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Material Properties

Curing behaviors' characterization of strong and weak crosslinking systems by thermal and dynamic mechanical methods

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ABSTRACT

Curing processes of weak- and strong-crosslinking curing systems, *e.g.*, epoxy asphalt and dicyandiamide cured epoxy resin systems, were studied by mechanical method of dynamic shear rheometer (DSR) and thermal method of differential scanning calorimetry (DSC), respectively. Results indicate that the two approaches are both sensitive to the whole curing process for strong-crosslinking system, whose curing exothermic process matches its mechanical properties' development. But for weak-crosslinking system, *i.e.*, incompletely cured rubber-like one, whose mechanical properties' improvement lags behind its curing exothermic process, DSC is sensitive in initial stage of curing reaction, and DSR is sensitive after gel point. Furthermore, with Avrami equation, it is possible to control the curing processes for preparing products with needed mechanical properties by DSR. Therefore, although DSC method is classical, DSR and alike mechanical methods should be comprehensively evaluated in terms of involved curing systems at different curing stages as well as researchers' study purposes.

1. Introduction

In general, small molecular isocyanate reacts with relative long chain lower functionality polyols formed three-dimensional crosslinking polymers with lower crosslinking densities, so that the resultants are usually soft elastomers (*e.g.*, polyurethane elastomers [1,2]); or long chain liquid rubber vulcanizes [3,4] by small molecular agents formed three-dimensional crosslinking soft vulcanized rubber with lower crosslinking densities. However, small molecules, such as epoxy resin [5], phenolic resin [6] and polyester [7] *etc.*, condense quickly with their small molecular curing agents with high functionality and release heat at the same time, so that the generated three-dimensional crosslinking network polymers with higher crosslinking densities are usually of rigid structural materials [8]. That is, with the increase of crosslinking density, the cured materials transform from soft elastomers with lower moduli into hard glass polymers with higher modulus at about room temperature, *i.e.*, their glass transition temperatures increase from low temperatures (usually lower than room temperature) to high temperatures (extremely higher than room temperature, and some of them even exceed 300 °C) [9]. From this viewpoint, crosslinking polymers are divided into weak- and strong-crosslinking systems, whose glass transition temperatures are around room temperature and much higher than room temperature, respectively.

As mentioned above, cured epoxy resins are usually hard fragile structural materials, *i.e.*, dicyandiamide cured epoxy resin, and its glass transition temperature is of about 140 °C [10,11], which indicates that the dicyandiamide cured epoxy resin is brittle and hard to be stretched at round room temperatures [12], so, it is widely used for its superior properties, such as excellent mechanical properties, higher thermostability, lower volume contraction ratio and so on. To toughen epoxy resins, kinds of long chain flexible curing agents, interpenetration networks, and special fillers have been widely investigated [13,14]. As is well known, properties of materials are determined by their microstructures, which are influenced greatly by their forming processes. Therefore, we have prepared weak-crosslinking epoxy elastomers, *i.e.*, rubber-like epoxy asphalt at room temperature, whose glass transition temperatures are in the range from 10 °C to 30 °C, and their tensile strengths and break elongations are about 2–8 MPa and 180%–800%, respectively [15,16], by using flexible curing agents and controlling the curing processes. That is, the curing process of epoxy resin could affect the final performance of product greatly. Therefore, studying on the curing kinetics of crosslinking systems is helpful to prepare high performance composites and establish the quantitative relation between the curing technology and curing products' performance.

Actually, there are many methods to characterize the curing behaviors according to the curing process' physical or chemical effects, *e.g.*,

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electric and magnetic effects, sonic effects, and thermal as well as mechanical properties *etc*. Therein, spectroscopic methods (such as infrared spectroscopy, Raman spectroscopy) [17–19] can analyze the chemical reaction mechanism in the curing reaction, but they are not sensitive to the subtle property changes at the latter curing process. Dielectric analysis (DEA) is to study the curing process by monitoring the system's dielectric properties in real time, and is sensitive to whatever the system is of liquid at the early curing stage or of solid at the latter curing stage [20,21]. As for ultrasonic method, it can monitor the change of material's internal structures; and it is possibly high sensitivity to the complete curing process [22,23]. However, neither the DEA nor the ultrasonic method is capable of providing thermal data for producers or mechanical properties for end users. Thermal analysis methods, including differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are the popular methods capable of obtaining the enthalpy data directly in curing reaction [24–27]. Notably, many weak-crosslinking systems' curing heat flux is much smaller at the stage after gel points than before, but their cure degree and mechanical properties enhanced greatly at stage after gel points than before. Since a small percent of the curing degree can have a big influence on T_g, consequently, it has a big influence on mechanical properties. Therefore, it is very important to monitor the mechanical properties change at the last stage of cure over which heat flux is negligible [28]. Therefore, mechanical methods, such as dynamic mechanical thermal analysis (DMTA), dynamic mechanical analysis (DMA) and dynamic shear rheometer (DSR), *etc.* [29–32], which directly monitor the mechanical properties during the curing process, are thought to be better for weak-crosslinking systems at the late stage of curing progress.

To verify this supposition, a weak-crosslinking system and a strong-crosslinking system, *i.e.*, epoxy asphalt system and dicyandiamide cured epoxy resin system, were investigated by DSC and DSR.

2. Experimental

2.1. Materials

Epoxy asphalt (NingJue®2910) was obtained from Ningwu Chemicals, Zhenjiang, China. The epoxy asphalt includes component A and component B. Component A is of epoxy resin component, and component B is of a mixture of bitumen, hardener, and catalyst. Dicyandiamide (DICYANEX®1400 F, Air Products Inc., USA) and aluminum hydroxide (MARTINAL® ON-921, Arbor Inc., USA) were used as received.

2.2. Experimental procedures

2.2.1. Epoxy asphalts

Firstly, the component A and component B were heated to 120 °C and then kept them 1 h at 120 °C in an oven, separately. Then, they were mixed (A: B = 1:2.9, *wt.*) carefully at a steel cup. Next, the blend was stirred mechanically for 2 min to be homogeneous, and it was poured into a 120 °C steel mold, vibrated to decrease small bubbles of air involved. Finally, steel mold with blend was put in the oven to cure for 10 h at the experimental temperature (120 °C, 140 °C and 170 °C, respectively).

Well-mixed uncured sample (120 °C, 9–10 mg) was sealed into an aluminum DSC pan. Then, DSC measurements were carried out on a Q2000 DSC (Waters Instruments, Milford Massachusetts, USA) at this temperature for 4 h at high purity nitrogen atmosphere with a flow rate of 50 mL/min. Empty crucible was used for instrument calibration. To eliminate the experimental error, each condition conducted three replicates.

Strain sweeps of epoxy asphalts were conducted by MCR302 dynamic shear rheometer (Anton Paar Inc., Graz, Austria) with a customized SRF5 solid torsion geometry. The temperature of strain sweep was equal to the curing temperature of epoxy asphalt (120 °C, 140 °C and 170 °C, respectively). Strains increased from 0.001% to 10%, and oscillation frequency was of 10 rad/s. The sample dimensions were of 20 mm × 10 mm × 2 mm. To eliminate the experimental error, each condition conducted three replicates.

The component A and component B were mixed at 120 °C (A: B = 1:2.9, *wt.*). Then, the mixture was stirred for 2 min. PP25 (25 mm diameter parallel plate geometry) was used to monitor the curing reaction within the 1 mm gap at temperatures from 120 °C to 170 °C at the interval of 10 °C for 10 h, respectively. The strain was set as 1% and oscillation frequency was of 10 rad/s. To eliminate the experimental error, each condition conducted three replicates.

2.2.2. Dicyandiamide cured epoxy resin

Dicyandiamide, epoxy resin and aluminum hydroxide were mixed at room temperature, and the weight ratio was 3:50:80.

As mentioned above, the DSC experiments of dicyandiamide cured epoxy resin were almost the same as those of epoxy asphalt, except for the curing time of dicyandiamide/epoxy resin was 2 h. To eliminate the experimental error, each condition conducted three replicates.

The curing experiments were conducted by MCR302 dynamic shear rheometer (Anton Paar, Austria) with the PP25 in a 1 mm gap. The selected strain was of 0.25% and the oscillation frequency was of 10 rad/s. And, the temperatures of curing experiments were of 110 °C, 120 °C, 130 °C, 140 °C and 150 °C, respectively. To eliminate the experimental error, each condition conducted three replicates.

3. Results and discussions

3.1. Cure behaviors' characterization by DSC

3.1.1. Epoxy asphalt

As shown in Fig. 1, in the initial stage of the curing reaction, exothermic rate was very fast and accompanied with a steeper exothermic peak measured by DSC at 120 °C, here, the maximum of heat flow was of 0.28 mW, which was much lower than that of dicyandiamide cured epoxy resin as shown in Fig. 2. Then, the heat flow gradually decreased with the curing reaction to zero at about 50 min. The following negative heat flow indicated that curing reaction of epoxy asphalt absorbed heat from outside to maintain the system's temperature.

At the beginning of the curing reaction, the epoxy asphalt was of liquid with lower viscosities, so, its complex modulus G^* ($G^* = G' + iG''$, where i is the imaginary unit.) was relatively small; with the curing progress, epoxy asphalt's complex modulus G^* still improved greatly after 10 h at 120 °C. However, the curing process was far away from finishing in only 50 min that the DSC measured. Therefore, DSC was sensitive to curing reaction of epoxy asphalt system

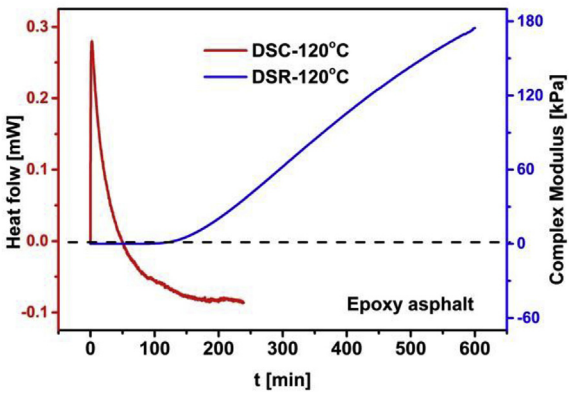

Fig. 1. Isothermal cure behavior of epoxy asphalt measured by DSC and DSR: heat flow *vs.* curing time (red) and complex modulus *vs.* curing time (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)