

High performance biodegradable thermoplastic starch—EMMT nanoplastics

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Abstract

Nanoplastics were prepared using the formamide/ethanolamine-plasticized thermoplastic starch (FETPS) as the matrix and ethanolamine-activated montmorillonite (EMMT) as the reinforcing phase. Wide angle X-ray diffraction (WAXD), scanning electron microscope (SEM) and transmission electron microscope (TEM) revealed that FETPS was successfully intercalated into the layers of EMMT and formed the intercalated nanoplastics with EMMT. When EMMT content was 5 wt%, the mechanical testing indicated that the tensile stress of the nanoplastics achieved 7.5 MPa, and the tensile strain achieved 85.2%, Young's modulus increased from 47.2 MPa of pure FETPS to 145.1 MPa of FETPS/EMMT nanoplastics, and the breaking energy increased from 1.34 to 1.81 N m after being stored at RH=25% for 14 days. Comparing with FETPS, the nanoplastics effectively restrained the recrystallization of starch. In contrast to pure FETPS, the strength of nanoplastics obviously improved, and the thermal stability and water resistance also improved.

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1. Introduction

Since the montmorillonite's homogeneous dispersion in a continuous polymer matrix in nanosheets could greatly improve the properties of polymers, and even could produce new properties that cannot be derived from other composites counterparts [1–8], the polymer/MMT nanocomposites developed rapidly in the recent decade, and the methods of polymer intercalation and intercalative polymerization resolved the dispersion and interface problems in the preparation of polymer nanoplastics [9,10]. Currently, the matrixes of nanocomposites were mainly synthesized polymers, such as polyolefin, polyamide, polyester, and so on. [11–13], however, the study on the natural polymers was few. Only Park et al. [14–16] studied the thermoplastic starch (TPS)/clay hybrids. This kind of hybrid was the compound of TPS and inorganic mineral in the size of nanometer. However, a mass of plasticizers were introduced

to make TPS flowed in the processing, and plasticizer contents reached 50% (native potato starch:glycerol:water were wt 5:3:2), so the mechanical properties were poor.

In order 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 [17]. 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 [18–20].

In the present study, biodegradable nanoplastics have been successfully prepared from formamide/ethanolamine-plasticized thermoplastic starch and ethanolamine-activated montmorillonite. In order to improve the mechanical properties, less proportional novel plasticizers were used (native cornstarch:formamide:ethanolamine were wt 10:1.5:1.5). In addition, the crystallization behavior, thermal stability, and water adsorption of nanoplastics were studied.

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2. Experimental section

2.1. Materials

Cornstarch (11.6% moisture) was obtained from Langfang Starch Company (Langfang, Hebei, China). Formamide was purchased from Tianjing Chemical Reagent Third Factory (Tianjin, China); ethanolamine was purchased from Tianjing Chemical Reagent Two Factory (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 (Hebei, China).

2.2. Activation of MMT

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

2.3. The preparation of nanoplastics

The FETPS/EMMT nanoplastics were prepared through two steps. At the first step, the formamide (15 wt%) was dissolved with the ethanolamine (15 wt%), and the solution was premixed (3000 rpm for 2 min) in the High Speed Mixer GH-100Y (made in China), and stored in the tightly sealed plastic bags for 36 h. Then these swelled mixtures were manually fed 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 were cut into small particles in order to be mixed with EMMT easily. At the second step, those FETPS granules were mixed with different proportional EMMT, and these mixtures were fed into the single screw Plastic Extruder again. The temperature profile along the extruder barrel was 120, 130, 130, 110 °C (from feed zone to die). The die was a round sheet with the diameter 3 mm holes.

2.4. X-ray diffractometry

The FETPS/EMMT nanoplastics, EMMT, MMT and FETPS 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 at a scanning rate of 2 °/min. The diffractometer was equipped with 1° divergence slit, a 0.16 mm receiving slit and a 1° scatter slit.

2.5. Microcosmic structure

The SEM and TEM performed the microcosmic structure characterization of nanoplastics. The scanning electron

microscope used in the present experiment was Philips XL-3. The samples were cooled in liquid nitrogen, and then broken. The fracture faces were vacuum coated with gold for SEM. The nanoplastics samples were performed with transmission electron microscope JEM-1200EX, operating at an acceleration voltage of 80 kV. The samples were sliced in liquid nitrogen with the Reichert-Jung Ultracut E extra-thin slice. The thickness of the slices was 50–70 nm.

2.6. Mechanical testing

According to the GB1040-79 standard of China, the tensile stress, strain, yield stress, yield strain, Young's modulus and breaking energy of nanoplastics were measured using Testometric AX M350-10KN Materials Testing Machines. The specimens were measured after being stored at RH=25% for two weeks. The crosshead speed was 10 mm/min. All measurements were performed for five specimens (8 cm × ϕ 3 mm in size) and averaged.

2.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of nanoplastics (5–10 mg) and FETPS (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.

2.8. Water absorption property

The samples were dried until constant weight in an oven to remove the moisture before water absorption testing by gravimetric methods and this weight was taken as initial weight (w_1). The samples were kept at different relative humidity conditions for 50 h and increase in weight was taken as final weight (w_2). The percentage of water absorption (K) was calculated by the formula, $K=(w_2-w_1)/(w_1) \times 100$.

3. Results and discussions

3.1. X-ray diffraction

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. The X-ray diffraction pattern of all samples is shown in Fig. 1. The WAXD patterns 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: $2d\sin\theta=\lambda$, the distances d_{001} between the layers were 1.01 and 1.25 nm, respectively, which indicated that the ethanolamine had intercalated into the layers of EMMT and the microenvironment between the layers was ameliorated. This profited the intercalation of

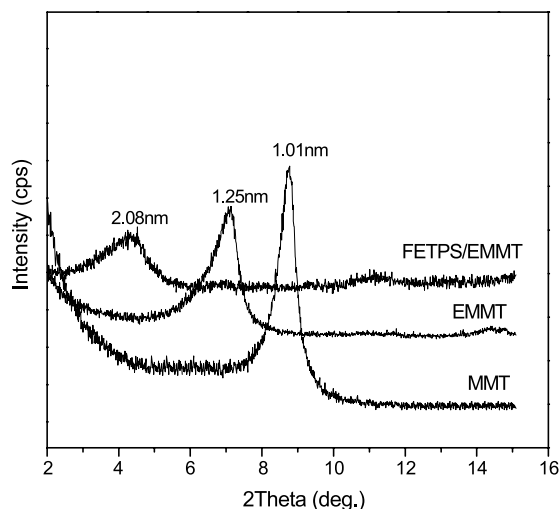


Fig. 1. WAXD patterns of MMT, EMMT and FEPTS/EMMT nanoplastics.

FETPS. WAXD pattern of FETPS/EMMT shows that the diffraction angle moved to 4.24° and the distance value d_{001} was 2.08 nm. It was longer than the distance value of montmorillonite layer, and the diffraction peak of materials was wider than montmorillonite and EMMT (the half width of the peak of montmorillonite was 1.26° , the one of EMMT was 2.03° , and the one of FETPS/EMMT was 2.58°). This indicated that melting FETPS molecule chains were intercalated into EMMT layers successfully, which made the structure of crystal lattice more dispersible, the distances between layers were widened, and the intercalated nanoplastics were formed.

3.2. Morphology of nanoplastics

The scanning electron microscope (SEM) photograph of FETPS/EMMT nanoplastics (5 wt% EMMT), which was magnified 5000 times, was shown in Fig. 2(a). It demonstrated that the EMMT dispersed well in the matrixes of FETPS. The transmission electron microscope (TEM) photograph of FETPS/EMMT nanoplastics (5 wt% EMMT), which was magnified 100 thousand times, was shown in Fig. 2(b). The white areas were FETPS phase and the black areas were the EMMT layers dispersed in FETPS phase. It indicated that in the cooperation of shear–stress effect and thermal effect of single strew plastic extruder and the ethanolamine, the melting FETPS molecular chains were intercalated in the EMMT gallery successfully, The montmorillonite layers were expanded and uniformly dispersed in the FETPS phase in the size of nanometer. The TEM results correspond well with the WAXD patterns.

3.3. Mechanical testing

The stress–strain curves of FETPS/EMMT nanoplastics and pure FETPS that were kept at $RH = 25\%$ for 14 days, were shown in Fig. 3. From Fig. 3 we can see that, when the

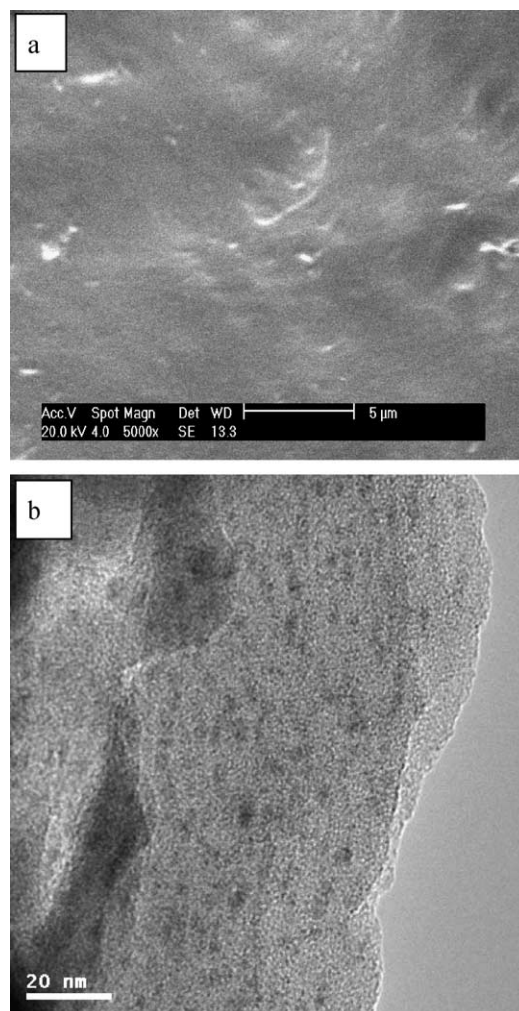


Fig. 2. 5000 \times SEM (a) and 100,000 \times TEM Micrographs (b) of nanoplastics.

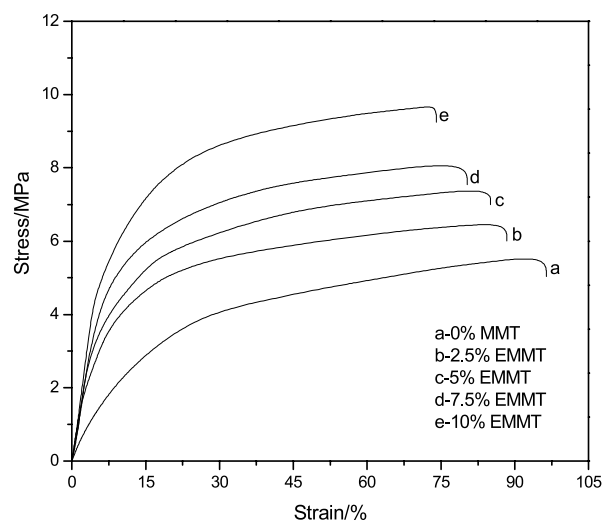


Fig. 3. The stress–strain curves of nanoplastics with different mass contents EMMT and FETPS.

mass fractions of EMMT in nanoplastics was 2.5, 5, 7.5 and 10%. The stress–strain diagrams of nanoplastics, just like the pure FETPS, present the typical pattern of rubbery starch plastic materials reported previously [21]. In other words, with the increasing of the strain the plots are essentially linear at low strain and curve towards the strain axis at higher strains. With the increasing of the stress, EMMT particles get rid of the viscosity, FETPS come into being cavity damage, and the material achieve the yield point. When getting to the yield point, the increasing of the stress is stopped, the strain increased continuously, the molecular chains configuration of FETPS changed, and the material came to the softening state. Then the thin neck phenomenon of the material occurred, simultaneously, the strong interaction between EMMT and FETPS inhibited the outside stress from destroying the structure of nanoplastics, viz. blocked the expand or passivation of the cavity in the FETPS matrix, and the nanoplastics got to the neck shrink state that was particular to the polymer. When the stress continuously increased, the tropism rigidification occurred, the surface energy between EMMT and FETPS was hard to make up for the energy exhausted by the yield and the energy getting rid of the interface viscosity, the molecular chains of FETPS achieved the maximal loading, then broke. In the whole tensile process, the strong interaction between EMMT and FETPS was presented. Since the more EMMT content induces the increase of the crystal lattice lacuna inside the nanoplastics and the energy exhausted by the yield and reducing viscosity of interface increases, the strain is relatively small when breaking.

As shown in Figs. 4–6, when EMMT content is in the range of 2.5–10%, the mechanical properties of FETPS/EMMT nanoplastics are obviously ameliorated. The tensile stress increases from 6.5 to 9.7 MPa, the yield stress of nanoplastics changes from 5.1 to 8.5 MPa, the Young's modulus increases from 68.5 to 184.1 MPa, the elongation

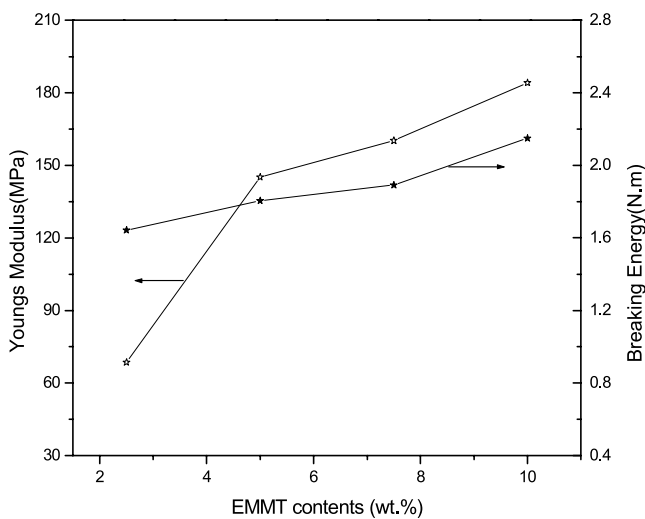


Fig. 4. The effect of the EMMT contents on Young's modulus and breaking energy of nanoplastics.

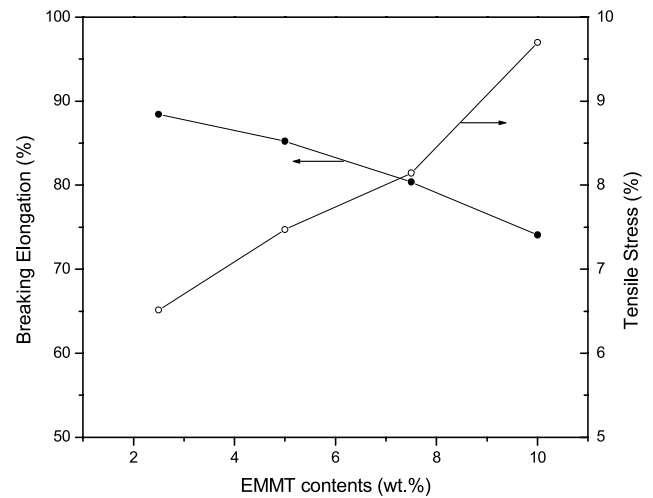


Fig. 6. The effect of the EMMT contents on breaking elongation and tensile stress of nanoplastics.

at break decreases from 88.4% to 74.1%, and the breaking energy increases from 1.64 to 2.15 N m. Those indicate that the mechanical properties of nanoplastics are very good. As far as the practical application is concerned, the nanoplastics containing 5 wt% EMMT was chosen, due to the perfect mechanical properties of this kind of material.

Table 1 shows the mechanical parameters of FETPS/EMMT nanoplastics and pure FETPS. As shown in Table 1, the mechanical properties of nanoplastics were better than those of pure FETPS except the strain peak.

3.4. Crystallization behavior

The starch crystallization is bad to the property of the material, because it can make the material brittle. However, the nanoplastics prepared in the present study get over the flaw, and restrain the crystallization behavior of FETPS.

Fig. 7 shows the X-ray diffraction patterns of FETPS and

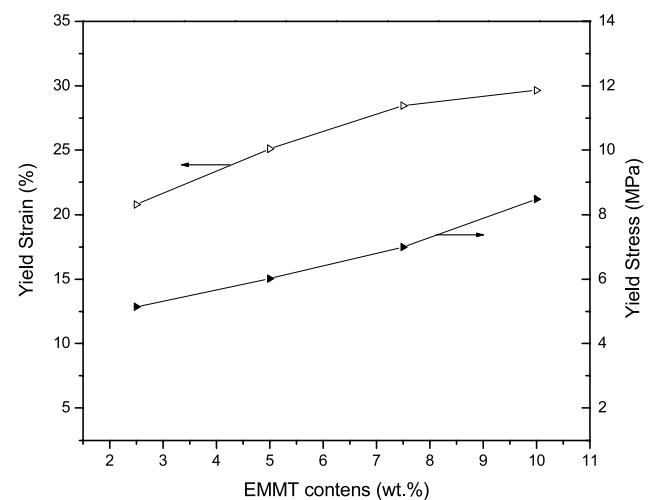


Fig. 5. The effect of the EMMT contents on yield strain and yield stress of nanoplastics.

Table 1
Mechanical parameters of nanoplastics and FETPS stored at RH25% for 14 days

Parameters	Yield stress (MPa)	Stress peak (MPa)	Yield strain (%)	Strain peak (%)	Young's modulus (MPa)	Energy break (N m)
Pure FETPS	3.7	5.6	23.5	96.4	47.2	1.34
Nanoplastics	6.0	7.5	25.1	85.2	145.1	1.81

were stored at RH=50% relatively for 30, 60, 90 days. We can see from the XRD patterns, there appear two kinds of crystallization peak after being kept for 30 days, one is the V_H type crystallization peak that is induced in the process of preparing thermoplastic starch; the other is the type A crystallization peak existing between the initial starch molecules. The height of the two crystallization peaks depends on the time, and it increases with the prolongation of the storing time. We found out that at about 14° there appeared newly type A crystallization peaks after being kept for 60 and 90 days, which made the material brittle, and that made against real practical use. Fig. 8 presents the X-ray diffraction patterns of nanoplastics that contained 5 wt% EMMT and were stored at RH=50% relatively for 30, 60, 90 days. We can see that no obvious crystallization peak occurred after nanoplastics being kept at RH=50% for 90 days. The contrastive analysis demonstrates that the formamide and ethanolamine mixture plasticizers cannot restrain the crystallization behavior of thermoplastic starch caused by long storing, so it is MMT sheets that contribute to the restraint of crystallization in nanoplastics. On the one hand, MMT sheets in nanoplastics restrained the growth of global crystal existing between starch molecules in FETPS; on the other hand, the growth of large number of crystal nucleus (nanometer MMT) in limited spaces caused the extrusion and the impact of global crystal, which made it

hard to form integrated global crystal, and restrained the occurrence of the crystallization behavior.

3.5. Thermal stability

Fig. 9 shows that the mass loss of pure FETPS and FETPS/EMMT nanoplastics was mainly water loss below 100 °C, however, from 100 °C to decomposition temperature the mass loss was mainly plasticizer loss. Before the decomposition temperature, the mass loss of FETPS composites was 15.1%, the onset decomposition temperature was 277 °C, and the ending decomposition temperature was 343 °C. The mass loss of FETPS/EMMT nanoplastics was 14.8%, the onset and ending decomposition temperature was 282 and 341 °C, respectively. The mass loss of nanoplastics was less than that of FETPS. MMT possess the high aspect ratio (width to thickness), and its homogeneous dispersion in a continuous polymer matrix in nanosheets improved greatly the properties of polymers, therefore, the good composites between MMT and FETPS effectively improved the stability of the nanoplastics.

3.6. Water absorption

Water absorption was an important index to estimate application of a composite. Fig. 10 shows the water

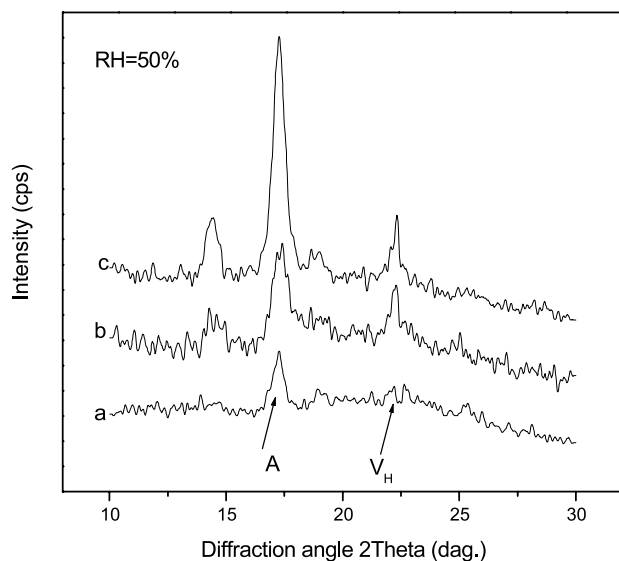


Fig. 7. The diffractograms of FETPS stored at RH=50% for 30 (a), 60 (b) and 90 days (c).

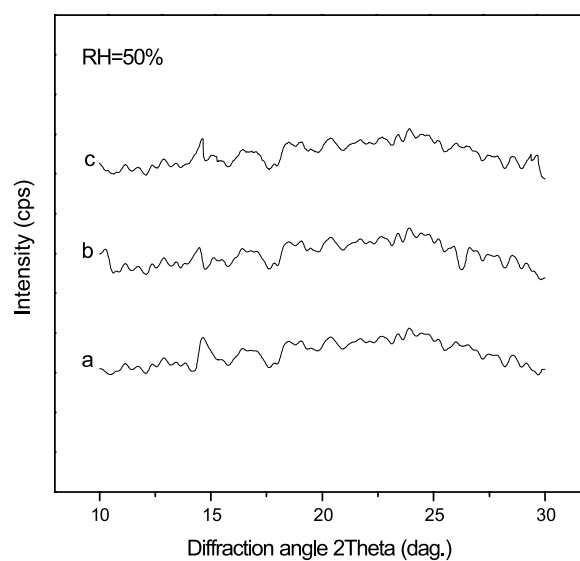


Fig. 8. The diffractograms of nanoplastic stored at RH=50% for 30 (a), 60 (b) and 90 days (c).

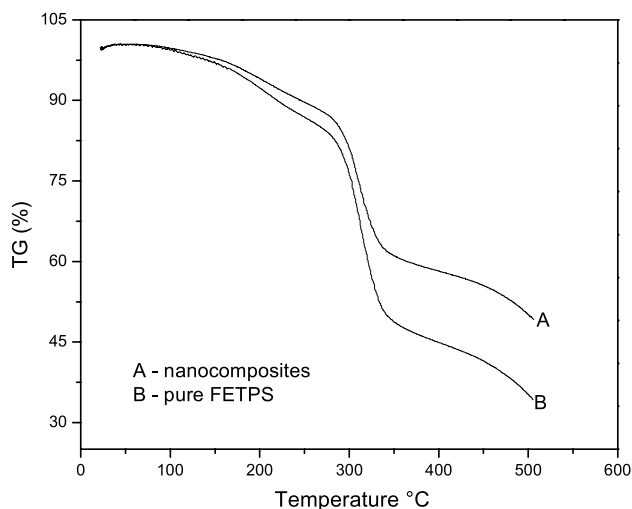


Fig. 9. TG curves for nanoplastics and pure FETPS.

absorption of nanoplastics containing 5 wt% MMT and FETPS at RH=75 and 100%. When the relative humidity was 75 and 100%, the water contents of nanoplastics were obviously less than that of FETPS. These indicated that the water resistance of nanoplastics was better than FETPS. The reason was that the maze structure was formed between the starch molecular chains that inserted in the MMT layers and the interbed of MMT. If water molecule wanted to permeate the materials, it had to through this winding channel (maze structure), which reduced the diffusion speed of water molecule in the material, and so improved the water resistance.

4. Conclusions

FETPS/EMMT nanoplastics were successfully prepared by the method of melt-intercalation. Wide angle X-ray diffraction (WAXD) revealed that the layer space distance of MMT in nanoplastics increased from 1.01 (original clay) to 2.08 nm. SEM and TEM show that FETPS was successfully intercalated into the layers of EMMT and formed the intercalation nanoplastics with EMMT. When EMMT content was 5 wt%, the mechanical testing indicated that the tensile stress of the nanoplastics achieved 7.5 MPa, and the tensile strain reached 85.2%, Young's modulus increased from the 47.2 MPa of pure FETPS to 145.1 MPa of FETPS/EMMT nanoplastics, and the breaking energy increased from 1.34 to 1.81 N m. The nanoplastics greatly restrained the recrystallization behavior resulting from longtime storing. In contrast to pure FETPS, the strength of nanoplastics obviously improved, and the nanoplastics had better thermal stability and water resistance.

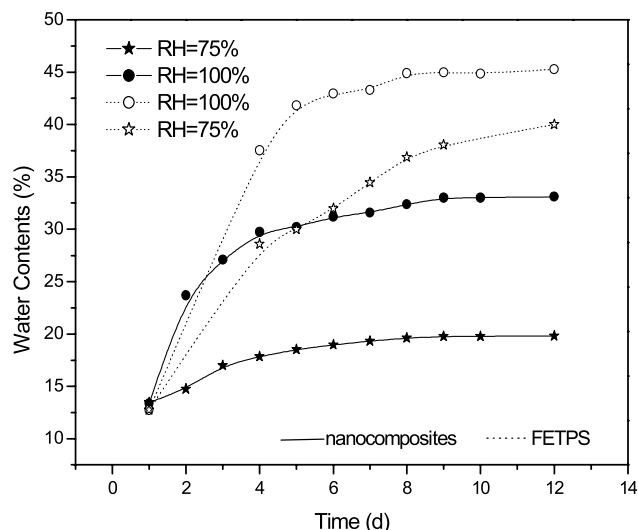


Fig. 10. The water adsorption curves of nanoplastics and FETPS at RH=75 and 100%.

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