Preparation of PSAN/FMMT nanocomposites by in situ intercalative polymerization in supercritical carbon dioxide

Qingzhi Dong and Jing Wang
Shanghai Key Laboratory of Advanced Polymeric Materials,
Key Laboratory for Ultrafine Materials of Ministry of Education,
School of Materials Science and Engineering,
East China University of Science & Technology
Room 225, 1st Lab Building, No.130, Meilong Rd
Shanghai 200237

ABSTRACT

Dispersion copolymerization of styrene-acrylonitrile (SAN) and fluorinated montmorillonite (FMMT) had been successfully performed in supercritical carbon dioxide. The effects of the different stabilizer in the polymerization were examined respectively. In this study, the intercalation result of PSAN-FMMT was characterized by XRD, SEM, TEM and TGA were performed to demonstrate the thermal stability of the nanocomposites.

1. INTRODUCTION

As we know, supercritical carbon dioxide has been used as environmentally friendly solvent for materials synthesis because of its relatively chemical characteristics [1]. In fact, $SCCO_2$ could only be regarded as a poor solvent for most hydrocarbon polymers. So an effective amphiphilic stabilizer must be employed in the polymerization [2]. Recently, the $SCCO_2$ also was applied in polymer/clay nanocomposites synthesis due to its diffusivity which makes it penetrate the platelet galleries easily. So $SCCO_2$ is expected to show more advantages on the preparation of polymer nanocomposites.

This paper reported a new way to prepare PSAN/FMMT nanocomposites with mixed surfactants in $SCCO_2$ by using poly(styrene-r-acrylonitrile)-b-poly(1,1,2,2-tetrahydro perfluorooctyl methacrylate) (PSAN-b-PFOMA) as the synthesis system stabilizer, and using perfluoroalkyl-sulfonyl quaternary ammonium iodides (FCAI), not only as the surfactant to modified the clay, but also as the guest stabilizer of the system.

2. EXPERIMENTAL

2.1 Instruments

Rigaku diffractometer (D/MAX 2550 VB/PC), transmission electron microscopy (TEM)(JEOL JEM-2010) and scanning electron microscope (SEM)(JSM-6360LV) were used to study the samples. Thermogravimetric analysis (TGA) was carried out using a TA model 2050 TGA instrument at a heating rate of 10°C /min from room temperature to 800°C under nitrogen atmosphere.

2.2 Synthesis and modification

Diblock copolymer consisting of PSAN and PFOMA (PSAN-b-PFOMA) was synthesized via atom transfer radical polymerization (ATRP). Fluorinated montmorillonite (FMMT) were prepared by a cation-exchange reaction between the sodium cations of NaMMT (CEC=110mmol/100g) and FCAI. Polymerizations were conducted in SCCO2 in a 48mL stainless steel autoclave equipped with a stirring bar.

3. CHARACTERIZATION

3.1 XRD patterns of PSAN-FMMT with different FMMT loadings

Five different FMMT concentration products were synthesized. The product PSAN/FMMT3 represented there was 3% FMMT weight loadings to the system.

Figure 1 shows the XRD diffraction patterns of PSAN/FMMT with different FMMT loadings. There is a lack of diffraction peak as the FMMT loading is low, which indicates that the layered silicates had been exfoliated completely. Even if FMMT loading is increased to 5wt% or 10wt%, the XRD patterns show relatively weaker peaks at lower 2θ angle, which suggest the composites with partially exfoliated FMMT are obtained.

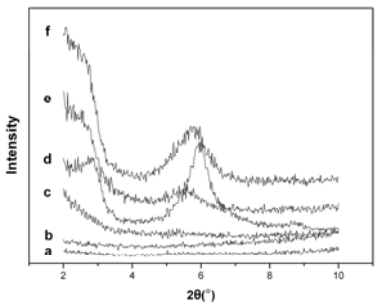

Figure 1. XRD patterns of the different FMMT contents nanocomposites (a) PSAN/FMMT1.5 (b) PSAN/FMMT3 (c) PSAN/FMMT5 (d) FMMT (e) PSAN/FMMT10 (f) PSAN/FMMT15

3.2 SEM analysis of PSAN-FMMT with different FMMT loadings

Figure 2 shows the scattered FMMT layers with different FMMT loadings. There are exfoliated FMMT platelets dispersing in the composite as 3wt% FMMT adding in the monomer. With the FMMT contents increasing, there are more unintercalated layers exist in the composite. Such corresponds to the result according to the XRD patterns.

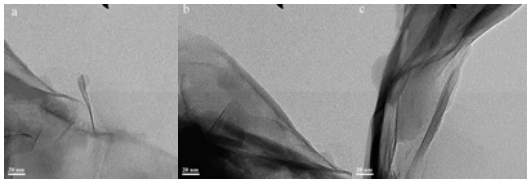

Figure 2. TEM micrograph of PSAN/FMMT (a) PSAN/FMMT3 (b) PSAN/FMMT5 (c) PSAN/FMMT10

Correspondence to qzdong@ecust.edu.cn

3.3 Thermal property of PSAN/FMMT with different FMMT loadings

Figure 3 shows the TGA curves of PSAN/FMMT with different FMMT loadings. It is obvious concluded that with the increasing of the FMMT loadings, the total thermal weight loss and the thermal degradation rate is gradually reduced. When more FMMT platelets are exfoliated and highly dispersed, the nanocomposite exhibits more excellent thermal stability.

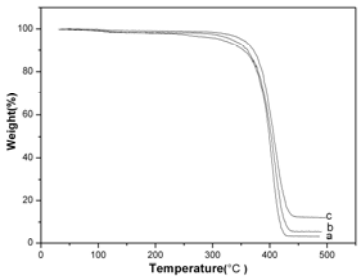

Fig 3. The TGA curves of the products containing different FMMT contents (a) PSAN/FMMT3 (b) PSAN/FMMT5 (c) PSAN/FMMT10

3.4 XRD patterns of PSAN-FMMT with different stabilizer contents

Polymerizations were conducted at three different concentration of stabilizer. Each had different stabilizer content to the monomers, and the product PSAN/Stab5 represented there was 5% stabilizer weight contents existed in the reaction. Figure 4 shows the XRD diffraction patterns of PSAN-FMMT with different stabilizer contents. 10wt% FMMT loading was exited in the reaction system. When the stabilizer content is 0wt% or 5wt% to monomer, there are diffraction peaks for the composites which are similar to those of the FMMT. But when the stabilizer content is 10wt%, the XRD patterns show relatively weaker diffraction peaks at lower 2θ angle, which suggest the FMMT are partially exfoliated because of the increasing of the stabilizer content.

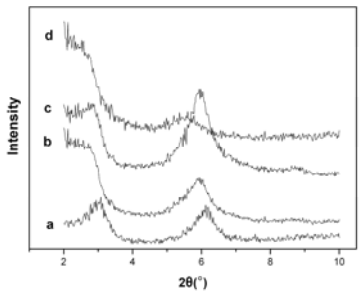

Figure 4. XRD patterns of the different stabilizer contents nanocomposites (a) PSAN/ Stab0 (b) PSAN/ Stab5 (c) FMMT (d) PSAN/ Stab10

3.5 Thermal property of PSAN-FMMT with different stabilizer contents

Figure 5 show the TGA curve with different stabilizer contents. The figure shows that PSAN/Stab10 has better thermal stability. When no stabilizer was in the system, the thermal degradation was rapid, and the weight of the degradation residues was higher than the others because of the low yield. The stabilizer showed the excellent effect on polymerization and exfoliating of the FMMT layers which improved the thermal properties of the nanocomposite.

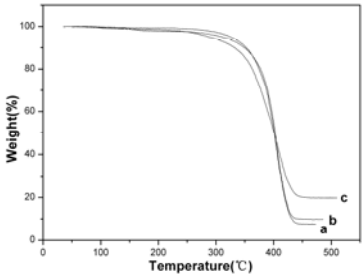

Figure 5. The TGA curves of the products containing different stabilizer contents (a) PSAN/Stab10 (b) PSAN/Stab5 (c) PSAN/Stab0

3.6 SEM analysis of PSAN-FMMT with different stabilizer contents

The morphology of PSAN-FMMT particles synthesized by dispersion polymerization could be observed directly by SEM photos. The figure 6 shows the particles with different stabilizer contents. With the increasing of stabilizer contents, the micelles formed by stabilizer supply more loci for dispersion polymerization and the particles present more small and fine sphericity.

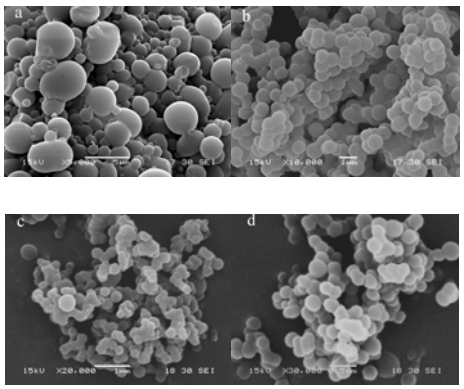

Figure 6. The SEM micrograph of PSAN/Stab

(a)PSAN/Stab0 (b) PSAN/Stab5 (c) PSAN/Stab10 (d) PSAN/Stab15

4. RESULTS

The blending system of stabilizer and fluorinate montmorillonite was successfully employed to synthesize PSAN-FMMT nanocomposites in $SCCO_2$. Up to 5 w/w% FMMT could be completely exfoliated during the copolymerization, and increasing PSAN-b-PFOMA content was favorable to the exfoliating of the FMMT interclayers and the nanocomposites polymerization. The effective impregnation, disaggregation and delamination of FMMT did positive effects to the thermal stability of the composites.

5. REFERENCES

1. Span, R., Wagner, W., "A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa." *J. Phys. Chem. Ref. Data.*, 5(1996): 1509-1596.

2. Desimone, J. M., Maury, E. E. & Menceloglu, Y., "Dispersion polymerization in supercritical carbon dioxide." *Science*, 265(1994): 356-359.