Synthesis and characterization of some polyimide-epoxy composites

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Abstract: Composites from some novel polyimide and commercial epoxy were prepared aiming to improve the thermal behavior of epoxy resins. Two diamines namely 4-4’-diamino-4’’-hydroxytriphenyl methane (DHTM) and 4-4’-diaminotriphenyl methane (DTM) were synthesized by reacting aniline and aldehydes according to a reported method. The synthesized diamines were blended with commercially available epoxy 1, 4-butanedioldiglycidylether (BDDE) to synthesize model epoxy amine networks which were compared with polyimide-epoxy composites. The polyimides were synthesized by reaction of these diamines with aromatic anhydride namely 3,3’,4,4’-benzophenone tetracarboxylic acid dianhydride (BTDA). These synthesized polyimides were dispersed in epoxy diamine networks to prepare composites. All the monomers and composites were characterized by making use of various analytical techniques including FTIR, NMR, TGA, DSC and XRD. Presence of hydroxyl group in the diamine helped in better dispersion of polyimide leading to high Tg and high char yield at 600 °C.

Key words: Epoxy resins, polyimide composites, network structure, thermal gravimetric analysis, dynamic scanning calorimetry

Introduction

Epoxy resins have the collective advantages of excellent chemical and corrosion resistances, thermal and dimensional stability, and great mechanical and electrical properties, ensuring their ample applications in laminating, adhesive, surface coating and semiconductor encapsulation [1-3]. However, the conventional epoxy resins are unable to satisfy some applications such as integrated circuit packaging [4] and advanced materials which need higher thermal resistance [4]. Hence it is essential to design and synthesize novel high heat resistant epoxy resin systems which broaden the applications in the field of construction, electronics, and adhesives and as matrix materials in aerospace composites [5]. Many approaches have been reported to enhance the heat resistance of epoxy resins, for example changing the structure of the starting resins which influences the properties of final cured epoxy polymers [6-11] by increasing ductility of epoxy resins, their range of applications can be enhanced [12]. Most frequently studied approach to improve properties of epoxy resins is their curing. A number of traditional curing agents are reported but curing with these agents presents a number of problems including overall resin modulus and in end use temperature [13, 14].

Polyimides are known to have high thermal stability, chemical resistance and mechanical properties. These have been used as a favourite candidate to improve the thermal stability and toughness [15, 16] of different epoxy amine matrices. In this context, polyimide or its precursor poly(amic acid) has been cured with epoxy resins, or they are used as reinforcement in the epoxy resin systems [17-20]. Gaw et al
studied the curing of epoxy with poly(amic acid, PAA) a precursor of polyimide, and reported an improved thermal stability along with shrinkage during cure [17, 18]. Hey et al reported the molding of linear unreactive polyimide for toughening of the epoxy–dianinodiphenylsulfone system [19] and had shown increased fracture toughness without the loss of modulus. However, there was a little influence on the thermal capability across the range of modifying polyimides. Synthesis of hydroxyl group containing reactive polyimide, and its use as curing agent for commercial epoxy resin has been studied by Agag et al. Their work had resulted in the increased thermal stability of the polymer with increase in polyimide contents [20].

The synthesis of soluble polyimide from 4,4’-diamino-4”-hydroxy triphenyl methane (DHTM) and pyromellitic dianhydride and its use in PI/SiO₂ hybrid nanocomposites has been reported by Chen et al [21]. It was observed that introduction of phenyl hydroxyl group to polyimide led to better solubility of polyimide and also enhanced compatibility with silica.

In this study, two structurally similar polyimides were synthesized. One polyimide (PI-1) was synthesized from DTM and BTDA. Second (PI-OH) containing pendant phenyl hydroxyl group, by the reaction of DHTM and BTDA. Both, DHTM and DTM were blended with BDDE separately to prepare epoxy-amine networks. These networks were used to compare the effect on increasing polyimide contents on thermal stability of polyimide-epoxy composites.

Thus two series (CR, and FR respectively) of polyimide–epoxy composites (PI-EP) were synthesized and characterized by their DSC, TGA and XRD analysis. The difference between the two series lied in the structure of the constituent diamines of epoxy matrix and polyimides, DHTM with hydroxyl group and DTM without it. Thus, DTM and DHTM were reacted with BTDA to give PI-1 and PI-OH, while their reaction with diepoxy resulted in the formation of epoxy amine matrix. The main purpose of this study was to compare the two systems, one having an unreacted polyimide without any chemical linkage between the matrix and polyimide, other where the reaction between hydroxyl group of polyimide might produce chemical linkage with matrix.

Results and application

The diamines DHTM and DTM were synthesized (scheme 1) according to the reported procedure [21]. The structure of diamines was confirmed by elemental analysis as well as FTIR and NMR spectroscopic techniques. In IR spectrum, characteristic absorption bands for amine hydrogens were observed at 3300-3450 cm⁻¹. In addition, another absorption band at 2860 cm⁻¹ due to stretching vibration of C-H group indicates the formation of diamines. In NMR spectra, a signal at 5.05 ppm for methine proton confirms the conversion of reactant into product. The diamine monomers were reacted with an aromatic dianhydride namely 3,3’,4,4’-benzophenone tetracarboxylic acid dianhydride (BTDA), to yield the polyimides of DHTM and DTM. A conventional two step procedure resulting in the formation of poly (amic acid), followed by sequential heating at 80 °C for 18 hours, 100 °C for 24 hours, and 150 °C for 24 hours was adopted to convert it into polyimide. The formation of polyimides was confirmed by IR analysis. Both polyimides exhibited characteristic imide group absorption around 1780 and 1725 cm⁻¹ typical of imide carbonyl symmetric and a symmetric stretching, and 720 cm⁻¹ (imide ring deformation). The disappearance of bands for amide (1680-1630 cm⁻¹ for carbonyl group, 3180 and
3350 cm\(^{-1}\) for amino group) and carboxylic acid group (3400-2400 cm\(^{-1}\)) indicated complete conversion of poly(amic acid) precursor into polyimide.

![FT-IR analysis of PI-OH.](image_url)

**Fig. 1.** FT-IR analysis of PI-OH.

Two neat epoxy-diamine networks were prepared by stirring overnight a mixture of diamines (DHTM, DTM) and BDDE in DMF, the formulations were cured for three hours at 100 °C followed by a three hours post-cure at 120 °C. During the curing process, epoxide ring of BDDE was opened by amino group of diamines and hydroxyl group is generated. This hydroxyl group further opens the epoxide ring (scheme 3). In case of DHTM, along with amino group, hydroxyl group also opens the epoxide ring as shown in Scheme 4. Polyimide-epoxy composites were prepared under the same curing conditions. The hydroxyl group of PI-OH can also be involved in opening of epoxide ring [20] of BDDE (Scheme 5). Viscosities of both polyimides were measured from a solution of 0.2g/dl at 25 °C and found to be 1.02 for PI-1, 1.07 for PI-OH.

**X-ray Diffraction Data**

Structural information of the neat epoxy-diamine network and their composites with polyimides was obtained from their wide-angle X-ray diffraction pattern in the region of \(2\theta = 0–80\) at room temperature. The representative X-ray diffractograms of epoxy diamine network and composites are shown in Fig 2. The peak patterns of diffractograms of epoxy diamine network exhibited that these have semicrystalline behavior. The peak at \(2\theta =72.5\) of neat epoxy diamine network disappeared.
completely by addition of 1% PI-OH. It means that the semicrystalline matrix is transformed to amorphous material. As the percentage of PI-OH was increased beyond 1% the peak at 2θ = 72.5 reappeared and its intensity increased gradually. This is due to phase separation at higher percentage of polyimide. In case of PI-1 which has no pendant hydroxyl group, the intensity of peak at 2θ = 72.5 decreased to some extent at 2.5% but remains unaffected at other percentages of polyimide.

Fig. 2. Wide-Angle X-ray diffractograms of composites (a) PI-OH; (b) PI-1.

**Thermal analysis**

The thermal stability of the neat epoxy-amine matrices and their polyimide reinforced composites were studied from the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. Figures 3a and 3b represent the thermograms and Table 1 lists the thermal properties of the composites. The thermal stability of the composites was determined in terms of T_{10},
The maximum degradation temperature $T_{\text{max}}$, $R_{600}$ and energy of activation. The maximum degradation temperature $T_{\text{max}}$ for the neat matrices derived from DHTM and DTM are 307 °C and 353 °C while those for the composites are 45 to 62 °C high as compared to the matrices. This shows the effect of chain rigidity conferred by PI-OH and PI-1 to the epoxy-amine neat networks. Comparing the thermal stabilities among the two polyimide series, it is evident that the PI-OH increases the $T_{\text{max}}$ of the neat matrix from 43-62 °C while PI-1 increases the $T_{\text{max}}$ of the neat matrix from 45-47 °C. Thus the reactive polyimide PI-OH probably established the chemical linkages between the two networks and thus resulted in a high thermal stability as compared to the non-reactive PI-1.

**Tab. 1.** Thermal analysis of composites.

<table>
<thead>
<tr>
<th>Composites</th>
<th>$T_{10}$ °C a</th>
<th>$T_{\text{max}}$ °C b</th>
<th>$R_{600}$ (%) c</th>
<th>$T_{\text{g}}$ °C d</th>
<th>Ea(kJ/mol) e</th>
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</thead>
<tbody>
<tr>
<td>FR 1(0%PI)</td>
<td>263</td>
<td>307</td>
<td>40.00</td>
<td>176</td>
<td>16.75</td>
</tr>
<tr>
<td>FR2(1%PI)</td>
<td>387</td>
<td>363.98</td>
<td>85.00</td>
<td>176</td>
<td>22.42</td>
</tr>
<tr>
<td>FR3(2.5%PI)</td>
<td>308</td>
<td>367.15</td>
<td>60.00</td>
<td>235</td>
<td>23.46</td>
</tr>
<tr>
<td>FR4(5%PI)</td>
<td>224</td>
<td>369.10</td>
<td>31.34</td>
<td>175</td>
<td>21.53</td>
</tr>
<tr>
<td>FR5(7.5%PI)</td>
<td>257</td>
<td>350</td>
<td>42.47</td>
<td>173</td>
<td>21.45</td>
</tr>
<tr>
<td>CR 1(0%PI)</td>
<td>327</td>
<td>353.21</td>
<td>19.65</td>
<td>125</td>
<td>20.27</td>
</tr>
<tr>
<td>CR2(1%PI)</td>
<td>345</td>
<td>398.40</td>
<td>23.00</td>
<td>147</td>
<td>25.03</td>
</tr>
<tr>
<td>CR3(2.5%PI)</td>
<td>319</td>
<td>398.60</td>
<td>24.30</td>
<td>109</td>
<td>23.23</td>
</tr>
<tr>
<td>CR4(5%PI)</td>
<td>319</td>
<td>398.90</td>
<td>19.82</td>
<td>93</td>
<td>21.30</td>
</tr>
<tr>
<td>CR5(7.5%PI)</td>
<td>320</td>
<td>399.55</td>
<td>23.77</td>
<td>73</td>
<td>21.28</td>
</tr>
</tbody>
</table>

a Temperature at which 10% weight loss occur (from TGA)
b Temperature at which maximum weight loss occur (from TGA)
c Residual weight at 600 °C. (From TGA)
d Glass transition temperature (from DSC)
e Energy of activation (from TGA)

The high values of glass transition temperatures also show the same trends i.e., higher values of $T_{\text{g}}$ are observed for PI-EP composites that epoxy amine network and among composites $T_{\text{g}}$ was higher for the composites containing PI-OH. Residual weights at 600 °C are again coherent with the above mentioned fact. $T_{10}$ values remain always higher for composites in comparison to networks and also higher for the FR series than the CR series. The energy of activation of pyrolysis was calculated with the Horowitz and Metzeger method [22] from the TGA curves and its value ranges from 16.75-25.03 kJ/mol.

In both the series it is also observed that the thermal stability initially increases with an increase in percentage of polyimide up to certain value after that it starts decreasing (Fig 3a, 3b). This decrease in the thermal stability may be attributed to decreases in the solubility of polyimides at higher polyimide percentages. The comparison of the glass transition temperature of neat epoxy-diamine network and epoxy-polyimide composites revealed that the value of $T_{\text{g}}$ increases with increase in the polyimide content up to certain percentage after which $T_{\text{g}}$ decreases due to decrease in solubility (Fig 4a, 4b). A comparison of the initial decomposition
temperature of neat epoxy-diamine network with that of composites show that it increases appreciably by the addition of polyimides as shown in the Figures 5a, 5b.

**Fig 3a.** TGA Curves of PI-Epoxy Composites (PI-OH).

**Fig. 3b.** TGA Curves of PI-Epoxy Composites (PI-1).

**Fig. 4a.** $T_g$ Vs. percentage of PI-OH.
Fig. 4b. $T_g$ Vs. percentage of PI-1.

Fig. 5a. DT vs. percentage of PI-OH.

Fig. 5b. DT vs. percentage of PI-1. DT: Temperature at which decomposition starts.

Conclusions

Two series of composites consisting different weight percentage of polyimide and epoxy-diamine matrix were prepared. The analysis showed that composites are
thermally more stable than the epoxy cured with diamines. Using the diamine with pendent hydroxyl group gives better dispersion of the polyimide in the epoxy-amine matrix which in turn, is reflected in higher glass transition temperatures and improved char yields at 600 °C of the resulting composites. Wide-angle X-ray diffraction pattern also shows the enhanced miscibility of polyimide with pendant hydroxyl group.

**Experimental part**

**Materials**

Chemicals of high purity were obtained from various commercial sources which include aniline (Fluka Switzerland), 4-hydroxybenzaldehyde (Merck, Germany), benzaldehyde (Merck, Germany), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (Fluka Switzerland), Hydrochloric Acid (Sigma Aldrich, Germany), Aradite LY564 (vantico, Switzerland). Dimethylformamide (Lab-Scan, Ireland) and Ethanol (Lab-Scan, Ireland).

**Measurements**

The solid state Fourier transform infrared spectra (KBr pallets, 4000-400 cm⁻¹) were recorded on Bio-Rad Excalibur FT-IR, Model 3000 MX spectrophotometer. ¹H NMR spectra were taken on NMR Bruker spectrometer at 300 MHz in DMSO d₆. ¹³C NMR spectra were recorded on NMR Bruker apparatus at 75 MHz. Tetramethylsilane (TMS) was used as internal reference. Elemental analysis was carried out on CHNS-932 LECO elemental analyzer. Particle size of polyimide was determined on Fritsch Analysette Economy Mode. Thermal stability of composites was determined using thermo gravimetric analyzer STAR™ SW 9.01 (25-800 °C, 10 /min, under nitrogen). Wide-angle XRD analysis of the polymers was carried out using 3040/60 X’Pert PRO diffractometer. Viscosity of both polyimides was calculated at 25 °C by Ostwald viscometer.

**Synthesis of Monomers**

The aromatic diamines were synthesized by following the reported procedure [21] as given in Scheme 1. The reaction flask was preheated to 50°C and purged with nitrogen for 30 min. The mixture of aromatic aldehyde (0.08 mol), aniline (0.24 mol), and aniline hydrochloride 1.07g was charged and refluxed at about 120 °C under nitrogen flow for 3 h. After the completion of the reaction, the mixture was cooled and 30 mL of ethanol was added. The entire mixture was then heated to 80 °C to dissolve the lumpy material, cooled and kept overnight. Purple crystal precipitated out, which were filtered off and washed with ethanol followed by water a few times to remove aniline residue and salt. Crude product was recrystallized from ethanol.

(i) 4,4′-diamino-4″-hydroxytriphenylmethane (DHTM)

The diamine DHTM was synthesized according to the reported procedure cited above by reacting 4-hydroxybenzaldehyde 10 g (0.08 mol) with aniline 22 mL (0.24 mol) and aniline hydrochloride 1.07g. (Yield 30%, m.p. 206°C). Elemental Analysis for C₁₉H₁₈N₂O in wt% Calcd: C = 78.60, H = 6.20, N = 9.60. found C = 78.42, H = 6.38, N = 9.44. IR (KBr pellet) in cm⁻¹: 2860 (C-H, aliphatic). ¹H NMR (DMSO-d₆) in δ (ppm): 9.16 (s, 1H, OH), 6.8 6.4 (m, 12H, PhH), 5.05 (s, 1H, CH), 4.84 (s, 4H, NH₂).
(ii) 4, 4′-diaminotriphenylmethane (DTM)

The diamine DTM was synthesized according to the reported procedure cited above by reacting benzaldehyde 8 mL (0.08 mol) with aniline 22 mL (0.24 mol) and aniline hydrochloride 1.07 g. (Yield 30%, m.p: 119 °C.). Elemental Analysis for C_{19}H_{18}N_2O in wt% Calcd: C=78.60, H= 6.20, N=9.60, Found: C=78.42, H=6.38, N=9.44. IR (KBr pelet) in cm\(^{-1}\): 2844 (C-H, aliphatic). \(^1\)H NMR (300 MHz, DMSO-d\(_6\)) in δ (ppm) 7.27-7.02 (m, 13H, PhH), 5.17(s, 1H, CH), 4.94 (s, 4H, NH\(_2\)).

Scheme 1. Synthesis of diamines.

Fig 6.(a). 3, 3’, 4, 4′-benzophenone tetracarboxylic acid dianhydride (b) 1,4-butanedioldiglycidylether.

Scheme 2. Synthesis of polyimide.
Synthesis of Polyimides

Polyimides were synthesized (Scheme 2) by stirring the solution of diamine (2.47 mmoles) in 16 mL of DMAc with gradual addition of 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (Fig 6 a) (2.47 mmoles). The mixture was stirred at room temperature for 24 hours under nitrogen atmosphere. Then the reaction mixture was poured into 200 mL of water. Polyamic acid was precipitated out, filtered, washed with water and dried under vacuum. The overall yield of polyamic acid was 93%. Polyamic acid was ground to powder form, and was heated at 80 °C for 18 hours, 100 °C for 24 hours, and 150 °C for 24 hours to convert it into polyimide.

Polyimide PI-OH

The polyimide PI-OH was synthesized following the above mentioned procedure, using 4,4'-Diamino-4''-hydroxytriphenylmethane (DHTM) 0.7g (2.47 mmol), 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride 1g (2.47 mmol). IR (KBr pellet) in cm⁻¹: 3480 (OH), 2856 (C-H, aliphatic), 1780, 1720 (C=O), 720 (C-N, tertiary). ¹H NMR (DMSO-d₆) in δ (ppm): 9.39 (s, 1H, OH), 8.23-6.75 (m, 18H, PhH), 5.54 (s, 1H, CH).

¹³C NMR (DMSO-d₆) in δ (ppm):  a (166), b (162), c (144), d (142), e (139), f(136), g (135), h (132), i (130), j (129), k (127), l (124), m (55)

Polyimide PI-1

The polyimide PI-1 was synthesized following the procedure mentioned above, using 4,4'-diamino-triphenylmethane (DTM) 0.67g (2.47 mmol), 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride 1g (2.47 mmol). IR (KBr): 2930 (s) cm⁻¹(C-H, aliphatic), 1781,1722 (m), (C=O), 716 (s) cm⁻¹ (C-N,tertiary). ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) 8.27-6.75 (m, 19H, PhH), 5.54 (s, 1H, CH).

¹³C NMR (DMSO-d₆) in δ (ppm):  a (166), b (160), d (141), e (140), f (137), g (134), h (132), i (130), k (126), l (124), m (57)
Synthesis of neat Epoxy–diamine Network

Epoxy-diamine network was synthesized in order to compare its properties with polyimide-epoxy composites. Commercially available 1,4-butanedioldiglycidylether (BDDE) (Fig. 6b) was cured with the two diamines to obtain networks (Scheme 3, 4).

Scheme 3. Epoxide ring opening by amino group of diamine.

Synthesis of Neat-Epoxy–diamine Network

Neat epoxy-amine system was synthesized by mixing an equimolar ratio of epoxy and amine keeping the ratio of functionalities N=1. N was defined as number of hydrogen in amine /number of epoxy functional groups in the resin. When N=1, there are equal numbers of hydrogen and epoxy in the sample mixture. For this purpose, 1, 4-butandioldiglycidylether (BDDE) (1.47g, 8.4 mmol) and diamine (1g, 3.4 mmol) was mixed in a flask using DMF as solvent. The mixture was stirred at room temperature for 24 hours. The clear solution thus formed was poured into clean dry Teflon coated Petri dish. Then the Petri dish was placed in vacuum oven at 100 °C for three hours and at 120 °C for next three hours to obtain transparent film.

Synthesis of polyimide-epoxy composite

Polyimides (PI-OH, PI-1) were ground to fine powder. Average particle size of ground polyimide (PI-OH) is 15 μ and for PI-1 is 10 μ.

Polyimide in different weight ratios (Table 2) was blended to mixture of BDDE and diamine in DMF solvent. The mixture was stirred at room temperature for 24 hours until a homogeneous solution was obtained.
Scheme 4. Epoxide ring opening by hydroxyl group of diamine.

Scheme 5. Epoxide ring opening by hydroxyl group of polyimide.
The solution was then transferred into Teflon coated petri dishes which were placed in vacuum oven at 100 °C for three hours and at 120 °C for next three hours. These films were peeled off from Petri dishes and were subjected to further analysis.

**Tab. 2.** Calculations for PI-Epoxy composites.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Epoxy (g)</th>
<th>Diamine (g)</th>
<th>Polyimide (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR1, CR1 *</td>
<td>1.47</td>
<td>1</td>
<td>0(0%)</td>
</tr>
<tr>
<td>FR2, CR2</td>
<td>1.47</td>
<td>1</td>
<td>0.02(1%)</td>
</tr>
<tr>
<td>FR3, CR3</td>
<td>1.47</td>
<td>1</td>
<td>0.06(2.5%)</td>
</tr>
<tr>
<td>FR4, CR4</td>
<td>1.47</td>
<td>1</td>
<td>0.12(5%)</td>
</tr>
<tr>
<td>FR5, CR5</td>
<td>1.47</td>
<td>1</td>
<td>0.35(7.5%)</td>
</tr>
</tbody>
</table>

* In FR series PI-OH while in CR series PI-1 was used.

**Acknowledgements**

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**References**