Chapter 5

Hyperbranched polyurethane/MWCNT nanocomposites

Highlights

This chapter also consists of two subchapters, one on thermoplastic and other on thermosetting hyperbranched polyurethane/triethanolamine functionalized MWCNT nanocomposites. The covalently functionalized MWCNT were characterized by the Fourier transform infrared spectroscopic and Raman spectroscopic studies. The formation of nanocomposites was supported by the Fourier transform infrared spectroscopic and TEM studies. The mechanical, thermal and shape memory behaviors were studied for the prepared nanocomposites. Microwave energy was used to investigate the shape memory behavior. In the second subchapter hyperbranched polyurethane/multi-walled carbon nanotube thermosetting nanocomposites were prepared using glycidyl ether epoxy of bisphenol-A. The thermosetting nanocomposites exhibited better performance including shape memory behaviors as compared to the thermoplastic one.

Parts of this work are published in
5A. Hyperbranched thermoplastic polyurethane/triethanolamine functionalized MWCNT nanocomposites

5A.1. Introduction

The importance of hyperbranched polyurethane and its nanocomposites along with their shape memory behaviors were discussed in Chapter 1. Since their discovery in 1991 by Iijima, carbon nanotubes have opened the door to augment mechanical properties of polymer by incorporating small amount of them into the polymer matrix. The efficient interfacial interactions between the carbon nanotubes and the polymer matrix are the most promising factors for significant improvement of the mechanical properties of the polymer which expand the applications of polymer materials in many fields. The extent of interfacial adhesion between the carbon nanotubes and polymer matrix depends on various factors such as the types, purity, structure, dimension, loading, alignment, degree of functionalization and degree of dispersion of the nanotubes in the polymer matrix. However, the preparation of nanocomposites with homogeneous distribution of carbon nanotubes in the polymer matrix is very difficult, because they tend to agglomerate as they are thermodynamically stabilized by van der Waals forces and numerous π-π interactions between the tubes as well as by high degree of entanglements. The agglomeration of nanotubes within a polymer matrix deteriorates the mechanical properties over the pristine polymer, due to easier crack initiation and propagation in the nanocomposites. Therefore, extensive investigations on chemical modification are undergoing where active organic groups are generated/grafted on the surface of carbon nanotubes. These groups enhanced the dispersion of carbon nanotubes in the polymer matrix due to improved compatibility between carbon nanotubes and polymer matrix. Therefore, by the modification of carbon nanotubes the interfacial adhesion between the carbon nanotubes and polymer matrix could be modified to enhance the load transfer capacity of the nanocomposites. In the current study, esterification reaction was used for grafting triethanolamine to acyl chloride activated multi-walled carbon nanotubes (MWCNT).

In the current study, therefore, hyperbranched polyurethane/triethanolamine functionalized MWCNT nanocomposites were prepared to investigate the performance including shape memory behavior.
5A.2. Experimental

5A.2.1. Materials

The monoglyceride of the *Mesua ferrea* L. seed oil, TDI, PCL, 1,4-butanediol and triethanolamine (TEA) used for the preparation of hyperbranched polyurethane were same as described in Chapter 2, section 2A.2.1.

MWCNT with diameter and length of about 10–20 nm and 20 µm, respectively, were purchased from Iljin Nanotech, South Korea and used as received.

5A.2.2. Modification of MWCNT

MWCNT were treated by a mixture of concentrated H$_2$SO$_4$ and HNO$_3$ (3:1 v/v) at 80 °C for 3 h. After washing thoroughly with water, they were dried under vacuum at 80 °C for 24 h. Required amount of dried acid treated MWCNT were dispersed in DMF by ultrasonication followed by the addition of excess SOCl$_2$. Then the reaction mixture was stirred at 70 °C for 12 h to form acid chloride functionalized MWCNT (MWCNT-COCl). After washing several times with anhydrous THF, they were dried in a vacuum oven at 40 °C for 6 h. Finally, the MWCNT-COCl was reacted with TEA at 70 °C under magnetic stirring for 12 h followed by washing with THF. The obtained solid was dried at 40 °C for 3 h.

5A.2.3. Preparation of hyperbranched polyurethane/TEA-f-MWCNT nanocomposites

The details of the synthesis of hyperbranched polyurethane were described in Chapter 2, section 2A.2.3. For the preparation of nanocomposite, required amount of dispersed TEA-f-MWCNT was injected into the polymerization reaction before 1 h of completion and the reaction was continued. After completion of reaction the solution was cast over the inert substrates followed by vacuum degassing and drying at 60 °C for different testing. The nanocomposites were denoted as MHBPU10, HPUCNT0.2, HPUCNT1 and HPUCNT2 corresponding to the TEA-f-MWCNT content of 0, 0.2, 1 and 2 wt%, respectively.
5A.2.4. Instrumentation

The hyperbranched polyurethane and its nanocomposites were characterized by different techniques such as FTIR, XRD and SEM as described in Chapter 2, section 2A.2.4.

The mechanical properties such as tensile strength, elongation at break, scratch resistance and impact resistance were measured by the same way as described in Chapter 2, section 2A.2.4. The thermal stability was studied by the same way as described in Chapter 2, section 2A.2.4.

The Raman spectra of MWCNT, a-MWCNT and TEA-f-MWCNT were recorded by Invia Renishaw Raman spectrometer, England (Argon ion laser 514.5 nm).

The shape memory behaviors of the samples were studied by the same way using microwave energy as described in Chapter 4, section 4A.2.4.

5A.3. Results and discussion

5A.3.1. FTIR study

The FTIR spectra of pristine MWCNT, a-MWCNT and TEA-f-MWCNT are shown in Fig. 5A.1. The FTIR spectra of acid treated MWCNT showed the absorption at frequency 1725 cm\(^{-1}\) (−C=O). However, there was no such absorption band in this region for the pristine MWCNT. This confirmed the functionalization of –COOH group on the acid treated MWCNT. The FTIR spectra of TEA-f-MWCNT showed the absorption frequency at 3145 cm\(^{-1}\) (−OH stretching), 2930 cm\(^{-1}\) (−CH stretching), 1732 cm\(^{-1}\) (−C=O of ester group), 1460 cm\(^{-1}\) (−CH bending), 1330 cm\(^{-1}\) (C−N stretching) and 1190 cm\(^{-1}\) (−C−O of ester group) indicating the presences of TEA functionalized on the surface of MWCNT. FTIR spectra of hyperbranched polyurethane and all the prepared nanocomposites are shown in Fig. 5A.2. The characteristic bands of urethane group of pristine polymer appeared at 3406-3430 cm\(^{-1}\) (N−H stretching) and 1728 cm\(^{-1}\) (−NHC0O− stretching) as already stated in the earlier chapter. The band at 3406-3430 cm\(^{-1}\) (N−H stretching) broaden after the nanocomposite formation. Further, the band at 1728 cm\(^{-1}\) of −NHC0O− was shifted to lower wavenumber (1720-1715 cm\(^{-1}\)) after the nanocomposites formation. All the above results confirmed the interactions of TEA-f-MWCNT with the polyurethane in the prepared nanocomposites.
Fig. 5A.1: FTIR spectra for (a) pristine MWCNT, (b) acid treated MWCNT and (c) TEA-f-MWCNT

Fig. 5A.2: FTIR spectra for (a) MHBPU10, (b) HPUCNT0.2, (c) HPUCNT1 and (d) HPUCNT2
5A.3.2. Raman spectroscopic study

The functionalization of MWCNT was further characterized by the Raman spectroscopy. The Raman spectra of pristine MWCNT, a-MWCNT and TEA-f-MWCNT are shown in Fig. 5A.3. All the Raman spectra showed D band at 1341 cm\(^{-1}\) and G band at 1571 cm\(^{-1}\). The intensity ratio between the D band and G band \((I_D/I_G)\) implies the degree of covalent functionalization of MWCNT. The value of intensity ratio was found to be 0.82, 0.91 and 1.10 for the pristine MWCNT, a-MWCNT and TEA-f-MWCNT, respectively. The increase in the value of intensity ratio indicated more defects are generated on MWCNT framework upon functionalization.

![Raman spectra](image)

**Fig. 5A.3:** Raman spectra for (a) pristine MWCNT, (b) a-MWCNT and (c) TEA-f-MWCNT

5A.3.3. X-ray diffraction study

The XRD patterns of TEA-f-MWCNT, hyperbranched polyurethane and all the prepared nanocomposites are shown in Fig. 5A.4. The peak appears at \(2\theta=25.4^\circ\) corresponding to the (002) plane of carbon atoms of MWCNT.\(^{11}\) There are two strong diffraction peaks at \(2\theta=21.90^\circ\) and \(2\theta=23.80^\circ\) due to the (100) and (200) planes of PCL crystals of the hyperbranched polyurethane. The peak intensity increased after the formation of nanocomposite. The results
showed that TEA-f-MWCNT serves as nucleating site to increase the crystallinity of hyperbranched polyurethane.

![XRD diffractograms](image)

**Fig. 5A.4:** XRD diffractograms for (a) TEA-f-MWCNT, (b) MHBPU10, (c) HPUCNT0.2, (d) HPUCNT1 and (e) HPUCNT2

5A.3.4. Morphology study

The morphology of the prepared nanocomposites was studied by using SEM. The fractured surface of the sample after tensile test was observed in SEM (Fig. 5A.5). The TEA-f-MWCNT appeared as bright lines in the micrographs of nanocomposites. TEM was used to examine the distribution of TEA-f-MWCNT in the polymer matrix. Fig. 5A.6 shows the TEM micrograph of nanocomposite (HPUCNT1). The micrograph depicts that TEA-f-MWCNT are well dispersed in the polymer matrix with average diameter 13 nm. Furthermore, TEA-f-MWCNT showed good dispersion in DMF and remained stable for 3 months. However, the pristine MWCNT in DMF settled down before 3 h from the date of sonication. The initial dispersion of MWCNT in the solvent has the great impact on the nanotubes dispersion in the polymer matrix.
**Fig. 5A.5:** SEM micrographs for (a) MHBPU10, (b) HPUCNT0.2, (c) HPUCNT1 and (d) HPUCNT2

**Fig. 5A.6:** TEM image for HPUCNT1
5A.3.5. Thermal property

The thermal stability of the prepared nanocomposites was studied by the TGA analysis and the thermograms are shown in Fig. 5A.7. The thermal decomposition of nanocomposites depends on the various factors such as size and nature of the nanomaterial, distribution of nanomaterial and interaction of nanomaterial in the polymer matrix.\textsuperscript{12} Thermal stability of the nanocomposites increased with the increase of amount of TEA-f-MWCNT. This is due to the increased of various physical interactions such as H-bonding and polar-polar interactions along with the chemical bond formation in the nanocomposites. Therefore, the volatile products formed during the thermal decomposition process have to travel longer zigzag path to escape the matrix because the well dispersed nanotubes act as gas barrier as well as absorption of free radicals that were generated during the degradation of polymer.\textsuperscript{13} Moreover, the molecular mobility of the chains decreases and confers the compactness in the structure of the nanocomposite. As a result, the bond breaking inside the bulk polymeric matrix needs more thermal energy. Incorporation of TEA-f-MWCNT in the polymer matrix enhances the thermal conductivity of the prepared nanocomposites that facilitates heat dissipation within the nanocomposites.

From Fig. 5A.8, it is seen that melting temperature ($T_m$) (39.1 °C to 44.2 °C) of the nanocomposites increased with the increase of amount of TEA-f-MWCNT. This is due to uniform dispersion of this MWCNT that resulted the enhanced interactions as stated earlier. Thereby decreases the free volumes present in the nanocomposites and the thermal transition temperature raised. Furthermore the enhanced crystallinity is also responsible for the increase in $T_m$ of the nanocomposites. This suggests that TEA-f-MWCNT act as a nucleating agent for the polyurethane.

5A.3.6. Mechanical property

The mechanical properties of the hyperbranched polyurethane and its nanocomposites are given in Table 5A.1. Mechanical properties of the nanocomposites depend on the nanotube type, aspect ratio, surface functionality, dispersion in solvent and the type of polymer matrix as these factors control the dispersion, distribution, alignment and interfacial interaction in the nanocomposites.\textsuperscript{14-16} From the result it is observed that tensile strength increased with the
Fig. 5A.7: TGA thermograms for (a) MHBPU10, (b) HPUCNT0.2, (c) HPUCNT1 and (d) HPUCNT2

Fig. 5A.8: DSC curves for (a) MHBPU10, (b) HPUCNT0.2, (c) HPUCNT1 and (d) HPUCNT2
increase of the amount of TEA-f-MWCNT. This is attributed to the increased chemical cross-linking and physical interactions between the TEA-f-MWCNT and the polymer matrix. After the modification MWCNT become more compatible with the polymer matrix as well as they are well dispersed in the polymer matrix. The modification of acid treated MWCNT with TEA leads to the functionalization of MWCNT that resulted weakening of the interactions among the MWCNT. This facilitates the dispersion of MWCNT in the polymer matrix. The high degree of dispersion leads to the extensive chemical derivatization and provides the highest interfacial area for stress transfer to the polymer matrix. The interactions such as physical cross-linking of the free –COOH and –OH groups of the nanotubes with the urethane linkages and free –OH of the polyurethane are taken placed. Moreover, chemical cross-linking such as urethane linkage may form between the free –OH of TEA-f- MWCNT and the free –NCO of the polymer matrix. As a consequence they make the material stiffer and lead to the enhanced load transfer from the polymer matrix to the carbon nanotubes. Furthermore the increased degree of crystallinity with the increase of amount of TEA-f-MWCNT increased the mechanical properties of the nanocomposites. However, the elongation at break of the nanocomposites decreases with the increase of amount of TEA-f-MWCNT. This may be due to the increased molecular restriction of the polymer chains by physical as well as chemical interactions on the surface of the MWCNT, result in decrease of flexibility. The scratch resistance of the nanocomposites increased with the increase of the content of TEA-f-MWCNT in the nanocomposite. This may be due to the enhancement of overall toughness of the nanocomposites arises from various interactions as stated earlier. The prepared nanocomposites exhibited sufficient flexibility as the films could be bent onto a rod of 0.001m diameter without any crack in the bent films as indicated in the bending test. This indicates retention of flexibility in all the nanocomposites. This is mainly due to the high flexibility of the soft segment and the presence of long chain fatty acid moiety in the structure of the polyurethane.
Table 5A.1: Mechanical properties of hyperbranched polyurethane and its nanocomposites

<table>
<thead>
<tr>
<th>Properties</th>
<th>MHBPU10</th>
<th>HPUCNT0.2</th>
<th>HPUCNT1</th>
<th>HPUCNT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>6.5 ± 0.4</td>
<td>13 ± 0.3</td>
<td>20.5 ± 0.3</td>
<td>28.5 ± 0.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>685 ± 3</td>
<td>480 ± 2</td>
<td>444 ± 2</td>
<td>405 ± 3</td>
</tr>
<tr>
<td>Scratch resistance (kg)</td>
<td>3.0 ± 0.1</td>
<td>4.2 ± 0.1</td>
<td>5.5 ± 0.1</td>
<td>7 ± 0.1</td>
</tr>
<tr>
<td>Bending (m)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Impact resistance* (m)</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
</tr>
</tbody>
</table>

* 1.0 m is the limit of the instrument

5A.3.7. Shape memory property

The shape memory behaviors of hyperbranched polyurethane and its nanocomposites under microwave irradiation are shown in Fig. 5A.9. All the prepared nanocomposites exhibited good shape fixity and the fixed shape was retained for a very long time at room temperature. The micro-Brownian movements of the molecular chains are frozen at low temperature and the strain energy is stored in the form of internal stress in the fixed shape. The shape recovery was studied under four different microwave powers at 140, 210, 350 and 455 W. The shape recovery effect was not observed when the microwave irradiation output power was 140 W. This can be attributed to the slow reorientation of the dipoles due to the low value of output power. Therefore, induced heat was not sufficient to activate the polymer chains due to the low molecular friction and collisions. The shape recovery increased with the increase of the microwave output power. The shape recovery time decreased with the increase of microwave output power (Table 5A.2). When the microwave irradiated on the sample, the dipole moment moves to align with the external electric field. This dipole movement generates friction inside the dielectric as a result heating effect arises as already discussed in Chapter 4, section 4A.3.7. The polymer chains are activated when the heat is close to the transition temperature ($T_{\text{trans}}$) and release the stored strain energy to recover the original shape. When the microwave output power increases, the temperature of the sample also increases due to the high molecular friction and collisions, which causes the high recovery speed. It can be noted that the shape recovery and shape recovery speed strongly dependent on the magnitude of the output microwave power. There are many reports available in the literature that the carbon nanotube has microwave
absorption capacity. However the nanocomposites showed higher recovery time as compared to the pristine polyurethane. This may be due to the increased $T_{\text{trans}}$ ($T_m$) (supported by the DSC) of the nanocomposites with increase in the loading of TEA-f-MWCNT, which required more heat energy to activate the polymer chains. This is due to the increased compactness as well as toughness of the nanocomposites. The prepared nanocomposites have shown good shape recovery and shape fixity. Thus the nanocomposites may be utilized as shape memory materials in sensors, actuators, self deployable sun sails in spacecraft, automobile, heat shrinkable tube and biomedical devices.

![Fig. 5A.9: Shape memory behaviors of hyperbranched polyurethane and its nanocomposites at microwave output power 455 W (a) original shape and (b) fixed shape](image)
Table 5A.2: Shape memory behaviors of hyperbranched polyurethane and its nanocomposite at different microwave output powers*

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Shape recovery$^a$ (%)</th>
<th>Shape recovery time$^a$ (s)</th>
<th>Shape recovery$^b$ (%)</th>
<th>Shape recovery time$^b$ (s)</th>
<th>Shape recovery$^c$ (%)</th>
<th>Shape recovery time$^c$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>75 ± 1.2</td>
<td>150 ± 2</td>
<td>100</td>
<td>65 ± 2</td>
<td>100</td>
<td>50 ± 2</td>
</tr>
<tr>
<td>HPUCNT0.2</td>
<td>71 ± 1.2</td>
<td>170 ± 2</td>
<td>100</td>
<td>72 ± 2</td>
<td>100</td>
<td>55 ± 2</td>
</tr>
<tr>
<td>HPUCNT1</td>
<td>65 ± 1.1</td>
<td>185 ± 2</td>
<td>100</td>
<td>85 ± 2</td>
<td>100</td>
<td>65 ± 2</td>
</tr>
<tr>
<td>HPUCNT2</td>
<td>60 ± 1.0</td>
<td>194 ± 2</td>
<td>100</td>
<td>90 ± 2</td>
<td>100</td>
<td>75 ± 2</td>
</tr>
</tbody>
</table>

*Microwave power output (W): $^a$210, $^b$350 and $^c$455

5A.4. Conclusion

The hyperbranched polyurethane/TEA-f-MWCNT nanocomposites were successfully prepared by ‘in-situ’ pre-polymerization technique. The nanocomposites exhibited good thermal and mechanical properties. The tensile strength and thermal stability was found to be increased with the increase of amount of TEA-f-MWCNT. Microwave was found to be an effective stimulus for the shape recovery of the hyperbranched polyurethane and its nanocomposites. The shape recovery rate as well as shape recovery time can be tuned by using the microwave output powers. All the prepared nanocomposites exhibited good shape fixity. Thus the prepared nanocomposites with tunable dose dependent performance may be utilized as microwave induced shape memory materials in different fields of application.
5B. Hyperbranched thermosetting polyurethane/triethanolamine functionalized MWCNT nanocomposites

5B.1. Introduction

From the above subchapter it has been found that the formation of hyperbranched polyurethane nanocomposites with covalent functionalized MWCNT by triethanolamine, enhanced the performance over the pristine polyurethane. Further, in Chapter 4, it is clearly demonstrated that the thermosetting nanocomposites of such hyperbranched polyurethane exhibited many superior properties including shape memory behavior compared to its thermoplastic counterpart. Thus the proposition for investigating the performance along with shape memory behaviors of such triethanolamine functionalized MWCNT/hyperbranched polyurethane thermosetting nanocomposites is worthy. Again, in Chapter 4, it is also found that glycidyl ether epoxy of bisphenol-A has good compatibility with such hyperbranched polyurethane, so attempt was made to form the thermosetting nanocomposites with this epoxy resin. The importance of glycidyl ether of bisphenol-A based epoxy was already discussed in Chapter 3, section 3.1. Further, the free hydroxyl groups present in the functionalized MWCNT as well as in the hyperbranched polyurethane would react with the oxirane rings of epoxy resin and thereby taking part in crosslinking reactions to form the dimensionally stable thermosets. In addition to that this phenomenon helps in uniform and stable dispersion of MWCNT into the polyurethane matrix and thus considerable and strong interfacial interactions would result, which in turn offer significant improvement in many desired properties including shape memory behaviors. The effect of crosslinking points or net points on the shape memory property of such polymeric materials is already described in subchapter 4B. A number of reports were found in literature on curing of MWCNT nanocomposites. Chapartegui et al. studied the curing behavior of epoxy/MWCNT nanocomposites.\textsuperscript{17} Tseng et al. reported the diamine cured maleic anhydride grafted CNT/epoxy nanocomposites.\textsuperscript{18}

In the present subchapter, therefore, hyperbranched thermosetting polyurethane/triethanolamine covalent functionalized MWCNT nanocomposites were fabricated to investigate the effect of epoxy resin along with the nanomaterial on the performance including shape memory behaviors of such nanocomposites.
5B.2. Experimental

5B.2.1. Materials

The monoglyceride of *Mesua ferrea* L. seed oil, TDI, PCL, 1,4-butanediol and triethanolamine used for the preparation of hyperbranched polyurethane were same as described in Chapter 2, section 2A.2.1.

The epoxy resin, a glycidyl bisphenol-A based epoxy used was same as described in Chapter 3, section 3.2.1.

MWCNT with diameter and length of about 10–20 nm and 20 µm, respectively, used were same as mentioned in subchapter 5A, section 5A.2.1.

5B.2.2. Modification of MWCNT

The covalent modification of MWCNT with triethanolamine was already described in subchapter 5A, section 5A.2.2.

5B.2.3. Preparation of hyperbranched thermosetting polyurethane/TEA-f-MWCNT nanocomposites

The nanocomposites were prepared by the same way as described in subchapter 5A, section 5A.2.3. This nanocomposite was then homogenized with 10 wt% of the epoxy resin (100% solid content) to obtain the desired thermoset. The polymer solution was cast on the inert substrates followed by vacuum degassing and finally cured at 120 °C for specified time (Table 5B.1). The cured films were coded as EHPUCNT0.2, EHPUCNT1 and EHPUCNT2 corresponding to 0.2, 1 and 2 wt% of TEA-f-MWCNT, respectively. Before curing, one representative nanocomposite was coded as BEHPUCNT1 with 1 wt% TEA-f-MWCNT content.

5B.2.4. Instrumentation

The hyperbranched polyurethane and its nanocomposites were characterized by different techniques such as FTIR, XRD and SEM as described in Chapter 2, section 2A.2.4.

The mechanical properties such as tensile strength, elongation at break, scratch resistance and impact resistance were measured by the same way as described in Chapter 2, section 2A.2.4.
The thermal stability was studied by the same instrument using same procedure as described in the Chapter 2, section 2A.2.4.

The shape memory behaviors of the samples were studied by the same way using microwave energy as described in Chapter 4, section 4A.2.4.

5B.3. Results and discussion

5B.3.1. Curing study

From the curing study it was found that the touch free time and the drying time decreased with the increase of the loading of TEA-f-MWCNT in the nanocomposites as cured at 120 °C (Table 5B.1). This is attributed to the increased degree of cross-linking reaction among the free –OH of TEA-f-MWCNT, epoxy/hydroxyl groups of the epoxy resin and free -OH groups of the hyperbranched polyurethane without using any additional external hardener (Scheme 5B.1). This is due to the fact that the number of free –OH and triethanolamine moiety increases with the increase of loading of TEA-f-MWCNT in the system. These intercross-linking network formations resulted three dimensional network structures. The absence of the epoxy band at 916 cm\(^{-1}\) after curing in FTIR spectra confirmed the formation of the network structure. The increased cross-linking density of the nanocomposites was also confirmed by the swelling test in DMF (Table 5B.2).

5B.3.2. FTIR study

The FTIR spectra of pristine MWCNT, a-MWCNT and TEA-f-MWCNT are already given in subchapter 5A, section 5A.3.1. FTIR spectra of hyperbranched polyurethane and its thermosetting nanocomposites are shown in Fig. 5B.1. The band at 3406-3432 cm\(^{-1}\) (N–H stretching) of nanocomposites was found to broaden as compared to the pristine polyurethane. Further, after the formation of nanocomposite the band of –C=O at 1728 cm\(^{-1}\) was shifted to lower wavenumber, 1719-1715 cm\(^{-1}\). All the above observations confirmed the interactions of TEA-f-MWCNT with the polyurethane chains in the prepared thermosetting nanocomposites.
Scheme 5B.1: Proposed crosslinking reactions
**Fig. 5B.1:** FTIR spectra for (a) MHBPU10, (b) BEHPUCNT1, (c) EHPUCNT0.2, (d) EHPUCNT1 and (e) EHPUCNT2

**Table 5B.1:** Composition and curing time of the nanocomposites at 120 °C

<table>
<thead>
<tr>
<th>Code</th>
<th>MHBPU10 (wt%)</th>
<th>Epoxy (wt%)</th>
<th>Touch free time (min)</th>
<th>Drying time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EHPUCNT0.2</td>
<td>100</td>
<td>10</td>
<td>45</td>
<td>54</td>
</tr>
<tr>
<td>EHPUCNT1</td>
<td>100</td>
<td>10</td>
<td>34</td>
<td>47</td>
</tr>
<tr>
<td>EHPUCNT2</td>
<td>100</td>
<td>10</td>
<td>30</td>
<td>42</td>
</tr>
</tbody>
</table>

5B.3.3. XRD study

The XRD patterns of TEA-f-MWCNT, hyperbranched polyurethane and the thermosetting nanocomposites are shown in Fig. 5B.2. The peak at $2\theta=25.4^\circ$ is due to the (002) plane of carbon atoms of MWCNT.\(^{11}\) The two strong diffraction peaks at $2\theta=21.9^\circ$ and $2\theta=23.8^\circ$ were observed because of the (100) and (200) planes of PCL crystals present in the
hyperbranched polyurethane. The peak intensity was found to be increased after the nanocomposite formation. This may be due to the nucleating effect of the TEA-f-MWCNT.

**Fig. 5B.2:** XRD diffractographs for (a) TEA-f-MWCNT, (b) MHBPU10, (c) EHPUCNT0.2, (d) EHPUCNT1 and (e) EHPUCNT2

5B.3.4. Morphology study

The morphology of the fractured surface of nanocomposites was observed by SEM (Fig. 5B.3). The TEA-f-MWCNT appeared as bright lines in the micrographs of nanocomposites. Furthermore functionalized MWCNT were broken rather than being pulled out on tensile fracture. This depicts a strong interfacial adhesion between the nanomaterial and the polyurethane matrix. TEM was used to observe the dispersion of TEA-f-MWCNT in the nanocomposite (Fig. 5B.4). From the micrograph it was observed that nanotubes were homogeneously distributed in the polymer matrix with an average diameter of 12 nm.
**Fig. 5B.3:** SEM micrographs for (a) MHBPU10, (b) EHPUCNT0.2, (c) EHPUCNT1 and (d) EHPUCNT2

**Fig. 5B.4:** TEM image of EHPUCNT1

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5B.3.5. Thermal property

The TGA thermograms of pristine MWCNT, a-MWCNT and TEA-f-MWCNT are shown in Fig. 5B.5. The pristine MWCNT did not show weight loss below 550 °C. However, the a-MWCNT gradually lost their weight with the increase of temperature due to the decomposition of –COOH groups from the surface of the MWCNT. The TGA thermogram of TEA-f-MWCNT showed an initial weight loss from 190 to 250 °C. This can be attributed to the decomposition of triethanolamine present on the surface of MWCNT. The thermal stability of the polymer nanocomposite plays a vital role in determining their processing and service life. The TGA thermograms of the hyperbranched polyurethane and the thermosetting nanocomposites are shown in Fig. 5B.6. The thermal stability increased with the increase of content of TEA-f-MWCNT in the thermosetting nanocomposites. This is due to the increased compactness and rigidity of the nanocomposites as cross-linking density increases with the same and supported by the swelling results (Table 5B.2). This is also attributed to the homogeneous distribution of the TEA-f-MWCNT as well as increased of various interactions such as polar-polar interaction, H-bonding, van der Waals forces etc. All these cause molecular restriction of the polymer chains in the nanocomposites and thus the volatile products formed during the decomposition have to follow a longer diffusion path to escape from the matrix.

The DSC curves of hyperbranched polyurethane and its thermosetting nanocomposites are shown in Fig. 5B.7. The melting temperature ($T_m$) was found to be increased (40 to 45 °C) with the increase of TEA-f-MWCNT content in the nanocomposites. This is attributed to the increased compactness of the structure due to the various interactions as stated in the earlier chapter.

5B.3.6. Mechanical property

The mechanical properties of the hyperbranched polyurethane and the thermosetting nanocomposites are shown in Table 5B.2. The tensile strength increases, whereas the elongation at break decreases with the increase of loading of TEA-f-MWCNT in the nanocomposites. This enhancement could be attributed to the well distribution of TEA-f-MWCNT that results efficient interfacial interactions between TEA-f-MWCNT and the polymer matrix. The presence of different physical interactions such as polar-polar, H-bonding etc. of free –OH of
Fig. 5B.5: TGA thermographs for (a) MWCNT, (b) a-MWCNT and (c) TEA-f-MWCNT

Fig. 5B.6: TGA thermograms for (a) MHBPU10, (b) EHPUCNT0.2, (c) EHPUCNT1 and (d) EHPUCNT2
TEA-f-MWCNT with the urethane linkages of the hyperbranched polyurethane as well as increased cross-linking density as supported by swelling values (Table 5B.2) resulted enhancement of tensile strength. The scratch hardness which is the resistance of materials to the dynamic surface deformation increases with the increase of content of TEA-f-MWCNT. The significant improvement of the scratch hardness is due to the increased compactness and rigidity of the nanocomposites. All the prepared nanocomposites exhibited good impact resistance. The gloss of the nanocomposites increases with the increase of the loading of TEA-f-MWCNT in the nanocomposites. This is attributed to the compatibility among epoxy resin, TEA-f-MWCNT and hyperbranched polyurethane and increased dimension stability of the nanocomposites.

Fig. 5B.7: DSC curves for (a) MHBPU10, (b) EHPUCNT0.2, (c) EHPUCNT1 and (d) EHPUCNT2
Table 5B.2: Mechanical properties of hyperbranched polyurethane and the nanocomposites

<table>
<thead>
<tr>
<th>Properties</th>
<th>MHBPUI0</th>
<th>EHPUCNT0.2</th>
<th>EHPUCNT1</th>
<th>EHPUCNT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>6.5 ± 0.4</td>
<td>16.5 ± 0.3</td>
<td>25 ± 0.3</td>
<td>34.5 ± 0.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>614 ± 3</td>
<td>389 ± 2</td>
<td>333 ± 2</td>
<td>305 ± 2</td>
</tr>
<tr>
<td>Scratch hardness (kg)</td>
<td>3.0 ± 0.1</td>
<td>5 ± 0.1</td>
<td>6.5 ± 0.1</td>
<td>8.5 ± 0.1</td>
</tr>
<tr>
<td>Bending (m)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Impact resistance* (m)</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
<td>0.95 ± 0.05</td>
</tr>
<tr>
<td>Swelling (%)</td>
<td>-</td>
<td>27 ± 1.2</td>
<td>20 ± 1.2</td>
<td>15 ± 1.1</td>
</tr>
</tbody>
</table>

* 1.0 m is the limit of the instrument

5B.3.7. Shape memory property

The shape memory behaviors of the hyperbranched polyurethane and its thermosetting nanocomposites are shown in Fig. 5B.8. The thermal motion of the molecular chains was activated during heating the samples at 60 °C for 5 min and facilitated to form ring shape. However, the molecular chains are frozen on cooling at low temperature (0-5 °C) and help to fix the shape. The hyperbranched polyurethane and the nanocomposites exhibited excellent shape fixity. Further the fixed shape was retained for long time at room temperature. The micro-Brownian movements of the molecular chains are frozen at low temperature and thereby prevent its reorientation of molecular chains, showing the perfect shape fixity.\textsuperscript{19, 20} The shape recovery test was studied under the microwave irradiation at 455 W. The hyperbranched polyurethane and the nanocomposites showed almost full shape recovery. No significant change of shape recovery of the nanocomposites was obtained over the ten cycles of test. The shape recovery time found to increase with the increase of loading of TEA-f-MWCNT in the thermosetting nanocomposites. This can be attributed to the increased transition temperature (supported by DSC) due to the increased physico-chemical interactions among the polymer chains, epoxy resin and TEA-f-MWCNT in the thermosetting nanocomposites.
Fig. 5B.8: Shape memory behaviors of hyperbranched polyurethane and its nanocomposites at microwave output power 455 W (a) original shape and (b) fixed shape

5B.4. Conclusion

The hyperbranched polyurethane/TEA-f-MWCNT thermosetting nanocomposites were prepared successfully by an ‘in situ’ polymerization technique. MWCNT were functionalized by TEA using a covalent approach. The mechanical and thermal properties of the thermosetting nanocomposites were significantly enhanced with the increase of content of TEA-f-MWCNT. The thermosetting nanocomposites exhibited the enhanced mechanical and thermal properties as compared to the thermoplastic one. All the prepared nanocomposites exhibited excellent shape fixity and shape recovery. The shape recovery time found to be lowered in the thermosetting nanocomposites as compared to the thermoplastic one. Thus the prepared nanocomposites could be utilized as advanced SMP in different suitable applications.
References


