In situ polymerization and performance of alicyclic polyimide/graphene oxide nanocomposites derived from 6FAPB and CBDA

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Abstract: A series of alicyclic polyimide/graphene oxide(PI/GO) nanocomposites were successfully prepared by in situ polymerization of 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene(6FAPB) and 1,2,3,4-cyclobutanetetracarboxylic dianhydride(CBDA) as well as GO, followed by thermal imidization. The effect of GO on the thermal stability, optical properties, mechanical properties, water absorption and water surface contact angle of the PI-based nanocomposites was investigated. The optical properties of the pure alicyclic PI and corresponding PI-based nanocomposite films showed that the addition of GO reduced the transparency of PI films in the range of 200-800nm obviously. With the increase of GO loading, the mechanical and thermal properties of alicyclic PI-based nanocomposites were enhanced. For the PI-1.0%GO nanocomposite films, the tensile strength was increased from 96 MPa (pure PI) to 109 MPa, and the Young's modulus was improved from 2.41 GPa (pure PI) to 3.83 GPa. The 10 wt% decomposition temperature for PI-1.0%GO nanocomposite films was increased from 464 (pure PI) to 481°C, while the glass transition temperature (T_g) of PI/GO was slightly increased. In addition, the water surface contact angle of PI/GO enhanced from 71° to 82.5°, and the water uptake of PI/GO decreased from 2.58% to 1.48% with increasing the GO loadings. The uniform dispersion of GO in PI matrix was proved, and the pure PI and PI/GO nanocomposite films were amorphous.

Keywords: polyimides, graphene oxide, nanocomposites, alicyclic, in-situ polymerization

Introduction

Because polyimides(PIs) show excellent mechanical properties, thermal stability, electrical

performance and so on, they have attracted wide interest [1-3]. Especially, PIs containing alicyclic unit have good optical transparency, low dielectric constant and good solubility in organic solvents [4, 5]. However, the thermal and mechanical properties of alicyclic PIs are poorer than those of aromatic ones. Therefore, these shortcomings of alicyclic PIs could limit their industrial applications.

As is well known, graphene exhibits excellent mechanical properties, thermal conductivity, electrical conductivity and optical transparency. Since 2004, graphene was successfully exfoliated, which has become the most perspective nano materials in future research [6]. Graphene oxide (GO) was prepared by the oxidative treatment of graphite. There are some functional groups containing oxygen on its surface, so GO also exhibits some excellent properties such as mechanical and thermal properties. Like carbon nanotubes, GO is an ideal nano-scaled filling material for improving polymer's properties. After chemical modification, the surface functional groups of GO make it more compatible with the polymer matrix, which provides good dispersion in a polymer matrix, resulting in composites with excellent mechanical and thermal properties [7, 8]. The polymer/GO nanocomposites used for wide range of applications have been discussed in detail [9-11].

In recent years, there are a lot of studies about PI/GO nanocomposites [12-14]. GO could be introduced to the PIs matrix by means of in situ polymerization and blending method. In the in situ polymerization method, using its hydrophilic nature, GO is highly dispersed into the polar solvents such as *N,N*-dimethylacetamide (DMAc) and *N,N*-Dimethylformamide (DMF) to form individual sheets under ultrasound. In the GO dispersion solution, the dianhydride and diamine monomers were added to undergo an in situ polymerization, obtaining poly(amic acid)(PAA) solution with GO nanosheets. Then, the PAA/GO solution was converted into PI/GO nanocomposites followed by thermal or chemical imidization method. For the blending method, the GO dispersion solution is directly blended with PAA solution to form PAA/GO solution, which is converted into PI/GO composites further. In addition, the GO dispersion solution could be blended with the PI solution directly. Because the GO surface includes some functional groups such as C=O, -OH, -COOH, as well as epoxy groups, GO nanosheets could be uniformly dispersed in the PIs matrix, and produced strong interface interaction between GO and PI molecular to enhance the thermal, electrical properties, permeation and mechanical performance of PI/GO composites [15-19]. Furthermore, GO platelets have excellent diffusion barriers, so the water/oxygen permeation of PI membranes could be controlled to improve the performance or service life of PIs using as substrates [20]. Moreover, GO also shows positive improvement on the tribological

behaviors of the PI matrix, due to the formation of the transfer film to protect the specimens [21, 22]. Therefore, it is a significant interest to investigate the effect of GO on various properties of PIs. In this work, GO was prepared by chemical exfoliated method and used as the nano-filler to in situ polymerize with the alicyclic dianhydride 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and aromatic diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB). Then, the pure PI and PI/GO nanocomposite films such as PI-0.05%GO, PI-0.1%GO, PI-0.3%GO, PI-0.5%GO and PI-1.0%GO were prepared by thermal imidization method. The chemical structures and various properties of the pure alicyclic PI and corresponding PI-based nanocomposites were explored by infrared spectrum (FTIR), UV-Vis spectra (UV-Vis), X-ray diffraction (XRD), scanning electron microscope (SEM), tensile test as well as water absorption (WA) and water surface contact angle (WSCA). The goal of this work is to study the effects of GO on the alicyclic PIs-based nanocomposites. The obtained results indicated that the GO nanosheets were dispersed homogeneously in the alicyclic PI matrix. In addition, due to the incorporation of GO, the mechanical properties, thermal performance and so on of alicyclic PI-based nanocomposites were enhanced, but their optical properties exhibited a serious loss.

Experimental

Materials

The alicyclic dianhydride 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) were obtained from China Anshan Huahui optoelectronic materials sci-tech Co., Ltd. CBDA was purified by acetic anhydride for use. *N,N*-dimethylacetamide (DMAc) was purchased from China Sinopharm Chemical Reagent Co., Ltd. Graphene oxide (GO) was prepared in the lab according to the literature [23-25].

Preparation of pure PI and PI/GO composite films

A typical process for the preparation of alicyclic PI-based nanocomposites consists of in situ polymerization and the thermal imidization, as shown in Scheme 1. Here, the -COOH group on the GO surface can react with -NH₂ group of 6FAPB to produce amide structure during the in-situ polymerization and thermal imidization process. The specific preparation procedure is as follows. A certain amount of GO, such as 0, 0.05, 0.1, 0.3, 0.5 and 1.0 wt % of PIs was added into the 250ml two-neck flask containing dry 35.4ml DMAc under ultrasonic for at least 2h. Next, 0.01mol (4.2833g) 6FAPB was put into the GO dispersion solution. After stirring for 0.5 h continuously, 0.01mol (1.9611g)

CBDA was introduced into the above-mentioned solution containing GO with mechanical stirring at R.T. for 18h to form a homogeneous and viscous poly(amic acid) (PAA) solution with the amount of GO. The synthesized PAA and PAA/GO solution were coated onto smooth and clean glass plates, followed by drying at 40°C for 24h to remove the most of the solvent. Then, these alicyclic PI-based nanocomposite films were prepared by the thermal imidization procedure at 80, 150, 200 and 250°C each for 1h in a far infrared oven, then naturally cooled to room temperature. Here, the imidization procedure is sensitive to the heating temperature. With the thermal temperature increasing, the imidization degree of PI will be improved in further, so the programmed heating process is necessary. After the programmed thermal imidization process, these films were soaked in water to be taken from the glass plates, and dried in a vacuum oven at 100°C for 12h. In the work, the amount of GO was controlled to 1.0 wt% to study the optical properties of alicyclic PI films.

Scheme 1 Schematic diagram for preparing alicyclic PI-based nanocomposite films with different GO loadings

Measurements

The Nicolet is 10 Fourier transform infrared (FTIR) spectrophotometer was used to characterize the chemical structures of pure alicyclic PI and corresponding PI-based nanocomposite films, scanning from 600 to 4000 cm^{-1} . Thermo gravimetric analysis was conducted with a thermo gravimetric analyzer (TGA, PE Instruments Co.) from 50 to 800°C at a heating rate of 20°C/min in nitrogen atmosphere. The 5 wt% and 10 wt% degradation temperatures ($T_{5\%}$ and $T_{10\%}$) were obtained from the thermal degradation curves. The crystallographic data of GO, pure PI, and PI/GO nanocomposites was obtained by using a X'Pert Powder X-ray diffractometer (PANalytical, Netherlands) at room temperature. The X-ray diffraction (XRD) pattern was measured from 5° to 60° (2θ value) with Cu K_{α} radiation

(conditions: $\lambda = 1.54\text{\AA}$, 40 kV, 40 mA). The morphologies of the cross-sectional surface of pure alicyclic PI and corresponding PI-based nanocomposite films were observed by a Zeiss-SIGMA HD field emission scanning electron microscope (SEM) with a working voltage of 2.0 kV. These films were fractured in liquid nitrogen and mounted on a metal block by means of double-sided conductive adhesive tape, and a thin layer of white gold was sputtered onto the cross-sectional surface. The optical transmittance of these films was examined by a UV-Vis spectrophotometer (PE Instruments Co.) in the range of 200-800nm. The dynamic mechanical properties of these films were measured by the thermal mechanical analyzer (TMA, Mettler Toledo Instrument, STDA861e) with an extension mode, at a heating rate of 5°C/min, with a tension force of 0.5 N, at a frequency of 1 Hz and under nitrogen. The HY-0580 stretching tester (Shanghai Yiheng Instruments Co., China) was used to measure the mechanical properties of thin films about 70 μm thickness, at a speed of 1mm/min. In the tensile test, at least three specimens were used for each sample.

Results and discussion

Structure characterization of GO, pure PI and GO/PI nanocomposite films

The chemical structure of GO samples was studied by the FTIR measurement. As shown in Fig. 1, the FTIR spectrum showed that the special absorption peaks at 1041 cm^{-1} (C-O), 1223 cm^{-1} (C-O-C), 1400 cm^{-1} (C-OH), 1614 cm^{-1} (C-C) and 1724 cm^{-1} (C=O) were consistent with reported values of GO in the literature [26]. Two relatively broad peaks at 3085 cm^{-1} and 3597 cm^{-1} are caused by the stretching vibration of -OH on GO surface as well as absorbed water [27]. The surface functional groups of GO, such as -OH, -COOH, C=O, and epoxy groups could be beneficial to the interaction between PAAs and GO in situ polymerization. In further, the GO is bonded to the PIs molecular chain after thermal imidization process. **Polymerization occurs via reaction of $-\text{NH}_2$ groups of 6FAPB diamine with anhydride functional groups of CBDA dianhydride, and it belongs to condensation polymerization.** The chemical structures of pure PI and PI/GO composites such as PI-0.05%GO, PI-0.1%GO, PI-0.3%GO, PI-0.5%GO and PI-1.0%GO were also confirmed by FTIR spectrum and shown in Fig.1. The FTIR spectra of alicyclic PIs-based composites derived from alicyclic dianhydrides CBDA and diamine 6FAPB containing $-\text{CF}_3$ and -O- linkage exhibited characteristic imide group absorptions at around 1780 and 1712 cm^{-1} (C=O asymmetrical and symmetrical stretching of imide ring), 1372 cm^{-1} (C-N stretching), and 738 cm^{-1} (C=O bending), together with the disappearance of absorption bands around 1660 cm^{-1} corresponding to C=O stretching of amide. These special peaks are consistent with reported

values in the literature [14, 20]. After the thermal imidization, the characteristic absorption bands of graphene can hardly be detected directly for their negligible amounts.

Fig.1 FTIR spectra of GO, pure PI, and PI/GO nanocomposite films **Fig.2** XRD patterns of GO, pure PI, and PI/GO nanocomposite films

The XRD patterns of GO, pure alicyclic PI, and corresponding PI-based nanocomposite films with various GO loadings are illustrated in Fig.2. The GO samples showed a strong diffraction peak at $2\theta=9.5^\circ$ because of the chemical oxidation process, and the interlayer spacing of GO was 0.93 nm according to the Bragg equation. According to the literature, the diffraction peak of graphite is around at $2\theta=26.5^\circ$ [16]. The new diffraction peak at $2\theta=9.5^\circ$ indicates that hydroxyl, carbonyl and epoxy groups have intercalated into the graphite sheets in the process of the chemical oxidation, and the interlayer distance has been enlarged [16]. There was no sharp diffraction peak at $2\theta=9.5^\circ$ for pure PI and PI/GO nanocomposites, but a broad diffraction peak around at $2\theta = 18.5^\circ$ was observed. The obtained XRD results indicate that the regular layered structure of GO disappeared, and the enough exfoliation of GO was confirmed in PIs matrix. In other words, the surface functional groups of GO nanosheets have made it form a uniform dispersion in PAA solution or PI matrix. Compared with pure PI, the incorporation of GO was conducive to the formation of short-range ordered structures as a result of the enhanced diffraction peak. Moreover, a broad XRD diffraction peak was mainly attributed to the amorphous nature of pure PI and PI/GO composites.

Thermal properties of pure PI and PI/GO nanocomposites

Thermal properties are more important properties for PI and PI-based composites in high-temperature applications. Fig.3 shows the TGA curves of pure alicyclic PI and corresponding PI-based nanocomposites including PI-0.05%GO, PI-0.1%GO, PI-0.3%GO, PI-0.5%GO and PI-1.0%GO. The

thermal stability of these films were evaluated by TGA under nitrogen, and their $T_{5\%}$ (5% weight-loss temperature) and $T_{10\%}$ (10% weight-loss temperature) were obtained from the TGA curves for comparison. The corresponding data of thermal properties is list in Table 1. The purpose in determining $T_{5\%}$ and $T_{10\%}$ is to discuss the effect of GO on the thermal stabilities of PI/GO nanocomposites. In general, when the weight loss of the material reaches 5%, the ideal performance will be not achieved. It is obvious that the TGA curves of PI-based nanocomposites are different from that of pure alicyclic PI. For example, $T_{5\%}$ of PI-1.0%GO was decreased from 443°C (pure PI) to 442°C. It indicates that the thermal stability of PI matrix decreased because the residual -COOH or -OH groups on GO surface easily decomposed in high temperature measurement. Compared with pure PI film, the $T_{10\%}$ moved to high temperature gradually due to the increase of GO loadings, the $T_{10\%}$ of PI-1.0%GO increased to 481°C, which was attributed to the uniform dispersion of GO in PI matrix. The $T_{10\%}$ of pure alicyclic PI and corresponding PI-based nanocomposite films were recorded in the range of 464-481°C in nitrogen atmosphere, and the residual weight at 700 °C of these resulting films was in the range of 44-50%, implying all these films with excellent thermal stability. In other words, GO can improve the thermal properties of PIs. Generally speaking, the decomposition temperature of the polymer-based nanocomposites was increased due to the incorporation of inorganic nano materials, which had been reported in many literatures [7, 12, 16, 21, 24]. In PI/GO nanocomposites, the reason for improvement of thermal properties is the strong interface interaction between GO and PI limits the movement of PI molecular. Therefore, the incorporation of GO improved the thermal properties of PI/GO composites with a lower GO loadings.

Fig.4 shows the $\tan\delta$ -T curves of pure PI, PI-0.5%GO, and PI-1.0%GO nanocomposites, and the glass transition temperature (T_g) according to the peak of the $\tan\delta$ curves are list in Table 1. It is not obvious that the position of $\tan\delta$ peaks shift to high temperature with increasing GO loadings, so the T_g value of the PI-based composites shows a slightly rising trend. The PI- 1.0%GO only has a 4°C higher T_g than that of the pure PI (T_g =304°C), maybe the amount of filled GO is too small. The increase of T_g value was attributed to the covalent bonding between GO and PI to enhance the interface interaction, which restricted segmental motions of PI polymer chain. Under the effect of restriction, the molecular chain relaxation and segmental movement of PIs need a broader temperature range as well as higher temperatures to occur.

Fig.3 TGA curves of pure PI and PI/GO nanocomposite films **Fig.4** Tan δ -T curves of pure PI and PI/GO nanocomposite films

Table 1 Thermal properties and optical performance of pure PI and PI/GO nanocomposite films

Samples	Thickness / μm	T_g / $^{\circ}\text{C}$	$T_{5\%}$ / $^{\circ}\text{C}$	$T_{10\%}$ / $^{\circ}\text{C}$	R_w /%	λ_{cutoff} /nm	$T_{450\text{nm}}$ /%
Pure PI	75	304	443	464	44	315	72
PI-0.05%GO	72	-	448	469	46	315	60
PI-0.1%GO	72	-	444	471	47	315	45
PI-0.3%GO	70	-	445	476	47	315	24
PI-0.5%GO	71	306	445	480	45	315	12
PI-1.0%GO	60	308	442	481	50	315	1.5

T_g , glass transition temperature obtained from Tan δ curves; $T_{5\%}$ and $T_{10\%}$, temperature at 5% or 10% weight loss in nitrogen; R_w , residual weight at 700 $^{\circ}\text{C}$ in nitrogen; λ_{cutoff} , UV cutoff wavelength; $T_{450\text{nm}}$, transmittance at 450 nm.

Optical performance of pure PI and PI/GO nanocomposite films

The alicyclic dianhydride CBDA and $-\text{CF}_3$ and $-\text{O}-$ containing diamine 6FAPB were selected to fabricate the flexible and light color PI films in the solvent of DMAc successfully. The UV-Vis transmission spectrum of pure alicyclic PI films with different thicknesses is illustrated in Fig.5. The pure alicyclic PI film with 15 μm thickness exhibited 90% transmittance in the whole visible light region. The results suggested the obtained PI films were light color and high transparency. As is known to all, the color of PI films is mainly caused by the formation of intermolecular or intramolecular charge transfer complex (CTC) in PI matrix [1]. The alicyclic structure of CBDA and bulky $-\text{CF}_3$ group

of 6FAPB reduced the conjugated structure and CTC of PI, resulting in less absorption of visible light. The transmittance of PI films at 450nm decreased with the film thickness increasing. For pure alicyclic PI film with 75 μm thickness, the optical transmittance at 450nm was 72%. It is demonstrated that the transparency of PI films was affected by the thickness obviously.

Fig. 6 illustrates the transmittance of pure alicyclic PI and corresponding PI-based nanocomposite films with about 70 μm thickness in the range of 200-800nm. For PI-0.05%GO nanocomposites, the transmittance at 450nm was 60%, compared with 72% for pure PI. With the increase of GO loadings, the transmittance at 450nm of PI-1.0%GO composite film was sharply decreased to 1.5%. It is obvious that the transparency of PI/GO composite films were remarkable influenced by the incorporation of GO based on the thickness of PI films. Therefore, to prepare the light colored and transparent PI/GO nanocomposite films, the thickness of film and GO loadings must be controlled strictly.

Fig.5 UV-Vis spectrum of pure PI films with different thickness

Fig.6 UV-Vis spectra of pure PI and PI/GO nanocomposite films with different GO loadings

Mechanical properties of pure PI and PI/GO composites

The TMA data of pure alicyclic PI and corresponding PI-based nanocomposite films is illustrated in Fig.7. The storage modulus (E') of PI/GO nanocomposite films increased due to the GO loadings increasing. At 100 $^{\circ}\text{C}$, the E' value of pure PI was 1427MPa, and E' value of PI-1.0%GO composites was increased to 2407MPa. The dynamic mechanical properties of PI/GO nanocomposite films was improved due to the incorporation of GO. The reason for it is that the GO was uniformly dispersed and highly orientated in PI matrix. Furthermore, the load could be efficiently transferred from the PI matrix to GO nanosheets due to strong interface interaction between PI and GO [20].

In order to enhance the mechanical properties of PI-based composites, the dispersion of GO in the PI

matrix must be homogeneous. And then, the covalent bonding at the interface could effectively transfer the stress from PI matrix to GO nanosheets. The typical stress–strain curves of pure alicyclic PI and corresponding PI-based nanocomposite films with different GO contents are shown in Fig. 8, and the corresponding mechanical strength and Young’s modulus are shown in Table 2. In general, the pure PI and PI-based nanocomposite films exhibit the characteristic of rigid material with high strength, high modulus, and without yield point in the stress–strain curves. Obviously, both the tensile strength and Young’s modulus of PI/GO composites increased with the increase of GO loadings. Compared with pure PI, the tensile strength of PI-1.0%GO composite film sharply increased from 96 MPa to 109 MPa, and Young’s modulus increased from 2.41 GPa to 3.83 GPa. The improvement of mechanical properties is caused by the excellent compatibility and strong interface interaction between GO and PI matrix. After in situ polymerization process, the -COOH groups on the GO surface can react with -NH₂ group of 6FAPB to form a strong covalent bond between the nanosheets and PAA, and also prevent the stacking and aggregation of GO to form a good dispersion in the PI matrix. After the thermal imidization, the load may be transferred successfully from the PI matrix to GO.

The different magnification SEM images of fracture surface morphology of the tensile samples for pure PI and PI-0.5%GO nanocomposites are shown in Fig.9, and there is an obvious difference between the pure alicyclic PI and corresponding PI-based composites. The fracture surface of pure PI after tensile test was flat and a little rough. Due to the incorporation of GO, the fracture morphology of PI-0.5%GO showed rather rough, which indicates that the toughness of PI/GO nanocomposite films was also improved to some extent. In addition, some micro pores were observed on the fracture surface because some functional groups on the surface of GO such as -OH and -COOH, decomposed to produce some small molecular gas. These results illustrate that the incorporation of a small amount of GO can improve the mechanical properties of the PI/GO composite films.

Fig.7 TMA measurement of storage modulus–T curves of pure alicyclic PI and PI-based nanocomposites **Fig.8**

Stress-strain curves of pure alicyclic PI and PI-based nanocomposites

Table 2 Mechanical properties and water uptake of pure PI and PI/GO nanocomposite films

Samples	Tensile strength / MPa	Tensile modulus / GPa	Water uptake / %
Pure PI	96 ± 6.5	2.41 ± 0.6	2.58 ± 0.7
PI-0.05%GO	99 ± 4.9	2.66 ± 0.5	2.14 ± 0.6
PI-0.1%GO	105 ± 5.6	2.76 ± 0.7	2.02 ± 0.5
PI-0.3%GO	107 ± 7.7	3.10 ± 0.8	1.86 ± 0.8
PI-0.5%GO	116 ± 5.2	3.27 ± 0.3	1.63 ± 0.5
PI-1.0%GO	109 ± 7.0	3.83 ± 0.4	1.48 ± 0.4

Fig.9 SEM photo of fracture morphology of tensile sample (a) pure PI film, ×10K; (b) pure PI film, ×2K; (c)

PI-0.5wt% GO nanocomposite films, $\times 10K$; (d) PI-0.5wt% GO nanocomposite films, $\times 2K$

Water absorption (WA) and water surface contact angle (WCA)

The WA is an important performance index to evaluate the service of PI films in the various applications. For example, PIs used in the field of microelectronic devices need lower water absorption. Here, as shown in Table 2, the pure PI and PI-based nanocomposite samples exhibited lower water uptake. With the increase of GO content, the water uptake of the PI-based nanocomposites decreased from 2.58% to 1.48% (pure PI). The results are attributed to the increase of hydrophobicity from GO. As we known, the surface of GO nanosheets have abundant hydrophilic groups such as C=O, -OH, -COOH, so it maybe absorbs some water. After thermal imidization, GO was reduced with less hydrophilic groups, so WA of PI/GO nanocomposites decreased due to the incorporation of GO. It is obvious that the hydrophobic nature of thermally reduced GO produced a positive effect on WA of the PI/GO nanocomposite films.

The digital photo of WCA and the corresponding WCA data of pure PI and PI/GO nanocomposite are shown in Fig.10. It can be seen that the pure PI film exhibits a WCA of 71° because the C=O of imide rings and -O- linkages are hydrophilic. For PI/GO nanocomposite films, the WCA data increased with the increase of GO content, and PI-1.0%GO exhibited a maximal WCA value of 82.5° . The reason for the improvement of hydrophobicity for PI/GO nanocomposites is that the thermally reduced GO has a hydrophobic nature, resulting in water drop aggregating on the film surface.

Fig.10 WCA of pure alicyclic PI and PI-based nanocomposite films

Morphological study of pure PI and PI/GO nanocomposite films

In order to improve the properties of alicyclic PI-based composites, inorganic GO nanosheets must be

homogeneously dispersed in PI matrix. Fig.11 shows the digital photos of the pure PI and PI/GO nanocomposite films. After the ultrasonic treatment and thermal imidization process, the GO was uniformly dispersed in the solvent DMAc, corresponding PAA and PI matrix. The pure PI film was light yellow, and the color of the PI-1.0%GO nanocomposite films became dark. In addition, all the PI/GO nanocomposite films from PI-0.05%GO to PI-1.0%GO were uniform in appearance, indicating the uniform dispersion of GO in the PI matrix. To evaluate the dispersion of GO in the PI matrix, the SEM images of the cross sections of the pure PI and PI/GO nanocomposites are shown in Fig.12. The different magnification SEM images of pure PI, PI-0.3%GO and PI-0.5%GO nanocomposite films showed a well-exfoliated and homogeneous dispersion without any agglomerates. It indicated that GO nanosheets had been homogeneously dispersed in PI matrix and produced a strong interface interaction between GO and PI after the ultrasonic treatment, in situ polymerization and the thermal imidization. Furthermore, some micropores were observed on the fracture surface of PI/GO nanocomposites. Thus, it will be an efficient approach to increase the gas separation properties of PI membranes via the incorporation of GO.

Fig.11 Photographs of pure PI and PI/GO nanocomposite films

Fig.12 SEM images of the cross sections of the pure PI and PI/GO nanocomposite films with 0.3wt% and 0.5wt% GO (a) pure PI, $\times 10K$; (b) pure PI, $\times 2K$; (c) PI-0.3wt% GO, $\times 10K$; (d) PI-0.3wt% GO, $\times 2K$; (e) PI-0.5 wt% GO, $\times 10K$; (f) PI-0.5 wt% GO, $\times 2K$.

Conclusions

In this study, 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) and 1,2,3,4-cyclobutane tetracarboxylic dianhydride (CBDA) as monomers, PI/GO nanocomposites with different content of GO were prepared using in situ polymerization method. The GO sheets were homogeneously dispersed in the PI matrix and produced good compatibility with the PI matrix due to the high hydrophilicity of the surface functional groups of GO, as well as a strong interface interaction between PI and GO because of the -COOH groups of GO reacting with -NH₂ of diamine. The incorporation of GO effectively improved the mechanical properties and thermal properties of alicyclic PI. The PI/GO nanocomposites exhibited an increase in tensile strength from 96 MPa to 109 MPa, improvement in Young's modulus from 2.41 GPa to 3.83 GPa. The thermal properties of PI/GO nanocomposites were improved with the increase of GO content, but the optical transparency was reduced significantly. The 10 wt% decomposition temperature for PI-1.0%GO nanocomposite films was increased from 464 (pure PI) to 481°C, while the glass transition temperature (T_g) of PI/GO was slightly increased. With increasing the GO loadings to 1.0wt%, the water uptake of PI/GO nanocomposite reduced from 2.48% (pure PI) to 1.58%, and the water surface contact angle of the PI/GO nanocomposites enhanced from 71° (pure PI) to 82.5°.

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In situ polymerization and performance of alicyclic polyimide/graphene oxide nanocomposites derived from 6FAPB and CBDA

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A series of alicyclic polyimide/graphene oxide (PI/GO) nanocomposites were successfully prepared by in situ polymerization of 1,4-bis(4-amino-2-trifluoromethoxy)benzene (6FAPB) and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) as well as GO, followed by thermal imidization. The effect of GO on the thermal stability, optical properties, mechanical properties, water absorption and water surface contact angle of the PI-based nanocomposites was investigated. The uniform dispersion of GO in PI matrix was proved, and the pure PI and PI/GO nanocomposite films were amorphous.