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Preparation of cured epoxy resin particles having one hollow by polyaddition reaction[☆]

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Abstract

In 1996, the authors proposed a novel method to prepare micron-sized, hollow cross-linked polymer particles. This method is based on the self-assembling of phase separated polymer at interface with water, which was named SaPSeP method, formed by suspension polymerization of divinyl monomer in toluene droplet dissolving previously polystyrene. The SaPSeP method was developed to be applicable to polyaddition reaction system of epoxy resin with diamine. The presence of PS dissolving in epoxy/diamine/toluene droplets promotes the phase separation of the epoxy resin reacted with the diamine. The epoxy resin molecules tend to adsorb at the interface of the droplets. These points were accord with the required conditions for the preparation of hollow particle by the SaPSeP method. Cured epoxy resin particles having one hollow were successfully prepared by the polyaddition reaction in the dispersed system of Epikote 806/630/604, of which equivalent ratio was 5/4/1.

Keywords: Hollow particle; Polyaddition; Epoxy resin

1. Introduction

A lot of submicron-sized polymer emulsions prepared by emulsion polymerization have been used as films in many industrial fields, for example, in painting, printing and manufacturing. Moreover, in recent years attention is focused to apply them directly as particle. As one of them, polymer particles having hollow(s) in the inside have received much attention as a hinding or opacifying agent in coatings and molding compositions [1–4].

Recently, many researchers in polymer colloids are concentrating their attentions on the preparation of micron-sized, monodisperse polymer particles [5–9] because there are attractive applications in the biomedical field, microelectronics, and other areas. In order to prepare monodisperse polymer particles having more than 5-μm-size, we suggested a novel swelling method of seed polymer particles with a large amount of monomer which was named the ‘dynamic swelling method’ [10]. Moreover, the technique was developed to prepare about 5-μm-sized, monodisperse, cross-linked polymer particles having one hollow by seeded polymerization for highly swollen polystyrene (PS) particles [11], and the formation mechanism was suggested [12]. On the basis of the formation mechanism, in a previous work [13], hollow polymer particles were also prepared by suspension polymerization for divinylbenzene (DVB)/toluene droplets dissolving PS and benzoyl peroxide (BPO), though they were polydisperse. When the PS was not dissolved in the droplets, no hollow particles were obtained. There were certain minimum values of the PS content and its molecular weight to obtain the hollow particles. Poinescu and coworker reported [14] that polyvinylacetate worked as polymeric porogen [15–18] for the preparation of macroreticular particles (no hollow particles) by suspension copolymerization of styrene and DVB. However, in the preparation of the

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hollow particles, the PS dissolved in the DVB/toluene droplets was needed as not porogen but accelerator for the phase separation of poly(divinyl benzene) (PDVB) formed therein during the polymerization [19]. The phase separation in the early stage was first required point for the formation of the hollow structure. Since the viscosity in the droplet is low at the low conversion, the PDVB can move and adsorb at the interface of the droplet. Moreover, the kinds of polymers [20] and of its end groups [21], which had different polarities, dissolved in DVB/toluene droplets greatly affected the formation of the hollow structure. Preferential adsorption of PDVB at the interface of the droplets over PS previously dissolved therein was second required point for the formation of the hollow structure. That is, the formation of the hollow structure is based on the self-assembling of phase separated polymer at the interface of the droplet. The method is named the self-assembling of phase separated polymer (SaPSeP) method. The method is applicable not only to the preparation of hollow particles but also to the encapsulation of chemicals. We have succeeded in encapsulating hinokitiol, which is abstracted from natural coniferous woods, and has aromaticity, antibacterial activity and mildew resistance [22]. However, the rate of the radical polymerization obviously decreased compared with that in the absence of hinokitiol, because of high chain transfer reaction to hinokitiol.

In this article, in order to clarify the formation mechanism of hollow particles by the SaPSeP method in more detail, and to develop it to polyaddition reaction system of epoxy resin with diamine where there is no problem of the chain transfer reaction in the radical polymerization, cured epoxy resin particles having hollow structure will be prepared.

2. Experimental

2.1. Materials

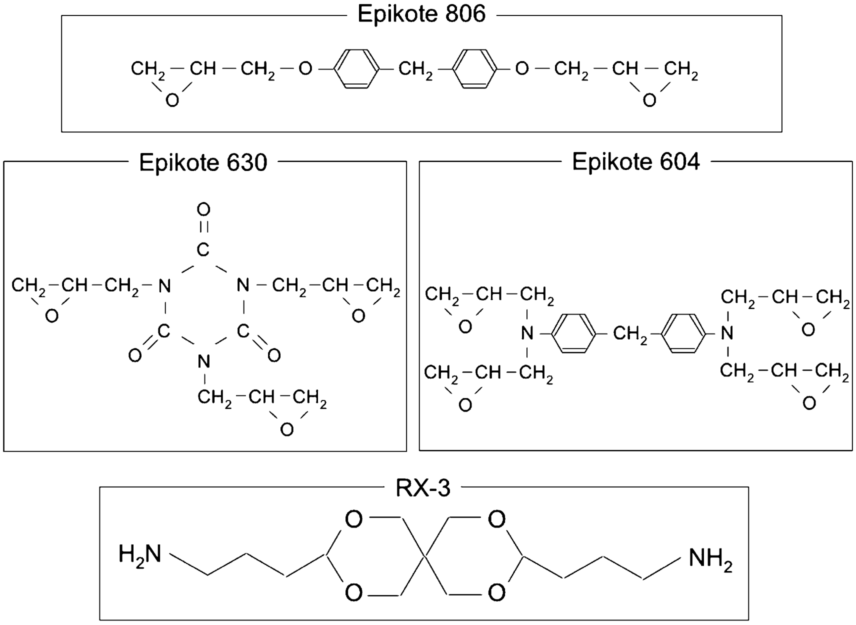
Epoxy resins (Epikote 604, 630, 806) and curing agent (Epomate RX-3) were supplied by Japan Epoxy Resins Co., Ltd, Tokyo, Japan. Epikote 806, 630, and 604 were, respectively, bisphenol F-, triglycidyl isocyanurate-, and tetraglycidyl diaminodiphenylmethane-typed epoxy resins as shown in Scheme 1. Epomate RX-3 consists mainly of 3,9-dipropanamine-2.4.8.10-tetraoxaspirodundecane. PS was prepared by solution polymerization with 2,2′-azobisisobuthyronitrile as initiator. The weight- and number-average molecular weights were, respectively, 1.5×10^5 and 8.2×10^4. Deionized water was distilled with a Pyrex distillator. Poly(vinyl alcohol) (PVA) used as a colloidal stabilizer was supplied by Nippon Synthetic Chemical Ind. Co., Ltd, Osaka, Japan (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%). The other materials were used as received.

2.2. Measurement of transmittance

The polyaddition reaction of Epikote 806 and RX-3 in toluene (631/31/941, w/w/w) dissolving PS or poly(methyl methacryrate) (PMMA) (2.4 wt%) was carried out in a spectrophotometer cell at room temperature. The transmittance of the solution was measured by a SHIMAZDU UV-2500 spectrophotometer at 550 nm.

2.3. Measurement of interfacial tension

The interfacial tensions between water and the solution of Epikote 806, RX-3 and toluene (631/31/941, w/w/w)



Scheme 1.

were measured by the du Noüy ring method at room temperature with a Shimadzu DN surface tensiometer. The measurement was carried out with a platinum ring (diameter, 19 mm).

2.4. Polyaddtion reaction in suspension system

Homogeneous solutions of epoxy resin, RX-3, toluene (250 mg), and PS (5–125 mg) were mixed with 0.33 wt% PVA aqueous solution (15 g), and stirred vigorously by NISSEI ABM-2 homogenizer at 1000 rpm for 2 min in glass cylindrical reactors. Polyaddtion reactions in suspension system were carried out at 70 °C for 24 h in sealed glass tubes. The tubes were horizontally shaken at 80 cycles/min (3-cm strokes). Particles were observed with a Nikon MICROPHOT-FXA optical microscope and a Hitachi S-2500 scanning electron microscope (SEM).

2.5. Ultrathin cross sections

The morphology of the cured epoxy resin particles was estimated with a Hitach H-7500 transmittance electron microscopic (TEM) observation of their ultrathin cross sections. Each cross section was prepared as follows. The dried particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO_4 solution, and then dispersed in epoxy matrix, cured at room temperature for 24 h, and microtomed.

3. Results and discussion

The key points of the SaPSeP method [19,21,23] for the preparation of hollow polymer particles by suspension polymerization of divinyl monomer in toluene droplets dissolving polymer, were phase separation of divinyl polymer in the early stage of the suspension polymerization and preferential adsorption of the separated polymer over PS to the interface of the droplets. In order to examine whether SaPSeP is applicable to polyaddition reaction system, a preliminary experiment on the phase separation in a polyaddition reaction system of epoxy resin with diamine as a curing agent was carried out in a homogeneous toluene solution.

Fig. 1 shows variations of transmittance of toluene solutions at 550 nm during the polyaddition reaction of epoxy resin (Epikote 806) and diamine (RX-3) (glycidyl group/amino group: 2/1, molar ratio) in the absence and presence of PS (M_w, 1.5×10^5) or PMMA (M_w, 2.4×10^5) at room temperature. In all cases, the transmittances of the solutions drastically decreased after certain times, which indicates the beginning of phase separation. The beginning times of the phase separation in the PS and PMMA-present systems were shorter than that (400 min) in the polymer-absent system. This satisfied the first required condition for the preparation of hollow particle by the SaPSeP method that the presence of dissolving polymer promotes the phase separation of the epoxy resin reacted with the diamine. The acceleration of phase separation by polymer previously dissolved in the droplet was already discussed thermodynamically in the radical polymerization system [19]. In the article, the experimental results were compared with bimodal curves calculated from the Flory–Huggins theory, which indicates that dissolved polymer and cross-linking reaction promote the phase separation. Strangely, the PS-present system became clear after the first turbid (100 min) and then the system became turbid again (200 min). On the other hand, in the PMMA-present system, such a phenomenon was not observed. The phenomenon was interesting, however, that is special for the PS-present system. This phenomenon might be based on the phase inversion in the heterogeneous structure formed by phase separation that proceeded with the polyaddition reaction of epoxy resin with diamine. Similar phenomenon was observed in the phase inversion during polymerization in the production of high impact PS [24]. Because the phenomenon essentially seems to have no relation to the preparation of hollow

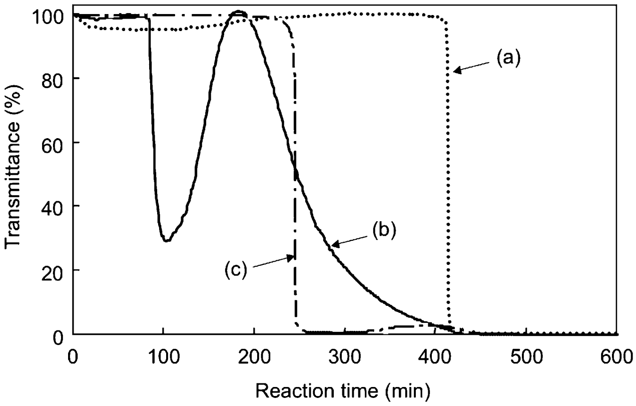


Fig. 1. Transmittances of toluene solutions at 550 nm as a function of polyaddition reaction time of Epikote 806 and RX-3 in the absence (a) and presence of PS (b) or PMMA (c) at room temperature.

Table 1
Interfacial tension between water and various solutions

Ingredient	Reaction time[a]	Interfacial tension (mN/m)
Toluene	–	36.0
Toluene, PS[b]	–	31.0
Toluene, PMMA[b]	–	18.4
Epikote 806, RX-3, toluene	–	7.7
Epikote 806, RX-3, toluene, PS	0 h	7.4
Epikote 806, RX-3, toluene, PS	1 h	6.8
Epikote 806, RX-3, toluene, PS	3 h	6.2

Measured by the du Noüy ring method at room temperature.

[a] Kept at room temperature.

[b] 0.01 wt% solution.

polymer particles, a detail discussion will be done elsewhere.

Table 1 shows the interfacial tension between water and oil phase (epoxy resin, diamine, toluene and PS or PMMA) measured by the du Noüy ring method at room temperature. The interfacial tension was much lower than that between water and toluene or toluene dissolving the PS or PMMA. Moreover, the interfacial tension decreased with the measurement time. These results satisfy the second necessary condition for the preparation of hollow particle by the SaPSeP method that the epoxy resin molecules reacted with the diamine (cured epoxy resin microgels) adsorb preferentially over the dissolving polymers at the interface of the droplets. In the previous paper [20], in which the radical polymerization of DVB in toluene droplets was carried out, hollow polymer particles were not obtained in the PMMA-present system. The reason was that the PMMA preferentially adsorbed over the PDVB microgels at the interface of the droplets, which prevent the formation of cross-linked PDVB shell at the interface. This was supported from the experimental data that the interfacial tension between water and toluene dissolving PMMA was lower than that between water and toluene dissolving shell polymer (PDVB). Interfacial tension values shown in Table 1 indicates that the cured epoxy resin microgels preferentially adsorb over PMMA at the interface of droplets, which satisfy the second necessary condition of SaPSeP method. Actually, in the PMMA-present system, the formation of shell structure was confirmed (data omitted), though almost all of the hollow particles were collapsed because of weak shell strength [25]. These results support the mechanism of SaPSeP method.

Fig. 2 shows optical micrographs of the particles prepared by polyaddition reaction in Epikote 806/RX-3/toluene droplets in the absence or presence of PS listed in Table 2. In both cases, heterogeneous structure in the inside of particle was not observed at just after the reaction, because of similar refractive indexes between the reacted epoxy resin and toluene. In order to visualize it, a small amount of the dispersions were separately mixed with a large amount of methanol, which is miscible with water and toluene, and its refractive index is relatively different from that of epoxy resin. In the PS-absent system, no difference was observed before and after the treatment with methanol. The particles had non-spherical shape based on heterogeneity of crosslink [26–28] and shell was not observed in the inside. On the other hand, in the PS-present system, the particles had spherical shape and a shell structure was observed after the treatment with methanol. The formation of the shell was confirmed in the TEM observation of ultrathin cross section of the particles. In Fig. 2(d), a high contrast region was observed inside the shell. This seems to consist of PS that was precipitated by replacement form the toluene to methanol. Methanol is non-solvent for PS. These results indicate that the PS previously dissolved in the droplets is important for preparation of hollow particles by the polyaddition reaction system as well as the radical polymerization system of divinyl monomer [13]. The PS dissolved in the droplets was needed as accelerator for the phase separation of cured epoxy resin formed during the polyaddition reaction. Cured epoxy resin microgels separated in the early stage can move and adsorb at the interface of the droplet because of low viscosity in the droplet and its high hydrophilicity [29], resulting in cross-linked shell as capsule.

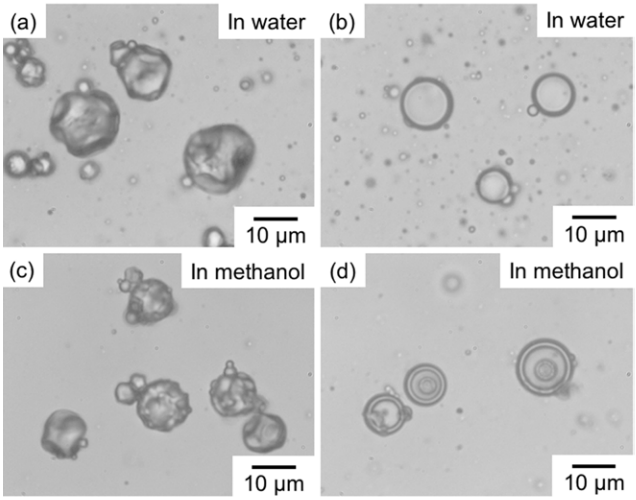


Fig. 2. Optical micrographs of epoxy resin particles prepared by polyaddition reaction in Epikote 806/RX-3/toluene droplets in the absence (a,c) or presence (b,d) of PS under the conditions listed in Table 2. A small amount of dispersions were separately mixed with a large amount of methanol (c,d).

As shown in Fig. 3, when toluene was removed from the dispersion by evaporation, the particles were transformed into a non-spherical shape. Such a phenomenon was already reported in the hollow PDVB particles prepared by the SaPSeP method [25]. The shell of the hollow particles was collapsed by the evaporation of toluene because the shell strength was not so high enough to maintain spherical shape.

Table 2
Recipes for the preparations of cured epoxy resin particles by polyaddition reaction in dispersion systems

Ingredients	No. 1	No. 2	No. 3
Epikote 806[a] (mg)	631	631	631
RX-3 (mg)	310	310	310
Toluene (mg)	941	941	941
PS (mg)	–	47	–
PMMA (mg)	–	–	47
PVA (mg)	47	47	47
Water (g)	10	10	10

70 °C; 24 h; shaking rate, 80 cycles/min (3-cm strokes). Abbreviations: PS, polystyrene; PMMA. Poly(methyl methacrylate); PVA, poly(vinyl alcohol); RX-3,3,9-dipropanamine-2,4,8,10-tetraoxaspiro[5,5]undecane.

[a] Diglycidyl ether of bisphenol-F epoxy resin (Japan Epoxy Resins Co., Ltd).

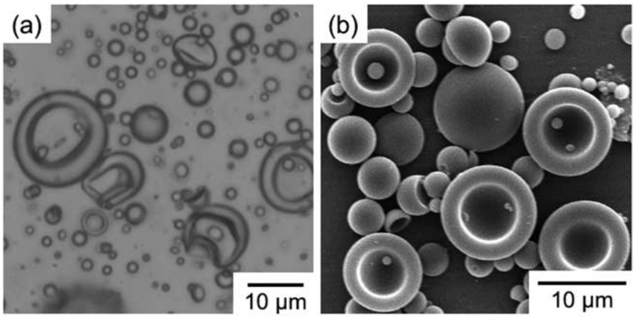


Fig. 3. An optical micrograph (a) and a SEM photograph (b) of the epoxy resin particles prepared by polyaddition reaction in Epikote 806/RX-3/PS/toluene droplets under the conditions of No. 2 listed in Table 2.

In order to maintain the spherical shape, the shell was strengthened by addition of tri- (Epikote 630) or/and tetra-functional (Epikote 604) epoxy resins.

Fig. 4 shows optical micrographs of epoxy resin particles prepared by polyaddition reaction in Epikote 806/630/RX-3/PS/toluene droplets under the conditions listed in Table 3. In all cases, the particles buckled though spherical shape had been observed before evaporation of toluene. Moreover, in order to promote the curing reaction, the reaction temperature was increased to 100 °C in the same composition. As a result, the particles still buckled after evaporation of toluene. The introduction of tri-functional epoxy resin was not so enough to maintain the hollow structure.

Figs. 5 and 6 show optical micrographs and SEM photographs of epoxy resin particles prepared by polyaddition reaction in Epikote 806/630/604/RX-3/toluene droplets having different compositions under the conditions listed in Table 4, which were separately mixed with a large amount of methanol. In Epikote 806/630/604 systems of 7/2/1 and 3/6/1 equivalent ratios, the particles were observed to be non-spherical. On the other hand, at the equivalent ratio of 5/4/1 the spherical polymer particles having shell were observed and maintained the spherical shape after the evaporation of toluene. This may be based on the high cross-linking density in the shell by introduction of tetra-functional epoxy resin, which was enough to maintain the spherical shape. However, the particles in the 3/6/1 system were not spherical. Because the solubility of Epikote 630 in water is high in comparison with Epikote 806 and 604, an increase in the ratio of Epikote 630 may inversely decrease the ratio of epoxy resin/diamine in the droplets. As the result, cross-linking density in the shell might be lower in the 3/6/1 system than in the 5/4/1 system.

Fig. 7 shows a TEM photograph of ultrathin cross sections of RuO_4-stained, cured Epikote 806/630/604 (5/4/1, equivalent ratio) particles. The thickness of shell was homogeneous, which indicates the particles had one hollow at the center. A very thin layer of high contrast was observed

Table 3
Recipes for the preparations of cured epoxy resin particles by polyaddition reaction in dispersion systems

Epikote 806/630 (equivalent ratio)	9/1	8/2	7/3
Epikote 806 (mg)	568	505	442
Epikote 630[a] (mg)	37	74	112
RX-3 (mg)	310	310	310
Toluene (mg)	915	889	864
PS (mg)	46	45	43
PVA (mg)	46	45	43
Water (g)	10	10	10

70 °C; 24 h; shaking rate, 80 cycles/min (3-cm strokes).

[a] 1,3,5-Triglycidyl isocyanurate (Japan Epoxy Resins Co., Ltd).

Table 4
Recipes for the preparations of cured epoxy resin particles by polyaddition reaction in dispersion systems

Epikote 806/630/604 (equivalent ratio)	7/2/1	5/4/1	3/6/1
Epikote 806 (mg)	442	316	180
Epikote 630 (mg)	74	149	223
Epikote 604[a] (mg)	45	45	45
RX-3 (mg)	310	310	310
Toluene (mg)	871	820	758
PS (mg)	43	41	38
PVA (mg)	87	82	77
Water (g)	10	10	10

70 °C; 24 h; shaking rate, 80 cycles/min (3-cm strokes).

[a] Tetraglycidyl diaminodiphenylmethane (Japan Epoxy Resins Co., Ltd).

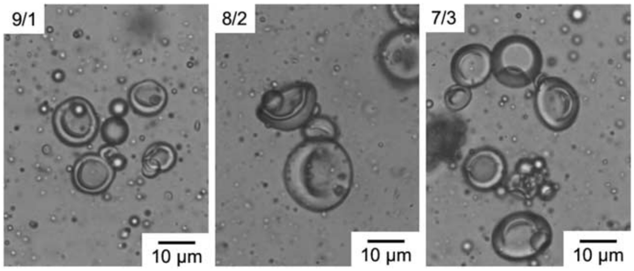


Fig. 4. Optical micrographs of epoxy resin particles prepared by polyaddition reaction in Epikote 806/630/RX-3/PS/toluene droplets under the conditions listed in Table 3. Ratios on the photographs indicate the equivalent ratios of Epikote 806/630.

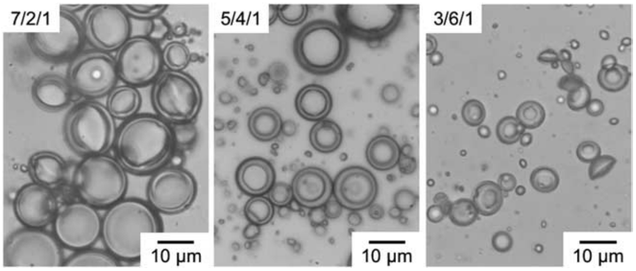


Fig. 5. Optical micrographs of epoxy resin particles prepared by polyaddition reaction in Epikote 806/630/604/RX-3/PS/toluene droplets under the conditions listed in Table 4, which were redispersed in methanol. Ratios on the photographs indicate the equivalent ratios of Epikote 806/630/604.

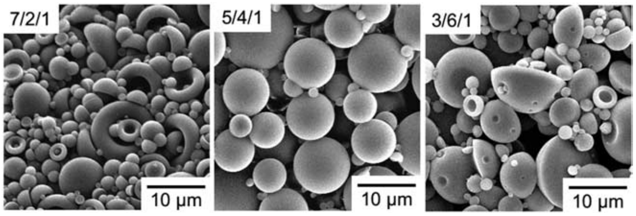


Fig. 6. SEM photographs of the epoxy resin particles prepared by polyaddition reaction in Epikote 806/630/604/RX-3/PS/toluene droplets under the conditions listed in Table 4. Ratios on the photographs indicate the equivalent ratios of Epikote 806/630/604.

around the inner wall of the hollow. This consisted of PS that previously dissolved in the droplets.

4. Conclusions

From above results, it is concluded that the SaPSeP method can be applied to the polyaddition reaction in the dispersed system. The polyaddition reaction system satisfied the required conditions for the preparation of hollow particle by the SaPSeP method. In actual, in the Epikote 806/630/604 system, cured epoxy resin particles having one hollow at the center were successfully prepared after evaporation of toluene.

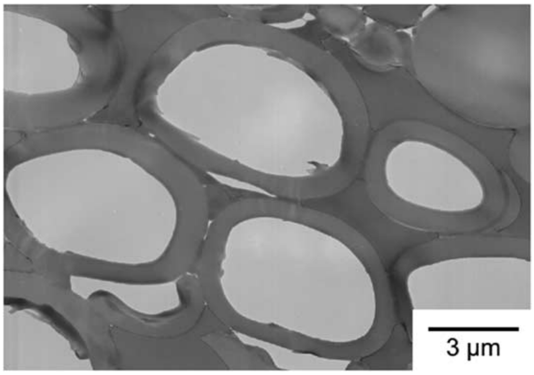


Fig. 7. A TEM photograph of ultrathin cross sections of RuO_4-stained cured Epikote 806/630/604 (5/4/1, equivalent ratio) particles.

Acknowledgements

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