CURING KINETICS OF EPOXIDIZED VEGETABLE OIL AND A GREEN HARDENER BASED ON NON-ISTHERMAL DSC METHOD

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Abstract

Vegetable oils have attracted a great deal of attention in polymer synthesis because of its abundant amount and people's increasing concern for environment. A new polymer with high bio-based content (>90%) has been developed in our laboratory through a curing process between epoxidized soybean oil (ESO) and a rosin-based hardener, maleopimaric acid (MPA). We also studied the non-isothermal curing kinetics of the system. The epoxy/anhydride ratio was 0.7 and the content of the catalyst, 2-ethyl-4-methylimidazole (EMI) was 1.0wt% based on the weight of ESO. Model-free isoconversional method was adopted to analyse the data obtained from differential scanning calorimetric (DSC) at the heating rates of 10, 12, 14 and 16 K/min respectively. The activation energy of the curing reaction is 71.53 kJ/mol. The Šesták–Berggren autocatalytic model has been employed to simulate the curing kinetics. The two parameters (*n, m*) of the model and the pre-exponential factor (*A*) of the Arrhenius equation are found to be 1.075, 0.5192 and $4.816*10^7$ s^{-1} respectively.

Keywords

Curing kinetics, Epoxidized vegetable oil, Maleopimaric acid.

Introduction

The thermoset materials play an irreplaceable role in our life. The majority of the polymeric thermosets used in daily life are synthesized from non-renewable petroleum at present. However, increasing attention is devoted into the exploration of renewable resources. Contrary to the high price and the small production of petroleum, the relatively low price and the large amount of these renewable materials make them attractive.

Vegetable oils are triglycerides of unsaturated fatty acids. ESO can be used as green plasticizer and new bio-based epoxy resin. While rosin is a kind of nature products with a huge hydrogenated phenanthrene ring in its molecular structure, which makes it possible similar to some petroleum-based aromatic or cycloaliphatic chemicals in rigidity when working as a curing agent for epoxy. Its derivative, MPA, owns an anhydride and a carboxyl group. Both of ESO and MPA are bio-based, so the polymer from them can own really high bio-based content. The study of the curing kinetics can be the guidance of the curing process.

Theory

The rate of the curing processes is generally a function of temperature and the curing degree, as Eq. (1) shows.

$$d\alpha / dt = k(T) f(\alpha) \tag{1}$$

where α is the curing degree, $d\alpha / dt$ is the curing rate and T is the reaction temperature in K. The function $k(T)$ can be written as

$$k(T) = AT^m \exp(-E / RT) \tag{2}$$

where E represents the activation energy, R stands for the universal gas constant, m is a constant value and A is the

pre-exponential factor. In the case of $m = 0$, $k(T)$ is known as Arrhenius equation.

Chen and Liu (2009) studied the approximate formula for the generalized temperature integral. In their study, E can be calculated by using Eq. (3).

$$\ln \beta / T^{1.89021+0.95479m} = const. - (1.00147 + 0.00057m)E / RT \quad (3)$$

where β is the heating rate. As mentioned in the literature, the relative error of E calculated by the new approximate formula is less than 0.8% when $E / RT \geq 10$ for commonly used value of m. So when $m = 0$, Eq. (3) can be rearranged into Eq. (4).

$$\ln \beta / T^{1.89021} = const. - 1.00147 \times E / RT \quad (4)$$

Usually, the curing process of epoxy resin and anhydride is an autocatalytic reaction (Ručigaj et al., 2014). So the autocatalytic model proposed by Šesták and Berggren (1971) can be adopted to fit the experimental data. Then the rate of the curing processes is as the following shows.

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A \exp(-\frac{E}{RT}) \alpha^m (1-\alpha)^n \quad (5)$$

The logarithm form of Eq. (5) is

$$\ln(d\alpha / dt) = \ln(\beta \times d\alpha / dT) = \ln A - E / RT + m \ln \alpha + n \ln(1-\alpha) \quad (6)$$

The parameters (A, m, n) can be obtained through nonlinear regression analysis.

Experiments

The experiments were carried out by DSC method. The epoxy/anhydride ratio was 0.7 and EMI was 1.0wt% based on the weight of ESO. The samples were heated from the room temperature to 300 °C at a rate of 10, 12, 14 and 16 °C/min respectively.

Results

According to Eq. (4), $\ln \beta / T^{1.89021}$ has a linear relationship with $1.00147 / RT$, and the slope is E. In this study, T is the peak temperature, and E obtained by the method mentioned above is 71.53 kJ/mol. The curing degree (α) can be calculated by Eq. (7).

$$\alpha = \Delta H_t / \Delta H_{total} \quad (7)$$

where ΔH_t is the heat releasing from the beginning to time t, and ΔH_{total} is the total heat releasing during the heating program. Other parameters calculated based on Eq. (6) are listed in table 1 and the comparison between experimental data and the autocatalytic model is shown in figure 1.

Table 1. calculated parameters required in curing kinetics

parameter	value
m	0.5192
n	1.075
A (s^{-1})	$4.816*10^7$

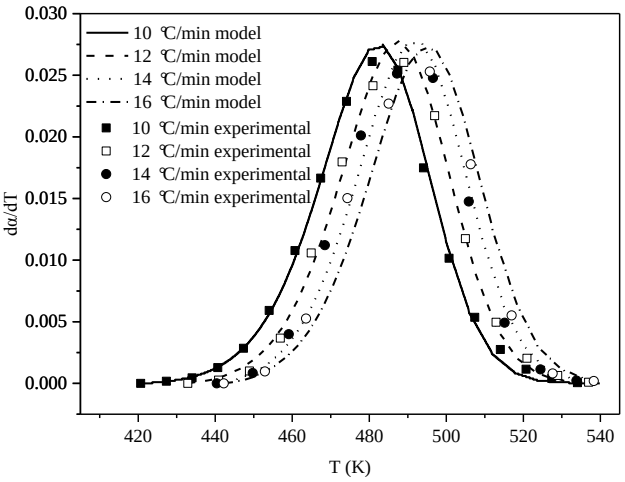

Figure 1. comparison between experimental data and the autocatalytic model

Conclusions

The curing kinetics of ESO and MPA catalyzed by EMI have been studied. The activation energy is 71.53 kJ/mol and other parameters, A, m, n, are $4.816*10^7$, 0.5192, 1.075 respectively. The calculated data from the autocatalytic model match well with the experimental data, and this model can be a useful guidance for curing process.

References

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