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Preparation of the Thermoplastic Starch/Montmorillonite Nanocomposites by Melt-intercalation

Ming Fu HUANG, Jiu Gao YU*, Xiao Fei MA

School of Science, Tianjin University, Tianjin 300072

Abstract: In this paper, the conception of melt-intercalation was introduced into the natural polymer field, and the thermoplastic starch/ethanolamine-activated montmorillonite (TPS/EMMT) nanocomposites were prepared by extruding the composites of EMMT and TPS, plasticized with ethanolamine/formamide. Wide angle X-ray diffraction (WAXD) and transmission electron microscope (TEM) revealed that TPS was intercalated into the layers of EMMT successfully and formed the intercalation nanocomposites with EMMT. When EMMT content was wt.10%, the mechanical testing indicated that the tensile stress of the nanocomposites reached 9.69 MPa, and the tensile strain reached 74.07%, Youngs modulus increased from the 47.23 MPa of TPS to 184.11 MPa of TPS/EMMT nanocomposites, and breaking energy increased from 1.34 N·m to 2.15 N·m after they had been stored at RH25% for 14 days.

Keywords: Thermoplastic starch, montmorillonite, nanocomposites, ethanolamine.

In last decade, the polymer/montmorillonite nanocomposites developed rapidly, and with the methods of polymer intercalation and intercalative polymerization, resolved the dispersion and interface problems in the preparation of polymer nanocomposites[1]. Currently, the matrixes of nanocomposities were mainly the synthesized polymers, such as polyolefin, polyamide and polyester[2~4], however the study on the natural polymers was few. Thermoplastic starch is a biodegradable material based on starch, an inexpensive and renewable natural polysaccharide, which has been widely investigated as the substitute of petroleum-derived plastics for the increasing environment and resources problems resulted from petroleum-derived plastics[5].

In this paper, EMMT was activated using ethanolamine, TPS was plasticized using the mixture of formamide and ethanolamine, and the TPS/EMMT nanocomposites were made by the method of melt-intercalation. The structure characterization and properties testing were performed by the method of WAXD, TEM and mechanical testing.

Experimental

The activation of montmorillonite: 1.462 g ethanolamine and 2.4 mL sulfuric acid (98%) were added into 450 mL water at 80℃ in turn. The gained solution was slowly added into 250 mL water solution containing 20 g MMT. The mixture was stirred at 80℃ for

* E-mail: mfhuang@21cn.com

3 h, then dried and cooled to room temperature. The activated MMT was gained after filtration, washed with water, dried, then ground.

The preparation of TPS/EMMT nanocomposities: formamide and ethanolamine was mixed, then blended (3000 rpm, 2 mins) with cornstarch (11.6 % moisture) and EMMT by use of High Speed Mixer GH-100Y (made in China), then stored for 36 hours. The weight ratio of cornstarch/formamide/ethanolamine was 100/15/15 and the weight ratio of EMMT was 2.5%, 5%, 7.5% and 10%, respectively. The mixtures were fed into the single screw Plastic extruder SJ-25 (s) (Screw Ratio L/D=25:1). The screw speed was 20 rpm. The temperature profile along the extruder barrel was 105℃, 110℃, 115℃, 120℃(from feed zone to die), respectively. The die was a round sheet with the diameter 3 mm holes.

Results and Discussion

Figure 1 revealed that when MMT was activated by ethanolamine, the diffraction peak of montmorillonite (001) crystal plane moved from 8.75° to 7.06°. According to the Bragg diffraction equation: 2dsin $\theta = \lambda$, the distances d_{001} between the layers were 1.01 nm and 1.25 nm, respectively, which indicated that the distance of EMMT layer expanded and the microenvironment between the layers was ameliorated. This was advantageous to the intercalation of TPS. WAXD pattern of TPS/EMMT showed that the diffraction angle moved to 4.24° and the distances value d_{001} was 2.08 nm, which was longer than the distances value of montmorillonite layer. The diffraction peak of materials was wider than montmorillonite and EMMT (the half width of peak of montmorillonite was 1.26°, one of the EMMT was 2.03°, and one of the TPS/EMMT was 2.58°). This indicated that TPS molecules were intercalated between MMT layers successfully, which made the structure of crystal lattice more dispersible, the distances between layers were widen, and the intercalation nanocomposites were formed.

Figure 1 WAXD patterns of MMT, EMMT and TPS/EMMT

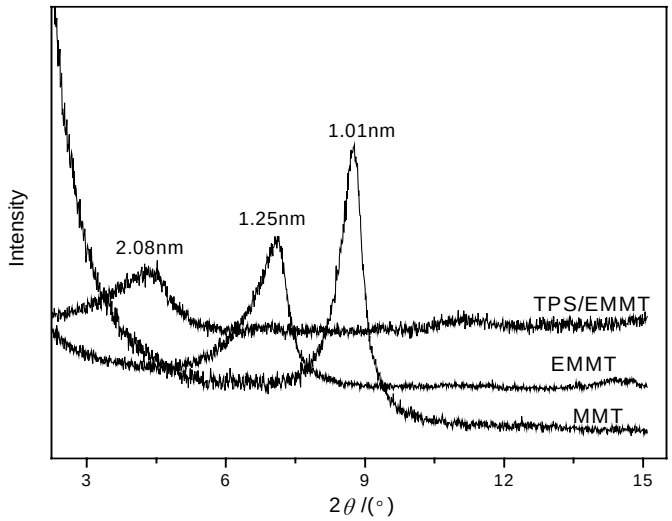


Figure 2 SEM photograph of TPS(A) and TEM photograph of TPS/EMMT(B)

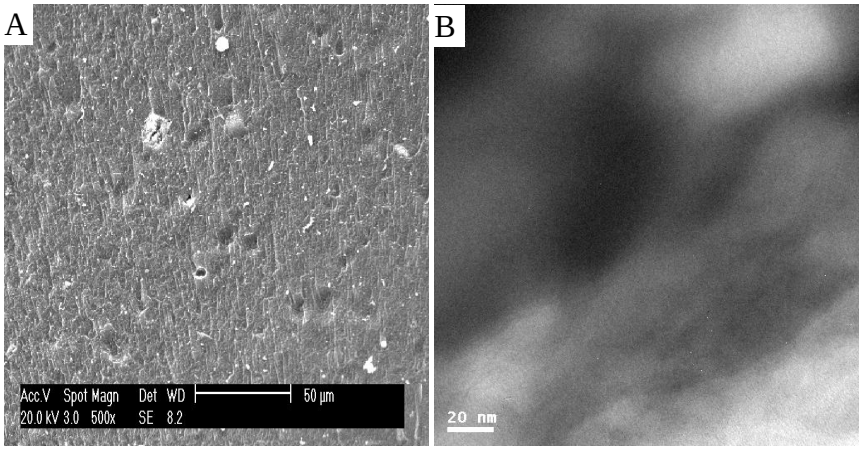
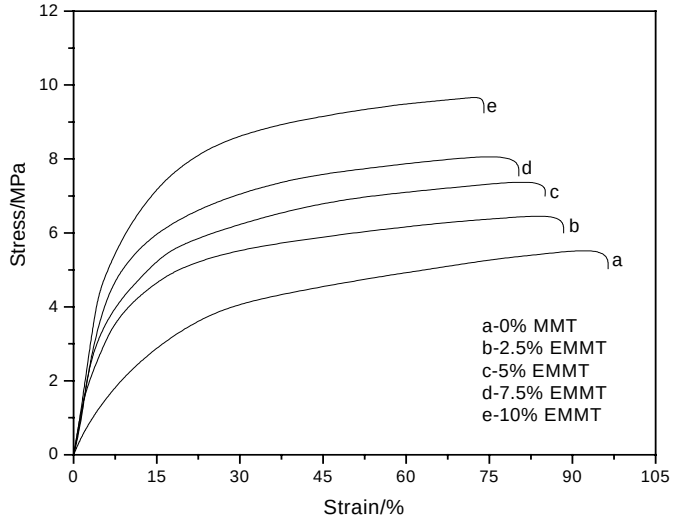


Figure 3 The stress~strain curves of TPS/EMMT nanocomposites and pure TPS



The scanning electron microscope of TPS (500x) and the transmission electron microscope photograph of TPS/EMMT nanocomposites (weight fraction of MMT was 10%), which was magnified 150 thousand times, were shown in **Figure 2**. The continuous TPS phase was formed in **Figure 2A**, the white areas were TPS phase and the black areas were the montmorillonite layers dispersed in TPS phase in **Figure 2B**. It indicated that during the processing chains of the melting TPS molecule were intercalated in the EMMT layers successfully. The montmorillonite layers were expanded and evenly dispersed in the TPS phase in the size of nanometer. This result agrees with WAXD.

Figure 3 showed the stress~strain curves of TPS/EMMT nanocomposites and the

pure TPS stored at relative humidity 25% for 14 days. Both TPS/EMMT nanocomposites and the pure TPS showed the typical pattern of rubbery starch plastic materials reported previously[6]. **Table 1** showed that when the weight content of EMMT was 10%, the mechanics properties of TPS/EMMT nanocomposites were improved greatly. The stress increased from 5.62 MPa of the pure TPS to 184.11 MPa of the TPS/EMMT nanocomposites, the strain was 74.07% and breaking energy increased from 1.34N.m of the pure TPS to 2.15 N.m of the TPS/EMMT nanocomposites. These illuminated that nanocomposites had good mechanical property. When the nanocomposites intercalatived in the space between MMT layers, the cooperation of starch molecule chain and EMMT endued the material a good stress, strain and energy break. The mechanical properties were obviously ameliorated.

Table 1 The mechanical parameters of TPS/EMMT nanocomoposites and pure TPS stored at RH25% for 14 days

Parameters	TPS/EMMT nanocomposites	TPS
Stress Yield (MPa)	8.48	3.74
Stress Peak (MPa)	9.69	5.62
Strain Yield (%)	29.63	23.54
Strain Peak (%)	74.07	96.41
Youngs Modulus (MPa)	184.11	47.23
Energy Break (N•m)	2.15	1.34

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