Structure and Properties of Thermoplastic Corn Starch/Montmorillonite Biodegradable Composites

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ABSTRACT: "Green" composites were successfully prepared from the thermoplastic cornstarch (TPCS) and activated-montmorillonite (MMT) by the method of blend extrusion. The thermoplastic cornstarch was plasticized with novel plasticizers urea and ethanolamine, and the activated-montmorillonites were obtained using ethanolamine as the activated solvent. The structure and morphology of "Green" composites were characterized by wide-angle X-ray diffraction (WAXD), scanning electron microscope (SEM), and transmission electron microscope (TEM). SEM and TEM images indicated that the composites presented reticulating fiber structure after being cooled by liquid nitrogen. The exfoliated MMT sheets in the composites acted as the inho-mogeneous nucleation effect. The melting urea was crystaled over on the MMT sheets in the inducement of ethanolamine, and the column-shape crystal whisker overlapped together. Comparing with normal temperature, the mechanical properties of composites evidently improved after being cooled by liquid nitrogen, which was proved by the mechanical testing. The thermal stability and water-resistance of the composites also were studied in this paper. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 170–176, 2006

Key words: themoplastic cornstarch; composites; degradation; ethanolamine

INTRODUCTION

To develop an environmentally friendly material, many efforts have been made to solve problems generated by plastic waste, particularly by one-time-use disposable commodity material. Most of the research attention is focused on the replacement of petro-based commodity plastics in a cost-effective manner by biodegradable material with competitive mechanical properties. Biopolymers have been considered as most promising materials for this purpose, as they exist abundantly and may form a cost-effective end product. In the family of biopolymers, starch has been considered as most promising candidate for the development of such materials.

Combinations of organic polymer matrices and inorganic particles have been developed over past decades for the synthesis of organic–inorganic hybrids.[1] These materials have often been shown to improve the physical, mechanical, and thermal properties, and the inorganic phase can be well distributed in the polymer matrix. A variety of approaches to hybrid materials have been developed, in which the methods of poly-mer intercalation and intercalative polymerization have developed rapidly in the recent decade.[2–5]

Nano-scale polymer/clay composites fabricated with crystallizable polymers have been shown to possess improved mechanical, physical, and thermal properties.[6] Recently, much attention has focused on the crystallization behavior of semicrystalline polymers in the presence of nano-scale clays. The addition of nano-scale clays can change the crystallization kinetics, the crystalline morphology, the crystal forms, and the crystallite size.[7] This difference in crystalline morphology, in turn, can significantly affect the overall mechanical and physical properties of the materials.

Currently, the matrices of nanocomposites are mainly synthetic polymers, such as polyolefin, polyamide, polyester, and so on.[8–12] However, studies on natural polymers are limited, and the material prepared from natural polymers has poor performance or a high cost. Thermoplastic starch/tunicin whiskers nanocomposites are expensive because of the high price of tunicin whiskers.[13,14] Park et al.[15–17] prepared the thermoplastic starch (TPS)/Clay hybrids in which the weight ratio of native potato starch/water/glycerol contained in TPS was 5/2/3, and they studied the combination of natural polymers and inorganic mineral at the nanometer level. However, the mechanical properties of the hybrids were poor. The thermoplas-

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tic cornstarch (TPCS) plasticized by different plasticizers was prepared in our previous study, in which the crystallization behaviors of these materials resulting from longtime storage were inhibited, but the mechanical properties were still poor.[18–20] Starch is known to be a renewable material because of its cheapness and very fast biodegradability.[21–23]

In this work, the composites were prepared from the ethanolamine-activated montmorillonite and the thermoplastic starch, in which the thermoplastic starch was plasticized by the novel plasticizers (urea/ethanolamine = 1/1) by melt-intercalation. It is interesting to note that the composites formed a reticulate fiber structure after being cooled in liquid nitrogen for 1 min. And we found that the strength and toughness of the material significantly improved. Consequently, we speculated that the reticulate fiber structure contributed to the improvement of the material properties. The thermal stability and water-resistance were also studied in this work.

EXPERIMENTAL

Materials

Cornstarch (11.5% moisture, 25% amylose) was obtained from Langfang Starch Company (Langfang, Heibei, China); Citric acid, urea, and ethanolamine were purchased from Tianjing Chemical Reagent Third Factroy (Tianjin, China); Sodium montmorillonite (Na^+-MMT) with a cation exchange capacity (CEC) of 90–100 mmol/100 g as an inorganic host material was supplied by Zhangjiakou Qinghe Chemical Plant (Heibei, China).

Activation of MMT

1.462 g ethanolamine and 2.4 mL sulfuric acid (98%) were in turn added to 700 mL water at 80°C. This solution was slowly added to the water solution that contained 20 g MMT. The mixture was stirred at 80°C for 3 h, then cooled to room temperature, filtrated, and dried. After being ground and sifted, the activated MMT was gained.

Preparation of composites

The urea and ethanolamine-plasticized thermoplastic cornstarch/ethanolamine-activated montmo-rillonite (UETPCS/EMMT) composites were prepared through two steps. At the first step, the urea (15 wt %) was dissolved with the ethanolamine (15 wt %) to obtain the plasticizer, and the plasticizer was premixed (3000 rpm/min, 2 min) with cornstarch (water content 11.5 wt %) in the High Speed Mixer GH-100Y (made in China), and retained in the tightly sealed plastic bags for 48 h to swell the granular cornstarch molecules.

Then, these swollen mixtures were transferred into the single screw Plastic Extruder SJ-25 (s) (Screw Ratio L/D = 25 : 1, Beijing, China) with a screw speed of 20 rpm and the UETPCS was obtained. After processing, the UFTPCS was cooled and cut into small granules to be easily mixed with MMT powder. These UFTPCS granules were then mixed with different proportions, and these mixtures were transferred to the single screw Plastic Extruder again. The temperature profile along the extruder barrel was 105°C, 110°C, 115°C, and 120°C (from feed zone to die). The die was a round sheet with 3 mm-diameter holes.

X-ray diffractometry

X-ray diffraction (XRD) analyses of UFTPCS/CMMT composites, CMMT, and MMT were carried out using a BDX3300 X-ray diffractometer (40 kV, 100 mA) equipped with a Ni-filtered Cu radiation and a curved graphite crystal monochromator. The scanning rate was 2°/min. The diffractometer was equipped with a 1° divergence slit, a 0.16 mm receiving slit, and a 1° scatter slit.

SEM and TEM

The Scanning Electron Microscopy (SEM) was obtained using Philips XL-3 instrument. The samples were cooled in liquid nitrogen, and then fractured. The fracture faces were vacuum-coated with gold for SEM. The composites specimens were performed with Transmission Electron Microscope (TEM) JEM-1200EX, operating at an acceleration voltage of 80 kV. The specimens were sliced in liquid nitrogen with the Reichert-Jung Ultracut E microtome, and the thickness was 50–70 nm.

Mechanical testing

According to the National Standard of China GB1040–79, the tensile stress and tensile strain of biodegradable composites were measured using Testometric AX M350–10KN Materials Testing Machines. The specimens were measured after being stored in a controlled chamber at RH50% for about two weeks. The crosshead speed was 10 mm/min. All measurements were performed for five specimens (80 mm × ø3 mm in size) and averaged.

Thermogravimetric analysis (TGA)

The Thermogravimetric analyses (TGA) of composites (5–10 mg) and UETPCS (5–10 mg) were carried out using a ZRY-ZP model TGA instrument under nitrogen atmosphere at a heating rate of 15°C/min. The range of scanning temperature was from room temperature to 500°C.
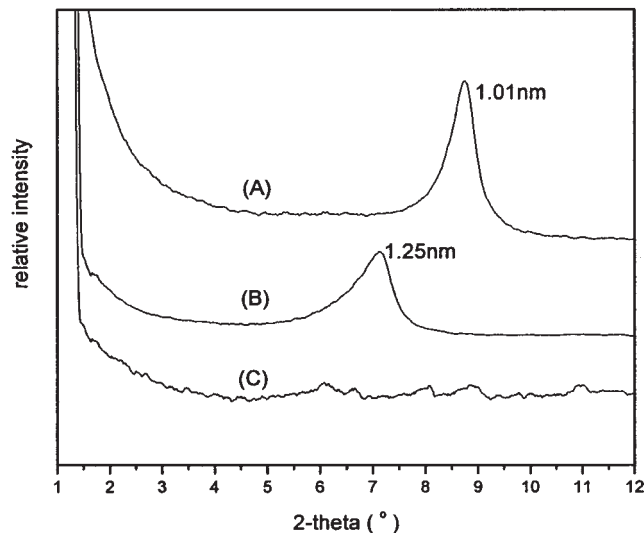
Figure 1 X-ray diffraction patterns of (A) original montrnorillonite, (B) Ethanolamine-activated montmorillonite, and (C) montmorillonite-UETPCS composites with about 8 wt % of nanofiller loading.

Water absorption properties

The bars of sample were cut into small pieces, and weighed immediately, then put into the oven, and dried at 105°C for 24 h. The water content rate (K) was calculated as the following formulation:

$$K = \frac{w_2 - w_1}{w_1} \times 100\% \tag{1}$$

in which, w_2 was the real mass of the sample, g; w_1 was the mass of the drying sample, g.

The samples were stored at different relative humidity conditions for a period of time, then weighed. The water content rates (K) at different relative humidity were calculated.

RESULTS AND DISCUSSION

X-ray diffraction

The X-ray diffraction data (XRD) and microscopy were used in this work to follow changes in the montomorillonite/natural polymer composites at 8 wt % nanofiller loading level, in which neither the extra MMT nor the insufficient MMT was good to mechanical performance.

The dispersion extent of MMT layers has typically been elucidated by WAXD, which allow a direct evidence of polymer chain confinement into the MMT gallery. Figure 1 shows the diffraction peak of montmorillonite (001) crystal plane moved from 8.75°to 7.06°, when MMT was activated by ethanolamine. According to the Bragg diffraction equation $2d\sin\theta = \lambda$, the spacing $d001$ between the layers are 1.01 and 1.25

nm, respectively, which indicates that the distances between the layers of MMT widened, and the ethanolamine had intercalated into the layers of MMT. The microenvironment between the layers was ameliorated and forms the MMT that was propitious to reacting with UETPCS. WXRD pattern of composites with 8 wt % shows that the diffraction peak $d001$ of composites disappeared. This means that the crystal lattice structure of MMT was totally dispersed, the slice layers were exfoliated into the UETPCS, and combined with UETPCS at the nanometer level, and so the exfoliated nanocomposites were formed.

Morphology

The SEM photograph of native cornstarch, which was magnified 5000 times, is shown in Figure 2(a). The cornstarch presents regular granule. From the SEM image (magnified 10,000 times) of the original montmorillonite [Fig. 2(b)], we can see that the MMT layers overlapped together. Figure 2(c) shows the bean-sprout-like crystal whisker structure of urea. The SEM image of the thermoplastic cornstarch plasticized by the urea and ethanolamine is shown in Figure 2(d). This indicated that the mixture plasticizers, urea and ethanolamine, penetrated inside the cornstarch granules in the cooperation of the shear stress and thermal effect of the single strew plastic extruder, the cornstarch granules were destroyed, and formed uniformly continuous phase.

The TEM image [Fig. 2(g)] of composites with 8 wt % EMMT shows that, in cooperation of the effects, including the combination effect of shear stress and thermal effect from the single strew plastic extruder, the strong adsorption and hydrogen bonding between the plasticizers and UETPCS, the melting UETPCS molecular chains successfully interacted into the EMMT gallery. The MMT layers were exfoliated (black areas) and uniformly dispersed in UFTPCS matrix at the nanometer level. The TEM results correspond well with the WAXD patterns. It is very interesting that after being frozen by the liquid nitrogen and sliced up, the exfoliated MMT sheets in thecomposites acted as the inhomogeneous nucleation effect. In the inducement of ethanolamine, the melting urea crystaled on the activated-MMT sheets, and the column-shape crystal whisker overlapped together, which presented reticulate crystal whisker structure. Figures 2(e) and 2(f) show the SEM images of UETPCS/EMMT composites, which were magnified 500 times and 10,000 times, respectively. The reticulate fiber structure can be more expressively observed in Figures 2(e) and 2(f).

Mechanical property

Figure 3 shows the tensile stress and tensile strain curves of composites and UETPCS. Three curves are very similar, and all shows the typical rubber state behavior. The stress and strain of composites (containing 8 wt % MMT) are
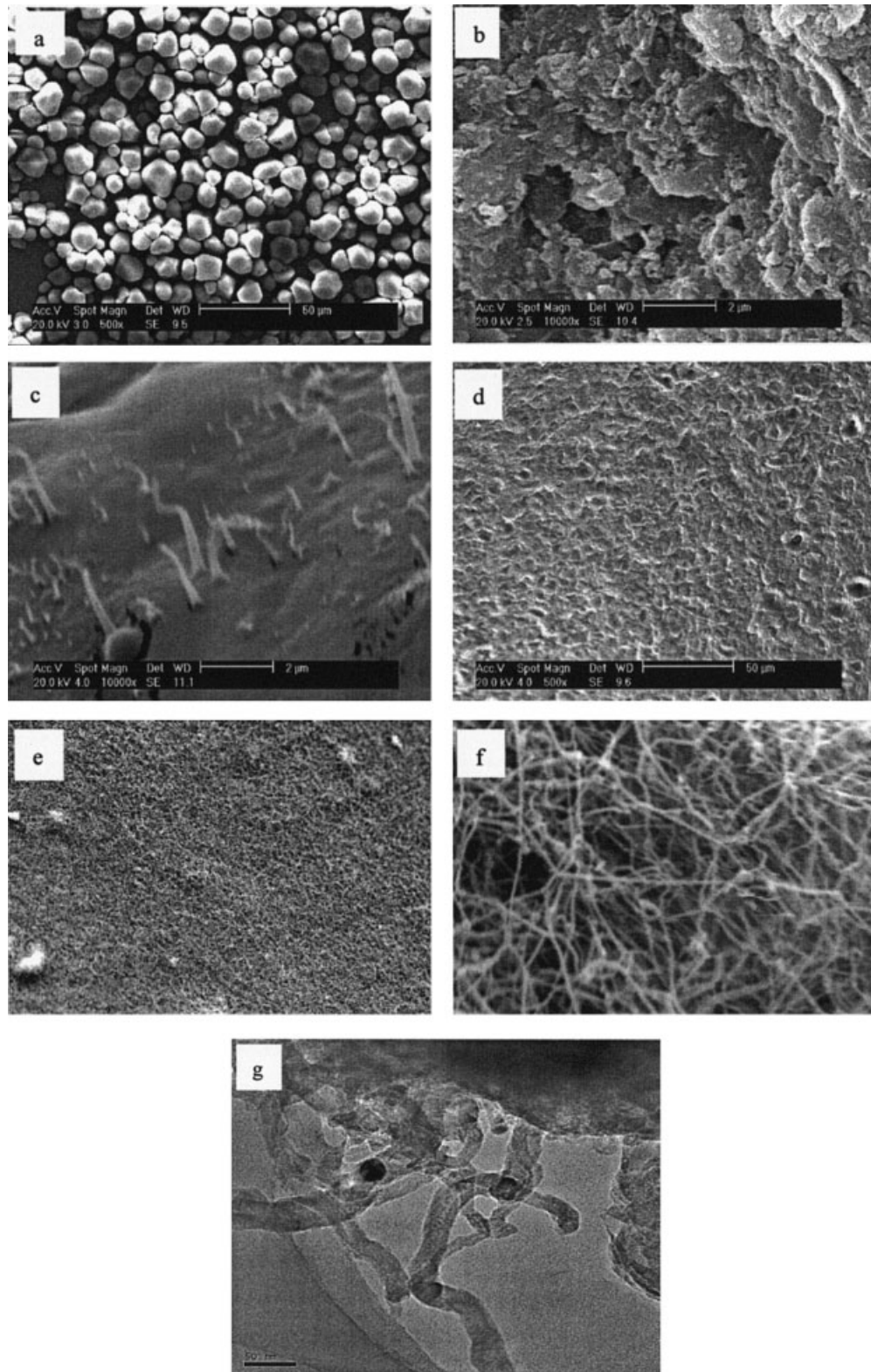
Figure 2 (A) Natural cornstarch SEM image. (B) Original montmorillonite SEM image. (C) Urea SEM image. (D) UETPCS SEM image. (E,F) SEM images of UETPCS/EMMT nanocomposites. (G) TEM image of UETPCS/EMMT nanocomnosites.

evidently better than those of pure UETPCS. After being cooled by liquid nitrogen, the range of rubber state enlarged, which indicated that reticulation fiber structure improved the mechanical properties of composites.

Table I shows the comparison of mechanical properties among different MMT composites, pure UFT-PCS and liquid nitrogen-cooled composites that containing 8 wt % MMT. From the Table I, we can
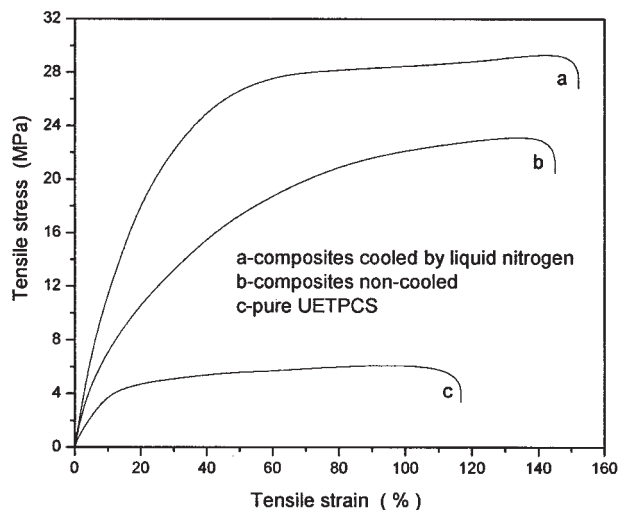
Figure 3 The tensile stress–tensile strain curves of composites and UETPCS.

Figure 4 TG scans of pure UETPCS, composites, and liquid nitrogen-cooled composites.

see that the mechanical properties of composites containing 8 wt % MMT are better than those of the other materials. The tensile stress of composites is obviously higher than that of pure UFTPCS, and as far as the strain is concerned, only the composites with 8 wt % MMT possess higher strain than pure UFTPCS does. These indicate that the mechanical properties of composites containing 8 wt % MMT are the best. It is interesting to note that the properties of liquid nitrogen-cooled composites improved evidently, compared with the composites containing 8 wt % MMT. The tensile stress and strain of the liquid nitrogen-cooled composites containing 8 wt % MMT achieved 29.81 MPa and 152.14%, respectively. Young's modulus and breaking energy, respectively, achieved 734.58 MPa and 3.05 N m. These results indicate that the occurrence of the reticulate fiber structure makes the tensile stress slightly improved and the tensile stress remarkably increased. We speculate that after being cooled by liquid nitrogen, the reticulate fiber structure forms, which contributes to the improvement of the material mechanical properties, since the extra-
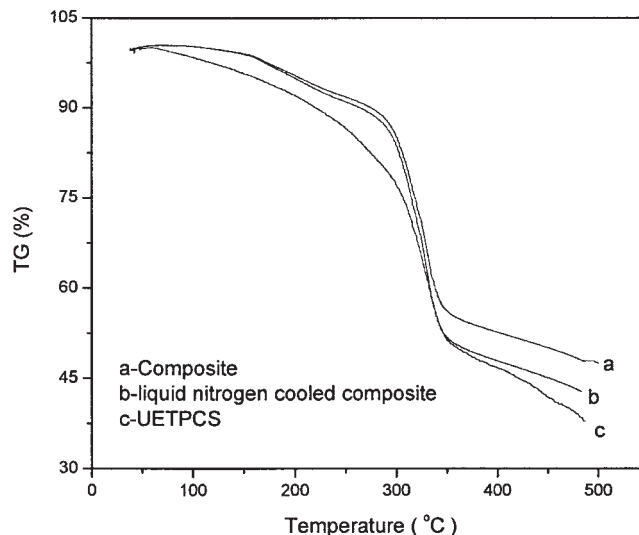
work getting over the reticulate fiber structure is needed in the tensile process. It is a beneficial inspiration to prepare the low-temperature-resistant material. The deeper insight into the formation mechanism of reticulate fiber structure is in progress.

Thermal stability

Comparing with organic material, the inorganic materials have better thermal stability and thermal resistant properties because of its configuration characteristics. Therefore, the introduction of inorganic particles will greatly improve the thermal stability of organic polymer materials.

Figure 4 shows that the mass loss of pure UETPCS and composites is mainly due to water loss below 100°C; however, from 100°C to decomposition temperature, the mass loss is mainly due to plasticizer loss. Before the decomposition temperature, the mass loss of UETPCS is 16.72%, the onset decomposition temperature is 271°C, and the ending decomposition temperature is 342°C. The mass loss of

TABLE I
Comparison of the Mechanical Properties Among Different Biodegradable Materials

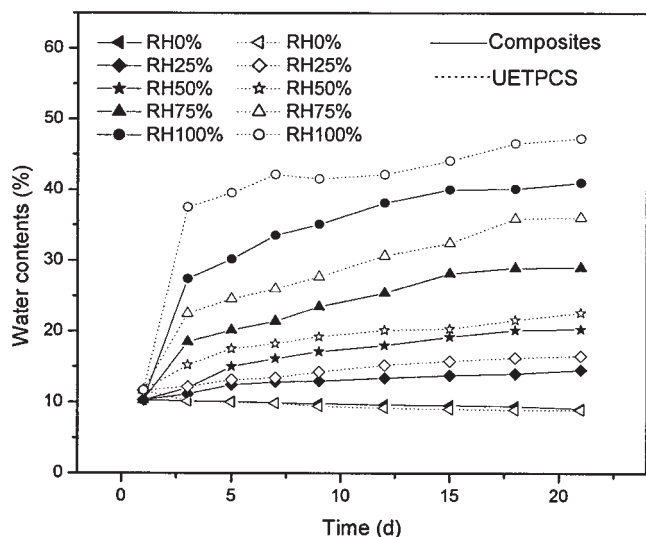| TPS material	UETPCS	Composite (2 wt %)	(5 wt %)	(8 wt %)	(11 wt %)	Liquid nitrogen-cooled composite (8 wt %)
Yield stress (MPa)	4.31	6.78	9.55	18.27	19.41	27.51
Yield strain (%)	13.42	32.14	51.19	56.08	12.05	58.56
Tensile stress (MPa)	6.38	10.19	14.75	23.46	25.15	29.81
Tensile strain (%)	116.71	84.8	64.20	145.07	37.81	152.14
Young's modulus (MPa)	124.73	254.96	387.14	599.42	611.4	734.58
Breaking energy (N m)	1.38	1.93	2.05	2.74	1.38	3.05

Figure 5 Water contents of composites and UETPCS with the storage times at different relative humidity.

composites with 8 wt % MMT is 11.53%, the onset and ending decomposition temperatures are 279 and 341°C, respectively. The mass loss of liquid nitrogen-cooled composites with 8 wt % MMT is 13.59%, the onset and ending decomposition temperatures are 282 and 339°C respectively. The mass loss of composite with 8 wt % MMT is less than that of UETPCS. For the composites being cooled by liquid nitrogen, the improvement of the mass loss may have some relationship with the reticulate fiber structure. The composites possess better thermal stability than pure UFTPCS does, that is because MMT possesses the high aspect ratio (width to thickness), and its homogeneous dispersion in a continuous polymer matrix in nanosheets greatly improves the properties of polymers. It is interesting to note that the TG scan of composites that are cooled by liquid nitrogen totally accords with that of composites at normal temperature [Fig. 4(a)]. This indicates that being cooled by liquid nitrogen had no effect on the thermal stability of composites.

Water absorption

Water absorption is an important index to estimate the utility of a composite. Figure 5 shows the water absorption of composites and UETPCS at different relative humidity. From Figure 5, we can see that the water-assistance of composites is obviously better than that of UETPCS. Both of the materials present water loss state, but the rate of water loss is less at RH = 0%. At the other relative humidity, both of the materials present water absorption state. The higher the relative humidity is, the larger is the water content of the material. The highest

water content of composites is 39.8% and that of UETPCS is 43.5% after being balanced at RH = 100% for 14 days. The perfect water resistance of composites contributes to the nanostructure of composites.

CONCLUSIONS

Composites have been successfully prepared from the thermoplastic cornstarch (TPCS) and the activated-montmorillonite (MMT) by blend extrusion. The thermoplastic cornstarch was plasticized with novel plasticizers urea and ethanolamine, and the activated-montmorillonites were obtained using ethanolamine as the activated solvent. WAXD presented the MMT in composites exfoliated. SEM and TEM images showed that composites presented reticulating fiber structure after being cooled by liquid nitrogen. The exfoliated MMT sheets in the composites acted as the inhomogeneous nucleation effect. The melting urea crystaled on the MMT sheets in the inducement of ethanolamine, and the column-shape crystal whisker overlapped together. Comparing with normal temperature, after being cooled by liquid nitrogen, the mechanical properties of composites evidently improved, which were proved by the mechanical testing. The tensile stress, tensile strain, Young's modulus, and breaking energy, respectively, achieved 29.81 MPa, 152.14%, 734.58 MPa, and 3.05 N m. And the thermal stability and water resistance of composites also improved.

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