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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

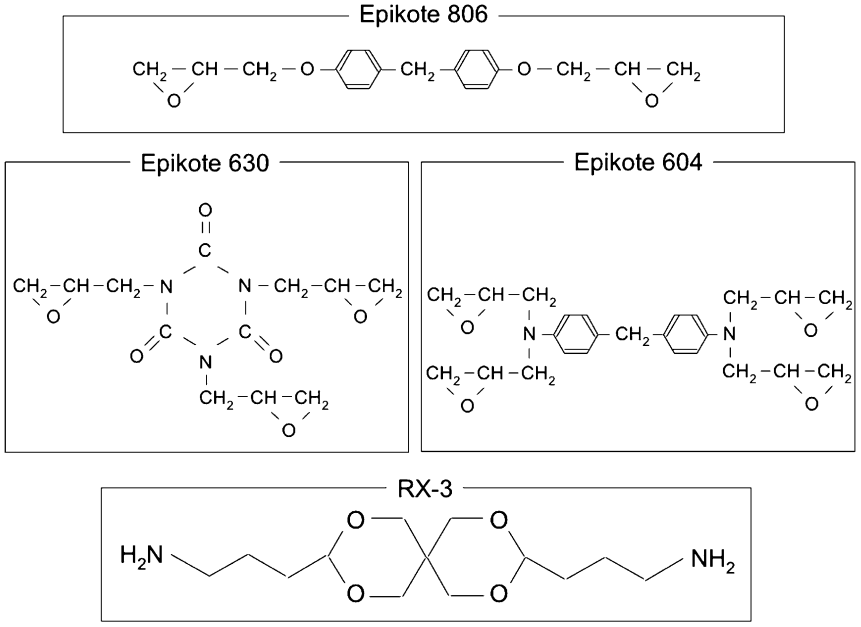
Epoxy resins (Epikote 604, 630, 806) and curing agent (Epomate RX-3) were supplied by Japan Epoxy Resins Co., Ltd, Tokyo, Japan. Epikote 806, 630, and 604 were, respectively, bisphenol F-, triglycidyl isocyanurate-, and tetraglycidyl diaminodiphenylmethane-typed epoxy resins as shown in Scheme 1. Epomate 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.