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Preparation of Semi-interpenetrating Polymer Network of Silicon Rubber and Poly(methyl methylacrylate) Using Supercritical CO_2

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Abstract: The heterogeneous free-radical polymerization of methyl methylacrylate (MMA) and divinylbenzene (DVB) as cross-linker within supercritical carbon dioxide-swollen silicon rubber (SR) has been studied as an approach to preparing semi-interpenetrating polymer network (semi-IPN) of SR and poly(methyl methylacrylate) (PMMA). The SR/PMMA semi-IPNs were characterized by scanning electron microscopy (SEM) and dynamic mechanical analyzer (DMA).

Keywords: Supercritical CO_2, interpenetrating polymer network, silicon rubber, poly(methyl methylacrylate), polymerization.

It is known that SR is immiscible with PMMA. One possibility to combine the properties of these two polymers is to form IPNs[1,2]. Recently, supercritical (SC) CO_2 has been utilized to fabricate polymer composites[3]. This is because SC CO_2 can dissolve vinyl monomers and swell most polymers. Moreover, its solvent strength is continuously tunable by temperature or pressure. This provides the ability to control the degree of swelling in a polymer as well as the partitioning of small molecule penetrates between a swollen polymer and the fluid phase. All these factors are helpful to the production of polymer composites. In this work, vinyl monomer MMA, cross-linker DVB, and initiator benzoyl peroxide (BPO) dissolved in SC CO_2 were infused into CO_2-swollen SR substrate and polymerized within it at a higher temperature. The resulting SR/PMMA semi-IPNs were determined by SEM and DMA.

Silicon rubber films with a thickness of 1 mm were supplied by Beijing Plastic Factory. MMA produced by Tianjin Special Chemical Reagent Development Center (A. R. grade) and DVB supplied by ICI Co. (Japan) were washed successively with 5% NaOH aqueous solution and deionized water until it was free from alkali, dried over anhydrous Na_2SO_4 for 24 hrs. BPO supplied by Beijing Jinlong Chemical Reagent Company was used after recrystallization in chloroform. CO_2 with a purity of 99.95% was provided by Huanxin Gas Co. The apparatus and procedures were similar to those used in our previous work to prepare the PS/PET blends[4]. The main difference was that a cross-linker was involved in this work. In a typical experiment, 2.0 g SR films were sealed in a stainless steel cell of 30 mL together with 1.5 mL BPO/MMA/DVB solution

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(0.3 mol% BPO and 5 wt% DVB on the basis of MMA). The cell was then put into a water bath of 35.0°C, and CO_2 was charged into the cell to 12 MPa. After the system was equilibrated for a desired time, the cell was drained, pressurized with N_2, and then heated to 120°C to initiate polymerization and crosslinking of MMA and DVB within SR substrate for 6 hours. The SR/PMMA semi-IPN was obtained. The composition of semi-IPNs was determined gravimetrically. The mass uptake of SR specimens increases with time initially, and is independent of soaking time after 5 hours. At equilibrium condition, the resulting semi-IPN contains 25 wt% PMMA.

The fracture topography of the fractured specimen at the liquid nitrogen temperature was studied using SEM (s-530). The SEM micrographs are shown in **Figure 1**. It is clear that the PMMA phase is uniformly dispersed and the domain diameter of the dispersed PMMA phase is much less than 1 μm. The dynamic mechanical properties of SR/PMMA semi-IPNs were examined using a dynamic mechanical analyzer (Perkin Elmer DMA-7). The mode of force loading was three-point bending. The testing frequency, heating rate, and temperature scanning range were 1 Hz, 10°C/min, and -150°C-150°C, respectively. The variation of the storage modulus (G') of virgin SR and the SR/PMMA semi-IPN (75/25) with temperature is shown in **Figure 2**, which indicates that the storage modulus of the semi-IPN is much higher at the higher temperatures.

Figure 1 SEM of SR/PMMA semi-IPN (75/25)

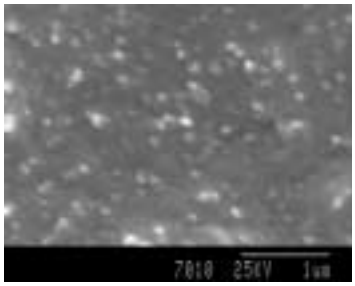
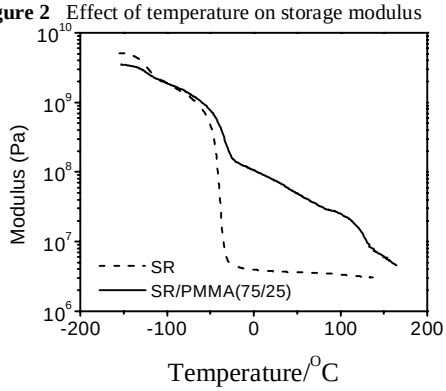


Figure 2 Effect of temperature on storage modulus



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