Fabrication of CPNBRs/epoxy composites with excellent impact strength, ideal thermal stabilities and dielectric properties

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Carboxyl powdery nitrile rubbers (CPNBRs) are blended with bisphenol A epoxy resin (E-51) to produce the corresponding CPNBRs/E-51 composites *via* casting method. The effects of the percentage mass of the CPNBRs on the impact strength, thermal stabilities and dielectric properties of the CPNBRs/E-51 composites are discussed and investigated. The impact strength of the resulting CPNBRs/E-51 composites is found to be optimal with 5 wt% addition of CPNBRs, enhanced from 14.2 kJ/m^2 to 20.8 kJ/m^2, increased by 46.5%. In addition, the dielectric constant and dielectric loss values of the resulting CPNBRs/E-51 composites are increased slightly, but the thermal stabilities are decreased with the increasing addition of CPNBRs.

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1. Introduction

Epoxy resins possess many remarkable properties, such as high mechanical and adhesion properties, excellent dimensional and thermal stability, good insulation, low cost, ease of processing, and so on [1-6]. Similar to most other thermosets, cured unmodified epoxy resins also suffer from brittleness owing to extensively high cross-linking density. To our best knowledge, many methods have been proposed to improve the toughness of epoxy resins, such as elastomers [7], rubbers [8-9], thermoplastics [10-11], thermosetting [12], liquid crystal polymer [13-14], fibre [15-16], inorganic particles [17-19], and so on. Powdery rubbers present good dispersing performance in the polymeric matrix, and can give the special properties of polymeric matrix effectively, especially for impact strength [20].

In our previous work, the results reveal that the addition of powdery nitrile butadiene rubbers (PNBRs) can effectively improve the impact strength of the bisphenol A dicyanate ester (BADCy) matrix [21]. In our present work, carboxyl powdery nitrile rubbers (CPNBRs) are performed to improve the impact properties of bisphenol A epoxy resin (E-51) composites. The effects of the addition of CPNBRs on the impact strength, thermal stabilities and dielectric properties of the CPNBRs/E-51 composites are discussed and investigated.

2. Experimental methods

2.1 Main materials

Bisphenol-A epoxy resin (E-51) is received from Xi'an Resin Factory (Shaanxi, China); Methyl hexahydrophthalic anhydride (MeHHPA) and 2, 4, 6-tris (dimethylaminomethyl) phenol (DMP-30) are purchased from Xi'an Hangang Chemical Group Co., Ltd (Shaanxi, China); Carboxyl powdery nitrile rubbers (CPNBRs) are supplied by the Beijing Research Institute of Chemical Industries (Beijing, China); Toluene and ethyl acetate are supplied by Tianjin Fu Yu Fine Chemical Co., Ltd (Tianjin, China).

2.2 Preparation of CPNBRs/E-51 composites

CPNBRs/E-51 composites are prepared by blending E-51, MeHHPA, DMP-30 and CPNBRs. The resulting mixtures are degassed in a vacuum vessel at first and then poured into a pre-heated glass die. Finally, the obtained mixtures are cured under the following conditions: 100°C for 1 hour, then 120°C for 2 hours, then 150°C for 4 hours, followed by post-curing at 190°C for 3 hours.

2.3 Analysis and characterization

Fourier transform infrared (FTIR) spectra of the samples are obtained on Bruker Tensor 27 equipment (Bruker Corporation, Germany) with thin films on KBr. Thermal-gravimetric analyzer (TGA) measurement of the samples is performed using a thermal analyzer (STA 449F3, Netzsch Group, Germany) in the temperature range of 40-800°C, with a heating rate of 20 K/min in an argon atmosphere. Scanning electron microscope (SEM) morphologies of the samples are analyzed by a VEGA3-LMH (TESCAN Corporation, Czech Republic). The impact strength of the samples is measured with a ZBC-4B impact testing machine (Shenzhen New Sansi Corp., China) *via* charpy method according to standard

ISO 179-1993. The dielectric constant and dielectric loss values of the samples are measured using a high frequency Q instrument (QBG-3D) and a dielectric constant detector (S914) from Aiyi Electronic Equipment Co. Ltd. (Shanghai, China), and the corresponding samples' dimension was 20mm×20mm×4mm.

3. Results and discussion

3.1 FTIR analysis

Fig. 1 presents the FTIR spectra of CPNBRs, original E-51 and cured CPNBRs/E-51 composite. In Fig. 1a, the bands at 914 cm^{-1} and 2240 cm^{-1} are ascribed to the adsorption peak of the vinyl group and the -C≡N group, respectively. The bands at 1735 cm^{-1} and 1450 cm^{-1} correspond to the characteristic adsorption peaks of the -COOH group. In Fig. 1b, the band at 910 cm^{-1} corresponds to the vibration adsorption peak of the epoxy group. In Fig. 1c, the adsorption peak of the epoxy group is weakened to the point of almost completely disappearing and the -C≡N peak at 2240 cm^{-1} is also weakened, which can be attributed to the decrease of the -C≡N group.

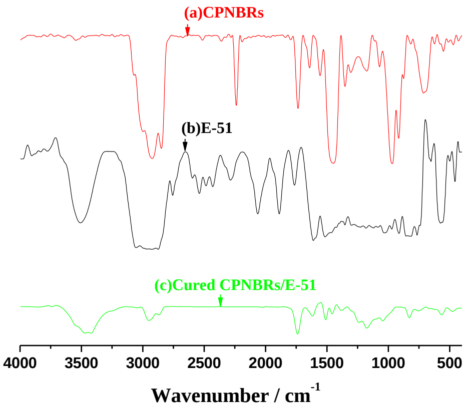


Fig. 1. FTIR spectra of CPNBRs, original E-51 and CPNBRs/E-51 composite

3.2 Mechanical properties of CPNBRs/E-51 composites

The effects of the addition of CPNBRs on the impact strength of the CPNBRs/E-51 composites are shown in Fig. 2. With the increasing addition of CPNBRs, the impact strength of the CPNBRs/E-51 composites is increased initially, but decreased with the increasing addition of CPNBRs. The impact strength of the resulting CPNBRs/E-51 composites is found to be optimal at 5 wt% addition of CPNBRs, and the corresponding impact strength is enhanced from 14.2 kJ/m^2 to 20.8 kJ/m^2, increased by 46.5%. The reason is that a small quantity addition of CPNBRs can enhance the shear zone and improve the ability to absorb the energy of impacts, resulting in inhibiting crazing and preventing the appearance of destructive cracks. With the excessive addition of CPNBRs, however, more interface defects and concentration points are easily introduced into the E-51 system, which lead to a reduction in the impact strength of the CPNBRs/E-51 composites.

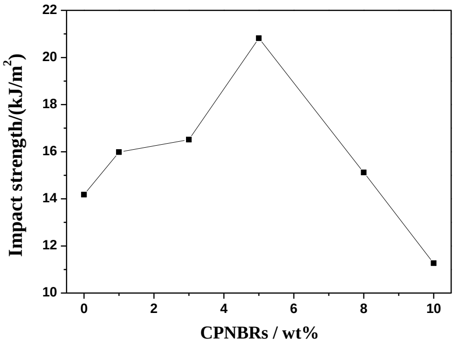
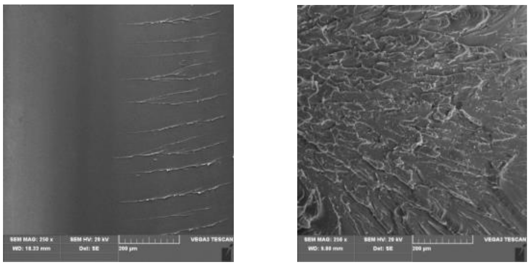
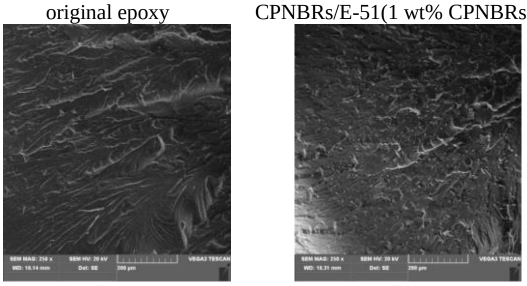


Fig. 2. The impact strength of the CPNBRs/E-51 composites

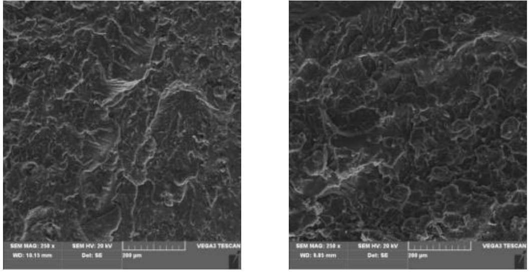
Fig. 3 shows the SEM morphologies of the original E-51 and CPNBRs/E-51 composites. The impact fracture of original E-51 displays smooth fracture morphology. With the addition of CPNBRs (1 wt%, 3 wt% and 5 wt%), the previous smooth fracture shape is disappeared, resulting in a river fracture morphology. The reason can be ascribed that the CPNBRs can effectively prevent the expanding, merging and transferring of inner cracks. With the excessive addition of CPNBRs (8 wt% and 10 wt%), the dispersion state of the CPNBRs is deteriorated, and more cracks are easily formed, which can negatively affect the impact strength of the CPNBRs/E-51 composites.



original epoxy CPNBRs/E-51(1 wt% CPNBRs)



CPNBRs /E-51(3 wt% CPNBRs) CPNBRs/E-51(5 wt% CPNBRs)



CPNBRs/E-51(8 wt% CPNBRs) CPNBRs/E-51(10 wt% CPNBRs)

Fig. 3. SEM morphologies of original E-51 and CPNBRs/E-51 composites

3.3 Dielectric properties of CPNBRs/E-51 composites

The effects of the addition of CPNBRs on the dielectric constant and dielectric loss values of the CPNBRs/E-51 composites are shown in Fig. 4. Both the dielectric constant and dielectric loss values are increased with the addition of CPNBRs. The reason is that CPNBRs has a relatively higher dielectric constant than that of the original E-51, and the interfacial polarization is improved with the increasing addition of CPNBRs. Therefore, the corresponding polarization performance of the CPNBRs/E-51 composites is improved, and the dielectric constant values are increased accordingly. Meanwhile, with the increasing addition of CPNBRs, more interfacial gaps and defects can form in the CPNBRs/E-51composites. Therefore, the corresponding dielectric loss values of the CPNBRs/E-51 composites are also increased.

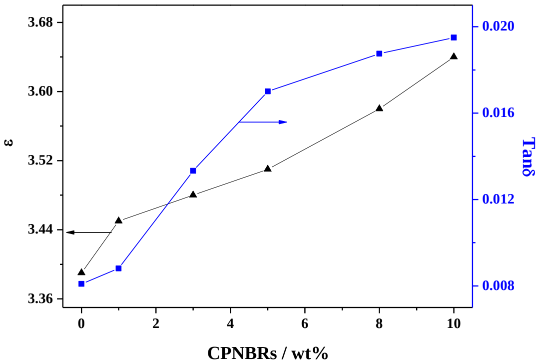


Fig. 4. The dielectric constant and dielectric loss values of the CPNBRs/E-51 composites

3.4 Thermal properties of CPNBRs/E-51 composites

The DSC curves of original E-51 and CPNBRs/E-51 composites are presented in Fig. 5. Compared to the original E-51, CPNBRs/E-51 composites present relatively lower T_g values. The reason is that the intrinsic T_g value of CPNBRs is far below that of the original E-51. In addition, the degree of cross-linking of the E-51 curing system is decreased with the increasing addition of CPNBRs, which enables an increase in the movement of the molecular chains.

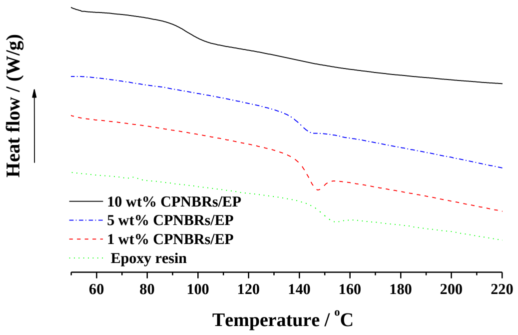


Fig. 5. DSC curves of original E-51and CPNBRs/E-51 composites

The TGA curves of the original E-51 and CPNBRs/E-51 composites are presented in Fig. 6. The thermal decomposition temperatures of the CPNBRs/E-51 composites are decreased with the increasing addition of CPNBRs for the same degree of weight loss. It reveals that the thermal stabilities of the CPNBRs/E-51 composites are decreased with the increasing addition of CPNBRs. The reason for this is that the heat resistance of CPNBRs is relatively poor in comparison to that of the original E-51, leading it to break down more easily, resulting in a decrease in the thermal stabilities of the CPNBRs/E-51 composites.

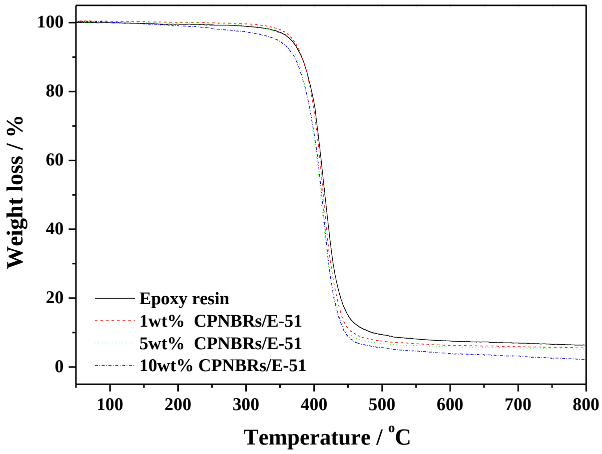


Fig. 6. TGA curves of original E-51 and CPNBRs/E-51 composites

4. Conclusions

With the addition of CPNBRs, the impact strength of the CPNBRs/E-51 composites is increased at first, but decreased with further addition of CPNBRs. The impact strength of the CPNBRs/E-51 composites is found to be optimal at 5 wt% addition of CPNBRs, and the corresponding impact strength is enhanced from 14.2 kJ/m^2 to 20.8 kJ/m^2, increased by 46.5%. The corresponding dielectric constant and dielectric loss values of the CPNBRs/E-51 composites are increased slightly, but the T_g values and thermal stabilities of the CPNBRs/E-51 composites are decreased slightly.

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