Advances in Natural Sciences, Vol. 7, No. 1 & 2 (2006) (49 – 55)

Materials Science

STUDY ON THE STRUCTURE AND PROPERTIES OF POLYPROPYLENE/CLAY NANOCOMPOSITES

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Abstract. Polypropylene/ maleic anhydride /organic montmorillonite nanocomposites (PP/ MA/ Org-MMT) have been prepared via direct melt intercalation in an internal mixer. Maleic anhydride (MA) was used as a compatibilizer to improve the dispersability of the clay. The structures of nanocomposites have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Mechanical properties and thermal stability were determined by tensile analysis and thermogravimetric analysis (TGA), respectively. The XRD patterns, TEM and SEM image showed exfoliation of Org-MMT layers in PP matrix and existence of both the exfoliated, intercalated structures of the formed nanocomposites in presence of 1% MA. The tensile strength, elongation at break, and thermal stability of PP/MA/Org-MMT nanocomposites was higher than those of neat PP. MA played a very important role in reduction of size of Org-MMT and improved its dispersion in PP matrix.

1. INTRODUCTION

Polymer-layered silicate (PLS) nanocomposites have attracted much attention recently as examples of a newly developed polymer reinforcement technique. A large number of polymers with varying degrees of polarity and chain rigidity have been studied as base polymers for PLS nanocomposites, including polystyrene, polyamide, epoxy resin, polyimide, poly(ε-caprolactone), poly(ethylene oxide), polypropylene, poly ethylene terephtalate, polyurethane, silicone rubber and so on. These nanocomposites exhibit improved modulus, decreased thermal expansion coefficient, reduced gas permeability, increased solvent resistance, and enhanced ionic conductivity in comparison to their parent matrix polymers [1-7].

PLS nanocomposites can be prepared by three different methods: solution intercalation, in-situ intercalative polymerization and direct polymer melt intercalation. Polymer melt intercalation is appealing because of its compatibility with current polymer processing techniques, and it is environmentally friendly due to the absence of solvent. Depending on the degree of polymer penetration into the silicate framework as well as the exfoliation of layered silicate, two idealized PLS structures are possible: intercalated and exfoliated. Significant property enhancements are often observed for exfoliated PLS nanocomposites [1,7,8].

However, it is very difficult to disperse unmodified clay in polymer due to difference of their nature and polarity. To improve dispersion of clay as well as to enhance properties of composite materials, one of most popular ways is modification of clay by organic substances. In the modified form clay surface may become organically and interact with organic compound including polymers [1, 6]. Preparation of polymer/organic modified clay nanocomposites using maleic anhydride by melt mixing is one promising method. Polypropylene is one of the most widely used polymers, and polypropylene/organic modified clay nanocomposites have been interested by many experts [1, 2, 5, 6]. In this article, we inform the results related to the structure and the properties of polypropylene/organic modified montmorillonite nanocomposites prepared by melt mixing in the presence of maleic anhydride.

2. EXPERIMENTS

2.1. Materials

Polypropylene (PP) was supplied by Cemen Thai Chemicals (Thailand). Organic montmorillonite (Org-MMT): montmorillonite (in Binh Thuan province, Vietnam) was modified by ion exchange with ammonium salt of trihexadecyl ammonium chloride. The basal interlayer spacing is 3.76 nm. Maleic anhydride (MA) was purchased from Aldrich Chemical Company, Inc. (USA).

2.2. Samples preparation

PP and Org-MMT were dried in vacuum oven at 80 ^{o}C for 8h prior to mixing. PP, Org-MMT and MA were mixed at the intended condition in a Haake intermixer (Germany). Table 1 shows the mixing weight ratios of all the samples.

Table 1. *The mixing weight ratios of the samples*

Samples	**MA** wt%	**Org-MMT** wt%	**Samples**	**MA** wt%	**Org-MMT** wt%
P00	0	0	P11	1	1
P01	0	1	P12	1	2

2.3. Physical measurements

The exfoliation and the dispersion of Org-MMT in the polymer matrix was evaluated with X-ray diffraction (XRD) (Siemens – D5000 instrument with Cu Kα radiation, $\lambda = 0.154$ nm). The basal interlayer spacing of Org-MMT was estimated by Braggs equation ($\lambda = 2d\sin\theta$) from peaks on XRD pattern.

The morphologies and structures of the composites were observed on TEM (transmission electron microscopy) images were obtained with a JEOL JEM 1010 (Japan) with the magnifications 400000 times, acceleration voltage of 80 kV and on SEM (scanning electron microscopy) images which were made by a JEOL 5300 instrument (Japan) with the magnifications of 15000 times in nitrogen gas.

2.4. Mechanical measurements

Tensile properties of PP/Org-MMT nanocomposites was determined on a Zwick machine (Germany), according to DIN 53503 (Vietnam Standard 1592-87) at a tensing rate of 100 mm.min^{-1}.

2.5. Thermogravimetric analysis (TGA)

TG curves of PP/Org-MMT nanocomposites were determined by a Shimadzu TGA-50H under air from room temperature to 600 ^{o}C at the heating rate of 10 ^{o}C.min^{-1}.

3. RESULT AND DISCUSSION

3.1. Morphology of PP/Org-MMT nanocomposites

Fig. 1 shows XRD patterns of Org-MMT(a), P12 (b), P11 (c) and P01 (d) in the region of $2\theta = 2 - 10^o$. Each pattern has one diffraction peak at $2\theta = 1.56$; 1.45; 1.40 and 2.35^o corresponding to the interlayer spacing of the Org-MMT d = 5.66; 6.09; 6.31 and 3.76 nm, respectively. The peaks of PP/Org-MMT nanocomposites shift to lower angle compared to that of Org-MMT. It means that interlayer spacing of Org-MMT in PP matrix was expanded. This phenomenon might be explained by following reasons: PP-grafted-MA (PP-g-MA) formed by in-situ melt blending played as a compatibilizer between PP and Org-MMT [1, 9]. The PP-g-MA and PP chains or both intercalated into the interlayer spacing of the clay. At the same time, PP-g-MA could act as a high molecular weight surfactant; the functional group of maleic anhydride anchored in the sheet of Org-MMT by the strong hydrogen-bonding between C=O of MA and HO- groups of the organically modified layer silicate [2, 3]. The non-reactive blocks of the compatibilizer will attempt to gain entropy by pushing the sheets apart under a strong shear field. The interlayer spacing of clay increases and the interaction of the layers should be weakened. Therefore, the easy miscibility PP with PP-g-MA dispersed at the molecular level, the exfoliation of the intercalated clay take place [3, 6,9].

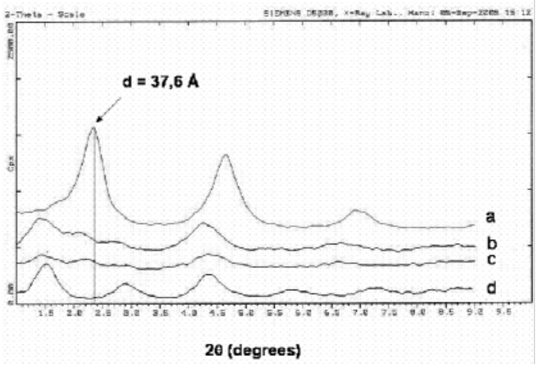
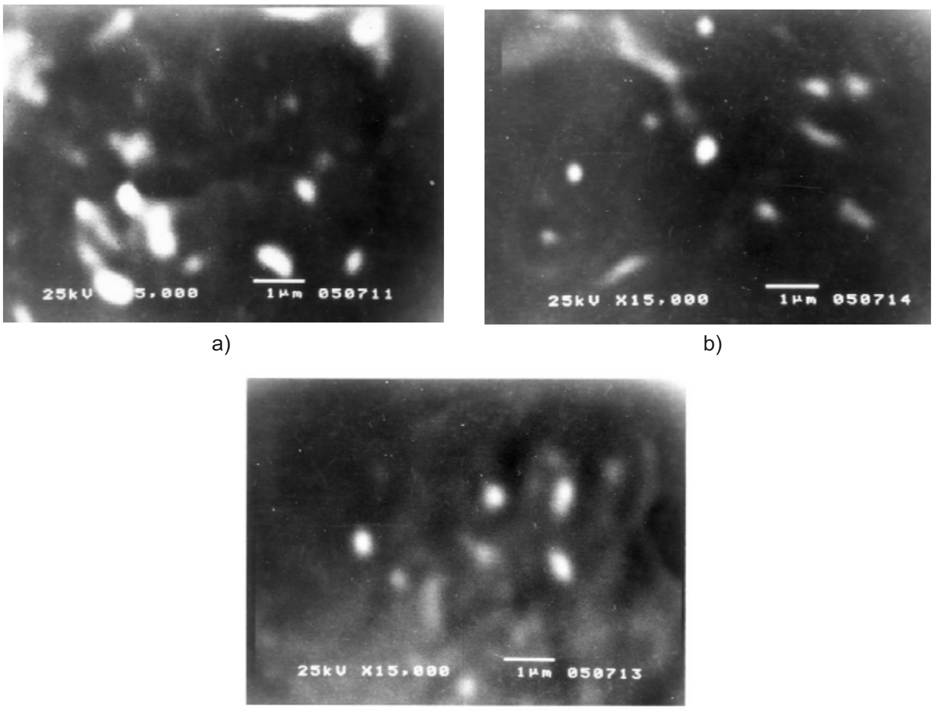


Fig. 1. XRD patterns of samples: Org-MMT (a), P12 (b), P11(c) and P01 (d).

Comparing the XRD patterns of samples P11 and P01 introduced in the Fig. 1, it is clear that the diffraction peak in the P01 (without MA) (Fig. 1.d) is stronger than that in the P11 (containing 1 wt% MA - Fig. 1.c). These results show that MA clearly affects the exfoliation and the dispersion of the Org-MMT in PP matrix and permits to presume that the obtained material containing exfoliated nanocomposites.

The SEM images in Fig. 2 showed that in the composites without MA (P01, Fig. 2d), size of dispersed particles (about 300 – 1000nm) is bigger than that on P11 containing 1 wt% MA (Fig. 2c). In this case, size of Org-MMT is only about 100-400 nm.

On the other hand, size of dispersed particles again increased when the content of Org-MMT in the composite reaches to 2 wt% (P12, Fig. 2c). In this case, size of Org-MMT is about 300-500 nm. This can be explained by a part of Org-MMT has not been exfoliated which agglomerated into micrometer size of particles. Comparing the SEM images indicated that the dispersion of Org-MMT in composite P11 (containing 1 wt% MA, 1 wt% Org-MMT) is finest.



a) b)

c)

Fig. 2. SEM images: a) P01, b) P11, c) P12

In sample P11, a part of Org-MMT was exfoliated, other formed intercalated nanocomposites.

This phenomenon was confirmed by TEM images (Fig. 3). The thickness of dispersed particles in the PP matrix is about 10 – 20 nm and the length is about 100 – 300 nm. Some of particles arranged parallel in PP matrix, the length is longer (about 500 – 1000 nm).

Consequently, the presence of MA promoted the dispersion of Org-MMT in PP matrix. XRD analyse and SEM, TEM observations determine the formation of intercalated and exfoliated structures in the nanocomposites and the good dispersion and exfoliation of Org-MMT in PP matrix was achieved in the composite containing 1 wt% Org-MMT with the presence of 1 wt% MA.

3.2. Mechanical testing:

After mixing PP with Org-MMT presence of fixed amount of MA, mechanical properties of the materials were remarkably enhanced, especially elongation at break as can

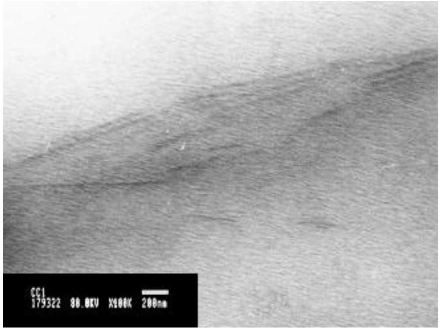


Fig. 3. TEM image of sample P11.

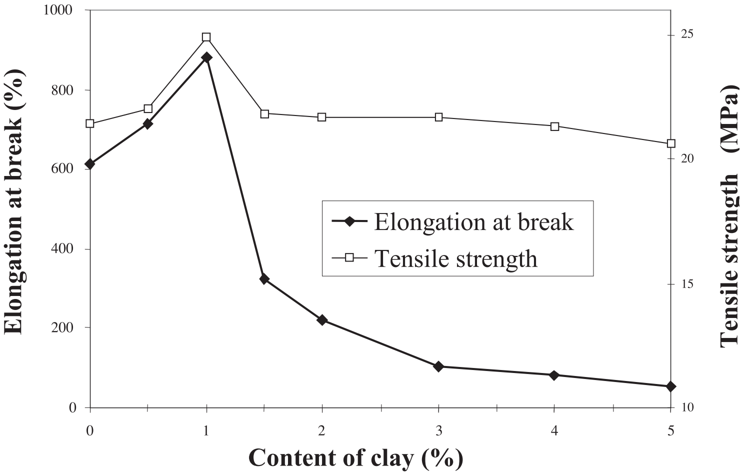


Fig. 4. Influence of content of Org-MMT on mechanical properties of nanocomposites.

be seen from Fig. 4. The results of stress strain testing showed that tensile strength and elongation at break of PP/ Org-MMT (100/1) nanocomposite using 1 wt% MA were increased 20.47 wt% and 220 wt% comparing with neat PP, respectively. MA improved the intercalation of PP chain into the interlayer spacing of Org-MMT and the exfoliation of its layers in PP matrix which are conducting to form a exfoliation nanocomposites.

Beside that, PP-g-MA formed by in-situ melting blending plays as a compatibilizer between PP and Org-MMT. Thus, the dispersion of Org-MMT in matrix PP became easier [1, 10, 11]. As a result, mechanical properties of the nanocomposites were dramatically improved. When content of Org-MMT in PP was higher than 2 wt%, tensile strength and elongation at break of the nanocomposites were remarkably decreased comparing with neat PP due to the existence of both structures nanocomposites and microcomposites. The loading of Org-MMT in PP more than 2 wt% is too high to allow exfoliation of whole amount of Org-MMT probably due to the large aspect ratio.

3.3. Thermo-gravimetric analysis (TGA)

Commonly, the incorporation of clay into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to volatile products generated during decomposition of the polymer [1, 2, 10].

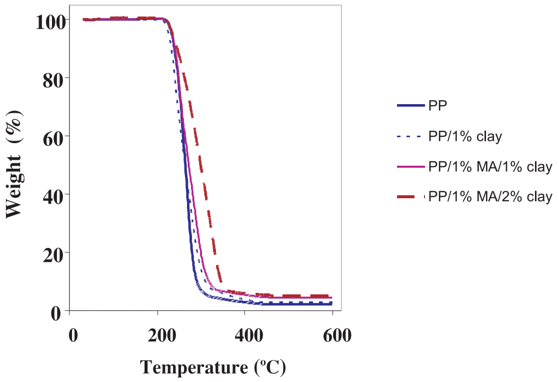


Fig. 5. TG curves of nanocomposites.

Fig. 5 shows TG curves of PP, P01, P11, P12 samples. In general, the major weight losses were observed in the range of 200 -350 ^{o}C and the rate of thermo-oxidative degradation of composites PP/MA/ Org-MMT were lower than those of neat PP and P01. Specifically, as can be seen in Table 2, the initial weight loss temperature (T$_i$) of PP, P01 samples is about 210 ^{o}C whereas P11, P12 samples is about 220 ^{o}C and the maximum weight loss temperature (T$_{max}$) of P11, P12 samples is also higher than that of the remaining samples.

Table 2. *The TG characterization of nanocomposites*

Samples	T$_i$ (^{0}C)	T$_{max}$ (^{0}C)	The remaining weight (wt%)	
			at 270 ^{0}C	at 330 ^{0}C
P00	211.5	266.9	37.10	4.58
P01	210.5	266.9	42.73	7.15
P11	218.8	268.9	52.40	7.62
P12	219.1	324.0	74.43	21.53

Particularly, T$_{max}$ of P12 sample is 324 ^{o}C which is higher than that P00 sample by 57 ^{o}C. The thermal stability of the nanocomposites increases with rising the content of Org-MMT up to 2 wt%.

The aforementioned results have confirmed once more an important role of MA. MA in content of 1 wt% and its copolymer with polypropylene (PP-g-MA) formed by in-situ melt blending have improved dramatically the interaction between PP chains and Org-MMT, hence, the structure of the nanocomposite becomes more finer than that of the composite without MA. As a result, the thermal stability of composite was enhanced.

4. CONCLUSION

Nanocomposites based on PP/MA/ Org-MMT was prepared by melt mixing. The XRD patterns, TEM and SEM image showed exfoliation of Org-MMT layers in PP matrix and existence of both the exfoliated, intercalated structures of the formed nanocomposites in presence of 1 wt% MA.

The tensile strength, elongation at break, and thermal stability of PP/MA/Org-MMT nanocomposites was higher than those of neat PP.

MA played a very important role in reduction of size of Org-MMT and improved its dispersion in PP matrix.

Acknowledgments. This work is result of Basic Research Project supported by the Ministry for Science and Technology.

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Received January 15, 2006.