Morphology and properties of blends of natural rubber and epoxidised natural rubber

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MORPHOLOGY AND PROPERTIES
OF BLENDS OF NATURAL RUBBER AND
EPOXYDISED NATURAL RUBBER

BY

HAIDZIR ABDUL RAHMAN
(DRPT, Bach. of Appl. Sci. Hons)

A Master's thesis

Submitted in partial fulfilment
of the requirements for the award of
Master of Philosophy of the Loughborough
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ABSTRACT

The degree of compatibility of two component blends have been examined by many experimental techniques. The criterion is important, as it influence the morphology and the mechanical properties of the blends.

The blends employed are NR/ENR-48 and ENR-26/ENR-48 over a range of compositions and a 50:50 latex blend of ENR-31/ENR-43. Mixing of rubbers and crosslinking agent (dicumyl peroxide) was done on a small two-roll mill. A simple vulcanizate system is used in order to simplify interpretation of the morphological structure.

Solubility parameter \( \delta \) is one of the properties which can be utilized to predict the degree of compatibility, via the Flory-Huggins segmental interaction parameter \( \chi_{AB} \). For NR and ENRs, \( \delta \) increases linearly with increased percent epoxide groups in the rubber. The smaller the difference in \( \delta \), the greater the segmental interaction between the two polymers.

A two-phase system was confirmed on these blends by identification of distinct glass transition, as determined from both DSC and DMTA.

The morphology of NR/ENR-48 blend vulcanizates was studied by DMTA and phase contrast microscopy techniques. At 10-20\% ENR-48 component in the blends, NR is the continuous phase and ENR-48 is the discrete phase. But, at 30-40\% ENR-48, both NR and ENR-48 components dominate to form co-continuous phases. At 50\% ENR-48 and beyond, ENR-48 is the continuous phase and NR is the discrete phase. Good agreement was obtained between the various techniques used to study the morphology. The results demonstrate that, the morphology
of NR/ENR-48 blend is dependence on blend composition and the viscosity of each component in the blends.

An attempt was made to relate the morphology with the physical properties, such as air permeability, tearing energy and tensile strength. The results shown that, air permeability and tearing energy can be interpreted in terms of blend morphology. Kerner's theory has been utilized to predict the moduli and loss angle properties of these blends. Within the limits of the theory good agreement was obtained with the experimental results.
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The author expresses his gratitude for invaluable service rendered by the staff of the compounding, analytical and physical testing groups.

Finally but not least, the author thanks all the staff who has offered assistance in connection with this work.
ABBREVIATIONS

The following abbreviations have been used in this thesis:

NR  natural rubber
ENR  epoxidised natural rubber
SMR-L  Standard Malaysian Rubber
d.r.c  dry rubber content
EV  efficient vulcanization
MG  methymethacrylate graft
DSC  differential scanning calorimetry
Tg  glass transition temperature
Td  dynamic glass transition temperature
NBR  nitrile-butadiene rubber
PPO  poly(2,6-dimethylphenylene oxide)
PVC  poly(vinyl chloride)
CED  cohesive energy density
PS  poly(styrene)
DMTA  dynamic mechanical thermal analyser
Td  dynamic glass transition temperature
TEM  transmission electron microscopy
R.I.  refractive index
SBR  styrene-butadiene rubber
EPDM  ethylene-propylene-diene terpolymer
LA-TZ  low ammonia-TMTD/ZnO
DCP  dicumyl peroxide
p.h.r.  parts per hundred rubber
I.R.  infra-red
NMR  nuclear magnetic resonance
RRIM  Rubber Research Institute of Malaysia
MRPRA  Malaysian Rubber Producers' Research Association
Hz  Hertz
ISO  International Standard Organization
IPTME  Institute of Polymer Technology and Materials Engineering
LIST OF SYMBOLS

The following symbols have been used in this thesis:

\( X_{AB} \) \hspace{1cm} \text{Flory-Huggins interaction parameter of component A and B}
\( X \) \hspace{1cm} \text{degree of polymerization of polymer}
\( \delta \) \hspace{1cm} \text{solubility parameter}
\( V_r \) \hspace{1cm} \text{molar volume of polymer}
\( \phi \) \hspace{1cm} \text{volume fraction of polymer}
\( \rho \) \hspace{1cm} \text{density}
\( F_i \) \hspace{1cm} \text{molar attraction constant of chemical groups}
\( M \) \hspace{1cm} \text{Molecular weight}
\( E' \) \hspace{1cm} \text{storage modulus}
\( E'' \) \hspace{1cm} \text{loss modulus}
\( E^* \) \hspace{1cm} \text{complex modulus}
\( \Theta \) \hspace{1cm} \text{loss angle}
\( G \) \hspace{1cm} \text{shear modulus}
\( K \) \hspace{1cm} \text{bulk modulus}
\( \nu \) \hspace{1cm} \text{Poisson's ratio}
\( V_{RN} \) \hspace{1cm} \text{volume of rubber network}
\( V_s \) \hspace{1cm} \text{volume fraction of solvent absorbed}
\( \lambda \) \hspace{1cm} \text{extension ratio}
\( V_0 \) \hspace{1cm} \text{molar volume of solvent}
\( M_c \) \hspace{1cm} \text{number average molecular weight of rubber chains between crosslinks}
\( a_T \) \hspace{1cm} \text{WLF shift factor}
\( T_s \) \hspace{1cm} \text{reference temperature}
\( F_m \) \hspace{1cm} \text{average tearing force}
\( \sigma \) \hspace{1cm} \text{tensile stress}
\( d \) \hspace{1cm} \text{thickness of sample}
\( w \) \hspace{1cm} \text{width of sample}
\( \alpha \) \hspace{1cm} \text{thermal expansion coefficient}
\( \beta \) \hspace{1cm} \text{compressibility}
\( \Delta G \) \hspace{1cm} \text{Gibbs free energy}
\( \Delta H \) \hspace{1cm} \text{enthalpy}
\( \Delta S \) \hspace{1cm} \text{entropy}
Dedication to my wife Ramlah and children Mohd. Harzufi, Hazimi and Mohd. Hazrool for their patience throughout the course of this work
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ABSTRACT

ACKNOWLEDGEMENTS

ABBREVIATIONS

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CHAPTER 1

AN INTRODUCTION AND GENERAL BACKGROUND

1.1 General introduction

Polymer blending has emerged in the last few decades, as a method for producing new types of materials. Both technical and economic advantages can be achieved. Essentially, there are two approaches for forming polymer blends. The first approach is a physical blend of two or more different polymers. The second approach is chemical blending of two or more polymers, e.g. graft and comb copolymers.

The properties of physical blends are different from those of the parent polymers and often are not simply an averaging of the two components. They can be quite unique. This has lead to interesting studies from both academic and industrial research organizations. The study of physical blend is an important subject, since more than 75% by volumes of rubbers are used in blends [1]. The major area is the tyre industry. In fact, polymer blends are classified into two groups, i.e. rubber-rubber blend and rubber-plastic blends. However, rubber-plastic blends are out of the scope of this thesis, although many of the same principles apply. Emphasis will be on the rubber-rubber blends.

The physical blending of rubber is widely carried out using open two-roll mills, internal mixers and extruders. The new materials formed after blending are often determined by the exact mixing technique which can influence the phase structure. Therefore, it is
important to understand the morphology of polymer blends, so that the properties can be more easily understood. Important factors that control the morphology of polymer blend are the ratio of compositions, physical state of the blend components and viscosities, as well as methods of preparation.

The morphology of polymer blends can be predicted from thermodynamics by employing the Gibbs free energy relationship. While, the use of analytical methods such as phase contrast microscopy can be used to characterise the blends.

In this section emphasis will be placed on the factors that affect the structure of polymer blends, technique used to characterise the blends and the properties of the two rubbers which form the bases of this blend study.
1.2 A brief review of NR

NR is available commercially in two forms, as a latex concentrate with a dry rubber content (d.r.c) of 60% and as a dry product, sold in 331/3 kg bales.

Malaysian dry rubber is available in a number of specified forms (Table 1.1). The products consists of approximately 94% polymer hydrocarbon with the remainder of the material being other natural products (Table 1.2). The NR used in this study was a Standard Malaysian Rubber (SMR L).

Chemically, NR hydrocarbon consists of 100% cis-1,4-polyisoprene units. It is essentially a linear long chain molecule with repeating isoprenic units \((C_5H_8)_n\), where \(n\) is about 10000, linked at the 1 and 4 carbon atoms in a head-to-tail arrangement as shown in Figure 1.1.

\[
\text{Fig. 1.1 : Structural unit of cis-1,4-polyisoprene}
\]

In the raw state NR has poor elastic properties which result from molecular entanglements. Because of its stereoregularity NR can crystallizes when stored at low temperature around 0°C and below or when it is

(3)
Table 1.1: Specifications of Standard Malaysian Rubber [2]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SMR L&lt;sup&gt;a&lt;/sup&gt;</th>
<th>SMR WF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>SMR CV&lt;sup&gt;b,d&lt;/sup&gt;</th>
<th>SMR LV&lt;sup&gt;a,d&lt;/sup&gt;</th>
<th>SMR 5&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SMR 10&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SMR GP&lt;sup&gt;c,d&lt;/sup&gt;</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt retained on 40 μm mesh (max. % wt)</td>
<td>0.03</td>
<td>0.05</td>
<td>0.10</td>
<td>0.20</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ash content (max. % wt)</td>
<td>0.50</td>
<td>0.60</td>
<td>0.75</td>
<td>1.00</td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen content (max. % wt)</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td>0.60</td>
<td></td>
<td></td>
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<tr>
<td>Volatile matter (max. % wt)</td>
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<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Wallace rapid plasticity, P&lt;sub&gt;0&lt;/sub&gt; (min)</td>
<td>30&lt;sup&gt;e&lt;/sup&gt;</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
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<td></td>
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<tr>
<td>PRI (min. %)</td>
<td>60</td>
<td>60</td>
<td>50</td>
<td>40</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colour (Lovibond max.)</td>
<td>6.0&lt;sup&gt;f&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mooney viscosity (ML 1+4, 100°C)</td>
<td>-&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-</td>
<td>-h</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cure</td>
<td>R&lt;sup&gt;l&lt;/sup&gt;</td>
<td>-</td>
<td>R&lt;sup&gt;l&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>From latex, <sup>b</sup>Sheet material, <sup>c</sup>Blend
<sup>d</sup>Viscosity stabilised; SMR LV contains 4% process oil,
<sup>e</sup>Only for SMR L and SMR WF, <sup>f</sup>Only for SMR L,
<sup>g</sup>Three grades SMR CV 50, CV 60, CV 70 with viscosity limits 45-55, 55-65, 65-75 units respectively; SMR LV with producer viscosity limits at 45-55 units
<sup>h</sup>SMR GP producer viscosity limits at 58-72 units
<sup>i</sup>Cure information provided for SMR CV, L, WF and GP in the form of rheograph (R)
Table 1.2: A typical analysis of NR [2]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Field Latex, %</th>
<th>Dry Rubber, %</th>
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<td>Rubber hydrocarbon</td>
<td>36.0</td>
<td>93.7</td>
</tr>
<tr>
<td>Protein</td>
<td>1.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Neutral lipids</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Glycolipids + phospholipids</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>Inorganic constituents</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Others</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Water</td>
<td>58.5</td>
<td>-</td>
</tr>
</tbody>
</table>
strained. The rate of crystallization varies with temperature [3].

To be practical useful, NR must be supplemented with elemental crosslinks to tie the NR molecules into a 3-dimensional network. The chemical reaction of NR with sulphur under heat, brings about the formation of crosslinking between long chain molecules. This is known as vulcanization, which was discovered by Charles Goodyear in 1839.

Currently, accelerated sulphur vulcanization system can be classified into three different types [4]: (1) conventional vulcanization system which predominately produce polysulphidic crosslinks, (2) efficient vulcanization (EV) system with short mono- and disulphur linkages and (3) semi-efficient vulcanization system. The conventional system consists of high sulphur/accelerator ratios. Generally, the properties are high tensile strength, resilience and resistance to fatigue and abrasion, but poor heat-ageing, creep and stress-relaxation. An EV system consists of high accelerator/sulphur ratios, confering improved heat-ageing, reversion resistance and low compression set. A semi-EV system is a compromise between the first two extremes. Besides the accelerated sulphur vulcanization systems, there are other systems, such as, urethane [5] and peroxide curing [6] systems. The latter form carbon to carbon crosslinks between the backbone of the rubber molecules.
1.3 Background of Epoxidised Natural Rubber (ENR)

One approach of producing new forms of NR is through chemical modification of the NR structure. In fact chemical modifications of NR have been extensively studied for many years. Such examples are: depolymerised NR [7], hydrochlorinated NR [8], chlorinated NR [9], cyclised NR [10] and methymethacrylate graft NR (MG rubber) [11]. Within the last year a new modified NR has appeared in the market place. It is formed from an epoxidation reaction with peroxo acids. An epoxidation reaction is referred to as the introduction of a three membered epoxide ring (oxirane) into unsaturated organic compound. Numerous methods are available for carrying out the epoxidation reaction. The most widely used is the single-step epoxidation of unsaturated compounds with peroxo acids. The reaction is shown in Figure 1.2.

\[
\text{R-CH} = \text{CH-R'} + \text{R}''\text{CO}_2\text{H} \rightarrow \text{R-CH} = \text{CH-R'} + \text{R'}\text{CO}_2\text{H}
\]

\( R = \text{H (peroxyformic acid)} \)
\( = \text{CH}_3 \) (peroxyacetic acid)

Fig. 1.2 : Peroxyacids epoxidation of unsaturated compound

This reaction was first discovered by Prileschajew [12] in 1909, who used peroxybenzoic acid as oxidising agent. Many others peroxy acids behave in a similar fashion, such as, peroxyacetic, peroxyformic and m-
chloroperoxybenzoic acids [13]. Indeed, epoxidation of NR was first demonstrated by Permmr et al. [14] in 1922, in their study of the structure of rubber molecules. They treated a CHCl₃ solution of rubber with peroxybenzoic acid. Others like Greenspan in 1964 [15] have studied oxidation of NR in the latex stage with peroxy acids. However, the products obtained always led to side reactions, i.e., ring-opening of the epoxide group [16]. As a result, the modified rubber had inferior properties, compared to those of unmodified NR. Thus, the modified rubber produced was of little interest. Renewed interest in epoxidation of NR occurred in the late 70s, when Gelling [17] claimed that epoxidised NR could be produced without side reaction, if the concentration of peroxy acid and the temperature were carefully controlled. Epoxidised NR can be produced by employing the reaction of NR in the latex stage with either a preformed peroxyacetic acid solution [17] or peroxyformic acid, formed 'in-situ' from hydrogen peroxide and formic acid [18], see Figure 1.3. An experimental method employing NR latex with peroxy-acetic acid can be found in section 2.3.

\[
\text{RCO}_2\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{RCO}_3\text{H} + \text{H}_2\text{O}
\]

carboxylic hydrogen peroxyacid peroxide

\[
\text{RCO}_3\text{H} + \text{NR}
\]

Fig. 1.3 : In-situ epoxidation of Natural Rubber

(8)
1.3.1 Peroxyacid epoxidation

The peroxyacetic acid epoxidation route is a useful laboratory method, as it is available commercially as a 40% solution in acetic acid. It is formed by the equilibrium reaction of hydrogen peroxide and acetic acid, with little or no loss of active oxygen (see Figure 1.4).

\[ \text{H}_2\text{O}_2 + \text{CH}_3\text{CO}_2\text{H} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \]

Hydrogen peroxide acetic acid peroxyacetic acid

Fig. 1.4: Preparation of peroxyacetic acid from hydrogen peroxide and acetic acid

Equimolar quantities of acetic acid and 90% hydrogen peroxide are mixed, in the presence of 1.0% sulphuric acid as a catalyst which yields an equilibrium mixture of 40% peroxyacetic acid in acetic acid. Peroxyacetic acid is relatively stable for long periods of time at 0°C. However, for use in epoxidation reaction it is essential to remove the sulphuric acid, since it results in the formation of secondary ring opened epoxide groups. This can be avoided by neutralising with sodium acetate or other bases or by distillation.

The other major peracid employed to epoxidise double bonds is peroxyformic acid. It can be formed very rapidly at room temperature from hydrogen peroxide and formic acid without an additional strong acid catalyst [18]. The formic acid is a sufficiently strong acid to
catalyse the reaction. This acid is less stable and loses its active oxygen rapidly even at 0°C. It is therefore due to this reason that peroxyformic acid is rarely prepared separately, but is generated and used in-situ. The in-situ epoxidation by peroxyformic acid was first reported by Niederhauser and Koroly [19] in 1949.

In-situ peroxyformic acid is a preferred industrial method as the mole ratio of formic acid to hydrogen peroxide used is only 0.2-0.5. The formic acid is recycled within the reaction sequence, as shown in the epoxidation reaction of Figure 1.3. But as mentioned earlier, conditions need to be carefully controlled to avoid secondary ring-opening reactions.

Currently, ENRs are produced in Malaysia. They are prepared from NR latex using the in-situ epoxidation route. Essentially, ENR of any epoxidation level can be produced. However, production is limited to 25 mole percent and 50 mole percent, which are designated as ENR-25 and ENR-50 respectively.
1.3.2 Properties of ENR

The epoxide groups in ENR are randomly distributed along the NR molecular backbone, as determined by $^{13}\text{C}$ NMR spectroscopy [20]. The chemical structure of ENR is shown in Figure 1.5. Like NR, ENR has a cis-1,4-polyisoprene structure because of the stereospecific nature of the epoxidation reaction [21].

\[ \text{Fig. 1.5: The chemical structure of ENR} \]

\[ n=0.5 \text{ (ENR-25)} \]
\[ n=1.0 \text{ (ENR-50)} \]

X-ray diffraction studies have shown that ENR, like NR can undergo strain crystallization [22]. The degree of crystallinity remains constant up to 50 mole % epoxide groups, but beyond this level it rapidly decreases. The volume of the polymer crystal lattice increases as the fraction of epoxide groups on the main chain increase.

Vulcanization systems used for NR can also be employed for ENR. However, conventional vulcanization system results in poor ageing characteristics, compared to unmodified NR. It would be expected that ENR could
Fig 1.6: Retention in tensile strength against number of days at 100 °C for NR and ENR-50 rubbers, cured with conventional sulphur and efficient vulcanization systems [16]
Fig. 1.7: Mechanism of ether crosslinking in epoxidised natural rubber
Fig. 1.8: The glass transition temperature of Epoxidised natural rubber [20]

Fig. 1.9: Relative air permeability of Epoxidised natural rubber compared with natural rubber, synthetic IIR and NBR, at 20 °C and 60 °C [24]
be more resistant to oxidative ageing than NR, since some of the double bonds have been replaced by the epoxide groups. But this behaviour was not observed, as can be seen from retention in tensile strength, Figure 1.6. Gelling et al. [23] have made model studies on the ageing behaviour of ENR-50. Poor ageing properties of ENR-50 are due to sulphur acids attacking the epoxide groups to give crosslinks, via ether group as illustrated in Figure 1.7. The use of semi-EV and EV vulcanization systems were recommended for ENR with the inclusion of bases to neutralize the sulphur acids.

Other vulcanization systems, such as peroxides can also be employed for ENR. In the peroxide system crosslinking is assumed to occur via the double bonds by a similar mechanism to that of NR.

A most interesting aspect of ENR is the glass transition temperature. The Tgs of ENRs increase linearly with increasing epoxide groups, as shown in Figure 1.8. For every 1 mole % epoxide, the Tg increases by approximately 1°C, as determined from differential scanning calorimetry (DSC). For example, the Tgs of ENR-25 and ENR-50 are -47°C and -22°C respectively.

As the mole percent of epoxide increases, the polymer properties move towards those of specialty materials. The change in Tg is reflected in the gas permeability of ENR. Figure 1.9 shows the relative air permeabilities of ENRs compared to NR and butyl rubber at temperatures ranging from 20°C to 60°C. Increasing the epoxidation levels substantially reduces air permeability. At higher levels of epoxidation, air permeability is comparable to butyl rubber. In applications where air permeability of rubber is
Fig. 1.10: Relationship of percentage rebound resilience against temperature of NR and various Epoxidised natural rubbers and the blend [24]

Fig. 1.11: Swelling behaviour of Epoxidised natural rubber in various ASTM oils and compared with natural rubber, CR and NBR (34%) [24]
important, halobutyl rubbers are normally used. In tyres halobutyls are blended with 30% NR to improve the adhesion of the inner liner to the carcass of the tyre. Since, both ENR-50 and butyl rubbers have similar air permeabilities. ENR-50 rubber can be used as a replacement of butyl rubber for tyre liners. Furthermore, ENR-50 has been found to give much better adhesion to natural rubber than butyl rubber [25].

Another consequence of the increase in glass transition temperature with epoxide level is the increase in hysteresis at ambient temperature. Ambient temperature resilience, as illustrated in Figure 1.10, decreases with increasing levels of epoxidation. However, at elevated temperatures, the resilience of ENR increase to approach that of NR. This characteristic means that ENR exhibits good heat buildup, i.e., dynamic cycling only produces a small temperature rise. Stress-relaxation or creep is comparable to NR [17], and is lower than that of synthetic high damping rubbers [26]. Therefore, with such a balance of properties, ENR seemed to be a good choice for some engineering applications. Examples are in vehicle suspension mountings, shock absorbers etc. The choice of materials is important since the product is subjected to different temperatures and frequencies. However, the temperature bandwidth at which high damping is exhibited is quite narrow for practical applications, as can be seen in Figure 1.10. A wider temperature bandwidth would be beneficial and an objective of this thesis is a study of blends of ENR to determine their temperature/frequency response.

The other interesting feature of ENR is the change in solvent resistance properties. Figure 1.11 shows the
swelling behaviour of ENRs compared with other polymers in the standard ASTM oils. It can be seen that the oil resistance of ENR-50 approaches that of NBR. In addition, ENR-50 also shows better physical properties than NBR [27]. Therefore, ENR-50 rubber has a potential for a range of applications which require both oil resistance and high strength properties.
1.4 Rubber blends

When two or more dissimilar rubbers are blended together, two basic results are possible: (1) a compatible or (2) an incompatible rubber blend results. The majority of rubber blends are comprised of two phase systems. That is, a mixture of discrete phases in a continuous phase of the other or the blends consist of co-continuous phases, as illustrated in Figure 1.12.

A limited number of compatible rubber blends are known, such as PPO/polysyrene [28] and ENR-50/PVC [29]. In the above examples compatibility is due to specific interactions between the two components.

For a compatible rubber blend, the basic criteria are negative Gibbs free energy ($\Delta G$) of mixing and a close to zero Flory-Huggin interaction parameter ($X_{AB}$). However, thermodynamics indicate that the entropy of mixing is very small for rubbery materials. As a result, it favours a positive $\Delta G$. In the case of $X_{AB}$, it requires the knowledge of solubility parameter ($\delta$) of each component A and B in the blend.

For incompatible rubber blends, the basic factors that govern the blend morphology are: (a) compositions, (b) viscosity of the components and (c) the method employed to produce the blend. These are sometime interrelated. The major blend component (by volume) will tend to form the continuous phase, while the second component the discrete phase. This behaviour has been supported by many workers [30-33].

The viscosity difference between components is of importance in determining the phase continuity. At equal component ratio the continuous phase is invariably found
Fig. 1.12: Schematic diagrams of morphology of polymer blends.
(a) dark region is the discrete phase and light region is the continuous phase,
(b) co-continuous phase
(c) light region is the discrete phase and dark region is the continuous phase

(20)
in rubber of lower viscosity [34]. A co-continuous phase system will tend to be produced if the blend ratio and viscosities of each components are equal.

Mixing rheology is an important factor in determining blend structures and hence the physical properties of the blend. The degree of shear determine the size of the discrete phase. At extended mix times, particles can coalesce to form larger particles, and obviously the extent of the above will be influenced by the rubber viscosity. Particular attention has been given by many workers to the morphology of this behaviour, such as Tokita [35], Roland and Bohm [36].

In addition, the effect of interfacial adhesion also important in determining the mechanical properties of incompatible rubber blends [37].

The techniques to characterize the rubber blend morphology will be discussed.
1.5 Characterization of polymer blend compatibility

1.5.1 Thermodynamics approach

The thermodynamic theory of phase separation in mixtures of polymers is, in principle, analogous to the phase separation in mixtures of small molecules. The behaviour of polymer towards solvents can be characterized using the Gibbs free energy of mixing ($\Delta G_{\text{mix}}$) relationship, which is defined as:

\begin{equation}
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}
\end{equation}

where the parameters $\Delta H_{\text{mix}}$ is the enthalpy of mixing and $\Delta S_{\text{mix}}$ is the entropy of mixing.

The criteria for two component systems to be compatible is $\Delta G_{\text{mix}} < 0$, i.e., the Gibbs free energy of mixing is negative. The entropies of mixing of polymers ($\Delta S$) are small because of the high molecular weights of the components. An important role of mixing is the enthalpies ($\Delta H$) which are generally positive. Thus, resulting in an overall positive free energy of mixing ($\Delta G$). The Flory-Huggins theory of polymer solutions [38-40] has been successfully applied to mixtures of polymers.

Scott [41] and Tompa [42] were the first to apply the Flory-Huggins equation in predicting the polymer blend compatibility, as given by,

\begin{equation}
\Delta G_{\text{mix}} = \frac{RTV_r}{V_r} [(\phi_A/X_A)\ln\phi_A + (\phi_B/X_B)\ln\phi_B + X_{AB}\phi_A\phi_B]
\end{equation}
where $V'$ is a total volume of two weakly interacting polymers, $V_r$ is a reference volume taken as close to the molar volume of the smallest polymer repeat unit as possible; $\Phi_A$ and $\Phi_B$ are the volume fractions of polymer A and B respectively; $X_A$ and $X_B$ are degrees of polymerization (molecular size) of polymer A and B in terms of the reference volume $V_r$ (e.g. 100 cm$^3$/mole) respectively and usually approximated by $X=M/100$ where $M$ is the polymer molecular weight; $X_{AB}$ is the interaction parameter between polymer A and polymer B and is related to the Hildebrand solubility parameter [43], $\delta_A$ and $\delta_B$ as given by the following equation,

$$X_{AB} = \frac{V_r}{RT}(\delta_A - \delta_B)^2$$

A negative or near zero $X_{AB}$ favours free energy of mixing. The individual solubility parameter of a polymer is determined from either the group contribution method [44,45] or by experiment. A detailed discussion can be found in section 1.5.2.
1.5.2 Solubility parameter: Hildebrand approach

The solubility parameter was first identified by Hildebrand [43] as a quantity for the characterization of the strength of interactions in simple liquids. The method analogous to this approach was first popularised by Bohn [46] for polymer-polymer blend systems. Solubility parameter is defined as the square root of cohesive energy density (CED). The CED is defined as the molar energy of vapourization divided by the molar volume, both are easily measured properties.

\[ \delta = (\text{CED})^{1/2} = (\Delta E/V)^{1/2} \]  

Thus, \( \delta \) is proportional to the cohesion of the material or the strength of interaction between molecules. Burrell [47,48] has discussed in detail various methods of estimating solubility parameters of materials. For high molecular weight materials (polymers) the solubility parameter cannot be determined directly because of their non-volatility. Therefore, an estimation has to be made.

One approach is to calculate the solubility parameter through the internal pressure [49],

\[ \delta^2 = P_i = T\alpha/\beta \]

where \( \alpha \) is the thermal expansion coefficient and \( \beta \) is the compressibility. The equation provides a means for direct estimation of solubility parameter of polymers because \( \alpha \) and \( \beta \) are measurable quantities.
Fig. 1.13: Swelling of natural rubber in solvents of various solubility parameter (δ). The point of maximum swelling can be taken as the solubility parameter of the polymer [53]
The other method which involves experimentation is the study of polymers in solution or swollen by solvent, i.e. the situation involves thermodynamic entropy contribution to the polymer-solvent interaction parameter. Two methods are generally used [50]:

* swelling of a crosslinked polymer, where it is assumed that the solubility parameter of the polymer is equal to that of the solvent which swells it most highly; and

* intrinsic viscosity of a soluble polymer sample, where it is assumed that the solubility parameter of the polymer is equal to that of the solvent in which the viscosity is maximum.

For the same polymers, these methods often give different results depending on the nature of the solvents: non-polar solvents, polar solvents and hydrogen bonding solvents [48,51,52]. A typical result of swelling NR in solvents with various solubility parameters is shown in Figure 1.13. A polymer of high $\delta$ tends to have a high value of $T_g$.

In the use of solubility parameter for the calculation of polymer-polymer compatibility, the most accurate predictions are based on calculated rather than experimental values of $\delta$. The values of solubility parameter determined experimentally are ultimately based on the solubility parameters of pure solvents [44]. Small found that the solubility parameter of a solvent depends, in general, on the structure of the solvent molecule, density and molecular weight. This method also works for polymers if,
Table 1.3: Tabulated values of group molar attraction constant according to Hoy, derived from vapour pressure measurement [45]

<table>
<thead>
<tr>
<th>Group</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>147.3</td>
</tr>
<tr>
<td>-CH₂⁻</td>
<td>131.5</td>
</tr>
<tr>
<td>&gt;CH⁻</td>
<td>85.99</td>
</tr>
<tr>
<td>&gt;C&lt;</td>
<td>32.03</td>
</tr>
<tr>
<td>CH₂=</td>
<td>126.54</td>
</tr>
<tr>
<td>-CH=</td>
<td>121.53</td>
</tr>
<tr>
<td>&gt;C=</td>
<td>84.51</td>
</tr>
<tr>
<td>-CH= aromatic</td>
<td>117.12</td>
</tr>
<tr>
<td>-C= aromatic</td>
<td>98.12</td>
</tr>
<tr>
<td>-O- (ether, acetal)</td>
<td>114.98</td>
</tr>
<tr>
<td>-O- (epoxide)</td>
<td>176.20</td>
</tr>
<tr>
<td>-COO⁻</td>
<td>326.58</td>
</tr>
<tr>
<td>&gt;C=O</td>
<td>262.96</td>
</tr>
<tr>
<td>-CHO</td>
<td>292.64</td>
</tr>
<tr>
<td>(CO)₂O</td>
<td>567.29</td>
</tr>
<tr>
<td>-OH</td>
<td>225.84</td>
</tr>
<tr>
<td>-H acidic dimer</td>
<td>-50.47</td>
</tr>
<tr>
<td>OH aromatic</td>
<td>170.99</td>
</tr>
<tr>
<td>NH₂⁻</td>
<td>226.56</td>
</tr>
<tr>
<td>-NH⁻</td>
<td>180.03</td>
</tr>
<tr>
<td>-N⁻</td>
<td>61.08</td>
</tr>
<tr>
<td>C≡N</td>
<td>354.56</td>
</tr>
<tr>
<td>NCO</td>
<td>358.66</td>
</tr>
<tr>
<td>-S⁻</td>
<td>209.42</td>
</tr>
<tr>
<td>Cl₂</td>
<td>342.67</td>
</tr>
<tr>
<td>Cl primary</td>
<td>205.06</td>
</tr>
<tr>
<td>Cl secondary</td>
<td>208.27</td>
</tr>
<tr>
<td>Cl aromatic</td>
<td>161.0</td>
</tr>
<tr>
<td>Br</td>
<td>257.88</td>
</tr>
<tr>
<td>Br aromatic</td>
<td>205.60</td>
</tr>
<tr>
<td>F</td>
<td>41.33</td>
</tr>
</tbody>
</table>
\begin{equation}
\delta = \rho \Sigma F_i / M
\end{equation}

where \( \rho \) is the density of the polymer at any temperature, \( M \) is the molecular weight of the repeat group in the polymer, and \( \Sigma F_i \) is the sum of all the molar attraction constant of the chemical groups in the polymer repeat unit. The values of \( F_i \) have been improved and updated by Hoy [45]. These revised version are tabulated in Table 1.3.
1.5.3 Glass transition temperature

The properties of polymers can be affected by a small change of temperature, e.g., as a result of crystallinity in the polymer (first-order transition) or by passing through the glass transition (second-order transition) [54]. The transition state is accompanied by marked changes in the specific volume, the heat capacity, the modulus etc. This state represents the boundary between a glassy and rubbery polymer.

Below the transition temperature, the motion in the polymer chain is restricted to small motions of individual atoms. When thermal energy is raised, a glass transition temperature is observed. In this state, the polymer has expanded to the extent that there is enough free volume in the material for segmental motion to jump from one position to another with respect to their neighbours. Above $T_g$, the coefficient of expansion is greater, as a result larger molecular motions are occurring in which whole segments of the polymer chain are in motion and the polymer loses its rigidity.

Techniques to determine $T_g$ can be divided into two categories, static and dynamic methods. For a static method, a change in temperature is dependent on density or heat capacity. Measurements are carried out slowly. This is to allow the sample to equilibrate and relax at each observation temperature. In dynamic mechanical method, the transition region is dependent on frequency of the applied force. Mechanical damping goes through a maximum, and the modulus may change by a factor of thousand on passing through the transition state. The temperature of maximum damping is associated with $T_g$ and
always higher than that obtained from the static methods. The discussions of each of these techniques will follow.

The most common method for assessing the degree of polymer blend compatibility is via the determination of glass transition temperatures. A compatible polymer blend will exhibit a single glass transition temperature (Tg) intermediate between those corresponding to the two component polymers. An incompatible polymer blend gives rise to two distinct transitions identical in temperature to those of the individual components. In semi-compatible polymer blends, a distinct transition of individual components may be observed, but shifted towards each other. A broadening of the width of the glass transition over a wide temperature range also suggests a semi-compatible polymer blend. If such broadening occurs, then it depicts microheterogeneity of a polymer blend [55].

The appearance of a single transition cannot be taken alone as evidence that the blend components are compatible. For example if the components have equal or close glass transition temperatures, then the resolution of the technique employed may not be sufficient.

1.5.3.1 Calorimetric method

Calorimetry is one of the techniques of detecting the transitional state of polymers and their respective blends. The most common instrument is the differential scanning calorimeter (DSC). In the last few decades, this type of instrument has rapidly gained prominance owing to its sensitivity. The DSC measures the amount of
heat required to increase the sample temperature by a value ΔT over that required to heat a reference sample by the same ΔT. In the glass transition region, caused by the onset of motion of chain segments in the amorphous region of a polymer, the change in heat capacity results in a shift of the thermogram baseline. This is monitored and plotted as a function of temperature. The thermograms are usually recorded during warm-up so that the baseline shift is endothermic in the glass transition region. A schematic diagram showing the behaviour of specific heat versus temperature of a polymer in the region of the glass transition temperature is shown in Figure 2.1.

The glass transition temperature (Tg) of a polymer can be defined as either the inflection point at the discontinuity in specific heat; the intersection point of the projection of the baseline with the tangent to the discontinuity or the temperature corresponding to the midpoint of the discontinuity \((1/2ΔC_p)\) [56]. The advantages of DSC are, a small sample (5-19 mg) is required; controlled rates of heating or cooling are possible with high accuracy of heat input and the measurement is quite rapid. The main disadvantage of DSC is the low sensitivity in detecting the Tg of polymer blends separated by <30° compared with the dynamic mechanical method. However, the glass transition temperature (Tg) determined from DSC has been successfully demonstrated for polymer blend compatibility, such as, PPO/PS [57], nitrile rubber/PVC [58] and ENR-50/PVC [59].
Fig. 1.14: Generalised behaviour of dynamic storage modulus and loss angle tangent of a compatible blend. $T_g(A+B)$ corresponds to the glass transition temperature of the 50:50 blend, occurring at intermediate positions between components A and B.

Fig. 1.15: Generalised behaviour of dynamic storage modulus and loss angle tangent of an incompatible blend. The Tgs occur at the positions of the respective components A and B.
1.5.3.2 Dynamic mechanical method

For a perfectly elastic material, the strain imposed is proportional to stress, which obeys Hooke's law. However, a polymer is not a perfectly elastic material; it has characteristics of both elasticity and a viscous liquid. Therefore, they are known as viscoelastic materials. James Clerk Maxwell was the first to discuss quantitatively the viscoelasticity nature of polymers [60]. A number of mechanical tests may be used to study viscoelastic properties of polymers. The most important tests include creep, stress-relaxation, stress-strain, and dynamic mechanical behaviour.

A dynamic mechanical test is one approach from which information can be obtained rapidly, where the stress response arising from an imposed strain is measured. Responses relate to transitional deformations occurring on the molecular segmental level. In a compatible polymer blend, a single transition corresponding to the glass transition temperature will appear. Likewise, in incompatible polymer blends, the transitional behaviour of the individual components will be unchanged. Generalised transitional behaviour of compatible and incompatible polymer blends is shown in Figures 1.14 and 1.15 respectively.

Dynamic mechanical testing can be accomplished using various experimental arrangements. They are free and forced vibrational techniques. Free vibrational dynamic mechanical testing devices include the torsional pendulum, free vibrating reed, and the torsional braid analyser. Forced vibration techniques are based on
Fig. 1.16: (a) Stress and strain as a function of time displacements for sinusoidal deformation of a viscoelastic material. The strain lags behind the stress by the loss angle $\theta$.

(b) The stress sine wave resolved into two components: one in phase with the strain and the other out-of-phase with the strain. The amplitudes of these two components determine the storage and loss modulus [61]
viscoelastometers or a forced vibrating reed. In this discussion, a forced vibration technique will be covered. This method is commonly employed to measure polymeric transitions. An example of this type of instrument is the dynamic mechanical thermal analyser (DMTA) [61]. It has great sensitivity in detecting any changes in internal molecular mobility, relating to morphological and transitional state behaviour.

The instrument operates on the principle that when a sinusoidal stress is applied to a viscoelastic material, the strain lags behind the stress by an angle <90°. The displacement of sinusoidal deformation of viscoelastic material is represented in Figure 1.16. Information such as dynamic modulus and mechanical damping or energy dissipation, can be obtained. Dynamic modulus is usually represented by a complex quantity, i.e., the ratio of stress amplitude to strain amplitude (A/B). For Young's modulus, the complex modulus is given by,

\[ E^* = E' + iE'' \]

where \( E' \) (storage modulus) is the ratio of the amplitude of the in-phase stress component to the strain amplitude (C/B), \( E'' \) (loss modulus) is the ratio of amplitude of the out-of-phase component to the strain amplitude (D/B).

Also, the loss tangent between stress and strain is \( \tan \theta = E''/E' \). It is defined as the ratio of energy loss (dissipation) to energy stored per cycle. The quantities are measured and plotted as a function of temperature over a wide range of frequencies to give dynamic mechanical spectra. The storage modulus (\( E' \)) measures
the amount of energy stored, while the loss modulus and loss tangent measure the energy dissipation in the material. The response of the measurement on polymers is dependent upon temperature, frequency, molecular structure, morphology and composition. At transition, the storage modulus shows a pronounced drop over a relatively small temperature range at constant frequency, usually of about $10^3$. While, the loss modulus ($E''$) and loss tangent go through a maximum (the latter is slightly higher than the former). The temperature at maximum transition is usually referred as dynamic glass transition temperature ($T_d$), which is much higher than $T_g$ measured by, for example, calorimetry, owing to the frequency applied.

The dynamic mechanical spectra, mostly in the form of the temperature response of Young's modulus and loss tangent, have been used with considerable success in predicting the morphology of polymer blends. The mechanical data can be used for predicting the morphology quantitatively using the existing theories of the elastic moduli of composites. The theoretical treatment will be discussed in section 1.6.

Other methods are also available to characterize polymer blend compatibility. They are dielectric relaxation (which is analogous to the dynamic mechanical method), thermo-optical, radiothermoluminescence methods, etc.
1.5.4 Microscopy techniques

Examinations using microscopy are now becoming increasingly important in characterizing the compatibility of polymer blends. Some blends appear to be compatible by transitional techniques (as previously discussed), but microscopically, two phases have been observed. Therefore, this has made many researchers turn to microscopy to investigate polymer blends.

At present, two main microscopy techniques are used for elucidating the morphology of polymer blends. They are transmitted light phase microscopy and transmission electron microscopy (TEM). The major limitation of polymer blend microscopy is in obtaining sufficient contrast between various phases. In phase contrast microscopy a difference in refractive index is required to observe the two phases. The electron microscopy technique requires thickness differences to account for the observed phenomena.

1.5.4.1 Transmitted-light phase contrast microscopy

In phase contrast microscopy, the sample is illuminated with light. Phase contrast can be measured either as transmitted or as reflected light, but the use of reflected light is very rare with polymer blends. Therefore, the discussion is confined to transmitted light microscopy.

Phase contrast microscopy requires sufficient fluctuation in refractive index within the sample to give rise to a contrast. Usually refractive index fluctuations in polymer systems are small and the
Fig 1.17: Illustrating a transparent sample with an inclusion whose RI differs from that of the matrix, $n_2 > n_1$, illuminated by coherent light. The rays passing through the inclusion are retarded by half a wavelength relative to those passing through the matrix.
visibility of the features in a common light microscope is difficult. A good contrast can be obtained in polymer blend system with the use of transparent materials. Usually the section thickness is 2µm or less. Thin sample can be prepared by ultramicrotoming. The sample is hardened before it is cut from the bulk. Hardening can be accomplished using liquid nitrogen and sectioning is done at below the glass transition temperature of the materials (see section 2.11.1). Any small particles (ingredients which are not homogeneous in the blend) will severely affect the interpretation of a phase contrast image because of many overlapping "halos" produced. These objects can show misleading structures when the illumination is not correctly centred. This is the major disadvantage of phase contrast microscopy. Staining is another method for obtaining contrast but is seldom used for polymer blend materials.

An illustration showing a section of non-absorbing transparent material that consists of a matrix containing an inclusion of higher refractive index, illuminating by a beam of coherent light is shown in Figure 1.17. As the beam passes through the sample, the phase of the rays passing through the inclusion lags behind that of the rays passing through the matrix. When the two sets of rays, which are of equal intensity, emerge from the sample they are out of phase by exactly half a wavelength and they interfere destructively causing the inclusion to appear dark, i.e. contrast is produced. This effect can be observed under bright-field conditions.

A schematic diagram of the arrangements of phase contrast microscopy employing transmitted light is shown
Fig 1.18: (a) A schematic diagram of transmitted-light phase contrast microscope, (b) Section through positive and negative phase plates; the shading represents the absorptive layer on the phase ring [64]
in Figure 1.18. The theoretical aspects of the basic operation of the microscope is well documented [62-64]. The features of the microscope are, an annular diaphragm located in the front focal plane of the condenser, so that it illuminates the sample with a hollow cone of light. The condenser is focussed so that an image of the annulus is formed in the back focal plane of the objective. A transparent phase plate, that carries an annulus the same size as the image of the condenser annulus, is inserted in this plane and is made to coincide exactly with it. The annulus of the phase plate accelerate or retards the phase of the direct beam. The maximum contrast in the final image of the two beams must be of about equal intensity, thus the annulus of the phase plate is coated with an absorbent material, usually antimony.

It has been mentioned earlier that the principle area of application for phase contrast microscopy is the study of polymer blend systems. This was first demonstrated by Walters and Keyte [30]. They examined a variety of two polymer blend systems. For SBR/BR, they have found that the blend formed discrete zones, with zones ranged from 0.2 micron to several microns in size. The blends are also incompatible even when blended in solution. However, Marsh, Voet, and Price [65] found that, after considerable mixing, blended SBR/BR appeared completely compatible. Keyek and Schoon [66] examined a range of blends of rubbers (not SBR/BR), but never found them to be completely compatible. They have found that under the most favorable circumstances the harder component is embedded in the softer in the forms of spheres. Callan, Topcik, and Ford [31] have studied the
blend between Butyl/EPDM. There is a tendency for low molecular weight EPDM to be compatible in Butyl rubber. For the blends of SBR/Neoprene and Butyl/SBR, a marked degree of incompatibility is apparent. In general, compatible or incompatible polymer blends depend on the types of polymer, relative viscosities, preparations and mixing conditions.
1.6 Mechanical behaviour at small strain

Small strain dynamic mechanical properties are mostly measured in terms of shear or Young's modulus and are widely used for elucidating polymer blend compatibility. Properties are dependent on blend composition and morphology. Changes in composition and morphology are reflected in dynamic properties by changes in the peak transitions, glass transitions and temperature bandwidth. However, the results of most of these cases are evaluated rather qualitatively. In principle, it is possible to obtain quantitative information on composition and morphology, with the use of a mathematical model describing the mechanical response of polymer blend components.

Many theories have been proposed to model the morphology and composition dependence on elastic and viscoelastic response of polymer blends. Such theories are, for example, Hashin [67], Takayanagi [68] and Kerner [69]. They have developed very promising mathematical models for predicting the morphology and composition of polymer blends. The work in this thesis is focused on the application of Kerner's theory. The mathematical calculations of Kerner's theory is based on the elastic properties of multiphase media.

1.6.1 Theoretical expressions

Kerner has derived the equations of shear (G) and bulk (K) moduli of isotropic homogeneous materials, in terms of the moduli and compositions of its components;
these components consisting of suspended grains. Several assumptions has been made in derivation of this model:
* the grains are suspended in and bonded to some uniform suspending medium (matrix),
* the grains are randomly distributed and spherical in shape,
* the grain particles adhere to the matrix phase at the interphase, but do not interact with one another, and
* Poisson's ratio is a real constant for elastic and viscoelastic material.

The results yield two decoupled expressions for the gross bulk and shear moduli of a multiphase suspension. For the case of one component suspended in a matrix phase, Kerner's equation for elastic shear modulus is [70-72],

\[
G = \frac{(1-\Phi)G_m + (\varepsilon+\Phi)G_i}{G_m (1+\varepsilon\Phi)G_m + \varepsilon(1-\Phi)G_i}
\]  

(1.8)

where \( G \) is elastic shear modulus of the blend, \( \Phi \) is the volume fraction of spherical inclusions (grain particles), subscript \( i \) designates a property of the grains or inclusions, subscript \( m \) designates a property of the matrix, and

\[
\varepsilon = \frac{2(4-5v_m)}{(7-5v_m)}
\]  

(1.9)

where \( v_m \) is Poisson's ratio of the matrix.

(44)
The expression for dynamic shear modulus (viscoelastic property) is analogous to that for static elastic shear modulus, with the use of the correspondence principle. The manipulation of eqn. 1.8 is convenient in the form of complex quantities. The correspondence principle states that [71], "expressions for the complex moduli of multiphase materials may be obtained by replacement of elastic moduli by complex moduli in exact expressions for the corresponding elastic moduli". Thus eqn. 1.8 can be rewritten in terms of the dynamic (complex) shear modulus,

\[ G^* = \frac{(1-\Phi)G_m^* + (\varepsilon+\Phi)G_i^*}{G_m^*} \]

(1.10)

The expression of Kerner's equation in terms of the dynamic Young's modulus \( E^* \) can be obtained by substituting eqn. 1.11 into eqn. 1.10,

\[ E^* = 2(1-v^*)G^* \]

(1.11)

where \( v^* \) is the Poisson ratio of viscoelastic material, and is assumed to be equal to Poisson ratio of elastic material [70], i.e. \( v = v^* \). Therefore,

\[ \frac{E^*}{E_m^*} = \frac{\Gamma(1-\Phi)E_m^* + \tau(\varepsilon+\Phi)E_i^*}{(1+\varepsilon\Phi)E_m^* + \varepsilon\tau(1-\Phi)E_i^*} \]

(1.12)
where,
\[ \Gamma = \frac{1 + v}{1 + v_m} \quad \text{and} \quad \tau = \frac{1 + v_m}{1 + v_i} \]  
(1.13)

Since,
\[ E^* = E' + iE'' \]  
(1.14)

where \( E' \) is the storage modulus and \( E'' \) is the loss modulus. Then substituting eqn.1.14 into eqn.1.12, we have
\[
(1.15) \quad E' + iE'' = \frac{\Gamma(1 - \phi)(E_m' + iE_m'')(E_m' + iE_m'')}{(1 + \phi)(E_m' + iE_m'') (\epsilon + \phi)(E_i' + iE_i'')(E_m' + iE_m'')} + \frac{\epsilon(1 - \phi)(E_i' + iE_i'')}{(\epsilon + \phi)(E_i' + iE_i'')(E_m' + iE_m'')} \]

For rubber material, \( v = v_m = v_i \), then \( \Gamma = 1 \) and \( \tau = 1 \). Therefore,
\[
(1.16) \quad E' + iE'' = \frac{(1 + \phi)(E_m' + iE_m'')(E_m' + iE_m'')}{(1 + \phi)(E_m' + iE_m'')(\epsilon + \phi)(E_i' + iE_i'')(E_m' + iE_m'')} \]
\[
= \frac{(1 - \phi)(E_m'^2 + 2iE_m'E_m'' - E_m'^2)}{(1 + \phi)(E_m' + iE_m'')(\epsilon + \phi)(E_i' + iE_i'')(E_m' + iE_m'')} \]
\[
= \frac{(1 - \phi)(E_m'^2 - E_m'^2)}{(1 + \phi)(E_m' + iE_m'') + (\epsilon + \phi)[(E_i' + iE_i'')(E_m' + iE_m'')]} \]
\[
+ \frac{i[(1 + \phi)E_m'' + \epsilon(1 - \phi)E_i']}{i[(1 + \phi)E_m'' + \epsilon(1 - \phi)E_i']} \]

Let \( A = (1 - \phi)(E_m'^2 - E_m'^2) + (\epsilon + \phi)[(E_i' + iE_i'')(E_m' + iE_m'')] \)
\( B = 2(1 - \phi)E_m'E_m'' + (\epsilon + \phi)(E_i' + iE_i'')(E_m' + iE_m'') \)
\( C = (1 + \phi)E_m' + \epsilon(1 - \phi)E_i' \)
\( D = (1 + \phi)E_m'' + \epsilon(1 - \phi)E_i'' \)

Rearranging real and imaginary part leads to the following equations:
\[ E' = \frac{AC + BD}{C^2 + D^2}, \quad E'' = \frac{BC - AD}{C^2 + D^2} \]

and \( \tan \Theta = E''/E' \)

(46)
1.7 Aim of present investigation

Factors affecting the structures and properties of polymer blends have been reviewed in the previous sections along with properties of NR and ENR whose blend structures and properties are the subject of this thesis.

A simple vulcanizate system is to be used in a model study of rubber-rubber blends. This is used in order to eliminate the effects of ingredients on the properties of rubber blends, so that the results obtained can more readily be interpreted.

The aims of the present investigation are as follows:

1) to study the compatibility of two components blend vulcanizates (NR and ENRs) via:
   (a) the prediction of Flory-Huggins segmental interaction parameter,
   (b) the determination of glass transition temperature of each component in the blends,
2) to study the morphology of two components rubber blends,
3) to study the factors that affects the morphology of the two components rubber blends,
4) to study the theoretical prediction of the dynamic mechanical data from the morphology,
5) to establish a compatible rubber blend and to study the damping properties over a wide temperature range,
6) to study the physical properties, such as air permeability, tearing energy, tensile strength and resilience and in relation to the morphology of rubber blends.
CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Natural rubber

Natural rubber (NR) used in this investigation was SMR L, which is a high quality grade rubber with minimum dirt content and other impurities, Table 1.1.

2.2 Epoxidised Natural rubber

Various grades of epoxidised natural rubber (ENR) were employed. Examples are ENR-26, ENR-48, ENR-31, ENR-38, ENR-43, ENR-64 and ENR-71. The first two rubbers are commercial Malaysian grades; while the other rubbers are specially prepared from LA-TZ latex.

2.3 Preparation of epoxidised NR

The NR latex used was LA-TZ (low ammonia-TMTD/ZnO), which is a Malaysian latex concentrate with 60% dry rubber contents (d.r.c). ENR was prepared using the method described by I R Gelling [18]. Table 2.1 records the reagent concentrations for the various ENRs prepared.

In preparation of ENR, LA-TZ latex was first stabilised with non-ionic surfactant (Texofor A30, ABM Chemical Ltd.) and diluted with the distilled water. Prior to the addition of peracetic acid (Interox Chemicals Ltd.), the latex was cooled to 10-15°C in an ice container. Sodium acetate solution (1% wt/wt) was added to the peracetic acid in order to neutralise any
Table 2.1: A typical formulation of ENRs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>ENR-31</th>
<th>ENR-38</th>
<th>ENR-43</th>
<th>ENR-71</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA-TZ (60% d.r.c.)</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Peracetic acid (38% wt/wt)</td>
<td>141</td>
<td>172</td>
<td>191</td>
<td>325</td>
</tr>
<tr>
<td>Sodium acetate anhydrous</td>
<td>2.4</td>
<td>3.4</td>
<td>3.8</td>
<td>6.5</td>
</tr>
<tr>
<td>Texofor A30 (20% sol.)</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Water</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>1000 cc</td>
</tr>
</tbody>
</table>

(50)
Table 2.2: Solubility parameter of solvents at 25°C [48]

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\delta \times 10^3$</th>
<th>$(\text{calcm}^{-3})^{1/2}$</th>
<th>$\phi \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>14.40</td>
<td>7.05</td>
<td>0.605</td>
</tr>
<tr>
<td>n-hexane</td>
<td>14.90</td>
<td>7.30</td>
<td>0.659</td>
</tr>
<tr>
<td>n-octane</td>
<td>15.45</td>
<td>7.55</td>
<td>0.703</td>
</tr>
<tr>
<td>decane</td>
<td>15.86</td>
<td>7.75</td>
<td>0.730</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>16.78</td>
<td>8.20</td>
<td>0.779</td>
</tr>
<tr>
<td>methyl i-butyl ketone</td>
<td>17.19</td>
<td>8.40</td>
<td>0.796</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>17.49</td>
<td>8.55</td>
<td>0.882</td>
</tr>
<tr>
<td>methyl propyl ketone</td>
<td>17.80</td>
<td>8.70</td>
<td>0.812</td>
</tr>
<tr>
<td>toluene</td>
<td>18.21</td>
<td>8.90</td>
<td>0.863</td>
</tr>
<tr>
<td>methyl propionate</td>
<td>18.41</td>
<td>8.90</td>
<td>0.915</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>18.62</td>
<td>9.10</td>
<td>0.901</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>19.03</td>
<td>9.30</td>
<td>0.799</td>
</tr>
<tr>
<td>acetone</td>
<td>20.47</td>
<td>10.0</td>
<td>0.791</td>
</tr>
<tr>
<td>methyl formate</td>
<td>20.87</td>
<td>10.2</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Table 2.3: Percentage loss of impurities after extraction

<table>
<thead>
<tr>
<th>Rubbers</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR (SMR L)</td>
<td>5.8</td>
</tr>
<tr>
<td>ENR-26</td>
<td>9.3</td>
</tr>
<tr>
<td>ENR-48</td>
<td>2.9</td>
</tr>
<tr>
<td>ENR-71</td>
<td>8.4</td>
</tr>
</tbody>
</table>
residual sulphuric acid remaining from the preparation procedure.

The acid was titrated dropwise to the stirred latex over 1-2 hrs. The latex was stirred for a further 2-3 hrs with the temperature maintained at 10-15°C. An ammonia solution was added dropwise to the stirred latex until the PH was >7. During this process the temperature was again maintained at 10-15°C.

The latex was then coagulated with methanol. Any trace of acetic acid present in the coagulum was thoroughly removed by washing on a creper mill. The coagulum was then soaked in 0.1M sodium carbonate solution overnight to ensure complete neutralization of any acid. The rubber was again washed with water and dried in an air oven at 50-60°C. The same procedure was adopted for high levels of epoxide groups, except the d.r.c of the latex was reduced to avoid high acetic acid concentrations and the amount of peracetic acid added increased correspondingly. The reason is to reduce ring-opened structures, which depend on the degree of epoxidation [73]. Therefore great care was taken to control the acid concentration and temperature during the process.

2.4 Solvents

The solvents used for equilibrium volume swelling measurements are listed in Table 2.2, together with the solubility parameter and density values. These were obtained from BDH and Aldrich with purity levels >99% and were used as received.
2.5 Preparation of blends

The Mooney viscosity of all rubbers were determined in accordance with ISO 289-1985 (E). In the preparation of rubber blends, rubber of the same Mooney viscosity was used. Blends were prepared by mixing the components on a laboratory two-roll mill. The mill temperature was 40-50°C and maintained constant by means of cooling water and steam regulation. The mill runs at a front-roll speed of 18 r.p.m. and frictional ratio of 1.65. The rubber was compounded with 1.5 p.h.r. dicumyl peroxide (DCP) unless otherwise stated. The blend time was five minutes. The compounded rubber was then sheeted into 5mm thick slabs and left overnight.

2.6 Moulding and curing

The rubber vulcanizates were prepared using compression moulding. Slabs of about 100X100mm were moulded in a tensile slab mould to yield sheets of 150X130X2mm. Initially the rubber was heated for 10 minutes at 100°C using an electrical press, to allow the rubber to flow prior to the onset of crosslinking. Then, it was transferred into the steam heated press for 50 mins at 160°C with a ram pressure of 6 MPa. The same procedure was adopted for other test pieces, with the use of appropriate moulds.
Fig. 2.1.: A typical IR spectrum of Epoxidised natural rubber sample
2.7 Acetone extraction

In order to obtain the vulcanizates free from non-rubber impurities and curative residuals, the samples were extracted with acetone under an atmosphere of nitrogen in a soxhlet apparatus. Extraction was carried out for 24 hrs. The initial weight was noted and recorded. After extraction the samples were vacuum dried until a constant weight was obtained. The percentage loss of impurities was calculated and tabulated in Table 2.3.

2.8 Analysis of ENR

The epoxide contents of ENR were analysed using the following analytical techniques: IR and $^1$H NMR spectroscopy.

2.8.1 IR spectroscopy

In IR spectroscopy technique, a thin film of sample was prepared by drying a latex sample on silver chloride (AgCl) plate. An example of an IR spectrum is shown in Figure 2.1. A baseline was drawn between the points at 940 and 720 cm$^{-1}$. The epoxide peak at 870 cm$^{-1}$ and olefin peak at 830 cm$^{-1}$ were measured. In each case, the intensity of a/b and c/d were measured and converted to $\log_{10}$ values. The ratio of epoxide to the total epoxide and olefin was calculated. The resulting ratio was then compared with the calibration curve [20] to determine the percentage of epoxide groups in the rubber.
Fig. 2.2: A typical $^1$H NMR spectrum of Epoxidised natural rubber sample
2.8.2 $^1H$ NMR spectroscopy

A second method for analysing the epoxide groups is by using proton nuclear magnetic resonance spectroscopy ($^1H$ NMR). The spectra were recorded at 90 MHz on a Perkin Elmer R32 spectrometer, linked to a BBC microcomputer. The samples were dissolved in deuterochloroform. Chemical shifts are given in parts per million downfield from tetramethylsilane. The peak signals of the olefin and epoxide, at 5.05 and 2.7 ppm respectively, are used to determine the degree of epoxidation. A typical example of a NMR spectrum is given in Figure 2.2. Integration of the area under the peak was done by a computer. The percentage of epoxide groups was calculated by dividing the area of the epoxide groups with the total area of the olefin and the epoxide groups.
2.9 Solubility parameter of rubbers

2.9.1 Equilibrium volume swelling measurement

Samples of the various vulcanizates, with dimensions of 30X5X2mm were weighed very accurately using an electrical analytical balance, and then immersed in a glass vessels containing the solvent (30 cm$^{-3}$) at 25°C. The vessels were placed in a dark cabinet. The reason is to avoid light which might caused oxidation. Each sample was then removed from the glass vessel. Excess surface solvent was removed with a lens blotting paper and the sample immediately placed in a closed vessel to prevent the solvent from being evaporated. The weight of the swollen sample was then determined. The sample was returned to the solvent and the process repeated until a constant swollen weight was obtained.

In order to find the volume fraction of solvent absorbed in the rubber, $V_s$, the sample was deswelled in vacuum at room temperature until the weight was constant. By knowing the density of the solvents used, the volume of the solvent absorbed in the rubber was calculated from the difference in weight of the swollen and deswollen samples. The volume fraction of rubber ($V_r$) was calculated using the formula [74], $V_r = V_{RN}/(V_{RN} + V_s)$, where $V_{RN}$ is the volume of the rubber network.
2.9.2 Stress/strain measurement

Stress/strain data of dry rubber networks were used to determine the $C_1$ values. Measurement was carried out using an equilibrium modulus' tensile machine, known as $C_1$ test. A detail description of the equipment can be found elsewhere in the text [75]. Basically, the test measures the stress-relaxation, i.e., the test piece is deformed to a fixed distance and the stress required to maintain this deformation is measured for a period of time.

The test piece used was a uniform parallel sided tensile strip taken from the vulcanized sheet used for equilibrium swelling measurement. The test piece was then placed in the grips. The initial length between the gauge marks ($l_0=10$ cm) was measured. The test piece was then deformed to a new fixed distance. The time chosen for stress-relaxation was 3 mins. After 3 mins relaxation, the stress required to maintain this deformation was noted. Then, the test piece was again deformed to a second fixed distance and the procedure was repeated for at least 9-10 extensions. Measurement was duplicated using different test piece. The stress-strain data were analysed and plotted using a computer.
Fig. 2.3: A typical plot of specific heat against temperature from DSC measurement.
2.10 Determination of glass transition temperature

2.10.1 Thermal analysis by DSC

The glass transition temperatures of rubber vulcanizates were measured by differential scanning calorimetry. The instrument used was a Perkin-Elmer model DSC 2, coupled with a computer recorder. Temperature reading of the equipment was calibrated with a reference SMRL sample. The glass transition temperature of which was taken to be -72°C. Calibration of heat capacity change was achieved using an indium standard. The X-axis of the plotter was adjusted to prevent base-line drift. The samples, about 10 mg, were cut from the vulcanized sheet using a cork borer and sealed in standard aluminium capsules. Initially, the sample was rapidly cooled to below its glass transition temperature (-110°C), using liquid nitrogen. The sample was then heated at a rate of 20°C/min. The rate is maintained constant since it can influence the Tg of rubber.

The difference in specific heat change between the sample and the reference was recorded. A typical transition is shown in Figure 2.3 along with the method used to determine the transition temperature, i.e., the intercept of the base line with tangent of the transition slope.
Fig. 2.4: Photograph showing the DMTA MK II instrument at MRPRA.
2.10.2 Dynamic analysis by DMTA

A dynamic mechanical thermal analyser (DMTA MK II-Polymer Laboratories) was employed to measure the dynamic mechanical properties of rubbers and rubber blends. The instrument is very versatile and well controlled through IEEE-488 interfaces, via an IBM microcomputer. The general specification of the dynamic mechanical thermal analyser is as follows: it has 16 frequencies in the range of 0.01 to 200 Hz.; the temperature ranges from -150°C to 300°C; and strain amplitudes from 11 μm to 256 μm. The strain has 9 levels in steps of √2. The modes of operation can be either isothermal (variable frequency) or isochronal (variable temperature) scans. Samples can be arranged in either bending or shear modes. A photograph of the instrument is shown in Figure 2.4.

2.10.2.1 Calibration and measurement

The instrument was calibrated before the start of each experimental run. Calibration is achieved by allowing the drive clamp attached to the drive shaft without the sample to vibrate sinusoidally. The analyser of the DMTA solves the equation of motion for the vibrating system using the following equation:

\[ F_p \sin \omega t = Mx + (\mu' + S'/w + kE'/w)x + (S'' + kE'')x \]

where \( F_p \) is the peak force from the vibrator (N),

\( M \) is the vibrating system mass (Kg),

\( w = 2\pi f \) is the angular frequency (rad.s\(^{-1}\)).
\( t \) is the times (s),
\( \mu' \) is the viscous damping term (Pa.s),
\( S' \) is the elastic response of the suspension, or the suspension stiffness in phase (Nm\(^{-1}\)),
\( S'' \) is the suspension stiffness out of phase (Nm\(^{-1}\)),
\( E' \) is the storage modulus of sample (Nm\(^{-2}\)),
\( E'' \) is the loss modulus of sample (Nm\(^{-2}\)),
\( k \) is the sample geometry factor (m) and
\( x \) is the displacement (m)

The in-phase and out-of-phase responses are given in equations 2.2 and 2.3 respectively.

\begin{align*}
(2.2) \quad \alpha' \cos \beta' &= (kE' + S' - \mu_2^2) / L \\
(2.3) \quad \alpha' \sin \beta' &= (kE'' + S'' + \mu_2^2) / L
\end{align*}

where \( L \) is the proportionality constant.

During calibration, the 'CAL' switch was pushed to ON position. The values of LOG MODULUS and LOG TAN \( \theta \) displayed correspond to \( \alpha' \cos \beta' \) and \( \alpha' \sin \beta' \) as defined in equations 2.2 and 2.3 respectively. If these quantities were denoted as \( A \) and \( B \) respectively, then,

\begin{align*}
(2.4) \quad kE' &= LA + \mu_2^2 - S' \\
(2.5) \quad kE'' &= LB - S'' - \mu_2^2
\end{align*}

Since \( LE' = LE'' = 0 \) (for calibration without the sample attached), then at 1 Hz, the terms \( \mu_2^2 \) and \( \mu_2' \) were insignificant. Therefore, By ignoring these two terms, we have,
Rearranging equations 2.6 and 2.7, we have,

(2.8) \[ A = \frac{S'}{L} \]
(2.9) \[ B = \frac{S''}{L} \]

At 30 Hz, \( M_w^2 \) is significant, then equation 2.4 becomes,

(2.10) \[ 0 = LC + M_w^2 - S' \]
(2.11) \[ C = \frac{(S' - M_w^2)}{L} \]

\( L \) is determined by changing the mass in equation 2.10, that is,

(2.12) \[ D = \log \frac{\Delta M_w^2}{\Delta C} \]

The calibration values were used in the computation of the storage modulus and the loss modulus using the equations given in 2.13.

\[ kE' = 10^D[A' + (A-C)(f/30)^2 - A] \]
\[ kE'' = 10^D(B' - B) \]

(2.13) \[ \tan \Theta = \frac{E''}{E'} \]
Fig. 2.5: (a) The set-up of the sample of dual-cantilever mode with the clamping bar attached on the sample. (b) The top view of the set-up of the sample.
2.10.2.2 Measurement in bending mode

Initially the instrument was allowed to stabilize for 15 mins. For the purpose of this work measurements were carried out in a dual-cantilever bending mode. This arrangement is extremely flexible and may be used to accommodate a huge range of sample types. The set-up of this mode together with drive shaft clamp and clamping frame is shown in Figure 2.5.

Rectangular strips (about 35X10X2 mm in dimensions) were cut from the vulcanized sheet. Their width and thickness were measured accurately with a travelling microscope. The strip was then inserted horizontally beneath the clamping bars on the clamping frame with both ends and central parts tightened slightly. The whole arrangement was enclosed in a heater/cooler oven. Sub-ambient temperature of the samples, for example, NR/ENR-48 blend were achieved by allowing the samples to cool to below their glass transition temperatures with the use of pressurised liquid nitrogen. The temperature is measured by a platinum resistance thermometer lying behind the sample. The reservoir of the dewar tank must be full at the start of the experiment. Due to rubber expansion, the sample was retightened at the glassy state, using a torque screw driver to eliminate over tightening.

Two modes of operation were used in this study. Firstly, an isochronal scan (variable temperature) at a fixed frequency of 20 Hz. Other frequencies are possible, but for gum vulcanized rubber, it is recommended to run at <50 Hz. The reason is due to the "toggle effect". The sample vibrates and slackens from
the clamping arrangement and the effect results in scattered data. The amplitude of 80 μm (ca.<0.01% strain) was imposed on the sample. Too high a strain level can cause low signal.

Secondly, the isothermal scan i.e., measurement at constant temperature with variable frequencies. The frequency used was varied from 0.01 to 50 Hz. at a number of temperatures.

The analyser monitors both the sinusoidal strain applied to the sample and the resulting stress response. Readings are automatically stored on computer disc once every 4 secs or 1 cps, whichever is greater. The measurement were taken during warming up at a heating rate of 2°C/min. This mode was adopted to avoid sample clamping problems. The results were computed in terms of moduli values and loss tangent. The curves of these parameters (storage modulus, loss modulus and loss tangent) as a function of both temperatures and frequencies were plotted.
Fig. 2.6(a): Photograph showing the LKB-Utrotome V instrument at MRPRA
Fig. 2.6(b) : Photograph showing the transmitted light Leitz Ortholux V microscope at MRPRA
2.11 Optical microscopy

2.11.1 Sample preparation

Samples of rubber vulcanizates were prepared by cryo-ultramicrotoming. This was accomplished using the LKB-Ultratome V instrument. A photograph of the instrument is shown in Figure 2.6(a). Initially, the sample was hardened and cooled to below its glass transition temperature (-120°C), using liquid nitrogen. The tip of the sample was sectioned to an ultra thin thickness between 0.25-0.30 μm. A glass knife was used for sectioning the sample, which was prepared using a LKB knifemaker. The thin sectioned samples were rolled-up, collected with a spatula and floated in a bath of water. The sample was collected again, placed on a glass slide and mounted with polybutene prior to examination.

2.11.2 Transmitted light phase-contrast microscopy

For the phase contrast microscopy observation, the morphology of polymer blends was examined under the transmitted light Leitz Ortholux V phase contrast microscope. A photograph of the instrument is shown in Figure 2.6(b). The principle and the features of the instrument are already discussed in section 1.5.4. The micrographs of the samples were taken on a polaroid film, and prepared at X1000 magnification.
2.12 Measurement of physical properties

2.12.1 Tensile strength

Tensile properties of rubber blends were measured using an Instron testing machine. Small dumbbell test pieces were used throughout. They were prepared and die stamped from vulcanized sheets. The measurements were carried out in accordance with ISO 37. A small test piece was used rather than a big test piece because of slippage problem, since the materials used were gum vulcanizates.
Fig. 2.7: (a) The diagramme showing the trouser test piece. The diamensions are in millimeters (b) The diagramme showing the position of the grip attached to the sample.
2.12.2 Tearing energy

A trouser test piece was used in this investigation. Measurements were made in accordance with ISO 34. Test pieces were prepared by die stamping from a vulcanized sheet. The shape and dimensions of the test piece is shown in Figure 2.7(a). Tearing measurements were carried out using an Instron 1122 test machine. The test piece was attached to the grip using "an air-actuated grip" which tightens automatically during tension. The position of the test piece on the grip is shown in Figure 2.7(b). The legs of the trouser test piece were separated at a constant rate of 100±10 mm/min. Displacement and tearing force were automatically recorded on a chart paper.

Tearing energy was calculated using the formula given below [76],

\[ \text{T.E} = \frac{F(\lambda + 1)}{h} \]  

(2.14)

where \( F \) is the average maximum tearing force in the steady state,
\( d \) is the thickness of the test piece and
\( \lambda \) is the extension ratio in the leg of the trouser test piece.
2.12.3 Rebound resilience

The apparatus used in this study was a pendulum Dunlop tripsometer. It consists of a steel disc of 42 cm in diameter with its periphery attached by an indentor or striker of diameter 4 mm. The test piece has the dimensions of 45 mm in diameter and 8 mm in thickness. The test can be carried out at both room and elevated temperatures. Measurements were made as described in BS 903:part A8.
Fig. 2.8: (a) A schematic diagramme of a Wallace permeability equipment
(b) A close view of the set-up of the sample in the test chamber.
2.12.4 Air permeability

Air permeability was measured based on the principle first used by Graham in 1866 [77]. It consists of placing a test piece between a high pressure chamber or reservoir containing air at given constant pressure and measuring the change in pressure or volume in the low pressure chamber of the system. In this investigation, a constant volume method was used and measured the change in pressure by a manometer. The apparatus used was a Wallace permeability tester, shown in Figure 2.8. A thin test piece of dimensions 50 mm in diameter and about 0.3 mm in thickness was specially prepared and moulded using a compression mould. The procedure of measurements is given in ISO 1399-1982 (E).

The rate of pressure rise was determined from the plot of pressure change against time. The slope was measured at a steady-state condition. Permeability coefficient was calculated using the equation given below,

\[
\frac{\text{dh}}{\text{dt}}Vxdx10^3x9.81x273
\]

\[\frac{\text{Pc}}{\text{AxApTXl0}^5}\]

where \(\frac{\text{dh}}{\text{dt}}\) is the rate of liquid in the manometer (ms\(^{-1}\)),

\(V\) is the effective volume on low pressure side (m\(^3\)),

\(d\) is the thickness of the test piece (m),

\(\rho\) is the density of manometer liquid (Mgm\(^{-3}\)),

\(A\) is the effective test piece area (m\(^2\)).
p is the pressure across the test piece (Nm\(^{-2}\)),

T is the test temperature (K) and

10^5 is the atmospheric pressure (Nm\(^{-2}\))

Permeability coefficient in SI unit is given as

\( m^{4} s^{-1} N^{-1}. \)
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Solubility parameter of NR and ENRs

The various factors that control the type of blends obtained when two polymers are mixed have been reviewed in the introduction. One such factor is the solubility parameters of the polymers to be blended.

The solubility parameter \( \delta \) of NR and ENRs used in the blends studied have been determined by equilibrium swelling measurements and calculation. Equilibrium swelling results of NR, ENR-26, ENR-48 and ENR-71 in a series of solvents of known solubility parameter are recorded in Table 3.1 and plotted in Figures 3.1(a-d). Density values of the solvents are given in Table 2.2. The types of solvents used were carefully chosen in order to avoid secondary bonding between the components. A "three dimensional" solubility parameter has been proposed by Hansen [78] and Crowley et.al [79] that splits the interactions, namely van der Waal dispersion forces, polar or dipole-dipole interaction and hydrogen bonding. The use of solvents which can hydrogen bond strongly with the rubber under study can lead to erroneous solubility parameter values. The energy of hydrogen bonding is not easily measured. Therefore, Burrell [47] has quantified and developed a practical system by arbitrarily categorizing solvents into three classes, depending in their tendency to hydrogen bond. (a) poorly hydrogen bonded, including hydrocarbons, chlorinated hydrogens and nitrohydrocarbons; (b)
Table 3.1  Swelling data of gum peroxide vulcanizates of NR, ENR-26, ENR-48 and ENR-71 in various solvents of known solubility parameter

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\sqrt{(Jm^{-3})} \times 10^3$</th>
<th>$\sqrt{(Calcm^{-3})}$</th>
<th>$M_O$</th>
<th>$M_S$</th>
<th>$M_I$</th>
<th>$V_S$</th>
<th>$V_{RN}$</th>
<th>$V_R$</th>
<th>$V_S/M_O$</th>
<th>$X$</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>14.40</td>
<td>7.05</td>
<td>0.1316</td>
<td>0.2790</td>
<td>0.1474</td>
<td>0.2356</td>
<td>0.1427</td>
<td>0.3772</td>
<td>1.7903</td>
<td>0.6179</td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>14.90</td>
<td>7.30</td>
<td>0.1376</td>
<td>0.3381</td>
<td>0.2005</td>
<td>0.3042</td>
<td>0.1492</td>
<td>0.3291</td>
<td>2.2108</td>
<td>0.5587</td>
<td></td>
</tr>
<tr>
<td>n-octane</td>
<td>15.45</td>
<td>7.55</td>
<td>0.1371</td>
<td>0.3710</td>
<td>0.2339</td>
<td>0.3327</td>
<td>0.1487</td>
<td>0.3089</td>
<td>2.4267</td>
<td>0.5126</td>
<td></td>
</tr>
<tr>
<td>decane</td>
<td>15.86</td>
<td>7.75</td>
<td>0.3712</td>
<td>0.990</td>
<td>0.6282</td>
<td>0.8605</td>
<td>0.4090</td>
<td>0.3222</td>
<td>3.3200</td>
<td>0.5100</td>
<td>(NR)</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>16.78</td>
<td>8.20</td>
<td>0.1344</td>
<td>0.5418</td>
<td>0.4074</td>
<td>0.5229</td>
<td>0.1458</td>
<td>0.2180</td>
<td>3.8906</td>
<td>0.4328</td>
<td></td>
</tr>
<tr>
<td>butyl acetate</td>
<td>17.49</td>
<td>8.55</td>
<td>0.1339</td>
<td>0.3638</td>
<td>0.2299</td>
<td>0.2607</td>
<td>0.1452</td>
<td>0.3577</td>
<td>1.9469</td>
<td>0.5891</td>
<td></td>
</tr>
<tr>
<td>methyl propyl ketone</td>
<td>17.80</td>
<td>8.70</td>
<td>0.1348</td>
<td>0.2557</td>
<td>0.1209</td>
<td>0.1489</td>
<td>0.1462</td>
<td>0.4954</td>
<td>1.1046</td>
<td>0.7355</td>
<td></td>
</tr>
<tr>
<td>decane</td>
<td>15.86</td>
<td>7.75</td>
<td>0.3250</td>
<td>0.5200</td>
<td>0.1950</td>
<td>0.2671</td>
<td>0.3345</td>
<td>0.5560</td>
<td>0.2218</td>
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</tr>
<tr>
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<td>8.20</td>
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<td>0.8800</td>
<td>0.5900</td>
<td>0.7574</td>
<td>0.2984</td>
<td>0.2826</td>
<td>2.6117</td>
<td>0.5264</td>
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</tr>
<tr>
<td>methyl i-butyl ketone</td>
<td>17.19</td>
<td>8.40</td>
<td>0.2850</td>
<td>0.9400</td>
<td>0.6550</td>
<td>0.8229</td>
<td>0.2933</td>
<td>0.2628</td>
<td>2.8874</td>
<td>0.4868</td>
<td>(ENR-26)</td>
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<td>butyl acetate</td>
<td>17.49</td>
<td>8.55</td>
<td>0.3250</td>
<td>1.2750</td>
<td>0.9500</td>
<td>1.0771</td>
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<td>0.2369</td>
<td>3.3140</td>
<td>0.4402</td>
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</tr>
<tr>
<td>methyl propyl ketone</td>
<td>17.80</td>
<td>8.70</td>
<td>0.3100</td>
<td>0.8300</td>
<td>0.5200</td>
<td>0.6600</td>
<td>0.3190</td>
<td>0.3326</td>
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<td>Solvents</td>
<td>$\sqrt{(Jm^{-3})}$ $\times 10^3$</td>
<td>$\sqrt{(Calcm^{-3})}$</td>
<td>$M_O$</td>
<td>$M_S$</td>
<td>$M_i$</td>
<td>$V_S$</td>
<td>$V_{RN}$</td>
<td>$V_r$</td>
<td>$V_S/M_O$</td>
<td>$X$</td>
<td>Polymer</td>
</tr>
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<td>cyclohexane</td>
<td>16.78</td>
<td>8.20</td>
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<td>0.6000</td>
<td>0.2700</td>
<td>0.3466</td>
<td>0.3137</td>
<td>0.4751</td>
<td>1.0503</td>
<td>0.7150</td>
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</tr>
<tr>
<td>methyl i-butyl ketone</td>
<td>17.19</td>
<td>8.40</td>
<td>0.3350</td>
<td>1.2800</td>
<td>0.9450</td>
<td>1.1872</td>
<td>0.3184</td>
<td>0.2115</td>
<td>3.5438</td>
<td>0.4479</td>
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</tr>
<tr>
<td>butyl acetate</td>
<td>17.49</td>
<td>8.55</td>
<td>0.3600</td>
<td>1.4900</td>
<td>1.1300</td>
<td>1.2812</td>
<td>0.3422</td>
<td>0.2108</td>
<td>3.5589</td>
<td>0.4217</td>
<td>(ENR-48)</td>
</tr>
<tr>
<td>toluene</td>
<td>18.21</td>
<td>8.90</td>
<td>0.3700</td>
<td>1.8500</td>
<td>1.4800</td>
<td>1.7159</td>
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<td>0.1701</td>
<td>4.6375</td>
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<tr>
<td>ethyl acetate</td>
<td>18.62</td>
<td>9.10</td>
<td>0.3300</td>
<td>1.1900</td>
<td>0.8600</td>
<td>0.9549</td>
<td>0.3137</td>
<td>0.2473</td>
<td>2.8936</td>
<td>0.5126</td>
<td></td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>19.03</td>
<td>9.30</td>
<td>0.3550</td>
<td>1.2600</td>
<td>0.9050</td>
<td>1.1327</td>
<td>0.3375</td>
<td>0.2296</td>
<td>3.1907</td>
<td>0.4979</td>
<td></td>
</tr>
<tr>
<td>butyl acetate</td>
<td>17.49</td>
<td>8.55</td>
<td>0.0600</td>
<td>0.2805</td>
<td>0.2205</td>
<td>0.2500</td>
<td>0.0568</td>
<td>0.1851</td>
<td>4.1670</td>
<td>0.4236</td>
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</tr>
<tr>
<td>methyl propyl ketone</td>
<td>17.80</td>
<td>8.70</td>
<td>0.0850</td>
<td>0.3919</td>
<td>0.3609</td>
<td>0.3780</td>
<td>0.0805</td>
<td>0.1757</td>
<td>4.4470</td>
<td>0.4352</td>
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<tr>
<td>methyl propionate</td>
<td>18.41</td>
<td>8.90</td>
<td>0.1800</td>
<td>0.8297</td>
<td>0.6497</td>
<td>0.7100</td>
<td>0.1706</td>
<td>0.1937</td>
<td>3.9440</td>
<td>0.4769</td>
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</tr>
<tr>
<td>ethyl acetate</td>
<td>18.62</td>
<td>9.10</td>
<td>0.1500</td>
<td>0.5949</td>
<td>0.4449</td>
<td>0.4940</td>
<td>0.1420</td>
<td>0.2232</td>
<td>3.2930</td>
<td>0.5896</td>
<td>(ENR-71)</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>19.03</td>
<td>9.30</td>
<td>0.1550</td>
<td>0.7103</td>
<td>0.5553</td>
<td>0.6195</td>
<td>0.1469</td>
<td>0.1917</td>
<td>3.9970</td>
<td>0.4797</td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>20.46</td>
<td>10.0</td>
<td>0.2000</td>
<td>0.6400</td>
<td>0.4400</td>
<td>0.5563</td>
<td>0.1895</td>
<td>0.2541</td>
<td>2.7820</td>
<td>0.5596</td>
<td></td>
</tr>
<tr>
<td>methyl formate</td>
<td>20.87</td>
<td>10.2</td>
<td>0.1100</td>
<td>0.4200</td>
<td>0.3100</td>
<td>0.3206</td>
<td>0.1042</td>
<td>0.2453</td>
<td>2.9150</td>
<td>0.5583</td>
<td></td>
</tr>
</tbody>
</table>
NOTES:

\[ \begin{align*}
M_o & = \text{weight of unswollen sample} \\
M_s & = \text{weight of swollen sample (after 2 weeks swelling)} \\
(M_i & = M_s - M_o) \\
V_s & = \frac{M_i}{\rho_s}, \text{where } \rho_s \text{ is the density of solvent (table 2.2)} \\
V_{RN} & = \frac{M_o}{P_{RN}}, \text{where } P_{RN} \text{ is the density of rubber} \\
V_r & = \frac{V_{RN}}{V_{RN} + V_s}
\end{align*} \]

Density of NR = 0.922 Mgm\(^{-3}\)

\[ \begin{align*}
\text{ENR-26} & = 0.972 " \\
\text{ENR-48} & = 1.052 " \\
\text{ENR-71} & = 1.055 "
\end{align*} \]
Fig. 3.1(a): Effect of equilibrium swelling of dicumyl peroxide of NR gum vulcanizate as a function of solubility parameter of solvents. The maximum swelling result is assigned as the solubility parameter of polymer.
Fig. 3.1(b): Effect of equilibrium swelling of dicumyl peroxide of ENR-26 gum vulcanizate as a function of solubility parameter of solvents. The maximum swelling result is assigned as the solubility parameter of polymer.
Fig. 3.1(c): Effect of equilibrium swelling of dicumyl peroxide of ENR-48 gum vulcanizate as a function of solubility parameter of solvents. The maximum swelling result is assigned as the solubility parameter of polymer.
Fig. 3.1(d) : Effect of equilibrium swelling of dicumyl peroxide of ENR-71 gum vulcanizate as a function of solubility parameter of solvents. The maximum swelling result is assigned as the solubility parameter of polymer.
### Table 3.2: Solubility parameter values of NR and ENRs

<table>
<thead>
<tr>
<th>Rubbers</th>
<th>$\delta^A \times 10^3$, (Jm$^{-3})^{1/2}$</th>
<th>$\delta^B$, (Jm$^{-3})^{1/2}$</th>
<th>$\delta^C$, (cal.cm$^{-3})^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>16.78 (8.20)$^*$</td>
<td>16.65 (8.14)</td>
<td>17.02 (8.32)</td>
</tr>
<tr>
<td>ENR-26</td>
<td>17.39 (8.50)</td>
<td>17.41 (8.51)</td>
<td>17.53 (8.57)</td>
</tr>
<tr>
<td>ENR-48</td>
<td>18.21 (8.90)</td>
<td>18.17 (8.88)</td>
<td>18.11 (8.85)</td>
</tr>
<tr>
<td>ENR-71</td>
<td>18.52 (9.05)</td>
<td>18.59 (9.09)</td>
<td>18.52 (9.05)</td>
</tr>
</tbody>
</table>

**Notes:**
- A - measurement from volume swelling
- B - measurement from the slope of line (eqn. 3.6)
- C - calculation using Small's method (eqn. 3.11), based on molar attraction constant in table 2.2.
- $^*$ - The values of $\delta$ in brackets are in (cal.cm$^{-3})^{1/2}$

### Table 3.3: $C_1$ values of extracted peroxide NR and ENR vulcanizes

<table>
<thead>
<tr>
<th>Rubbers</th>
<th>$C_1$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR (SMR L)</td>
<td>0.174</td>
</tr>
<tr>
<td>ENR-26</td>
<td>0.165</td>
</tr>
<tr>
<td>ENR-48</td>
<td>0.137</td>
</tr>
<tr>
<td>ENR-71</td>
<td>0.101</td>
</tr>
</tbody>
</table>
moderately hydrogen bonded, including ketones, esters and ethers and (c) strongly hydrogen bonded, such as alcohols. In this study, poor and moderate hydrogen bonding solvents were used in order to eliminate strong hydrogen bonding interactions with the rubber. The formation of hydrogen bonding will increase the interaction between the two components, and hence, result in an inaccurate swelling value.

As can be seen from the plotted figures, swelling initially increased with the increase of $\delta$ of the solvent, passing through a maximum before decreasing with further increase of $\delta$, giving a "bell-shaped" curve. In a "good" solvent, where the polymer-solvent compatibility is high, the segmental motion or end-to-end distance of rubber molecules increases. This allows more solvent molecules to diffuse into the bulk of the rubber molecules, resulting in a high degree of swelling. However, in a "poor" solvent, the rubber molecules are relatively contracted. The maximum swelling coincides with the maximum interaction of the rubber with the solvent. Thus, the solubility parameter of the rubber is assigned as that at which maximum swelling occurs. The values obtained from equilibrium swelling plots for NR, ENR-26, ENR-48 and ENR-71 are recorded in Table 3.2.

Swelling data can also be utilised to obtain solubility parameters via the modified Flory-Rehner equation [80]. This treatment enables the rubber-solvent interaction parameter $X$ to be determined from swelling data, and hence the solubility parameter of the polymer. The modified Flory-Rehner equation in terms of $X$ is given below:

\[ \text{(88)} \]
where \( Vo \) = molar volume of solvent,
\( V_r \) = volume fraction of the rubber network,
\( X \) = rubber-solvent interaction parameter,
\( M_c \) = number average molecular weight of rubber chains between crosslinks.

Mullins [81] has assumed that the physical degree of crosslinking, \( 1/2(M_c) \), is related to the expression,

\[
(3.2) \quad C_1 = \frac{\rho RT}{2(M_c)},
\]
\[
1/2(M_c) = C_1/(\rho RT)
\]

By substituting eqn. 3.2 into eqn. 3.1, then

\[
(3.3) \quad -\ln(1-V_r)-V_r-XV_r^2 = \left(2VoC_1/RT\right)(V_r^{1/3}-V_r/2)
\]

\( V_r \) was obtained from volume swelling measurement following the method described by Bristow and Porter [74], as discussed in section 2.9. \( C_1 \) has to be estimated independently from stress strain measurements based on unswollen samples, using the equation given by Mooney-Rivlin [82]. The use of unswollen and swollen samples is not critical in this work. For peroxide vulcanizates, Bristow and Porter [74] have shown that \( C_1 \) values are in close parity by making measurements on either swollen or unswollen samples. For this reason, unswollen samples were used to determine \( C_1 \). Mooney-Rivlin equation is:
Fig. 3.2(a) : The plot of $f/2A_0(\lambda - \lambda^{-2})$, x10^4 kgm^{-2} versus $\lambda^{-1}$ of dicumyl peroxide NR gum vulcanizate. $C_1$ value is obtained at the intercept of y-axis by extrapolating the linear portion of the curve to $\lambda^{-1}=0$. 

(90)
Fig. 3.2 (b) : The plot of \( f/2A_0(\lambda - \lambda^{-2}) \) versus \( \lambda^{-1} \) of dicumyl peroxide ENR-26 gum vulcanizate. \( C_1 \) value is obtained at the intercept of y-axis by extrapolating the linear portion of the curve to \( \lambda^{-1}=0 \).
Fig. 3.2(c): The plot of $\frac{f/2A_{o}}{(\lambda_{-}\lambda_{+})^2}$ versus $\lambda^{-1}$ of dicumyl peroxide ENR-48 gum vulcanizate. C value is obtained at the intercept of y-axis by extrapolating the linear portion of the curve to $\lambda^{-1}=0$. 
The plot of $f/2A_0(\lambda - \lambda^{-2}) \times 10^4$ kgm$^2$ vs. $\lambda$ of dicumyl peroxide ENR-71 gum vulcanizate. $C_1$ value is obtained at the intercept of $y$-axis by extrapolating the linear portion of the curve to $\lambda^{-1}=0$. 

Fig. 3.2(d): The plot of $f/2A_0(\lambda - \lambda^{-2})$ versus $\lambda^{-1}$ of dicumyl peroxide ENR-71 gum vulcanizate. $C_1$ value is obtained at the intercept of $y$-axis by extrapolating the linear portion of the curve to $\lambda^{-1}=0$. 

(93)
where $f$ is the force required to extend a test piece of unstrained cross-sectional area $(A_0)$ to an extension ratio $\lambda$. $C_1$ and $C_2$ are elastic constants which are assumed independent of the test method and strain. This assumption is valid for unfilled vulcanizates, as shown by Bristow and Watson [83].

The stress-strain data were analysed by plotting $f/2A_0(\lambda - \lambda^{-2})$ against $\lambda^{-1}$. In Figure 3.2(a-d) the stress-strain behaviour of NR, ENR-26, ENR-48 and ENR-71 are illustrated. $C_1$ value was obtained as the intercept of $y$-axis by extrapolating the linear portion of the curve to $\lambda^{-1}=0$. It was observed that for all the rubbers studied, the stress-strain data fitted quite well along a straight line plot.

The $C_1$ values of NR, ENR-26, ENR-48 and ENR-71 are tabulated in Table 3.3. $C_1$ values were observed to decrease with increased mole % epoxide groups. The decrease in $C_1$ values suggests that the efficiency of physical crosslinking decreases with the increase in mole % epoxide groups in the rubber. The reduction in $C_1$ value of ENRs is probably caused by the lower efficiency of crosslinking. This result is consistent with the work carried out by Gelling et al [23].

From eqn. (3.3), $X$ values were calculated for the various rubber-solvent interactions and the results are tabulated in Table 3.1.

Huggin [84] has deduced that $X$ is approximately related to the solubility parameter by,

\[(3.4) \quad f = 2A_0(\lambda - \lambda^{-2})(C_1 + \lambda^{-1}C_2)\]
Fig. 3.3 (a&b): The plots of Modified Flory-Rehner equation for the determination of solubility parameter of (a) NR and (b) ENR-26, using the equilibrium swelling data given in Table 3.1.
Fig. 3.3 (c&d) : The plots of Modified Flory-Rehner equation for the determination of solubility parameter of (c) ENR-48 and (d) ENR-71, using the equilibrium swelling data given in Table 3.1.
where $\beta'$ is the coordination number of the lattice and is equal to 0.3 for all solvents [85]; $\delta_1$ and $\delta_2$ are the solubility parameters of solvent and rubber respectively.

If this approximation is taken as a valid means of assigning the solubility parameter of the rubber, then rearrangement of eqn. (3.5) gives

$$\delta_1^2/RT - X/V_o = (2\delta_2/RT)\delta_1 - \delta_2^2/RT - \beta'/V_o$$  \hspace{1cm} (3.6)

By using the data determined in Table 3.1 and plotting $\delta_1^2/RT - X/V_o$ against $\delta_1$, a linear plot is obtained as illustrated in Figures 3.3 (a-d). Good straight line plots were obtained. The slope is equal to $2\delta_2/RT$. Therefore, $\delta_2$ of a polymer can be calculated from the slope of the plot. The results are recorded in Table 3.2. Thus, this represents an alternative method for estimating the solubility parameter of polymers.

Solubility parameters of polymers can also be determined by the use of "molar attraction constants". Small [44] worked out these physical constants from structural formula of the materials based on the concept proposed by Scatchard [86]. The Scatchard semi-empirical relationship of heat of mixing is given below:

$$\Delta H_{mix} = \Phi_1 \Phi_2 [(E_1/V_1)^{1/2} - (E_2/V_2)^{1/2}]^2$$  \hspace{1cm} (3.7)

$$= \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2$$

where $E$ is molar cohesive energy; $V$ is the molar volume; and $\Phi$ is the volume fraction of components 1 and 2. $E/V$
is the cohesive energy density and its square root is the solubility parameter.

Small has further proposed that, the cohesive energy \( E \) of a mixture consisting of \( n_1 \) moles of a liquid 1 with cohesive energy \( E_1 \) and molar volume \( V_1 \), and \( n_2 \) moles of liquid 2 is given by:

\[
E^{1/2}(n_1V_1+n_2V_2)^{1/2} = n_1(E_1V_1)^{1/2} + n_2(E_2V_2)^{1/2}
\]

That is, \( (EV)^{1/2} \) is an additive property over the structural formula of the material. The "molar attraction constant" of a chemical grouping is denoted by the symbol \( F \). \( \Sigma F \) summed over the groups present give the value of \( (EV)^{1/2} \) for one mole of the material. Therefore,

\[
(3.9) \quad (EV)^{1/2} = \Sigma F
\]

\[
E = (\Sigma F)^2/V
\]

But,

\[
(3.10) \quad \delta = (E/V)^{1/2}
\]

Substituting eqn. 3.9 into eqn. 3.10, we have

\[
(3.11) \quad \delta = \Sigma F/V = \rho \Sigma F/M
\]

where \( \rho \) is the density and \( M \) is the molecular weight of the polymer. Recently, Hoy [45] has redetermined the group molar attraction constants which are derived from vapour pressure measurement, (see Table 1.3). Hoy's values were used in the calculation rather than Small's, because the latter does not include the epoxide group.
Therefore, the solubility parameters of the structural configurational unit in a polymer chain can be calculated. Since, ENR is a random copolymer, the use of eqn. 3.11 was modified in order to take into account the fraction of NR and ENR molecules in the rubber. A calculated example for ENR-26 is given below: Now, from eqn. 3.11,

\[
\delta = \frac{\rho (\Sigma F_1 \Phi_1 + \Sigma F_2 \Phi_2)}{(M_1 \Phi_1 + M_2 \Phi_2)}
\]

Molecular weight of NR unit = 68.13 gmol\(^{-1}\)
Molecular weight of ENR unit = 84.13 gmol\(^{-1}\)
Density of rubber, \(\rho = 0.97\) Mg m\(^{-3}\)

Total molar attraction constants for NR unit:
1 \(-\text{CH}_3\) \hspace{1cm} 147.3
2 \(-\text{CH}_2\) \hspace{1cm} 2x131.5
1 \(-\text{CH}=\) \hspace{1cm} 121.53
1 \(-\text{C}=\) \hspace{1cm} 84.51

\(\Sigma F_i = 616.34\)

Total molar attraction constants for ENR unit:
1 \(-\text{CH}_3\) \hspace{1cm} 147.3
2 \(-\text{CH}_2\) \hspace{1cm} 2x131.15
1 \(-\text{C}\) \hspace{1cm} 32.03
1 \(-\text{CH}\) \hspace{1cm} 85.99
1 \(-\text{O}\) \hspace{1cm} 176.20

\(\Sigma F_i = 704.52\)
Fig. 3.4: Solubility parameters of ENRs as a function of per cent epoxide groups. Solid line is obtained from Small's calculation method. The points (●) and (○) are those obtained from the slope of the lines (Fig. 3.3) and equilibrium volume swelling measurements respectively.
Therefore,
\[
\delta = \frac{0.97(616.34x0.74 + 704.52x0.26)}{(68.13x0.74 + 84.13x0.26)} = 17.55x10^{-3} \text{ (Jm}^{-3})^{1/2}
\]

Note: the conversion factor to SI is
1 (cal.cm\(^{-3}\))\(^{1/2}\) = 2.046x10\(^{3}\) (Jm\(^{-3}\))\(^{1/2}\)

Figure 3.4 shows a plot of \(\delta\) against the mole percent epoxide groups in the rubber. The points (●) and (○) on the plot are those obtained from the slope of the line (obtained from eqn. 3.6) and from equilibrium volume swelling measurements respectively. For NR, the \(\delta\) determined from the slope is in accordance with the results obtained by Bristow et.al [83]. A good agreement was observed with values determined from Small's calculation represented by the solid line. It is found that the solubility parameter increases linearly with the increase in the mole % epoxide present in the rubber. As the mole % epoxide groups in the rubber increase, the movement of chain mobility decreases. This is due to the fact that epoxide groups restrict or hinder the rotation of the polymer chain. For example, in silicone rubber, the rotation around the bonds is nearly free, and thus silicone rubber has a low solubility parameter (\(\delta=7.3\)) [60]. Polymers with high Tgs tend to have high solubility parameters.

ENR has been suggested for use as an adhesive. A knowledge of solubility parameters will enable the correct choice of solvents to be made.
3.2 Segmental interaction parameter

A knowledge of the solubility parameters of polymers is useful to predict the compatibility of polymer blends. It has been discussed in section 1.5.1 that the segmental interaction parameter between two polymer chains is related to the solubility parameter by equation 1.3. A negative or near zero $X_{AB}$ of two polymer chains A and B results in a favourable free energy of mixing.

Segmental interaction parameters have been determined. A calculated example of $X_{AB}$ between NR and ENR-48 blend is given below. From eqn. 1.3,

$$X_{AB} = \frac{V}{RT}(\delta_A - \delta_B)^2$$

where $R = 8.314$ JK$^{-1}$mol$^{-1}$,
$T = 298$ K,
$V =$ molar volume of repeating unit of polymer chain and was assumed 100 cm$^3$mol$^{-1}$,
$\delta_A$ and $\delta_B =$ the solubility parameter of NR and ENR-48 respectively. The values used for the calculation were obtained from the group contribution of Small's method given in Table 3.2.

Therefore,

$$X_{AB} = \frac{100}{(8.314 \times 298)(17.02 - 18.11)^2}$$

$= 0.0479$

$= 4.79 \times 10^{-2}$

(102)
Table 3.4: Segmental interaction parameters of rubber-rubber blends at 25°C

<table>
<thead>
<tr>
<th>Rubber blend</th>
<th>$X_{AB} \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/ENR-26</td>
<td>1.05</td>
</tr>
<tr>
<td>NR/ENR-48</td>
<td>4.79</td>
</tr>
<tr>
<td>NR/ENR-71</td>
<td>9.08</td>
</tr>
<tr>
<td>ENR-26/ENR-48</td>
<td>1.36</td>
</tr>
<tr>
<td>ENR-26/ENR-71</td>
<td>3.96</td>
</tr>
<tr>
<td>ENR-31/ENR-43</td>
<td>0.27</td>
</tr>
<tr>
<td>ENR-48/ENR-71</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 3.5: Glass transition temperature of NR/ENR-48 blends by DSC

<table>
<thead>
<tr>
<th>Blend ratio (wt/wt%) NR/ENR-48</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENR-48</td>
</tr>
<tr>
<td>100:0</td>
<td></td>
</tr>
<tr>
<td>90:10</td>
<td>*</td>
</tr>
<tr>
<td>80:20</td>
<td>*</td>
</tr>
<tr>
<td>70:30</td>
<td>-22</td>
</tr>
<tr>
<td>60:40</td>
<td>-27</td>
</tr>
<tr>
<td>50:50</td>
<td>-25</td>
</tr>
<tr>
<td>40:60</td>
<td>-28</td>
</tr>
<tr>
<td>30:70</td>
<td>-25</td>
</tr>
<tr>
<td>20:80</td>
<td>-24</td>
</tr>
<tr>
<td>10:90</td>
<td>-27</td>
</tr>
<tr>
<td>0:100</td>
<td>-27</td>
</tr>
</tbody>
</table>

Notes: * no Tg detected
The calculated values of $X_{AB}$ between NR and ENRs, as well as between ENRs at different levels of epoxidation are given in Table 3.4. It was shown that, for blend between NR and ENRs, the $X_{AB}$ increases with the increase in the epoxide level. This indicates that blends are unlikely to result in truly compatible material when there is a significant difference in the level of epoxidation between the two polymers.

The values of $X_{AB}$ of blend between ENR-31/ENR-43 and ENR-48/ENR-71 were 0.0027 and 0.0068 respectively, which are small compared with values for other blends and some degree of compatibility may be expected. Evidence of this was observed from the dynamic glass transition temperature measurement which will be covered later. For a blend between PS and PPO in which the components have similar solubility parameters, the compatibility is well predicted [28].

In general, if $(\delta_A-\delta_B)$ is large, then the two polymers should be incompatible. The greater the difference between $(\delta_A-\delta_B)$, the more incompatible the polymer blend should be. However, if $(\delta_A-\delta_B)$ is small, then the two polymers should be compatible at that composition.
Table 3.6: Repeatibility results of NR/ENR-48 blends measured by DSC

<table>
<thead>
<tr>
<th>Blend ratio NR/ENR-48</th>
<th>Tg, °C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR</td>
<td>ENR-48</td>
<td></td>
</tr>
<tr>
<td>(100:0)</td>
<td>-70.0</td>
<td>-68.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-71.0±1.93)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(70:30)</td>
<td>-70.0</td>
<td>-68.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-70.0±1.29)</td>
<td>(-26.0±1.73)</td>
<td></td>
</tr>
<tr>
<td>(50:50)</td>
<td>-70.0</td>
<td>-68.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-71.0±0.71)</td>
<td>(-27.0±0.71)</td>
<td></td>
</tr>
<tr>
<td>(30:70)</td>
<td>-71.0</td>
<td>-68.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-72.0±0.82)</td>
<td>(-28.0±1.0)</td>
<td></td>
</tr>
<tr>
<td>(0:100)</td>
<td>-90.0</td>
<td>-68.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(29.0±0.87)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: figures in bracket are mean and standard deviation of 3 or 4 samples.
3.3 Thermal properties

The main purpose of the present study is to investigate and analyze a series of polymer blends. As stated in the introduction, useful information on blend structures can be obtained from a study of glass transition temperatures.

The glass transition temperatures (Tgs) of a range of NR/ENR-48 blends and parent materials are recorded in Table 3.5. Two main points arise from this table, i.e., no glass transition temperatures were observed for the ENR-48 component in the 90:10 and 80:20 NR/ENR-48 blends, and also no transition was observed for the NR component in the 10:90 NR/ENR-48 blend; a variation in Tg of the components was observed, which could suggest partial compatibility.

As a first step to clarify the position, a number of Tg determinations were repeated on each blend sample. The results are recorded in Table 3.6. The experimental error of a single determination is such that it can be safely stated the Tgs of the blends have not shifted. The absence of a Tg for the minor component could be due to compatibility, but this should be associated with a shift of the Tg of the major component. However, this behaviour was not observed. Therefore, the effect is assumed at this stage to be due to the lack of sensitivity of the instrument.

The detection of two Tg values over a range of NR and ENR blends suggests that the blends are incompatible, as distinct transitions are observed.

A range of blends of ENR-26 and ENR-48 were also examined. The Tg results of blends between ENR-26 and
Figure 3.7: Glass transition temperature of ENR-26/ENR-48 blends by DSC

<table>
<thead>
<tr>
<th>Blend ratio (wt/wt%) ENR-26/ENR-48</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENR-26</td>
</tr>
<tr>
<td>100:0</td>
<td>-46.0</td>
</tr>
<tr>
<td>80:20</td>
<td>-45.0</td>
</tr>
<tr>
<td>70:30</td>
<td>-47.0</td>
</tr>
<tr>
<td>65:35</td>
<td>-46.0</td>
</tr>
<tr>
<td>60:40</td>
<td>-45.0</td>
</tr>
<tr>
<td>50:50</td>
<td>-46.0</td>
</tr>
<tr>
<td>40:60</td>
<td>-45.0</td>
</tr>
<tr>
<td>30:70</td>
<td>-45.0</td>
</tr>
<tr>
<td>0:100</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.8: Glass transition of 50:50 latex blend of ENR-31/ENR-43

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENR-31</td>
<td>-44</td>
</tr>
<tr>
<td>ENR-43</td>
<td>-32</td>
</tr>
<tr>
<td>ENR-31/ENR-43</td>
<td>-46,-31</td>
</tr>
</tbody>
</table>
ENR-48 and its pure components are recorded in Table 3.7. Again, a similar variation in the Tgs was observed in these blends. Obviously, this also indicates two phase systems exist in these blends. A 50:50 latex blend of ENR-31 and ENR-43 was also examined by DSC. The results of the blend and its parent components are summarised in Table 3.8. The difference in solubility parameter between these two levels of ENR is only 0.0027 and hence some degree of compatibility may be expected. However, Tg measurement has shown two distinct glass transition temperatures at the positions of the parent rubbers. It would appear that even when there is only 12% difference in the epoxide level between the two components that they are basically incompatible.
3.4 Dynamic mechanical properties

Three principle areas can be studied by dynamic mechanical measurements. Firstly, rubber blend compatibility can be characterized through the glass transition phenomena. Separate glass transitions associated with the separate phase components can be distinguished. This is most clearly identified by the position of the dynamic transition and the moduli data over the temperature range scanned. Secondly, the mechanical properties, in particular hysteresis and moduli of rubber blends can be measured. Thirdly, the morphology of each component in the blends can be predicted.

To examine the above properties, two types of measurement were made. They are isochronal (fixed-frequency) over a range of temperatures and isothermal (fixed temperature) over a range of frequencies. The latter measurement allows the use of the time-temperature superposition principle, e.g. the WLF [87] equation, to master curve all the individual plots.

3.4.1 Isochronal measurement

3.4.1.1 NR/ENR-48 blends

Dynamic mechanical properties of rubbers as determined in terms of storage modulus ($E'$) and loss angle ($\tan \theta$) were measured at 20 Hz over a temperature range of $-60$ to $20^\circ C$. In order to ensure the test is within the linear viscoelastic region, measurements were initially made at variable amplitudes from 11 to 130 $\mu m$
Fig. 3.5: Effect of variable amplitudes on loss angle for dicumyl peroxide ENR-48 gum vulcanizate. The points are represented the loss angle peak.
Fig. 3.6: Dependence of storage modulus on temperature at 20 Hz for a series of NR/ENR-48 blends.
Fig. 3.7: Dependence of loss angle on temperature at 20 Hz for a series of NR/ENR-48 blends.
using an ENR-48 sample. The effect of variable amplitudes on loss angle is shown in Figure 3.5. The plotted figure shows that \( \tan \theta \) is independent of applied amplitude. Since the rubber is within its linear viscoelastic region over the whole amplitude range, an amplitude of 80 \( \mu \text{m} \) (ca. <0.01% strain) was chosen and used throughout the testing.

The storage modulus and loss angle of NR and ENR-48 dicumyl peroxide crosslinked rubber vulcanizates as a function of temperature are shown in Figures 3.6 and 3.7 respectively. The data points were recorded at 1-2°C temperature intervals. As can be seen from the figure, the storage modulus is independent of temperature in the glassy region. The storage moduli of NR and ENR-48 were found to be 0.15x10\(^{10}\) and 0.20x10\(^{10}\) Pa respectively. In this region, molecular motion of the chain segments is frozen, and deformation is primarily from the bending of valence angles of the atoms in the polymer chains, so that the modulus is high. The polymer behaves as a near perfect elastic material. A perfect elastic material stores energy as potential energy and does not dissipate it, and thus has no damping.

The modulus decreases very slowly as the temperature increases. Near the glass transition region, the modulus decreases very rapidly by a factor of a thousand over a small temperature range. In this region, the material is semi-rigid and hysteresis goes to a maximum, because some of the molecular chain segments are free to move.

At temperatures above the glass transition region, the modulus is again much less temperature dependent. At 20°C the storage modulus of NR and ENR-48 was 0.55x10\(^{6}\)
and $0.21 \times 10^7$ Pa respectively. In this region, the material is rubbery with free segmental motion. In defining the dynamic glass transition temperature ($T_d$), (which is analogous to glass transition temperature ($T_g$)), it is usual to define the $T_d$ as the temperature at which the maximum loss angle occurs. The $T_d$ of NR has been determined by many authors, albeit at different frequencies. As can be seen from Figure 3.7, the $T_d$s of NR and ENR-48 were found to be $-39.5\,^\circ C$ and $-2\,^\circ C$ respectively. The dynamic glass transition temperature is much higher than the actual glass transition temperature, as determined from DSC. The difference is due to the effect of translational forces occurring in mechanical deformation.

At $25\,^\circ C$, the loss angles of NR and ENR-48 were found to be 16.5 and 31.3$^\circ$ respectively. Thus, ENR-48 is a higher damping material than NR at room temperature.

Dynamic properties in terms of storage modulus and loss angle of NR/ENR-48 blends are also recorded in Figures 3.6 and 3.7 respectively. The blend compositions are in wt/wt percent. For blend compositions containing 80:20 and 90:10 NR/ENR-48, dynamic glass transition temperatures of both components were clearly observed. At the other end of the compositional range, i.e., 20:80 and 30:70 NR/ENR-48 blends, transitions due to both components were also observed.

The above observations substantiate the assumption made from DSC measurement, i.e., the minor components were not observed due to compatibility but because of the lack of sensitivity of the instrument. Distinct transitions for each component were observed over the full range of NR/ENR-48 blend compositions indicating
Table 3.9: Dynamic transition temperature and loss angle peak of ENR/ENR-48 blends

<table>
<thead>
<tr>
<th>Blend ratio NR/ENR-48</th>
<th>T&lt;sub&gt;d&lt;/sub&gt;, °C</th>
<th>Loss angle peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR</td>
<td>ENR-48</td>
</tr>
<tr>
<td>100:0</td>
<td>-39.5</td>
<td>-</td>
</tr>
<tr>
<td>90:10</td>
<td>-40.0</td>
<td>-7</td>
</tr>
<tr>
<td>80:20</td>
<td>-41.0</td>
<td>-8</td>
</tr>
<tr>
<td>70:30</td>
<td>-41.0</td>
<td>-7.5</td>
</tr>
<tr>
<td>60:40</td>
<td>-41.5</td>
<td>-6.0</td>
</tr>
<tr>
<td>50:50</td>
<td>-42.0</td>
<td>-5.5</td>
</tr>
<tr>
<td>40:60</td>
<td>-43.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>30:70</td>
<td>-43.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>20:80</td>
<td>-45.0</td>
<td>-2.5</td>
</tr>
<tr>
<td>0:100</td>
<td>-</td>
<td>-2.0</td>
</tr>
</tbody>
</table>

(115)
Table 3.10: Repeatability results of NR/ENR-48 blends, scanned at different temperatures

<table>
<thead>
<tr>
<th>Blend ratios wt/wt(%) NR/ENR-48</th>
<th>Scanned Temp., °C</th>
<th>Td, °C NR</th>
<th>Td, °C ENR-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/30</td>
<td>-60±20</td>
<td>-40.5</td>
<td>-7.5</td>
</tr>
<tr>
<td></td>
<td>-60±10</td>
<td>-41.0</td>
<td>-9.0</td>
</tr>
<tr>
<td></td>
<td>-20±20</td>
<td>-</td>
<td>-7.0</td>
</tr>
<tr>
<td></td>
<td>-10±20</td>
<td>-</td>
<td>-6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-40.75±0.25</td>
<td>-7.5±0.90</td>
</tr>
<tr>
<td>60/40</td>
<td>-60±20</td>
<td>-41.0</td>
<td>-6.5</td>
</tr>
<tr>
<td></td>
<td>-60±10</td>
<td>-42.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-10±20</td>
<td>-</td>
<td>-7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-41.75±0.75</td>
<td>-6.75±0.25</td>
</tr>
<tr>
<td>50/50</td>
<td>-60±10</td>
<td>-43.0</td>
<td>-6.5</td>
</tr>
<tr>
<td></td>
<td>-60±10</td>
<td>-43.0</td>
<td>-6.0</td>
</tr>
<tr>
<td></td>
<td>-20±20</td>
<td>-</td>
<td>-5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-43.0±0.0</td>
<td>-5.83±0.62</td>
</tr>
<tr>
<td>30/70</td>
<td>-60±20</td>
<td>-43.5</td>
<td>-3.5</td>
</tr>
<tr>
<td></td>
<td>-60±10</td>
<td>-43.5</td>
<td>-3.5</td>
</tr>
<tr>
<td></td>
<td>-20±20</td>
<td>-</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-43.0±0.0</td>
<td>-3.3±0.24</td>
</tr>
</tbody>
</table>
incompatibility. The Tds obtained from loss angle curves are summarised in Table 3.9, together with the loss angle peaks.

Two major effects were observed with these rubber blends. They are the shift in dynamic glass transition temperatures and the size of the loss angle transition.

For the range of blends studied, the shift in Tds of the NR and ENR-48 components were found to be approximately 5.5 and 6°C respectively. The shifts in Tds are quite significant. Therefore, in order to confirm that these shifts are not due to instrument error, a repeatability study was carried out on a number of NR/ENR-48 blends. The same conditions were used as with the previous measurements, but in this case samples were scanned over different temperature ranges. The results are recorded in Table 3.10 in terms of dynamic glass transition temperature. It is shown that the position of the Td of each component has shifted towards lower temperature. The standard deviation of the shift of NR and ENR-48 are respectively less than ±1.0. Therefore, the inference can be made that the shift in Td position in the blends is not due to instrument error, but must be attributed to other reasons.

A criterion for partial compatibility is the extent to which the transition temperature move towards each other. However, the loss angle curves demonstrate that both transition temperatures move towards lower temperature. Thus, the concept of partial compatibility cannot be used to explain the observations.

The other observed effect is the loss angle transition peak, as determined from the loss angle curve. The areas of the loss angle peak of each
component in the blends were observed not to be related to the composition of the blend. For example, in a 50:50 NR/ENR-48 blend, the ENR-48 contributed the major loss peak, in comparison with the NR component. Information of this type of behaviour is useful in interpreting the morphology of the blends.

For blend compositions consisting of 90:10 and 80:20 NR/ENR-48, the loss angle peak of the NR component was much higher than that of the ENR-48 component, see Table 3.9 and Figure 3.7. In the other extreme cases, i.e., the blends of composition 20:80 and 30:70 NR/ENR-48, a reverse effect was observed. In these blends, the major loss angle peak was the ENR-48 component. It would be expected that the continuous phase would dominate the phase angle spectrum with the discrete phase only having a minor contribution, i.e., acting as a polymeric filler. In these examples the experimental results are in agreement with the major blend component being the continuous phase and the minor component a discrete dispersed phase.

In the cases of 70:30 and 60:40 NR/ENR-48 blend compositions, approximately equal loss angle peaks were observed. On a compositional basis NR would be expected to be the continuous phase and dominate the phase angle spectrum, but this was not observed. Equal blend composition, 50:50 NR/ENR-48 would tend to favour a co-continuous blend morphology. However, the DMTA results had shown that the ENR component dominates. The morphology that can be interpreted from these blends is as follows: (1) For blends of 90:10 and 80:20 NR/ENR-48, NR component is the continuous phase and ENR-48 is the discrete phase. (2) For blends of 20:80, 30:70 and 50:50
Fig. 3.8 : Effect of Mooney viscosity on mastication time for raw SMR L and ENR-48.
NR/ENR-48, the ENR component is the continuous phase and NR is the discrete phase. (3) For blends of 70:30 and 60:40 NR/ENR-48, the morphology is not as simple as the above cases.

The viscosity of the two components in a blend can be a factor in determining the morphology [88]. The component of lower viscosity tends to form the continuous phase.

A mill breakdown study of raw ENR-48 and NR (SMR-L) under the conditions used to prepare the blends reveals that ENR-48 breaks down faster than NR, as illustrated in Figure 3.8, in terms of Mooney viscosity against mastication time. The mechanism of breakdown in ENR-48 is not yet understood. However, the breakdown in ENR-48 is believed to be controlled by the gel contents of the rubber [89]. In a blend system, it is difficult to measure the viscosity of each component, but it would be expected that the degree of breakdown is greater in ENR-48 than NR. As a result, ENR-48 would have a lower viscosity than NR. This probably explains the above results, i.e., the ENR-48 component has a greater tendency to form the continuous phase.
Fig. 3.9: Dependence of loss angle on temperature at 20 Hz for a series of ENR-26/ENR-48 blends.
Table 3.11: Dynamic glass transition temperature and loss angle peak of ENR-26/ENR-48

<table>
<thead>
<tr>
<th>Blend ratios ENR-26/ENR-48</th>
<th>TD, °C</th>
<th>Loss angle peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ENR-26</td>
<td>ENR-48</td>
</tr>
<tr>
<td>100:0</td>
<td>-17.0</td>
<td>-</td>
</tr>
<tr>
<td>80:20</td>
<td>-15.0</td>
<td>*</td>
</tr>
<tr>
<td>70:30</td>
<td>-16.0</td>
<td>-7.5</td>
</tr>
<tr>
<td>60:40</td>
<td>-18.0</td>
<td>-5.0</td>
</tr>
<tr>
<td>50:50</td>
<td>-19.0</td>
<td>-5.0</td>
</tr>
<tr>
<td>40:60</td>
<td>-19.0</td>
<td>-4.5</td>
</tr>
<tr>
<td>30:70</td>
<td>-19.0</td>
<td>-3.5</td>
</tr>
<tr>
<td>0:100</td>
<td>-</td>
<td>-2.0</td>
</tr>
</tbody>
</table>

Note: * undetectable transition

Table 3.12: Effect of crosslink density of 40:60 NR/ENR-48 blends

<table>
<thead>
<tr>
<th>DCP (phr)</th>
<th>MR100(Pa) at 23°C</th>
<th>E'(Pa) at 20°C</th>
<th>Td, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NR</td>
</tr>
<tr>
<td>1</td>
<td>0.451</td>
<td>0.139x10^7</td>
<td>-46.0</td>
</tr>
<tr>
<td>2</td>
<td>0.720</td>
<td>0.151x10^7</td>
<td>-44.5</td>
</tr>
<tr>
<td>3</td>
<td>1.052</td>
<td>0.167x10^7</td>
<td>-43.5</td>
</tr>
<tr>
<td>4</td>
<td>*</td>
<td>0.195x10^7</td>
<td>-42.5</td>
</tr>
<tr>
<td>5</td>
<td>*</td>
<td>0.222x10^7</td>
<td>-41.0</td>
</tr>
</tbody>
</table>

Notes: * Samples broken

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3.4.1.2 ENR-26/ENR-48 blends

A study of blends of ENR-26 and ENR-48 were also carried out. It is expected that these blends will have a greater degree of compatibility, since the materials have closer solubility parameters and a smaller segmental interaction parameter ($X_{AB} = 0.0136$). The same procedure was adopted as with the NR/ENR-48 blend system.

Dynamic mechanical properties of a range of ENR-26/ENR-48 blends are recorded in Figure 3.9, in terms of loss angles as a function of temperature. Tds and loss angle peaks are summarised in Table 3.11. Tds of single component of ENR-26 and ENR-48 occurred at $-17^\circ$ and $-2^\circ$C respectively. At room temperature, the loss angle ($\tan \theta$) of ENR-26 and ENR-48 are 0.44 and 0.61 units respectively.

Similar characteristics were observed with these blends as with the NR/ENR-48 materials. Two loss angle peaks were observed covering the composition range 30:70 to 70:30 ENR-26/ENR-48 blends. Again, the Tds of both components were seen to have shifted to lower temperature compared to the parent materials.

In the case of the 80:20 ENR-26/ENR-48 blend a transition temperature for the ENR-48 component was not observed and, there may be a slight shift in the temperature of the ENR-26 component towards higher temperature, i.e., $2^\circ$C. This behaviour might indicates a partially compatible blend. However, there is not enough evidence to state categorically that some degree of compatibility has occurred. In the case of the 70:30 ENR-26/ENR-48 blend, a broad transition was observed but
Fig. 3.10: Dependence of loss angle on temperature at 20 Hz for a single component ENRs and blends. Solid lines are single component of ENRs and broken lines with ______ and _._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._._.
clearly composed of two components. The Td of the ENR-48 phase had shifted (5.5°C) to a lower temperature as observed with the corresponding NR/ENR-48 blend. However, the ENR-26 component had shifted (1.0°C) in the opposite direction compared with the NR/ENR-48 blend. Again, this may suggest a limited degree of compatibility, but the exact position of this Td is doubtful.

3.4.1.3 ENR-31/ENR-43 blend

A 50:50 ENR-31/ENR-43 latex blend has also been examined. This material was prepared by blending the two latices together, followed by coagulation and drying of the latex. Crosslinking was achieved as for the other blends. In this case there is only 12% difference in epoxide content, i.e., the δ difference and (X_{AB}) are 0.26 and 0.0027 respectively. A considerable degree of compatibility may thus be expected between the components. This blend was compared with a homogeneous ENR-38 which has approximately the same overall epoxide content.

The results are recorded in Figure 3.10, in terms of loss angle. A broad peak with a shoulder was observed between -13°C to -11°C and -6°C to -4°C. These transition temperatures represent the blend components. Although, these materials have a close X_{AB}, obviously they are not completely compatible.
3.4.2 Reasons to explain the temperature shift

Beside partial compatibility which has already been discussed there are a number of other reasons which can result in a shift in Td. Partial compatibility will result in a shift of Td towards each other, but in the majority of blends both component peaks shift to lower temperature and thus needs to be explained.

One possible reason is a change in crosslink density. Increasing the crosslink density of a polymer will move the Tg to a higher temperature. This will obviously effect the Td. On blending NR and ENR-48, solubility differences could resulted in uneven distribution of DCP and hence crosslink density. Thus, the crosslink density of one phase increases, while the other reduces. An increase in crosslink density would thus be reflected in the transition temperatures. A 40:60 (NR/ENR-48) blend was chosen and increasing levels of DCP added to increase the crosslink density. The results in terms of MR100 (relaxation modulus at 100% extension) and storage modulus, as well as Td are summarised in Table 3.12. With increased DCP in the blends, the overall modulus increases proportionately. However, these results only relate to the overall blend and not to the crosslink density within the components. More meaningful data is obtained by examining the shifts in the transitions. The addition of 5 phr DCP to the blend has yielded a 5°C shift in the Td of the NR component, while the ENR-48 component shift was only 1°C. It was found that the Td of both components had shifted to a higher temperature with increased DCP. This observation is inconsistent with the observed shift in
Table 3.13: Effect of plastisizers on NR and ENR-48 vulcanizates

<table>
<thead>
<tr>
<th>Materials</th>
<th>Td, °C NR</th>
<th>loss angle peaks NR</th>
<th>ENR-48 NR</th>
<th>ENR-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-39.5</td>
<td>2.50</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>LNR</td>
<td>-39.0</td>
<td>2.42</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>LENR-50</td>
<td>-39.5</td>
<td>2.49</td>
<td>2.31</td>
<td></td>
</tr>
</tbody>
</table>
the component Tds. Even if arguments are put forward on an uneven distribution of curatives and differing efficiencies of crosslinking in the two components, a valid argument cannot be put forward to explain the observed phenomenon.

A second possible reason for the observed Td shifts could be due to the effect of a plasticizer. The presence of a plasticizer would move the position of a glass transition to lower temperature. Although it is difficult to visualize the formation of a plasticizer during blending, it is possible that one of the blend components degrades during mastication to produce a low molecular weight fraction which could plasticize both blend components. A study has been carried out on the effect of 5 phr of low molecular weight natural rubber (LNR) and epoxidised natural rubber (LENR-50) on NR and ENR-48 rubber vulcanizates. Both materials were readily available at MRPRA. The molecular weights (Mn) of both materials were 10,000. The compounds were vulcanized with 1.5 phr DCP. The Td results are shown in Table 3.13. It seems that the low molecular weight materials added have no effect on the Td of the NR component, but has shifted the Td of the ENR-48 component by 1.5°C. The overall effect was very small with respect to the amount of plasticizer added.

A more realistic explanation for the shift in dynamic glass transition temperatures can be envisaged in terms of a mechanical model. The viscoelastic form of the Kerner equation [69], employing a discrete and continuous phases system has been studied. This appears to be a realistic explanation of the observed shifts and will be discussed in section 3.5.

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However, a more quantitative interpretation of the morphology can be obtained from optical microscopy, which will be discussed in section 3.6.
Fig. 3.11: The isotherms of dicumyl peroxide NR gum vulcanizate plotted in terms of (a) storage modulus and (b) loss angle, as a function of frequency from 0.3 to 50 Hz run at a number of temperatures.
Fig. 3.12: The isotherms of dicumyl peroxide ENR-48 gum vulcanizate plotted in terms of (a) storage modulus and (b) loss angle, as a function of frequency from 0.3 to 50 Hz run at a number of temperatures.
Fig. 3.13: The isotherms of dicumyl peroxide 50:50 NR/ENR-48 gum blend vulcanizate plotted in terms of (a) storage modulus and (b) loss angle, as a function of frequency from 0.3 to 50 Hz run at a number of temperatures.

(132)/(133)
3.4.3 Isothermal measurement

The hysteresis data reported on ENRs and NR/ENR blends has been obtained at one frequency. However, in practice polymer based vibration isolation devices are required to operate over a range of frequencies, thus a knowledge of the frequency response of materials is necessary.

The frequency dependence of the dynamic properties of a gum NR vulcanizate over a range of temperatures is illustrated in Figures 3.11 (a) and (b), in terms of storage modulus ($E'$) and loss angle ($\tan \delta$) respectively. As can be seen from both curves, the transition occurred at $-50^\circ$C, with maximum hysteresis at 0.3 Hz. This transition is designated as the dynamic transition frequency ($T_f$). At low temperature the storage modulus was shown to be independent of frequency, when the rubber displays a glassy behaviour, but the storage modulus shows a sharp decrease with frequency through the transition region.

Figures 3.12 (a) and (b) respectively illustrate storage moduli and loss angle data for a gum ENR-48 vulcanizate. From the figures, a similar plot can be seen with that of NR. However, the transition is shifted and now occurs at $-5^\circ$C with a maximum hysteresis at 5 Hz.

For the 50:50 (NR/ENR-48) rubber blend, two transition regions were observed, i.e., each component of the incompatible blend exhibits its own hysteresis characteristics. These are illustrated in Figures 3.13 (a) and (b). The first region (A), corresponds to the NR phase, with maximum hysteresis occurring at $T_f$ of 1 Hz.
Fig. 3.14: Shift factors of dicumyl peroxide of NR and ENR-48 gum vulcanizates, calculated using the reference temperature of $T_s = T_g + 50^\circ C$. 
and -50°C. While the second region (B) corresponds to the ENR-48 phase with maximum hysteresis at 3Hz and -10°C.

Since the DMTA analyser is limited to 3 decades of frequency, the WLF (Williams, Landel and Ferry) transformation was used to obtain a better picture for a wide range of frequency. The WLF equation is given by [87]:

\[ \log a_T = -8.86(T - T_s)/(101.6 + T - T_s) \]

where \( a_T \) is a shift factor, \( T \) is the measurement temperature and \( T_s \) is the reference temperature. The equation holds for a wide range of polymers when \( T_s \) is taken to be 50° above the glass transition temperature \( (T_g) \). The \( T_g \)s of NR and ENR-48 are -72° and -27°C respectively, determined from DSC.

The shift factor of the WLF equation for both NR and ENR-48 rubbers is shown in Figure 3.14. As can be seen from the figure, the shift factor for both rubbers fits quite well along the master curve. Therefore, with the use of the WLF transformation, it is possible to demonstrate the dynamic properties of polymers over a wide range of frequency, which is much wider than can be obtained by experiment.

The next procedure in obtaining the master curve is to multiply all the storage moduli and \( \tan \theta \) data by a ratio of \( T_s/T \). The reason, according to a number of workers [90-92] is to make allowance for the change of these properties with temperature, since according to the statistical theory of rubber elasticity, modulus is proportional to temperature. It was determined that, if

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Fig. 3.15: The WLF transformation of dicumyl peroxide NR gum vulcanize plotted in terms of reduced modulus and loss angle, as a function of frequency.
Fig. 3.16: The WLF transformation of dicumyl peroxide ENR-48 gum vulcanize plotted in term of reduced modulus and loss angle, as a function of frequency.
no allowances were made, a smooth master curve cannot be obtained. The other procedure is to multiply the frequency by the shift factor to give the x-axis of the master curve. The process has been clearly described by Payne [93] and William, Landel and Ferry [87]. The computations of the data and the plots were done using the Prime minicomputer at MRPRA.

Using the experimental data obtained in Figure 3.11, the WLF transformation of NR in terms of reduced modulus and tan $\theta$ is shown in Figure 3.15. All the data seem to fit quite well along the WLF master curve. It can be categorised into 3 regions. Firstly, the plateau region at high frequency, which corresponds to the glassy behaviour of the rubber and is independent of frequency. Secondly, the central region which corresponds to the transition state. In this region, maximum damping occurs while the modulus is shown to drop very rapidly over 2 decades of frequency. Finally, the low frequency region, in which both modulus and damping are low and which corresponds to rubbery behaviour.

The WLF master curve for ENR-48 rubber is shown in Figure 3.16. A similar pattern was observed with that of NR. In the NR plot the scatter of the results at very low frequency is probably caused by the "toggle effect". This problem is often encountered in the double cantilever test arrangement. Thermal expansion causes the rubber bar to slacken between the grips. The problem can be eliminated by either applying a small tension to the sample when mounting it in the clamps, so that on raising the temperature the expansion no more than

(139)
compensates for the initial elastic strain or by retightening the sample in the glassy state.

It was observed from the master curve plots that the maximum damping of NR and ENR-48 was $10^3$ and $10^{4.5}$ Hz respectively. The difference of 1.5 decades of frequency relates the differences in the glass transition temperature.

A WLF transformation of NR/ENR-48 rubber blend is not possible due to the difficulty in defining a reference temperature.
3.5 Morphological studies: Theoretical consideration

Information can be deduced from the moduli and loss angle curves about the morphology and composition of the blends. For simple two phase systems, the morphology can be divided into 3 categories: (1) phase (A) may form discrete particles dispersed in a continuous phase (B), (2) vice versa and (3) a co-continuous phase, as illustrated in Figure 1.12. A continuous phase will contribute much more to a loss angle peak than a discrete phase, while a co-continuous phase at equal concentrations will exhibit equal contributions. These are well illustrated for the NR/ENR-48 blends shown in Figure 3.7.

It is possible to predict the dynamic response of a simple two-phase blend systems, with the use of a model proposed by Kerner [69]. This equation has been applied to the NR/ENR blends under study to compare the experimentally observed results with theoretical predictions. It is of particular interest to use Kerner's equation to predict any shifts in glass transition temperature. The derivation of the equation has been discussed in detail in section 1.6.1. In the use of Kerner's equation, two types of dispersed discrete phase are considered. Firstly, it is assumed that NR is the discrete phase and ENR-48 is the continuous phase. Secondly, it is assumed ENR-48 is the discrete phase and NR is the continuous phase. The Poisson's ratio of the two materials is assumed equal to 0.5. The volume fraction ($\Phi$) of each component is assumed to be volumetrically additive.
Fig. 3.17: Variation of storage modulus of 20:80 NR/ENR-48 blend vulcanizate with temperatures. Solid line is represented an experimental data. Broken line is calculated using Kerner's equation by assuming NR is the discrete phase and ENR-48 is the continuous phase ($\phi = 0.2$).
Fig. 3.18: Variation of loss angle of 20:80 NR/ENR-28 blend vulcanizate with temperatures. See Figure 3.17 for notations.
Fig. 3.19: Variation of storage modulus of 50:50 NR/ENR-48 blend vulcanizate with temperatures. Solid line is represented an experimental data. Broken line is calculated using Kerner's equation by assuming NR is the discrete phase and ENR-48 is the continuous phase (φ = 0.5).
Fig. 3.20 : Variation of loss angle of 50:50 NR/ENR-48 blend vulcanizate with temperatures. See Figure 3.19 for notations.
Fig. 3.21: Variation of storage modulus of 80:20 NR/ENR-48 blend vulcanizate with temperatures. Solid line is represented an experimental data. Broken line is calculated using Kerner's equation by assuming ENR-48 is the discrete phase and NR is the continuous phase ($\phi = 0.2$).
Fig. 3.22: Variation of loss angle of 80:20 NR/ENR-48 blend vulcanizate with temperatures. See Figure 3.21 for notations.
The storage moduli (log E') and loss angle (tan θ) data for 20:80 NR/ENR-48 are shown in Figures 3.17 and 3.18 respectively. Both calculated and experimental values are plotted. The former is depicted as the broken line and the latter is presented as the solid line. For this calculation it is assumed that NR is the dispersed discrete phase composed of spherical particles in a ENR-48 continuous phase. The volume fraction of NR was assumed to be 0.2. From these figures good agreement was observed between the two sets of data. This indicates that Kerner's theory is a good model for this blend composition and supports the morphology assigned to this blend system, i.e., NR is the dispersed discrete phase embedded in a ENR-48 continuous phase.

Figures 3.19 and 3.20 respectively show the plots of storage moduli and loss angle for a sample with a blend ratio of 50:50 NR/ENR-48. NR was assumed as a dispersed discrete phase, with a volume fraction of 0.5. As can be seen from the figures plotted, it is clear that the experimental and theoretical data do not agree. This is not too surprising and will be discussed later.

Figure 3.7 indicates that a phase inversion occurred for the sample with a blend ratio of 80:20 (NR/ENR-48). In this case, NR forms a continuous phase and ENR-48 is the discrete phase. In order to model this behaviour, the second type of inclusion is considered in the calculation. It was calculated by assuming ENR-48 is the discrete phase and NR is the continuous phase. The volume fraction was again assumed to be 0.2. The results are demonstrated in Figures 3.21 and 3.22, in terms of storage moduli and loss angle respectively. Although in
the case of the reverse blend good agreement was observed with the experimental data, the agreement was not as good with the 20:80 NR/ENR-48 blend.

Dynamic mechanical data of NR/ENR-48 blends can be used to model the morphology and the blend composition using Kerner's equation. From the above analysis, it was found that Kerner's equation can predict dynamic behaviour when the volume fraction of the dispersed discrete phase is 0.2. The model deviates from the Kerner's theory when the volume fraction of inclusion is greater than 0.2. This is in agreement with the results demonstrated by Dickie [70] and Takayanagi [68]. Therefore, the model calculations on the values of $E^*$ are very dependent on the volume fraction and morphology of the dispersed discrete phase.

The limitations of the theory are the assumptions made in its derivation, i.e., a spherical discrete phase. Thus, the theory cannot be used to predict the mechanical behaviour of a co-continuous phase system. In this case, Kerner's decoupled packed grain equation [94] would have to be used. However, no attempt has been made using this equation because of the limitation of the time period of this project.

It is of interest that Kerner's theory predicts a shift in dynamic glass transition temperature. If NR is the discrete phase and ENR-48 is the continuous phase, then the theory states that the dynamic glass transition temperatures of both components will shift towards lower temperatures, which is in agreement with the experimental data. But, if the reverse case were considered in the calculation, i.e., ENR-48 is the dispersed discrete phase and NR is the continuous phase,
then the dynamic glass transition temperatures will shift towards higher temperature [70]. This transition shift has been ascribed to the expansion mismatch caused by the heating/cooling effect for blends containing two phase systems. Alternatively Bohr [95] and Turley [96], have related the shift in temperature to low interfacial adhesion between the two phases.
Fig. 3.23: The plot of refractive index versus per cent epoxide groups, determined using Abbe refractometer
3.6 Phase contrast microscopy

The microscopy of polymer blends has been studied extensively by many workers [30-33]. The most versatile method of elucidating the morphology of polymer blends is light phase contrast microscopy. The method is particularly suitable for gum blend systems. For a filled blend system, TEM is the most suitable and frequently used. There are many variables that affect the morphology, as well as the mechanical properties of polymer blends [88]. However, the work undertaken here is confined to the effect on a particular blend ratio.

It has been mentioned in section 1.5.4, that in order to achieve a good contrast between the blend components, it is necessary to section the sample to a required thickness. The required thickness can be obtained using the relationship given below [97]:

\[ t = \frac{t_o}{(n_1 - n_2)} \]

where \( t \) is the actual physical thickness of the section; \( t_o \) is the optical thickness equal to 3 \( \mu \text{m} \); \( n_1 \) and \( n_2 \) are the refractive indices of the rubbers. The refractive index of the rubber can be determined using an Abbe refractometer. Figure 3.23 shows the plot of refractive index against mole percent epoxide groups. For example, refractive indices of NR and ENR-48 are 1.525 and 1.513 respectively. The required thickness of the blend between NR and ENR-48 was calculated to be 0.25 \( \mu \text{m} \). Therefore, the two phases can only be resolved if the thickness of the section is greater than this value.

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Fig. 3.24: Phase contrast micrographs of dicumyl peroxide; (A) NR and (K) ENR-48 gum vulcanizate. (X1000 magnification)
Fig. 3.25: Phase contrast micrographs for a series of dicumyl peroxide NR/ENR-48 blend vulcanizates. Dark and light areas are represented by the NR and ENR-48 phase respectively. (X1000 magnification)
Phase contrast micrographs of a dicumyl peroxide gum NR (micrograph A) and ENR-48 (micrograph K) rubber vulcanizates are illustrated in Figure 3.24. The appearance of the dark spots in the micrograph of the NR sample is due to dirt contamination. The NR micrograph was observed to be darker than that of ENR-48. This is due to the difference in refractive index of the rubbers.

The incompatibility of the two components in the NR/ENR-48 blend system is distinctly distinguished. This is clearly illustrated by micrographs in Figure 3.25. For blend consisting of 90:10 NR/ENR-48 (micrograph B), i.e., 10% ENR-48 in the blend, homogeneous spherical regions of ENR-48 dispersed in a NR continuous phase were observed. A similar morphology, i.e., ENR-48 dispersed in a continuous phase was observed for the 80:20 and 70:30 NR/ENR-48 blends (see micrographs C and D respectively). The discrete phase size increases, and in the 70:30 blend the tendency to form thread like domains is indicative of a more towards a co-continuous phase. For the 60:40 NR/ENR-48 blend (micrograph E), i.e., 40% ENR-48 in the blend, the discrete phase of ENR-48 is not apparent. This evidence would tend to suggest that the morphology of this type of blend is a co-continuous. At equal blend composition (micrograph F), ENR-48 component is clearly shown to dominate and form the continuous phase. In this blend, the NR phase exhibits a "mesh-like" appearance. In micrographs H and I, the spherical darker spots are the NR phase dispersed homogeneously in the lighter ENR-48 phase.

The morphology of a 50:50 ENR-26/ENR-48 blend vulcanizate was also examined using phase contrast
Fig. 3.26: Phase contrast micrograph of dicumyl peroxide of 50:50 ENR-26/ENR-48 gum blend vulcanizate. (X1000 magnification)
microscopy. The micrograph is shown in Figure 3.26. The morphology of this blend system is difficult to distinguish because of the difference in refractive index being too small to obtain a good micrograph.
Table 3.14: Unaged tensile properties of peroxide gum vulcanizates

<table>
<thead>
<tr>
<th>Blend ratios NR/ENR-48</th>
<th>M100</th>
<th>M300</th>
<th>TS</th>
<th>EB</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>0.67</td>
<td>1.66</td>
<td>13.1</td>
<td>608</td>
</tr>
<tr>
<td>90:10</td>
<td>0.63</td>
<td>1.52</td>
<td>12.2</td>
<td>591</td>
</tr>
<tr>
<td>80:20</td>
<td>0.69</td>
<td>1.77</td>
<td>9.88</td>
<td>540</td>
</tr>
<tr>
<td>70:30</td>
<td>0.64</td>
<td>1.57</td>
<td>8.76</td>
<td>562</td>
</tr>
<tr>
<td>60:40</td>
<td>0.61</td>
<td>1.44</td>
<td>7.85</td>
<td>549</td>
</tr>
<tr>
<td>50:50</td>
<td>0.61</td>
<td>1.36</td>
<td>7.84</td>
<td>569</td>
</tr>
<tr>
<td>40:60</td>
<td>0.60</td>
<td>1.41</td>
<td>7.01</td>
<td>549</td>
</tr>
<tr>
<td>30:70</td>
<td>0.57</td>
<td>1.29</td>
<td>6.61</td>
<td>558</td>
</tr>
<tr>
<td>20:80</td>
<td>0.52</td>
<td>1.13</td>
<td>6.10</td>
<td>589</td>
</tr>
<tr>
<td>10:90</td>
<td>0.54</td>
<td>1.16</td>
<td>5.70</td>
<td>642</td>
</tr>
<tr>
<td>0:100</td>
<td>0.52</td>
<td>1.06</td>
<td>4.23</td>
<td>594</td>
</tr>
</tbody>
</table>

Notes:
M100 = modulus at 100% elongation
TS = tensile strength
EB = elongation at break
Fig. 3.27: The plot of tensile strength against percent ENR-48 component in the blends.
3.7 Physical properties of NR/ENR-48 blends

From a practical point of view, blends are studied to obtain materials with properties that cannot be obtained from any single polymer. The physical properties of the blends were therefore evaluated.

3.7.1 Tensile properties

Tensile properties of dicumyl peroxide gum blend vulcanizates are given in Table 3.14. Tensile strength and moduli of an ENR-48 rubber were observed to be lower than those of NR. The reason is possibly due to the effect of the degree of crosslink density of the rubber network. In peroxide crosslinking system, it would be expected that the efficiency of crosslink density is lower in an ENR-48 than NR. This is probably due to the double bonds of unsaturated NR molecules having been replaced by 48% epoxide groups. This is reflected in the results shown in Table 3.3, i.e., $C_i$ which measures the degree of crosslinking decreases with the increase in epoxide groups.

An attempt was made to relate tensile properties with the morphology of the rubber blends. Figure 3.27 records tensile strength against percent ENR-48 in the blends. From this figure, tensile strength is observed to decrease rapidly in the range 0 to 20% ENR-48 blend composition. In this blend compositions, tensile properties are predominantly determined by the NR phase. A further gradual and steady drop in tensile strength occurs in the range 30 to 80% ENR-48 component in the blends. In this range, it is difficult to explain the
tensile properties on morphological grounds. However, tensile strength again shows a rapid drop at above 80% ENR-48 in the blends.

In general, it is difficult to relate tensile strength to the phase morphology. Other factors besides simple morphology possibly contribute to the strength properties. The distribution of crosslink density between the two phases will be a determining factor. ENR phase has a higher solubility parameter than the NR phase and hence the curative distribution of crosslink density between the two phases will be determined by the relative solubility parameter. The size of the dispersed discrete phase will influence interfacial adhesion and hence influence strength properties.
A typical plot of tearing force against displacement of NR/ENR-48 blend vulcanizate.
Fig. 3.29: The plot of stress versus strain for a series of NR/ENR-48 blend vulcanizates.
3.7.2 Tearing energy

An attempt to relate tear properties to the morphological structure of the blends has been made in this thesis. This is interesting to see how the rather complex tear phenomenon is related to other properties.

In the study of the tearing energy of rubber blends, trouser test pieces were used. The results are related to the fundamental behaviour of the rubber with the rate of tear propagation being related to the rate of grip separation [98]. Figure 3.28 illustrates a typical plot of tearing force against displacement for NR/ENR-48 blends. The tearing force fluctuates in a sequence from slow increase to a maximum and rapidly decrease to a minimum with time. This phenomenon is termed "stick-slip" tearing [99]. Stick-slip tearing was observed for all ranges of samples used here. The average tearing force (Fm) values were taken in the steady-state region between point (a) and (b) of five test pieces (see Figure 3.28). Tearing energy was calculated by adopting eqn. 2.14, taking into account a small strain in the legs of the trouser test piece. The stress, \( \sigma \), in the legs of the trouser test piece is given by,

\[
\sigma = \frac{2F_m}{dw}
\]

where \( d \) and \( w \) are thickness and width of the test piece respectively. Thus, by knowing the stress in the legs of the trouser test piece, the extension ratio, \( \lambda \), can be separately determined from the stress-strain curve, as shown in Figure 3.29.
Tearing energy, KJ m$^{-2}$

Fig. 3.30: The plot of tearing energy against percent ENR-48 component in the blends.
Fig. 3.31: Photograph showing tear failure of dicumyl peroxide NR/ENR-48 gum blend vulcanizates. Single component of NR and ENR-48 are represented by (A) and (K) respectively. (B) through (J) are samples with increasing ENR-48 component in the blends. (See Fig. 3.25 for notations).
Figure 3.30 records the tearing energy of NR/ENR-48 blends as a function of ENR-48 compositions. The results are analogous with tensile strength discussed earlier. Figure 3.31 shows the tear behaviour of rubber blends. In general, it was observed that tearing energy can be divided into three regions.

For samples in a range consisting 0 to 20% ENR-48 in the blends, a sharp drop of tearing energy was observed. Between 20 to 60% ENR-48 in the blends, tearing energy was observed to remain steady at 6 KJm⁻². Above 60% ENR-48 in the blends, tearing energy was again observed to decrease gradually.

The observed results may be related to the interfacial adhesion between the two phases. Between 0 to 20% ENR-48 in the blends, the morphology is expected to consist of NR in the dominant phase and ENR-48 in the discrete phase. A small volume of discrete phase in the blend may caused some interfacial interactions between the two phases. Hence, it creates weak points for crack initiation during tearing, resulting in a low tearing energy.

Between 60 to 100% ENR-48 in the blends, the morphology would be expected to reverse, i.e., ENR-48 is the continuous phase and NR is the discrete phase. A gradual drop in tearing energy is due to the characteristics of ENR-48, which has low tearing energy.

In the middle region between 20 to 60% ENR-48 in the blends, the morphology is represented by co-continuous phases and this results in a steady tearing energy.
Fig. 3.32: A typical diagramme showing the Rebound Resilience displacement of the Dunlop tripsometer.
3.7.3 Rebound resilience

The measurement of rebound resilience is widely used in rubber industry for quality control purposes. The apparatus is simple and inexpensive. Rebound resilience is a dynamic measurement, in which the test piece is subjected to half-cycle deformation. It is defined as the ratio of the energy of the indentor after impact to its energy before impact expressed as percentage. Resilience is an inverse measure of hysteresis, i.e., ratio of energy dissipated to energy stored.

A schematic diagram showing the displacement is recorded in Figure 3.32. It can be shown that,

\[ AB = h \cos \theta_r \]
\[ hr = AC - AB \]
\[ = h - h \cos \theta_r \]

\[ AE = h \cos \theta_f \]
\[ hf = AC - AE \]
\[ = h - h \cos \theta_f \]

Since the ratio of energy input and energy returned is proportional to the fall height and the rebound height, then rebound resilience is given by,

\[ R.\text{Resilience} = \frac{(h-h \cos \theta_r)}{(h-h \cos \theta_f)} \]
\[ = \frac{(1-\cos \theta_r)}{(1-\cos \theta_f)} \]

where \( \theta_f \) is fixed at 45° and therefore \((1-\cos \theta_f)\) is constant. The angle \( \theta_r \) is measured by means of a
Fig. 3.33: The plot of Rebound Resilience versus percent ENR-48 component in the blends, measured at 23°C and 75°C.
graduated scale which is converted into percentage rebound resilience.

Figure 3.33 shows the results of rebound resilience of NR/ENR-48 blends as a function of ENR-48 compositions, measured at 23° and 75°C. Rebound resilience of NR is observed to be much higher than ENR-48. This is in line with the known glass transition temperatures of the two materials. From the plotted figure, it is shown that rebound resilience decreases with the increase in percent ENR-48 in the blends. The reduction is much steeper when measurement was made at 23° than 75°C.

The straight line plot shown suggests that the test results cannot be related to the morphological properties of the blends, as determined from DMTA. In Dunlop resilience test, the frequency of the measurement is approximately 10 Hz, while in DMTA is 20 Hz. Also, the test temperature measured using Dunlop resilience was much higher than DMTA, i.e., 23° and 75°C, which is in the rubbery region and hence does not reflect changes in loss angles due to morphological differences.
Fig. 3.34: Pressure change for a series of NR/ENR-48 blend vulcanizates as a function of times. Single component of NR and ENR-48 are represented by (A) and (K) respectively. (B) through (I) are samples with increasing ENR-48 component in the blends. See Fig. 3.25 for notations.
Fig. 3.35 (a) : The plot of air permeability against percent ENR-48 component in the blends, measured at 23°C.
3.7.4 Air permeability

Air permeability is an important polymer property in a number of applications, e.g., inner tubes, tyre inner liners. The mechanism of air permeability involves the movement of small molecules through the polymer and hence will relate to polymer molecular motion. Thus, it should relate to glass transition phenomenon. Practically, air permeability is measured by the difference in pressure or concentration between opposite faces of a polymer membrane. In other words, the air molecule flow from high pressure/concentration to low pressure/concentration is monitored.

A study of the air permeability of NR/ENR-48 blends has been made. Measurement was based on the principle first used by Graham in 1866 [77], i.e., a constant volume method and measuring the pressure change manometrically [100].

Figure 3.34 illustrates the pressure change with time of NR and ENR-48 rubbers and the blend compositions of NR/ENR-48. As can be seen from the slopes, that of NR is greater than that of ENR-48. The rate decreases with increased % ENR-48 compositions in the blends. The inference is that the rate of diffusion through NR is much faster than through ENR-48 membranes.

Figure 3.35(a) shows the plot of air permeability against ENR-48 in the blends. As expected, ENR-48 has a lower air permeability than NR, which is consistent with the results shown earlier. The main factor which affects the permeability is the molecular structure of the rubber. It is known that ENR-48 has a higher Tg in NR. This is due to the presence of epoxide groups along the
Fig. 3.35 (b) : The predicted morphological behaviour of NR/ENR-48 blends on air permeability.
main chain, which restrict molecular mobility, and thus impede the movement of air molecules through the rubber membrane. In silicon rubber ($\sim$Si-O-Si$\sim$), the molecular structure confers very high internal mobility, and hence, results in high air permeability. The air permeability of silicone rubber is ten to twenty times higher than NR [101].

The air permeability curve of Figure (3.35(a)) can be described to consist of three straight lines, see Figure 3.35(b). These lines can be related to the morphology of the blends.

Between 0 to 20% ENR-48 in the blends, NR constitutes the continuous phase, i.e., there is a continuous NR pathway through the rubber and thus air permeability is high. At 50% ENR-48 and beyond, ENR-48 is the continuous phase and thus air permeability is low. Between the two cases, a co-continuous structure is believed to be present.

Air permeability properties in these blends are determined to a large extent by the phase morphology.
3.8 Interproperty and morphology relationships

It has been demonstrated in the previous sections that, the physical properties and the morphology of rubber-rubber blend can be interrelated. Experimental data has been obtained by dynamic mechanical analysis, optical phase contrast microscopy, air permeability, tear and tensile strength measurements. This section is devoted to a discussion of the interrelationship between the morphology and properties of dicumyl peroxide NR/ENR-48 gum vulcanizates. The most useful technique to characterize morphology is phase contrast microscopy which can determine the size and shape of the phases.

From dynamic mechanical analysis data, the loss angle peaks can be utilized to distinguish the morphology of blend compositions of NR/ENR-48 blends, see Figure 3.7. For blend compositions in the range 90:10 and 80:20 NR/ENR-48 systems, the contribution of loss angle peaks of NR is much higher than ENR-48 component. The morphology of this type of behaviour can be interpreted as: NR is the continuous phase and ENR-48 is the discrete phase. This is to be expected as NR is the major component.

With the 50:50, 30:70 and 20:80 NR/ENR-48 blends, the loss angle peak is reversed, i.e., the NR peak is much smaller than that of ENR-48. In this compositional range, the morphology can be regarded as NR is as the discrete phase and ENR-48 is the continuous phase.

In the intermediate compositional range, i.e., 70:30 and 60:40 NR/ENR-48 blend systems, almost equal contribution of loss angle peaks are observed. This is due to a co-continuous phase between the two components.
The recognition of the above morphology can be best described using phase contrast microscopy. For blend compositions in the range 90:10 and 80:20 NR/ENR-48 systems, small spherical lighter images were observed embedded in a darker continuous lighter region, see micrographs B and C of Figure 3.25. The size of the spherical regions increased in micrograph C. The spherical discrete phase is due to the ENR-48 component, which is homogeneously dispersed in a NR continuous phase.

With the 30:70 and 20:80 NR/ENR-48 blend systems, the morphology is reversed when compared with the previous results, see micrographs H and I of Figure 3.25. The spherical darker regions, NR, were observed dispersed in the continuous lighter region. The size of the spheres decreases with increasing ENR-48 component in the blends. In this case, NR is the discrete phase and ENR-48 is the continuous phase. Microscopy studies show that the morphology is very consistent with the loss angle peak data.

In the case of 70:30 NR/ENR-48 blend composition, short and long thread like areas were observed, see micrograph D. These are the ENR-48 component. The morphology of this blend is more towards the formation of co-continuous phases. The contribution of the major component (NR phase) is greater than that of the ENR-48 component, which is consistent with the dynamic loss angle peak. In the 60:40 NR/ENR-48 system, a co-continuous phase is apparent, see micrograph E. At an equal blend composition, i.e., 50:50 NR/ENR-48, see micrograph F, the lighter region of ENR-48 dominates and forms the continuous phase.
The air permeability properties of these NR/ENR-48 blends must be viewed in terms of their morphology. The air permeability curve shown in Figure 3.35(a) can be interpreted into three straight lines, which consists of three different zones, see Figure 3.35(b). These lines can be related to the morphology of the blends, as shown in a schematic diagram on the plot. For blend composition in the range 90:10 and 80:20 NR/ENR-48 systems, a drop in air permeability with increased ENR-48 component in the blend was observed, see Figure 3.35(b). NR is the continuous phase. The effect is due to the volume fraction (Vr) of the ENR-48 component in the blend. With increase Vr of ENR-48 in the blend, the tortuosity of the pathway through the continuous phase has decreases, and hence, result in a lower air permeability compared with the pure component. The morphology as determined from the dynamic loss angle data and microscopy studies has greatly shown that, in the first zone, NR is a continuous phase and ENR-48 is a discrete phase.

For blend compositions containing 50:50 NR/ENR-48 and beyond, there is a little change in air permeability. This is called second zone. A reversal effect to that of first zone was observed, i.e., NR is a discrete phase and ENR-48 is a continuous phase. The morphology as revealed from dynamic loss angle data and microscopy has suggested that, in this zone, NR is a discrete phase and ENR-48 is a continuous phase.

In the intermediate zone, i.e., 70:30 and 60:40 NR/ENR-48 component in the blends, a gradual and steady drop of air permeability was observed. Both NR and ENR-48 components in the blends formed the continuous phase.

(179)
i.e., a co-continuous phase structure is believed to be present, as shown in a schematic diagram in the figure. The morphology with regard to dynamic loss angle data and microscopy has confirmed that, in this zone a co-continuous phase exist. A phase inversion occurred for blend composition of 70:30 NR/ENR-48 blend, as revealed from dynamic loss angle and microscopy studies.

The previously described morphology can be used to try to interpret the tearing energies of the blend systems. In addition, the curative distribution between the two phases must be considered. The distribution of the curative, dicumyl peroxide, between the two phases will determined by the solubility parameters of the two phases. Tearing energy results, shown in Figure 3.30 can again be divided into three different regions. In the first region, i.e., 90:10 and 80:20 NR/ENR-48 blend systems, a sharp drop of tearing energy was observed. The tear behaviour is predominantly determined by the dominant phase, i.e., NR is the continuous phase and ENR-48 is the discrete phase. Interfacial adhesion between the two phases is an important factor. A small volume of a discrete phase may determine the path that a growing crack takes in a deformed rubber blend. It can also determine the extent to which stresses can be transferred between the continuous and the discrete phases.

In the 40:60 NR/ENR-48 blend and beyond, a gradual drops of tearing energy was observed. In this region, the morphology is reversed and ENR-48 dominates to become the continuous phase. However, tearing energy decreases with increased ENR-48 component in the blend.
This is due to the characteristic of ENR-48 which has lower tearing energy than NR.

In the intermediate region between 70:30, 60:40 and 50:50 NR/ENR-48 blend systems, a constant tearing energy was observed. In this region co-continuous phases are present.

In general, the morphology of the blends is interrelated with other properties. Tensile strength of the blends shows a similar trend to the tearing energies, but the trend is not as clear with other properties.
The blends studied were NR/ENR-48, ENR-26/ENR-48 and ENR-31/ENR-43. These rubbers were expected to differ substantially in solubility parameter \( \phi \), and hence, in their degree of compatibility. The compatibility between different phases of these polymer blends would be affected by the epoxide levels. The smaller the difference in epoxide level the greater potential for true compatibility between phases. At ambient temperatures ENR-48 is a high damping rubber and the degree of compatibility will determine the damping of the blend. Various techniques have been employed to investigate the blend properties.

As a first step to determine the degree of compatibility the solubility parameter of individual rubbers was measured. It was found that solubility parameters increased linearly with increasing epoxide levels. A good agreement was obtained from swelling measurements and Small's calculation method.

Solubility parameter data were used to predict the Flory-Huggins segmental interaction parameter \( X_{AB} \) of the blends. It was shown that \( X_{AB} \) of NR and ENR increased with increasing epoxide levels, indicating that the larger the difference in epoxide level the less likelyhood of blend compatibility.

Since the value of \( X \) cannot be taken as a sole indicator of blend compatibility, other specific interactions could be involved, a glass transition study was carried out. The techniques employed were DSC and
DMTA. Over a range of compositions the blends exhibited the glass transitions associated with the individual components. The only exceptions were believed to be due to lack of instrument sensitivity.

The loss angle of a rubber obtained from dynamic tests can be related to its glass transition. The loss angle data obtained from DMTA substantiated the DSC results, i.e. the components of these blends are incompatible.

Although the blends were incompatible the loss angle peaks of the components showed shifts to lower temperatures as measured by DMTA. Loss angle peak movement towards each other in a blend can indicate partial compatibility. Plasticization or changes in the crosslink density can be postulated as causes of the shifts to lower temperatures but neither of these reasons were substantiated.

The theory developed by Kerner to describe hysteresis properties of blends was examined. Measurements made from the small strain dynamic mechanical properties of the pure NR and ENR materials were used to calculate the blend properties. Shifts in the loss angle peaks were predicted that agreed with observation, i.e. movement to lower temperatures. However, an exact fit was only obtained when the composition of the blends were such that the morphology agreed with assumptions made by Kerner, i.e. a discrete spherical phase embedded in a continuous phase.

The morphology of rubber blends can be ascertained from the size of the dynamic loss angle peaks. The major loss angle peak is associated with the continuous phase and the minor with the discrete phase. In the case of a
co-continuous morphology equal loss angle contributions are observed. NR/ENR-48 blends were studied over the full composition range. At high NR concentrations this polymer formed the continuous phase. The morphology passed through a co-continuous phase and at high ENR-48 concentration the ENR formed the continuous phase. The ENR-48 had a greater tendency to form the continuous phase due to its lower viscosity.

Phase contrast microscopy substantiated these morphological conclusions.

A similar pattern was observed with the ENR-26/ENR-48 blends, i.e. the dynamic transition peaks of both components in the 30:70 to 60:40 blends moved to lower temperatures relative to the parent materials. With the 80:20 and 70:30 ENR-26/ENR-48 blends a slight shift of the ENR-26 loss angle peak to higher temperatures was observed. This could be interpreted as a limited degree of partial compatibility, but the evidence is slender. It was not possible to study the morphology of this system by phase contrast microscopy because the difference in refractive index of the two components was not great enough.

A single ENR-31/ENR-43 (50:50) blend was also examined in comparison to a homogeneous ENR-38. Due to the closeness in the transitions temperatures interpretation was difficult but it can be categorically stated that the components were not completely compatible.

The morphology of rubber blends is a major factor in determining their properties. A number of blend properties have been studied.
co-continuous morphology equal loss angle contributions are observed. NR/ENR-48 blends were studied over the full composition range. At high NR concentrations this polymer formed the continuous phase. The morphology passed through a co-continuous phase and at high ENR-48 concentration the ENR formed the continuous phase. The ENR-48 had a greater tendency to form the continuous phase due to its lower viscosity.

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A single ENR-31/ENR-43 (50:50) blend was also examined in comparison to a homogeneous ENR-38. Due to the closeness in the transitions temperatures interpretation was difficult but it can be categorically stated that the components were not completely compatible.

The morphology of rubber blends is a major factor in determining their properties. A number of blend properties have been studied.
Air permeability measurements on NR/ENR-48 blends over the full compositional range have shown that the continuous phase dominates permeability. Where NR was the continuous phase the rate of air permeation was high and when ENR-48 was the continuous phase the reverse was observed.

The strength properties, i.e. tensile and tear of these blends were also studied. Interpretation in terms of blend morphology was not straightforward as other factors such as crosslink distribution between phases and interfacial adhesion are also important.

Standard Dunlop resilience measurements were also made on the blends but it was found that the resilience was dominated by the blend composition and not the morphology as the temperature and frequency of this test do not coincide with the maximum loss angles.

This study has produced valuable data on the structure and properties of NR and ENR blends which will be of practical use in the consideration of ENR blends for industrial applications. Additional information, both academic and industrial could be obtained by extending the study to include:

- Determination of the difference in epoxide levels at which blends become compatible. Compatibility must occur at some point between blends as the levels of epoxidation in each component approach one another. A study to determine the epoxide difference at which compatibility occurs would be very informative particularly as the structure of the materials would be similar, only varying in composition. The point of compatibility would be related to values of $X_{AB}$, $\Delta G$ and
etc. However, practical difficulties are envisaged in determining compatibility using DSC and DMTA, due to insensitivity of the instruments. Thus, an alternative technique will be required.

* Utilization of Kerner's decoupled packed grain theory [94] to study co-continuous phase systems. Comparison of predicted small strain dynamic data should be made with that of experimental results.

* A systematic investigation in indentify the preferential phase crosslink density and to optimize interfacial adhesion to maximise blend properties.

* An Extension of the small strain dynamic property evaluation to black filled vulcanizates, which are more relevant to industrial applications.
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