



Developing high performance cyanate ester resin with significantly reduced postcuring temperature while improved toughness, rigidity, thermal and dielectric properties based on manganese-Schiff base hybridized graphene oxide



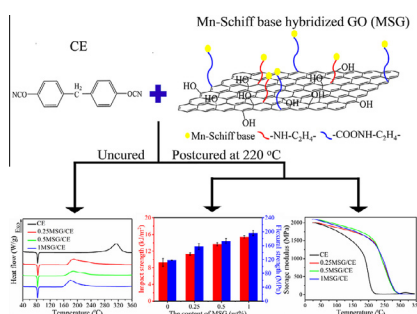
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HIGHLIGHTS

- A unique graphene oxide hybridized manganese-Schiff base (MSG) was developed.
- High performance resins based on MSG and cyanate ester (CE) were fabricated.
- MSG/CE resins have greatly reduced postcuring temperature and improved overall performances.
- Overall performances include toughness, rigidity, thermal and dielectric properties.
- The origin behind attractive results were intensively discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

New thermosetting resins with better integrated performances and easier processing characterization have been increasingly required by cutting-edge industries and energy-saving development. Herein, new high performance thermosetting resin was developed through building crosslinked network based on cyanate ester (CE) resin and a novel graphene oxide (GO) hybridized with manganese-Schiff base (MSG). The reactivity, crosslinked structure and comprehensive performances of MSG/CE resins were systematically studied. Compared with GO, MSG has better dispersion in CE resin, and a small addition of MSG (0.25 wt%) into CE significantly reduces the whole curing temperatures with a magnitude of 314–190 °C. This is because MSG uniquely integrates active hydrogen and manganese ions, and thus forms metal- π intermediates, which shows attractive catalysis on curing CE. Simultaneously, compared with CE resin, MSG/CE resins with suitable loadings of MSG have remarkably improved integrated performances including mechanical (toughness and rigidity), thermal and dielectric properties. Typically, the MSG/CE resin with 1 wt% MSG shows about 70% higher impact and flexural strengths, 75–15 °C enhanced glass transition and initial thermal degradation temperatures as well as lower dielectric loss. Above attractive performances of MSG/CE resins prove that MSG is superior and multi-functional filler, which can simultaneously act as curing catalyst, toughening agent, reinforcement while improving thermal and dielectric properties for heat resistant thermosetting resins. The origin behind attractive results was discussed through intensively investigating the structure of MSG/CE system.

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1. Introduction

Heat-resistant thermosetting resins (HRTSs) have been indispensable materials in many cutting-edge fields including aerospace, electronic information, electrical insulation, new energy [1–4], and so on. Cyanate ester (CE) resin is one typical kind of HRTSs [5–7], its biggest advantage is extremely low dielectric constant and loss over a wide frequency range compared with other HRTSs [8]. Therefore, CE resin is acknowledged as “the best candidate for preparing structure/function integration materials in the 21st century” [9]. However, almost all HRTSs have two big weaknesses, they are very brittle [10,11] and should be cured/postcured at high temperature (generally higher than 230 °C) [12]. These shortcomings not only bring complex processing and big energy consumption, but also make cured resins have big stress and/or easy to be broken, and thus greatly reducing the service reliability.

In fact, over past two decades, many researches were carried out to reduce curing temperature or improve toughness of HRTSs, and found that adding catalysts or toughening agents is the most effective method. Active hydrogen compounds [13–15] and transition metal salt/nonylphenol blend catalyst systems [16–18] are known to be efficient catalysts for curing CE. Of them, the latter has higher catalytic activity, and can reduce the peak curing temperature of CE by 100 °C when the content of transition metal ion is up to 0.11 mmol/mol; moreover, the catalytic role is enhanced with increasing the content of transition metal ion in the system [19]. Note that nonylphenol in the transition metal salt/nonylphenol blend catalyst system not only acts as a co-catalyst, but also a co-solvent to improve the dispersion of the transition metal salt in CE [20]; however, at high temperature curing stage, nonyl phenol will react with CE and generate carbamic acid ester [21], which tends to decompose into carbon dioxide and thus deteriorates the performances of CE resin. Therefore, developing an efficient transition metal catalyst without blending nonylphenol is attractive.

Among numerous toughening methods for thermosetting resins, toughening with inorganic nanoparticles has attracted many researchers in the last ten years. Reported researches suggest that toughening by using inorganic nanoparticles generally maintains or improves the rigidity and heat resistance of polymers [22,23], the thermal improvement was thought to be resulted from the high thermal stability of inorganic network as well as the interfacial adhesion between inorganic particles and polymers [24–26]. On the other hand, owing to high specific surface and surface energy, inorganic nanoparticles tend to aggregate easily [27,28]; moreover, inorganic particles generally contain few functional groups, and thus have weak interfacial adhesion with organic resins. These phenomena greatly decrease the toughening effect [29].

As an important derivative of graphene, graphene oxide (GO) keeps the stripping nano lamellar structure of grapheme, this is able to improve the mechanical properties of polymer composites [30]; simultaneously, GO has hydroxyl, carboxyl and epoxide groups on its surface due to oxidation, this feature is attractive for CE because active hydrogen compounds can catalyze and/or copolymerize with CE [31,32]. For example, Wang et al. [33] found that with the addition of 1 wt% or 4 wt% GO into CE, the exothermic peak of the resin shifts from 302 °C to 233 °C or 205 °C. However, the copolymerization of active hydrogen compounds with CE usually brings deteriorated heat resistance [34].

Reviewing the scientific data base on high performance thermosetting resins, it is reasonable to state that developing new thermosetting resins with remarkably improved integrated performances, including thermal, mechanical, dielectric and processing properties, etc., is still an interesting project with great difficulty at present.

To meet the challenge, this paper gives the first report on designing and synthesizing a novel multi-functional hybrid (MSG) by coordinating Mn^{2+} on the surface of GO, which was then added into CE resin to fabricate unique high performance HRTSs that completely overcome the two key drawbacks (high curing temperature and brittleness) of HRTSs reported previously, besides, they simultaneously show significantly improved thermal and dielectric properties. Some interesting results were found, and the origin was revealed through intensively discussing the structure–performance relationship.

2. Experimental

2.1. Materials

Natural graphite powders with an average size smaller than 30 μm were purchased from Sinopharm Chemical Reagent Co., China. Potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), four hydrated manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), anhydrous ethylenediamine (EDA), anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$), N,N' -dimethyl formamide (DMF) and N,N' -dicyclohexyl carbon imide (DCC) were commercial products with analytical grades and purchased from Sinopharm Chemical Reagent Co., China. Concentrated sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%) and salicylaldehyde (chemically grade) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. CE used herein is 2,2'-bis(4-cyanatophenyl) propane, which was got from Yangzhou Techia Material Co. Ltd, China.

2.2. Synthesis of MSG

MSG was synthesized through a three-step process as shown in Fig. 1, including the animation of GO, the grafting of Schiff base and the coordination of Mn ions, successively. Typically, GO (1 g) prepared from natural graphite using Hummers method [35] was dispersed in 500 mL of DMF with stirring and ultra-sonication for 0.5 h to obtain a homogeneous suspension, into which EDA (100 mL) and DCC (5 g) were added. The resultant mixture was stirred at 70 °C for 12 h. After cooling to room temperature, followed by filtrating and washing with absolute ethanol and water for three times, respectively, and then a black solid was dried at 60 °C to get animated GO (GO-NH_2).

GO-NH_2 (1 g) was dispersed in 300 mL of absolute ethanol with stirring and ultra-sonication for 1 h to get a suspension. Under a nitrogen atmosphere, excess salicylaldehyde (156 mL) and a few drops of acetic acid were added into the suspension. After reacted at 80 °C for 12 h, a black solid was obtained by filtering and washing with water and ethanol for three times, respectively, followed by drying at 60 °C to get Schiff base grafted GO (coded as GO-Schiff base).

Finally, GO-Schiff base (1 g) was mixed with $\text{Mn}(\text{C}_2\text{H}_5\text{O})_2$ (4.9 g) in absolute ethanol with stirring at 60 °C for 12 h. The resultant mixture was filtered and washed with water and ethanol for three times, respectively, followed by drying to get MSG.

2.3. Preparation of prepolymers for differential scanning calorimeter (DSC) measurements

Table 1 gives the compositions of various prepolymers for DSC tests. Typically, all compositions were blended at 90 °C for 40 min under sonication to get a mixture, which was then heated to 140 °C with stirring for 10 min to get a prepolymer.

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