Preparation and Properties of Polydimethylsiloxane-Modified Epoxy Resins

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ABSTRACT: In this work, polydimethylsiloxane (PDMS) with different molecular weight were used to modify diglycidyl ether of bisphenol A (DGEBA). A PDMS-block-DGEBA copolymer that acted as a compatibilizer was prepared via DGEBA, hydroxy terminated PDMS, and silane coupling agent in the presence of a catalyst. The reaction mechanisms and compatibilizing effects of the block copolymer were studied by means of Fourier transform infrared (FTIR) spectrum analysis and observation under scanning electron microscopy (SEM). The thermal and mechanical behaviors were analyzed as well. Results indicated that the block copolymer has good compatibilizing effect, and PDMS with low molecular weight could be dispersed in the DGEBA matrix more evenly. Moreover, the PDMS modified DGEBA systems had higher impact strength and lower weight loss rate than those of the pristine DGEBA system. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1683–1690, 2000

Key words: DGEBA; PDMS compatibilizer; thermal behavior; mechanical behavior

INTRODUCTION

Epoxy resins have been widely used as adhesives, coatings, composites, and so on, because of their excellent properties such as moisture, chemical, and corrosion resistance, high tensile strength and modules, and good dimensional stability.[1] However, due to brittleness caused by their highly cross-linked systems formed during their curing process, epoxy resins have low durability, poor heat resistance, and they are also liable to yield cracks. Therefore, the resins usually need to be modified in the occasions of high impact and fracture strength as well as high temperature.[2–4] In the past years, a large variety of toughening agents have been used including ductile engineering thermoplastic polymers, such as bisphenol-A-based polycarbonate (PC),[5] polyetherimide,[6] reactive liquid rubber acrylonitrile-butadiene copolymers terminated with carboxyl or amine end groups (CTBN, ATBN),[7–10] and organosiloxane polymers.[11–15]

Organosiloxane polymers have many unique characteristics such as very good thermal and thermooxidative stability, low glass transition temperature (−123°C), high moisture resistance, low stress resistance for reactive ion etching, and imparting nonflammability to the resins.[16–19] They thus can toughen epoxy resins, and bring them excellent synthetic properties at the same time.

In contrast to CTBN and ATBN, which are miscible with epoxy at first and only during the curing process can they generate two-phase morphology consisting of small rubber particles dispersed in the epoxy matrix,[9,10] organosiloxane polymers in essence are not compatible with the carbon-based epoxy resins because of their special silicone-based molecular structure, and the two-phase morphology has formed before their curing reaction.[20] Moreover, phase separation always macroscopically appears in their cured products.

Therefore there are many efforts contributing to improve the compatibility of the modified epoxy resins, for example, making good use of functional groups on polysiloxane to react with epoxy groups of the resins[21–26]; adding silane coupling agents for bridging polysiloxanes with epoxy resins[27]; controlling the morphology of polysiloxane for benefiting its homogeneous dispersion in the matrix[28]; diminishing the difference in solubility parameter between polysiloxane and epoxy resin via variation of substructure of polysiloxane,[29] and reinforcing epoxy network with a silica structure in situ formed by sol-gel process.[30]

Considering that there is a relationship between the size of the silicone phase and the toughness of the polysiloxane modified epoxy resins,[31] the compatibilizing effects and mechanisms were studied by using a PDMS-block-DGEBA copolymer as compatibilizer. The influences of the content of PDMS on the mechanical and thermal properties of the modified epoxy systems were analyzed as well.

EXPERIMENTAL

Materials

Epoxy resin, a diglycidyl ether of the bisphenol A (DGEBA), were purchased from Yueyang Chemical Factory (Hunan, China), and was used directly without further purification. Hydroxy-terminated Polydimethylsiloxane PDMSI (Mn = 577) was obtained from the Jilin Chemical Limited Co. (Jilin, China). Hydroxy-terminated Polydimethylsiloxane PDMSII (Mn = 1700) was gift from the No.2 Chemical Factory (Peking, China). Silane coupling agent (γ-aminopropyl-triethoxy silicone (KH-550) and anilinomethy-triethoxy silicone (ND-42) were from Dongfang Chemical Factory, Nanjing University (Jiangsu, China). Dibutyltin dilaurate was from the No. 3 Chemical Factory (Peking, China). 2-methyl imidazole was from Yancheng Chemical Factory (Jiangsu, China), and was used directly. Hexane (A. R.) was from the No.6 Chemical Factory (Tianjin, China).

Preparation of PDMSI-Modified Epoxy Resin

A 500-mL three-neck round-bottom flask, equipped with heating mantle, mechanical stirrer, and thermocouple, was charged with 100 g of epoxy resin and heated to 80°C under stirring. PDMSI (20 g), ND-42 (3 g), and dibutyltin dilaurate (0.3
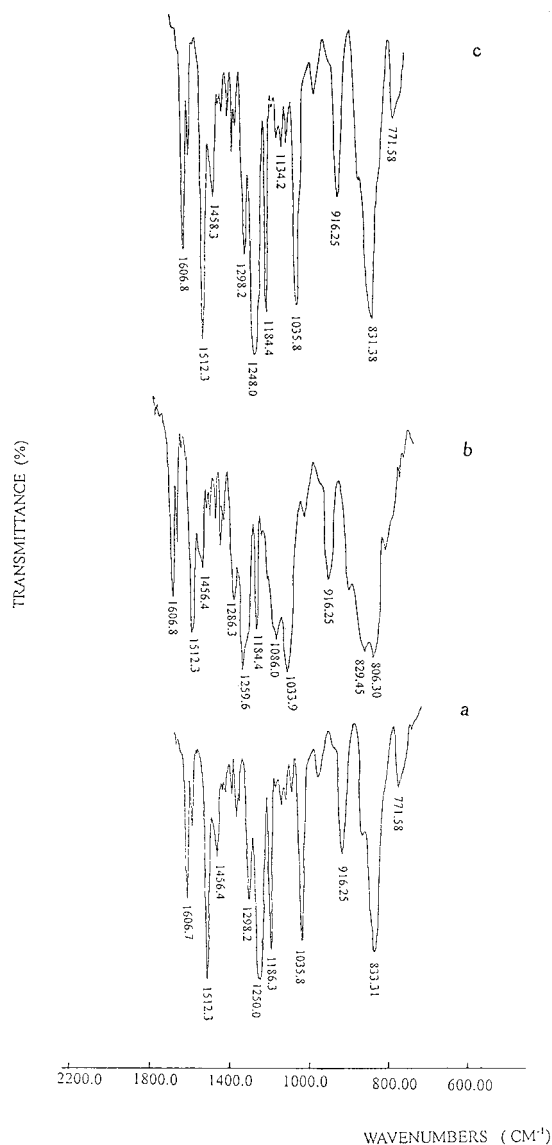

Figure 1 IR characterization of original DGEBA, ESDGI, and nonreaction DGEBA. (a) Original DGEBA; (b) ESDGI; (c) nonreaction DGEBA.

g) were then added dropwise while maintaining the reaction temperature at 80°C for 6 h. Then, a suitable amount of epoxy resin was incorporated, and agitation was kept at the same temperature for several minutes.

Preparation of PDMSII-Modified Epoxy Resin

For the preparation of PDMSII-modified epoxy resin, the same method was used as above, except that the amounts of PDMSII, KH-550, and dibutyltin dilaurate were changed to be 20 g, 5 g, and 0.3 g respectively.
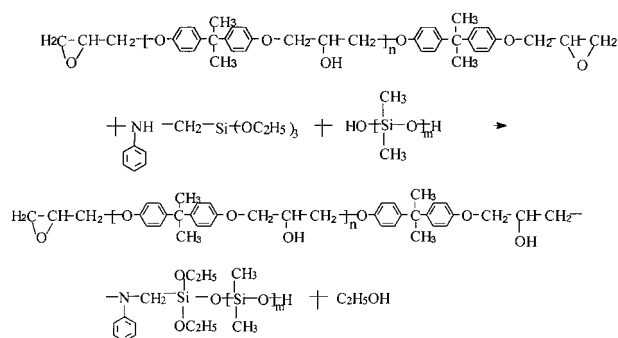
Scheme 1 Synthesis of ESDGI

Measurement of the Block Copolymer Structure

To remove the unreacted PDMS, the mixture obtained was immersed in a great deal of hexane. When the mixture formed two layers of liquid, the upper layer was dropped out. After the procedure was repeated several times, the residual hexane of the mixture was envaporized in vacuum, and then the block copolymer was obtained. The infrared (IR) spectrum of the block copolymer (on NaCl plate) was estimated on a Nicolet 50X IR spectrometer.

Curing of Resin Systems

Curing agent 2-methyl imidazole (4 wt % of prestine epoxy resin) was added in the epoxy resin or polydimethylsiloxane modified epoxy resin under stirring. Then the mixture was poured into a mold and degassed at 60°C under vacuum for several minutes. After that, the resin system was cured in a molding-press at 80°C, 20 Mpa for 3 h and postcured in an oven at 150°C for 4 h.

Measurement of the Impact Strength

The impact strength was tested according to Chinese Standard of Testing Methods GB1043-79 by using XCJ-40 hammer impacter. The dimensions of the specimens were 55L × 6B × 4Wmm. The specimens were impacted at controlled room temperature (23±1°C) or impacted immediately after been frozen in the low temperature (−65±2°C) environment that were prepared by dry ice, alcohol, and water mixture for 3 h.

Fracture Morphology of Modified Epoxy Resins

The PDMS modified epoxy resin specimens were vacuum-coated with gold after they were cooled and fractured in the liquid nitrogen. The micro-

fracture texture were observed by using a Hitachi X-650 scanning electron microscopy (SEM).

Thermodeformation Study

The deformation versus temperature curve of the specimen (4L × 4B × 4Wmm) was determined using a temperature-deformation analyzer (Polymer Laboratory, Tianjin University, China). The specimen was heated from 20°C to 200°C at a heating rate of 2°C/min while the deformation curve was recorded by a recorder.

Determination of Thermogravimetric Analysis

The thermogravimetric curve was determined using a TG-1 self-balance electric analytical microbalance (Polymer Laboratory). First, about 10 mg sample was put in a small cell and was heated from 20°C to 500°C at a heating rate of 5°C/min. Then it was heated from 500°C to 800°C at a heating rate of 10°C/min, and at last the temperature was kept for 30 min.

RESULTS AND DISCUSSION

Synthesis of Block Copolymer

Because silane coupling agents contain amine and alkoxyl groups, they can work as "molecular bridge" to react with not only the epoxy groups of DGEBA but also the hydroxy groups of PDMS. For example, DGEBA and PDMSI can be connected together by silane coupling agent ND-42 to yield block copolymer ESDGI. The reaction mechanism is shown in Scheme 1, and it can be confirmed by comparing the IR spectrum (Fig. 1a) of DGEBA with that of ESDGI (Fig. 1b). The IR spectrum of ESDGI exhibits major absorption peaks (cm^{-1}) at 1086.0 (Si-O-Si), 806.3 (Si-C),
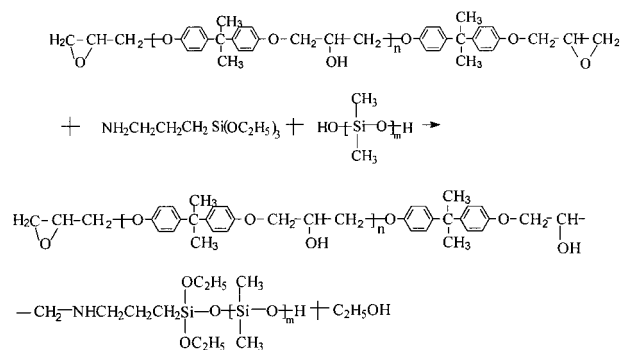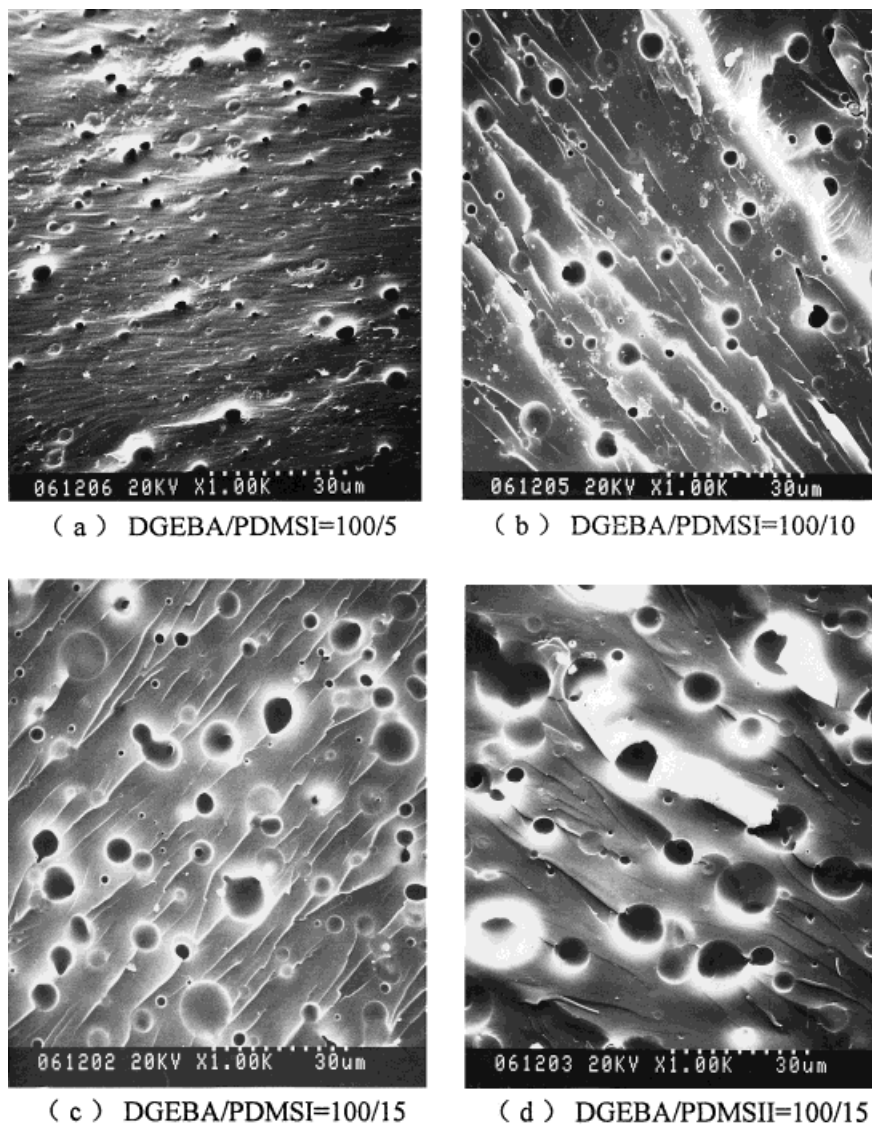

Scheme 2 Synthesis of ESDGII

Figure 2 Micrographs of the fracture surfaces for PDMS modified DGEBA at various ratio of DGEBA/PDMS by weight. (a) DGEBA / PDMSI = 100/5; (b) DGEBA / PDMSI = 100/10; (c) DGEBA / PDMSI = 100/15; (d) DGEBA / PDMSII = 100/15.

and 1259.6 (Si-C), illustrating that both of DGEBA and PDMSI have reacted with ND-42.

For the purpose of proving the mechanism, another synthesis methods was adopted, that is, DGEBA was first reacted with ND-42 at 80°C for 1.5 h, then PDMS and dibutyltin dilaurate were added respectively while maintaining the reaction temperature at 80°C for 4.5 h. However, the IR spectrum (Fig. 1c) shows that there is no absorption band of Si-O-Si existing but only the absorption at 1107.2 cm^{-1} (Si-C) becomes a little stronger. The phenomenon suggests that ND-42 only reacted with epoxy resin, and its alkoxyl

groups had already reacted with the trace water in the air, consequently, PDMS had reacted with neither epoxy nor ND-42.

The molecular weight of PDMS has an obvious influence on the selection of silane coupling agents. When the molecular weight of PDMS increases, it is necessary that a less-reactive silane coupling agent be selected to avoid gelation. For example, if PDMSII (Mn = 1700) is used instead of PDMSI (Mn = 577) to modify DGEBA, KH-550 needs to be selected as the silane coupling agent. Otherwise, if ND-42 is still utilized, gelation will occur in .5 h. The mechanism of the reaction of
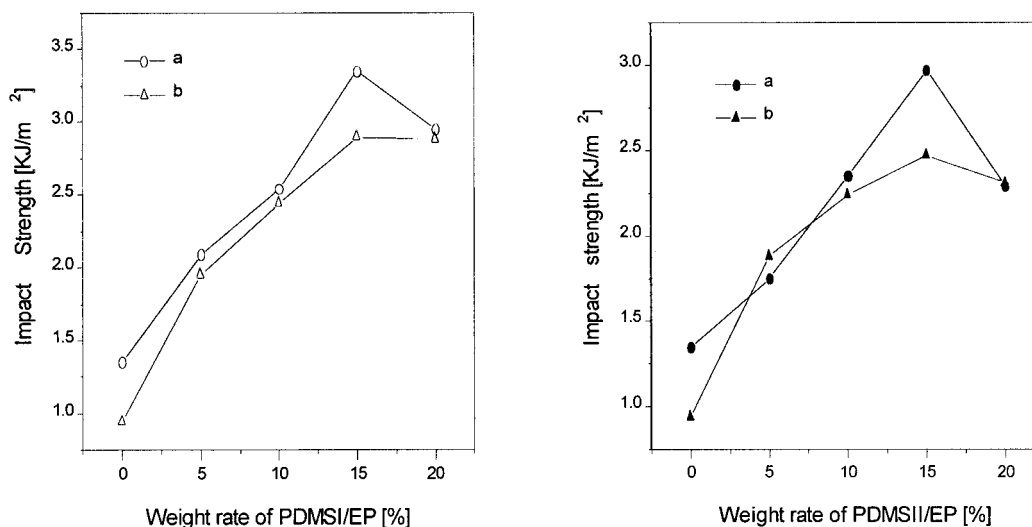
Figure 3 Impact strength of the PDMS-modified DGEBA systems. (a) Room temperature; (b) low temperature ($-65°$C).

DGEBA, KH-550 and PDMSII to yield block copolymer ESCGII is shown in Scheme 2.

Influence of Block Copolymer on the Microstructure of Modified DGEBA

When DGEBA is directly blended with PDMS, the ultimate cured sample separated macroscopically into two layers. The upper layer is white silicone rubber, whereas the lower one is cured DGEBA product. Nor is that all: the two layers almost have no adhesion. Nevertheless, in the presence of the synthesized block copolymer ESDG, which acts as a polymeric compatibilizer, PDMS rubber particles disperse more homogeneously in the DGEBA matrix (Fig. 2). It can also be inferred from Figure 2c,d that PDMSI, which has a low molecular weight, is comparatively easier to dis-

perse in the DGEBA matrix than PDMSII, which has a higher molecular weight.

Impact Strength of PDMS Modified DGEBA

The impact strength of PDMS modified DGEBA has a great variation depending on the content of PDMS (Fig. 3). It can be drawn from Figure 3 that with an increase in content of PDMS, the impact strength enhances also whether at room temperature ($23 \pm 1°$C) or at low temperature ($-65°$C), and reaches maximum value (2.7 times) when the content of PDMS is about 15 wt % of DGEBA. Figure 3 also suggests that in general, the impact strength of the modified resin system at $-65°$C can keep $80 \approx 90\%$ of that of the room temperature. That can attribute to the very low glass transition temperature of PDMS ($-123°$C). Even

Table I N and M_C of PDMS-Modified DGEBA Systems

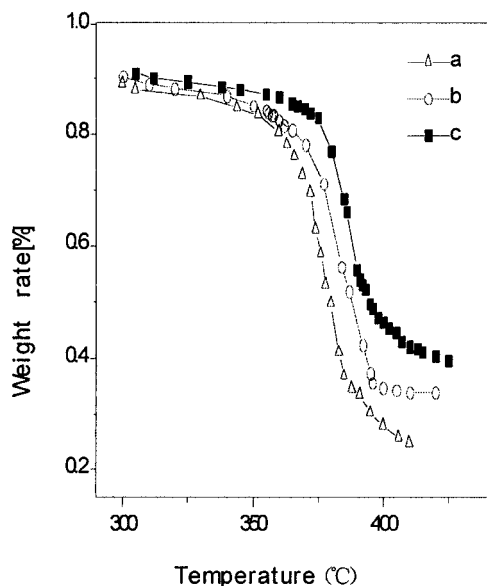| PDMS-Modified DGEBA Systems	Molecular Weight of PDMS (M_n)	Content of PDMS (%)	N	M_C
EP	—	—	3.24×10^{24}	216
EP/PDMSI	577	5	2.61×10^{24}	268
EP/PDMSI	577	10	2.34×10^{24}	298
EP/PDMSI	577	15	1.09×10^{24}	641
EP/PDMSI	577	20	9.28×10^{23}	752
EP/PDMSII	1700	5	2.97×10^{24}	235
EP/PDMSII	1700	10	2.78×10^{24}	251
EP/PDMSII	1700	15	1.51×10^{24}	462
EP/PDMSII	1700	20	1.28×10^{24}	546

Figure 4 TGA curve of PDMSI modified DGEBA systems. (a) DGEBA; (b) DGEBA/PDMSI = 100/10; (c) DGEBA/PDMSI = 100/20.

at −65°C, the PDMS molecule is still in a highly elastic state and possesses high molecular flexibility. Therefore, the low-temperature property of the DGEBA systems are benefited by the incorporation of PDMS.

As to the enhancement in the impact strength of PDMS-modified DGEBA system, in addition to
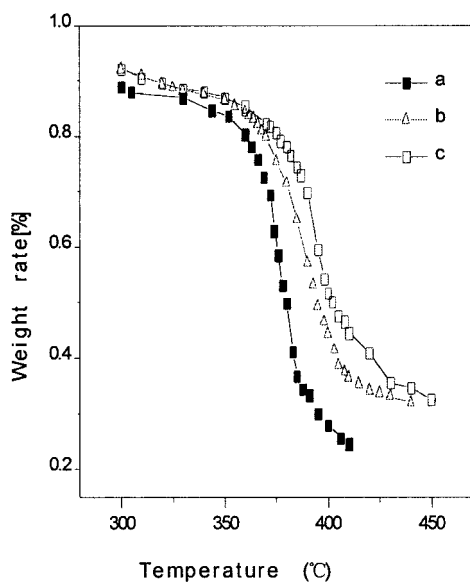

Figure 5 TGA curve of PDMS modified DGEBA systems. (a) DGEBA; (b) DGEBA/PDMS = 100/5; (c) DGEBA/PDMS = 100/20.
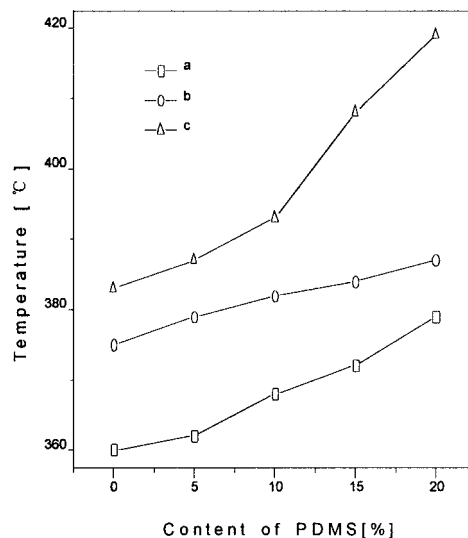

Figure 6 The influence of the content of PDMSI to the thermodegradation of PDMSI-modified DGEBA systems. Weight loss rate: (a) 20%; (b) 40%; (c) 60%.

the toughening effect of small PDMS rubber particles, PDMS also decreases the cross-linked density of the systems. According to the temperature-deformation curve, every modified DGEBA system has an obvious Tg transition district. After the transition region, the deformation tends to be comparatively small along with the raise of the temperature. Thus, a highly elastic state may be believed to exist. And then, the average number of chains in unit volume (N) can be calculated by the following cross-linked state equation[32] of rubber:

$$\sigma = NKT \ (\lambda - \lambda^{-2}) \qquad (1)$$

Where σ is the stress exerted on the sample; K is Boltzmann constant; T is temperature (K); λ is extension ratio and related to the nominal unit strain ε as follows:

$$\lambda = 1 + \varepsilon \qquad (2)$$

Next, based on the calculated value of N, M_c, the average molecular weight between cross-links, can be obtained by eq. (3):

$$M_c = \rho N_a / N \qquad (3)$$

Where ρ is the density of the modified DBEGA (kg/m^3), and N_a is Avogadro's number.

The average number of chains in unit volume (N) and the average molecular weight between
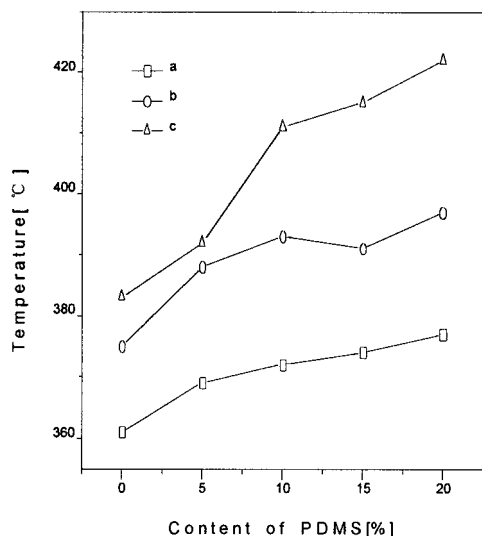
Figure 7 The influence of the content of PDMSII to the thermodegradation of PDMSII-modified DGEBA systems. Weight loss rate: (a) 20%; (b) 40%; (c) 60%.

cross-links (M_c) are listed in Table I. The data indicate that the more the content of PDMS, the less the average number of chains in unit volume, and the bigger the average molecular weight between cross-links. This illustrates that with an increase in the content of PDMS, the density of the modified DGEBA reduces. Moreover, the N of the PDMSI modified DGEBA system is smaller, whereas M_c is bigger than that of the PDMSII-modified DGEMA system when both of them contain the same content of PDMS.

Effect of the Content of PDMS on the Weight Loss of the Modified DGEBA Systems

The weight loss curves of PDMSI and PDMSII modified DGEBA systems (Figs. 4 and 5) that when the weight loss is determined, the thermogravimetric loss temperature all raises with the enhancement of the PDMS content. At the same time, the weight loss rate becomes smaller, and its transition district gets broader. Therefore, the incorporation of PDMS increased the thermostability of the DGEBA systems.

When the thermogravimetric loss is determined, the temperature curve of the modified DGEBA (Figs. 6 and 7) show that the weight loss temperature all enhance with the increase of the PDMS content. And when the temperature is determined, the thermogravimetric rate decreases. Moreover, the higher the temperature, the more obvious of the influence of the PDMS. From the

above analysis, one can see that although incorporation of PDMS can not prevent the thermodegradation of the DGEBA systems, it can improve the thermostability of the systems to some extent.

CONCLUSION

A kind of PDMS-block-DGEBA copolymer was synthesized via DGEBA, hydroxy terminated PDMS, and silane coupling agents in the presence of dibutyltin dilaurate. The block copolymers could be used as a compatibilizer for improving the PDMS dispersion within the DGEBA matrix. In addition, PDMS with low molecular weight could be dispersed well in the DGEBA matrix. The PDMS modified DGEBA systems had higher impact strength than those of the original DGEBA system. Moreover, their thermoresistances were also improved by this way.

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