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Novel silicon-modified phenolic novolacs and their biofiber-reinforced composites: Preparation, characterization and performance

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ABSTRACT

4,4′-(1,3-Dipropyl-tetramethyldisiloxane)bis-2-methoxyphenol (SIE), a novel silicone-contained biphenol type monomer, is synthesized from eugenol and 1,1,3,3-tetramethyldisiloxane, and used to modify phenolic novolac through copolymerization with phenol and formaldehyde to yield SIE-modified resins (SPNs). Then, the SPNs are used as resin matrix, while surface-treated chopped sisal fiber is used as the reinforced filler to produce the novel phenolic molding composites. Eugenol and sisal are biobased renewable materials. Due to modification of SIE, the ultimate composites expressed excellent electrical resistance, low water absorption and high thermal stability compared to the normal composites. Our work provides a facile and effective way to prepare the silicone modified, biofiber-reinforced phenolic composites with improved water resistance and electric property.

1. Introduction

Glass reinforced phenolic composites are widely applied from household appliances and kitchenwares to aerospace industries [1]. However, they are hard to process once they are out of use, and become environmental detrimental. Renewable resources attract a lot of attentions from energy and material industries. Using the renewable natural resources to replace traditional fibers to manufacture composites becomes a main issue of extensive studies. Natural fibers are cheap, low in density, easy to degradation, and most importantly, very efficient for sound interaction with matrix resin and in fracture resistance when compared with glass fibers [2]. In particular, sisal is a kind of important abundant plants that can be used as natural fibers to reinforce thermosetting phenolics [3–8], epoxy [5], and unsaturated polyester composites [5,9]. However, these fibers negatively affect composites' properties such as mechanical strength, water absorption rate and electrical resistance compared with commonly inorganic fibers, because of the numerous hydroxyl groups existed at the highly porous microstructure of the fibers [3]. Also, they have disadvantages such as inferior mechanical resistance compared to conventional fibers (asbestos, Kevlar, carbon/glass fibers) and express low thermal stabilities [10–12]. All these problems are urgently to be solved. Organic silicon shows many interesting properties such as low water absorption, low toxicity, high thermal stability and high molecular structural design flexibility. All these advantages could help a lot in improving properties of nature fiber reinforced phenolic composites.

In this paper, we intend to develop a novel high performance sisal fiber reinforced phenolic composites with low water absorption and excellent electric properties. We prepared a novel silicone compound, 4,4′-(1,3-dipropyl-tetramethyldisiloxane)-bis-2-methoxyphenol (SIE). Then the SIE was used to partially replace phenol to synthesize the silicone modified phenolic novolac (SPN). SPN was characterized, and its curing behavior with HMTA was studied. Then, phenolic composites are prepared by using the chopped sisal fiber as the reinforcement agent and SPN as the resin matrix. Note here that eugenol is a renewable natural resource that can be derived from plant oil, and sisal fiber is renewable too. Therefore, our phenolic composite not only contains chemically bonded silicone, but also is highly bio-contained. Our data will show that the composites have excellent properties, especially the lower water absorption and high electrical resistance.

2. Methods

2.1. Materials

Sisal fiber was obtained from the Guangxi sisal fiber Group, China. Phenol (99%), formaldehyde solution (37 wt%), oxalic acid (99%), sodium hydroxide (98%) and ethanol (99%) were purchased

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from Sinopharm Chemical Reagent Ltd. Eugenol (99%) was purchased from Sigma Aldrich Ltd. 1,1,3,3-Tetramethyldisiloxane (99%) was kindly provided by Jiaxing United Chemical Co., Ltd. Chloroplatinic acid (99%) was purchased from Shanghai Jiuling Chemical Co., Ltd. Other materials were kindly provided by Jiaming Plastic Ltd., Zhejiang province, China. All the chemical reagents were used as received.

2.2. Preparation of SIE modified novolac type phenolic resins

2.2.1. Preparation of SIE

To a three-necked 500 ml round-bottomed flask equipped with a magnetic stirrer, a dropping funnel, a thermometer and a condenser, eugenol (16.42 g, 0.1 mol) and chloroplatinic acid in isopropyl alcohol (1.44×10^{-2} g, Pt 0.8 wt%) were charged. The mixture was heated to 60 °C, and 1,1,3,3-tetramethyldisiloxane(6.72 g, 0.05 mol) was dropped slowly in 3 h. The exothermic reaction at 60–70 °C. When 1,1,3,3-tetramethyldisiloxane was dropped over, the reaction carried out for another 1 h. The unreacted reactants were removed using a rotary evaporator under vacuum at 80 °C. The acquired product was SIE (97% yield).

2.2.2. Synthesis of SIE modified novolacs type phenolic resins (SPN)

To a three-necked 500 ml round-bottomed flask equipped with a mechanical stirrer, dropping funnel, thermometer, and condenser, phenol (94 g, 1 mol), SIE and oxalic acid (3 g, 0.024 mol) were charged. The mixture was heated to 100 °C, and then 37 wt% formaldehyde water solution (64.93 g, 0.8 mol) was dropped in 1 h. When the formaldehyde was dropped over, the reaction was carried out at 100 °C for additional 2 h. After that, the viscous product was dried under reduced pressure up to 0.001 MPa at 150 °C to yield SPN with different silicon contents.

2.2.3. Theory on curing reaction kinetics of SPN

The data acquired from DSC test could be correlated with fractional conversion and reaction rate, which are assumed to follow Eq. (1) [13–16]:

$$\alpha = \frac{\int_0^t \frac{dH}{dt} dt}{\Delta H} \tag{1}$$

H is the heat flow. t is the reaction time. ΔH is the whole reaction exotherm value, and α represents the conversion.

From Eq. (1), the reaction rate ($d\alpha/dt$) can be derived as:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_o} = k(T)f(\alpha) \tag{2}$$

$f(\alpha)$ represents for function with α as independent variable, while $k(T)$ represents for reaction rate constant (temperature-related), and could be acquired according to the Arrhenius Equation Eq. (3). A is the frequency factor. E_α represents the activation energy, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

$$k(T) = A\exp\left(-\frac{E_\alpha}{RT}\right) \tag{3}$$

The model-free isoconversional kinetic analysis has been effectively applied in solving the issue of phenolic resin curing kinetics [17–19]. It follows the principle that conversion is only a function of temperature, whose analytic expression can be written as Eq. (4) [20], without assuming any specific reaction models:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_\alpha \tag{4}$$

These items attached to subscript α indicate kinetic parameters for a isoconversional conversion, because the function $f(\alpha)$ is unchanged at fixed conversion, Eq. (4) can be simplified to yield Eq. (5), through which the relationship between the activation energy with conversion could be established [21]:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha \tag{5}$$

2.3. Fiber surface treatment

Batches of sisal fiber were cleaned by soaking in alkali solution (2 wt.%) for 2 h, then washed with distilled water and dried in oven at 150 °C for 4 h to yield alkali-thermal treated sisal fiber (fiber length: 2–4 mm).

About 2 wt% of silane coupling agent (3-aminopropyl triethoxy silane) in alcohol/water solution (95:5/v/v) was hydrolyzed under a weak acid condition with a pH of 4–5 using acetic acid to adjust the acidity, and form transparent solution. Subsequently the solution was used to penetrate the alkali-thermal treated sisal fiber under stirring for about 1 h at room temperature. The soaked fiber was washed with distilled water and dried in vacuum at 80 °C over night.

2.4. Preparation of SIE modified phenolic composites (SIEC)

Surface treated sisal fiber (SF) (2–4 mm in length), inorganic filler, hexamethylenetetramine and other agents were milled with novolac type phenolic resin matrix on a heated two-roll mill to prepare the phenolic molding compounds based on the following composition: phenolic resin (SPN or NR): 40 wt%; hexamethylenetetramine (HMTA): 5.5 wt%; sisal fiber (SF), 30 wt%, 2–4 mm in length; mica powder: 20 wt%, 325 mesh pass; stearic acid: 2.5 wt%, stearic acid monoglycerides: 2 wt%. The test samples were shaped in a closed mold under following molding condition: pressure 30 MPa, molding temperature 175 °C, holding time 1 min/mm (see Fig. 1).

2.5. Instrumentation and characterization

2.5.1. NMR spectra

^{1}H NMR spectra of SIE (in $CDCl_3$) and ^{13}C NMR spectra of SPN (in CD_3OD) were recorded on a Bruker Avance 500 spectrometer at 300 K.

2.5.2. Molecular weight (GPC)

GPC analysis was carried out using a WATERS 1515 apparatus equipped with WATERS 2489 UV detectors under the following conditions: columns: WATERS Styragel HR0.5, HR1, HR3 and HR4; eluent: THF; flow rate: 0.8 ml/min; column temperature: 35 °C. The samples were dissolved in tetrahydrofuran (weight content: 0.5%). The calibration curves for GPC analysis were obtained by using polystyrene standards.

2.5.3. DSC measurement

All the DSC experiments were conducted on a DSC instrument (DSC 200F3, NETZSCH, Germany). The instrumental sensitivity and temperature were calibrated previously with a set of Hg, In, Sb, Bi and Zn standards. Finely pulverized novolacs were mixed with HMTA at room temperature with a weight ratio of 9:1, and placed into vacuum at 40 °C for 30 min to remove moisture. About 3 mg of the mixture was enclosed in an aluminum crucible and transferred into the DSC oven with an identical crucible as the reference. A series of non-isothermal curing reactions were conducted from room temperature to 250 °C with different heating rates of 3, 4.5, 6.7, and 10 °C/min. The isothermal cure was conducted at 140 °C. All the DSC measurements were conducted in high-purity nitrogen (protection gas flow: 60 ml/min; purge gas: 30 ml/min).