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Thermal properties of rigid rod epoxies cured with diaminodiphenylsulfone and dicyandiamide

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Abstract

The differences of thermal properties between rigid rod and flexible bisphenol A (DGEBA) epoxies were studied using modulated differential scanning calorimeter (MDSC), thermal gravimetric analyzer (TGA) and dynamic mechanical analyzer (DMA) techniques. The rigid rod epoxies of azomethine (AM), biphenol (BP) and tetramethyl biphenol (TMBP) were cured with diaminodiphenylsulfone (DDS) and dicyandiamide (Dicy), respectively. The DDS-cured epoxies have higher glass transition temperature (T_g) and decomposition temperature than the Dicy-cured epoxies due to the high functionality and rigid structure of DDS. The AM, BP and TMBP have higher T_g than DGEBA due to the rigid rod structure. The bulky methyl substitution on the BP main chain of TMBP epoxy decreases the order of polymer packing and reduces the T_g. The AM epoxy has the longest rigid rod structure, thus the AM epoxy has a higher T_g than that of BP and TMBP epoxies.
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1. Introduction

Epoxy resins have been extensively used in composite materials and as adhesives. The polymers with aromatic rigid rod moiety are known to have excellent thermal and mechanical properties [1,2]. Recently, epoxy resin containing rigid rod structure has been synthesized as a new class of high performance polymers. Most of rigid rod epoxies exhibit liquid crystalline behavior. Some of rigid rod liquid crystal epoxies retained liquid crystal behavior after cured with curing agent. They have exhibited excellent thermal properties [3,4].

The thermal properties of cured epoxies are determined by the structure of epoxy, cross-linking density and the functionality of epoxy and curing agent [1–6]. In this study, rigid rod epoxies, azomethine (AM), biphenol (BP) and tetramethyl biphenol (TMBP), were cured with diaminodiphenylsulfone (DDS) and dicyandiamide (Dicy), respectively. The selection of DDS was based on its high performance in the epoxy-based composite materials. The choice of Dicy was because of its low cost, good processability and electrical properties for printed wiring boards.

The effects of chemical structure changes on the thermal properties of cured epoxies are investigated. The results are reported and discussed in Section 3.

2. Experimental

2.1. Materials

The bisphenol A (DGEBA) (trade name DER 331) was obtained from Dow Chemical Company with an

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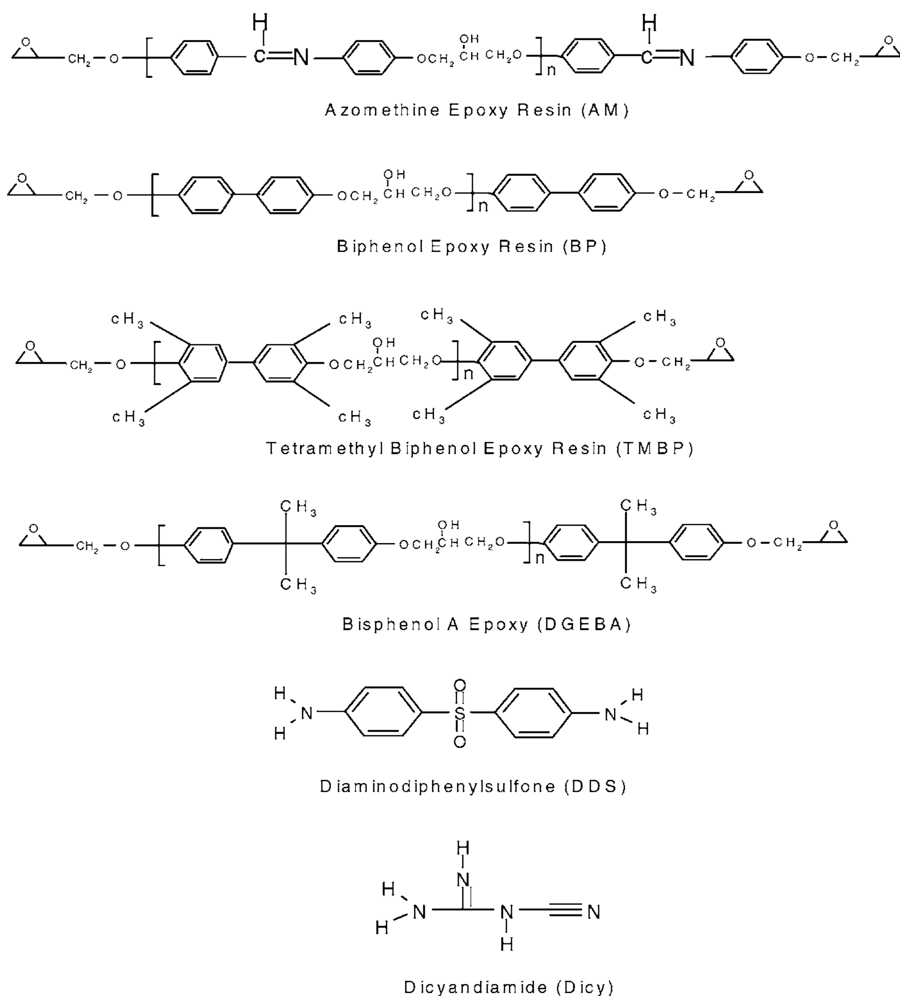

Fig. 1. Chemical structures of epoxy resins and curing agents.

epoxy equivalent weight of 185.5. The TMBP epoxy (trade name RSS1407) was supplied from Shell Chemical Company with an epoxy equivalent weight of 185. The AM (4,4′-bis(2,3-epoxypropoxy)benzylidene aniline) with an epoxy equivalent weight of 171 and the BP (4,4′-bis(2,3-epoxypropoxy)biphenyl) with an epoxy equivalent weight of 167.6 were synthesized according to literature procedure [2]. The curing agents (DDS and Dicy) were purchased from Aldrich. The structures of epoxy resins and curing agents are shown in Fig. 1.

2.2. Preparation of cured epoxies

A DuPont DSC 9900-910 was employed for the determinations of the curing conditions. All samples were mixed with stoichiometric amount of epoxy and curing agent. Fully cured samples exhibit no exothermal peak and no increasing in glass transition temperature (T_g). The curing conditions of each sample are shown in Table 1.

2.3. Instrumentation

A TA 2920 modulated differential scanning calorimeter (MDSC) (5 °C/min in 50 ml/min N_2) was used to determine the T_g of cured samples. A TA 2980 dynamic mechanical analyzer (DMA) (5 °C/min in air, 1 Hz, 20 μm amplitude) was used to measure the change in modulus and damping properties. A TA 2950 thermal gravimetric analyzer

Table 1
Curing conditions of epoxy resin systems

Sample	Pre-cure (°C/h)	Post-cure (°C/h)
AM/DDS	160/3 + 200/2 + 220/2	240/1
BP/DDS	180/6	220/4
TMBP/DDS	180/2 + 220/2	230/1
DGEBA/DDS	150/4 + 180/2 + 200/2	220/2
AM/Dicy	120/0.5 + 125/1 + 155/1	200/1
DGEBA/Dicy	150/6 + 175/2	200/3

(TGA) (10 °C/min in N_2) was used to study the thermal stability.

3. Results and discussion

Table 1 shows AM, BP and TMBP rigid rod epoxies need to be cured at higher temperature and longer time than flexible DGEBA epoxy. The results indicate that the rigid rod epoxies have a slower curing rate than that of flexible epoxy due to the slow molecular motions of rigid rod structure in the rigid rod epoxies. The AM epoxy has the longest rigid rod chain length, so it requires the highest post-cure temperature. The post-cure temperature of TMBP is higher than that of BP because of bulky methyl substitution on the BP main chain of TMBP.

From Table 2, AM, BP and TMBP, cured with DDS have higher T_g than the DGEBA epoxy due to their rigid rod structure. The AM epoxy contains the longest rigid rod chain length with the slowest molecular movement, so the AM epoxy has the highest T_g. The bulky substitution on TMBP epoxy decreases the ordered structure of the rigid rod moiety, so it has a lower T_g than BP.

Table 3 indicates that AM, BP and TMBP epoxies have better thermal stability than the flexible epoxy due to their rigid rod structure. The AM epoxy exhibits the lowest weight loss at 600 °C, which may be due to the formation of intermolecular hydrogen bonds [3]. The bulky substitution on TMBP epoxy reduces its thermal stability as compared with BP epoxy. The decomposition temperature of AM and BP epoxies are lower than that of DGEBA, the reason is not clear. However, it may be from the low curing rate of rigid rod epoxies.

Table 2
T_g of DDS-cured different epoxy resin systems

Sample	MDSC (°C)	TMA (°C)	DMA (°C) (tan δ)
AM/DDS	240	219	–
BP/DDS	211	213	235
TMBP/DDS	180	–	234
DGEBA/DDS	163	208	193

Table 3
TGA results of epoxy resin systems

Sample	Temperature at 5 wt.% loss (°C)	Percentage weight loss at 600 °C
AM/DDS	339	60.33
BP/DDS	339	69.64
TMBP/DDS	336	82.70
DGEBA/DDS	377	84.60

Table 4
T_g of epoxy cured with different curing agents

Sample	MDSC (°C)
AM/DDS	240
AM/Dicy	173
DGEBA/DDS	163
DGEBA/Dicy	138

Table 4 shows the DDS-cured epoxies have a higher T_g than Dicy-cured epoxies due to the high functionality and rigid structure of DDS. The Dicy-cured AM epoxy has a higher T_g than DGEBA epoxy because its rigid rod of AM epoxy.

4. Conclusions

The rigid rod AM, BP and TMBP epoxies exhibit higher T_g and weight retention at high temperature than the flexible DGEBA epoxy due to the low molecular motion and high thermal stability of rigid rod structure. The AM epoxy has the best thermal properties among the rigid rod epoxies because of its longest rigid rod chain and possible intermolecular chain formation in the cured network. The DDS-cured epoxies have a better thermal stability than Dicy-cured epoxies because of the high functionality and rigid structure of DDS.

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