Compatibilization of poly(vinylidene fluoride)/nylon 6 blends by intermolecular association

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/25382

Publisher: © K. Hashim

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
COMPATIBILIZATION OF POLY(VINYLIDENE FLUORIDE)/NYLON 6 BLENDS BY INTERMOLECULAR ASSOCIATION

by

KAMARUDDIN HASHIM

A Doctoral Thesis
Submitted in partial fulfilment
of the requirements for the award of
DOCTOR OF PHILOSOPHY
of the
LOUGHBOROUGH UNIVERSITY

1996

Supervisor: Dr L. Mascia

Institute of Polymer Technology and Materials Engineering

© K. Hashim, 1996
To my parent for their moral support
and

to my beloved wife for her patience and sacrifice
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Acknowledgements</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>II</td>
</tr>
</tbody>
</table>

## CHAPTER 1: INTRODUCTION

1.1 General Background
1.2 Polymer Blends
  1.2.1 Advantages of Blends
  1.2.2 Preparation of Blends
  1.2.3 Criteria for Miscibility
  1.2.4 Compatibility in Polymer Blends
1.3 Poly(vinylidene fluoride)
1.4 Polyamides (Nylons)
1.5 Objective and Approach of Research Project

## CHAPTER 2: LITERATURE SURVEY

2.1 Radiation Grafting and Graft Polymerization
  2.1.1 Direct Irradiation Method
  2.1.2 Pre-irradiation Method
  2.1.3 Graft Polymerization Applications
2.2 Ionomers
  2.2.1 Historical Background
  2.2.2 Structure
  2.2.3 Preparation
  2.2.4 Ionomeric Polymer Blends
2.3 Poly(vinylidene fluoride) Blends
2.4 Blends Based on Nylon 6

## CHAPTER 3: EXPERIMENTAL

3.1 Materials
3.2 Monomer Solubility Studies
3.3 Grafting Experiments
CHAPTER 4: RESULTS AND ANALYSIS

4.1 Absorption Studies 50
4.2 Grafting 52
4.3 Fourier Transform Infrared Analysis 58
4.4 Differential Scanning Calorimetry Analysis 71
4.5 Dynamic Mechanical Thermal Analysis 90
4.6 Phase Morphology of Blends 97
4.7 Extraction Tests 113
4.8 Tensile Tests 124
4.9 Rheological Studies 130
4.10 Solvent Resistance Test 142

CHAPTER 5: DISCUSSION AND CONCLUDING REMARKS 149

5.1 Effect of Acid Grafting on PVDF and Subsequent Ionomerisation 149
5.2 Effect of Acid Grafting on Nylon 6 and Subsequent Ionomerisation 152
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Compatibility of Blends</td>
<td>153</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Morphology of PVDF/N6 Blends</td>
<td>155</td>
</tr>
<tr>
<td>5.3.2</td>
<td>High Temperature Deformational Behaviour</td>
<td>167</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Mechanical Properties</td>
<td>171</td>
</tr>
</tbody>
</table>

**CHAPTER 6: CONCLUSIONS AND SUGGESTION FOR FUTURE WORK**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Conclusions</td>
<td>174</td>
</tr>
<tr>
<td>6.1.1</td>
<td>Grafting and Ionomerisation of PVDF</td>
<td>174</td>
</tr>
<tr>
<td>6.1.2</td>
<td>Grafting and Ionomerisation of Nylon 6</td>
<td>175</td>
</tr>
<tr>
<td>6.1.3</td>
<td>Effects of Grafting on Compatibilisation of PVDF/N6 Blends</td>
<td>176</td>
</tr>
<tr>
<td>6.1.4</td>
<td>Effects of Ionomerisation of Acid Groups of the Blend Components</td>
<td>177</td>
</tr>
<tr>
<td>6.2</td>
<td>Suggestions for Future Work</td>
<td>178</td>
</tr>
</tbody>
</table>

REFERENCES | 180 |
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my supervisor, Dr. Leno Mascia, for his guidance, advice and encouragement throughout the period of this study.

I would like to thank my friends, the IPTME staff and technicians for their assistance.

I am very grateful to Dr. E. Kronfli from Royal Military College of Science, Cranfield Institute of Technology for irradiating the samples, and also to Ing. A Valenza from Palermo University (Italy) for carrying out the rheological test.

Finally, I am grateful to Malaysian Government for financial support throughout my research work.
ABSTRACT

Blends of poly(vinylidene fluoride) (PVDF) and polyamide 6 (N6) are interesting for both scientific studies and commercial exploitation. PVDF is known to be miscible with polymers produced from monomers containing carbonyl side groups, eg. polyethyl acrylate, polyacrylamide etc., but is not miscible with polymers containing carbonyl groups in the main chain, eg. polyamides, polyester, etc. Although complete miscibility of the blend components is not always necessary, strong physical interactions between the two components are needed in order to obtain a compatible blend, i.e. one which exhibits good mechanical properties.

An investigation was carried out to explore the possibility to compatibilise blends of PVDF and N6 using γ-radiation to graft acid groups on either polymer and subsequently ionomerizing these with zinc cations. Graft copolymer type of compatibilizer was produced when the acid functionalized PVDF (grafted PVDF) was blended with N6 or acid functionalized N6 (grafted N6).

Fourier transform infrared analysis has confirmed the occurrence of reactions between acid groups in the grafted PVDF and amine groups in the N6. The compatibility of the PVDF/N6 blends was found to increase with increasing amount of carboxylic acid groups in the two polymers. This was accompanied by an increase in $T_g$ of the N6 phase in blend, which became more pronounced when both components were grafted. Tensile test and solvent resistance experiments were carried out to relate the compatibilization of the blend to the improvement in mechanical properties.

Ionomerization of the functionalized polymers with zinc cations was performed in order to study the effect on compatibility of the blend. The neutralization of the acid groups in either polymer in the blend by addition of zinc acetyl acetonate was found to suppress the chemical reaction with the amine end groups in the N6 phase, and to cause a reduction in the $T_g$ and a reduction in crosslinking of the N6 phase. However when both polymers were grafted, the crystallinity of the N6 phase was restored, which was accompanied by an increase in $T_g$.

Keywords: PVDF blends, radiation grafting, ionomeric associations, polyamide blends
1.1 GENERAL BACKGROUND

Polymer blending represents one of the fastest growing segments of polymer technology, from the standpoint of commercial applications and developments. It is an economically viable and versatile way in which new materials can be produced to obtain a wide range of properties. Another advantage is the potential opportunities for combining the attractive features of each material into one or for improving the deficient characteristics of a particular materials. Many reviews have been written on this subject (1-3).

Since most polymer blends are immiscible and consist of two distinct phases, it should not be surprising that most new blend products are formed from such mixtures. Continued growth in new products of this type is expected, driven by the need to combine high performance characteristics, such as strength and
toughness, with resistance to heat and aggressive chemical environments. This is aided by carefully controlling the morphology and the interface between phases by means of compatibilizers (4). In some cases the compatibilizer is added as a third component, bearing functional groups that are reactive towards one of the main polymers and are soluble in the other. In some other cases specific functional groups are introduced into one of the polymers that are reactive towards the other component, to form a graft copolymer which acts as an in-situ compatibilizer.

Compatibilizer performance in improving mechanical properties of immiscible polymer blends can be determined by their contribution to improved adhesion between the major and minor phase by reducing the interfacial tension between the two components, which results in smaller domains, and increases the interfacial adhesion. The compatibilizer should contain groups that form strong interactions with at least one of two components of the blend. When added to the blend, the compatibilizer is expected to migrate at the interface. It can be compared in some respects to the emulsifying action of surfactants. Figure 1.1 shows schematically how, by residing at the interface, graft and block copolymers could act as a compatibilizers.

**COMPATIBILIZER:**

**USUALLY A COPOLYMER WHICH**

**CAN BE ADDED AS A THIRD COMPONENT**

**OR**

**CAN BE FORMED IN SITU**

Figure 1.1: Schematic representation of a graft copolymer as a compatibilizer
The compatibility of polymer blends can also be enhanced by using an ionomer in which the metal cations form ionic association with anions from both polymer components of the blend, leading to the formation of ionomeric aggregates. These concepts have been explored for the past few years by Mascia and his co-workers (5-8), and have revealed the formation of strong interactions between carboxylate and alkoxide anions through common sodium cations in blends of phenoxy with polyolefin ionomers.

1.2 POLYMER BLENDS

When two polymers are blended, by whatever method, the most likely result is a two phase material. The reason why two polymers are not usually miscible becomes apparent from simple thermodynamic considerations. A necessary criterion for miscibility is that the free energy of mixing $\Delta G_m$ must be negative. This is given by,

$$
\Delta G_m = \Delta H_m - T\Delta S_m
$$

(1)

where $\Delta H_m$ is the enthalpy of mixing, $\Delta S_m$ is the entropy of mixing and $T$ the absolute temperature. $\Delta S_m$ is extremely small and therefore one relies entirely on a negative $\Delta H_m$ to achieve miscibility.

However, this criterion is not totally adequate as can be illustrated by examining the behavior of $\Delta G_m$ as a function of the mixture composition. First, equation 1 should be recast in a more amenable form following the treatment developed by Flory (9) and Huggins (10) for polymer-solvent mixtures, which is based on a rigid lattice model. For such mixtures the entropy term in equation 1 is expanded into combinatorial entropy of mixing term using the volume fraction $\phi_i$ as the concentration term:

$$
\Delta S_m = -R \left( \frac{V}{V_R} \right) \left\{ \phi_1 m_1 \ln \phi_1 + \phi_2 m_2 \ln \phi_2 \right\}
$$

(2)
where \( m_i \) is the number of segments per chain molecule (i.e. the degree of polymerization) of the ith component relative to the reference segment volume, \( V_R \).

The enthalpy of mixing can be expressed as a dimensionless interaction parameter per segment of polymer, \( \chi \), based on the Van Laar equation (11):

\[
\Delta H_m = RT(V/V_R) \chi_{1,2} \phi_1 \phi_2
\]  

This yields the final equation for the free energy of mixing:

\[
\Delta G_m = RT(V/V_R) \left\{ \phi_1/m_1 \ln \phi_1 + \phi_2/m_2 \ln \phi_2 + \chi_{1,2} \phi_1 \phi_2 \right\}
\]  

where \( V \) is the total molar volume of the two components.

The free energy change can now be plotted as a function of \( \phi_i \) for different \( \chi_{ii} \) values. Figure 1.2 shows three possible ways in which the free energy of mixing may vary with the composition of the mixture. The free energy of mixing is always negative for curve B for all compositions so that components are miscible in all proportions, whereas for the curve A, the free energy of mixing is always positive, and hence the two components are not miscible with each other to any extent. Even though the free energy of mixing is negative for curve C, it does not assume complete miscibility as illustrated in the Figure 1.2. Curve C represents a partially mixed (or compatible) mixture, which can achieve a state of lower free energy by forming two phases, each containing an amount of the other component. These considerations lead to a more rigorous thermodynamic definition of a miscible system. At constant temperature and pressure, the conditions of miscibility are given by the expression:

\[
[\partial^2 \Delta G_m / \partial \phi_2^2]_{T,P} > 0
\]  

4
Thus a mixture forms a one stable phase only as long as the above condition prevails.

Mixing can, however, be predicted to occur under three circumstances (12).

a) If the polymers are not of very high molecular weight then the entropy will not be negligible and may outweigh an unfavourable enthalpy of mixing. Thus one might expect oligomers mixtures to be more prone to form miscible systems.

b) If the enthalpy of mixing is positive but very small, then a small entropy of mixing may be sufficient to achieve a negative $\Delta G_m$. This may occur if the two polymers are chemically very similar.

c) If the enthalpy of mixing is negative, then two polymers would be expected to be miscible. This may occur if there are favorable interaction, such as a hydrogen bonds or ionic interactions, between the polymers components of the blend.

Figure 1.2: Free energy versus composition;
A: immiscible
B: miscible
C: partially mixed (or compatible)
1.2.1 Advantages of Blends

Beside the two reasons for mentioned earlier for blending polymers, other advantages are:

a) The possibility of producing unique materials with respect to processability and/or performance.
b) Easy modification of materials to suit a given application.
c) The possibility of improving performance at a reasonable price.
d) The possibility of using blends as a means of recycling polymers.

1.2.2 Preparation of Blends

In general, the methods to prepare polymer blends can be divided into three categories, mechanical mixing, solution blending and mixing via reaction. Each method has its own advantages and disadvantages. Most commercial polymer blends are prepared by mechanical mixing, largely because of its simplicity and low cost. The industrial method of mechanical mixing is to use a screw compounder or extruder that can be run continuously and generate a product in a convenient form for further processing. Where else on laboratory scale, the two roll mill or Banbury mixer are the tools used for mechanical mixing. With these methods, blending of polymers depends on the uniformity of shear and elongational stress, residence/mixing time, pressure, temperature control and efficiency of homogenisation. Low molecular weight liquid polymers mix to form one phase very easily but the low diffusion rate of high polymers makes the mixing process very slow. Prolonged mixing in the melt also causes problems due to the poor thermal stability of some polymers.

In the solution blending method, the blend is prepared by dissolving the two polymers in a common solvent. The blend can be recovered either by precipitation, cooling or evaporation of solvent. Commercially, this method would not be attractive unless the blend was required in film form, for example in membrane...
formation, or for coatings. This method has commercial disadvantages due to the cost and difficulty of solvent recovery as well as the potential environmental hazard associated with handling large volumes of toxic solvents. Beside this, the kinetics of solvent removal can influence the resulting morphology. In the case of film casting, three phase-separated types of morphology can be obtained, i.e. co-continuous, dispersed or layered depending on the selected solvent, the chemical nature of the two polymers as well as on the kinetic of the various processes involved.

There are several methods of reaction mixing. In the first method, the polymer is dissolved in a monomer and a fine dispersion of the two polymers produced when the monomer is polymerized. For example in the commercial production of high impact polystyrene (HIPS). In this case, polybutadiene is dissolved in styrene monomer which is then polymerized. Phase separation takes place when only a small amount of styrene has polymerized (13).

Many polymer blends are prepared by emulsion polymerization with sequential addition of different monomers. One example of this is the preparation of acrylonitrile/butadiene/styrene (ABS) plastics. The butadiene is polymerized first in the presence of a crosslinking agent and the other two monomers added in a later stage.

It is also possible to prepare homogenous (one phase) polymer mixtures by reaction mixing. One example is the in situ polymerization of vinyl chloride in the presence of polymers which are miscible with poly(vinyl chloride) (PVC). In this case, the polymerization of a 50:50 mixture of vinyl chloride and poly(butyl acrylate) (14) would produce a homogenous blend. If the mixture consists only 10 to 20% poly(butyl acrylate), which act as a rubber modifier or processing aid, then a heterogenous blend would be formed. This combination of polymers is an example of partially miscible blends.
1.2.3 Criteria for Miscibility

Several methods can be used to determine the miscibility of polymer blends and it is useful to recognize the strengths and limitation of each method.

Optical clarity is usually the first indication that two polymers are miscible though in itself it is not sufficient proof. It can be deceptive if the refractive indices of the two polymers are equal, or if the mixture has separated into two separate layers or the dispersed phase having dimension smaller than the wavelength of visible light. For transparency, the critical difference between refractive indices can be no greater than $0.01$ (15). The observation of an increase in turbidity or scattering has also often been used as a way of identifying the phase separation temperature of a mixture.

Perhaps the most commonly used and widely accepted criterion for polymer miscibility is the existence of a single glass transition temperature, $T_g$, whose temperature is intermediate between those corresponding to the two component polymers. Thus, a binary polymer mixture that is immiscible exhibits two $T_g$ values characteristic of the individual components, whereas a partially miscible system also displays two glass transitions which may be shifted closer to one another on the temperature scale. The most common techniques are differential scanning calorimetry, i.e. the measurement of heat capacity as a function of temperature, and dynamic mechanical thermal analysis, i.e. the measurement of storage and loss moduli as functions of temperature and possibly frequency. Other techniques are dielectric relaxation spectroscopy and dilatometry.

Limitations on the use of $T_g$ as a criterion for blend miscibility

a) Sensitivity problems can occur if the values of $T_g$ for the components are less than about 20 degree apart.

b) If one component represents less than 10% of the total.

c) For blends of amorphous and crystalline polymers, the glass transition of the amorphous region may be obscured at high levels of crystallinity for one or both of
the components. Crystallinity may also reduce the baseline shift expected at $T_g$ by thermal analysis, making this transition hard to detect.

d) These techniques also generally operate by scanning a property through the temperature range above the $T_g$ causing difficulties if the miscibility is temperature dependent, i.e. the temperature is scanned across the critical solution temperature. Beside the two factors, miscibility of the two components can also be assessed by monitoring such as melting point depression of a crystallizable polymer by differential scanning calorimetry analysis, reduction of domain size of disperse phase and improved morphological stability by scanning electron microscopy observation, interaction and/or chemical reaction between two components in the blend by FTIR analysis and an increase in blend viscosity by rheological studies (8).

1.2.4 Compatibility in Polymer Blends

Generally, immiscible blends must be compatibilized in order to obtain improved mechanical properties. Compatibilization may lower the interfacial tension between the two phases, reduce the physical size of the domains, stabilise the morphology, and provide for better adhesion between the phase.

There are two general routes to improve compatibility:

1) By adding a third component (compatibilizer) such as block and graft copolymers, or by a variety of low molecular weight reactive chemicals, capable of specific interactions and/or chemical reactions with one of the components and physically miscible with another component. The choice of a block or graft copolymer as compatibilizer is based on the miscibility or reactivity of its segments with at least one of the blend components. They are considered as interfacial agents since they tend to concentrate and act at the interface as emulsifiers. For most polyolefin/PS mixtures di- or tri-block copolymers of styrene and butadiene and hydrogenated butadiene or isoprene are effective compatibilizers, the rubber block exhibiting a certain miscibility with the polyolefin hydrocarbon backbone.
However, this method requires a separate synthesis step for the production of compatibilizers, which often is difficult to carry out and not economically viable for synthesis of such additives for systems of interest.

2) By blending suitably functionalized polymers is possible to produce graft copolymers which act as compatibilizers. Functionalization can be carried out in solution or in a compounding extruder and may involve the formation of block or graft copolymers, halogenation, sulfonation, hydroperoxide formation and end capping. During blending preparation, the block or graft copolymer is formed in situ via interfacial reaction of the functionalized polymeric components. This generates a copolymer at the interface which compatibilizes the two phases. HIPS and ABS are classical examples of systems compatibilized by graft copolymer formation.

1.3 POLY(VINYLIDENE FLUORIDE)

Poly(vinylidene fluoride) (PVDF) is the addition polymer of 1,1-difluorothene, CH2=CF2, commonly known as vinylidene fluoride (VDF or VF2). Vinylidene fluoride is polymerized readily by free-radical initiators to form a high molecular weight poly(vinylidene fluoride). It has good properties, such as impact strength, abrasion resistance, thermal stability, resistance to most chemicals and solvents, resistance to uv and nuclear radiation, and has an unusually high dielectric constant.

Properties of PVDF
PVDF is semicrystalline polymer that contains 59.4 % by weight fluorine and 3 % by weight hydrogen. The spatially symmetrical disposition of the hydrogen and fluorine atoms along the polymer chain gives rise to unique polarity influences that effect solubility, dielectric properties and crystal morphology.
a) Crystallinity
Crystallinity can vary from about 35 - 65%, depending on the method of preparation and thermomechanical history. PVDF exhibits a complex crystalline polymorphism absent in other synthetic polymers. It appears in at least four types of crystalline modification: alpha, beta, gamma and delta, depending on sample preparation. The alpha and beta forms predominate in practical situations. Generally, alpha form arises in normal melt-fabrication processes, whereas the beta form develops through mechanical deformations. The alpha form, being thermodynamically the most stable, is the most readily obtained under a variety of conditions. The density of alpha crystal is 1.92 g/cm\(^3\) (16) and the density of beta crystal is 1.97 g/cm\(^3\) (17). The density of amorphous PVDF is 1.68 g/cm\(^3\) (18). Hence, the typical 1.75-1.78 g/cm\(^3\) density reflects a crystallinity in the 40% range.

b) Melt and Transition Temperature
A variety of melting behaviours occur, depending on the polymerization method, thermomechanical history, and measurement technique. Thus, depending on type, PVDF resins melt from around 155°C up to 192°C. An oriented PVDF film with high beta crystal content melts at 166°C compared to 186°C when the specimen is restrained (19). However, below 300°C PVDF is extremely stable and degrades at 390°C with the evolution of hydrogen fluoride (HF). Chain relaxation behaviour indicates that the glass transition of PVDF lies in the range -30 to -50 °C (20), by dilatometry technique, dielectric method (21) and dynamic mechanical spectroscopy (22).

c) Mechanical
PVDF has a substantially greater strength, wear resistance, and creep resistance than PTFE, FEP and PFA. The tensile strength at break of PVDF is about 42-58.5 MPa at 25°C and 34.5 at 100°C. The elongation is in the range of 50 to 300 % at 25°C and 200 to 500 % at 100°C.
d) Chemical Resistance
PVDF exhibits exceptional resistance even at elevated temperatures to most inorganic acids, halogens, oxidants, weak bases, and aliphatic, aromatic, and chlorinated solvents. Strong bases, amines, esters, and ketones cause swelling, softening, and dissolution, depending on conditions. It has good weathering resistance and will not support combustion in air.

e) Electrical Properties
Polymorphism of PVDF and the two distinct dipole groups, -CF₂ and -CH₂ alternating along the polymer chain provide a unique polarity that influence its solubility and electric properties. It has a high dielectric constant about 8 to 9. Associated with the dielectric properties and polymorphism is the extraordinarily high piezoelectric properties (23) and pyroelectric activity of PVDF. Since polymorphism has a high dielectric loss factor, PVDF cannot be used as a primary insulating dielectric material for conductors of high frequency currents because considerable absorption of the electromagnetic energy occurs, thereby heating the insulation. In fact, PVDF can be melted readily by radio frequency or dielectric heating, and this is the basis of some fabrication or joining techniques (24).

f) Radiation Resistance
PVDF cross-links when subjected to electron beam radiation without detrimental effects on physical properties. It has radiation resistance to γ-Rays up to 10-12 MGy or 1000-1200 MRad. responds to high energy radiation mainly by cross-linking rather than degrading to lower molecular weight species. Interestingly, already at a dose as low as 20 kGy and in the absence of coagents, the gel content can be as high as 27% (25) and it increases rapidly to 54 % gel at a dose of 50 kGy, and then continues to rise moderately to 74 % gel at a dose of 200 kGy (26), if irradiation at high dose rate as in electron beaming. This retention of useful mechanical properties (27,28) can be used to achieve useful compositions with additives. The response to ionizing radiation in terms of cross-linking efficiency
and rate depends on the additive and the molecular weight of the polymer. The effectiveness is increased for high viscosity, broad molecular weight distribution polymers (29,30).

**Application**

PVDF is the basic raw material used in many diverse industrial products that require high mechanical strength and resistance to severe environmental stresses. Fluid handling system in the chemical process and related fields have been a growth market for PVDF products, e.g. solid and lining pipes, valves, pumps, tower packing, woven filter cloth, and tank lining (31). In the electronic field, PVDF insulated wire is used to connect panel boards and telecommunication systems. PVDF fabricated products utilizing radiation technology are heat-shrinkable tubing and insulated wire capable of withstanding high temperature. Pigmented thin film is cast from PVDF dispersions and is used by automobile manufacturers for body trim. PVDF is used in large quantities as a base for long-lasting decorative finishes for architectural metals, e.g. aluminium and galvanized steel.

1.4 **POLYAMIDES (NYLONS)**

Polyamides or Nylons are melt processable thermoplastic polymers that contain an amide group \(-\text{CONH}\) as a recurring part of the chain and are identified by numbers corresponding to the number of C - atoms in the monomers. In the case of Nylon 6, the polymer is made from \(\epsilon\)-caprolactam i.e.,

\[
\begin{align*}
n\text{H-N(CH}_2\text{)}_6\text{C}=\text{O} & \rightarrow \text{H[NH(CH}_2\text{)}_6\text{CO}]_n\text{OH} \\
\text{epsilon-caprolactam} & \quad \text{polycaprolactam (Nylon 6)}
\end{align*}
\]
Properties of Nylons

Nylons offer a combination of properties including high strength even at elevated temperatures, ductility, wear and abrasion resistance, low frictional properties, low permeability by gases and hydrocarbon, and good chemical resistance. Its limitations are hygroscopic behaviour, where moisture is slowly absorbed from the atmosphere, with resulting effect on dimensional and mechanical properties.

a) Crystallinity

Symmetrical, hydrogen-bonded, linear polyamides invariably are highly crystalline. Yield point, tensile strength, elastic and shear moduli, hardness, and abrasion resistance increase with increasing crystallinity, whereas moisture absorption and impact strength drop slightly. The maximum crystallinity that can be obtained varies with the nature of the polymer repeat unit, and high crystallinity (40-50 wt%) is obtained with polymers eg, Nylons -6, -6,6 and -6,10, whose regular structures permit good chain alignment and high degrees of hydrogen bonding in the planes of the chains. Chain stiffness, symmetry, and capacity to bond are especially important to provide good chain packing and high crystallinity in nylon.

b) Melting Temperature

They usually are semicrystalline polymers with melting temperatures in the range of 177 °C to 298 °C. Nylon - 6, 6/6 and 6/10 have melting temperature 220 °C, 255 °C and 215 °C respectively. The more C-atoms, that is the lower the concentration of amide groups, the lower the melting temperature, with a condition that nylons in which the amides are separated by an even number of C-atoms melt higher than those of similar amide concentration with an odd number of C-atoms.

c) Glass-transition Temperature

The glass-transition temperature $T_g$ of a polymer is determined by properties of the amorphous regions and by the degree of crystallinity. The $T_g$ of nylon depends on amide frequency and chain stiffness. A comparison of $T_g$ value for various
aliphatic polyamides e.g. Nylon -6, 6/6, 6/10, 11 and 12 shows that the T_g does not depend much on structure i.e. relaxations in the range of 40 - 50 °C (32, 33).

d) Chemical Resistance
Excellent resistance to hydrocarbon fuels, lubricants, and various organic solvents is a distinguishing feature of semicrystalline nylons compared to other engineering plastics. Nylon are attacked by strong acids, oxidizing agents and concentrated solutions of certain salts.

e) Thermal Effect
The rate and type of degradation depend on temperature, polymer structure, and whether the heating is carried out in the presence or absence of oxygen. In the degradation of Nylon -6 and -6,6 at 305 °C, the volatile products are carbon dioxide, water, ammonia, methyl/hexyl/heptyl amine and hexamethyleneimine. Degradation of many polyamides in the absence of air probably is associated with homolytic cleavage of the C—N bond with formation of a double bond and a nitrile group.

f) Radiation Effect
Irradiation of nylons with high energy electrons (eg. 2 MeV) or γ-rays produces cross-linking (34,35). In the process of irradiation, it produces free radicals with a characteristic colour (36). It is generally believed that the free radicals are on the carbon atom α to the amide nitrogen (37):

\[
\text{CH}_2\text{C—N—CH}_2 \quad \gamma \quad \text{CH}_2\text{C—N—CH}_2
\]

The predominant free radical in irradiated nylon is believed to be associated with the unpaired electron on the carbon adjacent to the amide nitrogen. For typical
aliphatic polyamides, such as Nylon -6 or -6,6, the free radical is yellow due to an absorption peak at 355 nm. The G yield (number of free radical per 100eV of absorbed radiation) for Nylon 6,6 has been reported (38) to be ca. 5.8, and the radical concentration per 10 kGy is ca. $6 \times 10^{-3}$ mol/L at lower radiation doses, i.e. up to 200 kGy. In air, oxygen diffusion accelerates this process of discoloration, but the rate of oxygen penetration is greatly reduced because of the irreversible reaction of oxygen with the free radical to produce peroxy groups. These can be used to initiate grafting reactions with vinyl monomers and other low molecular weight materials.

Application
Nylons are used in almost every industry and market. Transportation industry represents the largest single market for nylons in electrical connectors, wire jackets and light duty gears from unreinforced nylons while the glass-reinforced are used for engine fans, radiator headers, brake and power-steering fluid reservoirs and valve covers. Application in electrical and electronic parts include plugs, connectors, wiring devices, terminal blocks and coils form. In wire and cable, nylon is used mostly as a protective layer over primary insulation and lining of flexible cable. In mechanical applications include un lubricated gears, bearings and anti-fracture parts. Nylon tubing is used to convey brake fluid and refrigerants. Toughened nylons are important to the sporting good such as ski boots, ice and roller skate support, racquet sports equipment and bicycle wheels.

1.5 OBJECTIVE AND APPROACH OF RESEARCH PROJECT

Polyvinylidene fluoride (PVDF) and Nylon 6 are both semi-crystalline polymers and their combination in the form of blends could lead to new blends with interesting intermediate properties. Particularly important is the combination of the high melting point and high solvent resistance of Nylon 6 with the good hydrolysis
stability and thermoxidation resistance of PVDF. PVDF is known to be miscible with polymers produced from monomers containing carbonyl side groups, e.g. polyethyl acrylate (39), polyvinyl acetate (40), polyacrylamide (41), etc., but is not miscible with polymers containing carbonyl groups in the main chain, for example Nylon 6 and polybutylene terephthalate, based on the work by Frensch and Jungnickel (42) using Scanning Electron Microscopy observation of fractured surfaces of PVDF/N6 and PVDF/PBT blends.

The aim of the project is to study the blends of PVDF and Nylon 6 with the view to improve the compatibility of the PVDF with Nylon 6 by grafting of acrylic acid or methacrylic acid onto PVDF or Nylon 6 or both polymers and by subsequent ionomerisation and complexation with zinc cations, so as to increase the interactions between the two polymers. Bearing in mind that the modification of each polymer by acid functionalisation and subsequent ionomerisation could also be of direct interest, particularly with respect to adhesion and solvent resistance. This aim relies on achieving the following specific objectives:

i. To produce acid functionalised PVDF copolymer and acid functionalised Nylon 6 copolymer, by grafting methacrylic acid or acrylic acid monomers onto PVDF powder or Nylon 6 granule, separately. The method of grafting can be either coirradiation or preirradiation technique.

ii. To form an ionomer by reacting the acid functionalised PVDF copolymer with a source of zinc cations, such as zinc acetyl acetonate. This reaction is to be carried out in a melt.

iii. To study the effect of of grafting and ionomerization on the physical and mechanical properties of PVDF and Nylon 6 polymers, such as melting temperature, temperature of crystallization, crystallinity, glass transition temperature, tensile, elongation and solvent resistance.

iv. To study the reaction between acid functional group of grafted PVDF with amine group of Nylon 6 or grafted Nylon 6, in the process of making both
polymers more compatible in the blend, by FTIR, DSC, DMTA and SEM analysis, solvent extraction and rheology studies.

v. To examine the effect of zinc cations on the compatibility of PVDF and Nylon 6, especially on the interaction between the two polymers in the blend, with the same characterization study as in (iv).

v To study the effect of compatibilisation on the physical and mechanical properties of PVDF/Nylon 6 blends.
Chapter 2: Literature Survey

2.1 RADIATION GRAFTING AND GRAFT POLYMERIZATION

Radiation grafting and graft polymerization are well-known methods for the modification of the chemical and physical properties of polymeric materials. These can be achieved by ionizing radiation, ultraviolet light, or chemical initiators. Of these, radiation grafting is one of the most promising methods because of its extensive penetration into the bulk of a polymer, as well as providing a rapid and uniform formation of active sites. Hence, under appropriate experimental conditions, modification of polymer properties can be accomplished not only at the surface but also throughout the internal mass of the polymer. It allows a considerable degree of control to be exercised over structural factors, such as number and length of the grafted chains by careful selection of the dose and dose rate. The irradiation of polymers leads predominantly to the formation of free radicals and can be used quite conveniently to initiate block and graft copolymerization. Experimentally radiation synthesis of graft and block copolymers can be accomplished by two basic methods known as the direct irradiation method and the pre-irradiation method.
Elementary steps for the radiation-induced graft copolymerization of polymer (P) and vinyl monomer (M) may be written as follows (43)

Initiation

\[ \text{P} = \text{P} \rightarrow \text{P}' \]  

\[ \text{M} = \text{M} \rightarrow \text{M}' \] 

Propagation

\[ \text{P}' + \text{M} \rightarrow \text{PM}' \] 

\[ \text{P} + \text{M}' \rightarrow \text{PM}' \] 

\[ \text{PM}' + (\text{n}-1)\text{M} \rightarrow \text{PM}_n' \] 

Termination

\[ \text{PM}_n' + \text{M}' \rightarrow \text{PM}_{n+1} \] 

\[ \text{PM}_n' + \text{PM}_n' \rightarrow \text{P}_2\text{M}_{2n} \] 

\[ \text{M}_n' + \text{M}' \rightarrow \text{M}_{n+1} \] 

In all cases the initial radiation leads to the formation of free radicals in a polymer. From the reaction scheme above, all eight reactions are possible with the direct method, while reactions (1), (3), (5) and (7) prevail when the pre-irradiation method is used.

2.1.1 Direct Irradiation Method

The direct irradiation method involves the irradiation of a polymeric substrate in the presence of a monomer or the polymer is first impregnated with the monomer and then irradiated. Graft copolymerization of the monomer to the polymer is then initiated through the free radicals generated in the polymer. The direct method is the most efficient method for utilizing these radicals, since the radicals can be used immediately after they are produced, to initiate the polymerization of monomer. The most important aspect of this method is that the ionizing radiation is non-selective i.e. radiation affects not only the polymeric substrate but also the monomer, the solvent or any other substance present in the system. The disadvantage of this method is that some homopolymerization of monomer occurs as a result of the initiation by small free radicals such as \( \text{H}' \), \( \text{OH}' \) and \( \text{CH}_2\text{OH}' \) from the solvent. So this method of grafting is better suited for systems where the radical yield from the polymer is higher than that from the monomer, otherwise
excessive homopolymerization occurs. This effect is particularly pronounced if the polymer is irradiated in an excess of monomer.

The method for suppressing homopolymerization during direct grafting involves the introduction of transition ions into the system. Bonnecis and Puig (44) have found that the addition of Mohr salt and cupric chloride prevents homopolymerization of aqueous acrylic acid solution. In the grafting of acrylic acid and methacrylic acid on to polyester fibers (45), ferrous ammonium sulphate and copper sulphate in the case of acrylic acid, and copper sulphate in the case of methacrylic acid, were found to be the best additives capable of inhibiting homopolymerization without affecting the grafting process. Huglin and Johnson (46) also made a study on the effect of ferrous, ferric and cupric salts on the grafting of acrylic acid to Nylon 6 film in aqueous solution. They have found that anions have no effect on the grafting or homopolymerization, but both of these processes were suppressed by the cations in the following order of effectiveness: \( \text{Cu}^{2+} > \text{Fe}^{2+} > \text{Fe}^{3+} \).

In the direct irradiation method, grafting proceeds by a chain reaction of radical species which is influenced by many factors such as irradiation dose and dose rate, grafting in the presence or absence of air, monomer concentration, solvent or water and ratio of monomer. It has been established earlier that the number of radical species formed during irradiation is directly proportional to the dose rate (47). For the same total dose, the degree of grafting and graft rate are inversely proportional to the dose rate (48,49). This is largely because at low dose rates there is more time for monomers to diffuse to the radical sites before termination reactions occur. As the irradiation treatment gives rise to the formation of both monomeric as well as polymeric radical species, the former may react either with the polymer backbone (grafting) or with other monomer molecules (homopolymerization). At higher dose rate, the relative number of radicals present in the system will also be high. However, the rate of diffusion of monomer to the grafting sites will not alter. Under such circumstances, the greater availability of free radicals will increase the rate of homopolymerization.

As mentioned earlier, the disadvantage of this method is the limited supply of monomer during radiation grafting process. So there is a relation between percent of grafting with monomer concentration, which had been reported by Mukherjee and Gupta (48) in the grafting of methacrylic acid onto polypropylene fibers. For all doses, the percent grafting increases linearly only up to 2.0 molar concentration, beyond which the grafting levels off. The results show a very general trend and
have been confirmed by Koul et al. (49). On the grafting of acrylic acid onto polypropylene film, they have found that from 2.0 to 2.5 mole/litre concentration of monomer the homopolymer yield increases abruptly. This results in the depleting of monomer from the mixture, thus leaving little acrylic acid for grafting. During the grafting process, the monomer diffuses into the polymer matrix and, therefore, the ability of the polypropylene radical to capture the acrylic acid monomer depends upon the availability of acrylic acid from the solution. Hamil et al. (50) have also found that the grafting step of acrylic acid-grafted polyethylene film is determined by the diffusion of monomer and that the final copolymer composition can be controlled by controlling the concentration of acrylic acid in the grafting solution. The effect of monomer concentration on the grafting yield is not only for liquid phase grafting but also for vapour phase systems, as reported by El-Azmirly et al. (51), in the grafting of styrene on to Nylon 6 film. They discovered that not only the grafting yield increases with increasing the styrene concentration, but the grafting of styrene from the vapour phase system gives higher yields than from the liquid phase.

Since radiation grafting depend on the diffusion of monomer into the polymer radical sites, the composition and type of solvent greatly influences the rate and extent of grafting. Chapiro and Stannet (52) claim that irradiation in a dry system leads only to surface grafting, whereas, owing to the swelling effect of water, grafting occurs at greater depth in the fibre when water is present. El-Azmirly et al. (51) have reported that the degree of grafting at given radiation dose increases considerably up to a maximum when water added. Beside the swelling effect of water which make the amorphous regions loosen and become more accessible to monomer, the radicals produced by radiolysis of water (OH' and H') can undergo chain transfer with the polymer molecules, increasing the number of active sites for grafting. Such radicals can also initiate homopolymerisation of the monomer. Huglin and Johnson (46) have estimated that the reaction of OH' with vinyl monomer, CH₂=CHCOOH is $3 \times 10^4$ times faster than the reaction of OH' with a radical scavenger, such as cupric chloride.

Other factors that influence the degree of grafting such as type of polymer i.e. whether polar or non-polar, polymer form (fiber, powder or film), radiation in the present or absence of air and temperature, have also to be considered in the grafting by direct irradiation method.
2.1.2 Pre-irradiation Method

There are two types of graft polymerization by the preirradiation method; (a) Trapped radical graft polymerization and (b) Peroxide Graft Polymerization. In the grafting initiated by trapped radicals, the polymer is irradiated in the absence of air and then is brought into contact with monomer. Little or no homopolymerization of the monomer takes place, and grafting proceeds by the reaction of the monomer with trapped radicals within the polymer. In the second method, the polymer is irradiated in the presence of air forming peroxide groups, which are subsequently decomposed by heating the irradiated polymer in the presence of monomer, usually in the absence of air. Grafting occurs with some homopolymerization.

a) Trapped radical method

It is clear that the degree of grafting by this method depends directly on the efficiency of radical trapping and the concentration of trapped radical is proportional to the dose of irradiation. Hegazy et al. (53) in kinetic studies of preirradiation grafting of acrylic acid onto poly(tetrafluoro ethylene), have found that the rate of grafting and the final percent grafting increases with preirradiation dose. Since Dilli et al. (54) have demonstrated that in the γ-irradiation of paper, the production of trapped radicals is proportional to the dose, it appears that the degree of grafting is proportional to the concentration of trapped radicals. Kaji et al. (55) have found that final percent grafting (FGP) increased with increasing dose up to 50 kGy and levels off above 50 kGy. Thus at doses above 50 kGy, the higher concentration of released radicals will favour recombination reactions between radicals over grafting reaction between radicals and monomer, resulting in an efficient consumption of radicals for grafting.

In this method, generally, the initial rate should be largely dependent on the diffusibility of the monomer into the polymer matrix. Therefore, the rate of grafting in this system is mainly dependent on the swelling properties of polymer substrate. Lawrence and Verdin (56) have found that the high rate of grafting results from very rapid swelling of the cellulose matrix by water and fast diffusion of the acrylamide to the trapped radical sites. On the other hand, the final percent grafting depends on the rate of diffusion of monomer (monomer concentration) in the region of growing chains in the polymer matrix. This will increase the
propagation rate relative to the rate of termination, as a result of the formation of longer chains, since the number of initiating radicals will be unchanged.

The stability of the grafting sites in irradiated polymers is important because a major advantage of this method is that the polymer, after irradiation, may be transported to a new location and stored until required for grafting. Lawrence and Verdin (56) found that the degree of grafting decreases slowly with the period the samples has been kept before grafting. Since the extent of grafting is proportional to the trapped radical concentration, this phenomena must be due to the decay of trapped radicals during the storage. In general, the grafting yield depend on the stability of trapped radical in the polymer matrix. The decay of trapped radical also depends on the grafting temperature. The initial rate of grafting increases with temperature and the final percent of grafting has a certain maximum value (53,57). Since the decay of trapped radical is accelerated at higher temperatures, the grafting reaches the the final level much faster. The increase in grafting yield with temperature, may be due also to the increased diffusion of the monomer into the polymer matrix since the propagation reaction will be controlled by the diffusion of monomer.

b) Peroxide Method

In this method, the polymeric substrate (PH) is irradiated in air or oxygen to produce peroxide bonds (58). In most cases, the peroxidation is limited to the following process in which the peroxide is formed by radical-radical combinations involving peroxidic radicals:

\[
\begin{align*}
\text{PH} & \rightarrow \text{P'} + \text{H'} \quad (1) \\
\text{P'} + \text{O}_2 & \rightarrow \text{PO}_2' \quad (2) \\
\text{PO}_2' + \text{PH} & \rightarrow \text{POOH} + \text{P'} \quad (3) \\
\text{PO}_2' + \text{PO}_2' & \rightarrow \text{POOP} + \text{O}_2 \quad (4) \\
\text{PO}_2' + \text{P'} & \rightarrow \text{POOP} \quad (5)
\end{align*}
\]

The peroxide yield necessarily depends on both the \(G_R\) value of the irradiated polymer and the stability of the resulting peroxide at the irradiation temperature. Since diperoxides, P-O-O-P, are usually more stable than the corresponding hydroperoxides, P-O-O-H, the yield of the former species is expected to be higher except in the cases where hydroperoxides arise by chain reaction.
Graft polymerization is initiated by free radicals which are formed by thermal decomposition of dialkyl peroxide (P-O-O-P), as well as alkyl hydroperoxide (P-O-O-H) decomposition, in the presence of monomer at an elevated temperature. Hence, the efficiency of grafting will directly depend on the kinetics of the radiation-peroxidation process.

In the peroxide grafting method, the effect of oxygen during irradiation is one of the important factors controlling the grafting process as well as the other conditions such as preirradiation dose, grafting temperature, monomer concentration and so on. The efficiency of the grafting reaction will depend directly on the kinetics of the radiation peroxidation process. In the above process, although the dose-rate does not effect the peroxide yield, the rate of diffusion of oxygen within the polymer must keep up with the polymer radical formation, otherwise crosslinking and degradative reactions in the polymer predominate. A steady supply of oxygen must be secured to the reaction medium in order to compensate for oxygen consumption during irradiation. The best results are obtained if the polymer has a large free volume, i.e. above the T_g of the polymer, and the radiation dose-rate is not too high, in order to give time for oxygen to diffuse into the radical site.

It is clear that the concentration of polymeric peroxides will increase with radiation dose. For low doses, the concentration of peroxides is expected to build up linearly with dose; at higher doses, the radiolysis of the peroxide may become significant and a steady state may be reached when the rate of formation of peroxides equals their rate of destruction. The peroxide yield is not seriously affected by the irradiation dose rate if the peroxidation only occur through the above reaction and if supply of oxygen is not controlled by the rate of diffusion of this gas into the polymer. In the grafting of acrylic acid onto radiation-peroxidized polypropylene film, O’Neill (59) has found that in the range 16 - 80 kGy/s the initial grafting rate is independent of the peroxidation dose rate. The number of peroxidic sites in the polymer directly determines the number of grafted branches, and the concentration of peroxides determines the rate of inition of the polymerization of monomer and consequently the length of the grafted branches which can be controlled by appropriate selection of the grafting temperature and monomer concentration (60).

In some cases, for polymers containing labile hydrogen atoms such as polypropylene (61), irradiation in air also leads to the formation of hydroperoxides (POOH) on the polymer backbone. These, on heating, decompose to give a
hydroxyl radical (OH’) which can initiate the homopolymerization of the added monomer. This effect can be avoided to a large extent by the addition of a redox system or inhibitor with a good hydroxyl radical scavenger, according to a reaction such as:

$$\text{P-O-O-H} + \text{Fe}^{2+} \rightarrow \text{P-O'} + \text{Fe}^{3+} + \text{OH}^- \quad (6)$$

To inhibit efficiently the homopolymerisation of the monomer, the inhibitor must have a higher rate constant than the monomer for the reaction with the hydroxyl radical. O’Neill (59) has shown that the grafting rate increases at low concentration of Fe$^{2+}$, but at [Fe$^{2+}$] > 8 x 10$^{-4}$ molar a retarding effect occurs as a result of competition for P-O’ radicals between Fe$^{2+}$ and monomer, as described by the following reaction:

Chain Initiation:

$$\text{P-O'} + \text{M} \rightarrow \text{PO-M'} \quad (7)$$

Radical Scavenging:

$$\text{P-O'} + \text{Fe}^{2+} \rightarrow \text{PO}^- + \text{Fe}^{3+} \quad (8)$$

Thus, an increase in [Fe$^{2+}$] must at some point result in the predominance of the radical “wasting” reaction, eq. (8).

Gargan et al. (62) have found that ferrous sulphate is the most suitable inhibitor for grafting of acrylic acid onto LDPE powder and the degree of grafting is independent of inhibitor concentration (up to 0.2M), whilst for methacrylic acid, cupric sulphate or potassium ferrocyanide were preferred, but at low concentration of inhibitor (0.01M).

Beside this, homopolymer can also be formed by the dissociation of low molecular weight peroxides ROOR, ROOH, H$_2$O$_2$, which may be present in the irradiated polymer.

Although this method is less efficient than the direct grafting method, the preirradiation technique has the important advantage of the avoidance of direct radiation polymerization of the monomer.

2.1.3 Graft Polymerization Applications

Graft polymerization of suitable monomers on to the polymer backbone offers an effective means of introducing some desirable properties into the polymer without
affecting its original properties. Graft copolymers consist of a backbone chain carrying randomly distributed polymeric grafts. Their behaviour is governed by the strong repulsion between grafts and backbone. Various applications arise from the intramolecular phase-separation phenomena. Graft copolymers are used as membrane, emulsifiers, compatibilizers in polymer blends and surface modifying agents in coatings, adhesives, water repellents, and dye binders and so on.

Radiation grafting of properly selected functional monomers is a very powerful method for preparing a large variety of membranes with interesting properties. For example, acrylic acid-grafted polyethylene film is recognized as one of the most useful battery separators. The major role of separator membrane is to isolate physically the two half-cells of the battery in order to prevent contact or contamination of the active materials such as Ag₂O. The grafted membrane can suppress the migration of silver hydroxide which is formed from the dissolution of Ag₂O in highly concentrated alkaline solution of silver oxide-zinc battery.

Radiation induced grafting of hydrophilic monomers such as acrylic acid, methacrylic acid, 4-vinylpyridine and N-vinylpyrrolidone into polytetrafluoroethylene (PTFE) films generate various permselective membranes (43) with interesting properties. The resulting membranes of acrylic or methacrylic acid grafted PTFE film exhibit good performance in reverse osmosis and 4-vinylpyridine or N-vinylpyrrolidone grafted PTFE film have been successfully used in pervaporation, particularly for separating water from solvents such as formamide, dioxane or alcohol (63).

Preparation of copolymers possessing ion exchange properties by radiation grafting technique can also be seen in the copolymerized cellulose in chromatography (64). Celluloses grafted with styrene were unaffected by acids, bases and organic solvents commonly utilized in chromatography. It had high wet strength and the retardation factor (R_f) values for dyestuff, metal ion and fatty acids than the untreated paper.

Modification of the surface properties of polymers is one of the most important practical application of graft copolymerization. The introduction of carboxylic acid groups onto a hydrophobic support provides a good environment for subsequent enzyme immobilization. The immobilization of catalase on grafted membranes of poly(ethylene)-g-acrylic acid and poly(tetrafluoroethylene)-g-acrylic acid are used to make a single membrane hydrogen peroxide sensor (65).

Radiation grafting has been known as an excellent tool for hydrophilization of synthetic hydrophobic fibres, such as acrylic acid (AA) or acrylonitrile (AN).
grafted on polyester fibres (66), for the purpose of improving their hydrophilicity, dyeability, adhesion and antistatic properties, and it can be use for chemosorption. About 50% to 100% improvement in dyeability was observed with dispersed dyes in case of polyester fibres containing 22.4% and 9.0% graft of AA and AN, respectively. With increasing the number of polar groups (-COOH) on the surface of the fibre, the surface conductivity and moisture regain increased.

Radiation grafting have also been used to graft a flame retardant, monomer vinyl bromide, to polyethylene terephthalate filaments (67). Grafting of vinyl bromide can be localised either on the surface of the filament, uniformly throughout it, or predominantly at the core.

The application of ionization radiation allows grafting to be induced without catalysts and chemical initiators, which is an important factor in processing biomedical materials (68). Polytetrafluoroethylene surfaces have been grafted with polyacids to reduce thrombogenicity in order to make them suitable for use in prosthetic devices that come in contact with blood.

2.2 IONOMERS

Ionomers have long been reputed for such properties as greatly increased solvent resistance and mechanical properties at high temperatures compared to equivalent nonionic polymers. The term “ionomer” was coined by the Du Pont Co. to describe polymer materials composed of a hydrocarbon backbone containing pendant acid groups, neutralized partially or completely to form salts. The introduction of a small amount of bonded salt groups into a relatively nonpolar polymer has a profound effect on its morphology and properties.

Considerable industrial and academic research effort has been focussed on ionomers. This is evident from the scientific interest manifested in the technical literature and by the appearance of several monographs devoted to the subject. These materials have been used in a variety of applications, including permselective membranes, thermoplastic elastomers, packaging and films, and compatibilizing agents for polymer blends.

2.2.1 Historical Background

In the 1950s, Goodrich introduced one of the first elastomers based on ionic interactions, a copoly(butadiene/acrylonitrile/acrylic acid) and was followed by a
Du Pont's product under the trade name of Hypalon. Hypalon was based on the sulfonation of chlorinated polyethylene which, upon neutralization, changed from a material with the general properties of low density polyethylene to an extremely tough and optically clear rubbery polymer.

A breakthrough occurred in the mid 1960s when Du Pont introduced copoly(ethylene/methacrylic acid) under the trade name Surlyn; these copolymers were partially neutralized with sodium and zinc cations. The development of Surlyn was an important factor in stimulating research in ionomers.

2.2.2 Structure

The first attempt to predict the spatial arrangement of the salt groups in ionomers was the theoretical work of Eisenberg (69). In this work, the fundamental structural unit assumed to be the contact ion pair, where the anion and cation are separated from each other only by their ionic radii. Associated ion pairs, triplets, quartets, etc. in which the charges are as close to one another as possible are defined as multiplets which are dispersed in the matrix of low dielectric constant. Three factors which govern the formation of multiplets are considered:

i. the dimensions of polymer chains and ion pairs,
ii the tension on the chains resulting from ionic aggregation, and
iii the electrostatic (enthalpic) energy released upon multiplet formation, i.e. as in a crystallization type of transition.

Thus a single ion pair can be regarded as the smallest possible multiplet while the maximum multiplet size is governed by its geometry and the restriction that each ion pair must be attached to a hydrocarbon backbone. On the other hand, clusters are considered to be small microphase separated regions of aggregated multiplets.

2.2.3 Preparation

In general, the preparation of ionomers is a straightforward procedure. The particular acid group of interest can be introduced onto the hydrocarbon backbone either by: (1) direct copolymerization of a low level of functionalized monomer with an olefinically unsaturated comonomer or (2) direct functionalization of a preform polymer. The preparation of ethylene-based ionomers is an example of direct copolymerization. In this case, copolymers of ethylene and methacrylic or acrylic.
acid are synthesized by a high pressure, free radically initiated process. The resulting copolymer is then neutralized by fluxing with the metal-neutralizing agent by mixing in the melt state using plastics processing equipment. It is possible, however, to dissolve the copolymer in a suitable solvent and add the base, often as an alkoxide in methanol. The ionomer may then precipitate out as it forms.

The preparation of ionic elastomers in the sulfonation of poly(ethylene/propylene/diene monomer) (EPDM) (70) is an example of direct functionalization. This reaction is conducted in solution and so direct neutralization of the acid functionality to the desired level can be obtained. The ionic content in the ionomer is proportional to the amount of sulfonating agent. The neutralized ionomer is then isolated by conventional techniques such as coagulation in a nonsolvent or by solvent flashing.

2.2.4 Ionomeric Polymer Blends

Physical blending of two polymers generally results in a two-phase material as a consequence of a positive enthalpy of mixing. In order to improve their miscibility, specific interacting functionalities have to be introduced into the polymer pairs. The most common method is to employ hydrogen bonding or ionic interactions. The interactions are based on proton transfer from a donor site on one polymer to an acceptor site on another polymer, leading to ion-ion interactions. In others, the transfer of a metal cation from an ionomer to a polar polymer is the result of an ion-dipole interaction. Thus, it appears that chemical reactivity or ionic-cross interactions could lead to in situ compatibilising or miscibility enhancement during melt-mixing.

Eisenberg and coworkers have shown that it is possible to enhance the miscibility of two immiscible polymers by developing interactions involving one or more ionized species. Miscible blends were prepared using acid-base interactions, e.g. sulfonated polystyrene and poly(alkylene oxide) diamine (71), sulfonated polyisoprene and poly(styrene-co-4-vinylpyridine) (72), and using ion-dipole interactions, e.g. poly(styrene-co-lithium methacrylate) and poly (ethylene oxide) (73). Mascia et al. (7) have reported that sodium co-ionomeric mixtures of ethylene methacrylic acid copolymers and phenoxy act as surfactants in blends of poly(butylene terephthalate) and ethylene-butyl acrylate copolymers. They also reported that, the addition of sodium ethoxide (6) to the above stated polymer
mixtures change their morphology from that of a predominantly dispersed particle system to a co-continuous microstructure.

Peiffer et al. (74) have used transition metal complexation between a zinc neutralized sulphonated EPDM and poly(styrene-co-vinylpyridine) to improve the mechanical properties of the blend. Hirasawa et al. (75) have reported that the changes in the structure and properties of poly(ethylene-co-methacrylic acid) (EMAA) with increasing neutralization are larger in the alkaline and alkaline earth metal salts than in the transition metal salts. The microphase separation of salt group aggregates is observed with the former but not with the latter. Han and Williams (76) have reported that the alkaline and alkaline earth metal ionomers form the multiplet-cluster model while the transition metal such as copper and zinc ionomers form the coordination complex model. Jiang and co-workers have reported that introducing metal-ions to the blends of copolymers, i.e. poly(styrene-co-methacrylic acid) with poly(butyl methacrylate-co-methacrylic acid) (77) and poly(styrene-co-4-vinylpyridine) with poly(butyl methacrylate-co-4-vinylpyridine) (78) improves the miscibility and this miscibility enhancement depends on the nature and amount of the counter ions. In the blend of polystyrene ionomer and Nylon 6,6, Molnar and Eisenberg (79) have shown that lithium sulfonate groups are more effective than lithium or sodium carboxylate groups in enhancing the miscibility between the two components. Xie and Zhou (80) have reported that, the tensile strength of ionomers neutralized with different metallic ions decreased in the following order: Pb²⁺ > Zn²⁺ > Na⁺ > Ca²⁺ > Mg²⁺ > K⁺.

2.3 POLYVINYLIDENE FLUORIDE BLENDS

Poly(vinylidene fluoride) (PVDF) is among the few partially crystalline polymers that exhibit thermodynamic miscibility with other polymers (81), in particularly acrylate or methacrylate polymers. Mijovic et al. (82) have found that poly(vinylidene fluoride) and poly(methyl methacrylate) (PMMA) blends are miscible over a wide range of compositions, as indicated by the appearance of a single T_g in the dynamic mechanical spectra. The melting point of the PVDF/PMMA blend decreases, as the amount of PMMA in the blend is increased, indicating that the presence PMMA molecules around the PVDF chains reduce the energy required to melt the crystals.

PVDF is also miscible with poly(ethyl methacrylate) (PEMA) (83-89), but it is immiscible with higher members of the polymethacrylate series, such as
poly(isopropyl methacrylate) (PiPMA) and poly(isobutyl methacrylate) (PiBMA) (39). The immiscibility of PVDF with PiPMA and PiBMA appears to be the result of the interference of the bulky alkyl groups on the interaction between PVDF and carbonyl group.

These complex interactions have been the focus of numerous studies by Wahrmund et al. (39), on the transitional behavior of PVDF blends with poly(alkyl acrylate) such as poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA) and poly(isopropyl acrylate) (PiPA). Earlier work (90) has shown that PEA/PVDF and PMA/PVDF blends exhibit lower critical solution temperature (LCST) behavior, which is conclusive evidence of their miscibility. Poly(isopropyl acrylate) was also examined because it is a higher member of the homologous acrylate series and proved to be immiscible with PVDF.

From further investigation on the nature of the specific interaction leading to the miscibility of PVDF with certain oxygen containing polymers, Bernstein et al. (91) have reported that PVDF is miscible with poly(vinyl methyl ketone) (PVMK) but immiscible with poly(vinyl methyl ether) (PVME) and have concluded that PVDF interacts with the carbonyl group rather than the whole ester group. Furthermore, they also reported that PVDF is miscible with poly(vinyl acetate) (PVAc) (40) and suggested that placement of the carbonyl further from the main chain was responsible for the stronger interaction of PVAc with PVDF than that of poly(methyl acrylate) (PMA) (39). As mentioned earlier, PVDF is miscible with PMA and PEA, but not with PiPA and higher homologues of poly(alkyl acrylates) (39). The same situation occurs with the poly(vinyl esters), i.e. PVDF is miscible only with PVAc but not with the poly(vinyl propionate) (PVPr) and poly(vinyl butyrate) (PVBu).

In general, the presence of a high content of carbonyl groups in the additive polymer appears to be a prerequisite for miscible composition ranges. Interestingly all the miscible polymers, PMMA, PEMA, PMA, PEA and PVAc, have in common a -O-C-O- group as part of their pendant structures which evidently gives rise to some specific interaction with PVDF that results in miscibility. However, this is not a fixed rule; thus, although poly(ethyl acrylate) is miscible with PVDF, while poly(isopropyl acrylate) and higher homologues are immiscible. Strong dipolar interactions are important to achieve miscibility with PVDF, as suggested by the observation that poly(vinyl fluoride) (PVF) is immiscible with PVDF (90).
As mentioned earlier, PVDF is immiscible with PiPMA and PiBMA (39). As expected, blends of poly(n-propyl methacrylate) (PnPMA) with PVDF (92) show optical cloudiness and two T$_g$s, characteristic of an immiscible mixture. But the presence of an additional carbonyl group in the pendant alkyl group affects the miscibility behaviour of the poly methacrylate. By replacing the methylene groups in the pendant groups of PnPMA with carbonyl groups, the resulting poly(acetonyl methacrylate) (PACMA) becomes miscible with PVDF.

Poly(ε-caprolactone) (PCL) is a highly crystalline polymer and shows miscibility with a large number of polymers such as poly(vinyl chloride) (PVC), poly(hydroxy ether of bisphenol A), PVAc, etc (93). The miscibility of PCL and PVC has been attributed to a specific interaction between the carbonyl groups of PCL and the hydrogen of PVC. Based on the criterion for the miscibility of PVDF, Won Ho Jo et al. (94) have reported that PCL/PVDF blends are miscible when the content of PVDF is less than 30 wt%, based on melting point depression and cloud point measurements. However, this conclusion is not in agreement with that presented by previous workers (83,91) as they have found that the molecular weight of PCL and PVDF used in their work was lower than that used previously. Generally, it is known that cloud point curves are very sensitive to the molecular weight of polymers. The reason why PET and PBT are not miscible with PVDF is probably due to the unaccessibility of the PVDF dipoles to the carbonyl groups in the polyester chains which is further prevented by the rigidity of the aromatic rings in relation to aliphatic chains (such as in PCL).

Paul et al. (83) have suggested that the major driving force for miscibility results from dipolar interactions between PVDF and the carbonyl functions of the amorphous polymers. Since tertiary amide structures are well known for their strong dipolar character, Galin (41) has reported that poly(N-vinyl-2-pyrrolidone) (PNVP) and poly(N,N-dimethylacrylamide) (PDMA) both form miscible blends with PVDF. The miscibility of PVDF with PNVP or PDMA was based on the occurrence of a single glass transition temperature, intermediate between the parent homopolymers for the amorphous blends (PVDF : <60 wt.%) and the depression of the melting point for the semi-crystalline blends. Alfonso et al. (95,96) have reconfirmed these findings with differential scanning calorimetry and dynamic mechanical relaxation techniques.

As mentioned earlier, PVDF is miscible with PVAc (41) but immiscible with polystyrene (PS) (97). Rio and Acosta have studied the possibilities offered by PVAc for compatibilizing PVDF and PS. From calorimetric and dynamic
mechanical analyses, they demonstrate that PVAc tends to ‘compatibilize’ blends of PVDF/PS, although the results of the two analyses do not agree with each other. It is presumed that this is due to differences in the techniques employed. Even though PVDF is not miscible with PS, but is miscible with PMMA, Won Ho Jo et al. (98) have reported that PVDF is miscible with poly(styrene-co-methyl methacrylate) (SMMA) having an styrene content less than 13 vol.%. According to the binary interaction model (99), the maximum styrene content in SMMA for the blend to be miscible was predicted as 18.5 % by volume. Poly(vinyl chloride) (PVC) is an inexpensive utility polymer and it can mix well with many other polymers to form numerous useful blends. PVDF is a much more expensive polymer than PVC and it is not miscible with PVC. The miscibility of poly(neopentyl glycol adipate) (PDPA) with PVC and with PVDF has been reported (100,101) and is expected to play the role of compatibilizer between the incompatible PVC/PVDF blends. Lau et al. (102) have found, infact, that PVC/PDPA/PVDF blends are miscible for PVDF contents below 50 wt%.

2.4 BLENDS BASED ON NYLON 6

Blending has been practiced for years to improve the performance of commodity and engineering plastics to achieve wider applications. Polyamide-6 (Nylon 6) is an important class of commercial polymers with a wide variety of applications, from engineering thermoplastics to fibers. However, it has a number of deficiencies for certain applications, for examples, low impact strength, high moisture sorption and poor processability. Hence, the improvement of some of the properties of polyamides through blending with other polymers is an attractive route to follow. Polyethylene offers high impact strength and good barrier to moisture, hence it would constitute an attractive polymer to blend with Nylon. Polyethylene and Nylon 6, however, form incompatible blends (103), and give poor mechanical properties. Compatibilization can be achieve by addition of a compatibilizing agent or with the use of functionalized polyethylene in the form of copolymer. A particularly attractive feature of the Nylon 6 for reactive coupling to other polymers is their inherent chemical functionality through the amine or carboxyl end groups that may be present, and potentially, the amide linkage itself. Thus, there is no need to functionalize this component by further reaction or by physical addition of a functional component. Raval et al. (104) have used only 2.4% LDPE-g-(butyl
acrylate-co-maleic anhydride) with a 12% degree of grafting as compatibilizer for LDPE/N6 blends and have obtained remarkable improvements in impact strength along with a reduction in water absorption. Several workers (105-107) have successfully used maleic anhydride-g-polyethylene to compatibilize polyethylene/Nylon 6 blends. Serpe et al. (107) have reported that a succinimide group is formed during mixing, through reaction of anhydride with the terminal -NH2- groups of nylon by infrared spectroscopy. MacKnight et al. (108) in their investigation using poly(ethylene-co-methacrylic acid) (EMA) copolymer as compatibilizer, have suggested an amidation reaction between NH2 terminal groups of Nylon 6 and the COOH groups of the copolymer, in addition to possible hydrogen bonding between the two phases, at least when the copolymer is in the acid form. Functionalized polyethylene by photoxidation (109) or γ-irradiation (110,111) in blends with Nylon 6 has been found to improve the compatibility from interactions of carbonyl group formed during photoxidation/γ-irradiation with amine group, these gave rise also to a higher viscosity and improved tensile and impact properties.

Blending Nylon 6 with polypropylene (PP) leads to materials with improved chemical and moisture resistance, dimension stability, and reduced cost. However, to achieve these advantages some form of compatibilization is generally required; one successful approach involves the addition of maleic anhydride grafted polypropylene (PP-g-MAH) as third component (112,113) to the blend. The maleic anhydride units reacts during processing with the amine end groups of the Nylon 6 to form block or graft copolymers that act as the compatibilizer for the blend. The usefulness of the compatibilizer has also been demonstrated for the recycling of shredded industrial carpet waste containing PP and Nylon 6 (114). Dagli et al. (115,116) have used acrylic acid grafted PP in reactive compatibilization of Nylon 6 and PP blend. They have suggested that the acid/amine reaction (Fig. 2.1) to form a graft copolymer in-situ is the primary compatibilization reaction and an anhydride/amine reaction (Fig. 2.2) is also possible since under processing conditions, PP-g-AA may also form an anhydride (117).

Formation of cyclic imide have also been reported by Van Duin et al. (118) in the reaction of nylons with maleic anhydride containing polymers by 13C NMR spectroscopy. They have reported that, at a blending temperature between 180 °C and 220 °C, the amine and anhydride are coupled, resulting in a linear imide acid but above 220 °C a cyclic imide is formed and acid is split off. They have
remarked that it is quite difficult to distinguish between imide and acid groups with IR spectroscopy in real polymer systems, due to low chemical conversion.

**Acid / Amine Reaction**

\[
\text{PP} \quad \xrightarrow{\text{CH}_2\text{O}} \quad \text{CH} - \text{C} - \text{OH} + \text{H} - \left\{ \text{N} - \left(\text{CH}_2\right)_6 - \text{C} \right\}_n - \text{OH} \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{PP-g-AA} \quad \rightarrow \quad \text{PP-g-AH}
\]

**Anhydride / Amine Reaction**

\[
\text{PP} \quad \xrightarrow{\text{CH}_2\text{O}} \quad \text{CH} - \text{C} - \text{OH} + \text{H} - \left\{ \text{N} - \left(\text{CH}_2\right)_6 - \text{C} \right\}_n - \text{OH} \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{PP-g-AH}
\]

Fig. 2.1: Acid/amine reaction between carboxylic groups on grafted PP and amine end groups on Nylon 6

Nylon 6
Fig. 2.2: Anhydride/amine reaction between anhydride groups on grafted PP and amine end groups on Nylon 6 form imide.

In blends of Nylon 6 with polycarbonate (119-121), an aminolysis reaction occurred with the attack of active amine groups on the inner carbonate groups with the formation of a \( \text{N} 6-\text{NH}-\text{COO-PC} \) block copolymer;

\[
\text{N} 6-\text{NH}_2 + \text{PC-O-COO-PC} \rightarrow \text{N} 6-\text{NH}-\text{COO-PC} + \text{PC-OH}
\]

Besides the copolymer composition, NMR analysis (121) yielded evidence of the presence of urethane units interconnecting the Nylon 6 and polycarbonate block. They have found that the number of \( \text{NH}_2 \) terminal groups is the most important parameter in controlling the interchange reactions of the systems and that the degradative effect on \( \text{PC} \) is only due to the chemical reactions with Nylon 6 and not to the thermomechanical treatment.

Nylon 6 has not hitherto become a commodity plastic material because of its relatively high cost. Therefore, it is desirable to compromise properties and cost by blending it with cheap polymers like polystyrene (PS). It is often difficult to obtain good dispersion in polymer blends whose components are totally immiscible, particularly for blends of a polar Nylon 6 with a nonpolar PS. Poly(styrene-co-acrylic acid) (SAA) (122) has been used to control the morphology of the blend and formation of long branching between the amine end groups of Nylon 6 and the carboxylic acid of SAA that contributes to the compatibility of the blends. Beside the acid/amine reaction, Kuphal et al. (123) have shown the existence of hydrogen bonding interaction between SAA with aliphatic polyamide. Another way to compatibilize PS/Nylon 6 blends is to
functionalize PS with a small amounts of sulfonic acids groups. It has been shown that Nylon 6 can be miscible with sulphonated polystyrene (SPS), not only in its acid form but also as an ionomer neutralized with metal cations (124-129). Hydrogen bonding and complex formation between the cations and amide groups were responsible for miscibility of various SPS ionomers and Nylon 6. The nature of the specific sulfonate-amide interactions in SPS/N6 blends depends on the sulfonate cation used. For the free acid of SPS, hydrogen bonds form between the -SO\(_2\)H and -NHCO- species. For Li-SPS, Li\(^+\) complexes with the carbonyl oxygen, while the complex between N6 and Zn-SPS involves both the carbonyl oxygen and the amide nitrogen.

Thermoplastic elastomers or rubber-like polymers upon maleation have been used to increased the impact strength of Nylon 6. Styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS) (130), acrylonitrile-butadiene-styrene (ABS) (131) and ethylene-propylene rubber copolymer (EPM) (132) are successful examples of such rubbers that are useful for toughening Nylon 6. The pendant anhydride groups of maleated rubber-like polymers is reacted with the terminal amino groups and/or the backbone amide groups of polyamides while the elastomeric main chain of the compatibilizer is soluble and entangled with the elastomer phase of the blend. In this manner, which is similar to the classical mechanism of a surfactant, it brings about both a fine dispersion of the discontinued elastomeric phase surrounded by a continuous Nylon 6 matrix and a good adhesion between at the interface, which is required to achieve in significant toughening of the Nylon 6.

These suggest that a compatilizer has to added to blends with Nylon or that non-polar polymers have to be functionalized, in order to render them compatible with Nylon 6.
CHAPTER 3: Experimental

3.1 MATERIALS

a) Poly(vinylidene fluoride)

The homopolymer, poly(vinylidene fluoride) (PVDF), used was Kynar® 461, from Atochem North America, Inc. The PVDF grade used in this work was in powder form, having molecular weight (Mw) of $5.34 \times 10^5$, melting point 156 - 160°C, density 1.76 g/cm³ and particle size about 0.2 μm.

b) Nylon 6

The homopolymer Polyamide 6 (Nylon 6) was a high viscosity grade SNIAMID ADS 40 granules and Nylon 6 film with a 20 micron thickness were supplied by Sniaricerche S.C.P.A. The film was produced from the same polymer grade as for the granules. Nylon 6 has melting temperature 220 - 223°C and density 1.14 g/cm³.
c) **Functionalising Chemicals**

i) Monomers

Methacrylic acid (MAA), $\text{HC}_2=\text{C(CH}_3\text{)}\text{COOH}$ and acrylic acid (AA), $\text{H}_2\text{C}=\text{CHCOOH}$, both 99.9% grade.

ii) Inhibitor

Ferrous sulphate hexahydrate, $(\text{FeSO}_4\cdot6\text{H}_2\text{O})$

iii) Zinc cation source

Zinc acetyl acetonate hydrate, $[\text{CH}_3\text{COCH=COCH}_3\text{H}_2\text{O}]\cdot2\text{n.xH}_2\text{O}$ with melting point of 138 °C. The chemicals were purchased from Aldrich chemical Co. Ltd. and used as supplied.

d) Polyacrylic acid for PVDF calibration by FTIR, was purchased from Aldrich Chemical Co. Ltd. and used as supplied.

e) Standard materials for FTIR acid calibration were low MW ethylene-acrylic acid copolymer AC - 6702, AC - 540, AC - 5120 (supplied by Allied-Signal Inc.) and montanic acid, corresponding to acrylic acid grafting levels of 1.6%, 4.35%, 11.1% and 13.16%, respectively.

3.2 **MONOMER SOLUBILITY STUDIES**

a) **Absorption of Monomers by PVDF**

Absorption tests for PVDF in water, acrylic acid (AA) and methacrylic acid (MAA) were carried out at room temperature for 72 hours and at 80°C in an oven. Small plaques, 10 x 10 x 0.5 mm, were cut from the compression mould sheets of PVDF. For tests at room temperature, each specimen was immersed in 10 ml of liquid, i.e. water, AA and MAA, and measuring the weight increase after 72 hours. The surface of specimens was carefully wiped with a tissue before weighing. In the case of absorption at 80°C, each specimen were immersed in the 10 ml of liquid, i.e. water,
AA, MAA, 20% AA in water solution and 5% MAA in water solution, and the weight increase was determined at different time interval for 48 hours.

b) Absorption of Monomers by Nylon 6 Granule

Absorption tests of the Nylon 6 granule in water, acrylic acid (AA) and methacrylic acid (MAA) were carried out at room temperature for 72 hours and at temperature 80 °C in an oven. After 24 hours drying in a vacuum oven at 80 °C, accurately weighted Nylon 6 granules were immersed in the 10 ml of liquid, i.e. water, AA and MAA, and the weight increase measured after 72 hours. The excess liquid on the surface of Nylon 6 granules were carefully wiped out by squeeze gently on a tissue before weighing. For the absorption test at 80 °C, accurately weighed Nylon 6 granules were immersed in the 10 ml of liquid, i.e. water, AA, MAA, 10% AA in water solution, 10% MAA in water solution and 30% MAA in water solution, and the weight increase was determined at different time interval for 48 hours.

3.3 GRAFTING EXPERIMENTS

3.3.1 Grafting Procedures

a) Grafting by Direct Irradiation

The PVDF powder and the monomers either methacrylic acid (MAA) or acrylic acid (AA) at various weight ratios, were mixed in a high speed powder mixer for 5 minutes both with and without FeSO₄ inhibitor. They then were sent for γ-ray irradiation at the Royal Military College, Cranfield Institute of Technology, using a 60Co source at a dose rate of 1kGy/hr for 1.5 hours and 15 hours, respectively, i.e. the samples received a total dose of 1.5 kGy and 15 kGy. These low doses were used to graft the monomer on to the polymer without formation of crosslinks, confirmed by solubility test in DMF. After irradiation, the samples were heated up in the oven at 80° C for 24 hours, in a closed container, followed by thorough washing with hot water to remove any homopolymer which may have formed. The samples were dried in the
oven for 48 hours at 80 °C. The samples were made into KBr disc and analysed by FTIR. The degree of grafting was calculated from a previously produced FTIR calibration curves.

b) Grafting by Pre-irradiation

The PVDF powder was sent for irradiation with the same total dose as specified previously. For the preliminary studies, about 5 g of the irradiated PVDF powder were weighted accurately into a 250 ml volumetric flask. 100 ml of grafting solution was prepared by dissolving the required amount of ferrous sulphate in distilled water and then making the solution up to certain percent (v/v) either with acrylic acid or methacrylic acid. This solution was added to the powder in the volumetric flask which was then sealed with rubber stopper. The grafting solution was degassed by bubbling with oxygen-free nitrogen for 2 hours. The grafting reaction was initiated by placing the volumetric flask in a shaker water bath thermostatted at 80 °C (133). During the grafting process, the samples were shaken at 200 rpm to ensure constant agitation of the powder. After the grafting process, the grafted powder was filtered off and washed thoroughly with hot water to remove the excess monomer or homopolymer which formed by homopolymerisation of the monomer. The powder was dried at temperature 80 °C for 48 hours and then weighed. The degree of grafting was calculated as follows:

\[
\text{%Graft} = 100\left(\frac{W_2 - W_1}{W_2}\right)
\]

where \(W_1\) is the initial weight of the PVDF powder and \(W_2\) is the weight of the grafted powder. For the control, the unirradiated PVDF powder was used for the grafting process.

The aim of this preliminary studies was to find the optimum conditions for the grafting process such as effect of monomer concentration, time of grafting and effect of total absorbed dose.
c) Procedure for Grafting PVDF

In the larger scale experiments, about 100 g of irradiated PVDF powder were weighted accurately into a 1 litre reaction flask and 500 ml of grafting solution was added to the irradiated powder. The reaction was carried out under nitrogen in the temperature-controlled heating mantle at temperature 80 °C for 3 hours. During the grafting process, the powder was stirred with a propeller blade at 50 rpm and a condenser was used to maintain the acid in the reacting flask. After the grafting process, the grafted powder was filtered off and washed thoroughly with hot water. The powder was dried at 80 °C for 48 hours and then weighed.

d) Procedure for grafting Nylon 6 granule

The granules were vacuum dried at 70 °C for 48 hours and accurately weighted before sending for gamma irradiation with total dose 15 kGy. After irradiation, the granules were keep in the freezer until ready for use. The granules were placed into reaction solution in reaction flask and bubbled with nitrogen for 3 hours in order to remove air or oxygen in the solution. The reaction solution consists of 10% methacrylic acid monomer in 500 ml water with 0.01M FeSO₄ as inhibitor against polymerization of methacrylic acid monomer. After bubbling with nitrogen, the flask was sealed tight and left over night to allow the monomer to diffuse into the granules. The grafting procedure was the same as that used for PVDF powder.

e) Procedure for grafting of Nylon 6 film

Air trap type of paper was placed between layer of Nylon 6 film and then the films were send for irradiation to a total dose 15 kGy. The films were kept in the freezer after irradiation until ready for use. The irradiated Nylon 6 films were rolled on a piece of absorbent paper to prevent the film from touching each other and to allow the monomer to easily diffuse into the film. The rolled irradiated Nylon 6 films were placed into the reaction solution contained in a reaction flask, comprising 10% methacrylic acid in 500 ml water with 0.001M FeSO₄ or a 2 litre water solution with
0.01M FeSO₄ as inhibitor. The grafting process was the same for the grafting of PVDF powder or Nylon 6 granule, except for the lack of agitation.

3.3.2 Ionomerisation Procedure

Mixing of grafted PVDF with the zinc cations donor compound, zinc acetyl acetonate, was carried out in a Brabender Plastograph mixer with capacity of 25 cc. The amount of zinc compound used in the preparation of the ionomerise grafted PVDF was according to the stoichiometric mol ratio between acid of grafted PVDF and zinc cations. Melt mixing was carried out at 180 °C, for a total time of 15 minutes (5 minutes were required for melting grafted PVDF and adding the zinc compounds, and continued 10 minutes to achieve full mixing) at a rotor speed of 80 rpm. For the control, 10% w/w of zinc compounds was mixed with pure PVDF powder, the amount equivalent to that for the grafted polymer.

In the case of Nylon 6, 11% w/w of zinc acetyl acetonate compound was blended with Nylon 6 and grafted Nylon 6 granule separately at 240 °C for 5 minutes after melting the Nylon 6, at the rotor speed of 80 rpm.

3.3.3 PVDF/N6 Blend Procedure

PVDF, grafted PVDF (with 5% or 10% methacrylic acid) or ionomerised PVDF (half, full or 50% excess neutralization with zinc cations) were blended with Nylon 6 or grafted Nylon 6 (with 11% methacrylic acid) at weight ratios of 80:20 or 20:80 at 240 °C and a rotor speed of 80 rpm. The time of mixing was 5 minutes after melting the Nylon 6. Longer mixing times were not used due to the susceptibility of Nylon to degradation.

3.3.4 Preparation of Test Plaques

Compression moulding was used to prepare test plaques (110 x 110 x 0.5 mm). The plaques were produced using a "frame" type mould between steel plates. For PVDF samples, PET films were used to prevent the plaques from sticking to the plates.
However, with sample containing Nylon 6, PTFE impregnate glass cloth had to be used not only to prevent the plaques from sticking to the plates, but also to withstand temperatures around 240 °C, the processing temperature for Nylon 6. The appropriate amount of material (10% excess) was placed in the mould, the mould was loaded in the press and preheated at 180 °C for PVDF samples, and 240 °C for samples containing Nylon 6 over 3 minutes. A pressure of 15 tons was then applied for 3 minutes. For PVDF samples, the mould was transferred to a cold press and allowed to cool with running water in the platen for 3 minutes under the same pressure, in order to avoid deformation of the plaques. However, with samples containing Nylon 6, the hot press was switched off and the sample was allowed to cool down slowly by passing low rate of cold water through the platens.

3.4 CHARACTERISATION OF THE BLENDS

3.4.1 Fourier Transform Infrared (FTIR) Characterisation

Fourier transform infrared spectroscopy (FTIR) analysis was carried out using a Nicolet 20DXC spectrophotometer in order to quantify the grafting reactions and to illustrate the possible occurrence of acid/amine reaction and salt formation in the ionomerisation process.

a) Calibration of Grafted PVDF and Grafted Nylon 6

FTIR was used for calibration purpose to determine the extent of grafting of acrylic acid or methacrylic acid onto PVDF powder and Nylon 6 granule or film. A series of weight ratios of pure PVDF powder and poly(acrylic acid) powder, which gave a total amount of 3 mg samples, were mixed with 0.15 g KBr and then, were grinded in the mortar. The powder mixture was then transferred to the hydraulic press disc mould and a 15 ton pressure was applied to the powder for about 10 minutes to produce the KBr discs for FTIR measurement. The peaks absorbance area of C=O stretching of acid group at 1722 cm\(^{-1}\) and CH\(_2\) bending of PVDF at 1410 cm\(^{-1}\) were measured by integrating the peak absorbance area from the x-axis. The FTIR
calibration curve for PVDF samples was obtained from the plots of the ratio of peaks absorbance area \( \frac{A_{1722}}{A_{1410}} \) against the % polyacrylic acid in the mixture with PVDF. The standard grades of ethylene-acrylic acid copolymers and montanic acid containing known amounts of acrylic acid were compressed into thin film to about 5 to 10 micron thickness. From FTIR spectra, the peak absorbance areas of C=O stretching of acid group at 1714 cm\(^{-1}\) and CH\(_2\) stretching of polyethylene at 2867 cm\(^{-1}\) were measured by integrated the peak absorbance area to x-axis. The FTIR calibration curve for the Nylon 6 samples was obtained from plots of the ratio of peak absorbance areas: \( \frac{A_{1714}}{A_{2900}} \) against percentage of acrylic acid grafting.

b) Thin film samples

Small pieces from a plaque about 0.1 g were place between PTFE sheets in a hot press. The samples were preheated for 3 minute and melted for another 3 minute. In the case of PVDF samples, they were melted at 200 °C while the Nylon samples were melted at 240 °C. After applying the pressure, the samples were then cooled slowly for about 30 minutes under pressure. Samples of about 5 to 10 micron thickness were so produced for FTIR absorbance analysis.

3.4.2 Differential Scanning Calorimetry (DSC)

Thermal properties of the blend were examined by differential scanning calorimetry (DSC, du Pont 2000). The samples from compressed plaques were accurately weighted to about 10 mg and placed in a small aluminium pan with a lid, and a similar empty pan with a lid was used as a reference. To ensure a uniform thermal history, the PVDF samples were first heated to 200 °C from room temperature, and held at this temperature for 5 minutes followed by cooling to 70 °C. After holding the samples at this temperature for 1 minute, they were then heated to 200 °C to record the melting temperature. Throughout the process, the scanning rate is 10°C/min. under a nitrogen atmosphere i.e. 60 cc/min. For the samples containing Nylon 6, the same sequence was applied but the samples were first heated to 260 °C and then heated for second time to 260 °C after cooling to 70 °C, with scanning rate 20 °C/min in all cases. The
difference in heat flow per unit of time was recorded as a function of temperature or time. The melting temperature (T_m) and crystallization temperature (T_c) were taken at the maximum of the endothermic and exothermic peaks, respectively. The heat of fusion (∆H_f) and heat of crystallization (∆H_c) were measured from integration of the area under the endo/exothermic peaks, respectively. The percent crystallinity of each phases was calculated separately from the normalized heat of fusion of the Nylon 6 and PVDF melting peaks, on the assumption that ∆H_f of Nylon 6 was 190.8 J/g (134) and ∆H_f of PVDF was 104.7 J/g (135), at 100% crystallinity.

3.4.3 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical tests were carried out using the dynamic mechanical thermal analyser of Polymer Laboratories, model PL706. The samples from the compression moulded test plaques were cut into rectangular bars 0.5 mm thick by 10 mm wide and 35-40 mm long. A medium frame in the dual cantilever mode was used with an 4 mm free length. The sample was clamped to the frame and oscillated at its centre by a large knife edge spreader clamp, attached to a drive shaft and linked to a mechanical oscillator. The samples were subjected to an oscillating frequency of 1 Hz and 4 mm oscillation amplitude (strain) in the temperature range from -100°C to 100°C at a heating rate of 5°C/min. The force resulting from the applied deformation is recorded as a function of the magnitude and phase of the sample displacement. The signals are automatically used to calculate the dynamic storage modulus (E') and the loss tangent (tan δ) which were plotted as a function of temperature. The tan δ peak was taken as the glass transition temperature (T_g) of the sample.

3.4.4 Scanning Electron Microscopy (SEM)

A Cambridge Stereoscan 360 scanning electron microscope was used to examine the morphology of the blends. Samples from compression molded plaques, Nylon 6 granule and Nylon 6 film were fractured in liquid nitrogen to reveal the internal morphology for SEM analysis. The non-conductive specimens were gold coated so that a constant electric potential could be produced and images of the fractured
surfaces were observed. The average particle diameter of the disperse phases or depth of grafting penetration on surface of Nylon 6 granules were determined from SEM micrographs.

3.4.5 Extraction Tests

The compression moulded plaque samples were cut into a rectangular pieces 10 mm wide and 35-40 mm long, and dried in vacuum oven at 80 °C for 24 hours. After being kept in a desiccator for cooling to room temperature, the samples were then accurately weighted and placed between very fine stainless steel wire meshes. For boiling water extraction, the samples were immersed in boiling water and were weighed at different time interval after carefully wiping out the water from the surface of the sample. The extractions were carried out until the system was in equilibrium, normally more than 72 hours.

In the case of extraction with dimethyl formide (DMF) solvent, the samples were accurately weighted without and with wire mesh and about 5 - 6 samples were placed in 250 ml round bottom flask which contained 150 ml DMF solvent. After extraction for 48 hours at the DMF boiling temperature, the sample were dried in the vacuum oven at 80 °C for 48 hours to make sure all the DMF were evaporated from the samples. After cooling in a desiccator, the samples in the wire mesh were weighed accurately to calculate the amount extracted.

3.4.6 Tensile Tests

Tensile properties measurements of the dumbbell-shaped samples were carried out on a Lloyd 2000R tensile testing machine at room temperature following the procedure described in ASTM D638. For brittle samples, the sheet were heated to a rubbery state before cutting into dumb bell specimens. Tensile strength and elongation at break were determined at a crosshead speed of 5 mm/min. The reported values of all properties are the average of at least five determinations.
3.4.7 Rheological Studies

These studies were carried out at Palermo University (Italy) by Ing A. Valenza. The Rheological properties were measured on a Rheometrics R.D.A. II Dynamic Analyser using a 25 mm diameter cone and plate fixture. Sample discs of approximately 27 mm diameter were cut from the sample plaques. Prior to each experiment the R.D.A. II Analyser was allowed to ‘settle’ at the test temperature for 10 to 15 minutes before setting the zero value between the cone and plate. Samples were placed between the cone and plate, melted, the cone and plate gap then reduced to the recommended 50 μm separation. Measurement were taken once the sample had fully relaxed (indicated by a normal force of less than 10%) and excess material removed from the cone and plate periphery.

Logarithmic frequency sweeps were taken over a frequency range of 0.1 rad/s to 500 rad/s with 5 measurement points per decade. A fixed strain of 5% was used at test temperature of 200 °C for PVDF sample and 240 °C for sample containing Nylon 6. Plots of Complex viscosity ($\eta^*$) versus angular frequency, ($\omega$) were made on a logarithmic scale.

3.4.8 Solvent Resistance Tests

These were carried out according to the ASTM method D-1239. The samples with thickness 0.5 mm were cut into pieces, 1cm x 3cm. For each sample, triple measurements were carried out using either chloroform or butyl acetate solvents. The samples were dried in a vacuum oven at 60 °C for 24 hours and weighed accurately before use. The sample were dipped in the solvent for 72 hours at room temperature. Before measuring the weight, the solvent was wiped from the surfaces of the sample with a tissue paper.
Chapter 4: Results and Analysis

CHAPTER 4
RESULTS AND ANALYSIS

In this section are presented the main results of the investigations.

4.1 ABSORPTION STUDIES

The preliminary studies of the absorption of monomers, i.e. acrylic acid and methacrylic acid, by polyvinylidene fluoride and Nylon 6 are presented here in order to identify the effective monomer concentrations for the grafting process.

The equilibrium amount of liquid absorbed by PVDF sheets and Nylon 6 granules at room temperature for 72 hours are shown in Table 4.1. Figures 4.1 and 4.2, on the other hand, show the absorption of liquid by the PVDF sheets and Nylon 6 granules, respectively, at a temperature of 80 °C at different time intervals up to 48 hours. It is observed that PVDF absorbs more acrylic acid than methacrylic acid or water either at room temperature or at 80 °C. However, Table 4.1 shows that Nylon 6 absorbs more water than acrylic acid or methacrylic acid at room temperature. The amount of water absorbed is twice that for than acrylic acid.
Fig. 4.1: Absorption of water, monomer and monomer solutions in PVDF at 80 °C;
- water, → Acrylic acid, ⇐ Methacrylic acid, ⇣ 20%(v/v) acrylic acid in water and → 5%(v/v) methacrylic acid in water.

Fig. 4.2: Absorption of water, monomer and monomer solutions in Nylon 6 granule at 80 °C;
- water, ⇐ Methacrylic acid, → 10%(v/v) acrylic acid in water, ⇣ 10%(v/v) methacrylic acid in water and
→ 30%(v/v) methacrylic acid in water.
Liquid absorption tests on Nylon 6 granules at 80 °C, (Figure 4.2) show that the 30% methacrylic acid solution gives a higher level of absorption than 10% acrylic acid solution and water.

Table 4.1: Absorption by PVDF sheet (30 x 10 x 0.05 mm) and Nylon 6 granules at room temperature for 72 hours.

<table>
<thead>
<tr>
<th>Solution</th>
<th>PVDF</th>
<th>Nylon 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.06%</td>
<td>6.0%</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>0.32%</td>
<td>3.2%</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>0.19%</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

4.2 GRAFTING

Preliminary studies were carried out to select the optimum grafting conditions and to determine which monomer, acrylic acid or methacrylic acid, gave the higher degree of grafting onto PVDF powder, either by direct irradiation (coirradiation) or preirradiation methods.

a) Grafting by Direct Irradiation

In the experiments for the grafting of PVDF powder with monomers, acrylic acid (AA) or methacrylic acid (MAA) (10% by weight), by irradiating the sample in air at room temperature (after mixing in a high speed mixer), it was found that methacrylic acid does not form any grafting with PVDF at any of the doses used, either with or without homopolymerisation inhibitor. With acrylic acid, however, grafting onto PVDF occurs in the absence of inhibitor (Table 4.2).
Table 4.2: Grafting yield of monomers, acrylic acid (AA) or methacrylic acid (MAA), onto PVDF powder by direct irradiation method, determined by FTIR calibration method.

<table>
<thead>
<tr>
<th>Total Dose</th>
<th>AA without inhibitor</th>
<th>AA with inhibitor</th>
<th>MAA without inhibitor</th>
<th>MAA with inhibitor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 kGy</td>
<td>4.5%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15 kGy</td>
<td>5.2%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

b) Grafting by Pre-irradiation

For the grafting of pre-irradiated PVDF powder with monomers, acrylic acid (AA) or methacrylic acid (MAA), the data in Table 4.3 and Figure 4.3 show that the optimum grafting conditions, are 3 hours reaction time at temperature 80 °C (134) and with a total dose of 15 kGy for the preirradiate PVDF powder. Methacrylic acid gives a higher percentage grafting compared to acrylic acid. Figure 4.4 shows that degree of grafting depends on concentration of the monomer in the solution and that the extent of grafting for acrylic acid is always lower than methacrylic acid.

When the grafting process was upgraded to a larger scale, i.e. from 5 g to 50 g, the grafting yield was reduced from 13.79% to 8.83%. The results in Table 4.4 have reconfirmed the effect of total dose on the grafting yield. Increasing the total dose of preirradiated PVDF powder, gives a higher percentage of methacrylic acid grafting. Table 4.4 shows that increasing the concentration of methacrylic acid from 5% to 20% (v/v) in 300 ml water solution does not improve the grafting yield.
Fig. 4.3: Effect of reaction time on percentage grafting by the preirradiation method;
(a) Acrylic acid reacted onto 1.5 kGy irradiated PVDF powder,
(b) Methacrylic acid reacted onto 1.5 kGy irradiated PVDF powder and
(c) Methacrylic acid reacted onto 15 kGy irradiated PVDF powder.

N.B: The reaction conditions are 5%(v/v) monomers in 100 ml solution,
containing 0.1M FeSO₄ as homopolymerization inhibitor at 80 °C and
shaken at 200 rpm in the a water bath. Percentage grafting was measured
gravimetrically.
Table 4.3: Effect of irradiation dose and reaction time on the grafting yield of acrylic acid (AA) and methacrylic acid (MAA) onto preirradiated PVDF powder in the grafting by the preirradiation method. The reactions condition are 5% (v/v) of monomer in 100 ml water with 0.1M FeSO₄ at 80 °C and 200 rpm for constant agitation of the sample.

<table>
<thead>
<tr>
<th>Reaction Time (hr)</th>
<th>1.5 kGy</th>
<th>15 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetry</td>
<td>FTIR Calibration</td>
</tr>
<tr>
<td></td>
<td>MAA</td>
<td>AA</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>1.94</td>
<td>-</td>
</tr>
<tr>
<td>2.0</td>
<td>1.93</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>4.0</td>
<td>0.24</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4: Grafting of acrylic acid and methacrylic acid on a larger scale.

50g of preirradiated PVDF powder at 5 kGy and 15 kGy were reacted with 5% and 20% (v/v) methacrylic acid, and 10% (v/v) acrylic acid in 300 ml water solution with 0.1M FeSO₄, at temperature 80 °C for 3 hours under nitrogen and 50 rpm constant agitation with stirrer.

<table>
<thead>
<tr>
<th>Irradiation dose</th>
<th>% Grafting by Gravimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methacrylic acid</td>
</tr>
<tr>
<td>5 kGy</td>
<td>6.71⁴</td>
</tr>
<tr>
<td>15 kGy</td>
<td>8.83⁴</td>
</tr>
<tr>
<td>15 kGy</td>
<td>7.46⁵</td>
</tr>
<tr>
<td>15 kGy</td>
<td>1.70⁵</td>
</tr>
</tbody>
</table>

⁴ 5% methacrylic acid in 300 ml water solution with 0.1M FeSO₄

⁵ 20% methacrylic acid in 300 ml water solution with 0.1M FeSO₄

⁶ 5% methacrylic acid in 300 ml water solution with 1.64 x 10⁻⁵M FeSO₄
Fig. 4.4: Effect of acrylic acid concentration in the solution on the grafting yield;
(a) percentage grafting measured by gravimetry method and
(b) percentage grafting measured from FTIR calibration.

N.B.: Preirradiated PVDF powder at 15 kGy was reacted in 100 ml solution
(% v/v acrylic acid in water which content 0.1M FeSO₄), for 3 hours at 80
°C and 200 rpm in a shaker water bath.
Further studies show that when 100 g of preirradiated PVDF powder at 15 kGy were reacted with 5% methacrylic acid in 500 ml water solution with 0.1M FeSO₄ at the same temperature and reaction time under inert agitation conditions, it gave 5.03% grafting yield. When 50 g of preirradiated PVDF powder at 15 kGy, on the other hand, were reacted with 10% methacrylic acid in 500 ml water solution with 0.01M FeSO₄ and at the same reaction condition, the grafting yield was 10.1%.

In subsequent experiments, 50 g Nylon 6 granules were irradiated at 15 kGy and then grafted with 10% (v/v) methacrylic acid in 500 ml water solution with 0.01M FeSO₄ at temperature 80°C for 3 hours under nitrogen and 50 rpm constant agitation with stirrer. These correspond to the optimum condition for grafting the pre-irradiated PVDF powder with methacrylic acid. In this reaction, about 11% of methacrylic acid monomer were grafted onto Nylon 6 granules. Table 4.5 compares the preirradiation grafting yield of PVDF and Nylon 6 by the gravimetric technique and FTIR calibration measurement, as described in section (a) and (b) of the FTIR Analysis.

Table 4.5: Grafting yield data of PVDF and Nylon 6 from the gravimetric technique and FTIR calibration measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gravimetric</th>
<th>FTIR calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-g-MAA5</td>
<td>5.03 %</td>
<td>4.20 %</td>
</tr>
<tr>
<td>PVDF-g-MAA10</td>
<td>10.10 %</td>
<td>11.70 %</td>
</tr>
<tr>
<td>N6-g-MAA11</td>
<td>11.16 %</td>
<td>13.30 %</td>
</tr>
</tbody>
</table>

In the grafting of the Nylon 6 film with methacrylic acid, two levels of grafting were produced, i.e. 3% and 11% as measured by the FTIR calibration method. For the 3% grafting, the irradiated Nylon 6 films at 15 kGy dose were grafted in 10% methacrylic acid in a 2-litre water solution with 0.01M FeSO₄ at 80°C for 3 hours under nitrogen. In the case of 11% grafting, the 15 kGy irradiated Nylon 6...
film was immersed in 10% methacrylic acid in 500 ml water solution with 0.001M FeSO₄ and bubbling with gas nitrogen for nearly 3 hours before starting the grafting process at 80 °C for 3 hours.

4.3 FOURIER TRANSFORM INFRARED ANALYSIS

a) FTIR Calibration of PVDF

The infrared spectra of individual monomers and polymers are shown in Figure 4.5. Spectra of acrylic acid (AA) and methacrylic acid (MAA) contain carbonyl absorption peaks at 1732 cm⁻¹ and 1641 cm⁻¹ respectively, which are absent in the spectrum of PVDF. Hence, it is possible to use the area of these peaks for the purpose of calculating the amount of grafting of the monomers onto the PVDF polymer. The same situation also applies to the poly(acrylic acid) spectrum exhibiting carbonyl absorption peaks at 1722 cm⁻¹, which was used for the preparation of the calibration curve.

Figure 4.6 shows that the carbonyl group peak of poly(acrylic acid)-poly(vinylidene fluoride) mixture is in the same position as the carbonyl groups of grafted acrylic acid-PVDF and grafted methacrylic acid-PVDF. Figure 4.7 shows the FTIR calibration curve of the ratio “Peak absorbance area of carbonyl group” to “CH₂-bending (reference peak) i.e. (A₁722/A₁410)” as a function of composition, i.e. weight ratio of poly(acrylic acid) in a mixture of poly(acrylic acid) and poly(vinylidene fluoride).

b) FTIR Calibration of Nylon 6

The infrared spectra of homopolymer Nylon 6, grafted Nylon 6 and a reference ethylene-acrylic acid copolymer, with known amount of acrylic acid, are shown in Figure 4.8. Since the reference materials have carbonyl peaks at 1714 cm⁻¹ which are in the same position as carbonyl peaks for grafted Nylon 6, it is deduced that
Fig. 4.5: FTIR spectra for (a) PVDF, (b) polyacrylic acid, (c) monomer methacrylic acid and (d) monomer acrylic acid.

Fig. 4.6: FTIR spectra for (a) mixture of polyacrylic acid and PVDF, (b) methacrylic acid - PVDF grafted copolymer and (c) acrylic acid - PVDF grafted copolymer.
Fig. 4.7: FTIR calibration curve of ratio of peak absorbance area \(A_{1722}/A_{1410}\) as a function of ratio of polyacrylic acid in mixture of polyacrylic acid and PVDF.

Fig. 4.8: FTIR spectra for (a) Nylon 6, (b) methacrylic acid-Nylon 6 grafted copolymer and (c) Ethylene-acrylic acid copolymer (AC540).
the reference materials can be used for the calibration of the grafting yield of
grafted Nylon 6. The spectrum of Nylon 6 does not show any peaks at 1714 cm\(^{-1}\),
and hence this peak can be used to calculate the amount of methacrylic acid grafted
to the Nylon 6 polymer. Figure 4.9 shows FTIR calibration curve for the ratio of
"Peak absorbance area of carbonyl group" to "\(-\text{CH}_2\)- stretching (reference peak)"
i.e. \(\frac{A_{1714}}{A_{2867}}\) as a function of percent acrylic acid in the reference materials.

c) **FTIR Analysis**

Figure 4.10 shows the spectra of grafted PVDF by the DRIFT technique (a) and
pressed thin film technique (b). The DRIFT technique shows only one peak of
carbonyl group at 1714 cm\(^{-1}\) from methacrylic acid grafted to the PVDF polymer,
while the thin film technique produces 3 peaks, i.e. at 1811 cm\(^{-1}\), 1769 cm\(^{-1}\) and
1714 cm\(^{-1}\) for carbonyl group which represent anhydride, carbonate and acid
groups, respectively. It is possible that during blending and compression moulding
the thin film for FTIR analysis, the acid groups decompose to give a different type
of carbonyl groups. This is in agreement with the worked done by Grant and
Grassie (136) showing that polymethacrylic acid decomposed thermally at 200 °C
by elimination of water to form anhydropolymethacrylic acid with additional two
carbonyl signals at 1795 cm\(^{-1}\) and 1750 cm\(^{-1}\), beside the acid groups peak at 1714
cm\(^{-1}\). In the case of grafted Nylon 6, only one peak at 1714 cm\(^{-1}\) is observed in
Figure 4.12(b), even though the sample were treated in the same way as grafted
PVDF and at much higher temperature 240 °C.

Figure 4.11 shows the effect of ionomerization by zinc acetyl acetonate on grafted
PVDF. With half neutralization of the grafted PVDF i.e. PVDF-g-MAA5/ZnAA(0.5), the size of the absorption peaks for all three carbonyl groups is
reduced (as shown by spectrum (b)). With increasing the amount of zinc cations
to full neutralization, the carbonyl peaks reduce much further and nearly disappear
when an excess of zinc cations is used, as shown in spectrum (d). As a result of
the neutralization process, a new absorption peak at 1571 cm\(^{-1}\) is obtained which
Fig. 4.9: FTIR calibration curve of ratio of peak absorbance area ($A_{1714}/A_{2867}$) as a function of percent acrylic acid in the reference copolymer.

Fig. 4.10: FTIR spectra of 5% methacrylic acid - PVDF grafted, (PVDF-gMAA) using (a) DRIFT method and (b) thin film by compression moulding.
does not exist in spectrum (a) for grafted PVDF. This corresponds to zinc carbonate groups, \((\text{COO}')_2\text{Zn}^{2+}\). The same behaviour is also found for the grafted Nylon 6. Figure 4.12 shows that the peak for the carbonyl group at 1714 cm\(^{-1}\) in spectrum (b) nearly disappears when grafted Nylon 6 is full neutralized with zinc acetyl acetonate, as shown in spectrum (c). The peak for the zinc carbonate group cannot be seen in this case, because it overlaps with the -NH bending of amide II peak which appears at 1564 cm\(^{-1}\). Since the amide groups — NH—CO — will produce two peaks, in the case of Nylon 6, the amide I peak at 1640 cm\(^{-1}\) has been identified as carbonyl stretching group while amide II peak at 1564 cm\(^{-1}\) is corresponded to the -NH bending group.

For PVDF/N6 80:20 blend, the spectrum (a) in Figure 4.13 does not reveal any specific interaction between the two polymers since all the peaks correspond to the individual polymers. However, for the blend of grafted PVDF with Nylon 6, i.e. spectrum (c) corresponding to PVDF-g-MAA10/N6 80:20 blend, shows the formation of new a peak at 1712 cm\(^{-1}\), as a result of the interaction between acid groups of grafted PVDF with amine terminal groups of Nylon 6. The occurrence of this reaction is deduced also from the reduction in absorbance of the amine (NH\(_2\)) peak at 3300 cm\(^{-1}\) and the disappearance of acid peaks (triple peaks). The data in Table 4.6 show that the ratio of the peak height NH\(_2\)/CH\(_2\) for PVDF-g-MAA10/N6 80:20 blend decreases by 50% with respect to the NH\(_2\)/CH\(_2\) peak height ratio for the PVDF/N6 80:20 blend. The peak at 1712 cm\(^{-1}\) has been identified as a carbonyl conjugated double bond, i.e.

\[
\begin{align*}
\text{O} & \quad \text{C—N—C} \\
\end{align*}
\]

and there is also a possibility for the formation of imide groups, as indicated in Figure 2.2, when the anhydride PP-g-MAH reacts with amine terminal groups of Nylon 6 in blends of PP/N6 using PP-g-MAH as compatibilizer.

The same type of reaction occurs in PVDF-g-MAA10/N6-g-MAA11 80:20 blend. Spectrum (c) in Figure 4.14 shows the disappearance of the acid carbonyl peak
Fig. 4.11: FTIR spectra of grafted PVDF and subsequently ionomerised with zinc acetyl acetonate. (a) PVDF-g-MAA5, (b) PVDF-g-MAA5/ZnAA(0.5), (c) PVDF-g-MAA5/ZnAA(1), and (d) PVDF-g-MAA5/ZnAA(1.5).

Fig. 4.12: FTIR spectra for (a) Nylon 6, (b) N6-g-MAA11 and (c) N6-g-MAA11/ZnAA(1).

N.B.: Figures in brackets represent the molar fraction of cations used to the maximum required for full neutralization.
Fig. 4.13: FTIR spectra for (a) 80%PVDF/20%N6, (b) PVDF-g-MAA10 and (c) 80%PVDF-g-MAA10/20%N6

Fig. 4.14: FTIR spectra for (a) 80%PVDF/20%N6-g-MAA11, (b) PVDF-g-MAA10 and (c) 80%PVDF-g-MAA10/20%N6-g-MAA11
which is present in spectrum (b) for grafted PVDF, followed by the appearance of a new peak at 1712 cm$^{-1}$, while the size of NH$_2$ peak is reduced to about 70% in terms of NH$_2$/CH$_2$ peak height ratio when compared with the NH$_2$/CH$_2$ peak height ratio for PVDF/N6-g-MAA11 80:20 blend, as shown in Table 4.6. Based on the reduction in size of the NH$_2$ peak, it is deduced that the extent of acid/amine reaction in the PVDF-g-MAA10/N6-g-MAA11 80:20 blend is higher than in the PVDF-g-MAA10/N6 80:20 blend. It is presumed that the interaction between two components in PVDF-g-MAA10/N6-g-MAA11 80:20 blend leads to greater compatibility than in the PVDF-g-MAA10/N6 80:20 blend (see later). The small peak at 1714 cm$^{-1}$ in Figure 4.14(a) for PVDF/N6-g-MAA11 80:20 blend, at the shoulder of carbonyl amide I peak (at 1640 cm$^{-1}$), belong to the acid groups of grafted Nylon 6 since only 20% grafted Nylon 6 is present in the blend and therefore, cannot give rise to a strong peak.

However, with the addition of zinc acetyl acetonate to the blend, the presence of zinc cations has a considerable effect on the interaction between the two components. For half neutralization, spectrum (b) of PVDF-g-MAA10/ZnAA(0.5)/N6 80:20 blend in Figure 4.15 shows the gradual disappearance of 1712 cm$^{-1}$ peak. With increasing the amount of zinc cations, the 1712 cm$^{-1}$ peaks of PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend nearly disappears and the size of the -NH$_2$ peak increases with the NH$_2$/CH$_2$ peak height ratio becoming about 20% higher than for the PVDF-g-MAA10/N6 80:20 blend. There is a possibility that the zinc cations form a metal salt/complex with the acid group of grafted PVDF and prevents the interaction of the acid groups with the amine groups of Nylon 6. This cannot be verified, however, since the peak of zinc carbonate groups at 1571 cm$^{-1}$ overlaps with the NH bending of the broad amide II peak at 1564 cm$^{-1}$, as mentioned earlier. (N.B.: Figures in brackets in the composition code represent the molar fraction of cations used to the maximum required for full neutralization).

The same effect of the zinc cations can be seen in the blend of PVDF-g-MAA10 with N6-g-MAA11. FTIR spectra (b) of PVDF-g-MAA10/ZnAA(0.5)/N6-g-
Table 4.6: Ratio of peak absorbance height and peak absorbance area of -NH₂ group at 3300 cm⁻¹ to -CH₂ absorbance at 2939 cm⁻¹ from FTIR spectra.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Absorbance ratio of NH₂/CH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Height</td>
</tr>
<tr>
<td>80PVDF/20N6</td>
<td>1.31</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6</td>
<td>0.66</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6</td>
<td>0.88</td>
</tr>
<tr>
<td>80PVDF/20N6-g-MAA11</td>
<td>1.60</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA11</td>
<td>0.52</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA11</td>
<td>1.31</td>
</tr>
<tr>
<td>80PVDF/20N6-g-MAA3</td>
<td>1.45</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA3</td>
<td>0.58</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA3</td>
<td>1.10</td>
</tr>
<tr>
<td>80PVDF/15N6/5N6-g-MAA11</td>
<td>1.30</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/15N6/5N6-g-MAA11</td>
<td>0.65</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/15N6/5N6-g-MAA11</td>
<td>1.17</td>
</tr>
</tbody>
</table>

N.B. Figures in brackets represent the molar fraction of cations used to the maximum required for full neutralization.
Fig. 4.15: FTIR spectra for (a) 80%PVDF-g-MAA10/20%N6, (b) 80%PVDF-g-MAA10/ZnAA(0.5)/20%N6 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6.

Fig. 4.16: FTIR spectra for (a) 80%PVDF-g-MAA10/20%N6-g-MAA11, (b) 80%PVDF-g-MAA10/ZnAA(0.5)/20%N6-g-MAA11 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA11.
MAA11 80:20 and (c) of PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blends in Figure 4.16, for half and full neutralization respectively, show much more clearly the gradual disappearance of the conjugated carbonyl groups peaks at 1712 cm⁻¹, as a result of the interference of zinc cations with respect to the acid/amine reaction between the two components. This deduction is based on the size of the NH₂ peak for the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, which shows again an increase in the NH₂/CH₂ peak height ratio. This becomes about 50% higher than the NH₂/CH₂ peak height ratio for PVDF-g-MAA10/N6-g-MAA11 80:20 blend, as shown in Table 4.6.

In the blend of PVDF with grafted Nylon 6 film, which contains 3% methacrylic acid grafted onto Nylon 6 film, the FTIR spectrum for PVDF/N6-g-MAA3 in Figure 4.17(a) shows no peak for the conjugated carbonyl groups. However, in the blend of grafted PVDF with grafted Nylon 6 film, the FTIR spectrum for PVDF-g-MAA10/N6-g-MAA3 80:20 blend in Figure 4.17(b) shows the formation of a conjugated carbonyl peak at 1714 cm⁻¹ as a result of acid/amine reaction, based on the reduction of the peak height of the amine, as shown in the Table 4.6, as compared with the amine peak height of PVDF/N6-g-MAA3 80:20 blend. The extent of reaction is less than for PVDF-g-MAA10/N6-g-MAA11 80:20 blend, based on the reduction of the NH₂/CH₂ peak height ratio, which is about 60% of NH₂/CH₂ peak height ratio for PVDF/N6-g-MAA3 80:20 blend. This shows that the amount of methacrylic acid grafted to Nylon 6 is one of the factors that determines the effectiveness of interactions between the two components. With the addition of zinc cations, the size of NH₂ peak and the NH₂/CH₂ peak height ratio increases by 15% relative to peak height ratio for PVDF-g-MAA10/N6-g-MAA3 80:20 blend. At the same time the peak for conjugated carbonyl groups also disappears, indicating that no acid/amine reaction in the blend takes place in the presence of zinc cations. This presumes that compatibility between the two polymers may be decreased as a result.

The blend of PVDF with Nylon 6 film in the presence of third components i.e. 5% grafted Nylon 6 film (N6-g-MAA11) as compatibilizer is shown in the Figure 4.18.
Fig. 4.17: FTIR spectra for (a) 80%PVDF/20%N6-g-MAA3, (b) 80%PVDF-g-MAA10/20%N6-g-MAA3 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA3

Fig. 4.18: FTIR spectra for (a) 80%PVDF/15%N6/5%N6-g-MAA11, (b) 80%PVDF-g-MAA10/15%N6/5%N6-g-MAA11 and (c) 80%PVDF-g-MAA10/ZnAA(1)/15%N6/5%N6-g-MAA11
The FTIR spectrum (a) of PVDF/N6/N6-g-MAA11 80:15:5 blend does not show any interaction between the two polymers, even in the presence of 5% N6-g-MAA11, since there is no formation of either new peaks or a conjugated carbonyl peak. However, with grafted PVDF, the FTIR spectrum (b) for PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend shows some interaction between the two polymers, based on the reduction of the amine peak height and the formation of conjugated carbonyl peak, as a result of the acid/amine reaction. When compared to PVDF-g-MAA10/N6 80:20 blend, based on NH₂/CH₂ peak height ratio, it is deduced that the addition of a third component, i.e. 5% N6-g-MAA11, does not improve the interaction between the two polymers. It difficult to say whether having functionalized groups attached to the Nylon 6 films give more interactions than the case where this used as third component (i.e. as compatibiliser), although the reduction in the height of the amine peak for the PVDF-g-MAA10/N6-g-MAA3 80:20 blend is greater than for the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, since the amount of methacrylic acid in Nylon 6 phase is not quite the same in the two cases. In the case of N6-g-MAA3, the amount of methacrylic acid is 0.6% while for 5%N6-g-MAA11 added as compatibiliser, the amount is 0.55%.

When zinc cations are added to the blend, about 90% of NH₂ group in the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend do not react with acid group of grafted PVDF, based on NH₂/CH₂ peak height ratio. This shows that the zinc cations can form salts/complex with grafted PVDF more easily in this type of blend and almost totally prevents reactions between the two polymers.

4.4 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

In this section, the differential scanning calorimetry results for grafted and non-grafted polymers, the ionomerised system and PVDF/N6 blends are presented and summerised in Tables 4.7 to 4.10. These tests were carried out in order to check the effects of grafting, ionomerisation and blending on melting temperature (T_m),
heat of fusion ($\Delta H_f$), crystallization temperature ($T_c$), heat of crystallization ($\Delta H_c$) and degree of crystallinity of the polymers.

a) Thermal Analysis of Grafted, Non-Grafted and Ionomerized Polymers

The results obtained show that grafting of methacrylic acid on the backbone of the polymers has a significant effect on the thermal properties of PVDF and Nylon 6. In the case of PVDF, increasing the amount of methacrylic acid from 5% to 10%, causes a significant reduction in melting temperature ($T_m$), heat of fusion ($\Delta H_f$), heat of crystallization ($\Delta H_c$) and degree of crystallinity (\%Crys.) of PVDF (see Table 4.7). The same observation also can be made with the grafting of 11% methacrylic acid onto Nylon 6. In Figure 4.19 is shown a large reduction of the melting temperature ($T_m$), heat of fusion ($\Delta H_f$), crystallization temperature ($T_c$), heat of crystallization ($\Delta H_c$) and degree of crystallinity (\%Crys.). The effect of grafting is more pronounced for Nylon 6 than PVDF. This cannot be due simply to effects associated with hydrogen bonding between the hydrogen of N-H groups and oxygen of C=O groups from adjacent molecules that act as hydrogen acceptors, it is more likely, on the other hand, to result from chemical branching and/or crosslinking reactions which affects molecular packing (see later).

The results obtained from DSC analysis in Table 4.7 show that the thermal property of the ionomers depend on the amount of zinc cations present. For half neutralization of grafted PVDF with zinc acetyl acetonate, a small reduction in thermal property of the ionomer is observed, when compared with grafted PVDF. However, with increasing the amount of zinc cations, the thermal property of the ionomer increase to almost the value of grafted PVDF. May be that with small amounts of zinc cations in the blend, the salt formed was not evenly distributed in the matrix to reduce the overall interaction between the molecules, but with increasing the amount of zinc cations, larger amount of salts are formed and the interaction between molecules are through the ionic associations from the zinc salts. Ionomerisation of grafted Nylon 6 shows a large increase in melting
Table 4.7: DSC DATA FOR GRAFTED, NON-GRAFTED AND IONOMERIZED POLYMERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ °C</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$T_c$ °C</th>
<th>$\Delta H_c$ (J/g)</th>
<th>% Crys.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>162.5</td>
<td>65.4</td>
<td>135.3</td>
<td>53.2</td>
<td>62.5</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>222.0</td>
<td>87.6</td>
<td>182.2</td>
<td>72.6</td>
<td>45.9</td>
</tr>
<tr>
<td>PVDF-g-MAA5</td>
<td>162.4</td>
<td>64.0</td>
<td>136.4</td>
<td>49.7</td>
<td>61.2</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)</td>
<td>162.6</td>
<td>56.5</td>
<td>135.1</td>
<td>44.9</td>
<td>54.0</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)</td>
<td>161.3</td>
<td>61.9</td>
<td>136.3</td>
<td>48.6</td>
<td>59.2</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)</td>
<td>161.6</td>
<td>64.6</td>
<td>136.0</td>
<td>48.9</td>
<td>61.7</td>
</tr>
<tr>
<td>PVDF-g-MAA10</td>
<td>161.8</td>
<td>48.9</td>
<td>135.3</td>
<td>39.0</td>
<td>46.7</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)</td>
<td>160.9</td>
<td>42.1</td>
<td>134.4</td>
<td>35.0</td>
<td>40.3</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)</td>
<td>161.0</td>
<td>48.8</td>
<td>135.4</td>
<td>37.6</td>
<td>46.6</td>
</tr>
<tr>
<td>N6-g-MAA11</td>
<td>208.0</td>
<td>61.1</td>
<td>167.6</td>
<td>50.0</td>
<td>32.0</td>
</tr>
<tr>
<td>N6-g-MAA11/ZnAA(1)</td>
<td>218.8</td>
<td>62.7</td>
<td>183.2</td>
<td>54.8</td>
<td>32.9</td>
</tr>
</tbody>
</table>

(Note: The enthalpy data are normalised to 100% polymer and the crystallinity data are calculated from the heat of fusion ($\Delta H_f$))
Fig. 4.19: DSC Crystallization (top) and Melting (bottom) curves for (a) Nylon 6 homopolymer, (b) N6-g-MAA11 and (c) N6-g-MAA11/ZnAA(1)
temperature \( (T_m) \) and crystallization temperature \( (T_c) \) compared with the grafted Nylon 6, as shown in Figure 4.19, but only a small increase in heat of fusion \( (\Delta H_f) \), heat of crystallization \( (\Delta H_c) \) and degree of crystallinity \( (\% \text{Crys.}) \). The explanation for this can also be pointed to the zinc salt formation, which may prevent/reduce the extent of intermolecular reactions between COOH groups and NH\(_2\) groups (see page 63) for results from FTIR.

b) **Thermal Analysis of PVDF/N6 Blend**

Table 4.7 show that the crystallization and melting peaks of PVDF and Nylon 6 are, respectively, 47 °C and 60 °C, apart. The addition of 20% Nylon 6 to PVDF, causes a significant increase in melting temperature \( (T_m) \) of the PVDF phase and a large decrease in crystallization temperature \( (T_c) \), heat of fusion \( (\Delta H_f) \), heat of crystallization \( (\Delta H_c) \) and degree of crystallinity \( (\% \text{Crys.}) \). (Compare the data for PVDF/N6 80:20 blend in Table 4.8 with PVDF in Table 4.7) The presence of 80%PVDF in the blend however, only gives a small reduction in the melting temperature \( (T_m) \) and crystallization temperature \( (T_c) \) of Nylon 6 phase, despite the quite large reduction in crystallinity.

On the other hand, with methacrylic acid grafted to PVDF, for example PVDF-g-MAA10/N6 80:20 blend, there is a large reduction in melting temperature \( (T_m) \) and degree of crystallinity \( (\% \text{Crys.}) \) of the PVDF phase with a significant increase in crystallization temperature \( (T_c) \). (Compare with PVDF/N6 80:20 blend Figure 4.20) With respect to the thermal properties of PVDF-g-MAA10 (in Table 4.7), the addition of 20% Nylon 6 increases the melting temperature \( (T_m) \) and heat of crystallization \( (\Delta H_c) \), but reduces the crystallization temperature \( (T_c) \), heat of fusion \( (\Delta H_f) \) and also degree of crystallinity. The major effect, however, is on the thermal properties of the Nylon 6 phase. With 5% and 10% methacrylic acid in the grafted PVDF, the melting temperature \( (T_m) \) of Nylon 6 decreases by almost 16 °C and 30 °C, respectively (Table 4.8 and Figure 4.20). This is accompanied by a reduction in degree of crystallinity from 29% to 19% and 6% respectively, as a
### Table 4.8: DSC DATA FOR GRAFTED, NON-GRAFTED POLYMERS IN PVDF/NYLON 6 BLEND

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PVDF PHASE</th>
<th></th>
<th>NYLON 6 PHASE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ °C</td>
<td>$\Delta H_r$ (J/g)</td>
<td>$T_c$ °C</td>
<td>$\Delta H_c$ (J/g)</td>
</tr>
<tr>
<td>80PVDF/20N6</td>
<td>165.3</td>
<td>53.7</td>
<td>127.7</td>
<td>44.2</td>
</tr>
<tr>
<td>80PVDF-g-MAA5/20N6</td>
<td>162.7</td>
<td>52.0</td>
<td>131.4</td>
<td>44.5</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6</td>
<td>163.3</td>
<td>33.1</td>
<td>131.9</td>
<td>45.9</td>
</tr>
<tr>
<td>80PVDF/20N6-g-MAA11</td>
<td>162.3</td>
<td>45.3</td>
<td>132.9</td>
<td>38.4</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA11</td>
<td>161.7</td>
<td>50.3</td>
<td>130.3</td>
<td>36.2</td>
</tr>
<tr>
<td>20PVDF/80N6</td>
<td>160.5</td>
<td>26.9</td>
<td>119.9</td>
<td>44.9</td>
</tr>
<tr>
<td>20PVDF-g-MAA5/80N6</td>
<td>158.9</td>
<td>17.4</td>
<td>123.8</td>
<td>28.3</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/80N6</td>
<td>159.9</td>
<td>18.7</td>
<td>130.4</td>
<td>20.0</td>
</tr>
<tr>
<td>20PVDF/80N6-g-MAA11</td>
<td>161.8</td>
<td>12.0</td>
<td>130.6</td>
<td>23.1</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/80N6-g-MAA11</td>
<td>161.8</td>
<td>19.9</td>
<td>116.5</td>
<td>23.4</td>
</tr>
</tbody>
</table>

(Note: The enthalpy data are normalised to 100% polymer and the crystallinity data are calculated from the heat of fusion ($\Delta H_c$))
Fig. 4.20: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF/20%N6, (b) 80%PVDF-g-MAA5/20%N6 and
(c) 80%PVDF-g-MAA10/20%N6
result of the reduction in heat of fusion ($\Delta H_f$) from 56 J/g to 37 J/g and 12 J/g. The effect of 5% methacrylic acid in grafted PVDF can also be seen in the crystallization temperature ($T_c$) and heat of crystallization ($\Delta H_c$) of the Nylon phase, which reduces from 181 °C to 144 °C and from 56 J/g to 20 J/g, respectively (Table 4.8). A further increase in the amount of grafted methacrylic acid to 10%, the melting peak of the Nylon disappears as shown in Figure 4.20, which indicates that Nylon does not crystallize during the cooling process and does not diffuse out of the PVDF matrix. The depression of melting and crystallization temperatures of the Nylon 6 phase indicates the existence of interactions between the two components with a formation of a (partially) miscible blend. This interaction increases with increasing the amount of methacrylic acid in the blend.

When Nylon 6 is the major phase, the addition of 20% PVDF to Nylon 6 does not affect the $T_m$ of the Nylon, but causes a reduction in the heat of fusion ($\Delta H_f$) and degree of crystallinity. However, for blends of Nylon 6 with 20% grafted PVDF, there is a significant reduction in melting temperature ($T_m$) of the Nylon 6 phase but an increase in crystallization temperature ($T_c$). This trend continues with increasing the amount of methacrylic acid, as shown in Table 4.8. Although there is less than 2% methacrylic acid, in the blend of 20% grafted PVDF with 80% Nylon 6, the results in Table 4.8 show a significant effect on Nylon 6 thermal properties i.e. heat of fusion ($\Delta H_f$), heat of crystallization ($\Delta H_c$) and degree of crystallinity, when compared with PVDF/N6 20:80 blend. Since there is only 20% grafted grafted PVDF in the blend, the interactions between N6 and PVDF are diluted and the effect on the thermal property of N6 is consequently small.

The effect of Nylon 6 on the thermal property of PVDF/N6 20:80 blend can be seen from the large reduction in crystallization temperature ($T_c$), heat of fusion ($\Delta H_f$) and degree of crystallinity of the PVDF phase, accompanied by a significant decrease in melting temperature ($T_m$). However, for the blend of Nylon 6 with grafted PVDF, i.e. PVDF-g-MAA5/N6 20:80, there is a significant reduction in melting temperature of the PVDF phase and an increase in crystallization temperature, as compared to the PVDF/N6 20:80 blend. With increasing the
amount of methacrylic acid, there is an increase in melting and crystallization temperature of the PVDF phase in the PVDF-g-MAA10/N6 20:80 blend. When compared with the melting and crystallization temperatures of grafted PVDF in Table 4.7, it is deduced that the reduction in both temperatures are caused by the interaction of grafted PVDF with Nylon 6.

For the PVDF/N6-g-MAA11 80:20 blend, the addition of 20% grafted Nylon 6 increases the crystallization temperature ($T_C$) but reduces the melting temperature ($T_m$), heat of fusion ($\Delta H_f$), heat of crystallization ($\Delta H_c$) and degree of crystallinity ($\%\text{Crys.}$) of the PVDF phase, when compared with the PVDF/N6 80:20 blend. Although the crystallization temperature ($T_C$) increases, it is still lower than the crystallization temperature ($T_C$) of the homopolymer PVDF by itself. For the Nylon 6 phase, the results in Table 4.8 show an increase in melting and crystallization temperatures, compared with N6-g-MAA11 in Table 4.7. Since there is no depression in melting temperature for both phases compared with the polymers by themselves, PVDF/N6-g-MAA11 is considered to be an immiscible blend. However, in the PVDF-g-MAA10/N6-g-MAA11 80:20 blend, the melting temperature ($T_m$), crystallization temperature ($T_C$) and heat of crystallization ($\Delta H_c$) of the PVDF phase decrease, although there is an increase in degree of crystallinity, compared with PVDF/N6-g-MAA11 80:20 and PVDF-g-MAA10/N6 80:20 blends (Table 4.8). For the PVDF-g-MAA10/N6-g-MAA11 80:20 blend in Figure 4.21 is observed the disappearance of the crystallization and melting peaks of the Nylon 6, which means that a crystalline phase for the Nylon 6 does not exist in the blend, due to strong interactions between the two components. This is proved also by the FTIR analysis in Figure 4.14(c), which shows the formation of conjugated C=O peak and a reduction of the amine peak. The two components are more miscible, compared with the PVDF-g-MAA10/N6 80:20 blend, where the crystalline phase of Nylon 6 still exist (Figure 4.20).

For the PVDF/N6-g-MAA11 20:80 blend, the addition of PVDF does not affect the melting and crystallization temperatures of the Nylon 6 phase, as compared with grafted Nylon 6 by itself, but there is a small reduction in melting and
Fig. 4.21: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF/20%N6, (b) 80%PVDF/20%N6-g-MAA11 and
(c) 80%PVDF-g-MAA10/20%N6-g-MAA11
crystallization temperatures of the PVDF phase. This reduction in thermal properties of the PVDF phase is caused by the diffusion of the dispersed phase into the matrix. When both components are grafted polymers, e.g. PVDF-g-MAA10/N6-g-MAA11 20:80 blend, there is a further reduction in melting and crystallization temperatures of the Nylon 6 phase and a large reduction in the crystallization temperature (T_c) of the PVDF phase as shown in Figure 4.22. The data in Table 4.8 show that the PVDF-g-MAA10/N6-g-MAA11 20:80 blend is more miscible than the PVDF-g-MAA10/N6 20:80 blend, judged from the large reduction in thermal properties of the Nylon 6 phase, due to the former blend having more methacrylic acid in the blend.

c) Thermal Analysis of Ionomerised PVDF/N6 Blends

Table 4.9 shows the effect of the addition of zinc acetyl acetonate to the blend. The presence of zinc cations in the PVDF-g-MAA5/N6 80:20 blend, increases the melting and crystallization temperatures and also the crystallinity of the Nylon 6 phase. The crystallization temperature increases further with increasing the amount of zinc cations. At first, the melting temperature of the PVDF phase increases with the addition of zinc cations but decreases with higher amounts of zinc cations. However, the effect of zinc cations on the crystallization temperature of the PVDF is the opposite. In the PVDF-g-MAA10/N6 80:20 blend, the addition of zinc cations increase the melting temperature (T_m) of the Nylon 6 phase and the crystallization peak of the Nylon 6, which does not exist in the PVDF-g-MAA10/N6 80:20 blend, becomes more prominent, as shown in Figure 4.23. The melting temperature (T_m) of the Nylon 6 phase in the PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend is almost the same as in PVDF/N6 80:20 blend. It shows that the salt formation between acid groups and zinc cations, which has been proved from FTIR analysis in Figure 4.11, prevents the occurrence of interactions between two components and allows the Nylon phase to crystallize.

81
Fig. 4:22: DSC Crystallization (top) and Melting (bottom) curves for
(a) 20%PVDF/80%N6, (b) 20%PVDF/80%N6-g-MAA11 and
(c) 20%PVDF-g-MAA10/80%N6-g-MAA11
Fig. 4.23: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF-g-MAA10/20%N6,
(b) 80%PVDF-g-MAA10/ZnAA(0.5)/20%N6 and
(c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6.
An excess of zinc cations in the blend will prevent completely the acid/amine reaction. The same behaviour is observed for the ionomerisation of PVDF-g-MAA10/N6-g-MAA11 80:20 blend with zinc acetyl acetonate. Figure 4.24 shows the reappearance of crystallization and melting peaks of Nylon 6 by the addition of zinc cations in the blend. It shows that the crystalline Nylon 6 phase is reformed as a result of the salt formation from zinc cations and the acid groups of the grafted PVDF, which prevents the interaction between two polymer components. For the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, the crystallization temperature (Tc) of Nylon 6 is reduced further with increasing the amount of zinc cations, as shown in Table 4.9. There is a possibility that some of the zinc cations also react with acid groups of grafted Nylon 6 and the salts formed within the Nylon phase will affect the process of crystallization of Nylon, causing it to crystallize at lower temperatures.

However, when Nylon 6 is the major phase, the effect of zinc cations on the thermal property of the individual phases in the blend is not so significant even with increasing the amount of zinc cations in the blend. It may be that this is due to amount of zinc cations being very small, since the overall amount of methacrylic acid present is less than 2%. In blends where both components are grafted polymers, the addition of zinc cations e.g. PVDF-g-MAA10/N6-g-MAA11, gives significant effect on the thermal property of both components, as shown in Table 4.9. The melting temperature (Tm) of the PVDF phase is reduced while the crystallization temperature (Tc) is increased. The addition of zinc cations however, increases the thermal property of the Nylon 6 phase (Table 4.8). It seems that the effect on melting and crystallization temperatures of the PVDF phase is caused by the existence of acid groups in grafted Nylon 6 and there is a possibility that zinc cations will also react with this group. This could be the cause for the PVDF phase to crystallize at high temperature, due to nucleation effects.
Fig. 4.24: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF-g-MAA10/20%N6-g-MAA11,
(b) 80%PVDF-g-MAA10/ZnAA(0.5)/20%N6-g-MAA11 and
(c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA11

Table 4.9: DSC DATA FOR IONOMERIZED PVDF/N6 80:20 BLEND

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PVDF PHASE</th>
<th>NYLON 6 PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ °C</td>
<td>$\Delta H_f$ (J/g)</td>
</tr>
<tr>
<td>80PVDF-g-MAA5/ZnAA(0.5)/20N6</td>
<td>164.7</td>
<td>58.6</td>
</tr>
<tr>
<td>80PVDF-g-MAA5/ZnAA(1)/20N6</td>
<td>164.1</td>
<td>46.7</td>
</tr>
<tr>
<td>80PVDF-g-MAA5/ZnAA(1.5)/20N6</td>
<td>161.9</td>
<td>45.2</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(0.5)/20N6</td>
<td>161.4</td>
<td>38.6</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6</td>
<td>163.4</td>
<td>45.1</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(0.5)/20N6-g-MAA11</td>
<td>164.1</td>
<td>40.0</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA11</td>
<td>164.6</td>
<td>46.0</td>
</tr>
<tr>
<td>20PVDF-g-MAA5/ZnAA(0.5)/80N6</td>
<td>159.9</td>
<td>21.0</td>
</tr>
<tr>
<td>20PVDF-g-MAA5/ZnAA(1)/80N6</td>
<td>159.1</td>
<td>23.5</td>
</tr>
<tr>
<td>20PVDF-g-MAA5/ZnAA(1.5)/80N6</td>
<td>159.0</td>
<td>20.8</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/ZnAA(1)/80N6</td>
<td>159.1</td>
<td>21.0</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/ZnAA(1)/80N6-g-MAA11</td>
<td>157.0</td>
<td>16.2</td>
</tr>
</tbody>
</table>

(Note: The enthalpy data are normalised to 100% polymer and the crystallinity data are calculated from the heat of fusion ($\Delta H_f$). Figures in brackets represent the molar fractions of cations used to the maximum required for full neutralization.)
d) **Thermal Analysis of PVDF/N6 Film Blend**

This section presents the result of PVDF blends with Nylon 6 film and the effect of using grafted Nylon 6 film as compatibiliser. Table 4.10 shows that the addition of 20% grafted Nylon 6 film (N6-g-MAA3) to PVDF gives the same effect as the addition of 20% grafted Nylon 6 granule (N6-g-MAA11) (see Table 4.8) on the thermal properties of the PVDF phase, i.e. a reduction in the crystallization temperature ($T_c$), compared with PVDF by itself. This suggests that 3% methacrylic acid grafted to Nylon 6 film does not have much effect on the thermal properties of Nylon 6, as compared with 11% methacrylic acid grafted to Nylon 6 granule. This can be seen clearly when the results for PVDF/N6-g-MAA3 80:20 in Table 4.10 and PVDF/N6-g-MAA11 80:20 blend are compared with those for PVDF/N6 80:20 blend in Table 4.8. The only exception is the crystallization temperature ($T_c$) of the Nylon 6 phase in PVDF/N6-g-MAA3 80:20 blend, which increases significantly to 188 °C as compared to PVDF/N6-g-MAA11 80:20 blend which decreases to 178 °C from 181 °C for PVDF/N6 80:20 blend. It is shown that the amount of methacrylic acid grafted to Nylon 6 influences the way Nylon crystallizes in the blend.

The presence of 10% grafted methacrylic acid on PVDF, e.g. PVDF-g-MAA10/N6-g-MAA3 80:20 blend, shows a significant reduction in crystallization temperature ($T_c$) but increases the melting temperature ($T_m$) of the PVDF phase, as compared with the PVDF/N6-g-MAA3 80:20 blend. Figure 4.25 shows that the melting and crystallization peaks of Nylon 6 disappear, indicating that a crystalline phase of Nylon 6 does not exist in PVDF-g-MAA10/N6-g-MAA3 80:20 blend. With the addition of zinc acetyl acetonate to the blend, the melting and crystallization peaks of Nylon 6 reappeared, as shown in Figure 4.25. The thermogram shows that zinc cations have an effect on the reaction between two components by forming a salt with acid group of grafted PVDF, preventing the reaction with the amine groups of the Nylon 6 phase. However, the crystallization temperature ($T_c$) of the Nylon 6 phase in PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3
Table 4.10: DSC DATA OF PVDF/GRAFTED NYLON 6 FILM BLEND

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PVDF PHASE</th>
<th>NYLON 6 PHASE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m$ °C</td>
<td>$\Delta H_r$ (J/g)</td>
</tr>
<tr>
<td>80PVDF/20N6-g-MAA3</td>
<td>163.1</td>
<td>46.3</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA3</td>
<td>164.9</td>
<td>41.4</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA3</td>
<td>165.2</td>
<td>40.0</td>
</tr>
<tr>
<td>80PVDF/15N6/5N6-g-MAA11</td>
<td>164.4</td>
<td>44.0</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/15N6/5N6-g-MAA11</td>
<td>164.4</td>
<td>45.6</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/15N6/5N6-g-MAA11</td>
<td>165.0</td>
<td>39.2</td>
</tr>
</tbody>
</table>

(Note: The enthalpy data are normalised to 100% polymer and the crystallinity data are calculated from the heat of fusion ($\Delta H_f$))
Fig. 4.25: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF/20%N6-g-MAA3,
b) 80%PVDF-g-MAA10/20%N6-g-MAA3 and
c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA3
80:20 blend is lower than the crystallization temperature ($T_c$) of PVDF/N6-g-MAA3 80:20 blend. There is a possibility that some of zinc cations also react with acid groups of the grafted Nylon 6 phase and causes the Nylon phase to crystallize at a lower temperature. The melting and crystallization temperatures of PVDF phase increase as a result of the zinc salt formation (Table 4.10).

With addition of 5% N6-g-MAA11 as compatibilizer to PVDF/N6 80:15 blend, the melting temperature ($T_m$), heat of fusion ($\Delta H_f$), heat of crystallization ($\Delta H_c$) and degree of crystallinity of both components is decreased, but there is an increase in the temperature of crystallization ($T_c$) when compared with the PVDF/N6 80:20 blend, Tables 4.8 and 4.10. The blend with grafted PVDF, PVDF-g-MAA10/N6/6-g-MAA11 80:15:5 becomes a miscible blend, i.e. it shows only one melting and one crystallization peak corresponding to the PVDF phase (Spectrum (b) Figure 4.26, which can be compared with spectrum (c) in Fig. 4.20). Based only on DSC results it is not possible to determine whether the addition of third components, as compatibilizer, produces a different level of miscibility than the in-situ graft copolymer produced in blends of functionalized polymers.

The presence of zinc cations in the blend, was found to reduce the level of miscibility, giving rise to the formation of two melting peaks and two crystallization peaks as shown in Figure 4.26.

4.5 DYNAMIC MECHANICAL THERMAL ANALYSIS

The dynamic mechanical thermal analysis is widely used to relate the miscibility of the components to the molecular structure and transitions of the blend components.

a) High Temperature Transition of Nylon 6 and PVDF

The dynamic mechanical spectra in Figure 4.27 show that Nylon 6 has a main transition at about 50 °C and a small one at about 80 °C. The addition of zinc
Fig. 4.26: DSC Crystallization (top) and Melting (bottom) curves for
(a) 80%PVDF/15%N6/5%N6-g-MAA11,
(b) 80%PVDF-g-MAA10/15%N6/5%N6-g-MAA11 and
(c) 80%PVDF-g-MAA10/ZnAA(1)/15%N6/5%N6-g-MAA11
acetyl acetonate lowers the main transition to about 37 °C and increases the magnitude of the transition at about 80 °C. When Nylon 6 is grafted with 11% methacrylic acid, the DMTA spectrum shows only one very large (glass) transition at about 70 °C, which could be due to crosslinking effects within the polymer itself. Ionomerisation of grafted Nylon 6 with zinc acetyl acetonate reduces this transition to about 40 °C (i.e. somewhat higher than the N6/ZnAA) and gives a broad and large transition, starting at 80 °C going to above 100 °C.

Dynamic mechanical spectra of PVDF reveal a main transition at about -20 °C and large transition starting at about 40 °C going up to 100 °C. The presence of methacrylic acid grafts in the PVDF domains, (Figure 4.28) reduces the level of relaxation at -20 °C, it emphasizes the shoulder at 80 °C and lower level of damping at higher temperature. Ionomerisation of grafted PVDF with zinc cations reduce the shoulder and sharpens the high temperature transition.

b) **High Temperature Transition of PVDF/N6 Blend**

Figure 4.29 shows that the PVDF/N6 80:20 blend is dominated by the PVDF response, but an increase in dispersions (level of relaxation) at high temperatures could be due to interactions. The level of relaxation at $T_g$ of the PVDF phase is reduced but $T_g$ value remains the same. However, for the PVDF/N6 20:80 blend, Figure. 4.29 shows that $T_g$ of the Nylon 6 phase is reduced from 50 °C to 25 °C giving strong evidence for a large degree of plasticisation of the amorphous phases of the two polymers.

The DMTA spectrum of PVDF-g-MAA10/N6 80:20 blend in Figure 4.30 shows a very large and broad peak at 80 °C. In other words, the shifting of the tan δ peak to a lower temperature for the PVDF/Nylon 6 blend may be due to the solubilisation of Nylon 6 in the PVDF matrix. Figure 4.31 shows that PVDF-g-MAA10/N6 20:80 blend is dominated by the Nylon spectrum with $T_g$ of Nylon remaining at around 50 °C, but with greater dispersions, is probably due to some crosslinking of the amorphous Nylon.
Fig. 4.27: DMTA spectra of (a) Nylon 6, (b) N6/ZnAA, (c) N6-g-MAA11 and (d) N6-g-MAA11/ZnAA(1)

Fig. 4.28: DMTA spectra of (a) PVDF, (b) PVDF-g-MAA10 and (c) PVDF-g-MAA10/ZnAA(1)
Fig. 4.29: DMTA spectra of (a) PVDF, (b) Nylon 6, (c) 80%PVDF/20%N6 and (d) 20%PVDF/80%N6.

Fig. 4.30: DMTA spectra of (a) 80%PVDF/20%N6, (b) 80%PVDF-g-MAA10/20%N6 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6.
From the above observation, it can be deduced that the reduction in T_g of the Nylon 6 phase by the solubilisation of PVDF is counteracted by an increase in T_g of the Nylon 6 due to cross-linking induced by reactions with -COOH groups.

Ionomerisation of PVDF-g-MAA10/N6 80:20 with zinc acetyl acetonate gives a large depression of the high temperature peak, as shown by curve (c) in Figure 4.30. This may be due to the suppression of relaxations associated with the reaction of acid groups of PVDF grafts with Nylon 6. However, in the blend of 20PVDF-g-MAA10/ZnAA(1)/80N6, Figure 4.31 shows a similar trend to the equivalent blend at 20:80 ratio PVDF/N6, i.e. T_g of Nylon 6 is lowered slightly due to Zn cations (i.e. peak at 45 °C), but much less than in the absence of acid graft. This shows that, the solubility of PVDF in Nylon 6 is reduced and also confirms the reduction in the extent of reactions between -COOH groups and Nylon.

For the PVDF/N6-g-MAA11 80:20 blend, Figure 4.32 shows a very large depression of the height of PVDF relaxations from about 80 °C onwards. It may be due to solubilisation of Nylon 6 in PVDF in comparison to the equivalent 80:20 blend where Nylon 6 has not be grafted, giving strong interactions between -COOH groups in Nylon 6 and PVDF chain. However, with PVDF-g-MAA10/N6-g-MAA11 80:20 blend, there is a large increase in the PVDF dispersion with a wide peak at 60 °C to 80 °C, similar to the PVDF-g-MAA10/N6 80:20 blend. With the addition of zinc cations to the blend there is a large depression in the relaxation of the PVDF phase due to the Nylon 6 grafts.

c) High Temperature Transition of PVDF Blend with Nylon 6 Film

In Figure 4.33, the blend of PVDF with grafted Nylon 6 film (N6-g-MAA3) in the ratio 80:20 show a similar trend to PVDF/N6 80:20 blend, where Nylon 6 was used from granules, but the level of relaxation is much higher, indicating the occurrence of stronger interaction due to -COOH groups in the grafted Nylon 6 film. With the blend of PVDF-g-MAA10/N6-g-MAA3, again a similar type of spectrum was observed, as compared with PVDF-g-MAA10/N6-g-MAA11 80:20,
Fig. 4.31: DMTA spectra for (a) 20%PVDF/80%N6, (b) 20%PVDF-gMAA10/80%N6 and (c) 20%PVDF-g-MAA10/ZnAA(1)/80%N6.

Fig. 4.32: DMTA spectra for (a) 80%PVDF/20%N6-g-MAA11, (b) 80%PVDF-g-MAA10/20%N6-g-MAA11 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA11.
but a sharper transition ($T_g$) at about 75 °C is apparent. Also similar type depression is produced when zinc cations are added to the blend. With addition of 5% grafted Nylon 6 to the PVDF/N6 80:15 blend, again the same type of observation can be made when compared with the PVDF/N6 80:20 blend. However the blend PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 shows a large increase in the PVDF dispersion with sharp $T_g$ peak at 60 °C, Figure 4.34. Addition of zinc cations to the blend depresses the dispersion of PVDF as with the non grafted PVDF blend.

4.6 PHASE MORPHOLOGY OF BLENDS

Scanning electron microscopy was used to study the morphology of the grafted polymers, ionomerised polymers and various PVDF/N6 blends.

a) Phase Morphology of Grafted and Ionomerised Polymers

SEM micrograph in Figure 4.35 reveals that the size of the PVDF powder is about 4 μm and it comprises a large number of much smaller particles (about 0.2 μm) which indicate that the PVDF powder was produced by emulsion polymerisation process. The micrograph of grafted PVDF powder suggests that grafting takes place both on the surface and in the bulk of the powder. No homopolymerisation takes place within the space between primary particles as there is no indication of clogging of the interparticle pores. Figure 4.36 shows that after melt mixing the grafted PVDF produced fine dispersed particles in the PVDF matrix, and that the size of dispersed particles increases with increasing the amount of methacrylic acid in the grafted polymer. It is expected that such precipitated particles are formed during the melt mixing operation to prepare the plaques. Neutralization of the acid group with zinc acetyl acetonate breaks up the diffused particles and appears to solubilise them into the PVDF.

97
Fig. 4.33 DMTA spectra for (a) 80%PVDF/20%N6-g-MAA3,
(b) 80%PVDF-g-MAA10/20%N6-g-MAA3 and
(c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA3

Fig. 4.34 DMTA spectra for (a) 80%PVDF/15%N6/5%N6-g-MAA11,
(b) 80%PVDF-g-MAA10/15%N6/5%N6-g-MAA11 and
(c) 80%PVDF-g-MAA10/ZnAA(1)/15%N6/5%N6-g-MAA11
Fig. 4.35: Scanning electron micrograph obtained from powder and cryogenically fractured samples; (a) PVDF powder, (b) Grafted PVDF powder, (c) N6-g-MAA11 granule cross-section and (d) N6-g-MAA11 depth of grafting penetration
Fig. 4.36: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) PVDF, (b) PVDF-g-MAA5, (c) PVDF-g-MAA10 and (d) PVDF-g-MAA10/ZnAA(1)
SEM micrographs of the cross section of Nylon 6 granule, SEM Figure 4.35, show that grafting of methacrylic acid only takes place on the surface and the depth of grafting penetration is about 12 μm. Micrographs of grafted Nylon after mixing and pressing into plaques shows a single homogeneous phase (Figure 4.37). No substantial differences in the morphology of the Nylon samples are observed after grafting and also after subsequent ionomerisation.

b) Phase Morphology of PVDF/Nylon 6 Blends

The effects of grafting PVDF, Nylon 6 with methacrylic acid and subsequent ionomerisation on the microstructure of PVDF/N6 blend are shown in Figures. 4.38 to 4.41. Micrograph (a) in Figure 4.38 shows a very coarse dispersed phase of Nylon in the PVDF/N6 80:20 blend, i.e. particle size about 5 μm. This clearly shows that PVDF and Nylon 6 are not compatible due to the poor adhesion between two phases. However, with 5% methacrylic acid grafted onto PVDF, i.e. PVDF-g-MAA5/N6 80:20 blend there is a reduction in particle size of the dispersed phase and improved adhesion between phases (micrograph b) even though the level of compatibility is still low. Increasing to 10% methacrylic acid grafting to PVDF, i.e. PVDF-g-MAA10/N6 80:20 blend, the system appears to be almost homogenous with only a few dispersed particles which are less than 1 μm in size (micrograph c). When zinc acetyl acetonate is added to the blend, i.e. PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend, the structure appears to be heterogenous with very small particles dispersed in the matrix (micrograph d). The two phases with very fine domains, however, appears to be co-continuous. The reaction of zinc cations with acid groups in the grafted PVDF prevents the acid groups from reacting with the amine groups of Nylon 6, as shown by FTIR spectra in Figure 4.15(b).

The micrograph for PVDF/N6-g-MAA11 80:20 blend in Figure 4.39 (a) shows that the system is immiscible and the particle sizes of dispersed phase is nearly the
Figure 4.37: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) Nylon 6, (b) N6-g-MAA11 and (c) N6-g-MAA11/ZnAA(1)
Fig. 4.38: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) 80%PVDF/20%N6, (b) 80%PVDF-g-MAA5/20%N6, (c) 80%PVDF-g-MAA10/20% N6 and (d) 80%PVDF-g-MAA10/ZnAA(1)/20%N6
same as in the PVDF/N6 80:20 blend in Figure 4.38(a). However, when both components are grafted polymers (micrograph b), PVDF-g-MAA10/N6-g-MAA11 80:20 blend, the system is almost miscible, with very fine particles of dispersed phase. The DSC thermogram in Figure 4.21 confirmed the occurrence of strong interaction between the two components by the disappearance of melting and crystallization peaks of Nylon 6. Ionomerization of grafted PVDF with zinc acetylacetone appears to form a more homogenous phase. Both at half and full neutralization, the SEM micrograph of Figure 4.39 shows the disappearance of the dispersed phase even though DSC trace in Figure 4.24(b) shows small peaks which reveal the existence of a dispersed phase of grafted Nylon 6.

The phase morphology for various PVDF/N6 20:80 blends in Figures 4.40 and 4.41 shows the effect of grafted PVDF, grafted Nylon 6 and zinc cations on the microstructure of the blends. Figure 4.40 micrograph (a) for PVDF/N6 20:80 blend shows a very coarse dispersed phase of PVDF particles with particle size about 1-2 μm in the Nylon 6 matrix. However, the blend of Nylon 6 with grafted PVDF shows a significant decrease in particle size of the dispersed phase. Both micrographs (b and c) reveal a quite good adhesion between the particles of dispersed PVDF phase and matrix of Nylon 6. Previous data (FTIR) shown that ionomerization of grafted PVDF with zinc cations will lead to the formation of metal salt and prevents the reaction the two components. Despite this, the micrograph (d) in Figure 4.40 shows that the dispersed particles of PVDF have disappeared and the system is quite homogenous, with a very strong adhesion between the phase.

For the PVDF/N6-g-MAA11 20:80 blend, the SEM micrograph in Figure 4.41 shows a fine morphology of co-continuous phases. DSC analysis of this blend, indicates the presence of two distract phases, eventhough there is a small shift of the thermal peaks to the lower temperatures when compared with the PVDF/N6 20:80 blend. However when both components consist of grafted polymers, (micrograph b) Figure 4.41 i.e. PVDF-g-MAA10/N6-g-MAA11 20:80 blend, there appears to be a coarsening of the morphology. The DSC analysis (Figure 4.22c),
Fig. 4.39: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) 80%PVDF/20%N6-g-MAA11,
(b) 80%PVDF-g-MAA10/20%N6-g-MAA11,
(c) 80%PVDF-g-MAA10/ZnAA(0.5)/20%N6-g-MAA11 and
(d) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA11,
Fig. 4.40: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) 20%PVDF/80%N6, (b) 20%PVDF-g-MAA5/80%N6, (c) 20%PVDF-g-MAAI0/80%N6 and (d) 20%PVDF-g-MAAI0/ZnAA(1)/80%N6
Fig. 4.41: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples; (a) 20%PVDF/80%N6-g-MAA11, (b) 20%PVDF-g-MAA10/80%N6-g-MAA11 and (c) 20%PVDF-g-MAA10/ZnAA(1)/80%N6-g-MAA11
on the other hand, shows a depression of the melting point and a reduction of the crystallization temperature for the Nylon phase when compared PVDF/N6-g-MAA11 20:80 blend Figure 4.22(b). For the ionomerised grafted PVDF/grafted Nylon blend there appears a further desolubilisation of the dispersed PVDF phase, as indicated by the presence of small particles protruding from the surface of the matrix, as shown in Figure 4.41 micrograph (c).

c) Phase Morphology of Grafted Nylon 6 Film

Scanning electron microscopy was used to investigate the morphology of Nylon 6 film with a thickness about 20 μm after grafting with methacrylic acid. A cross-section of grafted Nylon 6 film (N6-g-MAA3) containing 3% methacrylic acid (Figure 4.42(b)) reveals a uniform morphology through the thickness. With increasing the amount of methacrylic acid grafted onto the Nylon 6 film, N6-g-MAA11 in micrograph (c) there appears to be the formation of fine particles within the bulk of the film. At higher magnification, N6-g-MAA3 morphology in micrograph (d) reveals the non-homogenous distribution of grafted Nylon 6 domains in the bulk. These suggest that areas of high concentration of grafted polymer is formed within a less grafted matrix.

d) Phase Morphology of PVDF/Nylon 6 Film Blend

In Figures 4.43 and 4.44 are shown the phase morphology for the PVDF/N6 film blend and those containing 5% N6-g-MAA11 film as compatibiliser.

In the blend of PVDF with grafted Nylon 6 film, Figure 4.43 micrograph (a) for PVDF/N6-g-MAA3 80:20 blend shows a coarse dispersed phase of grafted Nylon 6 particles about 1-3 μm in diameter. This indicates that the two components are not miscible. The DSC thermogram in Figure 4.25(a) confirms the lack of miscibility with the existence of melting and crystallization peaks in the same position as the components in isolation, Figure 4.19(a). However, for blends of
Fig. 4.42: Scanning electron micrograph obtained from cryogenically fractured samples; (a) Nylon 6 film cast, (b) 3% grafted Nylon 6 film (N6-g-MAA3), (c) 11% grafted Nylon 6 film (N6-g-MAA11) and (d) N6-g-MAA3 at higher magnification.
Fig. 4.43: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples for blends obtained from grafted nylon films; (a) 80%PVDF/20%N6-g-MAA3, (b) 80%PVDF-g-MAA10/20%N6-g-MAA3 and (c) 80%PVDF-g-MAA10/ZnAA(1)/20%N6-g-MAA3
grafted PVDF with grafted Nylon 6 film, PVDF-g-MAA10/N6-g-MAA3 80:20 blend, there is a large reduction in particle size of the dispersed phase. This indicates the occurrence of interactions between the two components, especially between acid groups of grafted PVDF and amine groups of Nylon, which is also shown by FTIR spectra in Figure 4.17(b). With addition of zinc acetyl acetonate in the system, the phase morphology of PVDF-g-MAA10/ZnAA(I)/N6-g-MAA3 80:20 blend, (Figure 4.43 c) appears to have become somewhat coarser.

With the addition of 5% N6-g-MAA11 to PVDF/N6 80:15 blend, the Nylon 6 particles, in this case the dispersed phase, can easily diffuse into the PVDF matrix (see Figure 4.44 micrograph (a) and compare with PVDF/N6-g-MAA3 80:20 and PVDF/N6-g-MAA11 80:20 blends in Figures 4.43(a) and 4.39(a), respectively).

Even though the SEM micrograph reveals a fairly homogenous morphology, the DSC thermogram in Figure 4.26(a) shows the existence of melting and crystallization peaks for both components without changes in the position of the peaks. Futhermore, FTIR spectra in Figure 4.18(a) do not give supporting evidence for the reduction in the absorbance of amine groups of the Nylon 6 resulting from reactions with the grafted acid groups. It is possible, however, that the FTIR technique used is not sufficiently sensitive to detect the small reduction in terminal amine groups and that an appreciable amount of branching may have resulted through reactions between the acid groups in the compatibiliser and the amine groups of the non-modified Nylon. The apparent compatibilisation indicated by micrograph (a) in Figure 4.44 is a manifestation of the co-continuity of phases, which may have resulted from a better match in rheological behaviour of the two components (see later).

When grafted PVDF was used in the blend, micrograph (b) Figure 4.44 for PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, an almost miscible type of blend appears to have resulted, although it may be that the two phases are very fine and interconnected. Note that the DSC thermogram in Figure 4.26(b) shows the disappearance of the melting and crystallization transition of the Nylon 6 phase but without affecting the melting transition of the PVDF phase. The reduction of
Fig. 4.44: Scanning electron micrograph obtained from cryogenically fractured compression moulded samples for blends produced from grafted Nylon 6 films: (a) 80%PVDF/15%N6/5%N6-g-MAA11, (b) 80%PVDF-g-MAA10/15%N6/5%N6-g-MAA11 and (c) 80%PVDF-g-MAA10/ZnAA(1)/15%N6/5%N6-g-MAA11
absorbance peaks at 3300 cm\(^{-1}\) of the amine groups of Nylon 6 from the FTIR spectrum in Figure 4.18(b) confirmed the occurrence of reactions between the two phases (compare with the FTIR spectrum in Figure 4.18(a) of PVDF/N6/N6-g-MAA11 80:15:5 blend). The presence of zinc cations through ionomerisation of the grafted PVDF by the addition of zinc acetyl acetonate gives rise to a heterogeneous phase morphology with very fine particles of the dispersed phase, Figure 4.44 micrograph (c). Interaction of zinc acetyl acetonate with acid groups of grafted PVDF produces carboxylate salts which prevent the reaction of acid groups in grafted PVDF with amine groups in Nylon 6. Nevertheless, the degree of compatibility of such blend is far better than that exhibited by blends of unmodified polymers. Hence, interactions between the two components are expected to have occurred.

4.7 EXTRACTION TESTS

Extraction tests were carried out in order to find additional supportive evidence for interactions between the two components and to determine the extent of interaction.

a) **Treatments with Boiling Water**

The purpose of treating the samples with boiling water was to study the diffusion of water into the material, which is related to phase morphology. Figure 4.45 shows that Nylon 6 absorbs about 10% of water whereas the water absorption for PVDF is almost nil. It is well known that Nylon 6 is hydrophilic and can take up large amounts of water due to hydrogen bonding possibilities, as shown below:
It is also known that PVDF is hydrophobic and does not absorb water. With the addition of zinc cations to Nylon 6, the percentage of water absorption is reduced to about 8 percent. This confirms that co-ordinated interactions are formed through ion-dipole interactions between zinc cations and carbonyl of amide groups, which reduces the extent of the bonding that water can form with amide groups. When 10% of methacrylic acid is grafted to PVDF, the absorption of water increases to nearly 5 percent because of the hydrophilic behaviour of acid groups. When compared with random copolymers of ethylene-acrylic (or methacrylic) acid of similar co-monomer concentration the 5% water absorption values appears to be very large. Hence, the methacrylic acid units in the grafts on to PVDF must be oligomeric rather than monomeric. This probably indicates that water is likely to be absorbed in the form of clusters rather than simple molecular association by H-bonding. With the full neutralization of acid groups with zinc acetyl acetonate, the percentage of water absorption, however, is reduced to half. This observation indicates that in addition to salt formation (which is not expected to decrease water absorption) there must be co-ordinated products formed. The FTIR spectra in Figure 4.11(c) for full neutralization indicates, however, that there is a small amount of acid groups in the ionomer of grafted PVDF which act as hydrogen donors to form hydrogen bonds with water molecules, thereby maintaining water absorption capability.

In the 80:20 blend of PVDF/N6 the percent water absorption is about 2 percent, which corresponds to the exact amount expected by simple additivity. When grafted PVDF is blended with Nylon 6, there is a large increase in water absorption by the PVDF-g-MAA10/N6 80:20 blend to about 3.5% which is 1.5% more than
PVDF/N6 80:20 blend Figure 4.46. From previous observations, PVDF-g-MAA10 has the capability to absorb about 5% water. So if there is no interaction between the two components, the total amount of water absorbed is expected to be about 6% (4% from 80%PVDF-g-MAA10 and 2% from 20%N6). The reduction from 6% to 3.5% indicate that there is interaction between both components involving acid groups of grafted PVDF and amine groups of Nylon 6. The interaction will reduce the amount of acid groups available to form hydrogen bonding with water molecules. The addition of zinc cations does not appear to affect significantly the intake of water, although a small increase is noted. Neutralization of acid groups by zinc cations reduce the extent of reaction between grafted PVDF and Nylon 6 and as a result Nylon 6 will absorb 2% of water due to 20%N6 in the blend. Since it was shown earlier that PVDF-g-MAA10/ZnAA still has the capability to absorb about 2.5% of water, the small increase in water absorption is probably a contribution from Nylon 6 and the remaining of carbonyl acid groups of ionomer.

For the blend of PVDF with 20% grafted Nylon 6, Figure 4.46 shows that about 2.5% water is absorbed by the PVDF/N6-g-MAA11 80:20 blend, which is 0.5% more than the amount of water absorbed by the PVDF/N6 80:20 blend. The increase in water absorption comes from the acid groups of 11% methacrylic acid grafted onto Nylon 6, in addition to the absorption by the Nylon 6 molecules equivalent to about 2%. The results show that 11% methacrylic acid in 20% grafted Nylon 6 gives a 0.5% reduction in absorption of water compare with the amount absorbed by 10% methacrylic acid in 20% grafted PVDF, i.e. 1% since PVDF-g-MAA10 (100%) absorbs 5% of water. From this observation, it can be deduced that some of the acid groups in grafted Nylon interact with the amine groups of Nylon 6 to produce branches and crosslinking intramolecularly. As a result of the reduction in free acid groups in grafted Nylon 6, a reduction in water absorption is expected. FTIR spectra in Figure 4.12 (b) show the occurrence of this interaction with the formation of a peak at 1712 cm⁻¹ which corresponds to conjugated carbonyl double bonds. The SEM micrograph in Figure 4.37(b) of N6-
Fig. 4.45: Percent water absorption (% w/w) against time after treatments with boiling water; ■ PVDF, □ Nylon 6, + PVDF-g-MAA10, × N6/ZnAA and ○ PVDF-g-MAA10/ZnAA

Fig. 4.46: Percent water absorption (% w/w) against time after treatments with boiling water; ■ 80PVDF/20N6, □ 80PVDF/20N6-g-MAA11, + 80PVDF-g-MAA10/20N6, × 80PVDF-g-MAA10/20N6-g-MAA11, ○ 80PVDF-g-MAA10/ZnAA/20N6 and ▲ 80PVDF-g-MAA10/ZnAA/20N6-g-MAA11

116
g-MAAI1 shows a continuous phase of grafted Nylon 6. When both components are grafted polymers, i.e. PVDF-g-MAAI0/N6-g-MAAI1 80:20 blend, the water absorption is about 5%. If there is no interaction between the two components, the total amount of water absorbed is expected to be 6.5%, based on 4% from 80% PVDF-g-MAAI0 and 2.5% from 20% N6-g-MAAI1, which were taken from the results on PVDF/N6-g-MAAI1 80:20 blend. The reduction in amount of water absorption indicates that there is interaction between the acid groups of grafted PVDF and amine groups of grafted Nylon 6. However, with addition of zinc cations, the water absorption for PVDF-g-MAAI0/ZnAA/N6-g-MAAI1 80:20 blend is reduced to about 4%. The complexation and salt formation between zinc cations and acid groups reduce the amount of acid available for absorption of water. The amount of water absorption, however, is higher than the PVDF-g-MAAI/ZnAA/N6 80:20 blend because grafted Nylon 6 has a higher water absorption of water than non-grafted Nylon 6.

In Figure 4.47 it is shown that the amount of water absorption for PVDF/N6 20:80 blend is 7 - 8% and is directly proportional to the amount absorbed by the PVDF/N6 80:20 blend, which is about 2%, based on the content of Nylon 6 in the blend. This clearly shows that in the absence of interactions between the two phases, the water absorption follows the additivity rule. When Nylon 6 is blended with grafted PVDF, the amount of water absorbed by the PVDF-g-MAAI0/N6 20:80 blend is slightly less or nearly the same as for PVDF/N6 20:80 blend, even though there is 2% methacrylic acid in the blend from 20% PVDF-g-MAAI0. This indicates that the amount of acid groups present in the blends is diminished by react with the amine groups of Nylon 6. With addition of zinc cations in the blend, there is small increase in water absorption, compare PVDF-g-MAAI0/ZnAA/N6 with PVDF-g-MAAI0/N6 and PVDF/N6 20:80 blends. The increase in water absorption indicates that there is a larger number carbonyl groups available to form hydrogen bonds with water molecules.

However, with PVDF/N6-g-MAAI1 20:80 blend, the amount of water absorption is lower than PVDF/N6 20:80 blend even though there are more acid groups in the
Fig. 4.47: Percent water absorption (\% w/w) against time after treatments with boiling water; ■ 20PVDF/80N6, □ 20PVDF/80N6-g-MAA11,
→ 20PVDF-g-MAA10/80N6, × 20PVDF-g-MAA10/80N6-g-MAA11,
○ 20PVDF-g-MAA10/ZnAA/80N6 and
▲ 20PVDF-g-MAA10/ZnAA/80N6-g-MAA11
grafted Nylon 6. The reduction in water absorption indicates the existence of interactions between acid groups and amine groups within the grafted Nylon itself. A further decrease in water absorption is experienced when both components in the blend are grafted polymers, as shown in Figure 4.47 for PVDF-g-MAA10/N6-g-MAA11 20:80 blend, and is much lower than the PVDF-g-MAA10/N6 20:80 blend. In other words, the increase in interaction between the acid groups of grafted PVDF and amine groups of grafted Nylon 6 reduces the capability of grafted nylon molecules to absorb water. With the addition of zinc cations, i.e. PVDF-g-MAA10/ZnAA/N6-g-MAA11 20:80 blend, the water absorption has not been affected, and is the same as for PVDF-g-MAA10/N6-g-MAA11 20:80 blend. This is at variance with general effect of zinc cations on PVDF-g-MAA10/N6 blends which is to increase the water absorption. This may be explained by the fact that beside the interaction with acid groups in grafted PVDF, there is a possibility that zinc cations will also neutralise the acid groups of grafted Nylon 6. The effect of zinc complex and salt formation on water absorption is more or less the same as that given by the interaction of both components in the PVDF-g-MAA10/N6-g-MAA11 20:80 blend.

b) Extraction with Dimethyl Formamide

Samples were extracted in dimethyl formamide (DMF) for 48 hours at the boiling temperature of the solvent in order to examine further the interactions between the two components, i.e. PVDF and Nylon 6, in the blend. Table 4.11 shows that PVDF is fully dissolved in DMF while Nylon 6 does not dissolve at all in DMF. From extraction tests, it is shown that only 49.6% of PVDF-g-MAA10 dissolves in the DMF, even though the expected amount of extraction is 100% since both PVDF and methacrylic acid, monomer and polymer dissolve in DMF. The results indicate that there is a possibility of the existence of crosslinks within the grafted PVDF itself. It is found that for N6-g-MAA11, 13.6% grafted Nylon 6 dissolves in DMF, the expected amount of extraction is 11% from the amount of methacrylic
TABLE 4.11: EXTRACTION TEST DATA WITH DIMETHYL FORMIDE

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Total Extract Experiment</th>
<th>Expected % Extract PVDF Phase</th>
<th>Expected % Extract Nylon 6 Phase</th>
<th>Expected % Extract, Total</th>
<th>%Expected - %Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PVDF-g-MAA10</td>
<td>49.6</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>50.4</td>
</tr>
<tr>
<td>N6-g-MAA11</td>
<td>13.6</td>
<td>-</td>
<td>11</td>
<td>11</td>
<td>-2.6</td>
</tr>
<tr>
<td>N6/6-ZnAA</td>
<td>8.4</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>-8.4</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA</td>
<td>46.7</td>
<td>43.2</td>
<td>-</td>
<td>43.2</td>
<td>-3.5</td>
</tr>
<tr>
<td>N6-g-MAA11/ZnAA</td>
<td>4.3</td>
<td>-</td>
<td>11.6</td>
<td>11.6</td>
<td>7.3</td>
</tr>
<tr>
<td>20PVDF/80N6</td>
<td>11.7</td>
<td>20</td>
<td>0</td>
<td>20</td>
<td>8.3</td>
</tr>
<tr>
<td>20PVDF/80N6-g-MAA11</td>
<td>19.8</td>
<td>20</td>
<td>10.9</td>
<td>30.9</td>
<td>11.1</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/80N6</td>
<td>10.6</td>
<td>9.9</td>
<td>0</td>
<td>9.9</td>
<td>-0.7</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/80N6-g-MAA11</td>
<td>51.1</td>
<td>9.9</td>
<td>10.9</td>
<td>20.8</td>
<td>-30.3</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/ZnAA/80N6</td>
<td>4.8</td>
<td>9.3</td>
<td>0</td>
<td>9.3</td>
<td>4.5</td>
</tr>
<tr>
<td>20PVDF-g-MAA10/ZnAA/80N6-g-MAA11</td>
<td>71.1</td>
<td>9.3</td>
<td>10.9</td>
<td>20.2</td>
<td>-50.9</td>
</tr>
<tr>
<td>80PVDF/20N6-g-MAA11</td>
<td>58.2</td>
<td>80</td>
<td>2.7</td>
<td>82.7</td>
<td>24.5</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA11</td>
<td>60.6</td>
<td>39.7</td>
<td>2.7</td>
<td>42.4</td>
<td>-18.2</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA</td>
<td>40.5</td>
<td>37.4</td>
<td>2.7</td>
<td>40.1</td>
<td>-0.4</td>
</tr>
<tr>
<td>20N6-g-MAA11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
acid present in the grafted Nylon 6. This shows that grafting of methacrylic acid onto Nylon 6 induces some of the Nylon 6 chains, about 2.6%, to dissolve in DMF even though Nylon 6 itself does not dissolve in DMF.

Neutralization of grafted PVDF with zinc acetyl acetonate increases the dissolution of PVDF-g-MAA10 in DMF to 46.7% from the expected 43.2% based on 49.6% grafted PVDF dissolving from 87% (w/w) PVDF-g-MAA10 in the PVDF-g-MAA10/ZnAA mixture. The increase in dissolution of the sample by about 3.5% is due to the complex and salt formation of zinc cations with carbonyl acid group of grafted PVDF, which reduces the intermolecular interactions and increases the amount of free PVDF in the sample. As a result, more PVDF dissolves in DMF.

In the case of the neutralization of N6-g-MAA11 with zinc cations, the dissolution of N6-g-MAA11 in DMF is reduced to 4.3% from the expected 11.6%, based on 13.6% dissolving from 85% (w/w) N6-g-MAA11 in N6-g-MAA11/ZnAA mixture. Complex and salt formation between carbonyl acid group and zinc cations is the main factor which makes the grafted Nylon dissolve less in DMF solvent. In the blend of Nylon 6 with 10% zinc acetyl acetonate, 8.4% was dissolved in DMF, which corresponds to the solubility of zinc acetyl acetonate in DMF.

For PVDF/N6 20:80 blend, the data in Table 4.11 show that only 11.7% PVDF dissolves in DMF instead of expected 20% PVDF. It indicates that 8.3% PVDF has diffused into the Nylon 6 phase and is prevented from dissolving in DMF solvent. In the PVDF-g-MAA10/N6 20:80 blend, 10.6% of the sample dissolve, in DMF as compare with 9.9% expected to be extracted i.e. 49.6% of the expected 20% PVDF-g-MAA10 which dissolves in DMF. The SEM micrograph in Figure 4.40(c), for PVDF-g-MAA10/N6 20:80 blend, reveals reduction in size of the dispersed particles as compared with the SEM micrograph Figure 4.40(a) for PVDF/N6 20:80 blend. There are two possible explanations: either more PVDF is dissolved in DMF as a result of the reaction of the amine groups in Nylon with grafted methacrylic acid, or some of the Nylon has been solubilised as the result of the reaction with carbonyl acid groups in the PVDF, as indicated by the increased 

121
amount of N6-g-MAA11 which dissolves in DMF, as a result of the methacrylic acid grafting.

With addition of zinc acetyl acetonate, the amount of PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend dissolved in DMF solvent is reduced to 4.8% which is substantially lower than the expected 9.3%, based on the calculation that 46.7% of the 20%PVDF-g-MAA10/ZnAA would dissolve in DMF. It has been shown earlier that the addition of zinc cations to grafted PVDF increases the solubility in DMF solvent. In this case, however, this has reduced the dissolution of PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend in DMF solvent. The most possible explanation is that zinc cations, although can prevent the reaction carbonyl acid group of grafted PVDF with amine groups in Nylon 6, it increases the overall amount free PVDF diffusing into Nylon 6 phase. This can be deduced from observations on the SEM micrograph in Figure 4.40(d), showing dispersed particle penetrating into the matrix, when compared with the SEM micrograph Figure 4.40(c) for PVDF-g-MAA10/N6 20:80 blend.

For PVDF/N6-g-MAA11 20:80 blend, 19.8% of sample dissolved in DMF as compared with the expected 30.9%, based on 20%PVDF dissolving in DMF and 10.9% dissolving from 13.6% of N6-g-MAA11 also dissolving in DMF solvent (i.e. 13.6% of 80%). The reduction in dissolution of the sample from the expected result indicates that more PVDF diffuses into the Nylon phase, which prevents it from being dissolved by DMF. This can be confirmed from observations on the SEM micrograph of PVDF/N6 20:80 and PVDF/N6-g-MAA11 20:80 blends in Figures 4.40(a) and 4.41(a), respectively. These reveal that more PVDF particles are present on the fractured surface of PVDF/N6 20:80 blend and less particles on the surface of the PVDF/N6-g-MAA11 20:80 blend.

When both components are grafted polymers, the amount of PVDF-g-MAA10/N6-g-MAA11 20:80 blend dissolving in DMF solvent is increased to 51.1% as compared with 19.8% for PVDF/N6-g-MAA11 20:80 blend. The expected amount of extracted matter is 20.8%, based on the calculation that 9.9% from 49.6% of PVDF-g-MAA10 content (20% content) and 10.9% from 13.6% of
N6-g-MAA (80% content). SEM micrographs in Figure 4.41 reveal that more particles of the dispersed phase on the fractured surface of the PVDF-g-MAA10/N6-g-MAA11 20:80 blend than for the PVDF/N6-g-MAA11 20:80 blend. This suggests that more PVDF particles from the former blend would dissolve in DMF. The results also indicate that more than 10.9% grafted Nylon dissolves in the DMF, since only 20% PVDF-g-MAA10 is present in the blend. With the addition of zinc acetyl acetonate to the blend, the amount of matter from the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80 blend which dissolves in DMF solvent increases to 71%, compared with 51% for the PVDF-g-MAA10/N6-g-MAA11 20:80 blend. This represents a large increase in amount of sample dissolved in DMF as compared with the expected 20.2%. Again, the SEM micrograph in Figure 4.41 provides the supportive explanation for the increased amount of PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80 dissolving in DMF. Complex and salts formed by zinc cations with carbonyl acid groups from grafted PVDF do not diffuse into the Nylon phase, in contrast with PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend. As a result, more PVDF is extracted by DMF as in the case of PVDF-g-MAA10/ZnAA. There is a possibility that some of the zinc cations complexing with Nylon amide groups, induces also some of the free Nylon to dissolve in DMF.

For PVDF/N6-g-MAA11 80:20 blend, the data in Table 4.11 show that 58.2% of sample dissolves in DMF, which is less than the expected 82.7% value. When both polymers are grafted, there is a small increase in the solubility of PVDF-g-MAA10/N6-g-MAA11 80:20 blend in DMF solvent as compared with PVDF/N6-g-MAA11 80:20 blend. The 60.6% value for the extraction in DMF is higher, however, than the expected 42.4%, (Table 4.11) based on 39.7% from 49.6% of PVDF-g-MAA10 (80% content) and 2.7% from 13.6% of N6-g-MAA11(20% content). The SEM micrograph in Figure 4.39(b) for PVDF-g-MAA10/N6-g-MAA11 80:20 blend reveals some interaction between the two components as compared with the SEM micrograph in Figure 4.39(a) for PVDF/N6-g-MAA11 80:20 blend. However, with addition of zinc cations, i.e. PVDF-g-
MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, a lesser amount dissolves in DMF solvent and approaches the expected value (see Table 4.11). This results from complex and salt formation between acid groups of grafted PVDF and zinc cations which prevents interaction between the two components.

4.8 TENSILE TESTS

In this section the results of the tensile tests on the various systems, grafted polymers, ionomer and PVDF/N6 blends, are presented (Tables 4.12 to 4.15). The purpose of the tests is to see the relation between the compatibility of the blend and the improvements in mechanical properties.

a) Tensile Test Data for Grafted and Ionomerised PVDF

The results in Table 4.12 show a reduction in tensile strength and elongation at break of grafted PVDF (PVDF-g-MAA5), but with increasing the amount of methacrylic acid grafted onto PVDF (i.e. PVDF-g-MAA10) there is an increase in tensile strength and a further reduction in elongation. The presence of small particles, acting as filler is believed to be the major cause for the observed changes in properties. With addition of zinc acetyl acetonate for ionomerisation of grafted PVDF, there is a significant improvement in the tensile strength. For PVDF-g-MAA10, the addition of zinc cations improves both tensile strength and elongation but reduce the latter with increasing the amount of zinc cations in the blend. It is difficult to correlate these data, however, with the morphology of the samples.

b) Tensile Test Data for the PVDF/N6 80:20 Blend

PVDF has higher elongation at break, but lower tensile strength than Nylon 6 (Table 4.13). The amide functions of Nylon 6 participate in hydrogen bonding, between adjacent molecules giving rise to high intermolecular forces. In the blend
Table 4.12: MECHANICAL PROPERTIES OF PVDF

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Tensile Strength at Yield, N/mm²</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>42.5</td>
<td>276</td>
</tr>
<tr>
<td>PVDF-g-MAA5</td>
<td>41.6</td>
<td>79</td>
</tr>
<tr>
<td>PVDF-g-MAA10</td>
<td>44.5</td>
<td>30</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)</td>
<td>44.5</td>
<td>20</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)</td>
<td>47.9</td>
<td>18</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)</td>
<td>47.7</td>
<td>14</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)</td>
<td>45.5</td>
<td>44</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)</td>
<td>44.3</td>
<td>14</td>
</tr>
</tbody>
</table>

Table 4.13: MECHANICAL PROPERTIES OF PVDF/N6 80:20 BLENDS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Tensile Strength at Yield, N/mm²</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>42.5</td>
<td>276</td>
</tr>
<tr>
<td>NYLON 6</td>
<td>57.6</td>
<td>235</td>
</tr>
<tr>
<td>PVDF/N6</td>
<td>17.6</td>
<td>3</td>
</tr>
<tr>
<td>PVDF-g-MAA5/N6</td>
<td>42.4</td>
<td>7</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)/N6</td>
<td>40.6</td>
<td>8</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)/N6</td>
<td>37.2</td>
<td>6</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)/N6</td>
<td>31.4</td>
<td>5</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6</td>
<td>35.7</td>
<td>6</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)/N6</td>
<td>44.3</td>
<td>9</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6</td>
<td>33.3</td>
<td>5</td>
</tr>
<tr>
<td>PVDF/N6-g-MAA11</td>
<td>35.4</td>
<td>8</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6-g-MAA11</td>
<td>37.4</td>
<td>6</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)/N6-g-MAA11</td>
<td>43.2</td>
<td>9</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11</td>
<td>50.6</td>
<td>9</td>
</tr>
</tbody>
</table>
of PVDF with 20% Nylon 6, the tensile strength and elongation of PVDF are reduced drastically. The presence of 5% methacrylic acid grafted to PVDF gives a large increase in tensile strength for the PVDF-g-MAA5/N6 80:20 blend. This can be easily attributed to improved compatibility of the blend, as shown in the SEM micrograph in Figure 4.38(b). With increasing the amount of methacrylic acid in the blend, the tensile strength and elongation at break of PVDF-g-MAA10/N6 80:20 blend is reduced. The reduction in tensile and elongation properties of PVDF-g-MAA10/N6 80:20 blend can be attributed to the reduction in crystallinity of the Nylon 6 phase in the blend, as indicated by the reduction in heat of fusion for the Nylon phase from DSC analysis in Figure 4.20(c).

For blends of PVDF-g-MAA5/N6, tensile strength and elongation are reduced with increase in amount of zinc cations. The complex and salt formation between acid groups of grafted PVDF and zinc cations will prevent interactions between the two components and produce a less compatible blend, resulting in a deterioration of mechanical properties. For PVDF-g-MAA10/N6 blend, half neutralization with zinc cations increase the tensile strength and elongation at break, but this effect reduces when the amount of zinc cations is increased to full neutralization. Complex and salt formation between zinc cations and acid groups of PVDF-g-MAA10 will reduce interactions between the two components in PVDF-g-MAA10/N6 80:20 blend, and since it is a half neutralization process, there is some acid available to react with amine groups of Nylon 6. A direct correlation with mechanical properties is difficult because of the complications arising from morphology and possible cross-linking reactions.

In the blend of PVDF with 20% grafted Nylon 6, tensile strength and elongation at break for PVDF/N6-g-MAA11 80:20 blend are increased as compared with the PVDF/N6 80:20 blend. With 10% methacrylic acid grafted to PVDF, i.e. PVDF-g-MAA10/N6-g-MAA11 80:20 blend, there is significant increase in tensile strength, but it reduces the elongation at break, as compared with the PVDF/N6-g-MAA11 80:20 blend. Even though the interaction between the two components in the PVDF-g-MAA10/N6-g-MAA11 80:20 blend is very strong than for
PVDF/N6-g-MAA11 80:20 blend, based on the formation of one melting peak and one crystallization peak compare to latter blend in Figure 4.21, it only shows small improvement in the tensile strength, compared to the latter case. This again highlights the difficulty of relating mechanical properties to structure.

However for the PVDF-g-MAA10/N6-g-MAA11 80:20 blend, the tensile strength and elongation at break are increased with increasing the amount of zinc cations in the blend Table 4.13. Since the grafted Nylon 6 contains acid groups, there is possibility that some interaction of grafted Nylon 6 molecules with zinc complex/salt in the PVDF phase, will produce a better distribution and diffusion of grafted molecules in the matrix. As a result of a more homogenous morphology will result which enhances the mechanical properties of the blend materials.

c) **Tensile Test Data for PVDF/N6 20:80 Blend**

When 20% PVDF is added to Nylon 6, tensile strength of PVDF/N6 20:80 blend is about the same as for the Nylon 6, but there is a reduction in elongation at break. This shows that PVDF acts like a filler with poor adhesion to the matrix. However, in the blend of Nylon 6 with grafted PVDF, i.e. PVDF-g-MAA5/N6 20:80 blend, the data in Table 4.14 show a reduction in mechanical properties, even though the SEM micrograph in Figure 4.40(b) indicates that the blend is semi-compatible, due to the reduction in particle size of dispersed phase. With increasing the amount of methacrylic acid, e.g. PVDF-g-MAA10/N6 20:80 blend, there is a further reduction in tensile strength, but an improvement in elongation property compared with the PVDF/N6 20:80 blend. The reduction in size of dispersed particles and interaction between the two components, the efficiency of the filler particles in improving the tensile properties of the blend is increased. Strong interactions will bond together the two components and improve elongation.

The degree of neutralization of grafted PVDF with zinc cations gives significant influence on mechanical properties of the blend. In the blend of Nylon 6 with
PVDF-g-MAA5, full neutralization improves the tensile strength while the elongation increases with increasing the amount of zinc cations in the blend. In the case of Nylon 6 blend with PVDF-g-MAA10, full neutralization of the PVDF-g-MAA10 gave a tremendous increase in elongation, but only a modest increase in strength (Table 4.14). Metal complex/salt formation of zinc cations with acid groups of PVDF-g-MAA10 prevents interaction between the two components and produce very fine particles of dispersed phase. The diffusion of these particles into matrix, as shown in the SEM micrograph Figure 4.40(d), is responsible for the large increase in elongation at break.

d) Tensile Test Data of PVDF/Nylon 6 Film Blend

Tables 4.15 and 4.13 show that tensile and elongation of PVDF/N6-g-MAA3 80:20 blend are lower than the PVDF/N6-g-MAA11 80:20 blend, but higher than PVDF/N6 80:20 blend. When both components are grafted polymers, i.e. PVDF-g-MAA10/N6-g-MAA3 80:20 blend, there is a reduction in tensile strength and elongation as compared with the PVDF/N6-g-MAA3 80:20 blend. Even though there is strong interaction between the two components with reduction in size particle of the dispersed phase, (SEM micrograph Figure 4.43(b)) the morphology of the blend when compared with PVDF-g-MAA10/N6-g-MAA11 80:20 blend are different. The addition of zinc cations reduces further the mechanical property of the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3 80:20 blend. Complex/salt formation between acid groups of grafted PVDF and zinc cations prevent interaction between the two components and reduce the compatibility of the system, as a result low mechanical properties are to be expected.

The addition of 5% N6-g-MAA11 to the PVDF/N6 80:15 blend gives the same effect on mechanical property as the PVDF/N6-g-MAA3 80:20 blend mentioned above. There is an increase in both tensile strength and elongation compared with PVDF/N6 80:20 blend. However, in the case PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, the presence of methacrylic acid grafts onto PVDF gives a
Table 4.14: MECHANICAL PROPERTIES OF PVDF/N6 20:80 BLEND

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Tensile Strength at Yield, N/mm²</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/N6</td>
<td>58.5</td>
<td>45.7</td>
</tr>
<tr>
<td>PVDF-g-MAA5/N6</td>
<td>57.2</td>
<td>20.2</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)/N6</td>
<td>55.8</td>
<td>68.6</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)/N6</td>
<td>58.4</td>
<td>67.6</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)/N6</td>
<td>55.7</td>
<td>75.7</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6</td>
<td>53.6</td>
<td>77.9</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6</td>
<td>53.9</td>
<td>187.6</td>
</tr>
</tbody>
</table>

Table 4.15: MECHANICAL PROPERTIES OF PVDF/NYLON 6 FILM BLEND

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Tensile Strength at Yield, N/mm²</th>
<th>Elongation at Break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>80PVDF/20N6-g-MAA3</td>
<td>24.7</td>
<td>6.3</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA3</td>
<td>18.8</td>
<td>5.8</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA3</td>
<td>12.7</td>
<td>4.6</td>
</tr>
<tr>
<td>80PVDF/15N6/5N6-g-MAA11</td>
<td>20.3</td>
<td>5.8</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/15N6/5N6-g-MAA11</td>
<td>21.4</td>
<td>6.1</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/15N6/5N6-g-MAA11</td>
<td>30.2</td>
<td>7.8</td>
</tr>
</tbody>
</table>
significant increase in the mechanical property, as compared with PVDF/N6/N6-g-MAA11 80:15:5 blend. This indicates that the effect of the addition 5% N6-g-MAA11 as a compatibilizer gives better mechanical properties than when the functional groups are all attached to the polymers. Neutralization of acid groups of the grafted PVDF by zinc cations improves further the mechanical properties of the PVDF-g-MAA10/ZnAA(1)/N6/N6-g-MAA11 80:15:5 blend. Even though complex/salt formation between zinc cations and acid groups of grafted PVDF prevent interaction between the two components, there is a possibility that some of the zinc cations are still involved in complex formation with the acid groups of 5% grafted Nylon 6.

4.9 RHEOLOGICAL STUDIES

In the rheology studies using an R.D.A. Analyser, the frequency sweep option was used to characterise the materials. From this studies, changes in viscosity of the materials and its frequency dependence can be used to determine the extent of interaction between the components in the blend.

a) Viscosity Measurements of PVDF

Figure 4.48 shows that the viscosity of the irradiated PVDF is slightly lower than the unirradiated sample. This indicates that there is a possibility of chain scission of PVDF taking place rather than crosslinking when irradiated to 15 kGy by γ-radiation. With 5% methacrylic acid grafted onto preirradiated PVDF, i.e. PVDF-g-MAA5, there is a further reduction in viscosity of the sample. However, with increasing the amount of methacrylic acid grafted to PVDF, the PVDF-g-MAA10 viscosity increases as compared with PVDF-g-MAA5. Neutralization of the acid groups with zinc cations produces a further increase in viscosity as a result of complex/salt formation with the acid groups. The frequency dependence of the
Fig. 4.48: Complex viscosity vs angular frequency of:
- PVDF,
- Irradiated PVDF,
- PVDF-g-MAA5,
- PVDF-g-MAA10 and
- PVDF-g-MAA10/ZnAA(1).
viscosity, however, remains the same irrespective of the type of chain modification. This indicates that chain branching is not occurring to any extent.

b) **Viscosity Measurements of Nylon 6**

The viscosity of Nylon 6 also decreases slightly as a result of γ-irradiation as shown in Figure 4.49 indicating the occurrence of some chain scission. With the grafting of methacrylic acid onto preirradiated Nylon 6, the viscosity of grafted Nylon (N6-g-MAA11) increases very drastically at lower frequency and becomes very sensitive to frequency (shear rate). This is a clear indication of extensive chain branching taking place, possibly accompanied by the formation of some crosslinked polymer. The viscosity values of these materials are much nearer to those of PVDF species.

The addition of zinc cations, i.e. N6-g-MAA11/ZnAA reduces the viscosity at low frequency as compared to the grafted Nylon, as a result of complex/salt formation. The viscosity dependence on frequency is also reduced, indicating that a lower degree of branching and crosslinking has taken place.

c) **Effect of Grafting Method on Viscosity of Nylon 6**

Figure 4.50 shows that types of grafting have an effect on the viscosity of the grafted Nylon 6. N6-g-AA9 is 9% acid acrylic grafted onto Nylon 6 which has been grafted by the coirradiation method, i.e. acrylic acid after was absorbed into the Nylon 6 granule and then irradiated together by γ-irradiation at 15 kGy. N6-g-MAA11 is 11% methacrylic acid grafted onto Nylon 6 by the preirradiation method using the same dose. Both systems show a higher viscosity at low frequencies and exhibit a similar frequency dependence, which indicate that both polymer systems are highly branched. Assuming the differences in acid content, i.e. 9% and 11% and CH₃ group in methacrylic acid are not significant, the difference on viscosity of N6-g-MAA11 and N6-g-AA9 could probably due to the
Fig. 4.49: Complex viscosity vs angular frequency of:

- [ ] Nylon 6
- [ ] Irradiated Nylon 6
- [ ] N6-g-MAA11
- [ ] N6-g-MAA11/ZnAA(1)
- [ ] Nylon 6 + ZnAA

Complex viscosity ($\eta^*$), Pa.s

Angular frequency ($\omega$), rad/s
Fig. 4.50: Complex viscosity vs angular frequency of:

- □ - Nylon 6
- △ - N6-g-AA9
- ○ - N6-g-MAA11
- ▲ - N6-g-AA9/ZnAA(1)
- ● - N6-g-MAA11/ZnAA(1)
way of monomers grafting onto the Nylon 6 backbone. Since the N6-g-AA9 has low viscosity and it was grafted by the coirradiation method, there is a possibility that it gives rise to more degradation, or that chain branches are fewer. The viscosity of N6-g-AA9 is increased by the addition of zinc cations because of complex/salt formation between acid groups and zinc cations. The rate of change in viscosity with frequency for N6-g-AA9/ZnAA is almost the same as N6-g-AA9, indicating a similar extent of chain branching.

d) Viscosity Measurements of PVDF/N6 blend

For the blend of PVDF with N6, Figure 4.51 shows a reduction in viscosity of PVDF/N6 80:20 blend as compared with PVDF in Figure 4.48. However, the viscosity at low frequencies is considerably higher. This a good indication that interactions are taking place between the two polymers. When grafted PVDF is blended with N6, i.e. PVDF-g-MAA5/N6 80:20 blend, there is a large reduction on the viscosity of the blend as compared with the PVDF/N6 80:20 blend. This is, however, mainly a reflection of the reduction in viscosity of the PVDF containing phase. With increasing the amount of methacrylic acid grafted to PVDF, the increase in viscosity of PVDF-g-MAA10/N6 80:20 blend is insignificant. The effect of the Nylon viscosity on the viscosity of PVDF/N6 blend can be further clarified in the blend of PVDF with grafted Nylon. As shown earlier, grafted N6 has higher viscosity than non-grafted N6 (Figure 4.49). For the blend of PVDF-g-MAA10/N6-g-MAA11 80:20, Figure 4.52 shows a small reduction in the viscosity as compared with the reduction on viscosity of PVDF-g-MAA10/N6 80:20 blend in Figure 4.51, even though it has been shown that the former blend is more compatible.

With grafted Nylon 6 as the main phase, addition of PVDF does not reduce the viscosity of PVDF/N6-g-MAA11 20:80 blend as shown in Figure 4.53 (compare with Figure 4.48). However, with grafted PVDF, the viscosity of PVDF-g-MAA10/N6-g-MAA11 20:80 blend is reduced as compared with the former blend,
Fig. 4.51: Complex viscosity vs angular frequency of:

- ○ --- PVDF/N6 80:20
- △ --- PVDF-g-MAA5/N6 80:20
- □ --- PVDF-g-MAA10/N6 80:20
- ○ --- PVDF-g-MAA10/ZnAA(1)/N6 80:20
Fig. 4.52: Complex viscosity vs angular frequency of:

- ••• PVDF/N6-g-MAA11 80:20
- ▲▲▲ PVDF-g-MAA10/N6-g-MAA11 80:20
- ■■■ PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20
Fig. 4.53: Complex viscosity vs angular frequency of:
- PVDF/N6 20:80
- PVDF/N6-g-MAA11 20:80
- PVDF-g-MAA10/N6-g-MAA11 20:80
- PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80
but the frequency dependence remains the same. Ionomerisation with zinc cations reduces further the viscosity of the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80 blend. The frequency dependence has been affected, however, to a less extent. This is a clear consequence of the reduced level of reactions between the two polymers giving less chain branching.

e) Viscosity measurements of PVDF/N6 film blends

Figure 4.54 shows that for the blend of PVDF with grafted Nylon 6 film, containing 3% methacrylic acid, i.e. PVDF/N6-g-MAA3 80:20 blend, the viscosity is lower than PVDF-g-MAA10/N6-g-MAA3 80:20 blend, but the difference gets smaller as frequency increases. This is a clear confirmation that there is interaction between the two components i.e. grafted PVDF and grafted Nylon 6. On the other hand, in the case of PVDF/N6-g-MAA3, the interaction is low or non-existent. The addition of zinc cations to the blend increases the viscosity of PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3 80:20 blend as compared with PVDF-g-MAA10/N6-g-MAA3 80:20 blend. Complex/salt formation between zinc cations and acid groups of both grafted polymers results in an increase the viscosity of the material.

Figure 4.55 shows that for the blend of PVDF and Nylon 6 with addition of 5% grafted Nylon 6 film (N6-g-MAA11) as compatibilizer, i.e. PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, the viscosity is the same as PVDF/N6/N6-g-MAA11 80:15:5 blend at low frequency. The rate of viscosity reduction with increased in frequency (shear rate) is higher for the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend than the PVDF/N6/N6-g-MAA11 80:15:5 blend. Ionomerisation of the blend with zinc cations seems to have increased the viscosity of the blend, but the effect of zinc cations does not influence the rate of viscosity reduction with increase frequency.
Fig. 4.54: Complex viscosity vs angular frequency of:
--- Δ --- PVDF/N6-g-MAA3 80:20
--- △ --- PVDF-g-MAA10/N6-g-MAA3 80:20
--- ◇ --- PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3 80:20
--- ★ --- N6 granule/N6-g-MAA3 80:20
Fig. 4.55: Complex viscosity vs angular frequency of:

- \(
  \Delta \quad \text{PVDF/N6/N6-g-MAA11 80:15:5}
\)

- \(\nabla \quad \text{PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5}
\)

- \(\nabla \quad \text{PVDF-g-MAA10/ZnAA(1)/N6/N6-g-MAA11 80:15:5}
\)
4.10 SOLVENT RESISTANCE TESTS

Butyl acetate and chloroform with solubility parameters of 17.4 (MPa)$^{1/2}$ and 19.0 (MPa)$^{1/2}$ respectively (137), have been chosen for the solvent resistance test on the PVDF/N6 blend. Since PVDF and Nylon 6 has solubility parameter of 23.2 (MPa)$^{1/2}$ (138) and about 23.0 (MPa)$^{1/2}$ (based on solubility parameter values of 24.0 (MPa)$^{1/2}$ and 22.87 (MPa)$^{1/2}$ for Nylon 4 and Nylon 6,6, respectively) (137), indicate that both are poor solvents for either polymers. Nevertheless, butyl acetate has been classified as moderately hydrogen-bonding and will give better interaction with Nylon 6 than chloroform, which is in the poorly-hydrogen-bonding group.

Tables 4.16 to 4.19 report the data for the solvent resistance of the blended sample after immersing in butyl acetate and chloroform separately for 72 hours at room temperature. When the result is positive, it means that absorption has taken place by the sample, while negative increments indicate some of the sample has been extracted by the solvent.

a) Solvent Resistance Data for PVDF and Nylon 6

Table 4.16 shows that PVDF absorbs about 0.6% butyl acetate whereas for Nylon 6 about 29% has been extracted by butyl acetate. However, with chloroform as a solvent, Nylon 6 absorbed 3.7% while PVDF absorbed only 0.4%. When 11% methacrylic acid is grafted to Nylon 6, there is a large reduction in solubility in butyl acetate causing an absorption of 41.7% compare with an extraction of 29%. There is also a reduction in absorption of chloroform i.e. down to 0.5% from 3.7%. For the case of grafted PVDF, i.e. PVDF-g-MAA5 there is an increase in absorption of both solvents but reduce with increasing the amount of methacrylic acid. Ionomerisation of grafted Nylon 6 with zinc cations reduce the absorption of butyl acetate to about 0.2%, but increase the absorption of chloroform to 1.13%.
However, the addition of zinc cations increased the absorption of grafted PVDF for both solvents.

b) Solvent Resistance Data of PVDF/N6 80:20 Blends

For the blend of PVDF with Nylon 6, the addition of 20% Nylon 6 gives an increase in absorption of butyl acetate and chloroform to about 1.1% (see Table 4.17) which is 0.5% and 0.7%, respectively, more than the PVDF itself (Table 4.16). When the grafted PVDF is blended with Nylon 6, i.e. PVDF-g-MAA5/N6 80:20 blend, there is a decrease in the absorption of butyl acetate and chloroform to about 0.2% and 0.5%, respectively, which is 0.9% for butyl acetate and 0.6% for chloroform, less than for the PVDF/N6 80:20 blend. With increasing in the amount of methacrylic acid, i.e. PVDF-g-MAA10/N6 80:20 blend there is a significant increase in absorption of chloroform i.e. 0.7%, but a very small increment in absorption of butyl acetate. With the addition of zinc cations in the blend, there is a significant increase in the absorption of butyl acetate and chloroform, and the absorption increases with increasing in the amount of zinc cations.

When the PVDF is blended with grafted Nylon 6, PVDF/N6-g-MAA11 80:20 blend there is an increase in the of absorption of butyl acetate and chloroform to 1.3% and 1.2%, respectively, which is about 0.1% more than for the PVDF/N6 80:20 blend. Based on the data from Table 4.16, the grafted Nylon 6 absorbs less chloroform than the Nylon 6. However, in this case the presence of grafted Nylon 6 does not seem to reduce the chloroform absorption for the PVDF/N6-g-MAA11 80:20 blend. When both components are grafted polymers, i.e. PVDF-g-MAA10/N6-g-MAA11 80:20 blend, the butyl acetate absorption is reduced to 0.5% which is 0.8% less than the PVDF/N6-g-MAA11 80:20 blend, and 0.3% higher than for the PVDF-g-MAA10/N6 80:20 blend. In the case of chloroform, the absorption is increased to 6.2% which is 5% more than the PVDF/N6-g-MAA11 80:20 and PVDF-g-MAA10/N6 80:20 blends, even though the
Table 4.16: SOLVENT RESISTANCE DATA FOR PVDF AND NYLON 6 SYSTEMS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% Absorption Butyl acetate</th>
<th>% Absorption Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>0.59</td>
<td>0.36</td>
</tr>
<tr>
<td>PVDF-g-MAA5</td>
<td>0.75</td>
<td>0.46</td>
</tr>
<tr>
<td>PVDF-g-MAA10</td>
<td>0.53</td>
<td>0.37</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)</td>
<td>0.93</td>
<td>0.53</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)</td>
<td>0.82</td>
<td>0.58</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)</td>
<td>0.87</td>
<td>0.62</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)</td>
<td>1.00</td>
<td>0.66</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)</td>
<td>0.97</td>
<td>0.65</td>
</tr>
<tr>
<td>NYLON 6</td>
<td>-29.03</td>
<td>3.67</td>
</tr>
<tr>
<td>N6-g-MAA11</td>
<td>41.70</td>
<td>0.45</td>
</tr>
<tr>
<td>N6-g-MAA11/ZnAA(1)</td>
<td>0.22</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table 4.17: SOLVENT RESISTANCE DATA FOR PVDF/N6 80:20 BLENDS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% Absorption Butyl acetate</th>
<th>% Absorption Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/N6</td>
<td>1.13</td>
<td>1.09</td>
</tr>
<tr>
<td>PVDF-g-MAA5/N6</td>
<td>0.19</td>
<td>0.48</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6</td>
<td>0.21</td>
<td>0.71</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)/N6</td>
<td>0.59</td>
<td>0.71</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)/N6</td>
<td>0.63</td>
<td>0.97</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)/N6</td>
<td>0.68</td>
<td>0.86</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)/N6</td>
<td>0.67</td>
<td>1.00</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6</td>
<td>0.46</td>
<td>1.18</td>
</tr>
<tr>
<td>PVDF/N6-g-MAA11</td>
<td>1.27</td>
<td>1.17</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6-g-MAA11</td>
<td>0.46</td>
<td>6.17</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(0.5)/N6-g-MAA11</td>
<td>0.47</td>
<td>0.94</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11</td>
<td>0.50</td>
<td>0.89</td>
</tr>
</tbody>
</table>

144
chloroform absorption by grafted Nylon 6 was 0.45% compared with 3.67% for nylon 6 itself. With the addition of zinc cations in the blend, there is no significant affect on the absorption of butyl acetate, even with increasing the amount of zinc cations. However, in the case of chloroform, the addition of zinc cations reduces the chloroform absorption, which is lower than the absorption by PVDF/N6-g-MAA11 80:20 blend (see Table 4.17).

c) Solvent Resistance Data for PVDF/N6 20:80 Blends

When 20% PVDF is blended with nylon 6, there is tremendous improvement in solvent resistance of Nylon 6 against butyl acetate. Table 4.18 shows that PVDF/N6 20:80 blends absorbed 0.2% butyl acetate, as compared with 29% extraction for the nylon 6 by itself (Table 4.16). In the case of chloroform as a solvent, the addition of 20% PVDF to nylon 6 gives a slight increase (possibly insignificant) in the chloroform absorption i.e. 4% compare with 3.7% chloroform absorption by nylon 6. For the blend of nylon 6 with grafted PVDF, i.e. PVDF-g-MAA5/N6 20:80 blend, the butyl acetate and chloroform absorptions are reduced to 0.02% and 0.3%, respectively. However, with increasing the amount of methacrylic acid in the blend, the butyl acetate and chloroform absorptions are increased to 0.3% and 5.2%, respectively, which is 0.1% and 1.2% higher than the butyl acetate and chloroform absorptions, by PVDF/N6 20:80 blend. Table 4.18 shows the effect of zinc cations on the solvents absorption by the blend. For the PVDF-g-MAA5/ZnAA(0.5)/N6 20:80 blend, the butyl acetate and chloroform absorption are increased to about 0.2% and 3.1%, respectively, as compared with 0.02% and 0.3% absorption of butyl acetate and chloroform by PVDF-g-MAA5/N6 20:80 blend. However, with increasing the amount of zinc cations to full neutralization, i.e. PVDF-g-MAA5/ZnAA(1)/N6 20:80 blend, the absorption of butyl acetate and chloroform is reduced to nil and 0.4%, respectively, which are almost equal to the values for the PVDF-g-MAA5/N6 20:80 blend. The same situation also happened for the full neutralization of PVDF-g-
MAA10/ZnAA(1)/N6 20:80 blend, where the amount of solvent absorbed is the same as the PVDF-g-MAA10/N6 20:80 blend. With an excess of zinc cations in the blend, i.e. PVDF-g-MAA5/ZnAA(1.5)/N6 20:80 blend, the absorption on both solvents is increased again to 0.2% and 2.5% for butyl acetate and chloroform, respectively.

When 20%PVDF is added to the grafted Nylon 6, i.e. PVDF/N6-g-MAA11 20:80 blend, the absorption of butyl acetate is reduced to 0.55% while the absorption of chloroform is increased to 10.3%, as compared with the absorption of butyl acetate and chloroform by grafted Nylon 6 itself equal to 41.7% and 0.5% respectively (see Table 4.16). It shows that the presence of PVDF in grafted Nylon 6 has a significant effect on the solvent resistant properties of grafted Nylon 6. When both components are grafted polymers, i.e. PVDF-g-MAA10/N6-g-MAA11 20:80 blend, Table 4.18 shows a further reduction in the absorption of butyl acetate i.e. 0.2% and also a decrease in the absorption of chloroform i.e. 3.2%. Ionomerisation with zinc cations seems to reduce further the solvent resistant properties of PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80 blend with the absorption of butyl acetate and chloroform to about 0.15% and 1.6%, respectively.

d) Solvent Resistant Data for PVDF/Nylon 6 Film Blends

Table 4.19 shows the solvent resistance results for the blend of PVDF with Nylon 6 films in the presence of a third component i.e. 5% grafted Nylon 6 film (N6-g-MAA11) as a compatibiliser. For the blend of PVDF with grafted Nylon 6 film (content 3% methacrylic acid grafting onto Nylon 6 film), i.e. PVDF/N6-g-MAA3 80:20 blend, the absorption of butyl acetate and chloroform are the same i.e. 1.37%, which is a little bit higher than the amount of butyl acetate and chloroform absorbed by the PVDF/N6-g-MAA11 80:20 blend (see Table 4.17). It shows that the solvent resistance of the blend depends on the amount of methacrylic acid grafted to Nylon 6. With addition of 5% grafted Nylon 6 film (N6-g-MAA11) as a
### Table 4.18: Solvent Resistance Data for PVDF/N6 20:80 Blends

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% Absorption Butyl acetate</th>
<th>% Absorption Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/N6</td>
<td>0.22</td>
<td>4.00</td>
</tr>
<tr>
<td>PVDF-g-MAA5/N6</td>
<td>0.02</td>
<td>0.30</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6</td>
<td>0.28</td>
<td>5.24</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(0.5)/N6</td>
<td>0.20</td>
<td>3.12</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1)/N6</td>
<td>0.00</td>
<td>0.39</td>
</tr>
<tr>
<td>PVDF-g-MAA5/ZnAA(1.5)/N6</td>
<td>0.22</td>
<td>2.46</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6</td>
<td>0.28</td>
<td>5.26</td>
</tr>
<tr>
<td>PVDF/N6-g-MAA11</td>
<td>0.55</td>
<td>10.33</td>
</tr>
<tr>
<td>PVDF-g-MAA10/N6-g-MAA11</td>
<td>0.24</td>
<td>3.16</td>
</tr>
<tr>
<td>PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11</td>
<td>0.15</td>
<td>1.60</td>
</tr>
</tbody>
</table>

### Table 4.19: Solvent Resistance Data for PVDF/N6 Film Blends

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>% Absorption Butyl acetate</th>
<th>% Absorption Chloroform</th>
</tr>
</thead>
<tbody>
<tr>
<td>80PVDF/20N6-g-MAA3</td>
<td>1.37</td>
<td>1.37</td>
</tr>
<tr>
<td>80PVDF/15N6/5N6-g-MAA11</td>
<td>1.43</td>
<td>1.87</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/20N6-g-MAA3</td>
<td>0.37</td>
<td>1.03</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/15N6/5N6-g-MAA11</td>
<td>0.41</td>
<td>2.12</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/20N6-g-MAA3</td>
<td>0.50</td>
<td>1.16</td>
</tr>
<tr>
<td>80PVDF-g-MAA10/ZnAA(1)/15N6/5N6-g-MAA11</td>
<td>0.47</td>
<td>1.05</td>
</tr>
</tbody>
</table>
third components, in the blend of PVDF with Nylon 6, i.e. PVDF/N6/N6-g-MAA11 80:15:5 blend, there is a significant increase in the absorption of chloroform to 1.87%, whereas a small increase is observed for the absorption of butyl acetate i.e. 1.43%, compared with the PVDF/N6-g-MAA3 80:20 blend. When both components are grafted polymers, i.e. PVDF-g-MAA10/N6-g-MAA3 80:20 blend, Table 4.19 shows a decrease in the absorption of butyl acetate and chloroform to about 0.37% and 1.03%, respectively, in comparison the solvent absorption by PVDF/N6-g-MAA3. However, in the case of PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, it also shows a reduction in the butyl acetate absorption, i.e. 0.41%, but a significant increase in the chloroform absorption, i.e. 2.12%, in comparison the solvent absorption by PVDF/N6/N6-g-MAA11 80:15:5 blend. The results show that by adding 5% grafted Nylon 6 as compatibiliser in the blend this will improve the solvent resistance of the blend in comparison to the blend based on the functionalised of the polymers. Ionomerisation with zinc cations improves the absorption of butyl acetate and chloroform by PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3 i.e. 0.5% and 1.16% respectively, in comparison the PVDF-g-MAA10/N6-g-MAA3 80:20 blend. However, full-neutralization of grafted PVDF with zinc cations, i.e. PVDF-g-MAA10/ZnAA(1)/N6/N6-g-MAA11 80:15:5 blend, does not improve the absorption of butyl acetate i.e. 0.47%, but decreases the chloroform absorption, i.e. 1.05%, in comparison with the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend.
CHAPTER 5: Discussion and Concluding Remarks

5.1 EFFECT OF ACID GRAFTING ON PVDF AND SUBSEQUENT IONOMERISATION

From the FTIR analysis on the grafted PVDF powder, Figure 4.10, are revealed carbonyl peaks at 1714 cm$^{-1}$ for methacrylic acid grafted to PVDF. This peak does not exist in the FTIR spectrum of PVDF in Figure 4.5(a). Ionomerisation with zinc acetyl acetonate of grafted PVDF shows the formation of a carbonate peak at 1571 cm$^{-1}$, as shown in Figure 4.11, which is caused by the reaction between zinc cations and acid groups of methacrylic acid. This is in good agreement with the FTIR analysis of the zinc salts of ethylene-methacrylic acid copolymers reported by Ishioka (139) which shows the antisymmetric stretching of carboxylate ion peak at 1587 cm$^{-1}$. Bonotto and Bonner (140) proposed that the reaction between divalent ions and acid groups of ethylene-acrylic acid copolymers do not give merely a “basic salt bond” $[M^2\text{OH}]^+$.
but more like a cluster of acid groups around the cations. They stated that metallic ions are not permanently associated to any particular carboxyl groups. Hirasawa et al. (141) proposed that the ordered structure of ionic salts in ethylene ionomers differs depending on the type of metal cations. For zinc cations it was found that 3 carbonyl groups were arranged around the metal cation. In the case of zinc-neutralized sulfonated polystyrene ionomers, on the other hand, Samuel Ding et al. (142) proposed a molecular model with four sulfonated groups around the zinc atom.

The presence of metallic cations further increase the capability of the polymers to absorb water (143). Figure 4.45 reveals, however, that ionomerisation of grafted PVDF reduces the water absorption. If the reaction between zinc cations and acid groups formed zinc carboxylate salt, an increase in water absorption would be expected. This shows that there is a possibility of cluster formation of acid groups around the zinc cations, as suggest by Bonotto and Bonner (140), and that the formation of such clusters will reduce ability of acid groups to absorb water. The introduction of acid groups into the PVDF tends to increase water absorption to 5%.

Comparing with this random copolymers of ethylene-methacrylic acid of similar co-monomer concentration, suggests that the values for methacrylic acid grafts to PVDF are in the form of oligomeric rather than monomeric units.

Extraction tests with DMF solvent on the grafted PVDF powder show that the grafting of methacrylic acid to PVDF gives only a 50% dissolution, suggesting the formation of a gel due to crosslinking. SEM micrograph of grafted PVDF in Figure 4.36 also suggests the presence of crosslinked matter with formation of dispersed particles in the PVDF matrix, the size of disperse particles becoming larger with increases in the amount of methacrylic acid. Ionomerisation of the grafted PVDF is expected to reduce the intermolecular interaction due to H-bonding and may give access to DMF solvent to dissolve more of the free PVDF. The SEM micrograph in Figure 4.36(d) supports the hypothesis on the reduction in intermolecular interactions in the form of a more even distribution of dispersed particles in the matrix and the reduction in size of dispersed particles, as a result of salt formation.

With methacrylic acid grafted to PVDF, there is a very small reduction in the melting temperature ($T_m$) of the PVDF, as a result of the interference in the molecular packing by the acid groups. However, Table 4.7 shows that there is large reduction in
crystallinity, heat of fusion (ΔH_f) and heat of crystallization (ΔH_c). Fairley and Prud’homme (144) reported that the incorporation of methacrylic acid units to polyethylene reduces the degree of crystallinity and its melting temperature due to the decrease of the chemical potential of the sample in the melt resulting from the incorporation of a different repeat unit into the (co)polymer chain. Beside the presence of methacrylic acid grafts, γ-irradiation alone is another factor which affects the properties of grafted PVDF. This conclusion is based on result of the rheological studies showing that the viscosity of the irradiated PVDF (Figure 4.48) being lower than the non-irradiated PVDF. These results indicate that some chain scission of PVDF takes place, which could effect the crystallinity and melting point of the grafted PVDF. The effect of ionomerisation on the thermal properties of grafted PVDF depends on the amount of zinc cations present. Based on the DSC results, there is no significant change in the thermal properties with full neutralization, which indicate that interaction between molecules is maintained through the ionic association of zinc cations and acid groups.

Reducing the degree of crystallinity affects the amorphous phase, displacing the T_g to a higher temperature and increasing the magnitude of the relaxation. However, the DMTA spectra in Figure 4.28 for grafted PVDF appear to indicate that crystallinity is not the only factor that influences the relaxation properties of the grafted PVDF. If this the case, there must be other factors which restrict the micro-Brownian motion of the molecular chains and the only possibility is the presence of crosslinks in grafted PVDF. Ionomerisation of grafted PVDF with zinc cations will reduce the ionic interaction within the molecules, resulting in a reduction in the magnitude of the damping peak.

Normally, the existence of acid groups in the polymers favour the formation of hydrogen bonding, which will reduce the mobility of the polymer chain segments and increases the modulus of the material. This effect could persist in the melt state giving rise to a higher viscosity. In the case of grafted PVDF, rheological studies reveals a contradicting result showing a reduction in viscosity of grafted PVDF, as compare with PVDF itself. However this effect could be due to chain scission reactions that have occurred by irradiation.
The cross-linked matter present forms precipitated particles and, therefore, will have only a small effect on viscosity. These will however increase the tensile strength and reduce the elongation as shown in Table 4.12 as is to be expected from a filler effect. Ionic association of zinc cations in the grafted PVDF improved the tensile strength, but reduced further the elongation properties of the ionomer at low level of grafting. With increasing the level of grafting, there is a possibility of increasing the level of crosslinking. Ionic associations with zinc cations, however, do not improve the tensile strength and reduce the elongation of ionomer. A reduction in elongation and an increase in tensile strength with increasing degrees of neutralization has also been reported by Bonotto and Bonner (140).

The fact that butyl acetate is moderately hydrogen bonded and chloroform is non-hydrogen bonded suggests that the introduction of acid groups in grafted PVDF will increase the absorption of butyl acetate more than the chloroform. With increasing the level of grafting, the absorption of butyl acetate and chloroform also reduce as a result of crosslinking taking place. Ionomerisation of grafted PVDF with zinc cations increase the solvents absorption since the ionomers have the capability to form clusters with molecules of solvent through plasticisation.

5.2 EFFECTS OF ACID GRAFTING ON NYLON 6 AND SUBSEQUENT Ionomerisation

The SEM micrograph in Figure 4.35 shows that the grafting of methacrylic acid takes place primarily on the surface of Nylon 6 granules, with a distinct layer about 12 μm thick. FTIR analysis reconfirmed the grafting with the carbonyl peaks at 1714 cm⁻¹ of methacrylic acid as shown in the Figure 4.12. Ionomerisation of grafted Nylon 6 with zinc acetyl acetonate will form zinc carboxylate salt as a result reaction between zinc cations and acid group. Eventhough the FTIR spectra in Figure 4.12 do not show the peaks of carboxylate groups at 1571 cm⁻¹ since it overlaps with the amide -NH peaks, the spectra show the disappearance of carbonyl acid groups. From the solubility studies by extraction with DMF solvent on the grafted Nylon 6, Table 4.11 supports the evidence for the grafting of methacrylic acid, giving an increased extraction of grafted Nylon 6.
When the methacrylic acid is grafted to PVDF, there is a large effect on the thermal properties of the grafted PVDF. This cannot be due simply to effects of hydrogen bonding but it is more likely to result from chemical branching and/or crosslinking which affects molecular configurations and packing. With addition of zinc cations, the melting and crystallization temperatures of grafted Nylon 6 is increased as a result of complex/salt formation, which reduces the branching and crosslinking of grafted Nylon 6 molecules.

The effect of grafting on the molecular arrangements in grafted Nylon 6 can be seen from the DMTA analysis showing a shift $T_g$ for the Nylon 6 phase to higher temperatures which could result from molecular restrictions. The same observation has been reported also by Shinohara (145) when acrylic acid is grafted to Nylon 6.

The occurrence of chain branching and/or crosslinking in the grafted Nylon 6 is also shown in rheological studies which reveals an increase in the viscosity and the viscosity dependence frequency or shear rate. Ionomerisation of grafted Nylon 6 reduces the viscosity of the ionomer through the formation of complex/salt which will reduce the level of branching and crosslinking. Without the occurrence of branching or crosslinking the viscosity of the ionomer would have increased.

As a result of branching and crosslinking, the grafted Nylon 6 has also been found to be more brittle. However, the solvent resistance of grafted Nylon 6 against butyl acetate is improved, and that against chloroform is reduced. The fact that butyl acetate is identified as a moderately hydrogen bonding solvent demonstrates that the effect of branching/cross-linking of the Nylon reduces the possibilities of H-bonding associations and therefore, increases the solubility in less polar solvents. It is also possible, however, that the increased absorption of chloroform can result from ion dipole coordination between zinc cations and chloride dipoles in chloroform.

5.3 COMPATIBILITY OF BLENDS

The terms compatibility and miscibility have in the past been used synonymously, to indicate that the mixture is homogenous at molecular level. More recently the term compatibility has been used to denote a state of mixing of two or more components which is between miscibility and immiscibility. This is sometimes also called partial
miscibility. Compatible systems will have two or more phases, but there will be a diffuse interphase which gives strong adhesion (Fig. 5.1). This is often achieved by adding a compatibiliser. Alternatively, the mixture may be in a state within the binodal curve so that each phase will contain a miscible mixture of the two components, but have different compositions, i.e. A becomes $A'$ and B becomes $B'$ without the occurrence of a diffused interphase.

![Figure 5.1: Morphologies of a blend of polymer A and polymer B (continuous phase).](image)

(a) immiscible and (b) partial miscible with an interphase between polymer A and B promoted by a compatibiliser

Compatibilisation of the blends of PVDF and Nylon 6 at weight ratios of 80/20 and 20/80, corresponding to volume ratios of 71/29 and 14/86, respectively, can be interpreted according to either mechanism mentioned above. Compatibility of the blends can be deduced from morphology and thermal analysis studies, high temperature deformational behaviour and mechanical properties. These are discussed below:
5.3.1 Morphology of PVDF/N6 Blends

a) Morphology of PVDF/N6 80:20 blends

When 20% Nylon 6 is added to PVDF, the melting point ($T_m$) of the PVDF phase exhibits a small but significant increase. This is accompanied by a large decrease in crystallization temperature ($T_c$) and degree of crystallinity compared to PVDF by itself. The melting temperature, crystallization temperature and degree of crystallinity of the Nylon 6 phase are reduced in relation to Nylon 6 in isolation. While the DSC analysis reveals some changes in thermal properties of the blend, the SEM micrographs in Figures 4.38(a), i.e. PVDF/N6 80:20 blend show the presence of very coarse dispersed particles in the matrix, with a sharp interphase between the two phases. This suggests that compatibilization is through "partial thermodynamic miscibility", i.e. each main phase containing small amounts of the second component. The fact that FTIR spectra in Figure 4.13(a) does not reveal any specific interaction between the two polymers is due to the low concentration of the second component in the main phases. Similar explanation can be used to account for the fact that no reduction in water absorption from the theoretical value. However, there is a significant increase in the absorption of butyl acetate, which supports the partial miscibility hypothesis, and demonstrates that the diffusion of butyl acetate is much more sensitive to low levels of miscibility than water. Further more the DMTA spectra in Figure 4.29 confirms it by showing a reduction in the magnitude of relaxation at -20 °C for the PVDF phase, due to the reduction in the mobility of molecular chains as a result of the solubilisation of Nylon 6 in the matrix.

When 20% grafted Nylon 6 is added to PVDF, there is also significant reduction in crystallization temperature and crystallinity of PVDF phase compared to PVDF itself, similar to the blends with ungrafted Nylon. For the Nylon 6 phase, there is an increase in melting point and significant increase in crystallization temperature, but a significant reduction in crystallinity, as compared to grafted Nylon 6 itself. Although there is some change in the thermal properties of the polymers, again, the SEM micrograph in Figure 4.39(a) reveals a non-miscible system. The size of dispersed particles, i.e. grafted Nylon, particles is much the same as for the PVDF/N6 80:20 blend. The FTIR
spectrum (a) in Figure 4.14 again does not show any specific interactions. Water absorption tests, however, show a small increase in the water absorption compared to PVDF/N6 80:20 blend, corresponding to the increase in absorption caused by the acid groups in the grafted Nylon 6. However, with methacrylic acid grafted to Nylon 6, the PVDF/N6-g-MAA11 80:20 blend shows a significant improvement in solvent resistance towards butyl acetate, compared to PVDF/N6 80:20 blend. The DMF solvent extraction also shows a reduction in extraction of about 24.5% from the theoretical (expected) value. This indicates that some interaction exists between acid groups of the grafted Nylon 6 and PVDF chains. The effect of the acid groups in the blend can be seen also from the DMTA spectra in Figure 4.32(a), which shows a very large depression of the height of PVDF relaxation from about 80 °C onwards compared to PVDF/N6 80:20 blends. This can not only be due to some solubilisation of the Nylon 6 phase but also to strong interactions between the COOH groups and PVDF chain. Although the PVDF/N6-g-MAA11 80:20 blend shows small degree of interaction the overall picture it is that of a not well compatibilised blend.

The morphology of the PVDF-g-MAA5/N6 80:20 blend in Figure 4.38 reveals an improved adhesion between the two components and a reduction in particle size of the dispersed phase. By further increasing the amount of methacrylic acid grafted to PVDF, i.e. PVDF-g-MAA10/N6 80:20 blend, the system appears to be come almost homogenous, i.e. one phase. The FTIR spectra in Figure 4.13 confirm the occurrence of the interaction between the two components with formation of a new peak at 1712 cm⁻¹ which has been identified as the conjugated double bond of carbonyl groups, resulting from the reaction between acid groups of grafted PVDF and amine groups of Nylon 6. This was accompanied by the disappearance of acid groups peaks and a reduction of peaks height absorbance ratio NH₂/CH₂, (Table 4.6), compared to the PVDF/N6 80:20 blend. The reaction between the terminal amine groups of Nylon 6 and acid functionality has been previously proposed by McKnight et al. (108). In a study of the binary blends of Nylon 6 and ethylene-methacrylic acid copolymers, they suggested that graft copolymers were formed at the interface between the two phases as a result of amidation reactions taking place during melt mixing. The FTIR analysis by Willis et al. (146) also confirmed the occurrence of the acid/amine reaction at the interface, which is responsible for the compatibilization of the blend. Furthermore, they
reported that there is no hydrogen bonding formation between the carboxylic acid groups and the amide carbonyl groups of Nylon 6.

Although Figure 4.46 reveals an increase in water absorption, i.e. about 3.5%, the increment is far less than the expected 6% water absorption value, which indicates that there is interaction between both components involving acid groups of grafted PVDF and amine groups of Nylon 6.

As a result of this interaction, there is large reduction in the thermal enthalpy of the Nylon phase in the PVDF-g-MAA5/N6 80:20 blend. With a further increase in the amount of methacrylic acid grafted to PVDF, i.e. 10% grafting, the DSC thermogram of PVDF-g-MAA10/N6 80:20 blend reveals only one crystallization peak. However, the effect of the interaction is not felt so much with respect to the thermal properties of the PVDF phase. The interaction also reduces the solvent resistance properties toward both butyl acetate and chloroform. With a further increase in extent of interactions i.e. by increasing the amount of methacrylic acid, the solvent resistance of PVDF-g-MAA10/N6 also increases, compared to PVDF-g-MAA5/N6 80:20 blend. The result of such interaction is to produce a very large and broad peak in the relaxations at 80 °C for the PVDF-g-MAA10/N6 80:20 blend, as shown in Figure 4.30, compared to the PVDF/N6 80:20 blend. It can be concluded that all the results confirm the occurrence of acid/amine reaction between grafted PVDF and Nylon 6 at the composition ratio 80:20.

When both components are grafted polymers, the SEM micrograph of PVDF-g-MAA10/N6-g-MAA11 80:20 blend (Figure 4.39) shows an almost miscible system. Based on the FTIR spectra in Figure 4.14, there is evidence of an acid/amine reaction with a reduction in the peak height of the NH₂ terminal groups of Nylon 6 and the disappearance of the acid carbonyl peak, accompanied by the formation of a conjugated double bond of carbonyl peak at 1712 cm⁻¹. As a result of the acid/amine reaction, the water absorption of PVDF-g-MAA10/N6-g-MAA11 80:20 blend is reduced to about 5%, compared to the 6.5% expected water absorption. The acid/amine reaction reduces the availability of acid groups in forming hydrogen bond with water molecules. From the DMF solvent extraction tests it is found that the amount extracted is much higher than expected i.e. 60.6% instead of 42.4%, which means that there is interaction between the two components. It shows that the
reaction between acid groups of grafted PVDF and amine group of Nylon 6 will reduce the interaction within the molecules of grafted PVDF and loosens the molecular packing of PVDF phase, producing access for the solvent to penetrate into the matrix. The effect on molecular packing increase also results in an chloroform absorption, as shown in the Table 4.17, compared with the PVDF/N6-g-MAA11 80:20 blend.

Based on the reduction in size of the NH$_2$ peak (see Table 4.6), it is deduced that the extent of acid/amine reaction in the PVDF-g-MAA10/N6-g-MAA11 80:20 blend is greater than in the PVDF-g-MAA10/N6 80:20 blend, which means that the first blend is more compatible than the second blend. This increase in compatibility has been confirmed by the results of the DSC analysis, in Table 4.8 and Figure 4.21, which shows only one melting peak and one crystallization peak for PVDF-g-MAA10/N6-g-MAA11 80:20 blend, compared to two melting peaks and one crystallization peak for the PVDF-g-MAA10/N6 80:20 blend in Figure 4.20. As a result of the increased interactions between the two components, the DMTA spectra of PVDF-g-MAA10/N6-g-MAA11 80:20 blend show a large increase in the PVDF relaxations with a wide peak at 60 °C to 80 °C, compared to the PVDF-g-MAA10/N6 80:20 blend. Hence, it can be concluded that the blend of grafted PVDF and grafted Nylon is more compatible than the blend of grafted PVDF and Nylon 6 at the same composition ratio i.e. 80:20.

Several authors (7,78,79,126) have reported that the addition of metal cations to produce ionomers into the blend improves the compatibility of the system. In this work the adding of zinc acetyl acetonate to the blend gives different results. The SEM micrograph in Figure 4.38 for the PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend shows a heterogenous blend with very small particles dispersed in the matrix, compared with PVDF-g-MAA10/N6 80:20 blends. The reduction in miscibility is due to the formation of zinc salt/complex between the acid groups of grafted PVDF and zinc cations in the blends, which prevents the acid/amine reaction from taking place. This was clearly shown in Figure 4.15 from FTIR analysis which reveals the disappearance of the conjugated carbonyl peak (as a result of acid/amine reaction) and the increase in absorbance intensity of NH$_2$ terminal of Nylon 6, as shown in Table 4.6. It is not possible to resolve the carboxylate stretching frequency at 1571 cm$^{-1}$ of zinc carboxylate salt/complex due to overlap with the Nylon 6 spectrum.
The DSC spectra confirmed that the system is incompatible forming two melting and two crystallization peaks, that are nearly in the same position as in the PVDF/N6 80:20 blend, clear evidence of no interaction between the two components. The explanation is that, probably, the reaction between zinc cations and acid group allows the Nylon 6 molecules to form only physical associations with themself, which allow them to recrystallize to the original form. Although the water absorption for PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend is increased, compared to the PVDF-g-MAA10/N6 80:20 blend, this is nearly the same as the calculated amount based on the absorption by the ionomer and the Nylon 6 phases, separately. It leads to the conclusion, therefore, that the interaction between PVDF-g-MAA10/ZnAA(1) and Nylon 6 must be rather weak.

As mentioned earlier, the zinc salt/complex formation will increase the solvent absorption of butyl acetate and chloroform by forming clusters with the solvent molecules. Increasing the concentration of zinc cations, the solvent absorption also increases, except for the PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend, which shows a reduction in butyl acetate absorption, compared to the PVDF-g-MAA10/N6 80:20 blend. The masking effect of zinc cations on the acid/amine reaction is to cause a depression in the relaxation peak at high temperatures for the PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend compared to the blends which allow acid/amine reactions, as shown in Figure 4.30. This is because crystallization has taken place for both components giving an increase in crystallinity (as shown in Table 4.9), which results in a reduction in the peak height of the blend, since relaxation are mostly due to the amorphous components of the blend. Taking all the results into consideration leads to the conclusion that zinc cations do not enhance the compatibility of grafted PVDF and Nylon 6, at the composition ratio 80:20, due to the formation of complex/salt with acid groups in the grafted PVDF.

Ionomerisation with zinc acetyl acetonate also produces non-compatible system for blends in which both polymers are grafted, i.e. PVDF-g-MAA10/ZnAA(0.5)/N6-g-MAA11 80:20 and PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blends. Although the SEM micrographs in Figure 4.39 show a nearly homogenous phase for the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, the DSC trace in Figure 4.24 reveals the presence of small thermal peaks as evidence of the existence of a dispersed phase.
of grafted Nylon 6. The events that lead to the formation of a homogenous phase may be related to the interaction between zinc cations and the acid groups of grafted Nylon 6, in addition to the reaction of zinc cations with acid groups of grafted PVDF. This conclusion is based on the effect of zinc cations in shifting the crystallization temperature of Nylon 6 to lower temperatures (see Table 4.9). However, FTIR spectra in Figure 4.16 cannot reveal the interaction between the acid groups of grafted Nylon 6 and zinc cations because the amount of acid groups in grafted Nylon 6 is so small compared to the acid groups of grafted PVDF. The spectra only show the disappearance of the conjugated carbonyl peaks at 1712 cm⁻¹ and the increase in intensity of the amine peak at 3300 cm⁻¹. The carboxylate peak at 1571 cm⁻¹ can not be identified because it overlaps with amide peaks of Nylon 6. On the other hand, the FTIR analysis confirmed the effect of zinc cations in preventing the acid/amine reaction. The DMF solvent extraction tests on PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 show a very small increase in amount extracted over the expected value, and which could have resulted from the zinc cations interaction with acid groups of grafted Nylon 6. As mentioned earlier, the addition of zinc cations increases the solvent resistance of the blend of grafted PVDF and Nylon 6 towards butyl acetate and chloroform, as shown in Table 4.17. However, the addition of zinc cations to the blend of both grafted polymers causes a large reduction in the absorption of chloroform and only small increased in the absorption of butyl acetate. The DMTA spectrum in Figure 4.32(c) for PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, compared to spectrum (c) in Figure 4.30 for PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend, also confirmed the occurrence of interactions with the formation of broad and large relaxations at about 50°C. The occurrence of interactions of zinc cations with acid groups of grafted Nylon 6 can also be predicted from the water absorption tests. The results of these tests show that the amount of water absorbed by PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 is nearly the same as the amount of water absorbed by the PVDF-g-MAA10/ZnAA(1)/N6 80:20 blend, although there are additional acid groups in the grafted Nylon 6 which are expected to increase the water absorption, as shown in Figure 4.46. Based on these results, it is concluded that there are some interactions between the two components via zinc cations. The thermal
properties of the blend indicate, however, that the interactions are rather weak and, therefore, the blend cannot be expected to be well compatibilised.

b) Morphology of PVDF/N6 20:80 Blends

In this part of the discussion, studies on the morphology of the blends are based on the Nylon 6 as the matrix and PVDF as the dispersed phase.

As mentioned earlier, the PVDF/N6 80:20 blend is an immiscible system. The SEM micrograph in Figure 4.40 show that the PVDF/N6 20:80 blend is also not miscible, with very coarse dispersed particles (about 1-2 micron) of PVDF. The DSC analysis confirms the immiscibility of two polymers with the existence of two melting peaks and two crystallization peaks, the positions of which being nearly the same as that of individual polymers, except for a significant decrease in crystallization temperature of the PVDF phase. It may be due to the diffusion of PVDF into the Nylon matrix that affects the crystallization process of PVDF, causing it to crystallize at a lower temperature. The occurrence of diffusion of PVDF into the Nylon matrix causes also a reduction in the extraction of PVDF by the DMF solvent, i.e. 11.7% compared to the expected value of 20%, based on the content of PVDF in the blend. As a result of this phenomenon, the solvent resistance of the blend, i.e. PVDF/N6 20:80 blend, towards butyl acetate improves tremendously i.e. only 0.22% absorption of butyl acetate, compared to an extraction of Nylon 6 of 29.0%. The diffusion has shifted the T_g of Nylon 6 to a lower temperature i.e. from 50 °C to 25 °C (see Figure 4.29), providing a strong evidence for large degree of plasticisation of the amorphous phases of the main polymer component. Based on the results for two compositions ratio, i.e. 80:20 and 20:80, PVDF and Nylon 6 only exhibit a partial miscibility at low concentration of PVDF.

When the matrix is the grafted Nylon 6, e.g. PVDF/N6-g-MAA11 20:80 blends, a fine morphology of co-continous phases is produced. This indicates that there are interactions between the two components which allow dispersed particles to diffuse into the matrix. Benedetti et al. (147) have reported that there are intermolecular interactions involving the carbonyl groups of functionalized polyolefins and the methylene groups of PVDF through hydrogen bonds in the amorphous region, based
on FTIR results showing a shift of the carbonyl stretching absorption toward lower frequencies. This explains the significant increase in the crystallization temperature and the small increase in melting temperature of the PVDF phase, compared with the PVDF/N6 20:80 blend (see Table 4.8). Since it is not a strong interaction, the decrease in melting temperature is small, while the small increase in the crystallization temperature is the natural consequence of the significant decrease in the crystallinity of Nylon 6 phase, compared with the thermal properties of grafted Nylon 6 (see Table 4.7). However, interactions alone are not sufficient to explain the reduction in water absorption, since there are acid groups grafted to Nylon 6, compared with the water absorption for the PVDF/N6 20:80 blend. These suggest that the presence of crosslinks in the grafted Nylon 6 molecules prevents the acid groups, the amide groups of Nylon 6 molecules from engaging into hydrogen bonding with water molecules. The possible interactions between the two components and crosslinking in the grafted Nylon 6 molecules also explains the reduction in solvent extraction by DMF, i.e. 19.8%, compared with the expected value of 30.9%. The solvent resistance tests, therefore, reveal how important is the miscibilisation of the dispersed phase into the matrix, beside interactions, with respect to solvent resistance of blends. Miscibilisation of the dispersed phase produces a large increase in the solvent resistant towards chloroform i.e. 0.45% by grafted Nylon 6 and 10.3% by the PVDF/N6-g-MAA11 20:80 blend, compared with the PVDF/N6 20:80 blend which contains coarse particles showing only a small increase in the resistance towards chloroform, i.e. from 3.67% to 4%. Based on all the results, it is concluded that the solubilisation of PVDF into the Nylon matrix and the morphology of the grafted Nylon 6 are mainly responsible for the improvement in the level of compatibility of the blend.

The introduction of acid groups into the blend by grafting methacrylic acid to PVDF improved the compatibility with Nylon. This was based on the SEM micrographs in Figure 4.40, which show that there is significant decrease in particle size of the dispersed phase and also a good adhesion between the two components. As a result of graft copolymer formation at the interface between the two components, the melting temperature and crystallinity of Nylon 6 phase are reduced, while the crystallization temperature is increased (see Table 4.8). The same effect is also observed with the PVDF phase, which undergoes a reduction in the melting temperature and crystallinity,
together with an increase in the crystallization temperature. Since the interaction reduces the crystallinity of both components in the blend, the DMTA spectra in Figure 4.31 for PVDF-g-MAA10/N6 20:80 blend shows the existence of a large relaxation peak, compared with the less compatible blend of PVDF/N6 20:80. Even though there are acid groups in the PVDF-g-MAA10/N6 20:80 blend, the amount of water absorbed is less than, or nearly the same as, the amount absorbed by the PVDF/N6 20:80 blend. This indicates that the capability of acid groups to absorb water has been reduced by the in reaction with the amine groups of Nylon 6. Further observations from the DMF solvent extraction test reveal that the acid/amine reaction induces some solubility of Nylon 6 in DMF solvent. The solvent resistant tests show that the level of interactions play an important part in determining the level of solvent resistance of the blend towards butyl acetate and chloroform. When more Nylon is involved in the interactions, i.e. by increasing in the amount of acid groups grafted to PVDF, the solvent resistant improves to a larger extent. The results show that even with 2% methacrylic acid grafted to PVDF an appreciable improvement in compatibility of the blend is obtained.

When both components are grafted polymers, i.e. PVDF-g-MAA10/N6-g-MAAII 20:80 blend, the SEM micrograph in Figure 4.41 show further improvements in compatibility, evidenced by a reduction in the size of dispersed particles, compared with the PVDF-g-MAA10/N6 20:80 blend (see Figure 4.40). This indicates that strong interactions between the two components have occurred during mixing. The DSC analysis confirms the occurrence of interactions with a decrease in the melting and crystallization temperatures of Nylon 6 phase, compared with the PVDF/N6-g-MAA11 20:80 blend (see Table 4.8 and Figure 4.22). The water absorption experiments further emphasize the occurrence of interactions by a reduction in amount of water absorbed. However, this blend shows a coarser morphology, compared with the PVDF/N6-g-MAA11 20:80 blend. In addition the DSC analysis reveals that the melting temperature of the PVDF phase is the same as for PVDF/N6-g-MAA11 20:80 blend, but a significant reduction in crystallization temperature and increase in the crystallinity is observed. Therefore, there must be other kinds of interaction between the two components besides the acid/amine reaction, which are responsible for the breakdown of particles in the matrix.
In the first part of the discussion on the morphology of the PVDF/N6 blend, it was shown that the ionomerisation improves the miscibility of the system. However, although the SEM micrographs in Figure 4.40 for PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend reveal the disappearance of dispersed particles of PVDF to produce a homogenous phase, the DSC analysis reveals the existence of two phases, corresponding to the melting and crystallization peaks of both components. The same kind of morphology structure have been reported by Willis et al. (146) when 80% Nylon 6 was blended with 20% ionomer i.e. a random terpolymer of ethylene, isobutyl acrylate and methacrylic acid, partially neutralized with zinc (approximately 70%). Through an etching process to remove the dispersed ionomer domains located at the surface, they found from SEM observation that the blend was heterogenous with a very small size of the dispersed ionomer domains in the matrix. The diffusion of dispersed particle into the matrix, as shown by the SEM micrograph, will reduce the amount extracted by the DMF i.e. 4.8% compared with the expected value of 9.3%. Water absorption tests also reveal the role of zinc cations in preventing interactions between the two components by showing an increase in water absorption for PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend, compared with the PVDF-g-MAA10/N6 20:80 blend. Figure 4.47 also shows that the water absorption for PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend is higher than for PVDF/N6 20:80 blend. It indicates that besides the water absorption by Nylon 6 there is small amount of carbonyl groups from grafted PVDF, which is not involved in the complex/salt formation and is available to form hydrogen bonding with water molecules. Again, ionomerisation does not enhance the miscibility by preventing the interaction between the two components.

For the ionomerised grafted PVDF/grafted Nylon 6 blend there appears to be a further desolubilisation of the disperse PVDF phase. This is a clear indication that by adding zinc cations into the blend does not enhance the miscibility of the two components. The DSC analysis also reveals the presence of two phases with a small increase in the melting point and crystallinity, and a significant increase in crystallization temperature of the Nylon phase, while there is significant increase in the crystallization temperature of PVDF phase. The decrease in melting temperature of the PVDF phase may be due to the affect of ionomerisation of the grafted PVDF. The small increase in the melting
and crystallinity of the Nylon phase can be explained from the result of water absorption test. Water absorption show no increase in the absorption of water when adding zinc cations in the blend, compared with the PVDF-g-MAA10/N6-g-MAA11 20:80 blend, although for the PVDF-g-MAA10/N6 20:80 blend there is an increase in water absorption when adding zinc cations. This shows that there is a possibility of interactions between the zinc cations and acid groups of grafted Nylon 6. The morphology of the sample from SEM observation, compared with the morphology of the PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend, can explain the large increase in amount extracted by DMF solvent and the significant reduction in the solvent resistance towards butyl acetate and chloroform. The results show that zinc cations reduce the miscibility of the system by salt/complex formation. The salt/complex formation alone, therefore, does not provide sufficiently strong interactions to provide large improvements in compatibility of the system.

From the studies on both 80:20 and 20:80 compositions of the PVDF/N6 blends, the PVDF-rich blend seems to be technologically more attractive than the Nylon-rich blend as it appear to provide better compatibility.

c) Morphology of PVDF/Nylon 6 Film Blend.

SEM micrographs of the PVDF blend with grafted Nylon 6 film, i.e. PVDF/N-g-MAA3 80:20 blend, reveals the same morphological structure as in the PVDF/N6-g-MAA11 80:20 blend which proved to be an immiscible system. DSC analysis confirmed the lack of miscibility with two melting and two crystallization peaks, corresponding to both components. Furthermore, FTIR analysis also proved that there is no interaction between the two components since all the peaks correspond to those of each components in isolation. The DMTA spectra show a similar trend to the PVDF/N6 80:20 blend, except for an increase in the level of relaxation, probably associated with the acid groups in the grafted Nylon 6. However, the blend of PVDF and Nylon 6 with addition of 5%N6-g-MAA11 third components, as compatibilizer, reveals a fairly homogenous morphology resolution from the diffusion of the dispersed phase into the matrix. Although the blend appear to be homogenous, the DSC analysis reveals the presence of two phases with the formation of two melting and two
crystallization peaks. There are, however, small depressions in melting and crystallization temperatures of the Nylon 6 phase, which indicate the existence of interactions between the two components. FTIR spectra do not show any other peaks beside the peaks of the individual components. However, the solvent resistance shows an increase, while the DMTA spectra show a wide dispersion and a generally lower level of relaxations, compared to the PVDF/N6-g-MAA3 80:20 blend, as a result of the diffusion of dispersed phase into the matrix. The results show that adding a third component as compatibilizer gives some improvement in the compatibility of the two components, and it is not necessary, therefore, to functionalise one component entirely.

For the blend of grafted PVDF with grafted Nylon 6 film, i.e. PVDF-g-MAA10/N6-g-MAA3 80:20 blend, SEM micrographs reveal a large reduction in the size of the dispersed phase due to the strong interaction between the two components. The blend with 5% compatibilizer, i.e. PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, on the other hand, shows a much improved morphology of the blend. The improved compatibility is confirmed by the DSC analysis because both blends show one melting and one crystallization peak, indicating that it is a miscible blend. FTIR analysis of both blends also reveal the existence of interactions between the two components, with the occurrence of acid/amine reaction, as evidenced by the disappearance of acid groups peaks, the reduction in intensity of amine peaks and the formation of new conjugated carbonyl peaks at 1712 cm⁻¹. Although the PVDF-g-MAA10/N6-g-MAA3 80:20 blend shows a reduction in height of the amine peak greater than for the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend (as shown in Table 4.6), it does not mean that the former blend exhibits stronger interactions because the amount of methacrylic acid in the blend is not quite the same, i.e. 0.6% and 0.55% respectively. However, the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend exhibit stronger interactions than the PVDF-g-MAA10/N6-g-MAA3 80:20 blend, based on the position of relaxation peaks i.e. 60 °C and 70 °C respectively, and the solvent resistance tests which show that the former blend has higher solvent resistance.

Ionomerisation of grafted PVDF with zinc acetyl acetonate produces a heterogeneous phase morphology for both blends, with the formation of two melting and two crystallization peaks and almost the same thermal properties (as shown in Table 4.10).
The FTIR analysis of both blends reveal the role of zinc cations in preventing the occurrence of the acid/amine reaction. The spectra in Figures 4.17 and 4.18, in fact, show an increase in intensity of the amine peak and the disappearance of the conjugated carbonyl peak as a result of zinc salt/complex formation. Similar observations for both blends are evident from the DMTA analysis. Finally, the salt/complex formation increased the absorption of butyl acetate, but the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA3 80:20 blend shows an increase in absorption of chloroform. On the other hand, the PVDF-g-MAA10/ZnAA(1)/N6/N6-g-MAA11 80:15:5 blend shows a decrease in absorption of chloroform.

5.3.2 High Temperature Deformational Behaviour

a) Dynamic Mechanical Thermal Analysis

The dynamic mechanical analysis from -100 to 100 °C reveals that there are two relaxation peaks for Nylon 6, i.e. the $\alpha$ peak ($T_\alpha$) at 50 °C and the $\beta$ relaxation at about -55 °C, which are in good agreement with the data reported by Gordon (148). The $\alpha$ peak is associated with the glass transition and the $\beta$ peak is attributed to the existence of the polar group forming the hydrogen bonds in the Nylon 6. Judging from the large increase in the $\alpha$ transition temperature, i.e. from 50 °C to 70 °C, for grafted Nylon there is a possibility that crosslinking has taken place within the molecules of grafted Nylon 6. N6-g-MAA11/ZnAA(1), on the other hand, produced a broad and large transition which indicated that ionomerisation depresses the crosslinking process. However, the PVDF main transition ($T_g$) is about -20 °C and there is a large transition at about 60 to 100 °C, which are in good agreement with the results given by Boyer (20) i.e. $\beta$ peak in the region of -30 to -50 °C and $\alpha$ peak in the region of 80 to 100 °C. The $\alpha$ relaxation is related to molecular motions in the crystalline regions and the $\beta$ relaxations are related to motions in amorphous regions. The reduction in magnitude of relaxation at higher temperature for grafted PVDF is due to reduction in the crystallinity and the possibility of crosslinking taken place within the grafted molecules. The ionomerisation by depressing the crosslinking process produces a small but sharp high temperature transition.
PVDF/N6 80:20 blend in Figure 4.29 shows an increase in the magnitude of the high temperature transition, which may be due to some interactions. The PVDF/N6 20:80 blend, on the other hand, reveals a reduction in $T_g$ to a lower temperature, giving strong evidence of plasticisation of the amorphous phase as a result of PVDF diffusion. The interaction between the two components, i.e. PVDF-g-MAAll/N6 80:20 blend, following the solubilisation of Nylon 6 into the matrix, produces a very large and broad peak at about 80 °C (see Figure 4.30). The depression of the interaction between the two components by the zinc cations reduces the high temperature relaxations.

When the matrix is Nylon 6, PVDF-g-MAAll/N6 20:80 blend, the $T_g$ of the Nylon phase does not shift, although there is interaction between the two components (Figure 4.31), but the mechanical spectra show a greater dispersion of relaxation, probably due to some crosslinking in the amorphous Nylon 6 phase. Based on the reduction in magnitude of the relaxations, it is clear that ionomerisation prevents interaction between the two components and reduces the diffusion of the PVDF into the matrix.

For the PVDF/N6-g-MAAll 80:20 blend, there is a large depression in the magnitude of the PVDF relaxation from about 80 °C upwards, compared with the PVDF/N6 80:20 blend. This is probably due to the solubilisation of grafted Nylon 6, which produces interactions between acid groups and PVDF chains. However, when both components are grafted polymers, the spectra of PVDF-g-MAAll/N6-g-MAAll 80:20 blend show large increases in the PVDF relaxations, with a wide peak at 60 °C to 80 °C, which an indication of the increase in interaction between the two components. Addition of zinc cations to the blend produced the same type of spectra as the PVDF/N6-g-MAAll 80:20 blend, but slightly depressed in magnitude of the relaxations. From this observation, it is can be inferred that zinc cations prevent interactions between the two components and reduce the solubilisation of grafted Nylon 6 into the matrix.

Figures 4.33 and 4.34 show the relaxation behaviour of two type of blends. For the first blend one or both polymers is functionalized with acid groups, while the second type of blend has a third components added as compatibiliser, i.e. 5% N6-g-MAAll. The PVDF/N6-g-MAAll 80:20 blend shows high level of relaxations at high temperatures, compared with the PVDF/N6/N6-g-MAAll 80:15:5 blend. This indicates that there is strong interaction between the two components in the
PVDF/N6-g-MAA3 80:20 blend. When the grafted PVDF is used instead of non-grafted PVDF, both blends, i.e. PVDF-g-MAA10/N6-g-MAA3 80:20 and PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blends, show strong interactions between the two components, with fairly sharp peaks and an increase in the magnitude of the relaxations at high temperatures. The position of the relaxation peak of the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend, however, is at lower temperature, i.e. 60 °C, compared with the PVDF-g-MAA10/N6-g-MAA3 80:20 blend, i.e. 70 °C. When both peaks are compared with the relaxation peak of the PVDF/N6 80:20 blend at about 80 °C, it shows that the components in the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend interact more strongly. This means that adding a compatibilizer to the blend produces better compatibility between the components in the blend than using only functionalized polymers. Ionomerisation with zinc cations reduce the interaction, based on the depression of the PVDF relaxations.

b) Rheological Studies

From rheological studies, it is revealed that PVDF undergoes chain scission when irradiated in the air at 15 kGy, evidenced by reduction in the viscosity. When 5% methacrylic acid is grafted to PVDF, there is further reduction in viscosity. Generally, the existence of acid groups attached to the polymer tend to increase the viscosity through the formation of hydrogen bonds within the molecules. In this case, there is the possibility that crosslinked materials containing the acid groups forms dispersed particles that have little affect on the viscosity. The increase in the viscosity of the PVDF-g-MAA10 i.e. containing 10% methacrylic acid is indicative of crosslinking reactions taking place in the grafted PVDF matrix, although precipitated particles are still present. The strong intermolecular forces created by ionomerisation is the main cause of the increase in viscosity, a well known phenomenon observed with ionomers and their blends (8).

Nylon 6 also undergoes chain scission when irradiated, causing a slight decrease in the viscosity. When methacrylic acid is grafted to Nylon 6, there is tremendous increase in viscosity, which indicates that there is extensive chain branching taking place and probably also crosslinking in the grafted Nylon 6. Ionomerisation with zinc acetyl
acetonate reduces the viscosity of the ionomer and also the viscosity dependence on frequency, which indicate that a lower degree of branching and crosslinking takes place, compared with the grafted Nylon 6.

Addition of 20% Nylon 6 does not give a significant effect on the viscosity of the blend, while the reduction in viscosity for the PVDF-g-MAA/N6 80:20 blend is mainly a reflection of the reduction in viscosity of the PVDF matrix. Increasing the amount of methacrylic acid grafted on to PVDF, has no significant further effect on the viscosity, although from SEM observation there are indication of a strong adhesion between the two components.

However the addition of 20% grafted Nylon 6 produces a significant effect on the viscosity of the blend because of the grafted Nylon 6 has intrinsically a higher viscosity. Although the PVDF-g-MAA10/N6-g-MAA11 80:20 blend shows stronger interactions than the PVDF-g-MAA10/N6 80:20 blend based on the DSC analysis, it only produces a very small reduction in viscosity. Note that the SEM micrograph reveals the formation of fine particles in the matrix and, therefore, these are not expected to contribute very much to the increased viscosity.

Addition of 20% PVDF to either Nylon 6 or grafted Nylon 6 does not effect the viscosity, as shown in Figure 4.53, compared with the viscosity of grafted and non-grafted Nylon 6 in Figure 4.49. Although the SEM micrograph in Figure 4.40(c) for PVDF-g-MAA10/N6-g-MAA11 20:80 blend reveals a strong adhesion between the two components, the rheological studies show reduction in viscosity compared with the PVDF/N6-g-MAA11 20:80 blend. The frequency dependence, however, remains the same. From the above discussion, ionomerisation of the blend with PVDF as the main phase, produces a significant increase in viscosity. For the PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 20:80 blend, however, ionomerisation produces a reduction viscosity due to reduction in the level of crosslinking reactions between the components and within the Nylon phase. Since the frequency dependence has been reduced, it shows that the Nylon component has less chain branching.

Figures 4.54 and 4.55 show the viscosities of two types of blends. The first figure is for the binary blend using functionalized groups and the other figure shows the effect of third components as compatibiliser, i.e. 5% N6-g-MAA11. The former blend, i.e. PVDF-g-MAA10/N6-g-MAA3 80:20 blend, shows that interactions between the
two components increase the viscosity. However, the PVDF-g-MAA10/N6/N6-g-MAA11 80:15:5 blend shows a decrease in viscosity as a result of the reduction in crosslinking reactions. From SEM observations on both blends, i.e. Figures 4.43 and 4.44, it is noted that both blends produce different types of morphology, which is probably also reflected in the viscosity data.

5.3.3 Mechanical Properties

Introduction of 5% methacrylic acid grafted to PVDF shows a reduction in the tensile strength and elongation properties of the materials. Generally, the introduction of acid groups into the backbone of polymers tends to improve the tensile strength with the formation of hydrogen bonding contributed by the carboxylic acid groups. In the present case, the effect is probably due to crosslinking rather than hydrogen bonding because with increasing the amount of methacrylic acid, the tensile strength is improved and becomes greater than PVDF itself, while the elongation continues to drop. Ionomerisation of grafted PVDF with zinc cations improved the tensile strength properties, as shown in Table 4.12. This is in good agreement with the results of Bonotto and Bonner (140) in their studies on the effect of ion valency on the physical properties of salts of ethylene-acrylic acid copolymers. As a result of crosslinking in the grafted PVDF, however, the mechanical properties of grafted and ionomerised PVDF do not improve so much. While, grafted Nylon 6 became too brittle and was not tested.

The addition of 20% Nylon 6 to PVDF reduces mechanical properties of the blend because it produces an incompatible blend. However, with the addition of 20% grafted Nylon to PVDF, the reduction in tensile strength is less than for the blend with non-grafted Nylon. It shows that, the PVDF/N6-g-MAA11 blend is more compatible than the PVDF/N6 blend at the same composition ratio. The introduction of 5% methacrylic acid into the blend, i.e. PVDF-g-MAA5/N6 80:20 blend, increased the tensile strength, demonstrating an improved compatibility of the blend. Increasing the amount of methacrylic acid in the blend, i.e. to 10%, results in a reduction in the tensile strength, although the interaction between the two components in PVDF-g-MAA10/N6 80:20 blend is higher than for PVDF-g-MAA5/N6 80:20, as evidenced by
the depression of melting temperature and the disappearance of the crystallization peak. A direct correlation between interaction and mechanical properties is difficult because of the complications arising from crosslinking reaction in the grafted PVDF. However, for the PVDF-g-MAA10/N6-g-MAA11 80:20 blend there is small increase in tensile strength, compared with PVDF/N6-g-MAA11 80:20 blend, although the DSC analysis reveals that the blend is miscible, i.e. with only one melting peak and one crystallization peak (as shown in Table 4.8). The possibility of crosslinking reactions within the acid groups of grafted Nylon 6 molecules makes it more difficult to relate the mechanical properties with the structure of the blend.

Ionomerisation with zinc acetyl acetonate in the blend of grafted PVDF with 20% Nylon 6, shows a decrease in the tensile strength with increasing the amount of zinc cations, except for the PVDF-g-MAA10/ZnAA(0.5)/N6 80:20 blend which reveals an increase in tensile strength. Poor compatibility of the system will give poor mechanical properties. In the case of the PVDF-g-MAA10/ZnAA(0.5)/N6 80:20 blend, since only half of the acid is reacted with zinc cations, there is some acid available to react with amine groups of Nylon 6 and that is why the tensile strength is almost the same as the PVDF-g-MAA5/N6 80:20 blend. However, for the blend with both components are grafted polymers, i.e. PVDF-g-MAA10/ZnAA(1)/N6-g-MAA11 80:20 blend, ionomerisation shows improvements in both tensile strength and elongation, although the FTIR analysis does not reveals any form of interaction between the two components. In this case, the coordination of zinc cations between the two components in the blend plays an important factor in improving the mechanical properties.

When the Nylon 6 is the major component, the part of the PVDF particles diffuse into the matrix, giving a good interfacial bond, giving a higher tensile strength but lower elongation properties. The strong interaction between the two components, i.e. PVDF-g-MAA10/N6 20:80 blend, gives rise to higher elongation at break but a reduction in the tensile strength of the blend. When ionomerisation taken place in the blend, very fine disperse particles are produced, which act like a filler that merge with the matrix and may cause an increase the elongation of the blend. From Table 4.14, it seems that increase the level of ionomerisation will increase the elongation, for example PVDF-g-MAA10/ZnAA(1)/N6 20:80 blend. Based on these results, it is
concluded that adding grafted PVDF or ionomerising the Nylon 6 gives a significant improvement in the elongation at break, but not in the tensile strength.

The mechanical properties in Table 4.15 are compared for two types of blends. The first blend uses functionalized polymers to improve compatibility and the second blend uses a third component as compatibilizer, i.e. 5%N6-g-MAA11. For the blend with 20% N6-g-MAA3, increased interactions reduce the mechanical properties of the blend and ionomerisation makes it even worse. However, for the blend with the compatibilizer, the increased interaction between the two components improved the mechanical properties and further improvements were obtained with ionomerisation. Based on these observations, it is concluded that adding a compatibilizer to the blend gave better properties than by using a functionalized polymer directly.
6.1 CONCLUSIONS

The main conclusions that can be derived from this work are as follows:

6.1.1 Grafting and Ionomerisation of PVDF

a) Grafting methacrylic acid on PVDF chains by pre-irradiation of the powders (γ-rays), and subsequent reactions in water solutions of the monomer produces an uneven distribution of grafts and gives rise to the formation of crosslinked products which cause the precipitation of fine particles in subsequent melt blending operations. Confirmation of these findings has been obtained by FTIR analysis, solvent extraction tests in DMF and rheological measurements.
The high level of water absorption exhibited by the grafted polymer suggests that the methacrylic acid is present in oligomeric, rather than monomeric, units. The presence of methacrylic acid grafts increases the solvent resistance of PVDF, particularly towards butyl acetate and chloroform.

b) Ionomerisation of methacrylic acid grafted PVDF can be accomplished by mixing it in the melt state with zinc acetyl acetonate. The extent of ionomerisation can be easily followed with FTIR by monitoring both the disappearance of the acid groups at the 1714 cm\(^{-1}\) peak and the appearance of a carboxylate anion peak at 1571 cm\(^{-1}\). Further evidence of ionomerisation is obtained from rheological measurements which have revealed an increase in melt viscosity. Ionomerisation of methacrylic acid grafted PVDF brings about a reduction in water absorption. This is a clear evidence that the ionic species are present in the form of localised clusters rather than being dispersed along the chains as isolated carboxylate groups.

6.1.2 Grafting and Ionomerisation of Nylon 6

a) Grafting of Nylon 6 granules by γ-radiation, with the pre-irradiation technique, produces a highly localised outer surface layer of grafted polymer. This is expected to contain a large number of oligomeric methacrylic acid units as side chains. Crosslinking takes place after mixing the grafted granules in the melt state. This is clearly indicated by the drastic changes in rheological behaviour, i.e. from a typical semi-Newtonian to a very viscous, but highly pseudoplastic, material. The reactions taking place as a consequence of the grafting process bring about a reduction in crystallinity which is accompanied by an increase in solubility in DMF. Grafting reactions carried out on thin films (≈ 20 \(\mu\)m) appear to have taken place through the entire body. From SEM examinations of fractured specimens there are some indications, however, that grafting does not take place homogeneously within the films, but through preferential paths.

b) Ionomerisation of the methacrylic acid grafted Nylon can be easily accomplished by mixing it in the melt state with zinc acetyl acetonate. The ionomerisation reaction can
not be followed satisfactorily by FTIR analysis, since the carboxylate anions absorption overlaps with the amide absorption bands. The disappearance of carboxylic acid groups at 1714 cm\(^{-1}\), however, can be readily monitored by FTIR.

The addition of zinc acetyl acetonate, to neutralise the carboxylic acid groups, reduces the extent of crosslinking reactions taking place during melt mixing. There is strong evidence (see later) that this is due to a reduction in the extent of reaction of carboxylic acid groups with terminal amino groups in the Nylon 6 chains.

The addition of zinc acetyl acetonate brings about a reduction in \( T_g \). Experiments on control sample, i.e. non-grafted Nylon, show that this phenomenon results primarily from the co-ordination reactions with the polyamide chains.

6.1.3 Effects of Grafting on Compatibility of PVDF/N6 Blends

a) A degree of miscibility exist in blends of Nylon 6 and PVDF in their natural (ungrafted) state. This is experienced, however, only in blends where Nylon 6 is the minor phase and is evidenced by an increase in the \( T_g \) of the PVDF phase and a reduction in its level of crystallinity, as a result of the solubilisation of the minor amounts of polyamide chains.

b) Blends of methacrylic acid grafted PVDF with Nylon 6 show a remarkable increase in miscibility (particularly when PVDF is the main component) as a result of the reactions of carboxylic acid groups in the PVDF chains and the terminal amine groups in the polyamide chains. The occurrence of these reaction has been clearly illustrated by the FTIR analysis which shows a distinct reduction in the concentration of amine groups, a depression of the carboxylic acid absorption band and a clear appearance of a conjugate carbonyl peak, corresponding to O=\( \equiv \)N—C=O, at 1712 cm\(^{-1}\). The occurrence of intermolecular reactions between Nylon and PVDF components in the blends is also supported from all other tests carried out:

— SEM examinations show the presence of much finer domains and a more diffused interphase (clear evidence of compatibilization).
DSC analysis shows a depression of the melting point and a reduction in degrees of crystallinity for both phases.

Solubility tests show that the solubility of the PVDF phase in DMF, and that of the Nylon 6 phase in butyl acetate, is decreased considerably. This is obviously an important improvement in properties, which could have considerable bearing on the commercial exploitation of these blends.

Blends of PVDF with grafted Nylon 6 do not show any particular difference in behaviour from the blends based on ungrafted polymers, other than the expected effects at high levels of grafted Nylon, as a result of intramolecular crosslinking reactions.

With blends produced from grafted PVDF and grafted Nylon, even larger improvements in miscibility are achieved. A homogenous blend is obtained when the grafted Nylon is the minor components. In this case, the Nylon component does not crystallise, but remains molecularly dissolved in the PVDF phase. This has to be attributed to intramolecular branching and crosslinking within the Nylon phase and to intermolecular branching reactions between the acid groups in the PVDF and amine groups in the Nylon. Such reactions are reduced when the grafted Nylon, produced from films, is used as a third component (i.e. compatibilizer). As a result, the blends show a higher level of compatibility, as indicated by the finer dispersion of the two phases.

6.1.4 Effect of Ionomerisation of Acid Groups of the Blend Components

The use of zinc acetyl acetonate in blends of grafted polymers produces carboxylate salts and decreases the extent of reactions that can take place between carboxylic acid groups and amine groups in the two respective polymers. Zinc acetyl acetonate, therefore, can be used for two purposes:

a) to produce ionomeric species in the blends, and
b) to control the extent of reactions leading to branching and crosslinking.

This is clearly illustrated by referring to the results from DSC which show the reappearance of the melting peak and crystallization peak of the Nylon 6 phase. The reduction in branching and crosslinking reactions increase the level of solvent absorption of butyl acetate and chloroform. Associated with the reduction in the level of intermolecular branching and crosslinking reactions is the large suppression in relaxation at high temperature, revealed by DMTA studies.

6.2 SUGGESTIONS FOR FUTURE WORK

The present work has revealed that there are significant advantages to be gained by grafting methacrylic acid on to PVDF for use in blends with Nylon 6. Grafting of acid groups on to Nylon 6, on the other hand, will lead to intramolecular branching and crosslinking reactions which could be difficult to control.

In order to achieve a better understanding of the findings obtained in the present work and to improve the "compatibility" and, hence, the properties of the blends produced by this method, the following suggestions are put forward:

— To achieve a deeper penetration of the grafting into the PVDF powder:
  a) Use a certain amount of DMF in the water solution of acrylic acid to increase the rate at which it can diffuse into the powder. Any residual DMF in the powder will evaporate out during drying.
  b) Pre-swell the PVDF powder with a small amount of DMF and methacrylic acid, from a water solution, and use the co-irradiation technique for grafting. The DMF will act as a diluent and will minimise the extent of crosslinking and homopolymerisation.

— To increase further the intermolecular reactions between the grafted PVDF and Nylon components, without the risk of intramolecular crosslinking, it should be possible to graft on Nylon chains some vinyl pyridine units from water solutions. These are expected to produce labile ionic bonds in the formation of quaternary salts with the acid groups in the PVDF.
— To gain a better insight into the structure of the compatibilised blends attempts should be made to use transmission electron microscopy (TEM) by ‘staining’ the Nylon phase with heavy metals such as osmium or ruthenium compounds. It is possible that these may co-ordinate with the polyamide chains in the same way as the zinc compounds.

Small angle X-ray scattering (SAXS) would also be useful to study the structure of the more highly ‘compatibilised’, (i.e. systems with a very fine domains of nanoscale dimensions), particularly for blends containing ionomeric clusters. SAXS could in fact, even differentiate between domains due to ionomeric clusters, normally very small, 3-5 nm, and the coarser polymer phase domains.
REFERENCES


33. R. Greco and L. Nicolais, Polymer, 17, 1049 (1976)

34. A. Charlesby, Nature, 171, 167 (1953)


42. H. Frensch and B.J. Jungnickel, Colloid Polymer Science, 267, 16 (1989)


52. A. Chapiro and V. Stannet, Intern. J. Appl. Radiation Isotopes, 8, 164 (1960)


61. Reference 47, pp 444
79. A. Molnar and A. Eisenberg, Polymer, 34, 1918 (1993)


136. D.H. Grant and N. Grassie, Polymer, 1, 125 (1960)


140. S. Bonotto and E. Bonner, Macromolecules, 1, 510 (1968)


