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Effect of Nanoparticulate Incorporation on Processability, Chemistry and Thermal properties of High Temperature Resin Systems

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A doctoral thesis submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy in Materials

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# CONTENT

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>I</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>V</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>VI</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>XIV</td>
</tr>
<tr>
<td>CHAPTER 1: INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Polymer Matrix Nanocomposites</td>
<td>1</td>
</tr>
<tr>
<td>1.2 High Performance Thermosetting Polymer Matrix Nanocomposites</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Introduction to Cyanate Ester</td>
<td>3</td>
</tr>
<tr>
<td>1.4 Aim and Objectives</td>
<td>5</td>
</tr>
<tr>
<td>CHAPTER 2: LITERATURE REVIEW</td>
<td>6</td>
</tr>
<tr>
<td>2.1 A brief story about cyanate esters and their nanocomposites</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1 Synthesis and thermal curing of cyanate esters</td>
<td>6</td>
</tr>
<tr>
<td>2.1.2 Development of cyanate ester matrix nanocomposites</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Current research in cyanate ester based nanocomposites</td>
<td>9</td>
</tr>
<tr>
<td>2.2.1 Cyanate ester/polyhedral oligomeric silsesquioxane (POSS) nanocomposites</td>
<td>9</td>
</tr>
<tr>
<td>2.2.2 Cyanate ester/clay nanocomposites</td>
<td>16</td>
</tr>
<tr>
<td>2.2.3 Cyanate ester/carbon nanotube nanocomposites</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Thermal curing kinetics and thermal curing monitoring study</td>
<td>28</td>
</tr>
<tr>
<td>2.3.1 Traditional catalysts employed for polymerisation of cyanate esters</td>
<td>28</td>
</tr>
<tr>
<td>2.3.2 Cure kinetics of cyanate ester based nanocomposites</td>
<td>31</td>
</tr>
<tr>
<td>2.4 Benzoxazine and its nanocomposites</td>
<td>32</td>
</tr>
<tr>
<td>2.4.1 A brief story about Benzoxazine</td>
<td>32</td>
</tr>
<tr>
<td>2.4.2 Benzoxazine based nanocomposites</td>
<td>34</td>
</tr>
<tr>
<td>CHAPTER 3: EXPERIMENTAL METHODOLOGIES</td>
<td>40</td>
</tr>
<tr>
<td>3.1 Materials</td>
<td>40</td>
</tr>
</tbody>
</table>
3.2 Preparation of CY mixtures incorporated with the nanofillers .................. 41
3.3 Preparation of CY based nanocomposites ......................................... 42
3.4 Preparation of BEN mixtures incorporated with the nanofillers .......... 42
3.5 Preparation of BEN based nanocomposites ....................................... 43
3.6 Characterization .............................................................................. 43

CHAPTER 4: PROCESSABILITY OF CYANATE ESTER BASED
NANOCOMPOSITES ........................................................................ 45
4.1: Catalysts, initiators, and solvents investigation ............................... 45
4.2 Morphology of the CY based mixtures ............................................. 53
4.3 Morphology of the CY based nanocomposites ................................ 54
4.4 Dispersion of the nanofillers in the CY ............................................. 56
4.5 Summary ......................................................................................... 60

CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE
ESTER BASED NANOCOMPOSITES ............................................. 62
5.1 Cyanate Ester Resin /Polyhedral Oligomeric Silsesquioxane (POSS)
Nanocomposites .................................................................................. 62
5.2 Cyanate ester resin/ clay nanocomposites ......................................... 80
5.3 Cyanate ester resin/ multi-wall carbon nanotubes (MWCNT) nanocomposites .. 108
5.4 Cyanate ester resin/ single-wall carbon nanotubes (SWCNT) nanocomposites... 125
5.4 Summary ......................................................................................... 136

CHAPTER 6: DEGRADATION DYNAMICS OF CYANATE ESTER BASED
NANOCOMPOSITES ....................................................................... 138
6.1 Analysis of the CY resin .................................................................. 138
6.2 Analysis of CY clay nanocomposites ................................................. 140
6.3 Analysis of CNT/CY nanocomposites .............................................. 147
6.4 Analysis of POSS/CY nanocomposites ............................................ 152
6.5 Activation energy calculation ............................................................ 154
6.6 Summary ......................................................................................... 160
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Processability of Benzoxazine based nanocomposites</td>
<td>162</td>
</tr>
<tr>
<td>7.1.1 Morphology of benzoxazine mixtures</td>
<td>162</td>
</tr>
<tr>
<td>7.1.2 Morphology of Benzoxazine based nanocomposites</td>
<td>163</td>
</tr>
<tr>
<td>7.1.3 Dispersion of the nanofillers in the benzoxazine</td>
<td>165</td>
</tr>
<tr>
<td>7.2 curing dynamic of benzoxazine and its nanocomposites</td>
<td>172</td>
</tr>
<tr>
<td>7.3 Network formation of benzoxzine and its nanocomposites</td>
<td>179</td>
</tr>
<tr>
<td>7.4 TGA analysis</td>
<td>189</td>
</tr>
<tr>
<td>7.5 comparative summaries</td>
<td>206</td>
</tr>
</tbody>
</table>

CHAPTER 8: CONCLUSIONS AND FURTHER WORK

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Conclusions</td>
<td>207</td>
</tr>
<tr>
<td>8.1.1 Processability of the cyanate ester and its nanocomposites</td>
<td>207</td>
</tr>
<tr>
<td>8.1.2 Curing dynamics and network formation of the cyanate ester and its nanocomposites</td>
<td>207</td>
</tr>
<tr>
<td>8.1.3 Thermal stability of the cyanate ester and its nanocomposites</td>
<td>209</td>
</tr>
<tr>
<td>8.1.4 Comparative study on the benzoxazine and its nanocomposites</td>
<td>209</td>
</tr>
<tr>
<td>8.2 Further work</td>
<td>210</td>
</tr>
</tbody>
</table>

REFERENCES                                                                 | 212  |
ABSTRACT:
Processability, curing dynamics, network formation, and thermal stability of cyanate ester resin (CY) nanocomposites with triSilanolphenyl polyhedral oligomeric silsesquioxane (POSS), natural montmorillonite clay (Na⁺), MT2EtOH (methyl, tallow, bis-2-hydroxyethyl, ternary ammonium) modified clay (30B), 2M2HT (dimethyl, dihydrogenatedtallow, quaternary ammonium) modified clay (20A), carbon nanotubes (CNTs) were studied by means of differential scanning calorimetry (DSC), modulated temperature differential scanning calorimetry (MTDSC), X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) and Raman spectroscopies. For comparison, the influence of the nanofillers on processability, curing dynamics, network formation, and thermal stability of a benzoxazine resin (BEN) were studied as well.

The influence of several catalysts, initiators and solvents on the curing dynamics of the CY was explored by means of DSC. Although the acetylacetonate and dilaurate based catalysts showed strong catalytic effect, the reaction enthalpy for the cure of CY dramatically declined, which implied that the incorporation of the catalysts led to incomplete network formation of the CY. For the initiators, the addition of dibenzoyl peroxide (BPO) and dicumyl peroxide (CPO) showed catalytic effect, and the strength increased with the concentration. For the solvents, chloroform, acetone, and cyclohexane did not show prominent catalytic effect on the CY. The DMF and THF showed catalytic effect, among which THF performed better. The clays and the POSS can be directly mixed with the CY resin to form homogenous mixtures, and there is no problem for further curing and processing of the nanocomposites. For the CNTs, in order to achieve good dispersion, assistance of solvent and ultasonication is necessary. The nano-scale dispersion of the POSS, Na⁺ and 30B clays, and MWCNTs was observed using SEM and TEM. XRD results indicate that the Na⁺ and 30B clays were exfoliated in the CY matrix. For the 20A/CY nanocomposites, visible aggregation was observed after the cure. For the SWCNT/CY nanocomposites, micro-scale aggregation was detected by means of SEM.

The incorporation of the POSS showed a strong catalytic effect on the curing reaction of CY. The activation energy of the CY decreased with increasing POSS content. The most effective catalytic effect was observed at 5wt% POSS. Both FTIR and Raman spectra monitored the
formation of triazine ring in the CY and its nanocomposites with the POSS. Raman spectra revealed that the CY resin preferentially reacted with –OH group in the POSS firstly to form a -O-(C=NH)-O- bond, rather than react with itself to form the triazine rings, during the network formation of the CY/POSS nanocomposites. The strong catalytic effect of the POSS on the curing process of the CY appears to be due to the formation of the -O-(C=NH)-O- bond.

The incorporation of the various clays showed different catalytic effects on the curing reaction of CY, among which 30B clay showed the most pronounced catalytic effect. For the CY/30B system, the activation energy of the CY decreased with increasing clay content. The most effective catalytic effect was observed at 3wt% of the 30B clay. The homogeneous dispersion of 30B and Na+ clays in the CY matrix was observed by using FEG-SEM. The aggregation of 20A clay was observed, which was due to the presence of the hydrophobic modifier. TEM images and XRD patterns confirmed that the 30B and Na+ clays were exfoliated in the CY matrix. FTIR was used to monitor the formation of triazine rings in the CY resin. For the CY/clay nanocomposites, the FTIR results indicated that the clays reacted with the CY to form a coordination complex, with the coordination complex then being transformed to –O–(C=NH)–O– bonds during the curing reaction. The strong catalytic effect of these clays on the curing process of the CY appears due to the formation of the coordination complex. Raman spectra revealed that the CY resin preferentially reacted with the hydroxyl groups in the clays firstly to form the coordination complex, rather than reacting with itself to form the triazine rings, during the network formation of the CY/clay nanocomposites. The formation of the 3-dimensional network for CY/clay nanocomposites was delayed until the mid to late stages of the cure, as determined by the absence of the triazine rings.

Incorporation of the various carbon nanotubes showed different accelerating effects on cure of the CY. Addition of the pristine multi-walled carbon nanotube (MWCNT) did not show prominent accelerating effect, and a carboxyl group functionalised multi-wall nanotube (MWCNT-COOH) displayed most effective accelerating effect. For a hydroxyl group functionalised multi-walled carbon nanotube (MWCNT-OH)/CY system, the most pronounced accelerating effect showed when the 1wt% to 2wt% MWCNT-OH was added. Nano-scale dispersion of both the pristine and the functionalised multi-walled carbon nanotubes in the CY matrix was observed by using FEG-SEM. In contrast, micro-scale
aggregation happened in a SWCNT-OH/CY system. The formation of triazine rings in the CY and its composites with CNTs was monitored using FTIR, and the results indicated that the CNTs reacted with the cyanate groups of the CY to form oxime C=N-O bond. The up-shifting of the bands for CNTs in Raman spectra confirmed nano-scale dispersion of MWCNTs in the CY matrix and strong interaction between the MWCNTs and the CY.

The incorporation of the clays showed good reinforcement on the thermal stability of CY under a nitrogen atmosphere, rather than that under an air atmosphere. It is remarkable that the char yield of 3wt% Na+/CY nanocomposite is 14 wt% higher than that of pure CY at 1000°C. The addition of the CNTs significantly impaired the thermal stability of the CY under an air atmosphere. Although leading to forward of decomposition process, the CNTs indeed helped the CY to be more stable under a nitrogen atmosphere. With incorporation of the 2wt% MWCNT-COOH, the char yield of CY increased up to 14%. The POSS/CY nanocomposites showed dramatic performance in both air and nitrogen. The full decomposition temperature was raised from 776°C to 916°C under an air atmosphere, with the incorporation of only 1wt% POSS. Under a nitrogen atmosphere, the char yield was increased by 15% up to 1000°C. The activation energies of the CY and its nanocomposites versus the conversion during decomposition process under air atmosphere, were calculated; the results are in accord with the TGA experiments. It is interesting that a negative activation energy appeared in the stage 2 for CY and its clay nanocomposites, due to the breakdown of triazine rings. The negative activation energy indicated the decomposition rate decreased with the increasing temperature, which may imply a very high decomposition barrier.

The processing procedure of the BEN/nanofiller mixtures is the similar with that of CY/nanofiller mixtures. The POSS and clays can be directly mixed with BEN to achieve the homogeneous mixtures. For CNTs, solvent and ultrasonication were necessarily applied to assist. The BEN did not show any advantages in processability comparing with that of the CY. For the BEN and its nanocomposites, there were large amounts of voids and cracks inside the samples after cure, which could not be prevented, and may result from the gas released during the cure, due to the nature of the BEN. High concentrations of the clays and the POSS impaired the shape stability of BEN, but high concentration of the CNTs help the BEN to retain its shape. TEM, SEM, and XRD proved the homogeneous dispersion of the nanofillers in the BEN matrix, which is similar with that of the CY. The incorporation of the various POSS, clays and CNTs showed different catalytic effects on the curing reaction of CY.
However, For the BEN, the incorporation of nanofillers rarely showed a catalytic effect, except CNTs. Both the cure of the BEN based mixtures and the CY based mixtures can be monitored by means of FTIR. The cure of the BEN followed a ring opening mechanism. With the curing time, the absorbance bands of oxazine ring disappeared due to the opening of the ring. All the functionalised nanofillers examined reacted with the BEN during the cure. However, the reaction between the nanofillers and the BEN did not lead to strong catalytic effect as that of CY. The incorporation of the nanofillers showed good reinforcement to the thermal stability of both BEN and CY. For the BEN, 10% POSS /BEN showed the best thermal stability before 567°C. 4wt% MWCNT/BEN nanocomposite became most thermally stable after 567 °C, under an air atmosphere. Interestingly, 5wt% POSS/BEN displayed the best thermal stability under nitrogen.
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LIST OF FIGURES

Figure 1. 1: Service temperature and toughness of various thermoset matrix polymer systems
......................................................................................................................................................... 4

Figure 2. 1: Synthesis of cyanate esters ............................................................................................... 6
Figure 2. 2: Cyanate ester chemical structures and cyclotrimerization reaction scheme. ........................ 7
Figure 2. 3: Semilogarithmic plot of gel time vs 1/T. ............................................................................. 8
Figure 2. 4: Experimental and model gel conversions for the cyanate resin ....................................... 8
Figure 2. 5: Structures of Silsesquioxane ............................................................................................. 10
Figure 2. 6: Cross-linked network formation through triazine ring formation (A), and fracture surface SEM micrographs of cyanate ester and its POSS nanocomposites (B). ................................................................. 12
Figure 2. 7: Synthesis of the PT-15/octaaminophenyl-POSS composites ............................................ 13
Figure 2. 8: (A) schematic of synthetic route to prepare the POSS/cyanate ester hybrid nanocomposites and (B) TGA of POSS/cyanate ester composites with different POSS molar contents ......................................................... 14
Figure 2. 9: TGA thermogram of 1, 3, 5, and 10 wt% POSS modified CE nanocomposites .................. 15
Figure 2. 10: Structure of sodium montmorillonite ............................................................................... 16
Figure 2. 11: Illustration of different states of dispersion of organoclays in polymers with corresponding WAXS and TEM results. ............................................................................................................. 17
Figure 2. 12: Effect of various additives on cyanate ester polymerization peak position. Compositions are: (A) cyanate ester plus 5 wt% 2MBHT MMT; (B) cyanate ester plus 5 wt% MT2EtOH MMT; (C) cyanate ester plus 2.5 wt% nonylphenol; (D) cyanate ester 5 wt% Na MMT, and (E) uncatalysed cyanate ester. ......................................................... 18
Figure 2. 13: SEM image of fracture surface of 4 wt% 2MBHT MMT in cure bisphenol E dicyanate ester ........................................................................................................................................ 19
Figure 2. 14: DSC thermograms for cyanate ester clay systems: (a) neat resin; (b) tetraphenylphosphonium clay. ............................................................................................................................. 20
Figure 2. 15: Schematic illustrations of the structures of (A) armchair, (B) zigzag, and (C) chiral SWNTs. Projections normal to the tube axis and perspective views along the tube axis are on the top and bottom, respectively. (D) Tunneling electron microscope
list of figures

Figure 2. 16: SEM images of the bending cross-sections of (A) neat CE and different CE composites with 0.5 wt % of (B) MW-CNT₁s, (C) MW-CNT₂s, (D) F-MW-CNT₁s, and (E) F-MW-CNT₂s. 118

Figure 2. 17: (left) Dynamic mechanical properties of the oligomeric cyanate ester/MWNT nanocomposites as a function of temperature and MWNT content: (A) storage modulus (G’), (B) loss modulus (G’’), and (C) damping factor [tan(delta)], and (right) thermal properties of the oligomeric cyanate ester/MWNT nanocomposites as a function of MWNT content: (A) thermo-oxidative and (B) thermal stability. The insets show an expansion of the data in the 5% weight loss region. 21

Figure 2. 18: processing route used to fabricate SWNT/CE nanocomposite fiber (A), Tensile stress-strain curves for neat CE fiber, p-SWNT(1 wt %)/CE composite fiber and f-SWNT(1 wt %)/CE composite fiber. (B) and FESEM images of f-SWNT(1 wt %)/CE composite fibers: a) Longitudinal image; b) crevice-interior image; c) cross-sectional image; d) cartoon of composite fiber with aligned SWNTs showing orientation of micrographs a–c. 119

Figure 2. 19: The electrical conductivity of M/CE composites (A) and M-OH/CE (B) as a function of weight fraction of MWCNTs. The inset shows the log–log plot of conductivity with p–pₑ for p > pₑ, and (C) TG and DTG curves for cured CE resin and composites. 120

Figure 2. 20: Proposed mechanism for the metal ion catalysed polymerisation of cyanate ester. 2

Figure 2. 21: Variation of normalized activation energy with concentration of DBTDL and ferric acetyl acetonate for the catalyzed polymerization of BACY. 4

Figure 2. 22: Conversion versus time for (a) neat cyanate ester resin and (b) 30 phr PPO blend cured at 210 °C. 123

Figure 2. 23: Synthesis of bisbenzoxazine monomer (A), and ring opening polymerization of bisbenzoxazines (B). 127

Figure 2. 24: TGA of polymeric benzoxazine composites containing different H-POSS
content (A), and SEM cross sectional micrographs of polybenzoxazine/POSS nanocomposites (B).

Figure 2. 25: Possible morphology for the benzoxazine/benzoxazine-POSS blends after thermal curing (A), and TGA analyses of benzoxazine/benzoxazine-POSS blends containing various VBa-POSS contents, after curing

Figure 2. 26: (A) Effect of organoclay on the Tg of the benzoxazine/clay nanocomposites, (B) TGA of PDS-MMT based hybrids; (a) neat resin, (b) 3% PDS-MMT hybrid, (c) 5% PDS-MMT hybrid, and (d) 10% PDS-MMT hybrid; and (C) TGA of ADS-MMT based hybrids, (a) neat resin, (b) 3% ADS-MMT hybrid, (c) 5% ADS-MMT hybrid, and (d) 7% ADS-MMT hybrid.

Figure 2. 27: (A) thermally-cured pellets of benzoxazine-functionalization MWCNTs. Photographs (a) and SEM micrographs (b, c), and (B) TEM micrographs of thermally cured nanocomposites of BPA-FBz and MWCNT-FBz.

Figure 3. 1: Schematic of molecular structure of (A) possible structure of the CY, (B) structure of the BEN, (C) POSS, (D) modifier for Cloisite® 30B, and (E) modifier for Cloisite® 20A. The anion is chloride, T is tallow (~65% C18; ~30% C16; ~5% C14), and HT is hydrogenatedtallow.

Figure 4. 1: DSC plots of the CY with different catalysts in nitrogen atmosphere (60 ml/min) with heating rate of 10ºC/min.

Figure 4. 2: DSC plots of the CY/BPO systems in nitrogen atmosphere (60 ml/min) with heating rate of 10ºC/min.

Figure 4. 3: DSC plots of the CY/ dicumyl peroxide systems in nitrogen atmosphere (60 ml/min) with heating rate of 10ºC/min.

Figure 4. 4: DSC plots of the CY prepared in various solvents in nitrogen atmosphere (60 ml/min) with heating rate of 10ºC/min.

Figure 4. 5: digital pictures of CY resins incorporated with different nanofillers. (A&B) neat CY resin, (C&D) 5 wt% POSS-OH/CY, (E) 2 wt% MWCNT-OH/CY, (F) 3 wt% Na+ clay/CY, (G) 3 wt% 30B clay/CY, and (H) 3 wt% 20A/CY.

Figure 4. 6: digital pictures of the CY based nanocomposites. (A) neat CY, (B) 5wt% POSS/CY, (C) 3wt% Na+/CY (D) 3wt% 30B/CY, (E) 3wt% 20A/CY, (F) 2wt% SWCNT-OH/CY, (G) 2wt% MWCNT-OH/CY, and (H) 2wt% MWCNT/CY.

Figure 4. 7: SEM images of the composites of CY with 1 wt% POSS (A and B), 5 wt%
POSS (C and D), and 10 wt% POSS (E and F). .................................................................56

Figure 4. 8: SEM images of (A) CY, (B) 3wt% 20A/CY nanocomposite, (C) 3wt% 
30B/CY nanocomposite, and (D) 3wt% Na⁺/CY nanocomposite, and TEM images of 
(E) 3wt% 30B/CY nanocomposite and (F) 3wt% Na⁺/CY nanocomposite ..............58

Figure 4. 9: XRD patterns for Na⁺ clay, 30B clay and their CY/clay nanocomposites. ....58

Figure 4. 10: SEM images of the composites of CY with 2 wt% MWCNT-COOH (A and 
B), 2wt% MWCNT-OH/CY (C and D), 2 wt% MWCNT (E and F), and 2 wt% 
SWCNT-OH (G and H) ..............................................................................................60

Figure 5. 1: DSC plots of the CY/POSS nanocomposites in nitrogen atmosphere (60 
ml/min) with heating rate of 10ºC/min. ........................................................................63

Figure 5. 2: Heat flow vs. temperature for CY resin with (60ml/min) and without 
nitrogen atmosphere. Heating rate of 10ºC/min was used .................................64

Figure 5. 3: Isothermal DSC plots for the CY/POSS nanocomposites at different 
isothermal temperatures (a) pure CY, (b) 1 wt% POSS/CY, (c) 5 wt% POSS/CY, and 
(d) 10 wt% POSS/CY ..............................................................................................66

Figure 5. 4: da/dt vs. α for the CY/POSS nanocomposites at different isothermal 
temperatures (a) pure CY, (b) 1 wt% POSS/CY, (c) 5 wt% POSS/CY, and (d) 10 wt% 
POSS/CY .............................................................................................................68

Figure 5. 5: Activation energy (A) and pre-exponential factor (B) vs. POSS content .....69

Figure 5. 6: Activation energy (a) and pre-exponential factor (b) vs. conversion for the 
CY/POSS nanocomposites .....................................................................................71

Figure 5. 7: FTIR spectra of the pure CY resin (A) with time cured at 225ºC and 5 wt% 
POSS/CY nanocomposite (B) with time cured at 210ºC in nitrogen atmosphere 
(60ml/min). For clarification, all the spectra were shifted parallel, and were 
calibrated basing the absorption band of phenyl ring symmetric breathing vibration 
near 1500 cm⁻¹. The peaks near 2350 cm⁻¹ are due to the presence of CO₂ ..........73

Figure 5. 8: FTIR spectra of the TriSilanolPhenyl POSS (A), and the comparison of neat 
CY with 5 wt% POSS/CY nanocomposite (B) ..........................................................74

Figure 5. 9: Raman spectra of the pure CY resin (A) cured at 225 ºC, 5% POSS/CY resin 
(B) cured at 210 ºC up to 100min, (C) A-enlarged, and (D) B-enlarged in nitrogen 
atmosphere (60ml/min). .....................................................................................77

Figure 5. 10: Raman spectra of the pure CY resin cured at 225 ºC and 5% POSS/CY 
resin cured at 210 ºC from 1250 to 2000 cm⁻¹ in nitrogen atmosphere (60ml/min)..79
Figure 5. 11: Scheme of crosslinked network formation through triazine ring and
-O-(C=NH)-O- bond for the POSS/CY nanocomposites.................................80
Figure 5. 12: DSC plots of the CY/clay systems in a nitrogen atmosphere (60 ml/min)
with heating rate of 10°C/min.................................................................81
Figure 5. 13: Isothermal DSC plots for the CY/clay systems at different isothermal
temperatures (A) pure CY, (B) 1 wt% 30B, (C) 3 wt% 30B, (D) 5 wt% 30B, (E) 3 wt%
20A and (F) 3 wt% Na⁺.................................................................84
Figure 5. 14: dα/dt vs. a for the CY/clay systems at different isothermal temperatures (A)
pure CY, (B) 1 wt% 30B, (C) 3 wt% 30B, (D) 5 wt% 30B, (E) 3 wt% 20A and (F) 3
wt% Na⁺.................................................................86
Figure 5. 15: Plots of heat flow and conversion versus time for 3 wt% Na⁺/CY cured at
180 °C.................................................................88
Figure 5. 16: plots of activation energy versus content of the 30B clay (A) and (B), and
comparisons of the activation energy for various CY/clay systems (C) and (D). .....89
Figure 5. 17: Activation energy (A) and pre-exponential factor vs. conversion for the
CY/clay systems.................................................................91
Figure 5. 18: FTIR spectra of the clays used for the CY/clay nanocomposites.............92
Figure 5. 19: FTIR spectra of (A) pure CY, (B) 3wt% 20A/CY nanocomposite, (C) 3wt%
30B/CY nanocomposite, and (D) 3wt% Na⁺/CY nanocomposite, in air atmosphere.
For clarification, all spectra were shift parallel, and were calibrated based on the
absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹.......95
Figure 5. 20: Comparison of the FTIR spectra of the pure CY and the clay/CY
nanocomposites under the condition of (A) cured at 190 °C for 1 hour, and (B) cured
at 190 °C for 1 hour and post-cured at 290 °C for another 1 hour, in air atmosphere.
.......................................................................................................................97
Figure 5. 21: Comparison of the FTIR spectra of the pure CY and the clay/CY
nanocomposites uncured (A), and CY cured at 222°C and CY/clay nanocomposites
cured at 180 °C for 320 min (B) in nitrogen atmosphere (60ml/min). .......................98
Figure 5. 22: Schematic of possible molecular structure for the coordination complex (A)
and the chemical compound (B) formed by reaction of the hydroxyl groups from the
clays and the cyanate groups from the CY..........................................................99
Figure 5. 23: FTIR spectra of (A) pure CY with time cured at 225°C, (B) 3wt% Na⁺/CY
nanocomposite (C) 3wt% 30B/CY nanocomposite and (D) 3wt% 20A/CY
nanocomposite with time cured at 180°C in nitrogen atmosphere (60ml/min). ......101
Figure 5. 24: Raman spectra of (A) the pure CY resin cured at 225°C, (B) 3wt% 20A/CY resin cured at 180°C, (C) 3wt% 30B/CY resin cured at 180°C, (D) 3wt% Na+/CY resin cured at 180°C, and (E) A-enlarged, in nitrogen atmosphere (60 ml/min) .....105

Figure 5. 25: Raman spectra of (A) the pure CY resin and the CY/clay resins uncured, (B) the pure CY resin cured after 10 minutes and the CY/clay resins cured after 320 minutes in nitrogen atmosphere (60 ml/min) ......................................................108

Figure 5. 26: DSC plots of the CY/CNTs nanocomposites in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min .........................................................109

Figure 5. 27: Plots of heat flow versus curing time for CY/CNT systems at different isothermal temperatures. (A) pure CY, (B) 1wt% MWCNT-OH/CY, (C) 2wt% MWCNT-OH/CY, (D) 4wt% MWCNT-OH/CY, (E) 2wt% MWCNT/CY, (F) 2wt% MWCNT-COOH/CY, and (G) 2wt% SWCNT-OH/CY ........................................112

Figure 5. 28: Plots of da/dt vs. a for various CY/CNT systems at different isothermal temperatures. (A) pure CY, (B) 1wt% MWCNT-OH/CY, (C) 2wt% MWCNT-OH/CY, (D) 4wt% MWCNT-OH/CY, (E) 2wt% MWCNT/CY, (F) 2wt% MWCNT-COOH/CY, and (G) 2wt% SWCNT-OH/CY ........................................114

Figure 5. 29: Activation energy E₁ (A) and E₂ (B) of CY/MWCNT-OH vs. weight fraction of MWCNT-OH ..............................................................................115

Figure 5. 30: Comparison of the activation energy E₁ (A) and E₂ (B) for various CY/CNT (2 wt%) systems ......................................................................................116

Figure 5. 31: Activation energy (A) and pre-exponential factor (B) vs. conversion for the CY/CNT systems ..............................................................................117

Figure 5. 32: FTIR spectra of (A) pure CY with time cured at 225°C, (B) 2wt% MWCNT/CY, (C) 2wt% MWCNT-OH/CY, (D) 2wt% MWCNT-COOH/CY (E) 2wt% SWCNT-OH/CY with time cured at 200°C, and (F) all samples cured after 320 min, in nitrogen atmosphere (60ml/min). For clarification, the spectra were shift parallel, and were calibrated based on the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹ .........................................................121

Figure 5. 33: Schematic of possible molecular reaction between hydroxyl group functionalised CNT (A), carboxyl group functionalised CNT (B) and the cyanate groups from the CY ......................................................................................................122

Figure 5. 34: Raman spectra of (A) the 2 wt% MWCNT/CY cured at 200 °C, and (B) 2% MWCNT-COOH/CY cured at 200 °C, in nitrogen atmosphere (60 ml/min) ........124

Figure 5. 35: DSC plots of the CY/SWCNTs nanocomposites in nitrogen atmosphere (60
ml/min) with heating rate of 10°C/min. .......................................................... 125

Figure 5. 36: Plots of heat flow versus curing time for CY/SWCNTs systems at different curing temperatures ................................................................. 128

Figure 5. 37: Plots of conversion rate versus curing time for CY/SWCNTs systems at different curing temperatures ......................................................... 129

Figure 5. 38: Activation energy of CY/SWCNT-OH vs. weight fraction of SWCNT-OH .......................................................................................................................... 131

Figure 5. 39: Comparison of the activation energy for the CY/functiona lised MWCNT (2wt%) systems .................................................................................. 131

Figure 5. 40: Kinetic activation energy versus conversion for the CY/SWCNT systems .................................................................................................................. 133

Figure 5. 41: FTIR spectra for the pure CY resin cured at 225°C (A) and for 2wt% SWCNT/CY (B), 2wt% SWCNT-OH/CY (C), and 2wt% SWCNT-COOH/CY (D), cured at 200°C in nitrogen atmosphere (60ml/min) For clarification, all the spectra were shift parallel, and were calibrated basing the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹ .................................................. 135

Figure 6. 1: TGA results of pure CY with a heating rate of 10 °C/min under air atmosphere (60 ml/min) (A) and under nitrogen atmosphere (60 ml/min) (B) ...... 139

Figure 6. 2: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under air atmosphere (60 ml/min). ................................................................. 141

Figure 6. 3: TGA results of CY/clay systems. (A) residual weight in percentage of CY/clay system vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min). .................................................. 142

Figure 6. 4: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/ Na⁺ system, (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/30B system with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min). .............. 144

Figure 6. 5: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/ Na⁺ system, (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/30B system with a heating rate of 10 °C/min under air atmosphere (60 ml/min). ...................... 146

Figure 6. 6: TGA results of CY/CNT systems. (A) residual weight in percentage vs.
temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under air atmosphere (60 ml/min)........................................................................................................148

Figure 6. 7: TGA results of CY/CNT systems. (A) residual weight in percentage of CY/clay system vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min). ..................................................................................149

Figure 6. 8: TGA results of CY/MWCNT-OH systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/MWCNT-OH system, with a heating rate of 10 °C/min under air atmosphere (60 ml/min), (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/MWCNT-OH system with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min). .151

Figure 6. 9: TGA results of CY/POSS systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/POSS system, with a heating rate of 10 °C/min under air atmosphere (60 ml/min), (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/POSS system with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min). ..................................................................................154

Figure 6. 10: TGA results of CY and its nanocomposites with different heating rates (A) CY, (B) 5 wt% POSS/CY, (C) 3 wt% 30B/CY, (D) 2 wt% MWCNT-OH under air atmosphere (20 ml/min)..................................................................................................................157

Figure 6. 11: activation energy of CY and its nanocomposites with clays during decomposition versus conversion rate under air atmosphere. ......................................159
LIST OF TABLES

Table 1. Parameters of several high performance thermosetting polymers

Table 4.1: General information of the catalysts investigated

Table 4.2: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of the CY with different catalysts

Table 4.3: General information of the initiators investigated

Table 4.4: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/BPO systems

Table 4.5: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/Dicumyl peroxide systems

Table 4.6: General information of the solvents investigated

Table 4.7: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/prepared in various solvents

Table 5.1: DSC results of the CY/POSS systems in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min

Table 5.2: Autocatalytic model constants for the CY/POSS nanocomposites

Table 5.3: Activation energy at different conversions for the POSS/CY nanocomposites

Table 5.4: Pre-exponential factor at different conversions for the POSS/CY nanocomposites

Table 5.5: Analytical results of the Raman spectra of the pure CY resin cured at 225 °C and the 5 wt% POSS/CY system cured at 210 °C

Table 5.6: DSC results of the CY/clay systems in nitrogen atmosphere (60 ml/min) with heating rate of 10 °C/min. \( \Delta H_{\text{post}} \) is the reaction enthalpy calculated from an isothermal post cure process at 330 °C after the dynamic DSC experiment

Table 5.7: Autocatalytic model constants for the CY/clays systems

Table 5.8: Activation energy at different conversions for the CY/clay systems

Table 5.9: Infra-red assignments on the clays used for the CY/clay nanocomposites

Table 5.10: Analytical results of the Raman spectra of the pure CY resin cured at 225 °C and its composites with addition of the clays

Table 5.11: Raman shift in the CY/CNT nanocomposites
Table 5. 12: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/SWCNT systems. \( \Delta H_{\text{post}} \) is the reaction enthalpy calculated from an isothermal post cure process at 330 \(^\circ\)C after the dynamic DSC experiment. 

Table 5. 13: Autocatalytic model constants for the CY/SWCNTs nanocomposites 

Table 5. 14: The kinetic activation energy and the pre-exponential factor for the CY/SWCNT systems 

Table 6. 1: experimental indicators for thermal stability from the TGA experiment 

Table 6. 2: parameters calculated based on Flynn-Wall-Ozawa method 

Table 6. 3: activation energy of the CY and its nanocomposites calculated using Flynn-Wall-Ozawa method 

Table 7. 1: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of the benzoxazine with different nanofillers 

Table 7. 2: Autocatalytic model constants for the Benzoxazine and its nanocomposites 

Table 7. 3: the kinetic activation energy and the pre-exponential factor for the benzoxazine and its nanocomposites 

Table 7. 4: Analytical results of the FTIR spectra of the pure BEN resin cured at 180 \(^\circ\)C 

Table 7. 5: Infra-red assignments on the clays used for the BEN/clay nanocomposites 

Table 7. 6: experimental indicators for thermal stability from the TGA experiment 

Table 7. 7: experimental indicators for thermal stability from the TGA experiment 

Table 7. 8: Experimental indicators for thermal stability of BEN and its POSS nanocomposite under air atmosphere 

Table 7. 9: experimental indicators for thermal stability of BEN and its POSS nanocomposite under nitrogen atmosphere 

Table 7. 10: experimental indicators for thermal stability from the TGA experiment 

Table 7. 11: experimental indicators for thermal stability from the TGA experiment
CHAPTER 1: INTRODUCTION

1.1 Polymer Matrix Nanocomposites

Nowadays, it is common that organic or inorganic fillers are added to a polymeric system. Polymer matrix composites have boosted many industries, such as sporting, aeronautics and automobiles. Since the 1990s, polymer nanocomposites have become a vital focus in the polymeric field. Polymer nanocomposites are generally defined as the combination of a polymeric matrix and nanofillers, which have at least one dimension (i.e. length, width, or thickness) in the nanometer size range. Profiting from the development of modern analysis techniques and computer technology, scientists are able to analyse the microstructure of materials in nanoscale, it also becomes easier to search the properties on the nanoscale via modelling and simulation. Therefore, the research and application on nanocomposites become possible.

Nanoparticles which have larger relative surface areas are significantly different from micro-particles. Since many important chemical and physical interactions are affected by the surface properties, the microstructure of nanocomposites, namely, the bonding of two phases, the structure and thickness of interphase, the continuity of two phases, the size and shape of the dispersed phase and so on, would be significantly different from conventional composites. Furthermore, the nanoparticles lead to quantum effects. Owing to these effects, the polymer nanocomposites offer many advantages over conventional composites. For example, the mechanical properties (strength, modulus, etc.), electrical conductivity, optical properties, magnetic properties, and transport properties would be changed with the addition of nanoparticles.

In general, nanocomposites perform efficient reinforcement due to their high aspect ratios. However, the properties of nanocomposites greatly depend on the size and shape of its component phases and the interaction between these phases. Thus, proper dispersion and optimizing interfacial bond between nanofillers and matrix are of vital importance in nanocomposite preparation. If these key points cannot be achieved, the nanocomposites cannot offer improved properties over those of conventional composites, indeed these might be even worse sometimes.
1.2 High Performance Thermosetting Polymer Matrix Nanocomposites

Both in polymer matrix nanocomposites science and industry, nanocomposites based on advanced thermosetting polymers matrix have become the focus of public concern. Traditional high performance thermosetting polymers include epoxy, polyimide, phenolic, BMI resins, and so on. The recognition of these materials is attributed to both the economy of weight saving and their key properties, such as high specific stiffness and strength, good dimensional and thermal stability, and desirable physical and mechanical properties. Owing to the development of the high performance thermosetting polymer matrix nanocomposites, many creative ideas are able to transform into technical realities. In aerospace and automotive industries, these materials showing an incredible impact in military and commercial vehicles, the rocket, satellites, and military and commercial aircraft, have found their undisputed place.

For example, epoxy resins are currently widely used in aircraft to make secondary non-load-bearing structures, such as engine nacelles, cowlings, fan containment cases, flaps, ailerons, spoilers, rudders, elevators, landing gear doors, etc.\(^2\) Besides, nozzle components in rocketry systems like honeycomb structures, cylindrical support structure, pressurant bottles, yoke, and solar panel substrates in satellites are preferably made of epoxy and polyimide nanocomposites. It has been reported that more than 80% of the structural components in modern small launch vehicles and satellites can be made using advanced thermosetting polymers nanocomposites. In the rocket motor cases of the space shuttle’s solid boosters, the structure can be composed of approximately 30 tons of graphite-reinforced epoxy composites. The application of light weight thermosetting polymer nanocomposite parts in aerospace and automotive industry leads to significant benefit, such as improving performance and fuel economy, and increasing range and payload capacity.

Although bringing many benefits to many advanced industries, traditional high performance thermosetting polymers also face various limitations. For epoxy resins, the upper use temperature limitation of 200°C cannot fit the requirement of aircraft engine and skin of supersonic aircraft and missiles which should be thermally stable at higher service temperatures. In launch vehicles and satellites, the manufacture of some structural components requires the use of high temperature resistant polymers which own better thermal insulation and dimensional stability than that of epoxy resins, to tailor the increasing demand.
Besides, for electrical/electronic applications, an alternate advanced thermosetting resin system with lower dielectric constant and moisture absorptivity is preferred. For polyimide resins, although with improved high temperature properties compared to epoxy resins, the crucial processing condition which requires long time and high pressure, has hampered their application. For phenolic resins owning good heat and flame resistance and low cost, brittleness and poor shelf-life become their fatal shortcomings for advanced applications. Against these backdrops, emergence of a new compromised high performance thermosetting polymer system is becoming more and more eager.

1.3 Introduction to Cyanate Ester

With technological development and increasing demand for materials with enhanced properties, cyanate ester resins have been brought to popular attention, due to their superior properties compared with the conventional thermosetting materials. As is shown in Figure 1.1, the glass transition temperature of cyanate esters is located between 250°C and 290°C, which fills a temperature regime intermediate between that of epoxy resins and hazardous polyimide or BMI resins. The high glass transition temperature makes the cyanate esters owning high dimensional stability and thermal stability even at the temperature as high as 350°C. Furthermore, unlike polyimide, cyanate ester resins are easy to process in a manner similar to epoxy. The moisture absorption (0.6%-2.5%) and moisture absorption rate of cyanate ester resins is also lower than those of epoxy, polyimide, and BMI resins. Besides, excellent mechanical properties, good radiation resistance, high flame resistance, low dielectric constant, low dissipation factor and low outgassing make cyanate esters currently in widespread use for high temperature applications, structural aerospace composites, microwave transparent composites, encapsulants, adhesives, and electronic insulating applications. However, one of universal issues that draws growing concern of scientists and engineers is the high curing temperature of cyanate esters, which has been hampering their application. Hence, looking for an appropriate catalyst for the curing process of cyanate esters is vitally important. On the other hand, although the cyanate esters own outstanding dimensional stability and thermal stability, they still can not meet the requirements at the crucial temperature above 400°C, for advanced military and aerospace engineering. Thus, the reinforcement of cyanate esters for high-performance applications becomes necessary.
Table 1: Parameters of several high performance thermosetting polymers.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Epoxy</th>
<th>Phenolic</th>
<th>Toughened BMI</th>
<th>Cyanate ester</th>
<th>Polybenoxazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg·m⁻³)</td>
<td>1200-2500</td>
<td>1240-3200</td>
<td>1200-3000</td>
<td>1100-3500</td>
<td>1190</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>3.1-3.8</td>
<td>3-5</td>
<td>3.4-4.1</td>
<td>3.1-3.4</td>
<td>3.8-4.5</td>
</tr>
<tr>
<td>Dielectric constant (1 MHz)</td>
<td>3.8-4.5</td>
<td>4.3-5.4</td>
<td>3.4-3.7</td>
<td>2.7-3.2</td>
<td>3-3.5</td>
</tr>
<tr>
<td>Mould Shrinkage (%)</td>
<td>0.06</td>
<td>0.2</td>
<td>0.7</td>
<td>0.4</td>
<td>~0</td>
</tr>
<tr>
<td>Cure temp (°C)</td>
<td>Room temp-180</td>
<td>150-190</td>
<td>220-300</td>
<td>180-250</td>
<td>160-220</td>
</tr>
<tr>
<td>Use temp (°C)</td>
<td>Room temp-180</td>
<td>200-250</td>
<td>around 200</td>
<td>200-250</td>
<td>130-280</td>
</tr>
<tr>
<td>Onset temp of degradation (°C)</td>
<td>260-340</td>
<td>300-360</td>
<td>360-400</td>
<td>400-420</td>
<td>380-400</td>
</tr>
</tbody>
</table>

Figure 1.1: Service temperature and toughness of various thermoset matrix polymer systems²
1.4 Aim and Objectives

In last decade, hybrid organic polymer-inorganic nanocomposites have attracted plenty of research interest for various applications, such as in mechanical, optical and electronic fields.\textsuperscript{1,10-14} Various inorganic nanofillers have been studied, including clays\textsuperscript{15-18}, carbon nanotubes\textsuperscript{19-21}, graphene\textsuperscript{22-27}, and polyhedral oligomeric silsesquioxanes (POSS). It is believed that inorganic nanoparticle/cyanate esters nanocomposites can be one of solutions for reducing the curing temperature of cyanate esters and improving their thermal stability, to meet the ever-increasing demand for high-performance polymeric materials.

The addition of nanofillers, such as POSS, clays, and carbon nanotubes, could influences significantly the cure and network formation of cyanate esters. However, these influences have never been clearly reported. In order to develop high performance cyanate ester based nanocomposites, the effects of the nanofillers on the curing dynamics need to be clarified. Furthermore, a clear understanding of network formation in the cyanate resin during cure is essential, so that the properties of the cyanate ester based nanocomposites can be successfully predicted and controlled. In this research, the effects of a POSS, three clays, and six carbon nanotubes on curing dynamics, network formation and thermal stability of a cyanate ester, PT-30, was revealed. Furthermore, the influence of the nanofillers on another novel thermosetting system, a benzoxazine, was also assessed for comparative study.
CHAPTER 2: LITERATURE REVIEW

2.1 A brief story about cyanate esters and their nanocomposites

2.1.1 Synthesis and thermal curing of cyanate esters

Basically, the synthesis of cyanate esters is based on the reaction of the corresponding phenols or novolac derivatives with cyanogen halides. In the presence of a tertiary amine as the acid scavenger, the hydrogen atom of the phenolic OH group is substituted by a cyanide group in a low temperature solution, as shown in figure 2.1. Cyanate esters can be divided into three species: dicyanates, cyanato telechelics, and cyanate esters of polyphenols and phenolic triazines. The cure of cyanate esters can be divided into three steps, which are polymerisation, gelation, and finally crosslinking network formation. The curing process is via a thermally driven cyclotrimerization of OCN groups to form triazine rings, each of which serves as a cross-linking site, as shown in Figure 2.2. The cure reaction can be significantly influenced by a few factors, such as, catalysts, solvent, and environment. For example, the carbon atom of the –OCN group is highly prone to attack by nucleophilic reagents, due to its strongly electrophilic nature. The cyanate esters also undergo a variety of reactions with hydrogen donating impurities, transition metal complexes, imidazoles and so on. Among these nucleophilic reagents, some act as catalysts, while some others hamper the formation of triazine rings. Thus, for synthesis and reaction of cyanate esters, scrupulous purification becomes vitally important.

![Figure 2.1: Synthesis of cyanate esters](image)

Figure 2.1: Synthesis of cyanate esters
During the curing process of thermoset resins, gel time and temperature are vitally important parameters. Due to the self-crosslinking behaviour of cyanate esters, their gelation studies have been one of interesting focus. Gelation happens at the time that the molecular motion of oligomers ceases on a macroscopic level. For moulding of the CY resin and its composites, determination of gelation point becomes one of importance, as it is the time for application of pressure for compaction. The gelation point depends on many factors, such as temperature of the cure, and catalysts applied. For cyanate esters, the gel time is related to temperature by an Arrhenius-type relationship, as shown in Figure 2.3 and Figure 2.4.\textsuperscript{29,30} It was also reported that the presence of various solvents showed the influence on the cure of cyanate esters.\textsuperscript{31}
Figure 2. 3: Semilogarithmic plot of gel time vs 1/T.$^{29}$

Figure 2. 4: Experimental and model gel conversions for the cyanate resin.$^{30}$
2.1.2 Development of cyanate ester matrix nanocomposites

Several research programmes on cyanate ester matrix nanocomposites have been done. The inorganic nanofillers being studied include polyhedral oligomeric silsesquioxanes (POSS), clays, and carbon nanotubes. According to the current research, the incorporation of POSS showed a remarkable improvement on the fracture toughness, flexural modulus, and thermal stability. For clays, both catalytic effect and improvement on fracture toughness and flexural modulus, were report. In cyanate ester/carbon nanotube research, significantly improvements on both the tensile strength and storage modulus were reported, which are attributed to good dispersion and strong interaction between matrix and the carbon nanotubes used. It is believed that inorganic nanoparticle/cyanate esters nanocomposites can be one of solutions for reducing the curing temperature of cyanate esters and improving its thermal stability, to tailor the ever-increasing demand for high-performance polymeric materials.

2.2 Current research in cyanate ester based nanocomposites

2.2.1 Cyanate ester/polyhedral oligomeric silsesquioxane (POSS) nanocomposites

POSS reagents, which own nanosized ladder, cage, or partial cage structures, are interesting silicon based compounds with the formula (RSiO\textsubscript{1.5})\textsubscript{n}. The R can be hydrogen, or a range of polar structures and functional groups. The size of POSS is between 1 to 3 nm in diameter, which is thought as one of the smallest particles of silica. Figure 2.5 shows the schematic structures of silsesquioxane. Unlike natural clays, silicones or other inorganic fillers, POSS contains an inner inorganic framework, which is covered by organic substituents. Due to their hybrid (inorganic-organic) nature, the POSS reagents become compatible with polymers, biological systems or any organic surfaces. Thus, incorporation of POSS reagents into organic polymers offers a unique opportunity to prepare nanocomposites with truly molecular dispersions of the inorganic fillers.\textsuperscript{3,32} POSS reagents have outstanding thermal stability and attractive oxidative resistance even at temperatures that higher than 500 °C. Furthermore, the insulating property and gas permeability of the POSS are also good.\textsuperscript{33} The enhancement of physical properties of polymeric materials by incorporation of POSS has been shown in a wide range of thermoplastics, such as polystyrene\textsuperscript{34,35}, polypropylene\textsuperscript{36,37}, ethylene and
propylene blends, ethylene copolymers, and polycarbonate, as well as thermosetting materials, which are polyimide, phenolic resins, epoxy resins, polyurethane, polyimide-epoxy blends and so on. Modification of cyanate ester properties with POSS has been attempted by several groups.

Liang et al. prepared cyanate ester (PT-15)/triSilanolphenyl-polyhedral oligomeric silsesquioxane (POSS) nanocomposites, with ratios of 99:1, 97:3, 90:10, and 85:15 in wt%. At the 1 and 3 wt% POSS loading, the POSS was molecularly dispersed and bonded into the continuous matrix phase. With the increasing POSS content, the POSS-enriched nanophases with sizes from a few nanometers to about 200 nm showed. The size distribution of these phases continuously broadens as the loading of the POSS increases, and larger aggregates formed at the higher loading. The storage bending moduli of the cyanate ester/POSS composites are significantly improved comparing to that of the pure cured cyanate ester at all loadings except 85wt%/15wt%, over the entire temperature range of 35 to 350 °C. The $T_g$ values of the 1, 3, and 5 wt % POSS composites are higher than those of neat PT-15.

![Scheme 1. Structures of silsesquioxane](image)
Furthermore, the storage modulus, high temperature properties, flexural strength and flexural modulus of the nanocomposites with the POSS loading lower than 5 wt%, are higher than those of neat PT-15. The good dispersion of the POSS into the PT-15 matrix is due to the reaction of the POSS with the cyanate esters to form iminosiloxycarbonates. However, continued curing results on aggregation of the POSS which is bound to resin molecules. The aggregation process depends on the concentration of the POSS in the cyanate ester resins.
Liang et al.\textsuperscript{50} also incorporated octaaminophenyl-POSS and cyanopropylcyclopentyl-POSS into the PT-15 cyanate ester resin to prepare the cyanate ester/POSS nanocomposites. The octaaminophenyl-POSS was totally dispersed and chemically bonded to the continuous matrix phase on a molecular scale in all samples. The amino functional groups of the octaaminophenyl-POSS reacted rapidly with the \(\text{–OCN}\) groups of cyanate ester before undergoing high-temperature curing. Apart from a sharp increase in 1wt\% octaaminophenyl-POSS loading, the \(T_g\) values of the PT-15/1 composites decreased as the POSS loading increased. The storage modulus values of the octaaminophenyl-POSS/cyanate esters nanocomposites were improved. In contrast to octaaminophenyl-POSS, the cyanopropylcyclopentyl-POSS did not react chemically with the cyanate ester below the cure temperatures, which leads to the occurrence of substantial phase separation into both nanometer and micrometer scales during curing. Increasing the concentration of cyanopropylcyclopentyl-POSS in the composites progressively raised the \(T_g\) values and the E’
values. In summary, both types of POSS additives can improve the high-temperature mechanical properties of cyanate ester resins despite their very different degrees of dispersion.

Figure 2. 7: Synthesis of the PT-15/ octaaminophenyl-POSS composites.\(^{50}\)

Lu et al.\(^ {32}\) introduced a multi-epoxy cubic silsesquioxane into a bisphenol A dicyanate ester resin to form the highly crosslinked organic-inorganic hybrid nanocomposites on a molecular level. The introduction successfully modified the local structure of the molecules. A multi-epoxy cubic silsesquioxane concentration of 4.8 mol% resulted in lower stiffness of the molecular chain, crosslinking density, \(T_g\) and thermal stability. In contrast, the concentrations of the POSS higher than 12.5 mol% led to a higher crosslinked hybrid network, bulk size, and mass cubic silsesquioxane structure. As a result, the thermal stability and flame retardancy of the cyanate ester were significantly improved.
Figure 2.8: (A) schematic of synthetic route to prepare the POSS/cyanate ester hybrid nanocomposites and (B) TGA of POSS/cyanate ester composites with different POSS molar contents.\textsuperscript{32}

Jothibasu et al.\textsuperscript{51} prepared POSS-cyanate ester (CE) nanocomposites through an in situ method by thermal curing with the use of diaminodiphenylmethane (DDM) as a coupling agent. The thermal and morphological properties of the CE incorporated with different weight
percentages (1, 3, 5 and 10%) of the POSS, were studied. The 5 wt% POSS/CE nanocomposite displayed the highest glass transition temperature among those studied. Furthermore, the thermal stability of nanocomposites increased with the increasing percentage composition of the POSS.

![TGA thermogram of 1, 3, 5, and 10 wt% POSS modified CE nanocomposites.](image)

It is believed that the addition of functionalized POSS could influence the cure dynamics and network formation of cyanate esters significantly. However, the mechanism of these influences is still not clarified. For example, what is the role of the POSS during the cure of the cyanate ester? Why does the incorporation of 5 wt% POSS show the best improvement in storage modulus and flexural moduli? When does the POSS react with the cyanate ester, at the very beginning, the mid-term, the very end, or throughout the whole curing process? The different reaction time will lead to the significant difference in the final network formation. In order to develop high performance cyanate ester resin/POSS nanocomposites, the effect of POSS on the curing dynamics needs to be fully understood. Furthermore, a clear understanding of network formation in the cyanate ester resin during cure is essential, so that the properties of the cyanate ester resin/POSS nanocomposites can be predicted and controlled. On the other hand, in order to tailor the ever-increasing demand for thermal stability of cyanate esters, it is very important to study the thermal decomposition of the
cyanate ester and its POSS nanocomposites in system. However, this work has not been done yet.

2.2.2 Cyanate ester/clay nanocomposites

A natural clay (montmorillonite) consists of an inner octahedral layer and two silicate tetrahedral layers, which form a sandwich structure, as shown in Figure 2.10. The sodium ions in the gallery of natural clay can be exchanged with organic cations, such as an ammonium salt, to form an organic clay. The exchanged ammonium salt usually acts as surfactant to improve the compatibility of the clay with other organic materials. In the natural state, clays exist as stacks of a lot of individual platelets. The presence of sodium ions or ammonium ions lead to the expansion of clays. The space between two individual platelets can be detected by means of X-ray Diffraction (XRD). For the natural clay, the thickness of an individual platelet is about 0.94 nm, while the d-spacing between two individual platelets is about 0.94. The d-spacing will be increased when the sodium ions are replaced by much larger ammonium ions.

Figure 2.10: Structure of sodium montmorillonite.

In the last decade, polymer-clay hybrid nanocomposites have attracted considerable research interest due to the reinforcing effect which clay can bring to the polymer matrix. It has been reported that the polymer-clay hybrid nanocomposites exhibit many attractive properties, such as improved mechanical properties, more effective thermal stability and inherent flame retardancy. Clays can be dispersed into polymer through a number of ways, including in situ
polymerization\textsuperscript{61-64}, latex\textsuperscript{65}, solution\textsuperscript{1}, and commercial melt processing\textsuperscript{66-72} which is most widely used. For polymer-clay composites, there are three types of morphology for clays in polymer matrix: immiscible, intercalated, and exfoliated, as shown in Figure 2.11. For most purposes, the ideal dispersion state for clays is exfoliation of the clay platelets, but this morphology is difficult to achieve in practice. The use of clays as a nanofiller to enhance properties of polymeric materials by incorporation of clays has been demonstrated on a wide range of thermoplastics, such as polystyrene\textsuperscript{73,74}, poly (methyl methacrylate)\textsuperscript{73,74}, polyaniline\textsuperscript{75}, polyethylene\textsuperscript{76}, polypropylene\textsuperscript{77}, nylon\textsuperscript{78}, and polybutadiene\textsuperscript{79}, as well as thermosetting materials, for instance, polyimide\textsuperscript{80}, epoxy resin\textsuperscript{81}, and polyurethane\textsuperscript{82,83}. There are a few studies focusing on modification of cyanate ester properties with clays.\textsuperscript{9,84-87}

Figure 2. 11: Illustration of different states of dispersion of organoclays in polymers with corresponding WAXS and TEM results.\textsuperscript{52}

Wooster et al.\textsuperscript{84} examined the influences of Na montmorillonite (Na MMT) and cation exchanged layered montmorillonite on the polymerization of a cyanate ester monomer (1,1-bis(4-cyanatophenyl)ethane). It is proved that the polymerization reaction of the cyanate
Ester resin was catalysed by the Na montmorillonite, which is a mixture of exfoliated layers and intercalated tactoids in the cyanate resin. The catalytic activity increased upon sodium cation exchange in the montmorillonite gallery. Montmorillonite catalyzed systems own superior properties in cross-link homogeneity and extent of polymerization, compared to traditionally catalyzed cyanate ester-montmorillonite polymers. During the curing process, the montmorillonite layers were firstly expanded due to monomer permeation into the gallery, and then were expanded again due to the monomer/polymer reorientation within the gallery.

Figure 2.12: Effect of various additives on cyanate ester polymerization peak position. Compositions are: (A) cyanate ester plus 5 wt% 2MBHT MMT; (B) cyanate ester plus 5 wt% MT2EtOH MMT; (C) cyanate ester plus 2.5 wt% nonylphenol; (D) cyanate ester 5 wt% Na MMT, and (E) uncatalysed cyanate ester.\textsuperscript{84}

Wooster et al.\textsuperscript{85} also studied the rheological properties and mechanical properties of percolated cyanate ester monomer/layered silicate mixtures. It was found that the change in rheology and mechanical properties was dominated by the dispersion state of the clays. With the incorporation of 4 wt% montmorillonite, the percolated network transferred from viscous liquid state to elastic solid state. Mechanical test revealed that the percolation of the montmorillonite in the cyanate ester significantly improved the crack resistance by 80% without a sacrifice of flexural strength.
Kissounko et al.\textsuperscript{86} studied the influence of an organically modified montmorillonite clay on cure mechanism of a cyanate ester resin by means of differential scanning calorimetry (DSC), FT-IR, NMR spectroscopy, and mass-spectrometry. The presence of the organically modified clay nanoparticles led to strong catalytic effect in the cure process. The catalytic effect resulted from the trace of moisture associated with the organic modifier molecules acting as moisture transport agents. Due to the presence of the clay, the polymerization mechanism of the cyanate ester was altered by firstly forming a carbamate intermediate, and then undergoing thermal decomposition by dual pathway.
Figure 2. 14: DSC thermograms for cyanate ester clay systems: (a) neat resin; (b) tetraphenylphosphonium clay.\textsuperscript{86}

Ganguli et al.\textsuperscript{9} dispersed organically modified layered silicates (OLS) into a phenolic-based cyanate resin, RS9RTM, to prepare OLS/cyanate nanocomposite. With the loading of 2.5 wt\%, the $T_g$ increased from 354 °C for neat resin to 387 °C. The fracture toughness and the flexural modulus was 30 \% higher than that of neat resin when 5 wt\% clay was added. Furthermore, the coefficient of thermal expansion and thermal stability was significantly improved as well.

Although several studies have focused on the cyanate ester/ clay nanocomposites, few have studied the curing kinetics of cyanate ester/clay nanocomposites systematically. This is vitally important, particularly for thermoset based nanocomposites. The processing ability and properties of thermoset based nanocomposites depends on various factors, such as the composition of nanocomposites (e.g. prepolymer, nanofiller, and catalyst), and influence of the nanofillers incorporated on the cross-linking reaction, which determines the final morphology. In order to develop high performance cyanate ester resin/clay nanocomposites, a clear understanding of curing dynamics and network formation in the cyanate ester resin during cure is essential, so that the properties of the cyanate ester resin/clay nanocomposites can be subsequently designed or controlled. The curing dynamics and network formation of cyanate esters may be significantly affected by the chemical behaviour of clays themselves, surface modifiers of clays, the degree of dispersion of the clay within the polymer matrix, and so on. However, the mechanisms responsible for these potential effects have never been clarified. On the other hand, in order to tailor the ever-increasing demand for thermal stability...
of cyanate ester, it is very important to study the thermal decomposition of the cyanate ester and its clay nanocomposites in system. However, this work has not been done yet.

2.2.3 Cyanate ester/carbon nanotube nanocomposites

Carbon nanotubes can be visualised as a graphene sheet that rolled into a tube. Currently, carbon nanotubes can be divided into two types, which are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The properties of nanotubes depend on varying factor, such as the diameter and length of the tubes, the atomic arrangement, and the morphology. The electrical properties of pristine carbon nanotubes are similar to that of semiconductor. The carbon nanotubes even act as superconductors when the temperature fall to ~5 K. The measured room temperature thermal conductivity of an MWCNT is as high as 3000 W/m.k. Furthermore, the calculated Young’s modulus of an individual nanotube is about 0.64 TPa. More impressively, the density-normalized modulus and strength of an individual SWNT are ~19 and ~56 times that of strongest steel wire, making it ideal for applications needing light structural materials.
Carbon nanotubes (CNTs) have been considered as one of the ideal reinforcing fillers, due to their high aspect ratio, low density and unique combination of excellent mechanical strength, electrical conductivity, thermal conductivity, and thermal stability. Polymer/carbon nanotube hybrid nanocomposites have been brought to popular attention due to the attractive reinforcement of carbon nanotubes bringing to thermoplastic matrices, such as polyethylene, polypropylene, polystyrene, poly (methyl methacrylate), and polyamide, as well as thermosetting matrices, for instance, polyimide and epoxy.
resins\textsuperscript{112-114}, phenolic,\textsuperscript{115} and polyurethane\textsuperscript{103,116,117}. Modification of cyanate ester properties with carbon nanotubes (CNTs) has also been attempted by several groups.

Fang et al.\textsuperscript{118} introduced both bundled and single multi-walled carbon nanotubes (MWCNTs) into a phenolic based cyanate ester, respectively. They found that bundled MWCNT was more easily dispersed and showed better reinforcement for toughness and stiffness of the cyanate ester. The dispersion of the two MWCNTs and mechanical and thermal properties of the nanocomposites may be further improved by grafting triethylene tetra amine groups.

Figure 2. 16: SEM images of the bending cross-sections of (A) neat CE and different CE composites with 0.5 wt % of (B) MW-CNT\textsubscript{1s}, (C) MW-CNT\textsubscript{2s}, (D) F-MW-CNT\textsubscript{1s}, and (E) F-MW-CNT\textsubscript{2s}.\textsuperscript{118}
Dominguez et al.\textsuperscript{21} improved the properties of an oligomeric cyanate ester polymer by the addition of multi-walled carbon nanotube (MWCNT). The storage modulus of a 1 wt\% MWCNT/cyanate ester nanocomposite was nearly 60\% and 600\% higher than that of the neat cyanate ester at 100 °C and 200 °C, respectively. With the incorporation of MWCNT, the glass transition temperature was increased by up to 30 °C and its thermal stability in air and nitrogen was raised by 58 °C and 25 °C, respectively. They attributed the improvements to good nanotube dispersion and effective interaction between the MWCNT and the cyanate ester.
Figure 2. 17: (left) Dynamic mechanical properties of the oligomeric cyanate ester/MWNT nanocomposites as a function of temperature and MWNT content: (A) storage modulus (G'), (B) loss modulus (G''), and (C) damping factor [tan(delta)], and (right) thermal properties of the oligomeric cyanate ester/MWNT nanocomposites as a function of MWNT content: (A) thermo-oxidative and (B) thermal stability. The insets show an expansion of the data in the 5% weight loss region.21

Che et al.119 reinforced dicyclopentadienyl bisphenol cyanate ester resin with aligned amino-functionalised signal wall carbon nanotube (SWNT), using reactive spinning involving three-stage curing. The mixture firstly underwent a pre-polymerisation at 120 °C for 100 minutes, and then was spun at 100 °C. Afterwards, the mixture was pre-cured at 80 °C for 2 hours, and then was cured at 120 °C, 140 °C and 160 °C each for 2 hours, followed by a postcure at 250 °C for 4 hours, to make dicyclopentadienyl bisphenol cyanate ester/SWNT nanocomposite fibres. The tensile strength and elongation of resulting fibres are 85% and 140 % higher than those of neat one. Furthermore, a remarkable increase of 420% in stress-strain curve area indicated that the cyanate ester was dramatically toughened by SWNTs. These improvements are believed to attribute to good dispersion, interfacial reaction and alignment of functionalised SWNTs.
Figure 2. 18: processing route used to fabricate SWNT/CE nanocomposite fiber (A), Tensile stress-strain curves for neat CE fiber, p-SWNT(1 wt %)/CE composite fiber and f-SWNT(1 wt %)/CE composite fiber. (B) and FESEM images of f-SWNT(1 wt %)/CE composite fibers: a) Longitudinal image; b) crevice-interior image; c) cross-sectional image; d) cartoon of composite fiber with aligned SWNTs showing orientation of micrographs a–c.119

Han et al.120 developed multi-walled carbon nanotubes (MWCNTs)/cyanate ester (CE) composites with low percolation threshold, high dielectric constant and excellent thermal property. It was found that the dielectric constant of all the composites increased firstly to a maximum value and then turned around to decrease. Furthermore, the dielectric constant and loss of both kinds of composites decrease dramatically with the increase of the tested frequency when reaching the percolation threshold. With the incorporation of pristine MWCNT, the glass transition temperature of CE decreased and the thermal stability was impaired. In contrary, the MWCNTs-OH significantly improved the thermal stability of CE resin.
Figure 2.19: The electrical conductivity of M/CE composites (A) and M-OH/CE (B) as a function of weight fraction of MWCNTs. The inset shows the log–log plot of conductivity with $p-p_c$ for $p > p_c$, and (C) TG and DTG curves for cured CE resin and composites. 

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27
However, few groups have focused on the curing kinetics and network formation of cyanate ester/carbon nanotube (CNTs) nanocomposites. This is vitally important, particularly for thermoset based nanocomposites. For example, the processing ability and properties of thermoset based nanocomposites depends on various factors, such as the composition of nanocomposites, dispersion of nanofillers, and influence of the nanofillers on the cross-linking reaction. In order to develop high performance cyanate ester resin/CNT nanocomposites, a clear understanding of curing dynamics and network formation in the cyanate ester resin during cure is essential, so that the properties of the cyanate ester resin/CNT nanocomposites can be subsequently designed or controlled. On the other hand, in order to tailor the ever-increasing demand for thermal stability of cyanate esters, it is very important to study the thermal decomposition of the cyanate ester and its carbon nanotube nanocomposites in system. However, this work has not been done yet.

2.3 Thermal curing kinetics and thermal curing monitoring study
In order to develop high performance cyanate ester matrix nanocomposites, the effect of nanofillers on the curing dynamics need to be clarified. Furthermore, a clear understanding of network formation in the cyanate resin during cure is essential, as it drives the complex changes in morphology and structure of the cyanate ester matrix nanocomposites during processing operations. Through the curing kinetics study, the properties of the cyanate ester based nanocomposites can be successfully predicted and controlled. There have been a number of reports on the catalysed network formation kinetics of cyanate esters and cyanate ester matrix nanocomposites. The common techniques employed to study mechanism and kinetics of polymerisation of cyanate ester resins, include solid state $^{13}$C NMR, FTIR spectroscopy, Raman spectroscopy, DSC and so on.

2.3.1 Traditional catalysts employed for polymerisation of cyanate esters
The cure reaction of cyanate esters is currently known to be catalysed by a large variety of materials, such as transition metal carboxylates (e.g. dibutyl tin dilaurate), acetyl acetonates, phenols, metal carbonyls and so on. Although cyanate ester based technology has been rapidly improved, the basic network formation and cure mechanism are remain disputed. It is generally accepted that the cyanate esters undergo cyclo trizmeration to form crosslinked...
polycyanurates. It has been reported that the actual mechanism appears to be catalyst dependent. It is believed that the cyanate groups are coordinated through the metal ion to allow ring closure through a step growth or ionic path, with the presence of active hydrogen donor, as shown in Figure 2.20. When an externally added catalyst is absent, the reaction is believed to be catalysed by adventitious water and residual hydrogen donating impurities, such as phenol.\textsuperscript{121}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{proposed_mechanism}
\caption{Proposed mechanism for the metal ion catalysed polymerisation of cyanate ester\textsuperscript{2}}
\end{figure}

Mathew et al.\textsuperscript{4} reported a kinetic study of the thermal cure reaction of bisphenol A dicyanate (BACY) in the presence of various catalysts. They investigated the catalytic efficiency of various transition metal acetyl acetonates and dibutyl tin dilaurate (DBTDL) in terms of the kinetic activation parameters and established the correlations between the catalytic efficiency and the characteristics of the transition metal acetyl acetonates, using dynamic differential scanning calorimetry (DSC). It is reported that the cure reaction was divided into two stages, a pre-gel stage corresponding to around 60% conversion and a post-gel stage beyond that. The activation energy (E), pre-exponential factor (A), and order of reaction (n) were derived by using Coats-Redfern Equation\textsuperscript{122}, which is shown as follows

\[
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\phi_E} \right) \left( 1 - \frac{2RT}{E} \right) - \frac{E}{RT} \hspace{1cm} 2.1
\]
Where, $\alpha$ is the fractional conversion at temperature $T$, $\theta$ is the heating rate, $E$ is the activation energy, $A$ is the Arrhenius frequency factor, $n$ is the reaction order, $g(\alpha) = [1-(1-\alpha)^{1-n}]/(1-n)$, and $R$ is the gas constant.

The reaction order of 1.5 was determined from the best fit linear plots of $\ln(g(\alpha)/T^2)$ against $1/T$ for different values of $n$. The other kinetic constants were determined from the linear plots of equation 2.1, using the predetermined optimum value of $n$, 1.5.

The normalised activation energy showed a systematic decrease with increase in catalyst concentration, as shown in Figure 2.21. The catalytic efficiency, measured in terms of the decrease in $E$ value, also varied depending on the nature of the coordinated metal and stability of the acetyl acetonate complex. The catalytic activity increased in the order of Mn$^{+2}$ > Ni$^{+2}$ > Zn$^{+2}$ > Cu$^{+2}$ for divalent ions and in the order of Fe$^{+3}$ > Co$^{+3}$ > Cr$^{+3}$ for the trivalent metals, which in both cases are opposite to the order of stability of the complexes. Manganese and iron acetyl acetonates were identified as the most efficient catalysts.

Figure 2. 21: Variation of normalized activation energy with concentration of DBTDL and ferric acetyl acetonate for the catalyzed polymerization of BACY$_4$
2.3.2 Cure kinetics of cyanate ester based nanocomposites.

Wu et al.\textsuperscript{123} studied the cure kinetics and mechanisms of a cyanate ester and its blends with poly(phenylene oxide) (PPO) by using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). To evaluate the cure kinetics of cyanate ester/PPO blends, an autocatalytic model (equation 2.2) which is derived from Simon and Gillham’s kinetic scheme\textsuperscript{5}, was used.

\[
\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^2
\]  

Both \(k_1\) and \(k_2\) depend on the temperature according to an Arrhenius law:

\[
k_i = A_i \exp \left( \frac{-E_i}{RT} \right)
\]

Where, \(\alpha\) is the degree of conversion, \(m\) is the reaction order, \(k\) is the rate constant, \(A\) is the pre-exponential constant, \(E\) is the activation energy, \(R\) is the gas constant, and \(T\) is the absolute temperature.

The results showed that the reaction rates of cyanate ester/PPO blends were higher than that of pure cyanate ester at the very beginning of the reaction. The conversion decreased with the increasing PPO content. Furthermore, a diffusion factor \(f(\alpha)\) developed by Chern and Poehlein\textsuperscript{124} was introduced to predict the cure kinetics over the whole range.

\[
f(\alpha) = \frac{k_2}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]}
\]
2.4 Benzoxazine and its nanocomposites

2.4.1 A brief story about Benzoxazine.

Recently, polybenzoxazine which is a newly developed polymerised phenolic system, has received a wide range of concerns, due to its good mechanical performance, molecular design flexibility, and thermal and flame retardance properties. More important point placed the polybenzoxazine under spotlight is that it overcomes the problems of traditional novolac and resole phenolic systems, such as, poor shelf life. The polybenzoxazine also performs several unique features, (a) near-zero shrinkage upon curing, (b) low water absorption, (c) Tg much higher than cure temperature for some polybenzoxazine based materials, (d) relatively
good thermal stability, (e) no strong acid catalysts required for curing, and (f) release of no by-products during curing.\textsuperscript{126}

As shown in Figure 2.23, Benzoxazine is a single benzene ring fused to another oxazine ring which contains one oxygen atom and a nitrogen atom. Synthesis of benzoxazine occurs through the reaction of phenol, formaldehyde, and amine. During thermal curing, the benzoxazine undergoes ring opening polymerization to form polybenoxazine. Furthermore, depending on the relative positions of the two heteroatoms of this oxazine ring, the benzoxazines can form a number of derivatives. Thus, the molecular structure of benzoxazines offers themselves great design flexibility for properties, to tailor for different applications.

![Synthesis of bisbenzoxazine monomer (A), and ring opening polymerization of bisbenzoxazines (B).\textsuperscript{127}](image)

Figure 2. 23: Synthesis of bisbenzoxazine monomer (A), and ring opening polymerization of bisbenzoxazines (B).\textsuperscript{127}
2.4.2 Benzoxazine based nanocomposites.

Although polybenzoxazines possess a lot of unique features, there are some shortcomings, for example, low process ability, and high curing temperature. In order to overcome these shortages during applications, benzoxazine is usually mixed with other polymers and fillers to prepare polymer blends and composites. It has been reported that benzoxazine was blended with rubber and polycarbonate to improve toughness, poly (e-caprolactone) (PCL) to improve process ability, polyurethane (PU), and epoxy. Apart from polymer blends, the influence of the incorporation of nanofillers on properties of benzoxazine has been studied by a few groups.

Lee et al. incorporated a hydrosilane-functionalized polyhedral oligomeric silsesquioxane (H-POSS) into vinyl-terminated benzoxazine monomer, and then subjected to ring opening polymerisation, to prepare POSS/polybenzoxazine nanocomposite. With the incorporation of 5wt% H-POSS, The glass transition temperature \( T_g \) increased from 307°C to 333°C. Furthermore, the improvement of thermal stability of POSS/polybenzoxazine nanocomposites was indicated by increase of the degradation temperature and char yield with the increasing POSS content.
Figure 2. 24: TGA of polymeric benzoxazine composites containing different H-POSS content (A), and SEM cross sectional micrographs of polybenzoxazine/POSS nanocomposites (B).  

Huang et al.\textsuperscript{142} prepared polybenzoxazine/POSS nanocomposites through the reactions of a multifunctional vinyl-terminated benzoxazine-POSS with a benzoxazine monomer at various compositional ratios. The mobility of the benzoxazine network was significantly hindered with the incorporation of the silsesquioxane core units. Furthermore, the thermal stability and mechanical properties of the nanocomposites were gradually improved with the increasing POSS content.
Agag and Takeichi\textsuperscript{143} demonstrated the preparation of polybenzoxazine-clay nanocomposites by the in-situ polymerization of allyl functionalised benzoxazine monomer, in the presence of two different types of organoclay. The glass transition temperature ($T_g$) of the nanocomposites decreased firstly, and then turned around to increase with the increasing organoclay content. These results implied that the change of curing mechanism and network formation of the benzoxazine with the incorporation of organoclays. Furthermore, the thermal stability of the nanocomposites was better than that of the neat resin.
Figure 2.26: (A) Effect of organoclay on the Tg of the benzoxazine/clay nanocomposites, (B) TGA of PDS-MMT based hybrids; (a) neat resin, (b) 3% PDS-MMT hybrid, (c) 5% PDS-MMT hybrid, and (d) 10% PDS-MMT hybrid; and (C) TGA of ADS-MMT based hybrids, (a) neat resin, (b) 3% ADS-MMT hybrid, (c) 5% ADS-MMT hybrid, and (d) 7% ADS-MMT hybrid.\textsuperscript{143}

Wang et al.\textsuperscript{144} firstly functionalised multi-walled carbon nanotubes (MWCNTs) using benzoxazine-containing compound (BPA-FBz) and polymer (PFBz) as modifiers through a Diels-Alder reaction. They then fabricated MWCNT-FBz and MWCNT-PFBz crosslinked nanomaterials by using press moulding and other thermal-forming processes. The surface electrical conductivities and electrical conductivities of the crosslinked pellets of MWCNT-FBz and MWCNT-PFBz were measured as 0.05 S cm\textsuperscript{-1} and 7 x 10\textsuperscript{-5} S cm\textsuperscript{-1}. It is believed that the attractive properties were attributed to the good compatibility between the polybenzoxazine matrix and MWCNT-FBz.
Figure 2.27: (A) thermally-cured pellets of benzoxazine-functionalization MWCNTs. Photographs (a) and SEM micrographs (b, c), and (B) TEM micrographs of thermally cured nanocomposites of BPA-FBz and MWCNT-FBz.144
However, few groups have focused on the curing kinetics and network formation of benzoxazine based nanocomposites. This is vitally important, particularly for thermoset based nanocomposites. For example, the processing ability and properties of thermoset based nanocomposites depends on various factors, such as the composition of nanocomposites, dispersion of nanofillers, and influence of the nanofillers on the cross-linking reaction. In order to develop high performance benzoxazine based nanocomposites, a clear understanding of curing dynamics and network formation in the benzoxazine resin during cure is essential, so that the properties of the benzoxazine based nanocomposites can be subsequently designed or controlled. On the other hand, in order to meet the ever-increasing demand for thermal stability of benzoxazine, it is very important to study the thermal decomposition of the benzoxazine and its nanocomposites in system. However, this work has not been done yet.
CHAPTER 3: EXPERIMENTAL METHODOLOGIES

3.1 Materials

Cyanate phenolic resin (CY), PRIMASET® PT-30, was purchased from Lonza Ltd. The CY has a low viscosity (80 c.p.s.) at its processing temperature (120 °C), and has less than 0.5% volatiles and generates no gaseous by-products during cure. Araldite® MT 35600 CH Bisphenol-A Benozoxazine resin (BEN) was provided by Huntsman Ltd. TriSilanolPhenyl POSS (C_{42}H_{38}O_{12}Si_{7} MW=931.34 g/mol) was purchased from Hybrid Plastics Inc. The unmodified sodium clay (Cloisite® Na+) and the organoclay (Cloisite® 20A and Cloisite® 30B) were purchased from Southern Clay Products, Inc. The modifier for Cloisite® 20A is dimethyl, dehydrogenated tallow, quaternary ammonium (2M2HT). For Cloisite® 30B, it is methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (MT2EtOH). The pristine multi-walled carbon nanotube (MWCNT), functionalised multi-wall carbon nanotubes (MWCNT-OH and MWCNT-COOH), and functionalised single-wall carbon nanotube (SWCNT-OH) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Science. The multi-wall carbon nanotubes (MWCNTs) have a length of approximate 50μm and a diameter of 8–15 nm. For the hydroxyl functionalised single-walled carbon nanotube used (SWCNT-OH), the length is between 5μm to 30μm, and the diameter is 1 to 2 nm. Figure 3.1 shows a schematic of the respective molecular structures for the CY, POSS, and modifier for Cloisite® 20A and Cloisite® 30B. All the solvents used were purchased from Sigma-Aldrich Ltd. UK.
Figure 3.1: Schematic of molecular structure of (A) possible structure of the CY, (B) structure of the BEN, (C) POSS, (D) modifier for Cloisite® 30B, and (E) modifier for Cloisite® 20A. The anion is chloride, T is tallow (~65% C18; ~30% C16; ~5% C14), and HT is hydrogenated tallow.

3.2 Preparation of CY mixtures incorporated with the nanofillers

CY/POSS mixtures were prepared as follows. The cyanate ester resin, CY, was firstly held at 100°C for 30 minutes with magnetic stirring to remove moisture. Afterwards, the CY was heated to 120°C, and then calculated amounts of the trisilanolphenyl POSS were added into the low viscosity resin to prepare the CY/POSS mixtures with different POSS contents. These mixtures were magnetically stirred at 120°C for 80 minutes. After mixing, all the CY/POSS resins prepared were sealed in glass bottles and were stored at -20°C until further use.

CY/clay mixtures were prepared as follows. The cyanate ester resin, CY, was firstly held at 100°C for 30 minutes in a vacuum oven to remove moisture. Afterwards, the CY was held at 90°C with magnetic stirring, and calculated amounts of the clays were added into the low viscosity resin. The resulting mixtures were then stirred for about 2 hours. After mixing, all the CY/clay resins prepared were sealed in glass bottles and stored at -20°C until further use.

CY/CNT mixtures were prepared by the following procedure. CNTs were firstly dispersed in chloroform (1mg/1ml) with assistance of ultrasonication (300 W power, 30 min) at room
temperature. The cyanate ester resin, CY, was held at 100°C for 30 min in a vacuum oven to remove moisture, and then was dissolved in chloroform. Following this, the CY/chloroform solution was mixed with the CNT/chloroform solution with magnetic stirring for 2 hours. The solvent was then volatilised. The resultant was further dried in a vacuum oven at 80°C. The CY/CNTs mixtures prepared were sealed in glass bottles and stored at -20°C for further use.

3.3 Preparation of CY based nanocomposites
The CY/POSS resins were firstly pre-cured at 100°C in vacuum oven for 30 minutes, to make sure all the moisture was removed. Afterwards, the CY/POSS resins were cured at 230°C for 1 hour, and followed by post-curing at 290°C for another 1 hour.

The CY/clay resins were firstly pre-cured at 100°C in vacuum oven for 30 minutes, to make sure all the moisture was removed. Afterwards, the CY/clay resins were cured at 190°C for 1 hour, and followed by post-curing at 290°C for another 1 hour.

The CY/CNT resins were firstly pre-cured at 100°C in vacuum oven for 30 minutes, to make sure all the moisture was removed. Afterwards, the CY/CNT resins were cured at 220°C for 1 hour, and followed by post-curing at 290°C for another 1 hour.

3.4 Preparation of BEN mixtures incorporated with the nanofillers
All BEN mixtures incorporated with clays and POSS were prepared as follows. The BEN resin was firstly held at 100°C for 30 minutes with magnetic stirring to remove moisture. Next, the BEN was heated to 120°C, and calculated amounts of the nanofillers were added into the low viscosity resin to prepare the mixtures. These mixtures were stirred at 120°C for 120 minutes. After mixing, all the mixtures prepared were sealed in glass bottles and stored at -20°C for further use.

BEN/CNT mixtures were prepared by the following procedure. CNTs were firstly dispersed in acetone (1mg/1ml) with assistance of ultrasonication (300 W power, 30 min) at room temperature. The BEN was held at 100°C for 30 min in a vacuum oven to remove moisture, and then was dissolved in acetone. Following this, the BEN/acetone solution was mixed with the BEN/acetone solution with magnetic stirring for 2 hours. The solvent was then volatilised.
The resultant was further dried in a vacuum oven at 80°C. The BEN/CNTs mixtures prepared were sealed in glass bottles and stored at -20°C for further use.

3.5 Preparation of BEN based nanocomposites

The BEN based mixtures were firstly pre-cured at 100°C for 30 minutes, to make sure all the moisture was removed. Afterwards, the mixtures were cured at 200°C for 2 hours, and followed by post-curing at 260°C for another 2 hours.

3.6 Characterization

A TA Instruments DSC 2920 calorimeter was employed for Differential Scanning Calorimetry (DSC) and Modulated-Temperature Differential Scanning Calorimetry (MTDSC) measurements. Nitrogen was used as the purge gas (60 ml/min). All the dynamic experiments were carried on using DSC. Samples were heated from 50°C to 350°C with a heating rate of 10°C/min. For all the quasi-isothermal experiments, MTDSC was employed. Samples were held at selected temperatures with a modulation amplitude of 0.5°C per 60 seconds.

Fourier transform infrared (FTIR) spectra of the sample coated on KBr pellet were recorded from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) using a Shimadzu FTIR-8400s spectrophotometer with a 4 cm\(^{-1}\) resolution over 128 scans. Raman spectra were recorded from 100 cm\(^{-1}\) to 3500 cm\(^{-1}\), on a Jobin Yvon Horiba high-resolution LabRam 800 Raman microscope system, which contains an optical microscope adapted to a double grating spectrograph and a CCD array detector. The laser excitation was provided by a Spectra-Physics model 127 helium–neon laser operating at 35 mW of 633 nm output. All the samples for FTIR and Raman experiments were cured in a DSC cell in N\(_2\) atmosphere (60ml/min).

To determine whether the clays were fully exfoliated in the CY matrix, X-ray diffraction (XRD) patterns of the CY/clay nanocomposites were obtained by using a Philip-X9 Pert X-ray diffractometer (anode 40 kV, filament current 35 mA) with nickel-filtered CuKa (\(\lambda\) = 0.1542 nm) radiation at a scan speed of 1°/min.

To observe the dispersion of the nanofillers in the CY matrix, scanning electron microscopy (SEM) images of the fracture surface of the CY/POSS nanocomposites were taken by field
emission gun scanning electron microscopy (FEGSEM) (LEO 1530VP instrument). The samples were fractured at room temperature. The samples with fractured surface on the top were placed on specimen holder using double-sided carbon conductive tap. Gold coating was applied for better conductivity. Transmission electron microscopy (TEM) was employed to observe the state of the nanofillers in the CY matrix as well, using a JEOL 2100 FX instrument. The CY based nanocomposites were cut into the ultra-thin films using a microtome, and then were dropped on a copper grid for direct TEM imaging.

Thermogravimetric Analysis (TGA) was performed on a DSC-TGA 2950 instrument. The samples were heated from room temperature to 1000°C at a heating rate of 10°C/min (5 and 15°C/min for the measurement of activation energy). The rate of gas (air or nitrogen) was 60ml/min.
CHAPTER 4: PROCESSABILITY OF CYANATE ESTER BASED NANOCOMPOSITES

4.1: Catalysts, initiators, and solvents investigation

One of universal issues that draws the growing concern of scientists and engineers is high curing temperature of cyanate esters, which has been hampering their application. In order to reduce curing temperature, catalysts can be applied. However, some side effects, such as incomplete network formation leading to poor performance, will be accompanied with the incorporation of some catalysts. On the other hand, although a few research studies about the influence of catalysts on the cure of cyanate ester have been carried out, the catalytic effect for different cyanate ester may be different. Thus, it is necessary to investigate the catalytic effect that traditional catalysts bring to the cure of the specific cyanate ester used in this project. Furthermore, in order to achieve good dispersion in some cyanate ester based nanocomposites, such as CNT/cyanate ester nanocomposites, addition of solvents to assist is necessary. Nevertheless, the influence of solvents to the cure of the cyanate ester has never been clarified. Here, the influence of several catalysts, initiators and solvents on the curing dynamics of the CY was explored.

Table 4.1 lists the general information of the catalysts investigated. Figure 4.1 shows DSC plots against temperature for the CY with different catalysts in a nitrogen atmosphere (60ml/min) with a heating rate of 10°C/min. Table 4.2 summarises onset, peak and end temperatures, enthalpy of the non-isothermal cure. The ferric (Iron(III)) acetylacetonate and dibutyltin dilaurate showed significant catalytic effect. The peak temperatures decreased by about 160 °C with incorporation of only 1 wt% of ferric (Iron(III)) acetylacetonate and dibutyltin dilaurate. It should be noticed that manganous (manganese(II)) acetylacetonate could display similar catalytic effect. The inapparently catalytic performance in the DSC experiment for manganous (manganese(II)) acetylacetonate should be relative to its low concentration. It can be concluded that the catalytic effect of acetylacetonate based metallic catalysts depends on their concentration. Furthermore, with the catalysts, the reaction enthalpy of the CY declined dramatically, which implied that the incorporation of the catalysts led to incomplete network formation of the CY. Thus, application of the traditional catalysts to reduce the curing temperature of the CY is not recommended, if good
performance of the cured CY and its nanocomposites is desired.

Table 4.1: General information of the catalysts investigated.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure scheme</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyanate ester resin, PRIMASET® PT-30</td>
<td><img src="image1.png" alt="Structure Scheme" /></td>
<td>Fe(C₅H₇O₂)₃</td>
<td>131 g/mol -OCN</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Ferric (Iron(III)) acetylacetonate</td>
<td><img src="image2.png" alt="Structure Scheme" /></td>
<td>Fe(C₅H₇O₂)₃</td>
</tr>
<tr>
<td></td>
<td>Manganous (manganese(II)) acetylacetonate</td>
<td><img src="image3.png" alt="Structure Scheme" /></td>
<td>[CH₃COCH=CHOCH₃]₂Mn</td>
</tr>
<tr>
<td></td>
<td>1,4,7,10,13,16-Hexaoxaacyclooctadecane (18-Crown-6)</td>
<td><img src="image4.png" alt="Structure Scheme" /></td>
<td>C₁₂H₂₄O₆</td>
</tr>
<tr>
<td></td>
<td>Dibutyltin dilaurate (DBTDL)</td>
<td><img src="image5.png" alt="Structure Scheme" /></td>
<td>(CH₃CH₂CH₂CH₂)₂Sn[OCO(CH₂)₁₀CH₃]₂</td>
</tr>
</tbody>
</table>
Figure 4.1: DSC plots of the CY with different catalysts in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

Table 4.2: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of the CY with different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (wt%)</th>
<th>Concentration (mmol/mol-OCN)</th>
<th>Onset Temperature (°C)</th>
<th>Peak Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CY</td>
<td>0</td>
<td>0</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
</tr>
<tr>
<td>Crown ether</td>
<td>1</td>
<td>5</td>
<td>210</td>
<td>299</td>
<td>340</td>
<td>13</td>
<td>304</td>
</tr>
<tr>
<td>DBTDL</td>
<td>1</td>
<td>2</td>
<td>81</td>
<td>137</td>
<td>176</td>
<td>9.5</td>
<td>318</td>
</tr>
<tr>
<td>Iron(III)</td>
<td>1</td>
<td>3.7</td>
<td>89</td>
<td>144</td>
<td>180</td>
<td>9.1</td>
<td>287</td>
</tr>
<tr>
<td>manganese(II)</td>
<td>0.04</td>
<td>0.2</td>
<td>124</td>
<td>295</td>
<td>345</td>
<td>22.1</td>
<td>492</td>
</tr>
</tbody>
</table>

Figure 4.2 shows DSC plots against temperature for CY/BPO in a nitrogen atmosphere (60ml/min) with a heating rate of 10°C/min. Table 4.3 lists the general information of the initiator investigated. Table 4.4 summarises onset, peak and end temperatures, enthalpy of the non-isothermal cure. The addition of BPO showed a catalytic effect, which was influenced by the concentration of BPO. The reaction of CY/BPO system involved two reactions, and this observation implies that the curing mechanism was changed due to the presence of the BPO. Furthermore, the reaction enthalpy did not decrease with the incorporation of BPO, which
indicated that the incorporation of BPO did not have a serious side effect on the network formation of the CY.

Table 4.3: General information of the initiators investigated.

<table>
<thead>
<tr>
<th>Catalogue</th>
<th>Material</th>
<th>Structure scheme</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
<th>$t_{1/2}=10\text{h}$ at</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator</td>
<td>Dibenzoyl peroxide (BPO)</td>
<td>![Structure]</td>
<td>(C$_6$H$_5$CO)$_2$O$_2$</td>
<td>242.23</td>
<td>73°C</td>
</tr>
<tr>
<td></td>
<td>Dicumyl peroxide (CPO)</td>
<td>![Structure]</td>
<td>[C$_6$H$_5$C(CH$_3$)$_2$]$_2$O$_2$</td>
<td>270.37</td>
<td>115°C</td>
</tr>
</tbody>
</table>

Figure 4.2: DSC plots of the CY/BPO systems in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.
Table 4.4: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/BPO systems.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Onset Temperature (°C)</th>
<th>Peak 1 Temperature (°C)</th>
<th>Peak 2 Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>$\Delta H_{peak1}$ (J/g)</th>
<th>$\Delta H_{peak2}$ (J/g)</th>
<th>$\Delta H_{total}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CY</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 wt% BPO</td>
<td>99</td>
<td>140</td>
<td>273</td>
<td>327</td>
<td>22.8</td>
<td>61</td>
<td>425</td>
<td>486</td>
</tr>
<tr>
<td>10 wt% BPO</td>
<td>99</td>
<td>141</td>
<td>261</td>
<td>314</td>
<td>21.5</td>
<td>98</td>
<td>340</td>
<td>438</td>
</tr>
<tr>
<td>15 wt% BPO</td>
<td>98</td>
<td>141</td>
<td>252</td>
<td>305</td>
<td>20.7</td>
<td>163</td>
<td>326</td>
<td>489</td>
</tr>
</tbody>
</table>

Figure 4.3 shows DSC plots against temperature for CY/CPO in a nitrogen atmosphere (60 ml/min) with a heating rate of 10°C/min. Table 4.5 summarises onset, peak and end temperatures, enthalpy of the non-isothermal cure. The CPO displayed a similar catalytic effect to BPO. The difference lies on the first stage reaction. The CPO showed higher reaction temperature in first stage reaction, which is due to its higher decomposition temperature.

Figure 4.3: DSC plots of the CY/dicumyl peroxide systems in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.
Table 4.5: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/Dicumyl peroxide systems.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Onset Temperature (°C)</th>
<th>Peak 1 Temperature (°C)</th>
<th>Peak 2 Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>△H_{peak1} (J/g)</th>
<th>△H_{peak2} (J/g)</th>
<th>△H_{total} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CY</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5 wt% CPO</td>
<td>157</td>
<td>186</td>
<td>275</td>
<td>320</td>
<td>16.3</td>
<td>11</td>
<td>284</td>
<td>295</td>
</tr>
<tr>
<td>5 wt% CPO</td>
<td>152</td>
<td>184</td>
<td>272</td>
<td>316</td>
<td>16.4</td>
<td>22</td>
<td>301</td>
<td>323</td>
</tr>
<tr>
<td>10 wt% CPO</td>
<td>137</td>
<td>186</td>
<td>253</td>
<td>313</td>
<td>17.6</td>
<td>376</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.4 shows DSC plots against temperature for CY prepared in different solvents in a nitrogen atmosphere (60ml/min) with a heating rate of 10°C/min. Table 4.6 lists the general information of the solvents investigated. Table 4.7 summarises onset, peak and end temperatures, enthalpy of the non-isothermal cure. For all samples, the CY firstly dissolved in the solvent with magnetic stirring for 1 h, and then the solvent was volatilised. The resultants were further dried in the vacuum oven. The chloroform did not show a prominent catalytic effect on the CY. The acetone and cyclohexane did not show remarkable catalytic effect, but the reaction enthalpy decreased. The DMF and THF showed catalytic effect, whilst the THF performed better. There are two reactions involved for the CY prepared in THF and cyclohexane, which indicates that the curing mechanism of the CY was changed. Thus, in order to investigate the influence of the nanofillers on the cure of the CY clearly, acetone and chloroform is the first choice.
Table 4.6: General information of the solvents investigated.

<table>
<thead>
<tr>
<th>Catalogue</th>
<th>Material</th>
<th>Structure scheme</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Cyclohexane</td>
<td></td>
<td>C₆H₁₂</td>
<td>84.16</td>
<td>80.7</td>
</tr>
<tr>
<td></td>
<td>Tetrahydrofuran (THF)</td>
<td></td>
<td>C₄H₈O</td>
<td>72.11</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Dimethylformamide (DMF)</td>
<td></td>
<td>HCON(CH₃)₂</td>
<td>73.09</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td></td>
<td>CH₃COCH₃</td>
<td>58.08</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>Methylidyne trichloride (Chloroform)</td>
<td></td>
<td>CHCl₃</td>
<td>119.38</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure 4. 4: DSC plots of the CY prepared in various solvents in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

Table 4. 7: Onset, peak and end temperatures, and enthalpy of the non-iso thermal cure of CY/ prepared in various solvents.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>Onset Temperature (°C)</th>
<th>Peak 1 Temperature (°C)</th>
<th>Peak 2 Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>ΔH_{peak1} (J/g)</th>
<th>ΔH_{peak2} (J/g)</th>
<th>ΔH_{total} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat CY</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>222</td>
<td>302</td>
<td>335</td>
<td>11.3</td>
<td>412</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
<td>123</td>
<td>157</td>
<td>292</td>
<td>345</td>
<td>22.2</td>
<td>32</td>
<td>430</td>
<td>452</td>
</tr>
<tr>
<td>DMF</td>
<td>145</td>
<td>243</td>
<td>322</td>
<td>17.7</td>
<td>604</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>123</td>
<td>167</td>
<td>230</td>
<td>300</td>
<td>17.7</td>
<td>450</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>227</td>
<td>299</td>
<td>333</td>
<td>10.6</td>
<td>491</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2 Morphology of the CY based mixtures

Figure 4.5 shows the digital pictures of CY resins incorporated with different nanofillers. It is showed clearly that the mixed resins are all homogenous. The neat CY resin is transparent and light yellow liquid with high viscosity. After incorporating with POSS, the resin stays transparent, but becomes dark yellow. With addition of the MWCNT, the resin turns to black, and the viscosity becomes very high. For the clay/CY systems, the Na⁺/CY resin is translucent and dark yellow. The 30B/CY resin is transparent and dark yellow. The 20A/CY resin is translucent and milky white.
4.3 Morphology of the CY based nanocomposites

Figure 4.6 shows the digital pictures of CY and CY based nanocomposites. For the POSS/CY and clay/CY nanocomposites, there are no problems with curing and further processing. For the CNT/CY system, in theory, there is no problem for preparation of mixed resins and the later nanocomposites. However, in practice, there are several problems. The residual solvent in the CNT/CY resins is very hard to remove, even if the resins remained at 120°C in vacuum for 7 days. When the CNT/CY resins were cured, the residual solvent separating out caused much smoke. During cure, the CNT/CY resins became extremely flammable, due to the presence of the residual solvent. Furthermore, the viscosity for the CNT/CY resins were too high to flow, thus, it is hard to shape the resins without pressure. After cure, the residual solvent separating out led to many voids and cracks in the nanocomposites, resulting in loose structures. Hence, if the CNT/CY nanocomposites are desired in further applications, a solvent free method for preparation will be essential.
Figure 4. 6: digital pictures of the CY based nanocomposites. (A) neat CY, (B) 5wt% POSS/CY, (C) 3wt% Na+/CY (D) 3wt% 30B/CY, (E) 3wt% 20A/CY, (F) 2wt% SWCNT-OH/CY, (G) 2wt% MWCNT-OH/CY, and (H) 2wt% MWCNT/CY.
4.4 Dispersion of the nanofillers in the CY

![SEM images of composites of CY with 1 wt% POSS (A and B), 5 wt% POSS (C and D), and 10 wt% POSS (E and F).](image)

Figure 4.7: SEM images of the composites of CY with 1 wt% POSS (A and B), 5 wt% POSS (C and D), and 10 wt% POSS (E and F).

Figure 4.7 shows the SEM images of the CY incorporated with POSS in different concentrations. It can be shown clearly that the dispersion of the POSS in the CY is homogeneous. For the CY/POSS nanocomposite with low concentration, such as 1 wt%, there is no aggregation of POSS found. For the CY/POSS nanocomposites with high concentration, such as 5 wt% and 1 wt%, a few particles with diameter of about 700 nm are observed. These results indicate that the aggregation of the POSS molecules occurred with the high percentages.
Figure 4.8 shows SEM and TEM images of the pure CY and the various CY/clay nanocomposites cured at 190°C for 1 hour and post cured at 290°C for a further hour. For the 3wt% 20A/CY nanocomposite, aggregation was observed. As shown in Figure 4.8 (C) and (D), for the 3wt% 30B/CY nanocomposite and the 3 wt% Na⁺/CY nanocomposite, the dispersion of the clays is quite good, no gross phase separation being shown. The difference between the three clays lies in the modifier. Owing to the presence of original inner hydroxyl groups, the Na⁺ clay is compatible with the hydrophilic CY resin. For the 30B clay, the modifier containing hydrophilic –OH groups make the clay more compatible with the CY resin than the unmodified Na⁺ clay. However, the modifier for the 20A clay is hydrophobic, which led to the aggregation of 20A clay. From Figure 4.8 (E) and (F), it is clear that the 30B and Na⁺ clays were exfoliated.
To examine the state of clay layers further for the different clays in the CY matrix, the d-spacings of 30B clay, Na\(^+\) clay, 3wt\% CY/30B nanocomposite and 3wt\% CY/Na\(^+\) nanocomposite were measured using XRD and the results are shown in Figure 4.9. The original d-spacings of the clays for Na\(^+\), and 30B were 1.17 nm and 1.85 nm, respectively. For the 3wt\% CY/30B nanocomposite and the 3wt\% CY/Na\(^+\) nanocomposite, it was noted that there was no peak in the range of 1° to 10°. This result also indicated the exfoliation of Na\(^+\) and 30B in the CY matrix.

![Figure 4.8: SEM images of (A) CY, (B) 3wt\% 20A/CY nanocomposite, (C) 3wt\% 30B/CY nanocomposite, and (D) 3wt\% Na\(^+\)/CY nanocomposite, and TEM images of (E) 3wt\% 30B/CY nanocomposite and (F) 3wt\% Na\(^+\)/CY nanocomposite.](image)

![Figure 4.9: XRD patterns for Na\(^+\) clay, 30B clay and their CY/clay nanocomposites.](image)
Figure 4.10 shows SEM images of the various CY/CNT nanocomposites (all at 2 wt%). All the MWCNTs were well dispersed at a nano-scale level in the CY matrix, with no indication of aggregation taking place. However, for the SWCNT-OH/CY system, SWCNT-OH bundles were visible on the micro-scale.
Figure 4. 10: SEM images of the composites of CY with 2 wt% MWCNT-COOH (A and B), 2wt% MWCNT-OH/CY (C and D), 2 wt% MWCNT (E and F), and 2 wt% SWCNT-OH (G and H)

4.5 Summary

The influence of several catalysts, initiators and solvents on the curing dynamics of the CY was explored by means of DSC. For the catalysts, ferric (Iron(III)) acetylacetonate and dibutyltin dilaurate showed significant catalytic effect. Furthermore, the catalytic effect of acetylacetonate based metallic catalysts depends on their concentration. However, with the catalysts, the reaction enthalpy of the CY declined dramatically, which implied that the incorporation of the catalysts led to incomplete formation of the CY network. For the initiators, the addition of BPO and CPO showed catalytic effect. The catalytic effect was influenced by the concentration. The reaction of the CY/initiator system involved two reactions, which implies that the curing mechanism was changed. For the solvents, chloroform, acetone, and cyclohexane did not show prominent catalytic effect on the CY. The DMF and THF showed catalytic effect, among which THF performed better. There are two reactions involved for the CY prepared in THF and cyclohexane, which indicates that the curing mechanism of the CY was changed.

The clays and POSS can be mixed directly with the CY resin to form homogenous mixtures. For the CNTs, in order to achieve good dispersion, assistance of solvent and ultasonication is necessary. For the POSS/CY and clay/CY nanocomposites, there is no any problem for curing and further processing. For the CNT/CY system, there are several problems. The residual solvent separating out made much smoke during the cure. During cure, the CNT/CY resins became extremely flammable, due to presence of the residual solvent. Furthermore, the
viscosity for the CNT/CY resins were too high to flow, thus, it is hard to shape the resins without pressure. After cure, the residual solvent separating out led to many voids and cracks in the nanocomposites, resulting in loose structures.

The nano-scale dispersion of the POSS, Na+ and 30B clays, and MWCNTs was observed using SEM and TEM. XRD results indicate that the Na+ and 30B clays were exfoliated in the CY matrix. For the 20A/CY nanocomposites, visible aggregation was observed after the cure. For the SWCNT/CY nanocomposites, micro-scale aggregation was detected by means of SEM.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

5.1 Cyanate Ester Resin /Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites

Figure 5.1 shows DSC plots of the curing process of CY/POSS systems in a nitrogen atmosphere (60ml/min) with a heating rate of 10°C/min. Table 5.1 lists the non-isothermal curing temperature, curing period and heat of reaction for the different CY/POSS systems. The onset temperature fell dramatically from 257°C for the pure CY until it reached a minimum of 199 °C for the incorporation of 5 wt% POSS. In contrast, the peak temperature continued to decrease with increasing POSS content. A 10 wt% loading of POSS, resulted in a reduction in the peak temperature by up to 26°C, compared with the pure CY. The total reaction enthalpy increased with increasing POSS content until 10 wt% of POSS was incorporated. These results indicate that the curing temperature of the CY resin can be reduced significantly with the addition of the POSS. The incorporation of POSS catalyzed the curing reaction of the CY. However, excessive addition of the POSS leads to an increase of onset temperature, and reduction in the total reaction enthalpy.

Figure 5.2 shows the DSC plots of the CY cured with and without a nitrogen atmosphere. Compared with the reaction in nitrogen atmosphere, the samples cured in air displayed a 39°C lower onset temperature and a 25°C lower peak temperature, which revealed the catalytic effect of oxygen on the curing process of the pure CY.
Figure 5.1: DSC plots of the CY/POSS nanocomposites in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

Table 5.1: DSC results of the CY/POSS systems in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset Temperature (°C)</th>
<th>Peak Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>ΔH_T (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CY</td>
<td>257</td>
<td>303</td>
<td>345</td>
<td>8.8</td>
<td>346</td>
</tr>
<tr>
<td>1 wt% POSS/CY</td>
<td>240</td>
<td>303</td>
<td>328</td>
<td>8.8</td>
<td>363</td>
</tr>
<tr>
<td>5 wt% POSS/CY</td>
<td>199</td>
<td>283</td>
<td>332</td>
<td>13.3</td>
<td>415</td>
</tr>
<tr>
<td>10 wt% POSS/CY</td>
<td>220</td>
<td>277</td>
<td>314</td>
<td>9.4</td>
<td>352</td>
</tr>
</tbody>
</table>
Figure 5.2: Heat flow vs. temperature for CY resin with (60ml/min) and without nitrogen atmosphere. Heating rate of 10°C/min was used.

For cure of a thermoset resin, the conversion at time, \( t \), can be defined as follows:

\[
\alpha_t = \frac{\Delta H_t}{\Delta H_T}
\]  

(5.1)

where, \( \alpha_t \) is the conversion at time \( t \), \( H_t \) is the reaction heat at time \( t \), and \( \Delta H_T \) is the total reaction heat shown on a typical non-isothermal experiment. In this experiment, the \( \Delta H_T \) was determined by scanning of uncured samples with a heating rate of 10°C/min, as shown in Table 5.1.

The conversion rate can be defined as follows:

\[
\frac{d\alpha}{dt} = \frac{dH_t}{dH_T dt}
\]  

(5.2)

where, \( \frac{d\alpha}{dt} \) is the conversion rate at time \( t \).

An autocatalytic model was employed for analysis of the cure of the CY/POSS nanocomposite. An empirical rate equation proposed by Kamal\(^{145,146}\) can be applied for thermosetting cure showing auto-catalytic behaviour:

\[
\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m)(1 - \alpha)^n
\]  

(5.3)

where, \( k_1 \) and \( k_2 \) are the rate constants, \( m \) and \( n \) are the reaction orders, and \( k_{\text{kin}} \) is the kinetic rate constant under chemically controlled condition.
Furthermore, the temperature dependence of any rate constant is given by the Arrhenius relationship:

\[ k = A \exp\left( -\frac{E_a}{RT} \right) \]  \hspace{1cm} \text{(5.4)}

Where, \( E_a \) is the activation energy, \( R \) is the gas constant, \( T \) is absolute temperature, and \( A \) is the pre-exponential or frequency factor.

Figure 5.3 shows the plots of heat flow versus time, recorded by MTDSC for the CY/POSS systems at different isothermal experimental temperatures. Figure 5.4 shows \( d\alpha/dt \) versus \( \alpha \) for the CY/POSS systems at different isothermal temperatures. Table 5.2 lists the results of kinetic analysis, based on the autocatalytic model (equation 5.3). According to equation 5.3, the parameters \( k_1, E_1, \) and \( A_1 \) reveal the effect of the POSS on the CY at the very beginning of the curing process in the presence POSS. In contrast, the parameters \( k_2, E_2, \) and \( A_2 \) are more important, as they show the effect of the POSS on network formation of the CY throughout the whole curing process.
Figure 5.3: Isothermal DSC plots for the CY/POSS nanocomposites at different isothermal temperatures (a) pure CY, (b) 1 wt% POSS/CY, (c) 5 wt% POSS/CY, and (d) 10 wt% POSS/CY.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

![Graphs showing curing dynamic and network formation at different temperatures](image)

- **Graph A** shows the curing dynamics at 215°C, 220°C, and 225°C.
- **Graph B** illustrates the curing dynamics at 210°C, 220°C, and 230°C.
- **Graph C** depicts the curing dynamics at 200°C, 205°C, and 210°C.
Figure 5.4: \( \frac{da}{dt} \) vs. \( a \) for the CY/POSS nanocomposites at different isothermal temperatures (a) pure CY, (b) 1 wt% POSS/CY, (c) 5 wt% POSS/CY, and (d) 10 wt% POSS/CY.

Table 5.2: Autocatalytic model constants for the CY/POSS nanocomposites

<table>
<thead>
<tr>
<th>Content of POSS (wt%)</th>
<th>Temperature (°C)</th>
<th>( k_1 ) ((\times 10^4 \text{ s}^{-1}))</th>
<th>( k_2 ) ((\times 10^4 \text{ s}^{-1}))</th>
<th>m</th>
<th>n</th>
<th>( \ln A_1 )</th>
<th>( \ln A_2 )</th>
<th>( E_1 ) (kJ/mol)</th>
<th>( E_2 ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>215</td>
<td>2.41</td>
<td>36.6</td>
<td>1.45</td>
<td>2.11</td>
<td>36.34</td>
<td>28.28</td>
<td>181.65</td>
<td>137.72</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>2.87</td>
<td>45.0</td>
<td>1.35</td>
<td>1.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>5.93</td>
<td>72.4</td>
<td>1.55</td>
<td>2.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>210</td>
<td>1.27</td>
<td>116</td>
<td>1.83</td>
<td>4.80</td>
<td>30.45</td>
<td>27.00</td>
<td>158.39</td>
<td>125.98</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>2.77</td>
<td>289</td>
<td>2.15</td>
<td>4.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>6.09</td>
<td>402</td>
<td>2.30</td>
<td>4.32</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>2.27</td>
<td>421</td>
<td>2.41</td>
<td>6.55</td>
<td>24.97</td>
<td>21.75</td>
<td>131.06</td>
<td>98.01</td>
</tr>
<tr>
<td></td>
<td>205</td>
<td>3.64</td>
<td>556</td>
<td>2.41</td>
<td>5.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>4.52</td>
<td>705</td>
<td>2.41</td>
<td>5.86</td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td>185</td>
<td>1.44</td>
<td>82.1</td>
<td>1.93</td>
<td>4.15</td>
<td>14.99</td>
<td>26.06</td>
<td>90.94</td>
<td>117.68</td>
</tr>
<tr>
<td></td>
<td>195</td>
<td>2.07</td>
<td>140</td>
<td>2.00</td>
<td>4.86</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.19</td>
<td>226</td>
<td>2.19</td>
<td>4.22</td>
<td></td>
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</tr>
</tbody>
</table>

Figure 5.5 illustrates the effect of the incorporation of POSS on the activation energy and the pre-exponential factor. Activation energy, \( E_1 \) and \( E_2 \), and the pre-exponential factor, \( A_1 \) and \( A_2 \), decreased with increasing POSS content, up to 5 wt%. Furthermore, the reaction order (see Table 5.2) increased significantly with increasing POSS content, up to 5 wt%. However, over 5 wt% POSS leads to an increase in the activation energy, \( E_2 \) and the pre-exponential...
factor, A2, and a decrease in reaction order. This result revealed that the incorporation of the POSS had a strong catalytic effect on the curing process of the CY. However, excessive addition hindered the cross-linking reaction of the CY.

![Graph A](image1)

**Figure 5.5**: Activation energy (A) and pre-exponential factor (B) vs. POSS content

From equation (5.3), the following equation can be deduced:

\[ k_{\text{kin}} = (k_1 + k_2 \alpha^m) \]  \hspace{1cm} (5.5)

Table 5.3 and Table 5.4 list the activation energy and the pre-exponential factor for different conversions for the POSS/CY nanocomposites.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPONENTS

Table 5.3: Activation energy at different conversions for the POSS/CY nanocomposites

<table>
<thead>
<tr>
<th>α</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS content (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>181.7</td>
<td>154.5</td>
<td>139.9</td>
<td>134.7</td>
<td>133.4</td>
<td>133.8</td>
<td>134.9</td>
<td>136.3</td>
<td>137.8</td>
<td>139.3</td>
<td>140.7</td>
</tr>
<tr>
<td>1</td>
<td>158.4</td>
<td>100.9</td>
<td>78.5</td>
<td>80.9</td>
<td>88.4</td>
<td>96.4</td>
<td>103.7</td>
<td>110.3</td>
<td>116.2</td>
<td>121.6</td>
<td>126.4</td>
</tr>
<tr>
<td>5</td>
<td>131.1</td>
<td>117.9</td>
<td>105.3</td>
<td>101.2</td>
<td>99.7</td>
<td>99.0</td>
<td>98.7</td>
<td>98.5</td>
<td>98.3</td>
<td>99.1</td>
<td>98.2</td>
</tr>
<tr>
<td>10</td>
<td>90.9</td>
<td>77.1</td>
<td>77.7</td>
<td>84.7</td>
<td>91.6</td>
<td>97.6</td>
<td>102.6</td>
<td>107.0</td>
<td>110.9</td>
<td>114.2</td>
<td>117.3</td>
</tr>
</tbody>
</table>

Table 5.4: Pre-exponential factor at different conversions for the POSS/CY nanocomposites

<table>
<thead>
<tr>
<th>α</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS content (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>36.34</td>
<td>30.14</td>
<td>27.02</td>
<td>26.13</td>
<td>24.14</td>
<td>26.50</td>
<td>26.99</td>
<td>27.52</td>
<td>28.06</td>
<td>28.58</td>
<td>29.08</td>
</tr>
</tbody>
</table>

Figure 5.6 shows changes of the activation energy with conversion for the CY/POSS systems. For the pure CY, the activation energy and the pre-exponential factor decreased with increasing degree of conversion until they reached a minimum value at a conversion factor of 0.4. When 1% POSS was added, the activation energy and the pre-exponential factor decreased dramatically below a degree of conversion of 0.2, which indicated a strong catalytic effect. However, after the conversion of 0.2, the activation energy and the pre-exponential factor increased significantly, which may be due to the exhaustion of POSS in the reaction. The activation energy at 5 wt% of POSS decreased throughout the whole curing process. The pre-exponential factor showed just a slight increase after the conversion of 0.2. However, for 10 wt% POSS/CY system, similar phenomenon with 1 wt% POSS/CY was observed. It is clear that the appropriate POSS content could continue to catalyze the cure of the CY. Although the excessive addition of the POSS showed better catalytic effect at the very beginning, it hindered the chemical reaction of the CY when the conversion reached
a certain level.

![Graph showing activation energy and pre-exponential factor vs. conversion for CY/POSS nanocomposites.](image)

**Figure 5.6:** Activation energy (a) and pre-exponential factor (b) vs. conversion for the CY/POSS nanocomposites.
Figure 5.7 (A) shows FTIR spectra for the pure CY resin with time cured at 225°C in nitrogen atmosphere. The characteristic absorption bands of the O-C≡N cyanate ester functional group were observed in the infrared spectrum between 2200 and 2300 cm\(^{-1}\). The band was split into a doublet of partially resolved peaks and was separated by approximately 35 cm\(^{-1}\). The cure of the CY cyanate ester resins can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring near 1360 and 1570 cm\(^{-1}\). With the curing time, the cyanate bands at 2250 cm\(^{-1}\) decreased and new bands appeared at 1565 cm\(^{-1}\) (\(\nu\)C=N\(\cdots\)C) and 1368 cm\(^{-1}\) (\(\nu\)N–C–O) due to triazine formation. Figure 5.7 (B) shows FTIR spectra for the CY/POSS (5wt%) nanocomposite with time cured at 210°C in nitrogen atmosphere. From the characteristic absorption bands of the O-C≡N cyanate ester functional group, it seems that the cure of cyanate ester resins and the formation of the triazine ring in the CY/POSS nanocomposites are the same as that of the CY.
Figure 5.7: FTIR spectra of the pure CY resin (A) with time cured at 225°C and 5 wt% POSS/CY nanocomposite (B) with time cured at 210°C in nitrogen atmosphere (60ml/min). For clarification, all the spectra were shifted parallel, and were calibrated basing the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹. The peaks near 2350 cm⁻¹ are due to the presence of CO₂.

For clarification, the FTIR spectra of the TriSilanolPhenyl POSS (A), and the comparison of neat CY with 5 wt% POSS/CY nanocomposite (B) in the range from 2000 cm⁻¹ to 1000 cm⁻¹ were given in Figure 5.8 (A) broad band near 3200 cm⁻¹ indicating stretching of Si-OH group, was observed in the infrared spectra of the TriSilanolPhenyl POSS. The aromatic C-H stretching at 3050 cm⁻¹ and the Si-C₆H₅ stretching at 1430 cm⁻¹ indicated the presence of phenyl group of the POSS. Furthermore, a sharp band appearing at 1075 cm⁻¹ indicated the asymmetric stretching of Si-O-Si group. The same band appearing as a shoulder, can also be observed in the infrared spectra of the 5 wt% POSS/CY nanocomposite in Figure 5.8 (B). From Figure 5.8 (B), no difference in the cure between the neat CY and the 5 wt% POSS/CY nanocomposite was observed. Raman spectra could reveal a difference.
Figure 5. 8: FTIR spectra of the TriSilanolPhenyl POSS (A), and the comparison of neat CY with 5 wt% POSS/CY nanocomposite (B).

Figures 5.9 (A) and (B) show the Raman spectra for the pure CY and its nanocomposites with 5 wt% POSS following different curing times. The curves recorded at 40 minutes became quite noisy, and it became hard to distinguish the peaks. As the curing reaction proceeded,
some vibrations of bonds in the CY were hindered by the rigid 3-dimensional crosslinking structure formed. Consequently, the vibrations can no longer be clearly detected by Raman scattering. In this case, one has to focus on the early stages of the cure.

Figures 5.9 (C) and (D) shows the details of Raman spectra for the pure CY and its nanocomposites with 5 wt% POSS in the early stages of the cure. Table 5.5 lists the analysis of the Raman spectra shown in Figure 5.9. From Figure 5.9 (C), it can be seen that the intensity of the absorption band at 2250 cm\(^{-1}\) indicating the stretching of \(-\text{O-C}≡\text{N}\) bond, and the intensity of absorption band at 340 cm\(^{-1}\) indicating the scissoring of \(-\text{O-C}≡\text{N}\) bond, decreased with increasing curing time. This observation indicated that the cyanate group of the resin started to react in the very early stages of the cure. The cure of the pure CY cyanate ester resin can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring at 1004 cm\(^{-1}\), 1304 cm\(^{-1}\), 1445 cm\(^{-1}\), and 1668 cm\(^{-1}\). As the curing reaction proceeded, the cyanate bands at 2250 cm\(^{-1}\) decreased and some new bands appeared due to stretching of \(-\text{O-C}≡\text{N}-\) at 1668 cm\(^{-1}\). This result is corresponded with that obtained in the FTIR experiments. Furthermore, the significant increase in the intensity of absorption band at 2921 cm\(^{-1}\) indicating stretching of \(-\text{CH}_2-\) bond may be caused by the formation of hydrogen bonding, which is due to the presence of triazine ring.

From Figure 5.9 (D), it can be seen that the major reaction of the 5 wt% POSS/CY system during cure is still the formation of the triazine ring, which is the same as that of the pure CY. The main reaction can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring at 991 cm\(^{-1}\), 1300 cm\(^{-1}\), 1445 cm\(^{-1}\), and 1675 cm\(^{-1}\), and monitoring the corresponding decrease in absorption band at 2235 cm\(^{-1}\) indicating stretching of \(-\text{O-C}≡\text{N}\) bond, and the absorption band at 345 cm\(^{-1}\) indicating scissoring of \(-\text{O-C}≡\text{N}\) bond. Compared with the pure CY, the intensity of absorption band at 345 cm\(^{-1}\) was almost the same, and the intensity of absorption band at 2235 cm\(^{-1}\) decreased just a little at the very beginning of the curing reaction. This phenomenon revealed that the cyanate group of the resin reacted very slowly and did not form the triazine ring in the very early stage of the cure.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

A

B

increasing time

increasing time
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

Figure 5.9: Raman spectra of the pure CY resin (A) cured at 225 °C, 5% POSS/CY resin (B) cured at 210 °C up to 100min, (C) A-enlarged, and (D) B-enlarged in nitrogen atmosphere (60ml/min).
Table 5.5: Analytical results of the Raman spectra of the pure CY resin cured at 225 °C and the 5 wt% POSS/CY system cured at 210 °C

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Assignment</th>
<th>Bond</th>
<th>Tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>340 (\delta_{C=N})</td>
<td>(R-C≡N)</td>
<td></td>
<td>decrease</td>
</tr>
<tr>
<td>2250 (\nu_{C=N})</td>
<td></td>
<td></td>
<td>decrease</td>
</tr>
<tr>
<td>627</td>
<td>Ring in-plane bending</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>1042 (\delta_{C-H})</td>
<td>1,2-disubstituted benzene ring</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>711 (\delta_{C-C}) for 1,2,4-trisubstituted benzene ring and (\nu_{\text{skeletal}}) for 1,2-disubstituted benzene ring</td>
<td></td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>1200 (\nu_{\text{skeletal}}) for substituted benzene ring</td>
<td></td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>1605 (\nu_{C=C}) of aromatic ring</td>
<td></td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>3055 (\nu_{C-H}) C-H stretching for benzene</td>
<td></td>
<td>constant</td>
<td></td>
</tr>
<tr>
<td>1304 (\nu_{C-N})</td>
<td></td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>1668 (\nu_{O-C=N}) usually strong doublet due to rotational isomerism</td>
<td></td>
<td>increase</td>
<td></td>
</tr>
<tr>
<td>1445 Triazine ring stretching</td>
<td></td>
<td>increase</td>
<td></td>
</tr>
<tr>
<td>1004 Triazine ring “breathing” vibration</td>
<td></td>
<td>increase</td>
<td></td>
</tr>
<tr>
<td>2921 (\nu_{as \ CH_2})</td>
<td>-CH(_2)-</td>
<td></td>
<td>Increase</td>
</tr>
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</table>
Enlarged Raman spectra for the pure CY resin cured at 225 °C and the 5% POSS/CY system cured at 210 °C from 1250 to 2000 cm\(^{-1}\) were shown in Figure 5.10 for clarification. For the neat CY, a band near 1668 cm\(^{-1}\) indicating the formation of triazine ring appeared at the very beginning of the curing process. In contrast, for the 5 wt% POSS/CY system, the band appearing at 1668 cm\(^{-1}\) is much weaker. Another band which is quite sharp showed at 1615 cm\(^{-1}\) indicated the formation of -O-(C=NH)-O- bond. These results implied that the cyanate ester resin reacted with –OH group of the POSS firstly to form -O-(C=NH)-O- bond. Thus, the curing mechanism of the CY/POSS nanocomposites is quite different from that of the pure CY. The strong catalytic effect of the POSS to the curing process of CY should be originated from formation of the -O-(C=NH)-O- bond. Figure 5.11 shows the scheme of crosslinked network formation through triazine ring and -O-(C=NH)-O- bond for the POSS/CY nanocomposites.

Figure 5. 10: Raman spectra of the pure CY resin cured at 225 °C and 5% POSS/CY resin cured at 210 °C from 1250 to 2000 cm\(^{-1}\) in nitrogen atmosphere (60ml/min).
5.2 Cyanate ester resin/ clay nanocomposites

Figure 5.12 shows the DSC curves relating to the curing process of CY/clay resins in a nitrogen atmosphere (60 ml/min) with a heating rate of 10 °C/min. Table 5.6 lists the non-isothermal curing temperature, curing period and heat of reaction for the different CY/clay systems. The addition of the three kinds of clays showed different catalytic behaviour, of which the 30B clay showed the most effective catalytic effect. With the incorporation of 5 wt% 30B clay, the onset temperature decreased by 62 °C, and the peak temperature fell to approximately 230 °C. The reaction enthalpy of the dynamic curing process and isothermal post curing process also varied with the incorporation of these clays. Generally, the total reaction enthalpy decreased. These phenomena implied that the addition of the clays significantly affected the network formation of the CY. Furthermore, as shown in Figure 5.12, the DSC plots of CY/Na⁺ and CY/20A systems are asymmetric, which indicates the reactions in CY/Na⁺ and CY/20A systems are more complicated than that in pure CY and CY/30B systems. These observations suggest that the curing temperature of the CY resin can be reduced significantly with the addition of these clays. The incorporation of the clays appeared to catalyse the curing reaction of the CY.
Figure 5.12: DSC plots of the CY/clay systems in a nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

Table 5.6: DSC results of the CY/clay systems in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min. $\Delta H_{\text{post}}$ is the reaction enthalpy calculated from an isothermal post cure process at 330°C after the dynamic DSC experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset Temperature (°C)</th>
<th>Peak Temperature (°C)</th>
<th>End Temperature (°C)</th>
<th>Duration (min)</th>
<th>$\Delta H_{\text{cure}}$ (J/g)</th>
<th>$\Delta H_{\text{post}}$ (J/g)</th>
<th>$\Delta H_T$ (J/g)</th>
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<tbody>
<tr>
<td>Pure CY</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
<td>166</td>
<td>667</td>
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<tr>
<td>1 wt% 30B</td>
<td>179</td>
<td>259</td>
<td>326</td>
<td>14.7</td>
<td>595</td>
<td>71</td>
<td>666</td>
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<tr>
<td>3 wt% 30B</td>
<td>156</td>
<td>234</td>
<td>314</td>
<td>15.8</td>
<td>479</td>
<td>69</td>
<td>548</td>
</tr>
<tr>
<td>5 wt% 30B</td>
<td>155</td>
<td>230</td>
<td>313</td>
<td>15.8</td>
<td>421</td>
<td>109</td>
<td>530</td>
</tr>
<tr>
<td>3 wt% 20A</td>
<td>176</td>
<td>230</td>
<td>316</td>
<td>14</td>
<td>537</td>
<td>67</td>
<td>604</td>
</tr>
<tr>
<td>3 wt% Na+</td>
<td>197</td>
<td>297</td>
<td>333</td>
<td>13.6</td>
<td>480</td>
<td>66</td>
<td>546</td>
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</tbody>
</table>
The kinetic analysis for the CY/CNT systems was based on an empirical rate equation showing auto-catalytic behaviour proposed by Kamal.\textsuperscript{145,146} The procedure generally followed our previous research on the CY/POSS nanocomposites.\textsuperscript{147}

Figure 5.13 shows the plots of heat flow versus time, recorded by MTDSC for the CY/clay systems at different isothermal temperatures. Figure 5.14 shows conversion rate (\(\frac{\text{d} \alpha}{\text{d} t}\)) versus conversion (\(\alpha\)) for the CY/clay systems at different isothermal temperatures. Table 5.7 lists the results of kinetic analysis for the CY/clays systems, based on the autocatalytic model (Equation 5.3). According to Equation 5.3, the parameters \(k_1\), \(E_1\), and \(A_1\) reveal the effect of the clays on the CY at the very beginning of the curing process. In contrast, the parameters \(k_2\), \(E_2\), and \(A_2\) are more important, as they show the effect of the clays on network formation of the CY throughout the whole curing process.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

- **Figure C:** Heat flow vs. time for sample C with 3 wt% 30B at 170, 180, and 190 °C.
- **Figure D:** Heat flow vs. time for sample D with 5 wt% 30B at 160, 170, and 180 °C.
- **Figure E:** Heat flow vs. time for sample E with 3 wt% 20A at 160, 170, and 180 °C.
Figure 5. 13: Isothermal DSC plots for the CY/clay systems at different isothermal temperatures (A) pure CY, (B) 1 wt% 30B, (C) 3 wt% 30B, (D) 5 wt% 30B, (E) 3 wt% 20A and (F) 3 wt% Na\(^+\).
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

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**Graphs:**

- **Graph B:** 1 wt% 30B
- **Graph C:** 3 wt% 30B
- **Graph D:** 5 wt% 30B

Each graph shows the da/dt versus a plot with different temperatures indicated by different line styles and colors for 170, 180, and 190°C.
Figure 5.14: $\frac{da}{dt}$ vs. $a$ for the CY/clay systems at different isothermal temperatures (A) pure CY, (B) 1 wt% 30B, (C) 3 wt% 30B, (D) 5 wt% 30B, (E) 3 wt% 20A and (F) 3 wt% Na$^+$. 
### Table 5.7: Autocatalytic model constants for the CY/clays systems

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>(k_1) ((\times 10^4 \text{ s}^{-1}))</th>
<th>(k_2) ((\times 10^4 \text{ s}^{-1}))</th>
<th>(m)</th>
<th>(n)</th>
<th>(\ln A_1)</th>
<th>(\ln A_2)</th>
<th>(E_1) (kJ/mol)</th>
<th>(E_2) (kJ/mol)</th>
</tr>
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<tr>
<td>Pure CY</td>
<td>195</td>
<td>0.698</td>
<td>12</td>
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<td>1.56</td>
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<td>154</td>
<td>137</td>
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<td></td>
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<td>215</td>
<td>3.39</td>
<td>50.6</td>
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<td></td>
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<tr>
<td>3 wt% 20A</td>
<td>160</td>
<td>1.11</td>
<td>13.0</td>
<td>1.28</td>
<td>1.45</td>
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<td>35</td>
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<td>31.4</td>
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<td>180</td>
<td>2.76</td>
<td>80.8</td>
<td>1.58</td>
<td>2.16</td>
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</table>

Figure 5.15 shows a typical reaction plot for the 3 wt% Na\(^+\)/CY system. For the system cured at 180 °C, three peaks showed at 6 minutes, 20 minutes, and 173 minutes, which indicated that there are three reactions. As the reaction process of Na\(^+\)/CY system is very complicated, the experimental data could not be well fitted using Kamal’s equation, therefore the activation energy was not calculated.
Figure 5.15: Plots of heat flow and conversion versus time for 3 wt% Na⁺/CY cured at 180 °C.

Figure 5.16 illustrates the effect of the incorporation of the 30B clay on the activation energy (Fig.6 (A) and (B)) and the comparison of the activation energy for various CY/clay systems (Fig.6 (C) and (D)). The activation energies, $E_1$ and $E_2$, decrease with increasing 30B clay content, up to 3 wt%. However, over 3 wt% 30B clay leads to an increase in both activation energy, $E_1$ and $E_2$. Furthermore, from the comparison of the activation energy, the CY/30B system showed the most effective catalytic effect. Both activation energy, $E_1$ and $E_2$, are lower than that of the pure CY. In contrast, the activation energy $E_2$ of the CY/20A system is higher than that of the CY. These results revealed that the incorporation of the clay 30B had a strong catalytic effect on the curing process of the CY. However, excessive addition hindered the cross-linking reaction in the CY. For the clay 20A, the catalytic effect was also strong at the beginning of the curing process, but was then impaired as the cure proceeded.
Figure 5.16: plots of activation energy versus content of the 30B clay (A) and (B), and comparisons of the activation energy for various CY/clay systems (C) and (D).

Table 5.8 lists the activation energy and pre-exponential factor at different conversions for the CY/clay systems. Figure 5.17 shows changes of the activation energy and pre-exponential factor with conversion for the CY/clay systems. For the pure CY, the activation energy and the pre-exponential factor decreased with increasing degree of conversion until they reached a minimum value at a conversion factor of 0.2. When the 30B clay was added, the activation energy and the pre-exponential factor decreased substantially below a degree of conversion of 0.1, which indicated a strong catalytic effect. However, after a conversion of 0.1, the activation energy and the pre-exponential factor started to increase, which may be due to the gradual consumption of the clay in the reaction. The activation energy at 3 wt% of 30B clay increased the most slowly after 10% conversion. For 5 wt% CY/30B system, the increasing rate for the activation energy is greater than that of 1 wt% CY/30B system. It is clear that there is a loading of approximately 3 wt% 30B displayed the most active catalytic effect. Excessive addition of the 30B hindered the chemical reaction of the CY. For the CY/20A
system, the most pronounced catalytic effect occurred at the very beginning of the reaction. With increasing time, the activation energy increased, and exceeded that of the pure CY after a conversion of 0.2. This observation corresponds to the result in the dynamic DSC experiment, where the CY/20A system firstly showed a very strong catalytic effect which is similar to that of the CY/30B system. However, with the continuing reaction, the activation energy increased significantly. Thus, the reaction became even more difficult than that of pure CY.

Table 5.8: Activation energy at different conversions for the CY/clay systems

<table>
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<th>Sample</th>
<th>a</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
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<td>E (kJ/mol)</td>
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</tr>
<tr>
<td></td>
<td>Ln A</td>
<td></td>
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<tr>
<td>1 wt% 30B</td>
<td>E (kJ/mol)</td>
<td>95</td>
<td>77</td>
<td>83</td>
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<td>98</td>
<td>105</td>
<td>110</td>
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<td>3 wt% 30B</td>
<td>E (kJ/mol)</td>
<td>71</td>
<td>76</td>
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<td>90</td>
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</tr>
<tr>
<td>5 wt% 30B</td>
<td>E (kJ/mol)</td>
<td>85</td>
<td>76</td>
<td>83</td>
<td>92</td>
<td>101</td>
<td>108</td>
<td>114</td>
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</tr>
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<td>3 wt% 20A</td>
<td>E (KJ/mol)</td>
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<td>82</td>
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<td>118</td>
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</tbody>
</table>
Figure 5.17: Activation energy (A) and pre-exponential factor vs. conversion for the CY/clay systems.
Figure 5.18 shows FTIR spectra of the clays used for the CY/clay nanocomposites, and the assignments on the clays used for the CY/clay nanocomposites are listed in Table 5.9.

Figure 5.18: FTIR spectra of the clays used for the CY/clay nanocomposites
Table 5.9: Infra-red assignments on the clays used for the CY/clay nanocomposites

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>3624</td>
<td>O-H stretching of the inner hydroxyl groups between tetrahedral and octahedral sheets</td>
<td>O-H</td>
</tr>
<tr>
<td>910, 880</td>
<td>O-H Bending</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>Si-O stretching</td>
<td>Si-O</td>
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<td>2920</td>
<td>Methylene symmetric C-H stretching</td>
<td>-CH$_2$</td>
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<td>2850</td>
<td>Methylene asymmetric C-H stretching</td>
<td>-CH$_2$</td>
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<tr>
<td>720</td>
<td>Methylene rocking</td>
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<td>1470</td>
<td>Methyl asymmetric C-H bending</td>
<td>-CH$_3$</td>
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<tr>
<td>1380</td>
<td>Methyl symmetric C-H bending</td>
<td></td>
</tr>
<tr>
<td>3300 for Clay 30B</td>
<td>O-H stretching of hydroxyethyl due to hydrogen bonding</td>
<td>O-H</td>
</tr>
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Figure 5.19 shows the FTIR spectra of the pure CY and the CY/clay nanocomposites in three stages which are uncured, cured at 190 °C for 1 hour and post cured at 290 °C for 1 hour in air atmosphere. The characteristic absorption bands of the O-C≡N cyanate ester functional group were observed in the infrared spectrum between 2200 cm$^{-1}$ and 2300 cm$^{-1}$. The band was split into a doublet of partially resolved peaks and was separated by approximately 35 cm$^{-1}$. The cure of the CY and the CY/clay nanocomposites can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring near 1360 cm$^{-1}$ and 1570 cm$^{-1}$. With the curing time, the cyanate bands at 2250 cm$^{-1}$ decreased and new bands appeared at 1565 cm$^{-1}$ ($\nu$C=N–C) and 1368 cm$^{-1}$ ($\nu$N–C–O) due to triazine formation.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED
NANOCOMPOSITES

A

CY 190C 1HR 290 1HR

CY 190C 1HR

CY 0 MIN

Transmission (%)
Wavenumber (cm$^{-1}$)

B

3wt% 20A/CY 190C 1HR 290 1HR

3wt% 20A/CY 190C 1HR

3wt% 20A/CY 0 min

Transmission (%)
Wavenumber (cm$^{-1}$)
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANO COMPOSITES

Figure 5. 19: FTIR spectra of (A) pure CY, (B) 3wt% 20A/CY nanocomposite, (C) 3wt% 30B/CY nanocomposite, and (D) 3wt% Na⁺/CY nanocomposite, in air atmosphere. For clarification, all spectra were shift parallel, and were calibrated based on the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹.
Figure 5.20 shows FTIR spectra of the pure CY and the clay/CY nanocomposites cured at 190°C for 1 hour (A) and then post-cured at 290°C for another 1 hour (B) in air atmosphere. It can be shown clearly that a weak absorbance band at 1735 cm\(^{-1}\) appeared in the FTIR spectra of 3wt% Na\(^+\)/CY nanocomposite and 3wt% 30B/CY nanocomposite. Apart from that, there are no obvious differences between the FTIR spectra. It should be noticed that the 3wt% 20A/CY nanocomposite showed phased separation after curing at 190°C for 1 hour. For the 3wt% Na\(^+\)/CY nanocomposite and the 3 wt% 30B/CY nanocomposite, the phase separation did not show throughout the curing process. To clarify whether there is any difference between the reaction mechanism of the pure CY and that of the CY/clay nanocomposites, further experiments were carried out using following procedure. The pure CY was cured at 225 °C and the CY/clay nanocomposites were cured at 180°C in nitrogen atmosphere (60 ml/min), up to 320 minutes. The FTIR spectra were recorded at various cure times. Recent work\(^{147}\) has demonstrated that the presence of an air atmosphere catalyses the curing reaction of CY resin. Carrying on the curing of CY and its nanocomposites under a nitrogen atmosphere and appropriately low temperature decelerates the cure reaction. By this method, the curing mechanism is easier to clarify.
Figure 5.20: Comparison of the FTIR spectra of the pure CY and the clay/CY nanocomposites under the condition of (A) cured at 190 °C for 1 hour, and (B) cured at 190 °C for 1 hour and post-cured at 290 °C for another 1 hour, in air atmosphere.

Figure 5.21 shows comparison of the FTIR spectra of the pure CY and the clay/CY nanocomposites uncured and cured for 320 min. It can be seen in Figure 5.21 (A) that a weak absorbance band at 1735 cm$^{-1}$ appeared in the FTIR spectra of all the clay/CY nanocomposites. As shown in Figure 5.21 (B), after curing at 180°C for 320 min, the absorbance band at 1735 cm$^{-1}$ disappeared for the 3wt% 20A/CY nanocomposite. In contrast, the absorbance band at 1735 cm$^{-1}$ (aliphatic C=O stretching for ester) became quite strong for the 3wt% Na$^+$/CY nanocomposite and the 3wt% 30B/CY nanocomposite. Furthermore, a new absorbance band at 1215 cm$^{-1}$ (C-N stretching) appeared for the 3wt% Na$^+$/CY nanocomposite and the 3 wt% 30B/CY nanocomposite. Associated with the presence of the bands at 1565 cm$^{-1}$ ($\nu$C=N) and 1368cm$^{-1}$ ($\nu$N–C–O), it is believed that the hydroxyl groups in the clays react with the cyanate groups of CY to form a coordination complex (shown in Figure 5.22 (A)). In contrast, for the CY/20A nanocomposite, the coordination complex was presented as well at the very beginning of the reaction, but then was transferred to –O–(C=NH)–O– compound (shown in Figure 5.22 (B)) immediately.
Figure 5. 21: Comparison of the FTIR spectra of the pure CY and the clay/CY nanocomposites uncured (A), and CY cured at 222°C and CY/clay nanocomposites cured at 180 °C for 320 min (B) in nitrogen atmosphere (60ml/min).
Figure 5.22: Schematic of possible molecular structure for the coordination complex (A) and the chemical compound (B) formed by reaction of the hydroxyl groups from the clays and the cyanate groups from the CY.

Figure 5.23 shows the FTIR spectra of the pure CY with time cured at 225°C, 3wt% Na⁺/CY, 3wt% 30B/CY and 3wt% 20A/CY systems with time cured at 180°C in nitrogen atmosphere (60 ml/min). Apart from the weak absorbance band presented at 1735 cm⁻¹ before 10 minutes for the 3wt% 20A/CY, the FTIR spectra of the pure CY and 3 wt% 20A/CY systems are almost the same. In contrast, the absorbance band at 1735 cm⁻¹ (aliphatic aldehyde C=O stretching) and the absorbance band at 1215 cm⁻¹ (C-N stretching) appeared in the FTIR spectra for 3wt% Na⁺/CY and 3wt% 30B/CY systems. It is interesting to note that the intensity of the absorbance band at 1735 cm⁻¹ decreased after 160 minutes for the 3wt% Na⁺/CY, and decreased after 100 minutes for the 3wt% 30B/CY. This is also evidence that the Na⁺ and 30B clays reacted with the CY to form the coordination complex, which were then converted to the –O–(C=NH)–O– bond as the cure proceeded. Furthermore, as shown in Figure 5.23 (C), the coordination complex was present at the very beginning of the cure and remained throughout the whole curing process for the 3wt% 30B/CY system. For the 3 wt% Na⁺/CY system, the coordination complex was present from the middle of the curing process. For the 3wt% 20A/CY system, the presence of the coordination complex was just shown at the very beginning, and then was disappeared as the reaction proceeded. This observation is associated with the catalytic behaviour shown in the dynamic DSC experiment. In this experiment, the 3wt% 30B showed the best catalytic effect throughout the cure. The 3wt% 20A showed a strong catalytic effect as well at the very beginning, but the catalytic effect was impaired with the proceeding of curing process. For the 3wt% Na⁺/CY system, the strongest catalytic effect was shown in the middle of curing process. Thus, it can be concluded that the catalytic effect originates from the formation of the proposed coordination complex. The level of catalytic behaviour depends on the concentration of the OH group in the clays. For 20A/CY nanocomposite, the impaired catalytic effect may be due to the occurrence of phase separation.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

![Graph A](image1.png)

![Graph B](image2.png)
Figure 5.23: FTIR spectra of (A) pure CY with time cured at 225°C, (B) 3wt% Na⁺/CY nanocomposite (C) 3wt% 30B/CY nanocomposite and (D) 3wt% 20A/CY nanocomposite with time cured at 180°C in nitrogen atmosphere (60ml/min).
Figure 5.24 shows the Raman spectra for the pure CY and its nanocomposites with various clays at different curing times. For the pure CY, the curves recorded after 10 minutes became quite noisy, and it became hard to distinguish individual peaks. As the curing reaction proceeded, some vibrations of the bonds in the CY were hindered by the formation of a rigid 3-dimensional crosslinked structure. Consequently, the vibrations can no longer be clearly detected by Raman spectroscopy. In this case, for the pure CY, we have to focus on the early stages of the cure. It is quite attractive that the Raman spectra can be recorded clearly even after curing for 320 minutes, for all the CY/clay nanocomposites. This is evidence that the formation of rigid 3-dimensional crosslinking structure was retarded with the incorporation of the clays. Further analysis will be given in the following discussion. Table 5.10 lists the analysis of the Raman spectra shown in Figure 5.24. Figures 5.24 (B) to (E) shows the details of Raman spectra for the pure CY and its nanocomposites with various clays. As shown in Figure 5.24 (E), for the pure CY, the intensity of the absorption band at 2250 cm\(^{-1}\) indicating the stretching of \(-\text{O-} \equiv \text{N}\) bond, and the intensity of absorption band at 340 cm\(^{-1}\) indicating the scissoring of \(-\text{O-} \equiv \text{N}\) bond, decreased with increasing curing time. The cure of the pure CY cyanate ester resin can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring at 1004 cm\(^{-1}\), 1304 cm\(^{-1}\), 1445 cm\(^{-1}\), and 1668 cm\(^{-1}\). As the curing reaction proceeds, the peak attributed to the cyanate bands at 2250 cm\(^{-1}\) decreased and new bands appeared due to the formation of a triazine ring. This result corresponds with that obtained in the FTIR experiments. Furthermore, the significant increase in the intensity of absorption band at 2921 cm\(^{-1}\), indicating stretching of \(-\text{CH}_2\)– bonds may be caused by the formation of hydrogen bonding, which is due to the presence of the triazine ring. For all the CY/clay nanocomposites, the reaction mechanism is significantly different from that of the pure CY.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

![Raman shift graphs](image)

**A**

- 100 min
- 60 min
- 30 min
- 10 min
- 5 min
- 2 min
- 0 min

Increasing time

**B**

- 320 MIN
- 160 MIN
- 80 MIN
- 40 MIN
- 20 MIN
- 10 MIN
- 5 MIN
- 0 MIN

Intensity vs. Raman shift (cm⁻¹)
Figure 5.24: Raman spectra of (A) the pure CY resin cured at 225°C, (B) 3wt% 20A/CY resin cured at 180°C, (C) 3wt% 30B/CY resin cured at 180°C, (D) 3wt% Na⁺/CY resin cured at 180°C, and (E) A-enlarged, in nitrogen atmosphere (60 ml/min)
Table 5.10: Analytical results of the Raman spectra of the pure CY resin cured at 225 °C and its composites with addition of the clays.

<table>
<thead>
<tr>
<th>Raman Shift (cm(^{-1}))</th>
<th>Assignment</th>
<th>Bond</th>
<th>Tendency</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>(\delta_{C≡N})</td>
<td>R-C≡N</td>
<td>decrease</td>
</tr>
<tr>
<td>2250</td>
<td>(\nu_{C≡N})</td>
<td></td>
<td>decrease</td>
</tr>
<tr>
<td>627</td>
<td>Ring in-plane bending</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>1042</td>
<td>(\delta_{C-H}) 1,2-disubstituted benzene ring</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>711</td>
<td>(\delta_{C-C}) for 1,2,4-trisubstituted benzene ring and (\nu_{\text{skeletal}}) for 1,2-disubstituted benzene ring</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>1200</td>
<td>(\nu_{\text{skeletal}}) for substituted benzene ring</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>1605</td>
<td>(\nu_{C=C}) of aromatic ring</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>3055</td>
<td>(\nu_{C-H}) C-H stretching for benzene</td>
<td></td>
<td>constant</td>
</tr>
<tr>
<td>1304</td>
<td>(\nu_{C-N})</td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>1668</td>
<td>(\nu_{O-C≡N}) usually strong doublet due to rotational isomerism</td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>1445</td>
<td>Triazine ring stretching</td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>1004</td>
<td>Triazine ring “breathing” vibration</td>
<td></td>
<td>increase</td>
</tr>
<tr>
<td>2921</td>
<td>(\nu_{\text{as CH}_2})</td>
<td>-CH(_2)</td>
<td>increase</td>
</tr>
</tbody>
</table>
Figure 5.25 shows the Raman spectra of the pure CY and its nanocomposites with the clays uncured (A) and cured after a period of time (B). As shown in Figure 5.25 (A), there is no obvious difference observed between the Raman spectra of the pure CY and its nanocomposites with the clays uncured. After curing for 10 minutes (Figure 5.25 (B)), the presence of the strong absorbance bands at 1004 cm\(^{-1}\), 1304 cm\(^{-1}\), 1445 cm\(^{-1}\), and 1668 cm\(^{-1}\) indicated the formation of the triazine ring for the pure CY. For all the CY/clay nanocomposites, after curing for 320 minutes, the band at 1304 cm\(^{-1}\) appeared, and a new band at 990 cm\(^{-1}\) was also apparent. Nevertheless, the bands at 1004 cm\(^{-1}\) (Triazine ring “breathing” vibration), and 1445 cm\(^{-1}\) (Triazine ring stretching) and 1668 cm\(^{-1}\) (\(v_{O-C=N}\)), which indicated the formation of the trazine ring were not observed. This observation revealed that the reaction mechanism is significantly different with and without the incorporation of these clays. Combining the Raman and FTIR results, it is believed that the triazine rings were no longer formed from the initial stage of the cure with the addition of these clays. The cyanate groups of CY resin preferred to react with the hydroxyl groups in the clays to form the coordination complex shown in Figure 5.22 (A). Thus, the formation of 3-dimensional network for CY/clay nanocomposites was retarded until the middle or even late stage of the cure, due to the absence of the triazine rings.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

Figure 5.25: Raman spectra of (A) the pure CY resin and the CY/clay resins uncured, (B) the pure CY resin cured after 10 minutes and the CY/clay resins cured after 320 minutes in nitrogen atmosphere (60 ml/min).

5.3 Cyanate ester resin/ multi-wall carbon nanotubes (MWCNT) nanocomposites

Figure 5.26 shows DSC plots against temperature for CY/CNT systems in a nitrogen atmosphere (60ml/min) with a heating rate of 10°C/min. The addition of MWCNT-OH, MWCNT-COOH and SWCNT-OH showed an accelerating effect. For the pristine MWCNT, no soon effect was observed. The onset temperature of the CY moved down from 217°C to 170°C with the incorporation of only 1wt% MWCNT-OH. With 4wt% MWCNT-OH, the peak temperature decreased by 57°C. The addition of MWCNT-COOH showed more pronounced accelerating effect than MWCNT-OH. Comparing with the MWCNT-OH, SWCNT-OH appeared to have a greater accelerating effect. With only 2wt% MWCNT-COOH or SWCNT-OH, the onset temperature decreased by about 40°C compared to a 10°C reduction for 2wt% MWCNT-OH/CY system. Furthermore, with the addition of CNTs, the reaction enthalpy $\Delta H_{\text{cure}}$ calculated from the dynamic DSC runs, became much larger than that of pure CY. $\Delta H_{\text{post}}$ calculated from an isothermal post cure process at 330 °C.
after the dynamic DSC experiment, decreased. The total reaction enthalpy generally increased. These phenomena implied that the addition of the CNTs could significantly affect the network formation of the CY.

Figure 5.26: DSC plots of the CY/CNTs nanocomposites in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.

Figure 5.27 shows the plots of heat flow versus curing time for various CY/CNT systems at different curing temperatures. Figure 5.28 plots conversion rate (da/dt) versus conversion (α) for the CY/CNT systems at different isothermal temperatures. Generally, a higher curing temperature resulted in greater curing rate.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED
NANOCOMPOSITES

A: pure CY

B: 1 wt% MWCNT-OH/CY

C: 2 wt% MWCNT-OH/CY
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

D: 4 wt% MWCNT-OH/CY

E: 2 wt% MWCNT/CY

F: 2 wt% MWCNT-COOH/CY

Heat Flow (W/g) vs Time (Min) for different temperatures.
Figure 5. 27: Plots of heat flow versus curing time for CY/CNT systems at different isothermal temperatures. (A) pure CY, (B) 1wt% MWCNT-OH/CY, (C) 2wt% MWCNT-OH/CY, (D) 4wt% MWCNT-OH/CY, (E) 2wt% MWCNT/CY, (F) 2wt% MWCNT-COOH/CY, and (G) 2wt% SWCNT-OH/CY.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

B: 1wt% MWCNT-OH/CY

C: 2 wt% MWCNT-OH/CY

D: 4 wt% MWCNT-OH/CY
Figure 5.28: Plots of $\frac{da}{dt}$ vs. $a$ for various CY/CNT systems at different isothermal temperatures. (A) pure CY, (B) 1wt% MWCNT-OH/CY, (C) 2wt% MWCNT-OH/CY, (D) 4wt% MWCNT-OH/CY, (E) 2wt% MWCNT/CY, (F) 2wt% MWCNT-COOH/CY, and (G) 2wt% SWCNT-OH/CY.
The kinetic analysis for the CY/CNT systems was based on an empirical rate equation showing auto-catalytic behaviour proposed by Kamal.\textsuperscript{145,146} The procedure generally followed our previous research on the CY/POSS nanocomposites.\textsuperscript{147} Figure 5.29 plots the activation energy $E_1$ and $E_2$ versus weight fraction of MWCNT-OH. With the exception of 1wt% MWCNT-OH/CY, the activation energy $E_1$ of the MWCNT-OH/CY systems is higher than that of the pure CY. The activation energy $E_2$ firstly decreased, and then increased with increasing weight fraction of MWCNT-OH. It is believed that the most effective acceleration effect is between 1wt% and 2wt% MWCNT-OH.

![Activation Energy E1 vs. Weight Content of MWCNT-OH](image1)

![Activation Energy E2 vs. Weight Content of MWCNT-OH](image2)

Figure 5.29: Activation energy $E_1$ (A) and $E_2$ (B) of CY/MWCNT-OH vs. weight fraction of MWCNT-OH.

Figure 5.30 compares the activation energy for different CY/CNT systems. It can be shown clearly that the activation energy $E_1$ of 2wt% MWCNT-OH/CY is much higher than that of pure CY, and the activation energy $E_2$ of 2wt% MWCNT /CY is over two times higher than that of pure CY. In comparison, both activation energies $E_1$ and $E_2$ of MWCNT-COOH are lower than that of the pure CY. Thus, it is believed that the addition of MWNT-COOH showed the greatest accelerating effect. These results are in accordance with the observation in the dynamic DSC experiment. It is remarkable that the activation energy $E_1$ of 2wt% SWCNT-OH/CY was almost the same as that of CY, and the activation energy $E_2$ was even higher than that of CY. This result implied that the addition of SWCNT-OH did not catalyse, or perhaps inhibited the curing reaction of CY. However, the observation in the dynamic DSC experiment indicated that the incorporation of SWCNT-OH displayed a strong accelerating effect. The reason for these two contrary results will be further explored.
Figure 5.30: Comparison of the activation energy $E_1$ (A) and $E_2$ (B) for various CY/CNT (2 wt%) systems.

The kinetic activation energy and pre-exponential factor were also calculated based on Kamal’s theory. Figure 5.31 shows changes of the activation energy and pre-exponential factor with conversion for various CY/CNT systems. For the pure CY, the activation energies decreased with increasing conversion until they reached a minimum value at a conversion factor of 0.2. For OH groups functionalised MWCNT, the activation energy becomes lower than that of CY after conversion of 0.4 for both 1wt% and 2wt%. But for 4wt% MWCNT-OH, the activation energy was higher than that of pure CY until a conversion of 0.9. These results implied that the most pronounced accelerating effect lies in the range of 1wt% to 2wt% MWCNT-OH. For the 2 wt% MWCNT/CY, the activation energy firstly decreased, and then increased rapidly with the conversion. The activation energy exceeded that of the pure CY after conversion of 0.4, and became two times higher at the conversion of 1. This observation indicated that the presence of MWCNT inhibited the curing reaction of the CY in the middle and late stages of the curing process. For the MWCNT-COOH/CY system, the activation energy is lower than that of the pure CY throughout the whole curing process. Thus, the incorporation of MWCNT-COOH showed the greatest accelerating effect. For the SWCNT-OH/CY system, the contrary result to the dynamic DSC experiment was shown as well. The activation energy is higher than that of the pure CY throughout the whole curing process, which means the addition of SWCNT-OH inhibited the curing reaction. The contrary results from the dynamic DSC experiment and isothermal MDSC experiments may be due to the poor dispersion of the SWCNT-OH in the CY matrix. The high concentration of SWCNT-OH in some local areas could lead to localised acceleration of the CY curing reaction of the CY, which could give rise to the apparently strong accelerating effect observed in the dynamic DSC experiment. However, the rapid cure occurring in some areas may have
inhibited the cure of the bulk resin, and impaired the network formation of the CY, resulting in the increase in activation energy observed in isothermal MDSC experiment.

Figure 5.31: Activation energy (A) and pre-exponential factor (B) vs. conversion for the CY/CNT systems.
Figure 5.32 shows FTIR spectra for the pure CY resin with time cured at 225 °C and various CY/CNT mixtures with time cured at 200 °C in nitrogen atmosphere. The characteristic absorption bands of the O-C≡N cyanate ester functional group were observed in the infrared spectrum between 2200 and 2300 cm⁻¹. This band was split into a doublet of partially resolved peaks and was separated by approximately 35 cm⁻¹. The cure of the CY and CY with different CNTs can be followed by monitoring the corresponding increase in the absorbance bands of the triazine ring near 1360 cm⁻¹ and 1570 cm⁻¹. With increasing curing time, the cyanate bands at 2250 cm⁻¹ decreased and new bands appeared at 1565 cm⁻¹ (νC=N–C) and 1368 cm⁻¹ (νN–C–O) due to triazine ring formation. For clarification, the FTIR spectra for the comparison of neat CY with 2 wt% CNT/CY nanocomposites in the range from 1800 cm⁻¹ to 800 cm⁻¹ were given in Figure 5.32 (F). For all the CY/CNT nanocomposites, a band at 1640 cm⁻¹ indicating oxime C=N–O stretching was shown, providing evidence that the CNT reacts with CY. In the CNT-OH/CY systems, it is the OH group which reacts with cyanate group of CY (Figure 5.33 (A)). For the COOH groups functionalised MWCNT, the band at 1750 cm⁻¹ indicating the C=O stretching disappeared after 20 min of the cure. This observation indicated that the C=O double bond of COOH groups broke to form the oxime bond with the CY at the very beginning of curing reaction (Figure 5.33 (B)). For the pristine MWCNT, the oxime C=N–O bonding is also shown, but there should be no functionalised group on the pristine MWCNT. It is inferred that the reaction may be due to the presence of impurity of pristine MWCNT.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

**Graph A:**
- Transmission (%)
- Wavenumber (cm\(^{-1}\))
- Data points at 0 min, 2 min, 5 min, 10 min, 20 min, 40 min, 100 min, 120 min, and 320 min are shown.
- The wavenumber range is from 4000 to 1000 cm\(^{-1}\).

**Graph B:**
- Transmission (%)
- Wave number (cm\(^{-1}\))
- Data points at 0 min, 2 min, 5 min, 10 min, 20 min, 40 min, 80 min, 160 min, and 320 min are shown.
- The wave number range is from 4000 to 500 cm\(^{-1}\).
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

Graph C and D show the transmission spectra over time, with wave number (cm$^{-1}$) on the x-axis and transmission (%) on the y-axis. The graphs display data at various time points, from 0 min to 320 min.
Figure 5.32: FTIR spectra of (A) pure CY with time cured at 225°C, (B) 2wt% MWCNT/CY, (C) 2wt% MWCNT-OH/CY, (D) 2wt% MWCNT-COOH/CY (E) 2wt% SWCNT-OH/CY with time cured at 200°C, and (F) all samples cured after 320 min, in nitrogen atmosphere (60ml/min). For clarification, the spectra were shift parallel, and were calibrated based on the absorption band of phenyl ring symmetric breathing vibration near 1500 cm\(^{-1}\).
Figure 5. 33: Schematic of possible molecular reaction between hydroxyl group functionalised CNT (A), carboxyl group functionalised CNT (B) and the cyanate groups from the CY.
Raman Spectroscopy is a vitally effective method to determine the structure change for carbon filler based polymer matrix composites. Raman has been applied to polymer/CNT nanocomposites, in order to determine the diameter, chirality type, the aggregation state of nanotubes in polymer matrix. Here, Raman was used to investigate the dispersion of CNTs and the interaction between polymer and CNTs. In the Raman spectra (Figure 5.34), CNTs displayed two characteristic bands, the D band located around 1330 cm\(^{-1}\) is derived from a disordered graphite structure. The G band located around 1595 cm\(^{-1}\) indicates the in-phase vibration of the graphite lattice which corresponds to the first order scattering of \(E_{2g2}\) mode. It can be clearly observed that the D band and G band shifted up by 17 cm\(^{-1}\) (shown in Table 5.11), and the bands became broader with curing time. The large up-shifting is attributed to strong hydrostatic compression that the polymer is giving to the carbon nanotubes. This result implied the disentanglement and subsequent good dispersion of the MWCNTs in the CY matrix, due to the penetration of the CY into the bundles of MWCNTs. The evolution of the shoulder peaks can be associated with very strong compressive forces between the MWCNTs and the CY matrix. These observations provide evidence for good dispersion and strong interaction between the MWCNTs and the CY matrix. Similar up-shifting of the G band was reported in CNTs reinforced polyethylene\(^{98}\) and polypropylene\(^{150}\), as well as polyurethane\(^{117}\) and epoxy resins\(^{149,151}\).
Figure 5. 34: Raman spectra of (A) the 2 wt% MWCNT/CY cured at 200 °C, and (B) 2% MWCNT-COOH/CY cured at 200 °C, in nitrogen atmosphere (60 ml/min)

Table 5. 11: Raman shift in the CY/CNT nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D band (cm⁻¹)</th>
<th>D band shift (cm⁻¹)</th>
<th>G band (cm⁻¹)</th>
<th>G band shift (cm⁻¹)</th>
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<tbody>
<tr>
<td>MWCNT</td>
<td>1328</td>
<td>12</td>
<td>1594</td>
<td>12</td>
</tr>
<tr>
<td>2 wt% MWCNT/CY 320 min</td>
<td>1342</td>
<td></td>
<td>1606</td>
<td></td>
</tr>
<tr>
<td>MWCNT-COOH</td>
<td>1333</td>
<td></td>
<td>1597</td>
<td></td>
</tr>
<tr>
<td>2 wt% MWCNT-COOH/CY 320 min</td>
<td>1343</td>
<td>10</td>
<td>1614</td>
<td>17</td>
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</tbody>
</table>
5.4 Cyanate ester resin/ single-wall carbon nanotubes (SWCNT) nanocomposites

Figure 5.35 shows DSC plots against temperature for CY/SWCNT systems. It can be seen clearly that all the SWCNTs systems showed a catalytic effect. Table 5.12 summarises onset, peak and end temperatures, enthalpy of the non-isothermal cure. The onset temperature of the CY moved down from 217°C to 177°C with the incorporation of only 1wt% SWCNT-OH. With 2wt% SWCNT-OH, the peak temperature decreased by 41°C. The addition of SWCNT-COOH showed more pronounced accelerating effect than SWCNT-OH. With only 2wt% SWCNT-COOH, the onset temperature decreased by about 79°C. Furthermore, with the addition of CNTs, the reaction enthalpy $\Delta H_{\text{cure}}$ calculated from the dynamic DSC runs, became much larger than that of pure CY. $\Delta H_{\text{post}}$ calculated from an isothermal post cure process at 330°C after the dynamic DSC experiment, decreased. The total reaction enthalpy generally increased. These phenomena implied that the addition of the SWCNTs could significantly affect the network formation of the CY.

![DSC plots of the CY/SWCNTs nanocomposites in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.](image-url)
Table 5.12: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of CY/SWCNT systems. $\Delta H_{\text{post}}$ is the reaction enthalpy calculated from an isothermal post cure process at 330 °C after the dynamic DSC experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset Temperature ($^\circ$C)</th>
<th>Peak Temperature ($^\circ$C)</th>
<th>End temperature ($^\circ$C)</th>
<th>Duration (min)</th>
<th>$\Delta H_{\text{cure}}$ (J/g)</th>
<th>$\Delta H_{\text{post}}$ (J/g)</th>
<th>$\Delta H_T$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CY</td>
<td>217</td>
<td>298</td>
<td>333</td>
<td>11.6</td>
<td>501</td>
<td>166</td>
<td>667</td>
</tr>
<tr>
<td>1 wt% SWCNT-OH/CY</td>
<td>177</td>
<td>283</td>
<td>353</td>
<td>17.6</td>
<td>643</td>
<td>91</td>
<td>734</td>
</tr>
<tr>
<td>2 wt% SWCNT-OH/CY</td>
<td>170</td>
<td>257</td>
<td>333</td>
<td>16.3</td>
<td>603</td>
<td>90</td>
<td>693</td>
</tr>
<tr>
<td>4 wt% SWCNT-OH/CY</td>
<td>184</td>
<td>272</td>
<td>353</td>
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<td>353</td>
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<td>64</td>
<td>768</td>
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<tr>
<td>2 wt% SWCNT-COOH/CY</td>
<td>120</td>
<td>219</td>
<td>330</td>
<td>21.0</td>
<td>634</td>
<td>93</td>
<td>727</td>
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Figure 5.36 shows the plots of heat flow versus curing time for CY/SWCNTs systems at different curing temperatures. Figure 5.37 shows the plots of conversion rate versus curing time for CY/SWCNTs systems at different curing temperatures.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED NANOCOMPOSITES

![Graphs showing heat flow vs. time for 1 wt% SWCNT-OH/CY, 2 wt% SWCNT-OH/CY, and 4 wt% SWCNT-OH/CY at different temperatures. The graphs depict the evolution of heat flow over time for each concentration level.](image-url)
Figure 5.36: Plots of heat flow versus curing time for CY/SWCNTs systems at different curing temperatures.
Figure 5.37: Plots of conversion rate versus curing time for CY/SWCNTs systems at different curing temperatures
The kinetic analysis for the CY/CNT systems was based on an empirical rate equation showing auto-catalytic behaviour proposed by Kamal. The procedure generally followed our previous research on the CY/POSS nanocomposites. Table 5.13 shows the kinetic parameters calculated from the isothermal MDSC experiments using Kamal’s equation, for various CY/SWCNTs nanocomposites. Figure 5.38 plots the activation energy E₁ and E₂ versus weight fraction of SWCNT-OH. With the incorporation of SWCNT-OH/CY, the activation energy E₁ of the SWCNT-OH/CY system decreased firstly, and then turned around to increase until 2wt%, followed by decreasing again. The activation energy E₂ showed similar trend. As the activation energy E₂ is more important, the most effective acceleration effect is believed to happen between 1wt% and 2wt% SWCNT-OH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>k₁ (×10⁴ s⁻¹)</th>
<th>k₂ (×10⁴ s⁻¹)</th>
<th>m</th>
<th>n</th>
<th>ln A₁</th>
<th>ln A₂</th>
<th>E₁ (kJ/mol)</th>
<th>E₂ (kJ/mol)</th>
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<td>50.6</td>
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<td>34.8</td>
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</table>
Figure 5.38: Activation energy of CY/SWCNT-OH vs. weight fraction of SWCNT-OH

Figure 5.39 compares the activation energy for different CY/SWCNT systems. There is no significant difference between $E_1$ of different systems. It can be shown clearly that the activation energy $E_2$ of 2wt% SWCNT-OH/CY is much higher than that of pure CY, and the activation energy $E_2$ of 2wt% SWCNT/CY is about half of that of pure CY. Thus, it is believed that the addition of SWNT showed more effective accelerating effect than that of SWCNT-OH. This is different from that of MWCNTs/CY systems. It is believed that the catalytic effect is significantly affected by the dispersion of SWCNTs and residual catalyst in SWCNTs.

Figure 5.39: Comparison of the activation energy for the CY/functionalisied MWCNT (2wt%) systems.
Table 5.14 shows the kinetic activation energy and the pre-exponential factor for the CY/SWCNT systems. Generally, the kinetic activation energy decreased with incorporation of SWCNTs. For SWCNT-OH systems, the activation energy firstly decreased with the conversion, and then increased rapidly with the conversion. For the 1wt% SWCNT-OH/CY system, the activation energy is lower than that of pure CY throughout the whole process. It is believed that the best catalytic effect should be showed when the incorporation content of SWCNT-OH is between 1wt% to 2wt%. The activation energy of 2wt% SWCNT/CY is decreased throughout the whole curing process, and is lower than that of pure CY after conversion of 0.5.
Figure 5.40: Kinetic activation energy versus conversion for the CY/SWCNT systems

Figure 5.41 shows the FTIR spectra for the pure CY resin cured at 240°C (A) and for 2wt%SWCNT/CY nanocomposite (B), 2wt%SWCNT-OH/CY (C), and 2wt%SWNT-COOH/CY nanocomposite (D) cured at 200°C in nitrogen atmosphere (60ml/min). From the FTIR spectra, the bands at 1055 cm⁻¹ which indicates the C-O stretching and at 1750 cm⁻¹ which indicates the C=O stretching disappeared after 20min of the cure. It could be concluded that the SWNT-OH and SWNT-COOH could react with the CY at the very beginning of the cure. The output of analysis is the same with that of CY/MWCNTs systems.
CHAPTER 5: CURING DYNAMIC AND NETWORK FORMATION OF CYANATE ESTER BASED
NANOCOMPOSITES

A

B

Transmission (%)

wave number (cm⁻¹)

Transmission (%)

wave number (cm⁻¹)
Figure 5.41: FTIR spectra for the pure CY resin cured at 225°C (A) and for 2wt% SWCNT/CY (B), 2wt% SWCNT-OH/CY (C), and 2wt% SWCNT-COOH/CY (D), cured at 200°C in nitrogen atmosphere (60ml/min) For clarification, all the spectra were shift parallel, and were calibrated basing the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹.
5.4 Summary

The incorporation of the POSS catalyzed the reaction of the CY. However, excessive addition leads to an increase of onset temperature, and reduction in the total reaction enthalpy. The results showed that the activation energy of the CY/POSS systems decreased with increasing POSS content, up to 5wt%. The most pronounced catalytic effect was observed with 5wt% POSS. Although the excessive addition of the POSS showed catalytic behaviour in the initial stages, it hindered the chemical reaction of the CY when the conversion reached a certain level. Both FTIR and Raman spectra can be applied to monitor the reaction of the CY/POSS nanocomposites through the formation of triazine ring. Raman spectra revealed that the CY resin preferred to react with –OH group on the POSS firstly to form -O-(C=NH)-O- bond in CY and its nanocomposites with the POSS. The strong catalytic effect of the POSS to the curing process of the CY should be originated from formation of the -O-(C=NH)-O- bond.

The incorporation of the Na\textsuperscript{+}, 20A, and 30B clays catalysed the reaction of the CY resin to various degrees. The most effective catalytic effect was shown with the addition of 30B clay. The results showed that the activation energy of the CY/30B clay systems decreased with increasing clay content, up to 3wt%. The most pronounced catalytic effect was observed with 3wt% 30B. Although the excessive addition of the clay showed catalytic behaviour in the initial stages, it hindered the chemical reaction of the CY when the conversion reached a certain level. The homogeneous dispersion of 30B and Na\textsuperscript{+} clays in the CY matrix was observed by the FEG-SEM. The aggregation of 20A clay was observed, which is due to the presence of the hydrophobic modifier. TEM images and XRD diffraction pattern confirmed that the 30B and Na\textsuperscript{+} clays were exfoliated in the CY matrix. FTIR spectra were used to monitor the formation of the triazine ring in the CY. The FTIR results indicate that the clay Na\textsuperscript{+} and 30B react with the CY to form a coordination complex, and then the coordination complex with this complex being converted to the –O–(C=NH)–O– bond with the proceeding of the curing reaction. In contrast, for the CY/20A system, the coordination complex was present at the very beginning of the reaction, but then was transformed to –O–(C=NH)–O– compound almost immediately. The catalytic effect of these clays on the curing process of the CY appears to be due to the formation of the coordination complex. The level of catalytic behaviour depends on the concentration of the hydroxyl group in the clays. For 20A/CY nanocomposite, the impaired catalytic effect may be due to the occurrence of phase separation. Raman spectra revealed that the CY resin reacts preferentially with the hydroxyl
groups in the clays firstly to form the coordination complex, rather than react with itself to form the triazine rings, during the network formation of the CY/clay nanocomposites. The formation of rigid 3-dimensional network for CY/clay nanocomposites was retarded until middle or even late stage of the cure, due to the absence of the triazine rings.

The incorporation of the various carbon nanotubes showed different accelerating effects on the curing reaction of CY. The addition of pristine MWCNT did not show a prominent accelerating effect. The MWCNT-OH and the MWCNT-COOH displayed strong accelerating effects, among which, the MWCNT-COOH performed better. For the MWCNT-OH/CY system, the most pronounced accelerating effect showed when the weight percentage of 1wt% to 2wt% was added. The nano-scale dispersion of MWCNTs in the CY matrix was observed by using FEG-SEM. The FTIR spectra monitored the formation of triazine rings in the CY and its composites with CNTs. The FTIR results also indicated that the CNTs react with the cyanate groups of CY to form the oxime, C=N-O. For the hydroxyl group functionalised MWCNT and SWCNT, reactions between OH group and cyanate groups were apparent. For the carboxyl groups functionalised MWCNT, reaction between C=O bond of COOH group and the cyanate groups appeared to occur at the very beginning of the reaction process. The up-shifting and broadening of the bands for MWCNTs in Raman spectra confirmed the nano-scale dispersion of MWCNTs in the CY matrix and strong interaction between MWCNTs and CY.
CHAPTER 6: DEGRADATION DYNAMICS OF CYANATE ESTER BASED NANOCOMPOSITES

6.1 Analysis of the CY resin

Figure 6.1 shows TGA results of CY under air and nitrogen atmosphere by TA instruments. The degradation of CY involved three reaction stages.\textsuperscript{9,152} Under air atmosphere, the first stage started from 415 °C, during which the thermoxidative degradation of oxygen bond between the phenyl and triazine rings led to approximate 10% weight loss. The second weight loss of 15% happened between 449 °C and 601 °C, due to the breakdown of the triazine rings. After 601 °C, the third reaction of benzene rings degradation resulted to approximately 75% weight loss. The decomposition process finished at 766 °C. Table 6.1 lists the analysis of TGA results. The CY became more durable under nitrogen atmosphere than that under air atmosphere. The first stage degradation happened from 418 °C to 451 °C, with about 14 % weight loss, followed by second stage degradation ending at about 701 °C. Even if the temperature raised to 1000 °C, the CY still did not completely degrade. Thus, the air showed an accelerating effect on the degradation of CY.
Figure 6.1: TGA results of pure CY with a heating rate of 10 °C/min under air atmosphere (60 ml/min) (A) and under nitrogen atmosphere (60 ml/min) (B).

Table 6.1: experimental indicators for thermal stability from the TGA experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{o1}$</td>
<td>$T_{c1}$</td>
<td>WL (%)</td>
</tr>
<tr>
<td>CY air</td>
<td>415</td>
<td>449</td>
<td>10</td>
</tr>
<tr>
<td>CY $N_2$</td>
<td>418</td>
<td>451</td>
<td>14</td>
</tr>
</tbody>
</table>

$T_{o}$: onset temperature at which decomposition started.

$T_{c}$: completion temperature at which decomposition finished.

WL: weight loss
6.2 Analysis of CY clay nanocomposites

Figure 6.2 and Figure 6.3 show the TGA results of CY/clay systems under both air and nitrogen atmosphere. Under air atmosphere, the thermal stability of the CY was slightly impaired with the addition of the clays. It is interesting that the heat released from the decomposition process the CY/clay nanocomposites is much lower than that of pure CY, under air atmosphere. The addition of the clays indeed enhanced the thermal stability of the CY in the nitrogen atmosphere. It is remarkable that the char yield of 3 wt% Na⁺/CY nanocomposite is 14 wt% higher than that of pure CY at 1000 °C. It should be noticed that the weight loss of the CY/clays nanocomposites was almost the same as that of pure CY before 670 °C. The dramatic improvement for the CY/clay nanocomposites happened when weight loss achieved about 31 %, which is at the end of stage 2 decomposition. This observation indicates that the incorporation of clays could not retard the stage 1 and stage 2 degradation. The improvement in stage 3 is possibly due to the formation of clay protection layers.
Figure 6.2: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under air atmosphere (60 ml/min).
Figure 6.3: TGA results of CY/clay systems. (A) residual weight in percentage of CY/clay system vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min).

Figure 6.4 and Figure 6.5 show the TGA results for two typical CY/clay systems with different clay ingredients. It is shown clearly that the clay/CY nanocomposites with different clay concentration did not show significant difference. If comparing in detail, the 3 wt% clay/CY systems displayed the best thermal stability under nitrogen atmosphere. According to the previous research, for the clay/CY systems, 3wt% clay incorporation led to lowest activation energy during the curing process. The activation energy is relative to Gibbs free energy. The lower Gibbs free energy means the lower internal stress between the molecules in the network, hence, the better network formation. The lower Gibbs free energy also implied better interaction between clay and CY resins, which may led to better dispersion. Thus, benefitted from more complete network formation and better interaction, the 3 wt% clay/CY systems showed best thermal stability.
Figure 6.4: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/Na\(^+\) system, (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/30B system with a heating rate of 10 \(^\circ\)C/min under nitrogen atmosphere (60 ml/min).
CHAPTER 6: DEGRADATION DYNAMICS OF CYANATE ESTER BASED NANOCOMPOSITES

Figure 6.5: TGA results of CY/clay systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/ Na\textsuperscript{+} system, (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/30B system with a heating rate of 10 °C/min under air atmosphere (60 ml/min).
6.3 Analysis of CNT/CY nanocomposites

Figure 6.6 and Figure 6.7 show the TGA results of CY/CNT systems under both air and nitrogen atmosphere. In air atmosphere, the CNT/CY nanocomposites showed poorer thermal stability than that of pure CY, except the MWCNT/CY nanocomposite. It is shown from Figure 6.6 (B) clearly that the heat release for functionalised CNTs is much higher than that of pure CY. This observation indicates that the presence of functionalised CNTs accelerated the decomposition process of CY. It is interesting that the incorporation of CNTs showed significant improvement in the thermal stability of CY, under nitrogen atmosphere. With incorporation of the 2 wt% MWCNT-COOH, the char yield of CY increased up to 14%. Furthermore, the trend of heat flow curves for the CNT/CY nanocomposites became totally different from that of pure CY, implying a change in the decomposition mechanism.
Figure 6.6: TGA results of CY/CNT systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under air atmosphere (60 ml/min).
Figure 6. 7: TGA results of CY/CNT systems. (A) residual weight in percentage of CY/clay system vs. temperature, (B) heat flow vs. temperature with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min).

Figure 6.8 shows the TGA results for the CY/MWCNT-OH systems with different MWCNT-OH ingredients under both air and nitrogen atmosphere. According to the result, the best thermal stability should be displayed with the incorporation of 1 wt% MWCNT-OH. This result is also in accordance with the previous research. For the CNT/CY systems, the incorporation of 1 wt% to 2 wt% CNT led to lowest activation energy during the curing process. The activation energy is relative to Gibbs free energy. The lower Gibbs free energy means the lower internal stress between the molecules in the network, hence, the better network formation. The lower Gibbs free energy also implied the better interaction between clay and CY resins, which may led to better dispersion. Thus, benefitted from more complete network formation and better interaction, the 1 wt% CNT/CY systems showed best reinforcement in the thermal stability of CY.
Figure 6. 8: TGA results of CY/MWCNT-OH systems. (A) residual weight in percentage vs. temperature, (B) heat flow vs. temperature for CY/MWCNT-OH system, with a heating rate of 10 °C/min under air atmosphere (60 ml/min), (C) residual weight in percentage vs. temperature, (D) heat flow vs. temperature for CY/MWCNT-OH system with a heating rate of 10 °C/min under nitrogen atmosphere (60 ml/min).
6.4 Analysis of POSS/CY nanocomposites

Figure 6.9 shows the TGA results for the CY/POSS systems with different POSS ingredients under both air and nitrogen atmosphere. It can be shown that the addition of POSS improved the thermal stability of CY significantly under both nitrogen and air atmosphere. The fully decomposition temperature raised from 776 °C to 916 °C under air atmosphere, with the incorporation of only 1 wt% POSS. Under nitrogen atmosphere, the char yield increased up to 15 %. The same as the clay/CY nanocomposites, the dramatic improvement happened when weight loss achieved about 31 %, which is at the end of stage 2 decomposition. This observation indicates that the incorporation of POSS could not retard the stage 1 and stage 2 degradation. The improvement in stage 3 is possibly due to the formation of POSS protection network.
6.5 Activation energy calculation

Studying thermal degradation kinetic of composites is vitally important for understanding the mechanisms of thermal decompositions of the composites. Activation energy for decomposition of materials is crucial parameter for estimation the thermal stability and decomposition kinetic of the materials. The activation energies of the CY and its nanocomposites versus the conversion during decomposition process under air atmosphere, were calculated. The calculation of activation energy is based on an integral method, Flynn-Wall-Ozawa (F-W-O) method\textsuperscript{153-156}, which leads to $-\frac{E_a}{R}$ from the slope of the line determined by plotting log (dT/dt) against 1/T at any certain conversion.
For a single reaction, the conversion $\alpha_i$ is defined as:

$$a_i = \frac{W_0 - W_{it}}{W_0 - W_{if}} \quad \text{...(6.1)}$$

Where, $W_0$, $W_{it}$, and $W_{if}$ are initial weight before the reaction, weight at time $t$ during the reaction, and final weight after the reaction, respectively.

If there are $n$ reactions during a typical decomposition process, the total conversion $\alpha$ is defined as:

$$\alpha = \frac{\sum_{i=1}^{n}(W_0 - W_{it})}{\sum_{i=1}^{n}(W_0 - W_{if})} \quad \text{...(6.2)}$$

The experiments were run at three heating rates. Thus, at the same conversion $\alpha$, the $T$ is different for different heating rate. According to F-W-O equation, heating rate $\beta$ was transformed to $\log(\beta)$, and temperature $T$ was transformed to $1/T$. The $\log(\beta)$ was plotted against $1/T$, to get a linear trend line. The activation energy of conversion $\alpha$, was calculated through the slope of the linear trend line, in which the slope equals to $-0.4567*E_a/R$

F-W-O equation is shown as follows:

$$\log \beta = \log \left( \frac{A E_a}{R g(\alpha)} \right) - 2.315 - \frac{0.4567 E_a}{RT} \quad \text{...(6.3)}$$

Where, $\beta$ is heating rate, $\beta=dt/dT$, $A$ is the pre-exponential factor (min$^{-1}$), $T$ is the absolute temperature (K), $R$ is the gas constant (8.314 J/K mol), and $E_a$ is the apparent activation energy.

Figure 6.10 demonstrates the TGA results for the calculation of activation energies. The poorer thermal stability was shown at higher heating rate. Table 6.2 shows the parameters calculated based on Flynn-Wall-Ozawa method. Table 6.3 shows the activation energy of the CY and its nanocomposites calculated using Flynn-Wall-Ozawa method.
CHAPTER 6: DEGRADATION DYNAMICS OF CYANATE ESTER BASED NANOCOMPOSITES

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[Graph A] Weight (%) vs. Temperature (°C) for CY series with different heating rates.

[Graph B] Weight (%) vs. Temperature (°C) for 5 wt% POSS series with different heating rates.

[Graph C] Weight (%) vs. Temperature (°C) for 3 wt% 30B series with different heating rates.
Figure 6. 10: TGA results of CY and its nanocomposites with different heating rates (A) CY, (B) 5 wt% POSS/CY, (C) 3 wt% 30B/CY, (D) 2 wt% MWCNT-OH under air atmosphere (20 ml/min).

Table 6. 2: parameters calculated based on Flynn-Wall-Ozawa method

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Table 6.3: activation energy of the CY and its nanocomposites calculated using Flynn-Wall-Ozawa method.

<table>
<thead>
<tr>
<th>stage</th>
<th>Conversion</th>
<th>Activation energy at conversion rate (kJ/mol)</th>
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<tr>
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Figure 6.11: activation energy of CY and its nanocomposites with clays during decomposition versus conversion rate under air atmosphere.

Arrhenius equation is shown as follows:

\[ k = A e^{-\frac{E_a}{RT}} \] ..........................................................(6.4)

Where \( k \) is Arrhenius type reaction rate constant, \( A \) is the pre-exponential factor, \( T \) is the absolute temperature, \( R \) is the gas constant, and \( E_a \) is the apparent activation energy.

Figure 6.11 shows the activation energy of the CY and the CY/clay systems. For the pure CY, the activation energy gradually increased in stage 1. However, it is quite interesting that in the stage 2, the activation energy increased significantly at the very beginning, and then decreased dramatically, became negative and reached its lowest value at conversion of 0.2, followed by a rapid increase again. The emergence of negative activation energy is relative to the reaction of nitrogenous chemicals, in this case, the degradation of triazine rings. Generally, an increase in temperature (T) increases the reaction rate (k) for most of reactions. According to Arrhenius equation, this situation results to a positive activation energy. However, there are a very small number of exceptions for elementary reaction, which the reaction rate decreased with the increasing temperature, leading to negative activation energy, for example, the oxidation of nitrogen monoxide. For a multistep mechanism reaction, it is also possible that the apparent activation energy is negative. The negative activation energy indicated that the
reaction rate decreased with the raising temperature, which may imply high barrier for the reaction. According to the current result, it is inferred that the reaction of stage 2 became a multistep mechanism reaction, or a reversible reaction, rather than the simple breakdown of the triazine rings for pure CY. The activation energy became stable in stage 3.

For the POSS/CY nanocomposites, the addition of the POSS increased the activation energy throughout the decomposition process, which means the higher reaction barrier. Thus, the thermal stability of the POSS/CY nanocomposites is better than that of pure CY in air atmosphere. It is remarkable that the activation energy in stage 2 became positive, which implied that the addition of the POSS changed the degradation mechanism of CY in stage 2. Generally speaking, for the clay/CY nanocomposites, the activation energy is slightly lower than that of CY, which indicated the lower degradation barrier.

For CNT/CY nanocomposites, the activation energy is much lower than that of the pure CY, which implied poorer stability. All these results are in accord with the previous TGA experiments.

6.6 Summary

The decomposition process of the CY and its nanocomposites involved three steps. The first stage is the thermoxidative degradation of oxygen bond between the phenyl and triazine rings, followed by the breakdown of the triazine rings (second stage). The decomposition ended by the third reaction of benzene rings degradation. Air showed accelerating effect on the degradation of CY.

The incorporation of the clays showed good reinforcement on the thermal stability of CY under nitrogen atmosphere, rather than that under air atmosphere. It is remarkable that the char yield of 3 wt% Na⁺/CY nanocomposite is 14 wt% higher than that of pure CY at 1000 °C.

The addition of the CNTs significantly impaired the thermal stability of the CY under air atmosphere. Although leading to forwarding of decomposition process, the CNTs indeed helped the CY to be more stable under nitrogen atmosphere. With incorporation of the 2 wt% MWCNT-COOH, the char yield of CY increased up to 14%.

160
The POSS/CY nanocomposites performed quite well under both air and nitrogen atmosphere. The fully decomposition temperature raised from 776 °C to 916 °C under air atmosphere, with the incorporation of only 1 wt% POSS. Under nitrogen atmosphere, the char yield increased up to 15 %.

The activation energies of the CY and its nanocomposites versus the conversion during decomposition process under air atmosphere, were calculated. The results are in accord with the TGA experiments. It is interesting that negative activation energy appeared in the stage 2 for CY, due to the reaction of triazine rings breakdown. The negative activation energy indicated the decomposition rate decreased with the increasing temperature, which may imply very high decomposition barrier.
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

7.1 Processability of Benzoxazine based nanocomposites

7.1.1 Morphology of benzoxazine mixtures

Figure 7.1 shows the digital pictures of the BEN resin incorporated with different nanofillers. It is showed clearly that the mixed resins are all homogenous. The neat BEN resin is powdered solid with light yellow colour. With addition of the MWCNT, the resin turned to black. After incorporating with the POSS, the resin became transparent with metallic yellow finishing. For the clay/BEN systems, the Na⁺/BEN resin is light green, the 30B/BEN resin is dark yellow, and the 20A/BEN resin stays light yellow.
Figure 7.1: digital pictures of BEN resins incorporated with different nanofillers. (A) neat BEN resin, (B) 2 wt% MWCNT-OH/BEN, (C) 5 wt% POSS-OH/BEN, (D) 3 wt% Na+/BEN, (E) 3 wt% 30B clay/BEN, and (F) 3 wt% 20A/BEN.

7.1.2 Morphology of Benzoxazine based nanocomposites.

Figure 7.2 shows the digital pictures of BEN and BEN based nanocomposites. For neat BEN, the POSS/BEN and the clay/BEN nanocomposites, there are a large amount of voids and cracks inside the samples after cure, which may have resulted from the gas released during the cure, due to the nature of the BEN. For the 5 wt% clay/BEN nanocomposites and 5 wt% POSS/BEN nanocomposites, the sample bent after cure, and there are more voids found compared with the nanocomposites with lower concentration, resulting in loose structure. For the CNT/BEN system with the concentration lower than 2 wt%, the situation is the same as the other nanocomposites. The difference is the amount of void decreased with the increasing concentration. The viscosity of the CNT/BEN resins increased with the concentration, The CNT/BEN resins can not flow any more with the incorporation of over 2 wt% CNTs, even if the temperature raised to 150 °C. Thus, it is hard to shape the resins without pressure. The benefit for the high concentration over 2 wt% is there were no any voids generated during cure. In conclusion, high concentration of the clays and the POSS impaired the shape stability of BEN, but high concentration of the CNTS help the BEN to retain its shape. Hence, if the BEN based nanocomposites are desired in further application, the concentration of the nanofillers should be carefully considered.
Figure 7. 2: digital pictures of the BEN based nanocomposites. (A) neat BEN, (B) 3 wt% Na⁺/BEN, (C) 5 wt% Na⁺/BEN (D) 3 wt% 30B/BEN, (E) 5 wt% 30B/BEN, (F) 3 wt% 20A/BEN, (G) 5 wt% 20A/BEN, (H) 5 wt% POSS/BEN, (I) 10 wt% POSS/BEN, (J) 1 wt% MWCNT-OH/BEN, (K) 2 wt% MWCNT-OH/BEN, (L) 4 wt% MWCNT-OH/BEN (M) 1 wt% MWCNT-COOH/BEN, (N) 2 wt% MWCNT-COOH/BEN and (O) 4 wt% MWCNT-COOH/BEN.

7.1.3 Dispersion of the nanofillers in the benzoxazine.

Figure 7.3 shows the TEM images of the cured BEN incorporated with POSS in different concentration. Generally speaking, the POSS was dispersed homogeneously in the BEN matrix. For the 1 wt% POSS/BEN nanocomposite, most of the POSS dispersed in the state of single particle sizing about 3nm, with some aggregates with sizes up to 50 nm observed. For the 5 wt% and 10 wt% POSS/BEN nanocomposites, the POSS was dispersed homogeneously with relatively high levels of aggregation. For the 5 wt% POSS/BEN nanocomposite, the size of aggregations ranged from 50nm to 100 nm. The size of the aggregations increased with the increasing concentration. The dimension of the aggregations was 200 nm in maximum with the incorporation of 10 wt% POSS.
Figure 7.3: TEM images of the nanocomposites of BEN incorporated with POSS in the concentrations of 1 wt% (A & B), 5 wt% (C & D), and 10 wt% (E & F).

To examine the state of clay layers for the different clays in the BEN matrix, the d-spacings of Na⁺ clay, 30B clay, 20A clay, 3 wt% BEN/Na⁺ nanocomposite and 3 wt% BEN/30B nanocomposite, and 3 wt% BEN/20A nanocomposite were measured using XRD and the results are shown in Figure 7.4. The original d-spacings of the clays for Na⁺, 30B, and 20A were 1.17 nm, 1.85 nm and 2.42 nm, respectively. For all the nanocomposites, it was noted that there was no peak in the range of 1° to 10°. This result indicated the exfoliation of the clays in the BEN matrix.
Figure 7. 4: XRD patterns for Na⁺ clay, 30B clay, 20A clay and their BEN/clay nanocomposites.
Figure 7.5 shows TEM images of Na⁺/BEN nanocomposites with various concentrations of Na⁺. It can be seen clearly from Figure 7.5 (B & D) that the Na⁺ clay layers were exfoliated in the BEN matrix. Although the Na⁺ clay layers were exfoliated, they aggregated into the particles with size of 1 µm.

![Figure 7.5](image)

Figure 7. 5: TEM images of (A & B) 1 wt% Na⁺/BEN nanocomposite and (C & D) 5wt% Na⁺/BEN nanocomposite.

Figure 7.6 shows TEM images of 30B/BEN nanocomposites with various concentrations. It is clearly shown from Figure 7.6 (B, D & F) that the 30B layers were exfoliated in the BEN matrix. Similar with the Na⁺/BEN nanocomposites, although the clay layers were exfoliated, they formed aggregations in the BEN matrix. The size of aggregations ranged between 1 µm to 5 µm, and increased with the increasing concentration of the 30B clay.
Figure 7.6: TEM images of (A & B) 1 wt% 30B/BEN nanocomposite, (C & D) 3wt% 30B/BEN nanocomposite, and (E & F) 5 wt% 30B/BEN nanocomposite.

Figure 7.7 shows TEM images of 20A/BEN nanocomposites with various concentrations. It is clearly shown from Figure 7.7 (B, & D) that the 20A layers were exfoliated in the BEN matrix. The aggregations are also observed, the size increased from hundred nanometers to 5 µm, with the increasing concentration.
Figure 7.7: TEM images of (A & B) 1 wt% 20A/BEN nanocomposite, and (C & D) 5 wt% 20A/BEN nanocomposite.

Figure 7.8 shows SEM images of the various BEN/CNT nanocomposites (all at 2 wt%). All the functionalised MWCNTs were well dispersed at a nano-scale level in the BEN matrix, with no any indication of aggregation taking place. However, for the pure MWCNT/BEN nanocomposite, and the SWCNT-OH/BEN nanocomposite, SWCNT-OH bundles were visible on the micro-scale were found.
Figure 7. 8: SEM images of the composites of BEN with 2 wt% MWCNT (A and B), 2 wt% MWCNT-OH/BEN (C and D), 2 wt% MWCNT-COOH (E and F), and 2 wt% SWCNT-OH (G and H)
7.2 curing dynamic of benzoxazine and its nanocomposites

Figure 7.9 shows DSC plots of benzoxazine and its nanocomposites in nitrogen atmosphere. Table 7.1 lists the parameters obtained from DSC experiments. It is clearly that the addition of POSSs did not show any catalytic effect. In contrast, the peak temperature of the curing process increased by up to 5 °C with the incorporation of clays. It is interested that the incorporation of MWCNTs showed good catalytic effect. For 2 wt% MWCNT-OH, the peak temperature decreased by 27 °C. Furthermore, the reaction enthalpy of 5 wt% POSS-OH/BEN system was 173 J/g, significantly lower than that of pure BEN which is 354 J/g. This observation indicates that the incorporation of POSS-OH hindered the network formation of the BEN.

Figure 7.9: DSC plots of benzoxazine and its nanocomposites in nitrogen atmosphere (60 ml/min) with heating rate of 10°C/min.
Table 7.1: Onset, peak and end temperatures, and enthalpy of the non-isothermal cure of the benzoxazine with different nanofillers.

<table>
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<tr>
<th>nanofillers</th>
<th>Onset Temperature (°C)</th>
<th>Peak Temperature (°C)</th>
<th>End temperature (°C)</th>
<th>Duration (min)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
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<td>Neat benzoxazine</td>
<td>210</td>
<td>246</td>
<td>288</td>
<td>7.8</td>
<td>354</td>
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<td>5 wt% POSS-OH</td>
<td>206</td>
<td>244</td>
<td>284</td>
<td>7.8</td>
<td>173</td>
</tr>
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<td>5 wt% POSS-NH₂</td>
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<td>246</td>
<td>291</td>
<td>8.2</td>
<td>304</td>
</tr>
<tr>
<td>3 wt% Na⁺</td>
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<td>248</td>
<td>292</td>
<td>8.5</td>
<td>325</td>
</tr>
<tr>
<td>3 wt% 30B</td>
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<td>249</td>
<td>288</td>
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<td>317</td>
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<tr>
<td>3 wt% 20A</td>
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<td>251</td>
<td>290</td>
<td>8.1</td>
<td>345</td>
</tr>
<tr>
<td>2 wt% MWCNT-OH</td>
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<td>219</td>
<td>294</td>
<td>10.9</td>
<td>351</td>
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<td>2 wt% MWCNT-COOH</td>
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<td>243</td>
<td>291</td>
<td>9.0</td>
<td>342</td>
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</table>

Figure 7.10 shows the plots of heat flow versus curing time for benzoxazine/nanofiller systems at different curing temperatures. Figure 7.11 shows the plots of conversion rate versus curing time for benzoxazine/nanofiller systems at different curing temperatures. It is clearly that higher temperature led to higher curing rate. Table 7.2 shows the kinetic parameters calculated from the isothermal MDSC experiments using Kamal’s equation, for the BEN and its nanocomposites.
Figure 7. 10: Plots of heat flow versus curing time for benzoxazine/nanofiller systems at different curing temperatures
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

Diagram A: Graph of a vs. time (min) for B: 3 wt% POSS-OH.

Diagram B: Graph of a vs. time (min) for C: 5 wt% POSS-OH.

Diagram C: Graph of a vs. time (min) for D: 2 wt% MWCNT-OH.
Figure 7.11: Plots of a versus curing time for benzoxazine/nanofiller systems at different curing temperatures

Table 7.2: Autocatalytic model constants for the Benzoxazine and its nanocomposites

<table>
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<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>$k_1$ ($\times 10^4$ s$^{-1}$)</th>
<th>$k_2$ ($\times 10^4$ s$^{-1}$)</th>
<th>m</th>
<th>n</th>
<th>lnA$_1$</th>
<th>lnA$_2$</th>
<th>$E_1$ (kJ/mol)</th>
<th>$E_2$ (kJ/mol)</th>
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<td>24.2</td>
<td>0.928</td>
<td>1.77</td>
<td>48</td>
<td>38</td>
<td>229</td>
<td>132</td>
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<tr>
<td></td>
<td>200</td>
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<td>1.469</td>
<td>2.629</td>
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<td>3.57</td>
<td>192.1</td>
<td>1.3</td>
<td>2.2685</td>
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<td>24.5</td>
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<td>34</td>
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<td>1.06</td>
<td>2.036</td>
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</table>
Table 7.3 shows the kinetic activation energy and the pre-exponential factor for the benzoxazine and its nanocomposites. Figure 7.12 shows the kinetic activation energy versus conversion for the benzoxazine and its nanocomposites. With the incorporation of the 30B clay and POSS, the activation energy is lower than that of pure benzoxazine at the very beginning of the cure, but then became higher at the conversion of 0.1 to 0.4. Thus, considering over all curing process, there is not obvious catalytic effect shown. On the other hand, the incorporation of the MWCNTs displayed good catalytic effect, the activation energy dropped dramatically at the very beginning, and was lower than that of neat benzoxazine throughout the whole curing process. The results are accordance with the dynamic DSC result.

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<td>96</td>
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<td>23</td>
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</table>
7.3 Network formation of benzoxazine and its nanocomposites.

Figure 7.13 shows the FTIR spectra for the pure BEN resin cured at 180 °C in nitrogen atmosphere (60ml/min). The characteristic absorption bands of the benzoxazine structure were observed at 1600 cm⁻¹, 1493 cm⁻¹, 1230 cm⁻¹, and 934 cm⁻¹, due to stretching of C-N-O group in oxazine ring, stretching of C=C bond in benzene ring, the asymmetric stretching of cyclic C–O–C ether group in oxazine ring, and the stretching of oxazine ring itself, respectively. The cure of the BEN resin can be followed by monitoring the corresponding absence in the absorbance bands of oxazine ring at 1600 cm⁻¹, 1230 cm⁻¹, and 934 cm⁻¹. The cure of the BEN followed a ring opening mechanism, as shown in Figure 7.14. With the curing time, the absorbance bands of oxazine ring disappeared due to the open of the ring. Another new band at 858 cm⁻¹ assigning to N-H wagging and twisting, indicated the occurrence of the ring opening as well. The characteristic band of trisubstituted benzene ring at 1493 cm⁻¹ shifted to 1573 cm⁻¹, which indicated the tetrasubstitution of the benzene ring. Furthermore, a new band at 1173 cm⁻¹ assigning to C-O stretching of phenol groups, indicated the formation of the phenol structure. The presence of absorbance bands at 1573 cm⁻¹ and 1620 cm⁻¹ indicating the C-N stretching and aromatic C=O stretching, also provided
an evidence of the oxazine ring opening and cure. It should be reminded here that the intensity of the absorbance bands of oxazine ring remained the same until 40 minutes, and then the absorbance bands suddenly disappeared or deceased. Furthermore, the intensity of the new bands changed little with the curing time. This observation reflected that the opening of the oxazine ring and the formation of benoxazine network completed in a short period, rather than gradually or step by step formation of the network which happened during the cure of cyanate ester.
Figure 7.13: FTIR spectra for the pure BEN resin cured at 180 °C in nitrogen atmosphere (60ml/min). (A) original and (B) enlarged. For clarification, the spectra were shift parallel, and were calibrated basing the absorption band of phenyl ring symmetric breathing vibration near 1500 cm⁻¹.
Figure 7.14: The cure scheme of benzoxazine rings opening.\(^{157}\)

Table 7.4: Analytical results of the FTIR spectra of the pure BEN resin cured at 180 °C

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Assignment</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>1230</td>
<td>Asymmetric C-O stretching</td>
<td>Cyclic ether C-O-C</td>
</tr>
<tr>
<td>1173</td>
<td>C-O stretching</td>
<td>Phenol C-OH</td>
</tr>
<tr>
<td>3520</td>
<td>O-H stretching</td>
<td>Phenol C-OH</td>
</tr>
<tr>
<td>1493</td>
<td>C=C stretching</td>
<td>trisubstituted benzene ring(^{153})</td>
</tr>
<tr>
<td>1483</td>
<td>C=C stretching</td>
<td>tetrasubstituted benzene ring</td>
</tr>
<tr>
<td>1600</td>
<td>Oxazine ring C-N-O stretching</td>
<td>N-C-O</td>
</tr>
<tr>
<td>1573</td>
<td>C-N stretching</td>
<td>C-N-C</td>
</tr>
<tr>
<td>1620</td>
<td>Aromatic C=O stretching</td>
<td>Aromatic C=O</td>
</tr>
<tr>
<td>934</td>
<td>Oxazine ring stretching(^{158})</td>
<td>Oxazine ring</td>
</tr>
<tr>
<td>858</td>
<td>N-H wagging and weisting</td>
<td>N-H</td>
</tr>
</tbody>
</table>

Figure 7.15 shows the FTIR spectra of the clays applied for the BEN/clay nanocomposites. Table 7.5 lists their assignments in the FTIR spectra.
Figure 7.15: FTIR spectra of the clays used for the BEN/clay nanocomposites

Figure 7.16 shows the FTIR spectra for the BEN/30B clay resin cured at 180 °C in nitrogen atmosphere (60ml/min). The characteristic bands at 1076 cm\(^{-1}\) and 998 cm\(^{-1}\) assigned to Si-O-C stretching and Si-O-Si asymmetric stretching respectively, indicated the presence of the 30 B clay. The procedure for monitoring the cure of the BEN/clay resin is the same as that of pure BEN resin. For the BEN/clay system, all the bands subjected to change after 20 minutes, quicker than that of the pure BEN system which changed after 40 minutes. Thus, it is clearly that the incorporation of the clay accelerated the cure process of the BEN. Apart from the bands present in the FTIR spectra of the cure of BEN, a new broad band is observed at 1027 cm\(^{-1}\) assigning to stretching of the ether C-O-C group. This observation indicated the reaction of the clay with the BEN during the cure. The scheme of the reaction is shown in Figure 7.17.
Table 7.5: Infra-red assignments on the clays used for the BEN/clay nanocomposites

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>3624</td>
<td>O-H stretching of the inner hydroxyl groups between tetrahedral and octahedral sheets</td>
<td>O-H</td>
</tr>
<tr>
<td>910, 880</td>
<td>O-H Bending</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>Si-O stretching</td>
<td>Si-O</td>
</tr>
<tr>
<td>2920</td>
<td>Methylene symmetric C-H stretching</td>
<td>-CH(_2)</td>
</tr>
<tr>
<td>2850</td>
<td>Methylene asymmetric C-H stretching</td>
<td>-CH(_3)</td>
</tr>
<tr>
<td>720</td>
<td>Methylene rocking</td>
<td></td>
</tr>
<tr>
<td>1470</td>
<td>Methyl asymmetric C-H bending</td>
<td></td>
</tr>
<tr>
<td>1380</td>
<td>Methyl symmetric C-H bending</td>
<td></td>
</tr>
<tr>
<td>3300 for Clay 30B</td>
<td>O-H stretching of hydroxyethyl due to hydrogen bonding</td>
<td>O-H</td>
</tr>
</tbody>
</table>
Figure 7.16: FTIR spectra for the BEN/30B clay resin cured at 180 °C in nitrogen atmosphere (60ml/min). (A) original and (B) enlarged. For clarification, the spectra were shift parallel, and were calibrated based on the absorption band of phenyl ring symmetric breathing vibration near 1500 cm\(^{-1}\).
The FTIR spectra of the cure of 5 wt% POSS/BEN nanocomposite with time are given in Figure 7.18. The procedure for monitoring the cure of the BEN/POSS nanocomposite is the same as that of pure BEN resin. There was no any accelerating effect with the addition of the POSS. The POSS reacted with the benzoxazine during the cure, proved by the presence of the band at 1050 cm\(^{-1}\), indicating the formation of Si-O-C bond.

![Figure 7.17: Scheme of crosslinked network formation of the BEN/clay nanocomposite.](image)

![Figure 7.18: FTIR spectra for the BEN/POSS resin cured at 180 °C in nitrogen atmosphere (60ml/min).](image)
Figure 7.19: Scheme of crosslinked network formation of the BEN/POSS nanocomposite.

Figure 7.20 shows the FTIR spectra for the BEN/MWCNT-COOH resin cured at 180 °C in nitrogen atmosphere (60ml/min). The characteristic band near 1650 cm$^{-1}$ assigned to C=O stretching, indicated the presence of the MWCNT-COOH. The procedure for monitoring the cure of the BEN/MWCNT-COOH resin is the same as that of pure BEN resin. For the BEN/MWCNT system, the addition of the CNT accelerated the cure process of the BEN. All the bands subjected to change after 20 minutes, quicker than that of the pure BEN system which changed after 40 minutes. Apart from the bands present in the FTIR spectra of the cure of BEN, two new bands are observed at 1250 cm$^{-1}$ and 1750 cm$^{-1}$ assigning to stretching of the C-O bond and C=O bond, respectively. These two bands indicated the reaction of the MWCNT-COOH with the BEN to form ester group. The scheme of the reaction is shown in Figure 7.21.
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

Figure 7. 20: FTIR spectra for the BEN/CNT resin cured at 180 °C in nitrogen atmosphere (60ml/min).

Figure 7. 21: Scheme of crosslinked network formation of the BEN/CNT nanocomposite.
7.4 TGA analysis

The thermal stability of the pristine BEN, and its nanocomposites incorporating with nanoclay, POSS, and CNT were evaluated by dynamic thermogravimetric analyses (TGA).

Figure 7.22 shows the TGA results of the BEN/clay nanocomposites under air atmosphere. Table 7.6 lists the experimental indicators for thermal stability from the TGA experiment. Under air atmosphere, the incorporation of the clays with high concentration showed significant improvement to the thermal stability of BEN. For the 20A/BEN nanocomposite and the 30B/BEN nanocomposite, the thermal stability increased with the increasing concentration. With the incorporation of 1 wt% 30B and 20A, the thermal stability of the BEN was impaired. The best performance was observed with the incorporation of the 5 wt% clays. For the Na+/BEN nanocomposite, the best result showed when 3 wt% Na+ was added. It should be noticed that the BEN became significantly less stable with the incorporation of the 1wt% clays. The onset decomposition temperature decreased about 40 °C. As shown in Figure 7.22 (D), the clays with best performance in each group were compared. There is no any obvious difference between them. The onset temperature increased from 320 °C to about 350 °C. The half life decomposition temperature increased by 30 °C as well. However, there is no improvement in full decomposition temperature. Thus, considering cost efficiency, 3 wt% Na+/BEN nanocomposite is recommended.
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANO COMPOSITES

[Graph A]

[Graph B]
Figure 7.22: TGA results of BEN/clay nanocomposites with residual weight in percentage vs. temperature (A) 20A/BEN, (B) 30B/BEN, (C) Na⁺/BEN, and (D) comparative results for the clays performed best in each group, with a heating rate of 10 °C/min under air atmosphere (20 ml/min).
Table 7.6: experimental indicators for thermal stability from the TGA experiment.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_c$</th>
<th>$T_{1/2}$</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>320</td>
<td>660</td>
<td>544</td>
<td>0</td>
</tr>
<tr>
<td>1 wt% 20A/BEN</td>
<td>280</td>
<td>644</td>
<td>551</td>
<td>1</td>
</tr>
<tr>
<td>3 wt% 20A/BEN</td>
<td>351</td>
<td>660</td>
<td>564</td>
<td>2</td>
</tr>
<tr>
<td>5 wt% 20A/BEN</td>
<td>351</td>
<td>660</td>
<td>576</td>
<td>5</td>
</tr>
<tr>
<td>1 wt% 30B/BEN</td>
<td>288</td>
<td>657</td>
<td>540</td>
<td>1</td>
</tr>
<tr>
<td>3 wt% 30B/BEN</td>
<td>329</td>
<td>664</td>
<td>555</td>
<td>2</td>
</tr>
<tr>
<td>5 wt% 30B/BEN</td>
<td>353</td>
<td>664</td>
<td>570</td>
<td>3</td>
</tr>
<tr>
<td>1 wt% Na$^+$/BEN</td>
<td>277</td>
<td>647</td>
<td>554</td>
<td>1</td>
</tr>
<tr>
<td>3 wt% Na$^+$/BEN</td>
<td>345</td>
<td>676</td>
<td>568</td>
<td>2</td>
</tr>
<tr>
<td>5 wt% Na$^+$/BEN</td>
<td>345</td>
<td>663</td>
<td>554</td>
<td>4</td>
</tr>
</tbody>
</table>

$T_o$: onset temperature at which decomposition started.

$T_c$: completion temperature at which decomposition finished.

$T_{1/2}$: half life decomposition temperature at which 50% weight loss of the initial weight occurred.

Figure 7.23 shows the TGA results of the BEN/clay nanocomposites under nitrogen atmosphere. Table 7.7 lists the experimental indicators for thermal stability from the TGA experiment. Under nitrogen atmosphere, the BEN and its nanocomposites did not fully degrade even if the temperature raised to 800 °C. The incorporation of the clays with high concentration showed significant improvement to the thermal stability of BEN. For the 20A/BEN nanocomposite and the 30B/BEN nanocomposite, the thermal stability increased with the increasing concentration. The best performance was observed with the incorporation of the 5 wt% clays. For the Na$^+$/BEN nanocomposite, the best result showed when 3 wt% Na$^+$ was added. It should be noticed that the BEN became less thermally stable with the incorporation of the 1wt% clays under nitrogen atmosphere. As shown in Figure 7.23 (D), the clays with best performance in each group were compared. The best enhancement for the thermal stability of the BEN was shown with the incorporation of 5 wt% 30B clay. The onset temperature increased by 70 °C. It is remarkable that the half time decomposition temperature increased from 493 °C to 729 °C, which is an improvement of 336 °C. Furthermore, the char yield at 800 °C increased 8 wt%. Thus, for applications under nitrogen atmosphere, 5 wt% 30B/BEN nanocomposite is recommended.
Figure 7.23: TGA results of BEN/clay nanocomposites with residual weight in percentage vs. temperature (A) 20A/BEN, (B) 30B/BEN, (C) Na+/BEN, and (D) comparative results for the clays performed best in each group, with a heating rate of 10 °C/min under nitrogen atmosphere (20 ml/min).
Table 7.7: experimental indicators for thermal stability from the TGA experiment.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_{1/2}$</th>
<th>Char yield at 800 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>257</td>
<td>493</td>
<td>36</td>
</tr>
<tr>
<td>1 wt% 20A/BEN</td>
<td>257</td>
<td>481</td>
<td>36</td>
</tr>
<tr>
<td>3 wt% 20A/BEN</td>
<td>283</td>
<td>640</td>
<td>39</td>
</tr>
<tr>
<td>5 wt% 20A/BEN</td>
<td>315</td>
<td>671</td>
<td>40</td>
</tr>
<tr>
<td>1 wt% 30B/BEN</td>
<td>282</td>
<td>489</td>
<td>38</td>
</tr>
<tr>
<td>3 wt% 30B/BEN</td>
<td>253</td>
<td>513</td>
<td>39</td>
</tr>
<tr>
<td>5 wt% 30B/BEN</td>
<td>328</td>
<td>729</td>
<td>45</td>
</tr>
<tr>
<td>1 wt% Na$^+$/BEN</td>
<td>275</td>
<td>512</td>
<td>40</td>
</tr>
<tr>
<td>3 wt% Na$^+$/BEN</td>
<td>282</td>
<td>538</td>
<td>43</td>
</tr>
<tr>
<td>5 wt% Na$^+$/BEN</td>
<td>289</td>
<td>639</td>
<td>42</td>
</tr>
</tbody>
</table>

Figure 7.24 (A) shows the TGA results of the BEN/POSS nanocomposite under air atmosphere. Table 7.8 lists the experimental indicators for thermal stability from the TGA experiment. Under air atmosphere, the incorporation of the POSS with high concentration showed good improvement to the thermal stability of BEN. With the incorporation of 1 wt% POSS, the thermal stability of the BEN was slightly impaired when temperature lower than 400 °C, with good reinforcement above 400 °C in contrast. The onset decomposition temperature reduced by 56 °C. When the concentration is higher than 1 wt%, the thermal stability increased with the increasing content. The best performance was observed with the incorporation of the 10 wt% POSS. Thus, 10 wt% POSS/BEN nanocomposite is recommended under air atmosphere.

Figure 7.24 (B) shows the TGA results of the BEN/POSS nanocomposites under nitrogen atmosphere. Table 7.9 lists the experimental indicators for thermal stability from the TGA experiment. Under nitrogen atmosphere, the BEN and its POSS nanocomposites did not fully degrade even if the temperature raised to 800 °C. With the incorporation of 1 wt% POSS, the BEN became less thermally stable at the beginning, with then turning to be more stable. The best performance was observed when 5 wt% POSS was incorporated. The half life decomposition temperature and char yield enhanced by 280 °C and 13 wt%. The thermal stability of the BEN/POSS nanocomposite is still better than that of pure BEN, with the incorporation of 10 wt% POSS, but not as good as that of 5 wt% POSS/BEN nanocomposite.
In conclusion, 5 wt% POSS was the first choice when applied under nitrogen atmosphere.

Figure 7.24: TGA results of BEN/clay nanocomposites with residual weight in percentage vs. temperature (A) under air atmosphere (20 ml/min), and (B) under nitrogen atmosphere (20 ml/min), with a heating rate of 10 °C/min.
Table 7.8: Experimental indicators for thermal stability of BEN and its POSS nanocomposite under air atmosphere.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_c$</th>
<th>$T_{1/2}$</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>320</td>
<td>660</td>
<td>544</td>
<td>0</td>
</tr>
<tr>
<td>1 wt% POSS/BEN</td>
<td>264</td>
<td>668</td>
<td>558</td>
<td>0</td>
</tr>
<tr>
<td>5 wt% POSS/BEN</td>
<td>278</td>
<td>673</td>
<td>564</td>
<td>3</td>
</tr>
<tr>
<td>10 wt% POSS/BEN</td>
<td>338</td>
<td>684</td>
<td>578</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 7.9: Experimental indicators for thermal stability of BEN and its POSS nanocomposite under nitrogen atmosphere.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_{1/2}$</th>
<th>Char yield at 800 °C(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>257</td>
<td>493</td>
<td>36</td>
</tr>
<tr>
<td>1 wt% POSS/BEN</td>
<td>263</td>
<td>537</td>
<td>43</td>
</tr>
<tr>
<td>5 wt% POSS/BEN</td>
<td>278</td>
<td>773</td>
<td>49</td>
</tr>
<tr>
<td>10 wt% POSS/BEN</td>
<td>278</td>
<td>619</td>
<td>47</td>
</tr>
</tbody>
</table>

Figure 7.25 shows the TGA results of the BEN/CNT nanocomposite under air atmosphere. Table 7.10 lists the experimental indicators for thermal stability from the TGA experiment. In general, the addition of CNT improved the thermal stability of BEN, but the situation became very complicated. For the MWCNT/BEN nanocomposites, the incorporation of 1 wt% MWCNT impaired the thermal stability. For the 2 wt% and 4 wt% MWCNT/BEN nanocomposites, the thermal stability was enhanced, with the 2 wt% MWCNT/BEN nanocomposite performing better before 569 °C. For the MWCNT-OH/BEN nanocomposites, the 1 wt% and 4 wt% MWCNT-OH/BEN nanocomposites showed similar enhancement to the thermal stability of BEN. For the MWCNT-COOH/BEN nanocomposites, the 2 wt% MWCNT-COOH/BEN nanocomposite was most thermally stable before 412 °C, with 1 wt% MWCNT-COOH/BEN nanocomposite performing best after 412 °C. Furthermore, the thermal stability of 2 wt% SWCNT-OH/BEN nanocomposite is better than that of pure BEN. It can be seen from Figure 7.25 (E) that 2 wt% MWCNT/BEN showed best thermal stability before 566 °C, and 4 wt% MWCNT/BEN nanocomposite became most thermally stable after 566 °C. Thus, the pure MWCNT displayed best performance among all the CNTs, and concentration of the MWCNT should be carefully chosen to fit typical application temperature range.
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

C

D

2% SWCNT-OH-BEN

Weight (%) vs. Temperature ($^\circ$C) for BEN and MWCNT-COOH-BEN

Weight (%) vs. Temperature ($^\circ$C) for BEN and SWCNT-OH-BEN

1% MWCNT-COOH-BEN

2% MWCNT-COOH-BEN

4% MWCNT-COOH-BEN
Chapter 7: A Comparative Study on Benzoxazine Based Nanocomposites

Figure 7.25: TGA results of BEN/CNT with residual weight in percentage vs. temperature (A) MWCNT/BEN, (B) MWCNT-OH/BEN, (C) MWCNT-COOH/BEN, (D) SWCNT-OH/BEN, and (E) comparative results, with a heating rate of 10 °C/min under air atmosphere (20 ml/min).

Table 7.10: Experimental indicators for thermal stability from the TGA experiment.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_c$</th>
<th>$T_{1/2}$</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>320</td>
<td>660</td>
<td>544</td>
<td>0</td>
</tr>
<tr>
<td>1 wt% MWCNT/BEN</td>
<td>305</td>
<td>665</td>
<td>529</td>
<td>0</td>
</tr>
<tr>
<td>2 wt% MWCNT/BEN</td>
<td>319</td>
<td>675</td>
<td>577</td>
<td>2</td>
</tr>
<tr>
<td>4 wt% MWCNT/BEN</td>
<td>319</td>
<td>692</td>
<td>590</td>
<td>1</td>
</tr>
<tr>
<td>1 wt% MWCNT-OH/BEN</td>
<td>310</td>
<td>662</td>
<td>573</td>
<td>1</td>
</tr>
<tr>
<td>2 wt% MWCNT-OH/BEN</td>
<td>254</td>
<td>643</td>
<td>550</td>
<td>0</td>
</tr>
<tr>
<td>4 wt% MWCNT-OH/BEN</td>
<td>311</td>
<td>663</td>
<td>573</td>
<td>4</td>
</tr>
<tr>
<td>1 wt% MWCNT-COOH/BEN</td>
<td>317</td>
<td>662</td>
<td>575</td>
<td>3</td>
</tr>
<tr>
<td>2 wt% MWCNT-COOH/BEN</td>
<td>310</td>
<td>672</td>
<td>552</td>
<td>1</td>
</tr>
<tr>
<td>4 wt% MWCNT-COOH/BEN</td>
<td>316</td>
<td>662</td>
<td>579</td>
<td>0</td>
</tr>
<tr>
<td>2 wt% SWCNT-OH/BEN</td>
<td>313</td>
<td>640</td>
<td>565</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 7.26 shows the TGA results of the BEN/CNT nanocomposite under nitrogen atmosphere. Table 7.11 lists the experimental indicators for thermal stability from the TGA experiment. In common with the analysis that under air atmosphere, the addition of CNT improved the thermal stability of BEN, but the situation became very complicated. For the MWCNT/BEN nanocomposites, the incorporation of 1 wt% MWCNT did not show much improvement to the thermal stability. The strongest reinforcement was observed with the incorporation of 4 wt% MWCNT. For the MWCNT-OH/BEN nanocomposites, the 1 wt% and 4 wt% MWCNT-OH/BEN nanocomposites showed similar enhancement to the thermal stability of BEN. 2 wt% MWCNT-OH/BEN nanocomposite performed better before 464 °C. For the MWCNT-COOH/BEN nanocomposites, the 2 wt% MWCNT-COOH/BEN nanocomposite was relatively thermally stable before 425 °C, with 4 wt% MWCNT-COOH/BEN nanocomposite showing significantly enhancement after 412 °C. Furthermore, the thermal stability of 2 wt% SWCNT-OH/BEN nanocomposite is better than that of pure BEN. It can be shown from Figure 7.26 (E) that 4 wt% MWCNT/BEN nanocomposite showed best thermal stability before 465 °C, and 4 wt% MWCNT-COOH performed best after 465 °C. In conclusion, the type of CNT and concentration should be carefully chosen to fit typical application temperature range.
CHAPTER 7: A COMPARATIVE STUDY ON BENZOXAZINE BASED NANOCOMPOSITES

B

C

Weight (%) vs. Temperature (°C) for different compositions of BEN and MWCNT-based nanocomposites.
Figure 7. 26: TGA results of BEN/CNT nanocomposites with residual weight in percentage vs. temperature (A) MWCNT/BEN, (B) MWCNT-OH/BEN, (C) MWCNT-COOH/BEN, (D) SWCNT-OH/BEN, and (E) comparative results, with a heating rate of 10 °C/min under nitrogen atmosphere (20 ml/min).
Table 7.11: experimental indicators for thermal stability from the TGA experiment.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_o$</th>
<th>$T_{1/2}$</th>
<th>Char yield at 800 °C(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BEN</td>
<td>257</td>
<td>493</td>
<td>36</td>
</tr>
<tr>
<td>1 wt% MWCNT/BEN</td>
<td>292</td>
<td>483</td>
<td>37</td>
</tr>
<tr>
<td>2 wt% MWCNT/BEN</td>
<td>304</td>
<td>654</td>
<td>39</td>
</tr>
<tr>
<td>4 wt% MWCNT/BEN</td>
<td>331</td>
<td>752</td>
<td>49</td>
</tr>
<tr>
<td>1 wt% MWCNT-OH/BEN</td>
<td>319</td>
<td>677</td>
<td>47</td>
</tr>
<tr>
<td>2 wt% MWCNT-OH/BEN</td>
<td>310</td>
<td>599</td>
<td>38</td>
</tr>
<tr>
<td>4 wt% MWCNT-OH/BEN</td>
<td>295</td>
<td>677</td>
<td>45</td>
</tr>
<tr>
<td>1 wt% MWCNT-COOH/BEN</td>
<td>285</td>
<td>575</td>
<td>44</td>
</tr>
<tr>
<td>2 wt% MWCNT-COOH/BEN</td>
<td>253</td>
<td>532</td>
<td>34</td>
</tr>
<tr>
<td>4 wt% MWCNT-COOH/BEN</td>
<td>323</td>
<td>779</td>
<td>50</td>
</tr>
<tr>
<td>2 wt% SWCNT-OH/BEN</td>
<td>318</td>
<td>594</td>
<td>46</td>
</tr>
</tbody>
</table>

Comparing with the TGA thermograms of the various BEN based nanocomposites under air atmosphere, it can be seen that 10% POSS /BEN showed the best thermal stability before 567 °C, 4 wt% MWCNT/BEN nanocomposite became most thermally stable after 567 °C. Interestingly, when comparing the TGA thermograms of the BEN based nanocomposites under nitrogen atmosphere, 5% POSS-OH-BEN performed the best thermal stability.
Figure 7.27: TGA results of BEN based nanocomposites with residual weight in percentage vs. temperature (A) under air atmosphere (20 ml/min), and (B) under nitrogen atmosphere (20 ml/min), with a heating rate of 10 °C/min.
7.5 comparative summaries

The processing procedure of the BEN/nanofiller mixtures is the similar with that of CY/nanofiller mixtures. The POSS and clays can be mixed directly with BEN to achieve homogeneous mixtures. For CNT, solvent and ultrasonication were necessarily applied to assist. For the CY, there was no problem to cure with the incorporation of the clays and the POSS. With the incorporation of CNTs, it is unavoidable that the generation of voids and cracks due to release of the solvent during cure. For the BEN, the processability is worse than that of CY. For the BEN and its nanocomposites, there were a large number of voids and cracks inside the samples after cure, which could not be prevented, and may result from the gas released during the cure, due to the nature of the BEN. High concentration of the clays and the POSS impaired the shape stability of BEN, but high concentration of the CNTs help the BEN to retain its shape. Hence, if the BEN based nanocomposites are desired in further application, the concentration of the nanofillers should be carefully considered. TEM, SEM, and XRD proved the homogeneous dispersion of the nanofillers in the BEN matrix, which is similar to that of the CY.

The incorporation of the various POSS, clays and CNTs showed different catalytic effects on the curing reaction of CY. However, For the BEN, the incorporation of nanofillers rarely showed a catalytic effect, except for CNTs. Both the cure of the BEN based mixtures and the CY based mixtures can be monitored by means of FTIR. The cure of the BEN followed a ring opening mechanism. With the curing time, the absorbance bands of oxazine ring disappeared due to the opening of the ring. All the functionalised nanofillers examined reacted with the BEN during the cure. However, the reaction between the nanofillers and the BEN did not lead to strong catalytic effect as that of CY.

The incorporation of the nanofillers showed good reinforcement to the thermal stability of both BEN and CY. For the BEN, 10% POSS/BEN showed the best thermal stability before 567 °C, 4 wt% MWCNT/BEN nanocomposite became most thermally stable after 567 °C, under air atmosphere Interestingly, 5% POSS/BEN performed the best thermal stability under nitrogen atmosphere.
CHAPTER 8: CONCLUSIONS AND FURTHER WORK

8.1 Conclusions

8.1.1 Processability of the cyanate ester and its nanocomposites
The influence of several catalysts, initiators and solvents on the curing dynamics of the CY was explored by means of DSC. Although the acetylacetonate and dilaurate based catalysts showed strong catalytic effect, the reaction enthalpy for the cure of CY dramatically declined, which implied that the incorporation of the catalysts led to incomplete network formation of the CY. For the initiators, the addition of BPO and CPO showed catalytic effect, and the strength increased with the concentration. For the solvents, chloroform, acetone, and cyclohexane did not show prominent catalytic effect on the CY. The DMF and THF showed catalytic effect, among which THF performed better. The clays and POSS can be directly mixed with the CY resin to form homogenous mixture, and there is no problem for further curing and processing of the nanocomposites. For the CNTs, in order to achieve good dispersion, assistance of solvent and ultrasonication is necessary. For the CNT/CY system, there are several problems. The nano-scale dispersion of the POSS, Na+ and 30B clays, and MWCNTs was observed using SEM and TEM. XRD results indicate that the Na+ and 30B clays were exfoliated in the CY matrix. For the 20A/CY nanocomposites, visible aggregation was observed after the cure. For the SWCNT/CY nanocomposites, micro-scale aggregation was detected by means of SEM.

8.1.2 Curing dynamics and network formation of the cyanate ester and its nanocomposites
The incorporation of the POSS catalyzed the reaction of the CY. However, excessive addition leads to an increase of onset temperature, and reduction in the total reaction enthalpy. The results showed that the activation energy of the CY/POSS systems decreased with increasing POSS content, up to 5 wt%. The most pronounced catalytic effect was observed with 5 wt% POSS. Although the excessive addition of the POSS showed catalytic behaviour in the initial stages, it hindered the chemical reaction of the CY when the conversion reached a certain level. Both FTIR and Raman spectroscopy can be applied to monitor the reaction of the CY/POSS nanocomposites through the formation of triazine ring. Raman spectra revealed
that the CY resin preferred to react with –OH group on the POSS firstly to form the -O-(C=NH)-O- bond in CY and its nanocomposites with the POSS. The strong catalytic effect of the POSS to the curing process of the CY should be originated from formation of the -O-(C=NH)-O- bond.

The incorporation of the Na+, 20A, and 30B clays catalysed the reaction of the CY resin to various degrees. The most effective catalytic effect was shown with the addition of the 30B clay. The results showed that the activation energy of the CY/30B clay systems decreased with increasing clay content, up to 3 wt%. The most pronounced catalytic effect was observed with 3 wt% 30B. Although the excessive addition of the clay showed catalytic behaviour in the initial stages, it hindered the chemical reaction of the CY when the conversion reached a certain level. The homogeneous dispersion of 30B and Na+ clays in the CY matrix was observed by the FEG-SEM. The aggregation of 20A clay was observed, which is due to the presence of the hydrophobic modifier. TEM images and XRD diffraction pattern confirmed that the 30B and Na+ clays were exfoliated in the CY matrix. FTIR spectra were used to monitor the formation of the triazine ring in the CY. The FTIR results indicate that the clay Na+ and 30B react with the CY to form a coordination complex, and then the coordination complex with this complex being converted to the –O–(C=NH)–O– bond with the progress of the curing reaction. In contrast, for the CY/20A system, the coordination complex was present at the very beginning of the reaction, but then was transformed to the –O–(C=NH)–O– compound almost immediately. The catalytic effect of these clays on the curing process of the CY appears to be due to the formation of the coordination complex. The level of catalytic behaviour depends on the concentration of the hydroxyl group in the clays. For 20A/CY nanocomposite, the impaired catalytic effect may be due to the occurrence of phase separation. Raman spectra revealed that the CY resin reacts preferentially with the hydroxyl groups in the clays firstly to form the coordination complex, rather than react with itself to form the triazine rings, during the network formation of the CY/clay nanocomposites. The formation of rigid 3-dimensional network for CY/clay nanocomposites was retarded until the middle or even the later stages of the cure, due to the absence of the triazine rings.

The incorporation of the various carbon nanotubes showed different accelerating effects on the curing reaction of CY. The addition of pristine MWCNT did not show a prominent accelerating effect. The MWCNT-OH and the MWCNT-COOH displayed strong accelerating effects, among which, the MWCNT-COOH performed better. For the MWCNT-OH/CY
system, the most pronounced accelerating effect was shown when 1 wt% to 2 wt% was added. The nano-scale dispersion of MWCNTs in the CY matrix was observed by using FEG-SEM. The FTIR spectra monitored the formation of triazine rings in the CY and its composites with CNTs. The FTIR results also indicated that the CNTs react with the cyanate groups of CY to form the oxime, C=N-O. For the hydroxyl group functionalised MWCNT and SWCNT, reactions between OH group and cyanate groups were apparent. For the carboxyl groups functionalised MWCNT, reaction between C=O bond of COOH group and the cyanate groups appeared to occur at the very beginning of the reaction process. The up-shifting and broadening of the bands for MWCNTs in Raman spectra confirmed the nano-scale dispersion of MWCNTs in the CY matrix and strong interaction between MWCNTs and CY.

8.1.3 Thermal stability of the cyanate ester and its nanocomposites.

The incorporation of the clays showed good reinforcement on the thermal stability of CY under nitrogen atmosphere, rather than that under air atmosphere. It is remarkable that the char yield of 3 wt% Na+/CY nanocomposite is 14 wt% higher than that of pure CY at 1000 °C. The addition of the CNTs significantly impaired the thermal stability of the CY under air atmosphere. Although leading to forwarding of decomposition process, the CNTs indeed helped the CY to be more stable under nitrogen atmosphere. With incorporation of the 2 wt% MWCNT-COOH, the char yield of CY increased up to 14%. The POSS/CY nanocomposites showed dramatic performance under both air and nitrogen atmosphere. The fully decomposition temperature raised from 776 °C to 916 °C under air atmosphere, with the incorporation of only 1 wt% POSS. Under nitrogen atmosphere, the char yield increased up to 15 %. The activation energies of the CY and its nanocomposites versus the conversion during decomposition process under air atmosphere, were calculated. The results are in accord with the TGA experiments. It is interesting that negative activation energy appeared in the stage 2 for CY, due to the reaction of triazine rings breakdown. The negative activation energy indicated the decomposition rate decreased with the increasing temperature, which may imply a very high decomposition barrier.

8.1.4 Comparative study on the benzoxazine and its nanocomposites

The processing procedure of the BEN/nanofiller mixtures is the similar with that of CY/nanofiller mixtures. The POSS and clays can be mixed directly with BEN to achieve the
homogeneous mixtures. For CNT, solvent and ultrasonication were necessarily applied to assist. The BEN did not show any advantage in processability when compared with CY. For the BEN and its nanocomposites, there were a large amount of voids and cracks inside the samples after cure, which could not be prevented, and may result from the gas released during the cure, due to the nature of the BEN. High concentrations of the clays and the POSS impaired the shape stability of BEN, but high concentrations of the CNTS help the BEN to retain its shape. Hence, if the BEN based nanocomposites are desired in further application, the concentration of the nanofillers should be carefully considered. TEM, SEM, and XRD supported the homogeneous dispersion of the nanofillers in the BEN matrix, which is similar with that of the CY. The incorporation of the various POSS, clays and CNTs showed different catalytic effects on the curing reaction of CY. However, For the BEN, the incorporation of nanofillers rarely showed a catalytic effect, except for CNTs. Both the cure of the BEN based mixtures and the CY based mixtures can be monitored by means of FTIR. The cure of the BEN followed a ring opening mechanism. With the curing time, the absorbance bands of oxazine ring disappeared due to the opening of the ring. All the functionalised nanofillers examined reacted with the BEN during the cure. However, the reaction between the nanofillers and the BEN did not lead to a strong catalytic effect as that of CY. The incorporation of the nanofillers showed good reinforcement to the thermal stability of both BEN and CY. For the BEN, 10% POSS/BEN showed the best thermal stability before 567 °C, 4 wt% MWCNT/BEN nanocomposite became most thermally stable after 567 °C, under air atmosphere Interestingly, 5% POSS/BEN offered the best thermal stability under nitrogen atmosphere.

8.2 Further work

1. The problems have been found in the curing and further processing of the CY/CNT nanocomposites. According to current study, assistance of solvent and ultrasonication is necessary, in order to achieve good dispersion for the CY/CNT nanocomposites. However, the residual solvent separating out made much smoke during the cure. Furthermore, the CNT/CY resins became extremely flammable in the cure process, due to presence of the residual solvent. After cure, the residual solvent separating out led to many voids and cracks in the nanocomposites, resulting in loose structure. Thus, for further application, it is necessary to develop a solvent free process for mixing and processing of the CY/CNT systems. For the BEN and its nanocomposites, it is necessary to develop new processing
method to remove the gas released during cure, or a new formula to avoid the generation of the gas.

2. The polymerization and crosslinking network formation of the CY has been comprehensively studied in the current curing kinetic study. Nevertheless, the diffusion factor and diffusion controlled kinetics of the CY did not take into account. It was reported that the diffusion factor showed significant influence on the network formation at the end of the cure reaction.\textsuperscript{2,123,124} Thus, in order to study the cure kinetics of cyanate ester based nanocomposites more systematically, the diffusion controlled kinetics can be considered in the further research.

3. According to the current research, the incorporation of the nanofillers showed significant influence on the curing dynamic and network formation of the CY. The structure of network of the CY is directly related to its properties. As shown in the SEM results of Chapter 4, the morphology of fracture surfaces of the CY based nanocomposites was totally changed, due to presence of the nanofillers. This observation implied a toughening phenomenon. Thus, the research to investigate properties of the CY based nanocomposites and the BEN based nanocomposites can be done further. Based on this research, the further application of the nanocomposites can be determined.
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213


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