Novel Processing Technology of Nanocomposites Using supercritical fluids

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Introduction

The increasing interest during the last few decades in decreasing the environmental effects of the release of organic compounds and aqueous waste has motivated the development of polymerization in supercritical fluids(SCF) [1,2]. However, the advantages of using SCF are not only environmental but also chemical and economical. One of the most practical advantages is a solvent-free polymer product by simply venting the solvent. It eliminates the need for energy intensive drying and devolatilization processes. Moreover there is no chain transfer to CO_2 in free radical polymerizations. Most studies focus on supercritical carbon dioxide, which is a solvent environmentally harmless, accessible and inexpensive, non-toxic and non-flammable. It has been noted that CO_2 behaves like hydrocarbons with respect to its capability to dissolve small molecules, and thus many monomers exhibit good solubility in CO_2 [3]. However, it is a rather poor solvent for most high molecular weight polymers [4, 5] except for some fluoropolymers and silicones. In consequence, We must have chosen any other supercritical fluids because carbon dioxide cannot dissolve polyester polymers. Chlorodifluoromethane(HCFC-22) is a good solvent which has critical point (Tc=96.2℃, Pc=49.7bar). Recently, the study of polymerization or study of creating particle using supercritical fluids has been progressed. But, the study of polyester polymerization and the study of making composites with nanoparticles such as CNT using RESS process have not been advanced.

In this paper, the polyester/clay nanocomposites using SCF process has been studied. And the CNT or clay nanocomposites which have great physical and electrical properties have been progressed.

Experimental

1. Materials

In this study, dichloromethane (99.8% CH_2Cl_2, Aldrich) was used for synthesizing cyclic ester oligomers as a solvent. Terephthaloyl chloride (99% $C_6H_4(COCl)_2$, TCI), 1,4-butanediol(99% $HO(CH_2)_4OH$, Aldrich), ethylene glycol(99.8% $HOCH_2CH_2OH$, Aldrich) were used as a monomer. Diazabicyclo[2,2,2]-octane (98% $C_6H_{12}N_2$, Aldrich), triethylamine (99.5% $(C_2H_5)_3N$,Aldrich) were used as a catalyst. Hydrochloric acid(35% HCl, Daejung) was used for washing. And To remove linear oligomers from synthesized cyclic oligomers, we used Celite® 521 (95% SiO_2, Aldrich).

2. Synthesis of Cyclic Ester Oligomers

One liter of dry CH_2Cl_2 (< 20ppm water) and 0.57 mol of triethylamine (78.3ml) and 13.3 mmol of 1,4-diazabicyclo [2,2,2] octane (DABCO) (1.49g) were filled in the 2L reactor. The 1,4-butandiol (24g ; 0.27 mol) and tetraphthaloyl chloride (TPC) was added using a peristaltic pump. After about 20min, deionized water was added and the reaction was completely stopped. And NH_4OH (10ml) was added.

3. Polymerization Procedure in Supercritical Chlorodifluoromethane

Polymerization was conducted in a 50mL stainless steel high-pressure cell equipped with a magnetic stirring bar and an electrically heating mantle. Butylene terephthalate cyclic oligomer(0.2g), cyclic stannoxane(0.01g), and clay(30B) were added to the cell. The reactor heated to 50℃, and purged with nitrogen for 5 min. When the reactor was cooled to room temperature, it was evacuated for 2h using a liquid nitrogen cooled trap and then purged with nitrogen for an additional 10min. The cell was then disconnected from the nitrogen line, evacuated, and connected to the HCFC-22 feed system. The cell was filled with liquid HCFC-22 to 30 bar at 50℃ by using an air-driven gas compressor and then gradually heated to 110℃ to achieve a pressure 200 bar. Polymerization was allowed to proceed for the predetermined times.

4. Rapid Expansion of Supercritical Solution (RESS)

The rapid expansion of supercritical fluid solutions through a small nozzle produces an abrupt decrease in dissolving capacity of the solvent as it is transferred from a supercritical fluid state, having near liquid density, to a very low density phase after the expansion. This abrupt transition in solvent characteristics results in the nucleation and growth of any low-vapor-pressure solute species that were present in the solution prior to expansion. The solute products which are generated during RESS expansions can have a number of different forms, depending on specific RESS processing parameters.

5. Characterization

For MALDI-TOF (Matrix Assisted Laser Desorption Ionization Time of flight) measurement, the synthesized cyclic oligomers were dissolved by tetrahydrofuran(THF). And 2,5-dihydroxybenzoic acid was mixed. For H-NMR measurement, the cyclic oligomers were dissolved by $CDCL_3$ including tetramethylsilane 1v/v%. Using FT-IR, the nonexistence of the hydroxyl end group in the synthesized cyclic oligomers and cyclic stannoxane 1 was confirmed. For GPC test, the samples were dissolved using THF(0.5%w/v), and injected THF at 1 ㎖/min speed. DSC was used for measuring T_m of synthesized polymers. TAG was used for analyzing synthesized cyclic stannoxame 1 catalyst by increasing temperature from 50℃ to 400℃ at 10℃/min speed. Capillary viscometer was used for measuring the viscosity molecular weight using a phenol and tetrachloroethane (60:40) mixture.

Results

The cyclic butylene terephthalate oligomers were successfully synthesized. The composition of butylenes terephthalate cyclic oligomers was 51.2% of dimer, 28.1% of trimer, 7.9% of tetramer, 8% of pentamer and 4.8% of hexamer. MALDI-TOF spectrum and H-NMR and FT-IR spectrum of butylenes terephthalate cyclic oligomer show sucessful synthesis of cyclic oligomer. Figure 1 shows FT-IR of BTC oligomer. Using there BTC oligomers, we polymerize the polybutylene terephthalate under the melt condition and the supercritical condition. PBT/clay nanocomposite from melt polymerization shows the molecular weight over 30,000. Figure 2 shows DSC of PBT polymerized from supercritical fluid process.

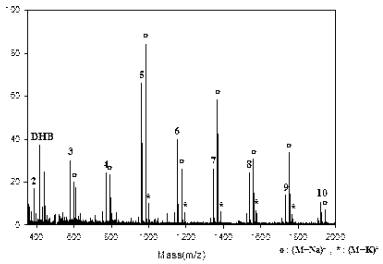

Figure 1. MALDI-TOF spectrum of BTC oligomer

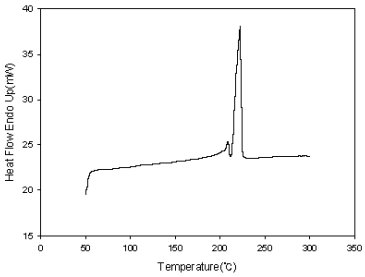

Figure 2. DSC of polymerized PBT from SCF process.

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