

# Novel silicon-modified phenolic novolac resins: Non-isothermal curing kinetics, and mechanical and thermal properties of their biofiber-reinforced composites



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## ABSTRACT

A silicone-contained biphenol type monomer, 4,4'-(1,3-dipropyl-tetramethyldisiloxane)bis-2-methoxyphenol(SIE), was used to modify phenolic novolac resin by being copolymerized with phenol and formaldehyde to yield SIE-modified phenolic resins (SPNs). The curing behavior of SPNs with hexamethyleneteramine (HMTA) was analyzed by DSC tests, and the non-isothermal curing kinetics were analyzed using the model-fitting and model-free isoconversional methods. Then, SPN/HMTA was used as the resin matrix, while surface-treated chopped sisal fiber was used as the reinforced filler to produce the silicon modified phenolic molding composites (SIEC). The finished composites expressed improved mechanical and thermal resistance properties compared with unmodified composites.

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## 1. Introduction

Phenolic resin is first kind of synthetic polymer materials. Since its invention one century ago, it is extensively applied in our daily life. It is easy to produce at low cost, and cured phenolic resin has excellent rigidity, dimensional stability and fire retardancy. However, traditional phenolic resin always suffer from inherent brittleness, high shaping pressure, and dark in color due to easy oxidation of phenolic groups. To improve properties of traditional phenolic resin, many researchers tried various methods, mainly by blending them with elastomers, thermoplastic polymers, nanofillers and fibers. However, these methods are highly dependent on processing conditions, because the condensation state and microstructure of added modifiers should be carefully controlled and highly optimized. Moreover, for practical industrial production, the costs of some modifiers such as POSS and carbon tubes, the energy and solvents consumption should be taken into consideration.

As an alternative, modification of the phenolic resin by introducing heteroatoms such as silicon [1–15], boron [16–18], phosphorus [19–21], sulfur [22], etc. into their backbone or side chain seems to be a more straightforward and effective way to improve their properties. Moreover, by this way the production process of phenolic based composites hardly need any significant change, which

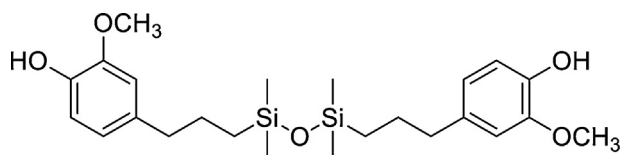
will greatly reduce production cost. Especially, silicone has many interesting properties such as low water absorption, low toxicity, high thermal stability and high molecular structural design flexibility. The introduction of the organic silicone to the backbone or side chains of phenolic resin is an effective way to improve the properties of phenolic resins. As far as we know, however, there are limited successful examples of small molecule silicon modification in phenolic resin have been reported up to date.

Natural fibers are cheap, low in density, easy to degradation, and most importantly, very efficient for sound interaction with matrix resin. Among them, sisal is a kind of important abundant plants that can be used as natural fibers to reinforce thermosetting phenolics [23–28], epoxy [25], and unsaturated polyester composites [25,29]. However, these fibers increase the water absorption of the resulting composite materials compared with inorganic fibers, resulting from the numerous hydroxyl groups existed at the highly porous microstructure of the fibers [23]. Also, compared with conventional fibers, they have disadvantages such as inferior mechanical resistance and low thermal stabilities [30–32]. All these problems should be solved before their further application.

In our previous work, we have developed high-performance sisal fiber-reinforced silicon modified phenolic composites [33]. In this paper, we continue to do further study on their curing kinetics, mechanical and thermal stability properties. We prepared a silicone contained bisphenol compound, 4,4'-(1,3-dipropyl-tetramethyldisiloxane)bis-2-methoxyphenol (SIE) (see Scheme 1). 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 examined and simulated by

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Scheme 1. Molecular structure of SIE.

isoconversional methods systematically. Then, phenolic composites are prepared by using the chopped sisal fiber as the reinforcement agent and SPN as the resin matrix. Our research results will show that the composites have excellent mechanical and thermal properties.

## 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 from Sinopharm Chemical Reagent Ltd. and were used without further purification. 1,1,3,3-tetramethyldisiloxane (99%) was kindly provided by Jiaying United Chemical Co., Ltd. Chloroplatinic acid (99%) was purchased from Shanghai Jiuling Chemical Co., Ltd. Eugenol (99.7%) was purchased from Sigma Aldrich Ltd. Other materials were kindly provided by Jiaming Plastic Ltd., Zhejiang province, China. All the chemicals were used without further purification.

### 2.2. Preparation of SIE modified novolac type phenolic resins

#### 2.2.1. Preparation of SIE

To a three-necked 500 ml round-bottom 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 ( $1.44 \times 10^{-2}$  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 underwent at 60–70 °C. When 1,1,3,3-tetramethyldisiloxane was exhausted, the reaction was carried out for another 1 h. The unreacted reactants were removed using a rotary evaporator under vacuum (up to 0.001 MPa) at 80 °C. The remained product was SIE (97% yield).

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

To a three-necked 500 ml round-bottom flask equipped with a mechanical stirrer, dropping funnel, thermometer, and condenser, phenol (94 g, 1 mol), SIE (0 g for NR; 9.4 g for SPN 10; 18.8 g for SPN 20) and oxalic acid (3 g, 0.02 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 exhausted, the reaction was carried out at 100 °C for additional 2 h. The viscous product was dried under reduced pressure (up to 0.001 MPa) at 150 °C to yield NR, SPN10 and SPN20.

#### 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 as Eq. (1) [34–37]:

$$\alpha = \frac{\int_0^t \frac{dH}{dt} dt}{\Delta H} \quad (1)$$

$H$  is the heat flow,  $t$  is the reaction time,  $\Delta H$  is the whole reaction exotherm value, and  $\alpha$  represents the conversion.

From Eq. (1), the reaction rate ( $d\alpha/dt$ ) can be derived as expressed by Eq. (2):

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} = k(T)f(\alpha) \quad (2)$$

where  $f(\alpha)$  represents for function with  $\alpha$  as independent variable, while  $k(T)$  represents for temperature-related reaction rate constant, and could be acquired according to the Arrhenius equation (3):

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

where  $A$  is the frequency factor,  $E_\alpha$  represents the activation energy, and  $R$  is the universal gas constant (8.314 J/mol/K).

A statistic method proposed by Málek [38,39] was chosen to analyze the nonisothermal experiment data. The Málek method contains two functions,  $y(\alpha)$  and  $z(\alpha)$ , for determining an appropriate kinetic model. See Eqs. (4) and (5):

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \exp(x) \quad (4)$$

$$z(\alpha) = \pi(x) \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} \quad (5)$$

where  $x$  represents the reduced activation energy ( $-E_a/RT$ ), and  $\beta$  is the heating rate.  $\pi(x)$  is the expression of the temperature integral that can be approximated well with Eq. (6) [40]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (6)$$

According to the Málek method,  $E_a$  should be estimated independently using other methods. Then, the function curves of Eqs. (4) and (5) could be drawn, from which the two parameters can be obtained: conversion  $\alpha_M$  at the maximum value of  $y(\alpha)$  and conversion  $\alpha_p^\infty$  at the maximum value of  $z(\alpha)$ . By comparing  $\alpha_M$ ,  $\alpha_p^\infty$  and  $\alpha_p$ , and checking whether they meet some specific relationship suggested by Málek, a kinetic model could be identified, and then the model parameters can be estimated by a specific algorithm to result in the rate equation.

The model-free isoconversional kinetic analysis has been effectively applied in calculating phenolic resin curing kinetics [41–43]. The model-free isoconversional methods take the principle that conversion is only a function of temperature [44], without assuming any specific reaction models (see Eq. (7)):

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_\alpha \quad (7)$$

The items attached with subscript  $\alpha$  indicate kinetic parameters for an isoconversional conversion, because the function  $f(\alpha)$  is unchanged at fixed conversion, Eq. (7) can be simplified as Eq. (8):

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha \quad (8)$$

According to Eq. (8), the relationship between the activation energy and conversion can be established, and this relationship is very useful for analyzing the kinetic mechanisms in complicated thermal stimulated polymerization processes [45]. However, direct derivation of the conversion with time to yield kinetic rate yields remarkable deviation, thus seriously affects the precision. To address these problems, the Vyazovkin method is chosen to analyze the nonisothermal reaction [44]. In particular, this method is applicable to any arbitrary temperature programs with

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