Chapter 4

Hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites

Highlights

This chapter consists of two subchapters, one on thermoplastic and other on thermosetting hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites. The first subchapter describes the preparation, characterization and properties evaluation of hyperbranched polyurethane/Fe$_3$O$_4$ thermoplastic nanocomposites. The prepared nanocomposites were characterized by Fourier transform infrared spectroscopy and X-ray diffraction studies. The mechanical, thermal and shape memory behaviors were studied for the prepared nanocomposites. The shape memory behaviors were studied by using microwave energy as the stimulus. While in the second subchapter epoxy modified thermosetting hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites were demonstrated. The thermoset nanocomposites were characterized similarly by using Fourier transform infrared spectroscopy and X-ray diffraction studies. The performance of the nanocomposites was also studied exactly on the same ways. The study showed that the thermosetting nanocomposites are better compared to their thermoplastic analogs with respect to their overall performance including shape memory behaviors.

Parts of this work are published in

4A. Hyperbranched thermoplastic polyurethane/Fe$_3$O$_4$ nanocomposites

4A.1. Introduction

The importance of shape memory polymers (SMP) and their nanocomposites are already discussed in Chapter 1. The shape memory polyurethanes (as discussed in Chapter 2) have some disadvantages such as low mechanical properties, low recovery, low cycle life that make the barrier for the advanced applications. In Chapter 3, it has been found that the modification with epoxy and hardener can improve the performance including shape recovery of hyperbranched polyurethanes. However, the pristine hyperbranched polyurethanes or their epoxy modified thermosets cannot be addressed the demands of many advanced applications. Now recently, it is clearly understood that the fabrication of suitable polymer nanocomposites has significant importance to overcome these problems. Fe$_3$O$_4$ nanoparticles were chosen here as nanomaterials due to their easy synthesis, low toxicity and good microwave absorption characteristic.\textsuperscript{1-5} Again, the shape memory behaviors were studied by the direct heating, in most of the cases.\textsuperscript{6-8} On the other hand, transition temperature ($T_{\text{trans}}$) of many of such SMP is far from the normal human body’s temperature and causes adverse impact in the clinical applications. Recently, thus research is focused on induced heating actuation of SMP by indirect ways. Cai et al. studied the magnetic field responsive shape memory behaviors of Fe$_3$O$_4$/poly($\varepsilon$-caprolactone)-polyurethane nanocomposites.\textsuperscript{9} Xiao et al. reported the electro-active shape memory properties of poly($\varepsilon$-caprolactone)/functionalized MWCNT nanocomposite.\textsuperscript{10} Microwave energy is used in the present study to investigate the shape memory behaviors of the nanocomposites. Microwave is an electromagnetic wave in the range of 300 MHz to 300 GHz. The corresponding wavelengths are 1 m to 1 mm. It can be used as stimulus in a non-contact way to actuate the SMP. The absorbed microwave energy is transferred to heat energy through the molecular friction and collisions and the shape memory effect is observed once the induced heat is close to the $T_{\text{trans}}$. Thus in this chapter thermoplastic hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites were prepared to investigate the effect of Fe$_3$O$_4$ nanoparticles on the performance including shape memory behaviors of the nanocomposites.
4A.2. Experimental

4A.2.1. Materials

The monoglyceride of the *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.

Iron (III) chloride hexahydrate was purchased from Merck, India. The minimum assay is 96.0%. The impurity present is 1.0% iron (II) chloride. It was used as received.

Iron (II) chloride tetrahydrate was purchased from Merck, Germany. The minimum assay is 99.0%. The other impurities are 0.01% sulphate, 0.0005% arsenic, 0.002% copper, 0.2% iron (III) salt, 0.001% lead and 0.003% zinc. It was used as received.

Polyethylene glycol (PEG) was obtained from Merck, India. The number average molecular weight ($M_n$) is 4000 g/mol. It was used as received.

Ammonia solution was purchased from Qualigens Fine Chemicals Ltd., India. The concentration and specific gravity are 30% and 0.89, respectively.

4A.2.2. Preparation of Fe$_3$O$_4$ nanoparticles

Fe$_3$O$_4$ nanoparticles were prepared by the co-precipitation method. Required amount of FeCl$_3$.6H$_2$O (2.0 g), FeCl$_2$.4H$_2$O (1.225 g) and PEG (1.5 g) were dissolved in deionized water (50 mL) under the nitrogen atmosphere with vigorous stirring at room temperature. An aqueous solution of ammonia (30%) was then added slowly into the mixture until it turns black. The black solution was then stirred continuously for 30 min. The resultant magnetic nanoparticles were separated by magnetic decantation and rinsed with deionized water followed by acetone until the supernatant become neutral. Finally, the washed Fe$_3$O$_4$ nanoparticles were dispersed and stored in DMF.

4A.2.3. Preparation of hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposite

Hyperbranched polyurethane was prepared by the pre-polymerization technique by the same method as described in Chapter 2, section 2A.2.3. For the preparation of nanocomposite, required amount of dispersed Fe$_3$O$_4$ was injected into the polymerization reaction before 1 h of completion and the reaction was continued. After completion of reaction the solution was cast on
the inert substrates followed by vacuum degassing and drying at 60 °C for 24 h for the different testing and analyses. The nanocomposites were denoted as MHBPU10, HPU2, HPU5 and HPU10 corresponding to the Fe₃O₄ content of 0, 2, 5 and 10 wt%, respectively.

4A.2.4. Instrumentation

The hyperbranched polyurethane and its nanocomposites were characterized by the same techniques such as FTIR, XRD and SEM as described in Chapter 2, section 2A.2.4. The distribution of Fe₃O₄ in the nanocomposite was studied by using transmission electron microscope (TEM) JEM 2100, JEOL, Japan at operating voltage of 200 kV. Lakeshore vibrating sample magnetometer (VSM; Model 7410) within the range of +20000 to −20000 Oe at room temperature was used to study the magnetic behavior of Fe₃O₄ and nanocomposite.

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.

In order to observe the shape memory effect strip like samples (0.04 m × 0.002 m × 0.0007 m) were heated at 60 °C (Tₘ + 20 °C) for 5 min and then folded to a ring shape. Immediately, the folded samples were put into the fixing temperature at 0 to 5 °C (Tₘ – 40 °C) for 5 min to fix the temporary shape. Subsequently, the samples were exposed to the microwave irradiation (Scientific microwave system, catalyst systems, 2450 MHz, output power: 140-700 W, India) for the shape recovery study at microwave output power 350 W. The shape recovery and shape fixity are two shape memory parameters calculated from the following equations:

\[
\text{Shape recovery (\%)} = \left(\frac{90 - \theta}{90}\right) \times 100 \quad \text{----------------------------- (4A.1)}
\]

\[
\text{Shape fixity (\%)} = \frac{\theta}{90} \times 100 \quad \text{------------------------------------ (4A.2)}
\]

where \(\theta\) in degree denotes the angle between the tangential line at the midpoint of the sample and the line connecting the midpoint and the end of the curved sample.

4A.3. Results and discussion

4A.3.1. FTIR study

FTIR spectra of Fe₃O₄, hyperbranched polyurethane and the nanocomposites are shown in Fig. 4A.1. The characteristic absorption band of Fe₃O₄ at 580 cm⁻¹ corresponding to Fe-O
stretches vibration. The band at 3429 cm\(^{-1}\) is assigned to the stretching vibration of Fe-OH groups absorbed on the surface of Fe\(_3\)O\(_4\) nanoparticles. The characteristic bands of urethane group appeared at 3406-3430 cm\(^{-1}\) (N-H stretching) and 1728 cm\(^{-1}\) (-C=O stretching of urethane linkage) as already discussed in the earlier chapter. The disappearance of band at 2250-2270 cm\(^{-1}\) indicates that there was no free –NCO group present in the hyperbranched polyurethane structure. The band at 3406-3430 cm\(^{-1}\) (N-H stretching) of nanocomposites was found to be broadened after the nanocomposite formation as compared to the pristine polyurethane. This confirmed the presence of strong interaction of Fe\(_3\)O\(_4\) nanoparticles with the polymer matrix. Further, the characteristic band corresponding to Fe-O of Fe\(_3\)O\(_4\) nanoparticles was also broadened after the formation of nanocomposite. This indicates that polymer chains are bound to the surface of the nanoparticles. The above results showed overall strong interactions between the nanoparticles and the polymer matrix.

4A.3.2. X-ray diffraction study

The X-ray diffractograms of Fe\(_3\)O\(_4\), hyperbranched polyurethane and the nanocomposites are shown in Fig. 4A.2. The peaks appear at \(2\theta=30.35^\circ, 35.51^\circ, 56.71^\circ\) and 62.73\(^\circ\) corresponding to (220), (311), (511) and (440) planes of Fe\(_3\)O\(_4\), respectively.\(^{11}\) The two peaks at \(2\theta=21.90^\circ\) and \(2\theta=23.80^\circ\) are due to the (100) and (200) planes of PCL crystals of the hyperbranched polyurethane. The intensity of these peaks decreases after the formation of nanocomposite. This may be due to the increased molecular restriction through the different interfacial interactions.

4A.3.3. TEM study

The size and distribution of Fe\(_3\)O\(_4\) nanoparticles in the polymer matrix was studied by the TEM analysis (Fig. 4A.3). The TEM micrograph indicates the homogeneous distribution of Fe\(_3\)O\(_4\) nanoparticles with an average diameter of 13 nm in the polyurethane matrix. This can be attributed to the good interfacial interaction between the nanoparticles and the polymer matrix.
Fig. 4A.1: FTIR spectra for (a) Fe$_3$O$_4$, (b) MHBPU10, (c) HPU2, (d) HPU5 and (e) HPU10

Fig. 4A.2: XRD diffractograms for (a) Fe$_3$O$_4$, (b) MHBPU10, (c) HPU2, (d) HPU5 and (e) HPU10
4A.3.4. Thermal property

The thermal stability of the nanocomposites was studied by TGA and the thermograms are shown in Fig. 4A.4. Inorganic compounds are more thermo-stable as compared to the organic polymers. Thermal stability of the nanocomposites depends on the size, shape, nature, loading of nanoparticles, dispersion and degree of interfacial interaction between the nanoparticles and the polymer matrix. Incorporation of Fe$_3$O$_4$ nanoparticles into the hyperbranched polyurethane matrix increases its thermal stability (240 to 270 °C). This is due to the uniform distribution, compatibility and strong interfacial interactions of Fe$_3$O$_4$ nanoparticles with the polymer matrix. Due to the various interfacial interactions such as physical cross-linking, polar-polar interactions and H-bonding, the polymer chains were immobilized on the surface of the nanoparticles. Thus the segmental motion of the polymer chains in the nanocomposites was restricted and thereby making the material more rigid. Hence the bond breaking requires high thermal energy.
Furthermore volatile products formed during the thermal degradation process have to follow a longer path to escape from the matrix. The DSC thermograms for all the samples were found to almost similar, but the melting temperature ($T_m$) was enhanced from 40.2 to 42.1 °C with the increase of Fe$_3$O$_4$ nanoparticles content in the nanocomposites (Fig. 4A.5). This may be due to the formation of rigid and compact structure in the nanocomposites arises from the various interactions between the nanoparticles and the polymer matrix as stated earlier.

4A.3.5. Mechanical property

From Table 4A.1, it is found that nanocomposites possess good mechanical properties viz. tensile strength, impact resistance and scratch resistance along with adequate elongation at break. The mechanical property of the nanocomposite depends on the several factors such as distribution, dimension, aspect ratio of nanomaterials as well as degree of interfacial interactions between the matrix and the nanomaterials. The tensile strength increases with the increase of
Fe$_3$O$_4$ nanoparticles content in the nanocomposites. This is due to the well distribution and enhanced interfacial interactions of Fe$_3$O$_4$ nanoparticles with the polymer matrix. The interfacial interactions increased the load transfer capability of the polymer matrix to the nanoparticles. However, the elongation at break decreases with the increase of Fe$_3$O$_4$ nanoparticles content in the nanocomposites. This is due to the increased molecular restrictions of the polymer chains in the nanocomposites.\(^\text{13}\) The scratch resistance of the nanocomposites increases with the increase of content of Fe$_3$O$_4$ nanoparticles. This can be attributed to the overall increase in toughness of the nanocomposites. The bending test results indicated that all the samples have sufficient flexibility as the films could be bent onto a rod of 0.001m diameter without any crack generation. 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 hyperbranched polyurethane. Moreover all the films showed the excellent impact resistance.
**Table 4A.1:** Mechanical properties of hyperbranched polyurethane and the nanocomposites

<table>
<thead>
<tr>
<th>Property</th>
<th>MHBPU10</th>
<th>HPU2</th>
<th>HPU5</th>
<th>HPU10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>6.2 ± 0.4</td>
<td>9.2 ± 0.2</td>
<td>12.3 ± 0.2</td>
<td>15 ± 0.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>607 ± 3.1</td>
<td>492 ± 1.4</td>
<td>441 ± 1.4</td>
<td>403 ± 1.1</td>
</tr>
<tr>
<td>Scratch resistance (kg)</td>
<td>3 ± 0.1</td>
<td>5 ± 0.1</td>
<td>5.6 ± 0.1</td>
<td>6 ± 0.15</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 ± 0.02</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>
</tbody>
</table>

* 1.0 m is the limit of the instrument

4A.3.6. Magnetic property

The magnetic hysteresis loops of Fe₃O₄ and nanocomposite (HPU2) at room temperature are shown in Fig. 4A.6. From the figure it is confirmed that the prepared Fe₃O₄ showed the super-paramagnetic behavior as their low coercivity ($H_c$) and remanence ($M_r$) on the magnetization loop. The saturation magnetization of the nanocomposite was much lower than that of the pure Fe₃O₄ nanoparticles. This can be attributed to the low content (2 wt%), smaller size as well as surface coating of Fe₃O₄ by the polymer chains in the nanocomposite.

4A.3.7. Shape memory property

The shape memory behaviors of the hyperbranched polyurethane and the nanocomposites are shown in Fig. 4A.7. All the samples exhibited almost full shape fixity behavior (Table 4A.2). This is due to the frozen of micro-Brownian movements of molecular chains during the vitrification. The shape recovery behavior was observed under the microwave irradiation. All the nanocomposites also exhibited almost full shape recovery. This is due to the fact that on microwave irradiation to the samples the dipole moment moves to align to the external field. But the electric field component of the wave oscillates and hence the dipole field attempts to follow these oscillations. These molecular friction and collisions resulted the required heat generation. Again, the polymer chains are activated when the heat is close to the transition temperature ($T_{trans}$) and thereby releasing the stored strain energy to recover the original shape. No significant
change of shape recovery of the nanocomposites was observed over the five cycles of test. The shape recovery time was decreased (81-49 s) with the increase of Fe₃O₄ nanoparticles content in the nanocomposites (Table 4A.2). This can be attributed to the increased store energy with the
loss of elastic entropy as a result of homogeneous distribution of the Fe$_3$O$_4$ nanoparticles and increased physical cross-linking in the polymer matrix. Furthermore, the increased shape recovery speed may be due to the enhanced microwave absorption characteristic of the nanocomposites with the increase of Fe$_3$O$_4$ nanoparticles content.$^{4,5}$ From the above result it is seen that the prepared nanocomposites showed the excellent shape recovery and shape fixity behaviors. Thus these materials might be used as advanced shape memory materials in various potential fields.

Table 4A.2: Shape memory behaviors of hyperbranched polyurethane and the nanocomposites

<table>
<thead>
<tr>
<th>Code</th>
<th>Shape fixity (%)</th>
<th>Shape recovery (%)</th>
<th>Shape recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>98.7 ± 0.5</td>
<td>98.5 ± 0.6</td>
<td>81 ± 4</td>
</tr>
<tr>
<td>HPU2</td>
<td>99.3 ± 0.2</td>
<td>99.2 ± 0.1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>HPU5</td>
<td>99.3 ± 0.2</td>
<td>99.2 ± 0.1</td>
<td>60 ± 2</td>
</tr>
<tr>
<td>HPU10</td>
<td>99.3 ± 0.2</td>
<td>99.2 ± 0.1</td>
<td>49 ± 2</td>
</tr>
</tbody>
</table>

Fig. 4A.7: Shape memory behaviors of hyperbranched polyurethane and the nanocomposites (a) original shape and (b) fixed shape
4A.4. Conclusion

In this study, we have successfully prepared *Mesua ferrea* L. seed oil based hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites. The prepared nanocomposites showed improved mechanical and thermal properties. The hyperbranched polyurethane and the nanocomposites exhibited almost full shape fixity and almost full shape recovery under the application of microwave stimulus. The shape recovery speed increases with the increase of Fe$_3$O$_4$ nanoparticles content in the nanocomposites. Thus the hyperbranched polyurethane/Fe$_3$O$_4$ nanocomposites might be utilized as advanced shape memory materials in the different fields especially in the biomedical domain like smart surgical sutures, catheters, stents, drug delivery materials etc.
4B. Hyperbranched polyurethane/Fe$_3$O$_4$ thermosetting nanocomposites

4B.1. Introduction

The effects of the chemical modification using glycidyl ether epoxy of bisphenol-A on the performance including shape memory behavior of the hyperbranched polyurethane thermosets is discussed in the third chapter of this thesis. From this study it is clear that the properties of such polyurethane can be improved by chemical cross-linking. However, as already mentioned in the above subchapter that this modification is unable to address many advanced applications, so more improvement is demanded. The above subchapter also showed that the formation nanocomposites with Fe$_3$O$_4$ nanoparticles also enhance the performance including shape memory property of such polyurethane. It is an apt proposition to investigate the effect of such nanomaterial on different properties of above thermosetting polyurethane. This is due to the fact that the epoxy ring is reactive towards polyurethane linkages leading to cross-link through a rearrangement polymerization of reaction as well as the hydroxyl groups present in the surface of Fe$_3$O$_4$ nanoparticles would interact both the epoxy and hyperbranched polyurethane. This process is expected to help in overall crosslinking reactions of the system and hence cycloaliphatic amine which is used as a hardener in Chapter 3 along with epoxy for obtaining hyperbranched polyurethane thermoset is not necessary. Thus in the present study the vegetable oil based hyperbranched polyurethane thermosetting nanocomposites were prepared without any additional external hardener. It is also assumed that the presence of various physico-chemical interactions significantly improved the performance of nanocomposite. Further, the shape memory properties of the polymers also depend on the degree of net point in the system. Large numbers of reports are available to improve the shape memory behaviors of the polymers by incorporation of suitable nanomaterials and/or crosslinking with the other compatible materials. Again, the importance of noncontact actuation of shape memory polymers is already discussed in subchapter 4A, section 4A.1. Although there are many reports on noncontact actuation of shape memory polyurethanes using magnetic field, electric field, IR radiation etc., here the microwave energy was used to investigate the shape memory behaviors of the thermosets polyurethane nanocomposites as described in subchapter 4A, section 4A.1. In this
subchapter, therefore, hyperbranched polyurethane/Fe$_3$O$_4$ thermosetting nanocomposites were prepared to investigate the performance including shape memory behaviors.

4B.2. Experimental

4B.2.1. Materials

The monoglyceride of the 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. Iron (III) chloride hexahydrate (Merck, India), iron (II) chloride tetrahydrate (Merck, Germany), polyethylene glycol (PEG, Merck, India, $M_n = 4000$ g/mol) and ammonia solution (Qualigens Fine Chemicals Ltd., India) used were same as described in subchapter 4A, section 4A.2.1.

4B.2.2. Preparation of Fe$_3$O$_4$ nanoparticles

Fe$_3$O$_4$ nanoparticles were prepared by the co-precipitation method and taking required amount of FeCl$_3$.6H$_2$O (2.0 g), FeCl$_2$.4H$_2$O (1.225 g) and PEG (1.5 g) by using the same procedure as described in subchapter 4A, section 4A.2.2.

4B.2.3. Preparation of hyperbranched polyurethane/Fe$_3$O$_4$ thermosetting nanocomposite

Hyperbranched polyurethane nanocomposites were prepared by the same technique as described in subchapter 4A, section 4A.2.3. To prepare the thermosetting polymer the above nanocomposite solution was mixed with 10 wt% of glycidyl bisphenol-A based epoxy resin (100% solid content) by vigorous mechanical stirring followed by 20 min ultra-sonication. The polymer solution was cast on the inert substrates followed by vacuum degassing to remove the air bubbles and curing was done at 120 °C. The cured films were denoted as EHPU2, EHPU5 and EHPU10 corresponding to the Fe$_3$O$_4$ content of 2, 5 and 10 wt%, respectively.
4B.2.4. Instrumentation

The hyperbranched polyurethane and its thermosetting nanocomposites were characterized by the same 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 method as described in Chapter 2, section 2A.2.4.

The shape memory behaviors of the thermosets were measured by the same method using microwave as a stimulus as described in subchapter 4A, section 4A.2.4.

4B.3. Results and discussion

4B.3.1. Curing study

The curing reaction occurred due to the presence of functionalities such as hydroxyl, urethane and epoxy groups in the system. It is pertinent to mention here that no additional cross-linking agent is required to obtain the desired thermosets. The touch free time at room temperature and drying time at 120 °C were decreased with the increase of loading of Fe₃O₄ in the nanocomposites (Table 4B.1). This is due to the increased cross-linking density as a result of various chemical reactions among the hydroxyl/urethane groups of polyurethane, epoxy resin and hydroxyl groups of Fe₃O₄ nanomaterials (Scheme 4B.1). Further, the increased of interactions is due to the homogeneous dispersion of Fe₃O₄ in the polymer matrix that causes the more restriction of polymer chains on the surface of the nanoparticles. Therefore the increased intercross-linking offers the compact three dimensional network structure formation. The absence of the epoxy band at 915 cm⁻¹ in the FTIR spectra and the increased of cross-linking density (supported by swelling study in DMF, Table 4B.1) confirmed the formation of thermoset.
Scheme 4B.1: Proposed crosslinking reactions

D = dendritic unit, L = linear unit and T = terminal unit
R = mixture of linoleic, oleic, stearic and palmitic acid

Hyperbranched polyurethane

Fe$_3$O$_4$ nanoparticle

Epoxy resin

Hydrogen bonding
Table 4B.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>
<th>Swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EHPU2</td>
<td>100</td>
<td>10</td>
<td>55</td>
<td>59</td>
<td>30</td>
</tr>
<tr>
<td>EHPU5</td>
<td>100</td>
<td>10</td>
<td>44</td>
<td>51</td>
<td>23</td>
</tr>
<tr>
<td>EHPU10</td>
<td>100</td>
<td>10</td>
<td>36</td>
<td>42</td>
<td>16</td>
</tr>
</tbody>
</table>

4B.3.2. FTIR study

The FTIR spectra of Fe₃O₄, hyperbranched polyurethane and the thermosetting nanocomposites are shown in Fig. 4B.1. The bands at 3429 cm⁻¹ and 581 cm⁻¹ are due to the stretching vibration of Fe-OH groups present on the surface of Fe₃O₄ nanoparticles and Fe-O stretching vibration, respectively. The band of urethane linkage at 3405-3431 cm⁻¹ (N-H stretching) was found to broaden after the nanocomposite formation. This implies the well dispersion of the nanoparticles and the presence of strong interaction of Fe₃O₄ nanoparticles within the polyurethane matrix. Moreover, the band corresponding to Fe-O of Fe₃O₄ nanoparticles was broadened in the nanocomposites. This ascribed that polymer chains are immobilized on the surface of Fe₃O₄ nanoparticles. The results confirmed the presence of interactions among the nanoparticles, epoxy resin and the polyurethane chains.

4B.3.3. X-ray diffraction study

The X-ray diffractograms of Fe₃O₄, hyperbranched polyurethane and the nanocomposites are shown in Fig. 4B.2. The peaks appear at 2θ=30.34°, 35.53°, 56.72° and 62.74°, which correspond to (220), (311), (511) and (440) planes of Fe₃O₄, respectively as already discussed in the earlier subchapter. The diffraction peaks at 2θ=21.81° and 2θ=23.72° are due to the (100) and (200) planes of PCL crystals of the hyperbranched polyurethane. The crystalline domain size of Fe₃O₄ was found to 10 nm, which was determined by using the Scherrer equation.
Fig. 4B.1: FTIR spectra of (a) Fe$_3$O$_4$, (b) MHBPU10, (c) EHPU2 before curing, (d) EHPU2, (e) EHPU5 and (f) EHPU10

Fig. 4B.2: XRD diffractograms of (a) Fe$_3$O$_4$, (b) MHBPU10, (c) EHPU2, (d) EHPU5 and (e) EHPU10
4B.3.4. TEM study

A representative TEM micrograph and histogram of Fe₃O₄ nanoparticles in the polymer nanocomposite are shown in Fig. 4B.3. The average diameter of the nanoparticles was found to be 12 nm, which is in good agreement with XRD result. Therefore the average surface area of Fe₃O₄ nanoparticles in the nanocomposite was 452.16 nm². The TEM image indicates the homogeneous distribution with almost no aggregation or agglomeration of Fe₃O₄ nanoparticles in the polyurethane matrix. This is due to the good interfacial interaction between the nanoparticles and the polyurethane chains. The distribution of spherical Fe₃O₄ nanoparticles in the nanocomposites clearly indicated that more than 50% of the nanoparticles are within the size range of 10-15 nm.

![TEM micrograph and histogram of Fe₃O₄ nanoparticles](image)

**Fig. 4B.3:** (a) TEM image and (b) distribution of nanoparticles for EHU5

4B.3.5. Thermal property

The DSC curves of hyperbranched polyurethane and the nanocomposites are shown in Fig. 4B.4. The melting temperature \( (T_m) \) and melting enthalpy are given in Table 4B.2. From the table it is clear that the melting temperature increases with the increase of the loading of Fe₃O₄ nanoparticles. This can be attributed to the increased restricted movement of the polymer chains due to the various physical and chemical cross-linking in the systems. The slight decrease in melting enthalpy value of the nanocomposites with loading of Fe₃O₄ nanoparticles as compared
to hyperbranched polyurethane (Table 4B.2) indicated the decrease of crystallinity of the polymer matrix in the presence of nanoparticles. In other words Fe₃O₄ nanoparticles have retarding effect on the crystallization process of hyperbranched polyurethane.

The thermo-gravimetric profiles of hyperbranched polyurethane and the thermosetting nanocomposites are shown in Fig. 4B.5. The thermal stability of the nanocomposites increased with the increase of content of Fe₃O₄ nanoparticles. From the figure it is seen that the initial decomposition starts at 240 °C, 258 °C, 264 °C and 275 °C for the 0, 2, 5 and 10 wt% of Fe₃O₄ loading, respectively. This beneficial effect can be attributed to the increased various physico-chemical interactions among the epoxy, polyurethane and Fe₃O₄ nanomaterials. Therefore the polymer chains configuration were changed as well as mobility restricted on the surface of nanoparticles, which conferred the rigidity and compactness of the nanocomposites. The improvement of thermal stability of the nanocomposites can also be attributed to the presence of Fe₃O₄ nanoparticles, which acted as gas barriers to reduce the permeability of oxygen and volatile degradation products throughout the nanocomposite.

![DSC curves](image)

Fig. 4B.4: DSC curves of (a) MHBPU10, (b) EHPU2, (c) EHPU5 and (d) EHPU10
Table 4B.2: Melting temperature and melting enthalpy of the thermosetting nanocomposites

<table>
<thead>
<tr>
<th>Code</th>
<th>Melting temperature ($T_m$ °C)</th>
<th>Melting enthalpy ($\Delta H_m$ J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>40.3</td>
<td>42.8</td>
</tr>
<tr>
<td>EHPU2</td>
<td>40.9</td>
<td>41.6</td>
</tr>
<tr>
<td>EHPU5</td>
<td>41.4</td>
<td>39.8</td>
</tr>
<tr>
<td>EHPU10</td>
<td>42.5</td>
<td>39</td>
</tr>
</tbody>
</table>

Fig. 4B.5: TGA thermograms of (a) MHBPU10, (b) EHPU2, (c) EHPU5 and (d) EHPU10

4B.3.6. Mechanical property

The effect of Fe$_3$O$_4$ nanoparticles loading on the performance characteristics such as tensile strength, elongation at break, scratch hardness, impact resistance etc. of the thermosetting nanocomposites are shown in Table 4B.3. The tensile strength increases from 6.2 to 18 MPa with the increase of loading of Fe$_3$O$_4$ from 2 to 10 wt%. This can be explained from the homogeneous dispersion of Fe$_3$O$_4$ nanoparticles and the increased physico-chemical interactions among the epoxy resin, urethane linkages and hydroxyl groups of Fe$_3$O$_4$ nanoparticles.\textsuperscript{20, 21} Therefore stress in the nanocomposites is transferred easily to the rigid nanoparticles, as a result, the tensile
strength of the nanocomposites was enhanced. Furthermore the increased cross-linking density (supported by the swelling values, Table 4B.1) is also responsible for the improvement of the tensile strength. However, the elongation at break decreased with the increase of the loading of Fe₃O₄ nanoparticles due to the molecular restriction of the polymer chains on the surface of the nanoparticles. The scratch resistance was found to be increased (Table 4B.3) with the increase of loading of Fe₃O₄ nanoparticles as a result of the increase of stiffness and compactness of the material. This is due to the presence of various interactions as stated earlier. This combined effect produced the tough surface that becomes more difficult for penetration. All the nanocomposites showed good impact resistance (~1m) that is the ability of the material to absorb the applied energy. The flexibility of pristine polymer remains intact even after the formation of nanocomposites as indicated by the bending test results. The gloss of the nanocomposites increased as compared to the neat polymer with loading of the nanoparticles. This can be attributed to the compatibility among the components, higher cross-linking density, higher dimension stability and the smoothness of the surface compared to pristine hyperbranched polyurethane.

**Table 4B.3:** Mechanical properties of hyperbranched polyurethane and the thermosetting nanocomposites

<table>
<thead>
<tr>
<th>Property</th>
<th>MHBPU10</th>
<th>EHPU2</th>
<th>EHPU5</th>
<th>EHPU10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>6.2 ± 0.4</td>
<td>11 ± 0.2</td>
<td>14.3 ± 0.2</td>
<td>18 ± 0.2</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>595 ± 3.1</td>
<td>482 ± 1.4</td>
<td>432 ± 1.4</td>
<td>396 ± 1.1</td>
</tr>
<tr>
<td>Scratch resistance (kg)</td>
<td>3 ± 0.1</td>
<td>5.4 ± 0.1</td>
<td>6.2 ± 0.1</td>
<td>7 ± 0.15</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 ± 0.02</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>Gloss (60°)</td>
<td>83 ± 2</td>
<td>87 ± 2</td>
<td>92 ± 2</td>
<td>95 ± 2</td>
</tr>
</tbody>
</table>

* 1.0 m is the limit of the instrument

4B.3.7. Magnetic property

The magnetic hysteresis loop of the nanocomposite (EHPU5) at room temperature is shown in Fig. 4B.6. The saturation magnetization value was found to be 0.22 emu/g. The low value of magnetization of the nanocomposite is due to the low content of the nanomaterials (2
wt%), smaller size and the surface coating of the Fe$_3$O$_4$ nanoparticles by the polymer chains as described in subchapter 4A, section 4A.3.6.

**Fig. 4B.6: Magnetic hysteresis loop for EHPU5**

4B.3.8. Shape memory property

The shape memory behaviors of the hyperbranched polyurethane and the thermosetting nanocomposites are shown in Fig. 4B.7. The nanocomposites exhibited good shape fixity over the repeated cycles of test. The micro-Brownian movements of the polymer chains and the applied stress are frozen during the cooling process. This resulted good shape fixity of the nanocomposites (Table 4B.4). The fixed shape can be retained for a long time at the room temperature. The nanocomposites also showed good shape recovery under the application of microwave energy. When the microwave irradiated on the samples, the dipole moment oscillates due to the oscillation of electric field component of the microwave. Therefore heat is generated due to the molecular friction and collisions, and the shape recovery was observed when the induced heat is close to the $T_{\text{trans}}$. The shape recovery speed was found to increase with the increase of loading of Fe$_3$O$_4$ nanoparticles (Table 4B.4). This can be attributed to the homogeneous distribution of the nanoparticles and increased various physico-chemical
interactions in the system. Furthermore this can be attributed to the increased of microwave absorption characteristic of the nanocomposites due to the increase of loading of Fe$_3$O$_4$ nanoparticles as Fe$_3$O$_4$ nanoparticles are microwave absorbing material.\textsuperscript{4, 5} The nanocomposites showed good shape fixity and shape recovery over the repeated cycles of test and might be utilized as advanced shape memory materials in different potential fields.

![Fig. 4B.7: Shape memory behaviors of the hyperbranched polyurethane and the thermoset nanocomposites (a) original shape and (b) fixed shape](image)

<table>
<thead>
<tr>
<th>Code</th>
<th>Shape fixity (%)</th>
<th>Shape recovery (%)</th>
<th>Shape recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHBPU10</td>
<td>98.7 ± 0.5</td>
<td>98.5 ± 0.6</td>
<td>83 ± 4</td>
</tr>
<tr>
<td>EHPU2</td>
<td>99.2 ± 0.2</td>
<td>99.1 ± 0.1</td>
<td>66 ± 2</td>
</tr>
<tr>
<td>EHPU5</td>
<td>99.2 ± 0.2</td>
<td>99.1 ± 0.1</td>
<td>54 ± 2</td>
</tr>
<tr>
<td>EHPU10</td>
<td>99.2 ± 0.2</td>
<td>99.1 ± 0.1</td>
<td>40 ± 2</td>
</tr>
</tbody>
</table>

Table 4B.4: Shape memory behaviors of hyperbranched polyurethane and the nanocomposites
4B.4. Conclusion

The \textit{in-situ} polymerization of hyperbranched polyurethane in the presence of Fe$_3$O$_4$ nanoparticles and subsequent modification with epoxy resulted mechanically strong thermosetting nanocomposites as microwave induced shape memory material. The incorporation of iron oxide nanoparticles in the epoxy modified hyperbranched polyurethane leads to significant improvement of tensile strength and thermal stability. In addition, the nanocomposites showed excellent shape fixity over the repeated cycle of test and exhibited almost full shape recovery under the application of microwave energy. Furthermore, the dose dependent shape recovery speed was observed, which is accelerated with the content of Fe$_3$O$_4$ nanoparticles. Moreover the thermosetting nanocomposites exhibited the better performance including shape memory behaviors as compared to the thermoplastic nanocomposites. Thus the studied nanocomposites could be utilized as a microwave induced non-triggering shape memory materials.
References


