

Note

MICRO-PHASE SEPARATION IN EPOXY RESIN WATERBORNE PARTICLES DURING CURING PROCESS*

Xi-yan Liu^{a, b}, Dong Qiu^a, Mei-li Guo^{b**} and Zhen-zhong Yang^{a**}

^aState Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

^bSchool of Materials Science and Engineering, BeiHang University, Beijing 100083, China

Abstract Sub-micron sized phenolic epoxy resin waterborne particles were prepared by phase inversion emulsification. Micro-phase separation occurred during the curing process at high temperature. The as-prepared samples possessed one glass transition temperature (T_g) and two exothermal processes during DSC heating scanings. After being thermally treated above the exothermal peak temperature, they possessed two glass transition temperatures with the disappearance of exothermal peaks, whilst a core/shell structure was formed. This was likely related with the outward diffusion of reactive oligomers to the outer layer of particles.

Keywords: Curing process; Phenolic epoxy resin; Waterborne dispersions; Micro-phase separation; Core/shell structure.

INTRODUCTION

Crosslinked polymeric resins are thermally and chemically resistant materials^[1]. Their spheres are useful in various applications, including biomedical fields^[2], information technologies^[3, 4], microelectronics^[5] and reinforcement fillers. We have previously prepared crosslinkable waterborne dispersions of epoxy resin and epoxy resin/silica nanoparticle composites by phase inversion emulsification in the presence of a curing agent^[1, 6–9]. Due to the presence of epoxide groups, they are latently curable both in aqueous media and in polymer matrices. They can be used as additives for emulsions or fillers for multiphase polymeric materials. In order to explore their applications, studying their curing process and phase behavior is required.

This communication reports the investigation of curing process of the resin particles and their morphological change using DSC and TEM.

EXPERIMENTAL

Materials

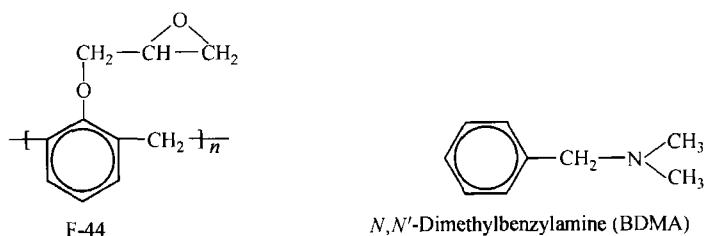
Phenolic epoxy resin F-44 with a softened point lower than 40°C was supplied by the Shanghai Resin Company and used as received. A curing agent *N,N*-dimethyl-benzylamine (BDMA) was purchased from Huabei Special Chemical Reagent Center and used without purification. Their structures are given in Scheme 1. A multi-block copolymer E1 of bisphenol A epoxy resin E-20/poly (ethylene glycol) 10000 (0.9:1.0 mol/mol) was prepared and used as an emulsifier during the phase inversion emulsification process^[10].

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** Corresponding authors: Zhen-zhong Yang (杨振忠), E-mail: yangzz@iccas.ac.cn

Mei-li Guo (过梅丽), E-mail: mlg@buaa.edu.cn

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Scheme 1 Chemical structure of the materials

Preparation of Curable Waterborne Dispersions^[1, 9]

After F-44 was mixed thoroughly with E1 (*e.g.* 10 wt% with respect to F-44) under stirring at 50°C for 30 min, the mixture was cooled to 30°C. A definite amount of BDMA was added under stirring in 20 min. Afterwards, water was added dropwise at a rate of 1 mL/min to initiate the phase inversion until the conductivity increased abruptly, and a concentrated waterborne dispersion was obtained. An excess amount of water was added to dilute the concentrated dispersion to ensure a solid content at about 40 wt%. Afterwards, the waterborne dispersion was heated to 95°C to conduct polymerization for various times in the aqueous medium.

Characterization

A thin layer of dispersion was spread on a glass slide and dried under vacuum at an ambient temperature for 30 min. The sample was then sputtered with Au under vacuum and observed with a scanning electron microscope (JSM-6301F). Powders for DSC measurements were obtained by freeze-drying the dispersion. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used to monitor the curing process. The DSC measurement was carried out in nitrogen atmosphere by temperature programming in the range 20–250°C at a rate 20 K/min. A very diluted dispersion was spread onto a carbon coated copper grid and observed with a transmission electron microscope (JEM-100CX).

RESULTS AND DISCUSSION

DSC Analysis of the Waterborne Particles

An as-prepared epoxy resin waterborne dispersion A containing 10 wt% BDMA (with respect to F-44) was polymerized at 95°C for 1, 2 and 3 h, respectively, leading to the formation of other three dispersions B, C and D. Their DSC curves are shown in Fig. 1. Each sample was scanned twice. During the first temperature scanning, no glass transition was found for sample A but a broad exothermic peak appeared around 137°C. The enthalpy was –278 J/g. The other three samples B, C and D possessed a glass transition temperature and two distinct exothermic peaks around 120°C and 160°C. This reveals that the particles could be further crosslinked at increasing temperature, which is important for reactive fillers in polymeric materials. For example, crosslink reaction could be completed at 150°C in 25 min. Glass transition temperature was related with the polymerization, which increased slightly from 60°C (sample B) to 65°C (sample D) with the increase in polymerization time. The enthalpy of the three samples was nearly the same, about –65 J/g, which was much lower than that of the sample A. This indicates that the polymerization of waterborne dispersion could occur below 100°C, which is important for the emulsions to form films in the presence of reactive additives at low temperature. During the first DSC temperature scanning in the range of 20–250°C, the samples experienced an equivalent thermal treatment. Another cycle of temperature scanning was performed to study the effect of thermal treatment on phase behavior. Two glass transition temperatures (T_{g1} , T_{g2}) were found, while all the exothermic peaks disappeared, meaning that the whole stage of crosslinking has been completed. The second glass transition region was rather broad.

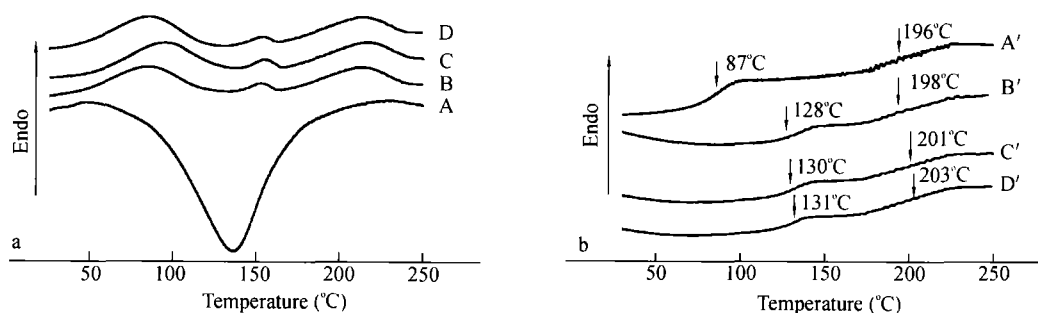


Fig. 1 Differential scanning calorimetric traces of the samples

a) The first temperature scanning; b) The second scanning

Table 1. Glass transition temperature and enthalpy

Samples	A	B	C	D
Polymerization time at 95°C (h)	–	1	2	3
ΔH (J/g)	–278	–64	–56	–69
T_g (°C)	–	60	63	65
T_{g1} (°C)	87	128	130	131
T_{g2} (°C)	196	198	201	203

T_g was obtained from the first DSC temperature scanning.

T_{g1} and T_{g2} were obtained from the second scanning.

As listed in Table 1, T_{g1} of sample A is about 87°C far lower than those of samples B, C and D. T_{g2} of all the samples is nearly the same around 200°C. In order to determine the extent of crosslinking, a good solvent acetone was used to extract the soluble components from the crosslinked epoxy resin. After being immersed in acetone for 1 day, sample A lost (43 ± 1) wt% and severely agglomerated, indicating that crosslinking reaction could partially occur at an ambient temperature. In contrast, (1.08 ± 1) wt% was extracted from samples B, C and D without aggregation among the particles. This reveals that almost all epoxy resin molecules have participated in the formation of crosslinked networks in the individual particles after polymerization at 95°C in water for more than 1 h.

Besides, the effect of aging at an ambient temperature on the curing behavior of samples A and B was studied. They were stored at 10°C for two months in order to get the corresponding derivatives A1 and B1. As shown in Fig. 2 and Table 2, one glass transition region was found for sample B1 with two distinct exothermic peaks during the first DSC temperature scanning, similar to its original behavior (curve B in Fig. 1a). This indicates that no remarkable crosslinks are formed in sample B during aging. For sample A1, the enthalpy is about –117 J/g far lower than that of the original one –278 J/g (in Table 1) and a glass transition temperature around 50°C was observed, indicating that polymerization has progressively occurred in sample A at low temperature. During the second temperature scanning, T_{g1} of sample A increased with the aging treatment but T_{g2} was less affected. This reveals that T_{g1} is closely related to the curing reaction at low temperature. The two T_g s and enthalpy of sample B are less affected by the aging treatment, indicating that the step curing process at low temperature for long time could be completed by the polymerization at 95°C for 1 h.

Table 2. DSC data from Fig. 2

Sample	A	A1	B	B1
T_g (°C)	–	50	60	60
ΔH (J/g)	–278	–117	–64	–60
T_{g1} (°C)*	88	92	128	127
T_{g2} (°C)*	196	195	198	198

*Measured from the second DSC temperature scanning

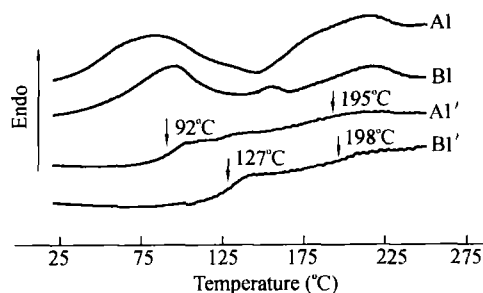


Fig. 2 DSC curves of samples A1 and B1
The curves with superscripts were obtained by the second temperature scanning.

Morphological Analysis of the Waterborne Particles

The pure epoxy resin used in this study was a viscous fluid, but the particles of as-prepared sample A without polymerization could preserve their individual spherical shape (Fig. 3a). This can be explained by the hardening of epoxy resin due to the increase of molecular weight through crosslinking at low temperature. This result is also consistent with the partial extraction from the particles. After the polymerization in aqueous medium at 95°C, the particle size and its distribution (Figs. 3b and 3c) are less influenced.

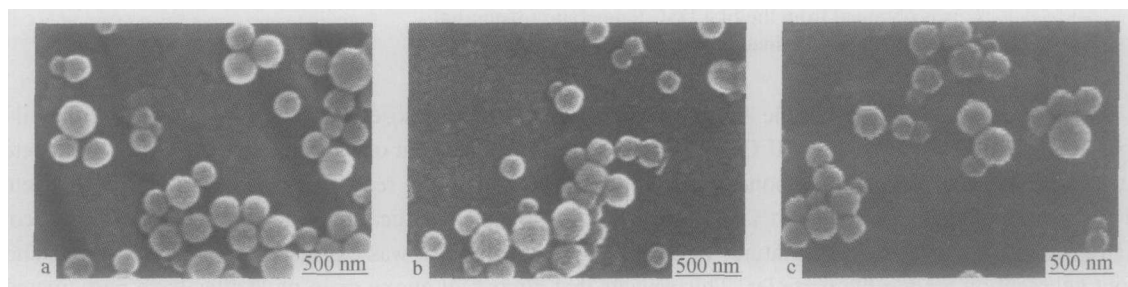


Fig. 3 Scanning electron micrographs of the particles (a) as-prepared sample A, (b) and (c) sample A after polymerization at 95°C for 1 h and 2 h

After the sample particles were thermally treated under the condition similar to that of the first DSC measurement, their morphology changed remarkably. Before such a treatment, the particles were uniform in size under TEM observation (Fig. 4a). After the treatment, a distinct core/shell structure was clearly observable (Fig. 4b). Thus, the two T_g s after the first temperature scanning during DSC measurement are closely related with the core/shell structure.

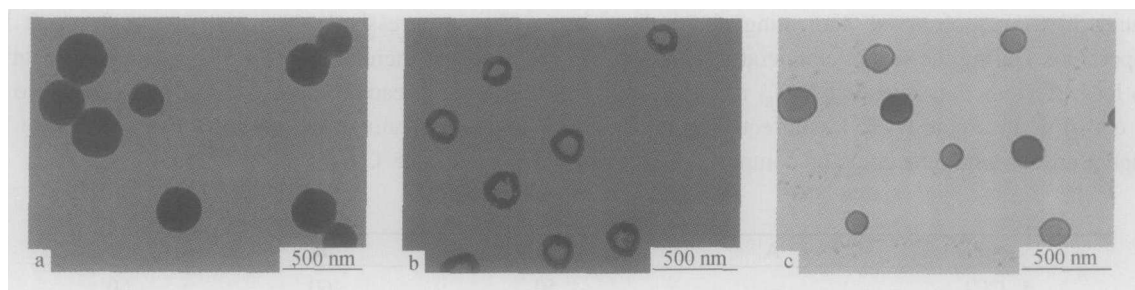


Fig. 4 Transmission electron micrographs of the samples (a) and (b) sample B before and after being thermally treated at high temperature, (c) the sample containing low BDMA content (5 wt%) after being thermally treated

The two T_g s and the formation of core/shell structure could be understood as follows. According to the previous report^[11], an anionic propagating site of quaternary ammonium alcoholate formed during the curing reaction of epoxy resin catalyzed by BDMA. Both the initiated active species and the propagating epoxy resin chains act as zwitter-ions and thus they can be used as emulsifiers. This has been proved by the successful preparation of curable waterborne emulsions of epoxy resin in the absence of surfactants^[10]. The molecular length of the initiated active species and the propagating epoxy resin chains were polydispersed. The shorter chains were more hydrophilic and tended to diffuse outward onto the particle's outer surface and enrich therein. This process was facilitated by the viscosity decrease at increasing temperature. Thus, phase separation occurred during the curing process at high temperature, and a core/shell structure with different extent of crosslinking was resulted. At an intermediate temperature (e.g. 95°C), the first step crosslinking was fast in the less viscous outmost layer, resulting in an abrupt increase in viscosity. In the core region, the reaction was retarded by the declined diffusion of longer chains in a highly viscous system. When the sample was heated to a high temperature (250°C), the crosslinking reaction within the outer layer became more complete, while the core started to crosslink with the formation of a network composed of longer molecular segments. Two distinct regions with varied crosslinking density were thus formed corresponding to the core/shell regions. This process was similar to the interfacial tension gradient driven formation of egg-type microstructure^[11]. In order to further verify the aforementioned supposition, another two experiments were designed. In the first experiment, the core/shell structure was still formed with decreasing BDMA content (e.g. 5 wt%) but with thinner shell thickness (Fig. 4c), and two glass transition temperatures were also found after being thermally treated (Fig. 5). This was in agreement with the shell formation related with BDMA. In the second experiment, only one glass transition temperature appeared between T_{g1} and T_{g2} (Fig. 5) in the composite particles containing 5 wt% silica nanoparticle^[9] after being thermally treated, and no core/shell structure was observed. This was attributed to the immobilization of the propagating epoxy resin chains by the silica nanoparticles and thus homogeneously dispersed within the particles^[12]. The supposition proposed in this study needs further experimental confirmation.

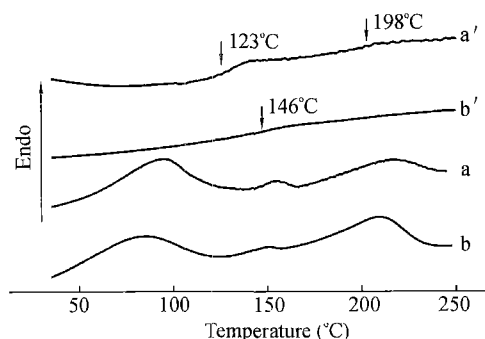


Fig. 5 DSC curves of (a) the sample containing 5 wt% BDMA and (b) the sample containing 5 wt% silica nanoparticles. The curves denoted with superscripts were obtained from the second temperature scanning.

CONCLUSIONS

Crosslinkable phenolic epoxy resin waterborne dispersions were prepared by phase inversion emulsification in the presence of the curing agent BDMA. Two glass transition temperatures were found after the samples were thermally treated. Morphological analysis indicated that a core/shell structure was formed. This was explained by the outward diffusion of the amphiphilic reactive epoxy resin chains of smaller molecular weight and their enrichment at the outer layer of the particles.

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