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Polymerization of Styrene in Supercritical CO_2-swollen Poly(ethylene terephthlate)

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Abstract: Polystyrene/Poly(ethylene terephthlate) (PET) blends have been prepared by the heterogeneous free-radical polymerization of styrene within supercritical carbon dioxide-swollen PET substrates. Composition of the blends and the average molecular weight of polystyrene in the blends can be controlled by equilibration time and reaction condition.

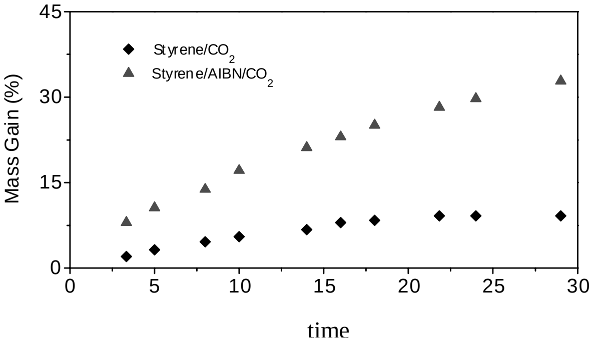
Keywords: Supercritical CO_2,, PET, styrene, impregnation, polymerization.

Supercritical fluids(SCFs) have many features, such as high compressibility, high diffusivity and low viscosity, which make them attractive for many industrial processes. Supercritical (SC) CO_2 is the most popular because it is non-toxic, non-flammable, and easy to obtain and has a near-ambient critical temperature. SC CO_2 can swell glassy polymers[1]. Additives in the SC CO_2 can diffuse into the swollen polymer and the CO_2 can be removed completely on depressurization, leaving most additives in the polymer. Thus solvent-free impregnation of additives can be achieved. If additives are monomers and initiator existing in the system, the monomer polymerizes in the matrix polymer, which is a new route to make polymer composites[2]. In this work, polystyrene/PET blends were produced on the basis of this principle.

Experimental The experimental apparatus consisted mainly of a high-pressure reactor of 50 ml, a circulation pump, and a constant temperature air bath. In a typical experiment, PET film with a thickness of 0.3 mm was placed in the high-pressure reactor. The temperature of the air bath was controlled at 35°C. Desired amount of styrene and CO_2 was charged into the system until the pressure reached 105 bar. The circulation pump was started. The concentration of styrene was controlled to be 0.4 mol/L which contained 0.3 wt% initiator 2,2'-Azobisisobutyronitrile (AIBN). The styrene and AIBN could dissolve into CO_2. At same time, the CO_2 swelled the polymer, which allowed styrene and AIBN molecules to diffuse into the polymer. The fluid in the system was vented after suitable equilibrating time. The mass of styrene in PET was determined.

Weight percent of styrene in PET Figure 1 gives dependence of the weight percent of styrene (wt%) in PET on equilibration time. Two interesting conclusions can be obtained from the figure. First, the wt% of styrene in PET is much higher when AIBN exists in the system. Second, when there is no AIBN in the system, the wt% increases

Figure 1 Dependence of weight percent of styrene in PET on equilibration time



with equilibration time(t) for t<22 hours, and then becomes independent of equilibration time(t). The wt%, however, increases monotonously with t in the presence of AIBN. The main reason is that polymerization of styrene occurs in the presence of AIBN, although the temperature is low (35°C). The styrene oligomers in PET were extracted by toluene and the average molecular weights were up to 10400 determined by viscosity method. Without AIBN, the styrene is adsorbed in PET and thus equilibrium can be reached.

Molecular weight of polystyrene in PET PET impregnated with styrene oligomers and AIBN obtained from the above procedures was put into a high-pressure cell. The oligomers were allowed to polymerize within PET substrates at 70°C for 11 hours under the protection of N_2. PET/polystyrene(PS) blends were obtained. The PS was extracted using toluene and the average molecular weights were determined by viscosity method. The results are listed in **Table 1**. The results show that the molecular weight increases with the wt% of PS in PET.

Table 1. Average molecular weight (Mη) of the PS in the blends

wt% of PS	10.614	17.154	23.025	29.742
AMW(Mη)	97,182	127,615	144,632	166,177

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