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ORIGINAL CONTRIBUTION

K. Hibino
Y. Kimura

Epoxy resin particles. I. Spontaneous particle formation by the polymerization reaction of epoxy resin in a stationary system using polyethers as organic media

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K. Hibino (✉)
EC Intracorporation
Sanyo Chemical Industries Ltd.
11-1 Ikkyonomoto-cho
Higashiyama-ku Kyoto 605-0995, Japan
e-mail: hibino@mvj.biglobe.ne.jp
Tel.: 81-75-541-6325
Fax: 81-75-561-5700

Y. Kimura
Department of Polymer Science
and Engineering
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku
Kyoto 606-8585, Japan

Abstract A thermosetting epoxy resin was found to form polymer particles spontaneously in a stationary reaction system using polyethers as solvents. Poly(oxypropylene) and its copolymer with poly(oxyethylene) were effectively used as reaction media. The diameter of the resultant particles depended on the structure of the amines used as hardeners as well as on the molecular weight and composition of the polyether media. The glass-transition temperatures of the particles revealed that a small amount of polyether used as the medium was incorporated in the epoxy resin particles during the polymerization.

Key words Particle formation · Epoxy resin particles · Polyether · Stationary reaction system

Introduction

Many kinds of polymer particles have been made of polyacrylates, polyamides, melamine and phenol resins, and other polymeric materials. These particles are most easily prepared in aqueous media by emulsion or dispersion polymerization of vinyl monomers such as vinyl acetate, acrylates, vinyl chloride, etc. or by interfacial polycondensation of some combinations of monomers [1]. Polymer particles dispersed in aqueous solutions are widely used as paints, adhesives, sealants, binders, and molding compounds. Polymer particles can also be formed in organic media when the dispersion polymerization is carried out in some types of organic solvents [2–4]. In this method, the monomers are dissolved in the organic medium and the polymer produced is deposited as particles from the solution as the polymerization proceeds. This method is generally called non-aqueous dispersion polymerization and is frequently applied to the polymerization of hydrolysis-sensitive monomers such as epoxy resin.

This article reports the novel preparation of epoxy resin particles in polyether as an organic medium. Previously, similar epoxy resin particles were prepared by reaction of a hardener with an epoxy resin dispersed in aqueous media [5]. In this case, thermoplastic epoxy resin particles with a low degree of cross-linking were obtained. In our method, thermosetting epoxy resin particles that are fully cross-linked can be spontaneously added to a stationary reaction system, i.e., without stirring the mixture in which both the epoxy compound and the hardening agent are dissolved in a viscous polyether medium. Therefore, the resultant particle dispersion in the polyether medium can be subjected directly to solidification with other hardening agents such as isocyanate and epoxy compounds.

Experimental

Materials

The epoxy resin and the amines used as hardeners are listed in Table 1. The polyethers used as media are listed in Table 2. Three

Table 1 The epoxy resin and hardeners used and the solubility parameters of the epoxy resin–hardener (1/1 mol ratio) reaction products

Epoxy resin	Epoxy equivalent (g/Eq)	Abbreviation	Supplier
2,2′-[(1-Methylethylidene)bis(4,1-phenylene-oxymethylene)]bisoxirane	189	BAE	Mitsui Chemical
Hardener	Active hydrogen equivalent (g/Eq)	Abbreviation	Supplier
Bis(4-aminophenyl)methane	49.5	MDA	Sumitomo Chemical
1,2-Diaminoethane	15.0	EDA	Sumitomo Seika
(2-Aminoethyl)-aminoethylamine	20.6	DTA	Sumitomo Seika
5-Amino-1,3,3-trimethylcyclohexylmethylamine	42.5	IPDA	BASF Japan
Epoxy resin	Hardener (amine)	Solubility parameter [(cal/cm^{3})$^{1/2}$]	
BAE	MDA	12.95	
BAE	EDA	13.01	
BAE	DTA	12.94	
BAE	IPDA	12.44	

Table 2 The polyethers used as media. 1,2-Epoxyethane and 1,2-epoxypropane are represented by *EO* and *PO*, respectively

Polyether	Molecular weight (Da)	Composition (wt%)		Solubility parameter [(cal/cm^{3})$^{1/2]}$	Abbreviation	Supplier
		EO	PO			
Poly[oxy(methyl-1,2-ethanediyl)]	ca. 2000	0	100	9.04	PPG2000	Sanyo Chemical Ind.
Poly[oxy(methyl-1,2-ethanediyl)]	ca. 3000	0	100	8.92	PPG3000	Sanyo Chemical Ind.
Poly[oxy(methyl-1,2-ethanediyl)]	ca. 4000	0	100	8.85	PPG4000	Sanyo Chemical Ind.
Poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)]	ca. 4000	20	80	8.99	P-E4020	Sanyo Chemical Ind.
Poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)]	ca. 4000	40	60	9.13	P-E4040	Sanyo Chemical Ind.
Poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)]	ca. 5000	20	80	8.95	P-E5020	Sanyo Chemical Ind.

of them were poly(oxypropylene)s with different molecular weight [poly(propylene glycol) (PPG) series] and the other three were ABA triblock copolymers of poly(oxypropylene) (B) and poly(oxyethylene) (A) with different composition (P-E series). All these compounds were from commercial sources and were used without further purification.

Preparation of epoxy resin particles

A typical procedure is as follows. 2,2′-[1-Methylethylidene)bis(4,1-phenylene oxymethylene)]bisoxirane (BAE) (189 g, 1Eq) and bis(4-aminophenyl)methane (MDA) (49.5 g, 1Eq) were dissolved in poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)] with a molecular weight of about 5000 Da (P-E 5020) (238.5 g). Here, the total weight of epoxy resin and hardener was equal to the weight of the reaction medium. The mixture was then heated at 100 °C without stirring for 10 h and it turned to a milky white paste. It was then cooled and 500 g methanol was added to this paste to precipitate the resulting particles. The precipitates were then filtered, washed well with methanol, and thoroughly dried in vacuo.

Measurements

The particle diameter shown as a median value was measured on a light scattering particle meter (Horiba Seisaku-sho LA-700). Scanning electron microscopy (SEM) was performed using a Hitachi S-800 with a platinum–palladium-coated sample. Differential scanning calorimetry (DSC) was conducted on a Seiko Electronics DSC-220 C calorimeter with about 5.0 mg sample packaged in an aluminum pan. Under a nitrogen atmosphere, the temperature was first raised from room temperature to 250 °C at a rate of 20 °C/min. The temperature was then held at 250 °C for 10 min, lowered to 0 °C at a rate of 90 °C/min, and maintained at 0 °C for 10 min. The temperature was again raised from 0 to 250 °C at a rate of 20 °C/min in the second heating. The glass-transition temperature (T_g) was determined both in the first and second heating runs.

Results and discussion

It is well known that epoxy resins such as BAE can be readily hardened by reaction with various amines to form a three-dimensionally cross-linked tough solid. This reaction proceeds with and without solvent under mild conditions. We observed during the hardening study of epoxy resin that the reaction system turned opaque when the hardening was done in some polyether media. A close study of this color change revealed that many particles had been formed during the hardening reaction. It was also found that the particles could be formed only when poly(oxypropylene) and its copolymers were used as media and the mixture of epoxy resin, hardener, and medium was kept standing without stirring. If the reaction system was stirred, the polymer produced agglomerated instead of forming particles.

Typical results of formation of the epoxy resin particles by the reaction of BAE with various amine-type hardeners in different polyether media are shown in Table 3. Ordinary aliphatic amines, 1,2-diaminoethane and (2-aminoethyl)aminoethylamine, reacted with BAE at room temperature to produce an agglomerate in the P-E5020 medium, and no small particles were formed. When BAE was reacted with 5-amino-1,3,3-trimethylcyclohexylmethylamine (IPDA), a cycloaliphatic amine, in the same medium at 25 °C, spherical particles were formed in the polyether medium in high yield. The particles isolated showed their T_g at 72 °C in the first DSC run. Since the T_g increased to 145 °C in the second DSC run, it is suggested that the reaction of epoxy resin and amine proceeded during the first heating of the particles, resulting in a much higher degree of cross-linking. The latter T_g value was even lower than that (154 °C) of the same resin that was hardened in the ordinary method, i.e., at 25 °C for 10 h in a bulk state and heated at 200 °C for 1 h. This fact suggests that a small amount of polyether medium polymerized into the epoxy resin during the particle formation by the reaction of the hydroxyl groups of the polyether with the epoxy group that is driven in the presence of amine as a catalyst. When an aromatic amine, MDA, was used as the hardener, no reaction occurred at low temperature, and the polymerization was conducted at 100 °C to obtain the particles. BAE/MDA particles were formed in most of the media examined, except in poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)] with a molecular weight of about 4000 Da; their size changed depending on the medium used. There was a general tendency that their particle size decreased with increasing content of oxyethylene units of the medium in the P-E series, i.e., the PPG–poly(ethylene glycol) copolymer type. When the oxyethylene content was over 40 wt%, no particle formation was observed. The T_g of the resultant BAE/MDA particles was around 120 °C in the first DSC run and reached 150 °C in the second run. The latter T_g value was almost 10 °C lower than that (161 °C) of the BAE/MDA resin hardened in the ordinary bulk state, as for the BAE/IPDA series, because of the incorporation of the polyether medium in the resin. The amine value of the particles (for the primary and

Table 3 Formation and characteristics of epoxy resin particles. The particle yield was over 94% in each case

No.	Epoxy resin	Amine	Medium	Reaction temperature (°C)	Reaction time (h)	Particle median diameter (μm)	Standard deviation of particle diameter (μm)	T_g (°C)	
								1st run	2nd run
1	BAE	EDA	P-E5020	25	10	– (*)	–	–	–
2	BAE	DTA	P-E5020	25	10	– (*)	–	–	–
3	BAE	IPDA	P-E5020	25	10	10	3.8	72	145
4	BAE	MDA	PPG2000	100	10	12	4.5	121	151
5	BAE	MDA	PPG3000	100	10	10	4.2	120	151
6	BAE	MDA	PPG4000	100	10	7.4	2.7	120	152
7	BAE	MDA	P-E4020	100	10	5.6	1.9	121	150
8	BAE	MDA	P-E4040	100	10	– (*)	–	–	–
9	BAE	MDA	P-E5020	100	10	3.3	1.5	120	150

(*) Agglomeration

Table 4 Particle formation at a reaction temperature of 100 °C as a function of reaction time (epoxy resin: BAE, amine: MDA, polyether: P-E5020) after isolation by precipitation

Reaction time (h)	Appearance of the reaction system	Particle yield (%)	Particle median diameter (μm)	Standard deviation of particle diameter (μm)	T_g (°C)	
					1st run	2nd run
1	Clear liquid	0	–	–	–	–
2	Translucent	15	3.4	0.9	98	154
4	Opaque	60	3.2	1.2	112	158
6	Opaque	90	3.4	1.1	118	157
8	Opaque	95	3.3	1.2	120	158
10	Opaque	95	3.4	1.2	120	158

secondary amines involved) was found to be zero. This fact indicates that most of the amine hardener in the feed was consumed in the hardening of the epoxy resin.

The formation times of the particles in the reaction of BAE and MDA in P-E5020 are shown in Table 4. At 100 °C the reaction mixture turned translucent after 2 h and gradually became turbid with an increase in the yield of the particles; however, the median diameter of the resultant particles was almost constant at 3 μm regardless of the reaction time and yield. When the reaction time was over 8 h, the particle formation was over 95% in isolated yield in spite of the loss during the precipitation. The T_g of the particles increased with increasing reaction time and yield, although it did not exceed 132 °C even after a long reaction time. To increase the T_g value the second heating in the solid state was necessary.

The effects of reaction temperature on the particle formation of the BAE/MBA system in P-E5020 and poly[oxy(methyl-1,2-ethanediyl)] with a molecular weight of about 4000 Da (PPG-4000) are summarized in Tables 5 and 6, respectively. At 60 °C no particle formation was observed in either medium. On increasing the reaction temperature from 70 to 120 °C stepwise, the particle yield increased at a constant reaction time of 10 h. The particle diameter also increased with the reaction temperature. It was again revealed that the particle size was much smaller in P-E5020 containing a poly(oxyethylene) block than in PPG-4000. The particles formed at higher temperature showed higher T_g in the first heating, while the T_g values observed in the second heating became similar for all the samples. At the same reaction temperature the particles formed in the two media showed almost identical T_g. This fact suggests that the rate of the hardening reaction is similar in both media and that the degree of cross-linking should not differ. Therefore, the difference in particle diameter in both media may be attributed to the difference in affinity between the epoxy resin and the medium in spite of their similar solubility parameters. In the medium having the higher affinity to the epoxy resin the cross-linking polymer should deposit at a slower rate and its deposition should happen in a catastrophic manner so as to make the particle size smaller. Considering that the epoxy resin has a higher affinity for the poly(oxyethylene)-containing medium, the particle size should be smaller in P-E5020.

The effect of reaction temperature on the particle formation of the BAE/IPDA system in P-E5020 is shown in Table 7. Since the reactivity of IPDA was very high in comparison with MDA, the particle formation was driven even at 25–50 °C. At a higher temperature of 100° C no particle formation was observed because the whole system turned to an agglomerate. The particle size and yield were not so different at the reaction temperatures examined, while the T_g value became slightly higher at the higher reaction temperature.

Typical SEM photographs of the epoxy resin particles obtained for the BAE/MDA system in P-E5020 are shown in Fig. 1. It is shown that each particle kept a completely spherical shape with a narrow size distribution. Interestingly, these particles were formed in the stationary reaction system without stirring. At present the mechanism for the particle formation is not known,

Table 5 Effect of reaction temperature on the particle formation of the BAE/MDA system in P-E5020

Reaction temperature (°C)	Reaction time (h)	Yield (%)	Particle diameter (μm)	Standard deviation of particle diameter (μm)	T_g (°C)	
					1st run	2nd run
60	10	–	–	–	–	–
70	10	45	2.6	0.9	79	147
80	10	78	2.9	0.9	84	155
90	10	89	3.0	1.0	100	158
100	10	90	3.4	1.2	120	159
120	10	94	3.8	1.2	120, 132	158

Table 6 Effect of reaction temperature on the particle formation of the BAE/MDA system in PP-4000

Reaction temperature (°C)	Reaction time (h)	Yield (%)	Particle diameter (μm)	Standard deviation of particle diameter (μm)	T_g (°C)	
					1st run	2nd run
60	10	–	–	–	–	–
70	10	30	6.9	2.8	78	157
80	10	65	7.2	3.3	85	158
90	10	88	7.2	3.3	99	156
100	10	91	7.4	3.4	120	158
120	10	94	7.7	3.4	125	157

Table 7 Effect of reaction temperature on the particle formation of the BAE/IPDA system in P-E5020

Reaction temperature (°C)	Reaction time (h)	Yield (%)	Particle diameter (μm)	Standard deviation of particle diameter (μm)	T_g (°C)	
					1st run	2nd run
25	5	95	10	3.4	72	151
30	5	93	12	4.2	75	153
40	5	94	13	4.5	76	152
50	5	95	13	4.5	81	155
100	5	–	–	–	–	–

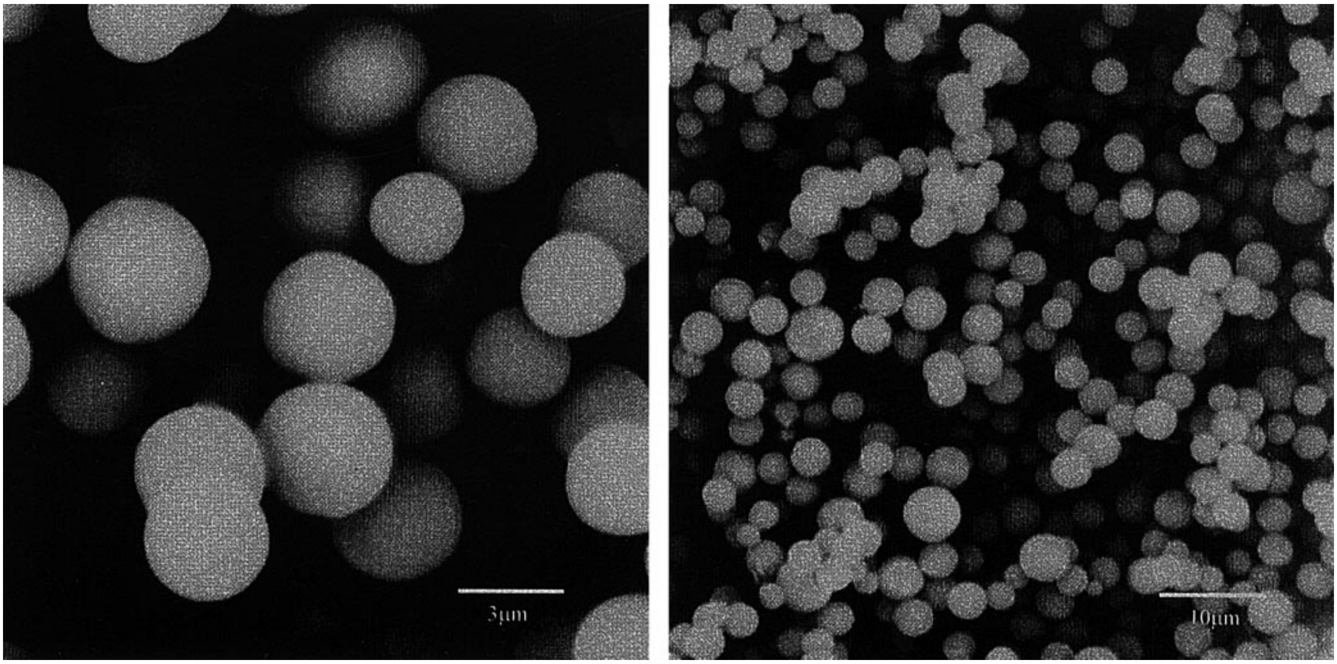

Fig. 1 Scanning electron microscope photographs of epoxy resin particles, 2,2′-[(1-methylethylidene)bis(4,1-phenyleneoxymethylene) bisoxirane and bis(4-aminophenyl)methane system, produced in poly[oxy(methyl-1,2-ethanediyl)]-*b*-poly[oxy(1,2-ethanediyl)]

but the spontaneous deposition of such well-shaped particles is to be attributed to a spinodal decomposition of the polymer–medium binary system. As the cross-linking reaction of the epoxy resin proceeds in the polyether medium, phase separation of the insoluble epoxy resin is induced at a limited solubility of the polymer. Generally, this limited solubility of polymer may be determined by the balance of its degree of cross-linking and the polymer–medium affinity. Particularly, the former should be closely related to the polymer deposition. In the present system, however, the degree of cross-linking changed with the conversion of the reaction between the epoxy resin and the amine and could not easily be monitored in such a heterogeneous system. Therefore, the phase diagram of the present reaction system was not given for further quantitative analysis. The fact that resultant particles became larger with increasing temperature is also problematic. The particle size is generally determined by various factors arising in the course of the phase separation, for example, polymer/solvent ratio, polymer aggregation, and so on. We think that in the present system the polymers before deposition became larger because of the increased polymer–medium interaction at higher temperature. Further study will be necessary for analysis of the formation mechanism of the particles.

In conclusion, epoxy resin particles were formed spontaneously in a stationary reaction system using polyethers as solvents. The epoxy particles thus prepared are characterized by their small size and narrow size distribution as well as by their high thermal and chemical stability in comparison with other conventional polymeric particles. The particle dispersions in the polyether media can be applied directly to the hardening reaction with other reactants, such as diisocyanate, for preparing particle-filled composite materials. These applications are also under study in our laboratories.

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