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Material properties

Preparation of poly(methyl methacrylate) and polystyrene-composite-filled porous epoxy microparticles via in-situ suspension polymerization

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ABSTRACT

Both poly(methyl methacrylate) (PMMA) and polystyrene (PS) were synthesized through suspension polymerization, and porous epoxy microparticles (PEMP) were incorporated *in-situ* during polymerization. It was discovered that the hollow structure available in the PEMP was able to successfully establish an interlocking mechanism with the PMMA and PS matrices, as revealed by SEM micrographs. Due to the epoxy structures, the PEMP could trigger MMA polymerization of two species of PMMA (different in molecular weight), which resided in two different locations, i.e., the outer and inner portions of the PEMP. In contrast, only one species of PS was obtained after polymerization. The glass transition temperature (T_g) for PMMA and PS decreased to approximately 14 and 8 °C, respectively. The thermal stabilities of the resultant composite beads were improved by approximately 56 °C for PMMA-PEMP and by 30 °C for PS-PEMP. It was hypothesized that the unique microstructure of the newly discovered and novel particles was responsible for enhancing the thermal properties of the composites.

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1. Introduction

Hybridization of two or more components is quite useful and attractive for enhancing polymer properties, such as mechanical properties, thermal stability and solvent resistance. A modification mechanism is usually exploited by virtue of *in-situ* phase separation of two or more multi-phase polymers. In the case of two multi-phase polymers, the resultant composite would be in the form of initially dispersed polymer particles as a filler in a second continuous polymer matrix [1–8]. The introduction of epoxy resin particles into a thermoplastic matrix can be generally accomplished by *in-situ* polymerization and curing of the epoxy phase. However, this process is not simple, and the morphology of the obtained composite materials is

unpredictable and strongly dependent on the chemically-induced phase separation. Therefore, it is difficult to control the process and to obtain a stable morphology.

The addition of a filler and pre-formed core-shell particles in polymers during *in-situ* polymerization of a monomer is commonly exploited to partially surmount this difficulty [9–14]. The morphology and properties of core-shell particles can be tuned in advance so that a more controlled composite can be prepared with a predetermined morphology that is independent of the curing process. The idea of synthesizing a core-shell or ready-made particles has been investigated by several researchers [15,16].

In this investigation, we incorporated porous epoxy particles with multiple, micron-sized holes into poly(methyl methacrylate) (PMMA) or polystyrene (PS) via suspension polymerization. These novel porous epoxy particles (PEMP) were prepared using an advanced aqueous method, and their morphology comprise multiple, micro-holes on the surface [17]. In this study, the experiment was focused on

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assessing the effect of PEMP on methyl methacrylate (as a polar monomer) and styrene (as a relatively nonpolar monomer) polymerization, and this effect was evaluated using gel permeation chromatography (GPC). The thermal properties of the obtained PMMA-PEMP and PS-PEMP composites were analyzed using DSC and TGA. The results of these thermal analyses were used to indirectly assess the contribution of the PEMP microstructure to the polymerization process and the enhancement of the thermal stability imparted by the developed microparticles.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) and styrene were purchased from Wako Pure Chemical Industries, Ltd. and purified by washing with aqueous sodium hydroxide solution and deionized water, followed by distillation under reduced pressure. Poly(vinyl alcohol) (PVA) 87–89% hydrolyzed was purchased from Sigma-Aldrich and used as a dispersing agent during polymerization. Benzoyl peroxide (BPO) (Acros Organics) was purified through precipitation using methanol from a chloroform solution, and 2,2-azobisisobutyronitrile (AIBN) (Wako Pure Chemical Industries, Ltd.) was purified by recrystallization in methanol. Distilled water was used in all the polymerization procedures. The porous epoxy microparticles (PEMP) were prepared in-house [17]. To provide a good comparison, two types of fillers were prepared and used: porous epoxy micro particles with CaCO_3 (PEMPCa) and without CaCO_3 (PEMP) as shown in Fig. 1.

2.2. Suspension polymerization

A typical procedure for suspension polymerization of MMA in the presence of PEMP is described as follows. Distilled water and PVA were placed in a cylindrical, 500 ml, separable three-necked flask under argon. The mixture was stirred at 600 rpm, heated at 80 °C and then cooled to approximately 50 °C after dissolution of PVA (approximately 1 h). A mixture of MMA and initiators was prepared separately in a 100 ml beaker and then stirred until all of the initiators were completely dissolved in the MMA phase. PEMP filler was then added to the MMA-initiator mixture and further stirred for 30 min. The resultant MMA-PEMP mixture was placed in the reactor, and the mixture was stirred at 600 rpm and 90 °C for 7 h (Table 1). Next, the obtained PMMA-PEMP beads were filtered and then stirred in an excess amount of hot water overnight to remove the PVA. A cycle of filtering and washing was performed at least five times with hot water. The resulting beads were dried at 60 °C under vacuum. The same procedure was employed for the PS-PEMP system (Table 1).

2.3. Measurement

Scanning electron microscopy (SEM) was performed using a JEOL JSM-5600. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200 (SEIKO Instruments Inc.) with a heating rate of 10 °C/min in air. Differential scanning calorimetry (DSC) was implemented using a DSC

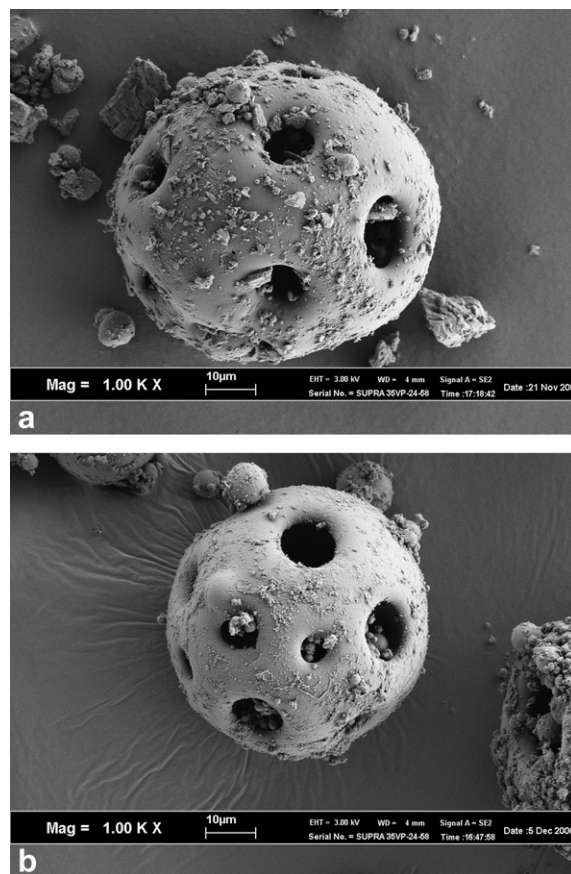


Fig. 1. SEM images of (a) PEMPCa and (b) PEMP.

6220 (SEIKO Instruments Inc.) with a heating rate of 10 °C/min in nitrogen flow. Powder X-ray diffraction patterns were taken using $\text{CuK}\alpha$ radiation with a Shimadzu XRD-600 at a scan speed of 1°/min. The molecular weights of the PMMA and PS components were determined by gel permeation chromatography (GPC), using a Model HLC8020 (Tosoh Ltd.) that was equipped with a GPC K804L column (Shodex) (CHCl_3 as an eluent, polystyrene calibration, at 40 °C). Fourier transform infrared spectroscopy (FTIR) was conducted using a Perkin Elmer system 2000 employing the KBr pellet method.

3. Results and discussion

3.1. Synthesis of polymer-PEMP composites by suspension polymerization

The polymerization conditions and particle size of the resultant polymer composite beads are shown in Table 1. The composite yield was almost 85% for all of the proposed recipes. In general, composite beads with PEMP were more yellowish and exhibited a similar color to that of a polyamide-cured epoxy system but with a larger size compared to composites with PEMPCa. The most yellowish composite beads were MEB and PSEAB for the PMMA and PS series, respectively. Composite beads that formed faster

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