Hyperbranched polysiloxane functionalized graphene oxide for dicyclopentadiene bisphenol dicyanate ester nanocomposites with high performance

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Abstract. We report an efficient and novel method to functionalize graphene oxide (GO) with hyperbranched polysiloxane and successfully compound them with dicyclopentadiene bisphenol dicyanate ester (DCPDCE) to prepare nanocomposites. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectra (FT-IR) were employed to examine the surface functionalization of GO. The effects of functionalized GO on the curing reaction, mechanical, dielectric and thermal properties of DCPDCE resin were investigated systematically. Results of DSC show that the addition of modified GO can facilitate the curing reaction of DCPDCE and decrease the curing temperature of DCPDCE. Compared with pure DCPDCE resin, the impact and flexural strengths of the nanocomposite materials are improved markedly with up to 66 and 50% increasing magnitude, respectively. Meanwhile, the modified GO/DCPDCE systems exhibit lower dielectric constant and loss than pure DCPDCE resin over the testing frequency from 10 to 60 MHz. In addition, the thermal stability and moisture resistance of modified GO/DCPDCE nanocomposites are also superior to that of pure DCPDCE resin.

Keywords: nanocomposites, graphene oxide, cyanate ester, mechanical properties, dielectric properties

1. Introduction

Cyanate ester resin has been regarded as the candidate with the great competition to fabricate advanced functional/structural materials for electronic and aerospace industries due to its excellent integral properties, such as outstanding mechanical properties, good molding workability as well as outstanding dielectric properties, etc. [1–3]. Unfortunately, like most thermosetting resins, the biggest shortcoming of cyanate ester resin is its brittleness, which is the major disadvantage to restrict further expansion into the advanced industrial applications. Therefore, the potential applications as cost-effective replacement of engineering polymers by composite materials based on cyanate ester resin have attracted considerable attention and has been widely investigated. To

improve the toughness, several methods have been developed to modify cyanate ester resins, such as polymer blending [4, 5], filling with mineral fillers [6, 7] and fiber reinforcement [8]. The advantage of these methods is that the fracture toughness can be improved dramatically. However, it is found to be difficult to obtain a resin system with both good mechanical and dielectric properties; in other words, the improvement of mechanical properties is generally accompanied by a decrease the other properties of the original cyanate ester resin. Therefore, there is a great interest to develop a new method to overcome the key shortcomings of original cyanate ester resin at the same time without deteriorating its original outstanding properties including excellent thermal property, dielectric property and moisture resistance.

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Graphene, which is recognized as one of the strongest materials in the world, has generated much excitement among materials scientists due to its unique physical, chemical, and mechanical properties [9, 10]. Polymer/graphene nanocomposites have been intensively studied in the recent years with the aim to obtain high-performance materials [11–17]. However, pristine graphene is not quite ready for using as a filler due to the strong tendency of the monolayer graphene sheet to form irreversible agglomerates into monolayer graphite through strong π - π stacking and van der Waals interaction. Poor dispersability in most common organic polymers has been a hurdle in the way of exploitation [18]. Therefore, processing and dispersion of graphene in the polymeric hosts constitute the main challenge to use it in nanocomposites, the control of the interfacial interaction being crucial [19–21].

Hyperbranched polymers are special kinds of polymers with highly branched structure, they have good solubility, low melt viscosity, and extremely high density of functional groups, so they can be utilized advantageously as surface modifiers [22]. Anchoring the hyperbranched polymers on the silica nanoparticles [23] and carbon nanotubes [24] has been studied for improving solubility of the inorganic materials, and the obtained hybrid nanoparticles exhibited some novel properties. Among reported hyperbranched polymers so far, hyperbranched polysiloxanes are beginning to attract interests as new organic inorganic hybrid materials because they combine the unique chemical structure of polysiloxane and hyperbranched topology structure, and thus possess low viscosity, high reactivity, low surface energy and interface tension [25, 26]. Gu's group [27–29] investigated the effects of hyperbranched polysiloxane on the properties of cyanate ester resin, and the results show that hyperbranched polysiloxane has good compatibility with cyanate ester matrix and the incorporation of hyperbranched polysiloxane in cyanate ester leads to an obvious improvement in the mechanical and thermal properties. In order to develop graphene-based cyanate ester nanocomposites with high performance, hyperbranched polysiloxane functionalized graphene oxide (GO) can be a useful method for achieving homogeneous dispersion of GO sheets in polymeric matrix because the hyperbranched polysiloxane can offer stronger interactions between matrix and GO by covalent linkage. In this paper, we propose a

facile method to modify dicyclopentadiene bisphenol dicyanate ester by introducing GO functionalized by a hyperbranched polysiloxane which contains active $\text{C}=\text{CH}_2$ groups, expecting dispersal of GO in dicyclopentadiene bisphenol dicyanate ester resins. The effects of functionalized GO on the curing reaction, mechanical, dielectric and thermal properties of dicyclopentadiene bisphenol dicyanate ester resins were investigated to develop high performance materials.

2. Experimental

2.1. Reagents and materials

The GO nanosheets were produced from natural graphite flakes by the modified Hummers's method [30]. Dicyclopentadiene bisphenol dicyanate ester (DCPDCE, >99% pure) was purchased from Jiangdu Wujiao Resin Plant (Jiangsu, China), the structure of DCPDCE was shown in Figure 1. Methylbis(dimethylallylsiloxy)silane was prepared according to the literature [31]. Vinyltriethoxysilane was purchased from Jingzhou Jiangnan Fine Chemical Co. Ltd (Hubei, China). Platinum-carbon catalyst (Pt/C) was purchased from Shaanxi Kaida Chemical Engineering Co. Ltd (Shaanxi, China). Ethanol, carbon tetrachloride and hydrochloric acid (HCl) were purchased from Tianjin Fuyu Fine Chemical Co. Ltd (Hebei, China). Acetone was purchased from Tianjin Ruijinte Chemicals Co., Ltd (Tianjin, China). Distilled water was produced by our laboratory. Other reagents were all commercial products with analysis grades.

Figure 1. The structure of DCPDCE

2.2. Preparation of vinyltriethoxysilane grafted GO

GO nanosheets (1.0 g), vinyltriethoxysilane (10.0 mL), ethanol (95%, 100 mL) and distilled water (15.0 mL) were combined in a glass beaker. HCl (0.1 mol/L) was slowly dropped into the glass breaker with stirring to adjust the pH value to 3~4. Then the mixture was dispersed through ultrasonication for 2 h. After that, the solution was transferred into a 250 mL three-neck round-bottom flask equipped with a mechanical stirrer, reflux-con-

Figure 2. The synthesis route of vinyltriethoxysilane grafted GO

denser and thermometer. Then the mixture was heated to 60–70°C and held for about 5 h. The synthetic route was shown in Figure 2. After the reaction, the mixture was filtrated and washed with acetone to remove the unreacted vinyltriethoxysilane. Finally, the resulting product was collected and dried in a vacuum oven at 50°C for 12 h.

2.3. Preparation of hyperbranched polysiloxane functionalized graphene oxide (HBPGO)

In a four-neck round-bottom flask holding a nitrogen inlet, mechanical stirrer, reflux-condenser, constant-pressure funnel and thermometer, vinyltriethoxysilane grafted GO (0.2 g), Pt/C catalyst (6 mg) and carbon tetrachloride (100 mL) were added. At 25°C, the methylbis(dimethylallylsiloxy) silane (1.0 g) was slowly dropped into the flask through the constant-pressure funnel. The reaction mass was then slowly heated to 50°C at which the reaction continued for 5 h. The synthetic route was shown in Figure 3. After the reaction, the product was filtered and washed with copious amounts of ethanol (95%). Finally, the resulting product was collected and dried in a vacuum oven at 50°C for 24 h before use.

Figure 3. The synthesis route of HBPGO

2.4. Preparation of HBPGO/DCPDCE nanocomposites

The DCPDCE was heated to 100°C in a glass beaker and kept at this constant temperature until melting. The appropriate amount of HBPGO was then carefully mixed with the melted DCPDCE using a mechanical high shear dispersion process. The mixture, consisting of prepolymer and HBPGO, was heated to 140°C in an oil bath and kept at this temperature for 15–20 min with stirring. Then the mixture was put into a preheated mold with release agent followed by degassing at 140°C for 1 h in a vacuum oven. After that, the mixture was cured and post-cured via the procedures of 160°C/1 h + 180°C/1 h + 200°C/2 h + 220°C/2 h and 240°C/2 h, respectively. Finally, the mold was cooled to room temperature and demolded to get the samples of HBPGO/DCPDCE systems.

The samples of pure DCPDCE resin were prepared in the same manner as above. All samples were dried at 120°C under vacuum for 6 h and kept in a dry environment prior to testing.

2.5. Characterization

Fourier Transform Infrared (FTIR) spectrum was recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1} on a Nicolet FTIR 5700 spectrometer (USA). The samples were mixed with potassium bromide (KBr) powder, to form the homogeneous mixtures using a grinder, and then the mixtures were compression moulded at 10 bar pressure to make a thin disc for the test.

X-ray photo-electron spectroscopy (XPS, Thermal Scientific K-Alpha XPS spectrometer) was used to investigate the surface elemental composition of GO and HBPGO. The analysis was performed under 1027 Torr vacuum with an AlKa X-ray source using a power of 200 W.

Transmission electron microscopic (TEM) images were obtained by a HITACHIS-600 (Japan) transmission electron microscope operating at 200 kV.

For TEM samples preparation, GO and HBPGO were dispersed in ethanol and chloroform, respectively. The dispersions of GO/ethanol and HBPGO/chloroform were dropped on a copper grid for TEM imaging, respectively.

Gel time was measured on a temperature-controlled hot plate by the standard knife method, the time required for the resin to stop legging and becomes elastic is recorded as the gel time.

Differential scanning calorimetry (DSC, MDSC2910, TA Instruments) experiments were performed at a heating rate of 5°C/min in a nitrogen atmosphere, heating from 25–350°C.

Impact strength was determined according to GB/T 2571-1995. Samples were cut into strips of $(50\pm0.02)\times(7\pm0.02)\times(4\pm0.02)$ mm³ by a cutting machine. The impact strength tests were performed using a Charpy impact machine tester (XCJ-L, China). Five samples were tested for each composition, and the results are presented as an average for tested samples.

Flexural strength was measured according to GB/T 2570-1995. Samples were cut into strips of $(80\pm0.02)\times(10\pm0.02)\times(4\pm0.02)$ mm³. The flexural tests were performed using an electronic universal testing machine (RIGER-20, China) at a crosshead speed of 2 mm·min⁻¹. Five samples were tested for each composition, and the results are presented as an average for tested samples.

Scanning electron micrographs (SEM) were performed on a HITACHIS-570 instrument. For SEM samples preparation, the fracture surface of the specimens was sputtered with a thin layer (about 10 nm) of gold by vapor deposition on a stainless steel stub using a vacuum sputter coater.

Thermogravimetric analysis (TGA) tests were performed by using Perkin Elmer TGA-7 (USA) at

a heating rate of 10°C/min in a nitrogen atmosphere from 25 to 800°C.

The dielectric constant and loss factor were measured by a high frequency QBG-3 Gauger and a S914 dielectric loss test set (China) at the frequency range from 10 to 60 MHz. The sample dimension was $(25\pm0.02)\times(25\pm0.02)\times(3\pm0.02)$ mm³. For each condition, five samples were tested the data was averaged.

The water absorption of a sample was determined by swelling the sample in distilled water for 48 h at 100°C. The sample dimension was $(10\pm0.02)\times(10\pm0.02)\times(3\pm0.02)$ mm³. The percentage of water absorbed by the specimen is calculated using equation. Percentage of water absorption = $(w_2 - w_1)/w_1$. Where w_1 is the initial weight of the sample and w_2 is the weight of the sample after immersion in water for 48 h at 100°C.

3. Results and discussions

3.1. Characteristics of HBPGO

X-ray photoelectron spectroscopy (XPS) is used for the investigation of elementary composition on the surface of the GO and HBPGO. Figures 4a and 4b show the board scan XPS spectra of the GO and HBPGO, respectively. Table 1 lists the elementary composition of HBPGO. Compared the board scan XPS spectrum of the GO (Figure 4a) with that of HBPGO (Figure 4b), successful grafting of the hyperbranched polysiloxane onto the GO can be confirmed due to the detection of silicon (Si) element. The Si element only derives from the hyperbranched polysiloxane, the C element and the O element derive from both the HBPGO and the GO.

Further evidence on the successful grafting of the hyperbranched polysiloxane onto the GO and the covalent bonding between the GO and the hyper-

Figure 4. Board scan XPS spectra of GO (a) and HBPGO (b)

branched polysiloxane chains can be demonstrated by FTIR spectra, as shown in Figure 5. Compared

Table 1. Elementary composition of HBPGO

Element	Bonding energy [eV]	Peak	Atom composition [%]
C	285.15	1s	40.78
O	532.85	1s	40.97
Si	154.11	1s	9.15
	103.10	2p	9.11

Figure 5. FTIR spectra of GO (a), vinyltriethoxysilane grafted GO (b) and HBPGO (c)

the FTIR spectrum of the GO with that of HBPGO, significant changes in the range of 3500 to 500 cm^{-1} can be observed, which indicates the occurrence of chemical reaction. The details are discussed as follows.

Figure 5a shows the FTIR spectrum of the GO. Intense absorption peak at 3421 cm^{-1} represents hydroxyl ($-\text{OH}$) groups, and the strong intensity may be affected by the absorbed water molecules. Peaks at 1626, 1055 and 1737.79 cm^{-1} are generated by $\text{C}=\text{C}$, $\text{C}-\text{O}$ and $\text{C}=\text{O}$ vibrations, respectively. Peaks at 864 and 1250 cm^{-1} are generated by bending and stretching vibrations of epoxy groups. Therefore, it can be concluded that the oxygen-containing functional groups of GO mainly are hydroxyl, epoxy and carboxyl groups. In the case of vinyltriethoxysilane grafted GO, as seen in Figure 5b, the peaks at around 3424, 1737 and 1622 cm^{-1} , which are assigned to $-\text{OH}$, $\text{C}=\text{O}$ and $\text{C}=\text{C}$, respectively, continue to be observed, and peaks at 1254 and 909 cm^{-1} are generated by bending and stretching vibrations of epoxy groups. New peaks at 1130 and 1564 cm^{-1} , are assigned to $\text{Si}-\text{O}-\text{C}$ and $\text{Si}-\text{C}=\text{C}$ vibrations, respectively and are clearly visible. After the grafting of the hyperbranched monomers on the surface of vinyltriethoxysilane grafted GO, an obvious change can be observed in the FTIR spectrum as shown in Figure 5c, a new peak is found at 1041 cm^{-1} , which is ascribed to $\text{Si}-\text{O}-\text{Si}$ vibration. These results provide an evidence of the successful covalent grafting of the hyperbranched polysiloxane onto the GO through the chemical reaction.

The nanosheets morphology of GO and HBPGO were investigated by TEM imaging as displayed in Figure 6. TEM analysis (Figure 6a) shows that the GO nanosheets are very thin and have some wrinkles and folded regions, and the surface of the GO nanosheets is fairly smooth, which is consistent with the morphology typically reported in the literature [32, 33, 17, 37]. In contrast, HBPGO (Figure 6b) exhibits a different morphology. Compared with GO, the nanosheets of HBPGO become less transparent, and some black regions on the surface of HBPGO can be observed. The black regions of HBPGO can be attributed to the hyperbranched polysiloxane layer attached onto the GO surface from both sides.

Figure 6. TEM images of GO (a) and HBPGO (b)

3.2. Curing behavior of HBPGO/DCPDCE system

Gel time is generally used to evaluate the curing behavior of a resin, a shorter gel time indicates a bigger curing activity. Figure 7 depicts the gel time of DCPDCE resin and HBPGO/DCPDCE systems at different temperatures, it can be observed that the addition of HBPGO can effectively decrease the gel time of DCPDCE, indicating that the addition of HBPGO can catalyze the gelation of DCPDCE. This phenomenon is mainly attributed to the intensive promotion of the curing reaction of DCPDCE by $-OH$ groups in the molecule of HBPGO [34], and the copolymerization between active $-C=CH_2$ at the end of molecular chains of HBPGO with $-OCN$ in DCPDCE [27].

Figure 7. Dependence of gel time on temperature for DCPDCE and HBPGO/DCPDCE systems

In order to further confirm the role of HBPGO on the curing reaction of DCPDCE prepolymer, comparative DSC analyses of DCPDCE resin and 0.6 wt% HBPGO/DCPDCE composites at the heating rate of $5^{\circ}\text{C}/\text{min}$ were carried out, and the corresponding curves are depicted in Figure 8. The whole peak of DCPDCE appears at the temperature from about 180 to 221°C , while that of HBPGO/DCPDCE system is between 160 and 196°C . Comparing with DCPDCE, the maximum curing temperature of HBPGO/DCPDCE shifts to lower temperature by about 15°C , demonstrating that the whole curing process of DCPDCE can be accelerated by a small amount of HBPGO loading. The decreased curing and post-curing temperature is beneficial to manufacture cyanate ester-based composites for industrial application.

Figure 8. DSC curves of DCPDCE and 0.6 wt% HBPGO/DCPDCE system

3.3. Mechanical properties of HBPGO/DCPDCE system

Figure 9 shows the impact strengths of DCPDCE and HBPGO/DCPDCE systems. It is observed that all the HBPGO/DCPDCE composites exhibit higher impact strengths than pure DCPDCE resin, and the 0.6 wt% HBPGO/DCPDCE system has the maximum impact strength (16 kJ/m^2), which is increased by 66% compared with that of pure DCPDCE, indicating that the addition of HBPGO can significantly improve the toughness of DCPDCE resin. Figure 10 shows the flexural strengths of DCPDCE and HBPGO/DCPDCE systems, and a similar trend can be observed. The 0.6 wt% HBPGO/DCPDCE system has the maximum flexural strength (142 MPa), which is increased by about 50% compared with that of pure DCPDCE resin. Therefore, it can be concluded that the addition of HBPGO can efficiently improve the mechanical properties of DCPDCE resin. The enhancement of impact and flexural strength may be attributed to the outstanding mechanical properties of GO and the increased interface

Figure 9. Relationship of impact strength on HBPGO content for HBPGO/DCPDCE systems

Figure 10. Relationship of flexural strength on HBPGO content for HBPGO/DCPDCE systems

bonding strength between GO and matrix. On one hand, the chain of hyperbranched polysiloxane grafted on the surface of GO nanosheets can bring stronger mutual exclusion and steric hindrance effect, thus the restacking of GO nanosheets is restrained and the agglomeration tendency of GO in matrix can be controlled effectively. On the other hand, the $-\text{C}=\text{CH}_2$ groups in the molecule of HBPGO can react with $-\text{NCO}$ in DCPDCE, leading to improved interfacial bonding strength between GO and matrix. For the HBPGO/DCPDCE system, the probability of forming a strong organic-inorganic combination will be enhanced. Therefore, the mechanical properties of HBPGO/DCPDCE system are increased as the contents of HBPGO from 0.0 to 0.6 wt%. However, when the fillers content is high enough ($>0.6 \text{ wt\%}$), the mechanical properties of the composites decrease with the increasing concentration of fillers. When the content of nanosheets is too large, the concentration of GO nanosheets is big enough to form aggregates, and thus reducing the mechanical properties. But the 0.8 wt% HBPGO/DCPDCE system still possesses much better mechanical properties than neat resin.

In order to further confirm the effect of HBPGO on the toughness of DCPDCE resin, SEM images of the fracture surfaces of samples after impact tests are taken and shown in Figure 11, it can be observed that pure DCPDCE resin has a smooth and river-like fracture surface (Figure 11a), exhibiting a typical brittle feature. While with the addition of HBPGO into DCPDCE resin, the fracture surfaces become rougher and are accompanied with more ductile sunken areas, which is consistent with the improved impact strength of the nanocomposites. In the case of 0.2 wt% HBPGO/DCPDCE system, as shown in Figure 11b, the surface becomes coarse and some ductile sunken regions can be observed, which can absorb the energy of fracture and hinder the crack propagation. For the 0.6 wt% HBPGO/DCPDCE system, as shown in Figure 11c, the fracture surface of the composite is much rougher than those of pure DCPDCE and 0.2 wt% HBPGO/DCPDCE system, and there exist large amount of ductile sunken areas, exhibiting a typical rough feature. However, when the concentration of HBPGO is 0.8 wt%, as shown in Figure 11d, large clusters in the matrix appear due to the aggregation of HBPGO at high concentration, which will lead to more rapid crack initiation and impact failure. Therefore, the impact

Figure 11. SEM images of the fracture surfaces of the HBPGO/DCPDCE systems with various contents of HBPGO (a: 0.0 wt%, b: 0.2 wt%, c: 0.6 wt%, d: 0.8 wt%)

strength of the nanocomposite with high HBPGO content is decreased. The features of the fracture surfaces of HBPGO/DCPDCE systems accord well with the mechanical properties.

3.4. Dielectric properties of HBPGO/DCPDCE system

One of the most attractive features of DCPDCE resin is its excellent dielectric properties including

low and stable dielectric constant (2.8–3.2) and loss (0.002–0.008) over a wide range of frequency, which enables DCPDCE resin to be used in many advanced industries. Therefore, it is necessary to retain the outstanding dielectric properties of the original DCPDCE resin to develop a new modified DCPDCE system. Figures 12 and 13 show dependence of dielectric constant and loss factor on frequency for pure DCPDCE resin and other modified systems,

Figure 12. Dielectric constants of DCPDCE resin and HBPGO/DCPDCE systems versus frequency

respectively. It can be seen that the dielectric constant and loss values of HBPGO/DCPDCE system are lower than that of pure DCPDCE resin, and the higher the HBPGO concentration is, the lower the dielectric constant and loss. Meanwhile, the dielectric constant and loss of HBPGO/DCPDCE system remain stable over the testing frequency band from 10 to 60 MHz. With regard to a composite, its dielectric properties are determined by those of both matrix and fillers as well as interfaces [35]. Firstly, GO is an insulator, with oxygen atoms randomly attached at graphene sites, which undergo conversion from sp^2 -hybridized carbon atoms in graphene, to sp^3 -hybridized carbon in GO. This process reduces conjugation and confines π -electrons [36]. So GO exhibits very low dielectric constant values. When GO sheets are used as interlayers in the polymer matrix, there is much less electron mobility. Wang

et al. [37] investigated the effect of NH_2 -functionalized GO on the dielectric constant of polyimide, and the results showed that the addition of GO/modified GO can efficiently decrease the dielectric constant of polyimide matrix. HBPGO has excellent dielectric properties due to the chemical structure of polysiloxane and special unoccupied spaces of hyperbranched polymers as well as the outstanding dielectric properties of GO, so modified DCPDCE systems with higher HBPGO concentration have smaller dielectric constant values. Secondly, the addition of HBPGO into CE resin promotes the self-polymerization of $-NCO$ groups, thus increases the productivity of symmetrical triazine rings [38]. As a result, the modified DCPDCE system tends to form networks with greater symmetry and larger space hinder, which is beneficial for reducing the dielectric constant and loss. Thirdly, the incorporation of nanofillers can fill the space between polymeric chains of DCPDCE, so the number of movable molecular chains and polarized groups in the network is decreased [39], which also provides contribution to the decrease in dielectric constant and loss. In addition, a good adhesion between HBPGO and DCPDCE matrix will reduce the interfacial polarization and restrict the mobility of chain segments, leading to reduced dielectric constant and loss factor. Therefore, both the dielectric constant and loss factor of HBPGO/DCPDCE system decrease compared with those of pure DCPDCE resin.

3.5. Thermal properties of HBPGO/DCPDCE system

Overlay TGA and DTG curves of DCPDCE resin and 0.6 wt% HBPGO/DCPDCE system are shown in Figure 14. It can be seen that the modified DCPDCE system has higher decomposition temperatures than pure DCPDCE resin. The decomposition temperature at 5% weight loss of pure DCPDCE resin is $390^\circ C$, while that of HBPGO/DCPDCE system is $405^\circ C$. The char yield at $800^\circ C$ of pure DCPDCE is 38%, while that of HBPGO/DCPDCE system is 46%. The higher decomposition temperatures and char yields of the composite materials suggest that the HBPGO/DCPDCE system possesses better thermal stability than pure DCPDCE. The enhanced thermal stability of the HBPGO/DCPDCE nanocomposite may be mainly attributed to the excellent thermal stability of HBPGO, and the increased

Figure 13. Dielectric loss factors of DCPDCE resin and HBPGO/DCPDCE systems versus frequency

Figure 14. Overlay TGA and DTG curves of DCPDCE and 0.6 wt% HBPGO/DCPDCE system

cross-linking degree of HBPGO/DCPDCE system which results from the catalytic effect of HBPGO in DCPDCE [27], as well as the fact that the mobility of polymer segments at the interfaces between the HBPGO and the DCPDCE matrix is suppressed by strong interactions [40]. In addition, compared with pure DCPDCE, the HBPGO/DCPDCE system is subject to a mass loss proceeding in two major steps. The former mass loss is attributed to the degradation of triazine rings, while the latter mass loss may mainly be caused by the pyrolysis of HBPGO because the thermal stability of the hyperbranched polysiloxane grafted on the surface of GO is better than that of triazine rings.

3.6. Water absorption of HBPGO/DCPDCE system

Outstanding moisture resistance is a very important property of a material, especially those requiring stably high performance, because in general absorbed water will decline almost all properties of the original material including thermal, mechanical and dielectric properties, etc., so very low water absorption is one important target for developing new resin systems with high performance [41]. One of the advantages of the DCPDCE resin is its low water absorption. Figure 15 gives the water absorption values of HBPGO/DCPDCE systems and that of pure DCPDCE resin for comparison. It can be seen that the water absorption decreases from 0.57 to 0.51 wt% with the small addition (0.2 wt%) of HBPGO into DCPDCE resin, and which continually decreases with the continuous increase of HBPGO content in HBPGO/DCPDCE systems. In case of 0.6 wt% HBPGO/DCPDCE system, its water absorption is

Figure 15. Water absorption of DCPDCE resin and HBPGO/DCPDCE systems

0.35 wt%, which is much lower than that of pure DCPDCE resin. The improvement of water-resistant property of HBPGO/DCPDCE systems may be ascribed to the following reasons. Firstly, as discussed earlier, the addition of HBPGO can effectively promote the curing reaction of DCPDCE, and thus leads to increasing conversion of the -OCN groups, which is a positive role on reducing the water absorption of DCPDCE resin. Secondly, Si-O-Si chains in HBPGO have excellent hydrophobic properties, which is beneficial to improve the water-resistant property of HBPGO/DCPDCE systems. Thirdly, a large number of functional groups on the HBPGO surface can enhance inorganic/organic phase compatibilization at the interface, which can effectively prevent water from entering the network of nanocomposites.

4. Conclusions

A kind of high-performance polymer composite has been fabricated using DCPDCE resin as matrix and GO as filler employing the method of melting mixing, in which the GO was modified with a hyperbranched polysiloxane before use in order to improve its dispersability and compatibility with the DCPDCE matrix. The incorporation of HBPGO into DCPDCE resin can not only effectively promote the curing reaction of DCPDCE, but also brings a lot of changes in the properties of HBPGO/DCPDCE nanocomposite materials. The impact and flexural strengths are increased obviously with suitable content of HBPGO within the matrix. In addition, the HBPGO/DCPDCE systems also exhibit better dielectric property, thermal stability and moisture resistance than pure DCPDCE resin. Especially, when

the concentration of HBPGO is 0.6 wt%, the best overall performance of HBPGO/DCPDCE nanocomposites can be achieved.

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