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Effect of Layered Silicates on the Crystallinity and Mechanical Properties of HDPE/MMT Nanocomposite Blown Films

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Summary

The highdensitypolyethylene (HDPE)/montmorillonite (MMT) nanocomposites were prepared by melt blending using twin screw extruder with two step process. The master batches were manufactured by melt compounding with maleic anhydride grafted HDPE (HDPE-g-MAH) and MMT. The HPDE/MMT master batches were subsequently mixed with HDPE. The blown nanocomposite films were obtained by a single screw extruder attached film blowing and take-off unit. The MMT dispersion in the nanocomposite films was characterized by X ray diffraction (XRD) and transmission electron microscope (TEM). The influence of MMT on the crystallinity, thermal properties and mechanical properties as a function of compatibilizer was investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and universal testing machine, respectively. X ray and TEM images showed the partially exfoliated nanocomposites which have the 5:1 – 20:1 ratios of HPDE-g-MAH and MMT. The thermal and mechanical properties of nanocomposites were enhanced by increasing the contents of MMT and in the presence of compatibilizer.

Introduction

Recently, silicate layers such as montmorillonite (MMT) have been widely studied as property enhancers for polymeric materials. There has been much research into polymer nanocomposites, due to the improvement in mechanical [1-3] and thermal [4] properties.

Generally, it has been known that melt intercalation process is the most cost effective process as compared to other methods of preparing polymer/layered silicate nanocomposites.

High density polyethylene (HDPE) is widely used in flexible film packaging produced by the blown film process. The information concerning the relationship between blown film structure and property is very important to PE film manufacturers. The mechanical response of HDPE film is a strong function of its morphological texture. This structure is controlled by a combination of the melt process variables and the structure characteristics of the resin. To achieve the desired properties and make better packaging films, it is important to understand the processing variables that affect the film crystallization, orientation and morphology and the correlation between the orientation/morphology with the final film properties [5-6].

The objective of the present work is to enhance the thermal and mechanical properties of HDPE blown film using the nanotechnology. HDPE/MMT nanocomposites having a various compositions were prepared by a melt blending technique with a twin screw extruder. HDPE/MMT nanocomposite films were prepared by blown film process. The morphologies and thermal properties of the nanocomposites were characterized by X ray diffraction (XRD), transmission electron microscope (TEM) and thermogravimetric analysis (TGA), respectively. The mechanical properties of nanocomposites were obtained with a universal testing machine (UTM).

Experimental

High density polyethylene (HDPE, YUZEX® 2800, MI=0.028g/10 min, density= 0.955g/cm^3) as the matrix and maleic anhydride grafted high density polyethylene (HDPE-g-MAH, ADPOLY® EM510H, MI=0.6g/10 min, density= 0.955g/cm^3, MAH contents=0.3wt%) as the compatibilizer (C) were obtained from SK Corporation and Honam Petrochemical Corporation, respectively. The layered silicate used in the study is a Cloisite 15A (Southern Clay Products), which is a natural sodium montmorillonite modified with a quaternary ammonium salt, 2M2HT (M: methyl; HT: hydrogenated tallow with ~65%C18, ~30%C16 and ~5%C14).

A master batch of HDPE-g-MAH/MMT and HDPE/MMT nanocomposites were prepared by melt mixing using a twin screw extruder (Baker Perkins, MPC 30, L/D=13). The mixing temperature was controlled at 180~190°C, the screw speed was 250 rpm. The master batch was first prepared with HDPE-g-MAH and MMT in order to enhance the dispersion of MMT. The ratios of HDPE-g-MAH and MMT were 3:1, 5:1, 10:1 and 20:1 as shown in Table 1. The HDPE/MMT nanocomposites were prepared by mixing of HDPE with MMT or master batch.

Table 1. Compositions of HDPE-g-MAH/MMT Master Batch

Sample	HDPE-g-MAH	MMT
MB-3	3	1
MB-5	5	1
MB-10	10	1
MB-20	20	1

The compositions of the HDPE/MMT nanocomposites studied in this work are summarized in Table 2. The blown films were produced with single screw extruder attached with blowing equipment. The temperatures of melting zones and the die of single-screw extruder were 230°C. The take up speed was 40 rpm. The blow-up ratio was maintained at 3:1.

The ultrathin sectioned nanocomposite samples for TEM experiment were prepared by microtome equipped with diamond knife. Ultrathin section samples were collected and placed on a 200 mesh copper grid. The TEM micrographs were obtained with a Tecnai G2 gun type (FEI company) apparatus running at an acceleration voltage of 200kV.

The thermal stability was investigated by thermogravimetric analysis using TGA Q500 system of TA instruments at the heating rate of 20°C/min under a flowing nitrogen atmosphere. The temperature was changed from 25 to 800°C.

The tensile tests were performed according to ASTM D822, a standard test method for tensile properties of thin plastic sheeting. A crosshead speed of 500mm/min and a 0.1kN cell with rubber clamps were used.

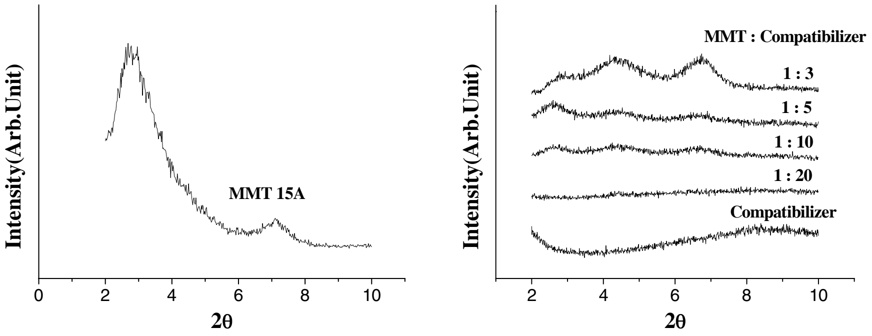
Table 2. Compositions of HDPE/MMT Nanocomposites

	HDPE	HDPE-g-MAH	MMT(phr)
HDPE	100		
HDPE/MMT0.5	100		0.5
HDPE/MMT1	100		1
HDPE/MMT2	100		2
HDPE/ MB-20	90	10	0.5
HDPE/ MB-10	90	10	1
HDPE/ MB-5	90	10	2

Results and Discussion

X ray diffraction patterns of MMT and HDPE/MMT nanocomposites with different MMT content are shown in Figure 1. XRD patterns of organically modified MMT (a) and HDPE-g-MAH/MMT nanocomposites (b) with different ratios of HDPE-g-MAH/MMT are also displayed in Figure 1.

The accurate description of nanoscale structure of nanocomposite could be explained by additional descriptors, such as partially intercalation, intercalation, partially exfoliation or exfoliation [7]. Figure 1(b) showed the formation of different types of nanocomposites by varing the composition of compatibilizer with MMT. That is, Figure 1(b) showed the formation of partially intercalation structure with composition MMT:Compatibilizer (1:3), intercalation structure with composition (1:5), partially exfoliation structure with composition (1:10) and exfoliation structure with composition (1:20), respectively.

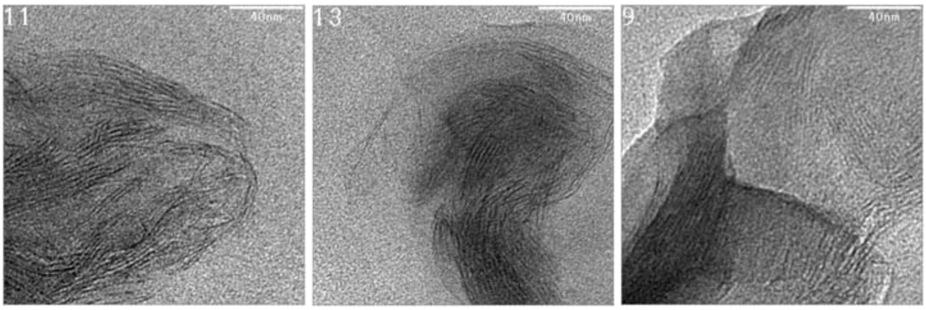


(a) (b)

Figure 1. XRD patterns of MMT (a) and compatibilizer/MMT composites (b).

It is obvious that the specific peak of MMT disappears and the corresponding gallery spacing is widened by intercalation and exfoliation at the HDPE-g-MAH/MMT ratio 5~20:1. Particularly, at the HDPE-g-MAH/MMT ratio, specific peak of MMT disappears at 20:1. Furthermore, it is also noted that HDPE-g-MA is an effective compatibilizer in HDPE-g-MA/MMT ratio, 5~20:1.

The dispersion of MMT in the HDPE matrix with and without compatibilizer is shown in Figure 2 and 3. Figure 2 shows the intercalated structure in HDPE/MMT nanocomposites prepared without the compatibilizer. The distribution of MMT in HDPE is almost uniform, and the tactoid structure still remains. A master batch process was applied to enhance the degree of exfoliation of nanocomposites, a master batch process was applied.

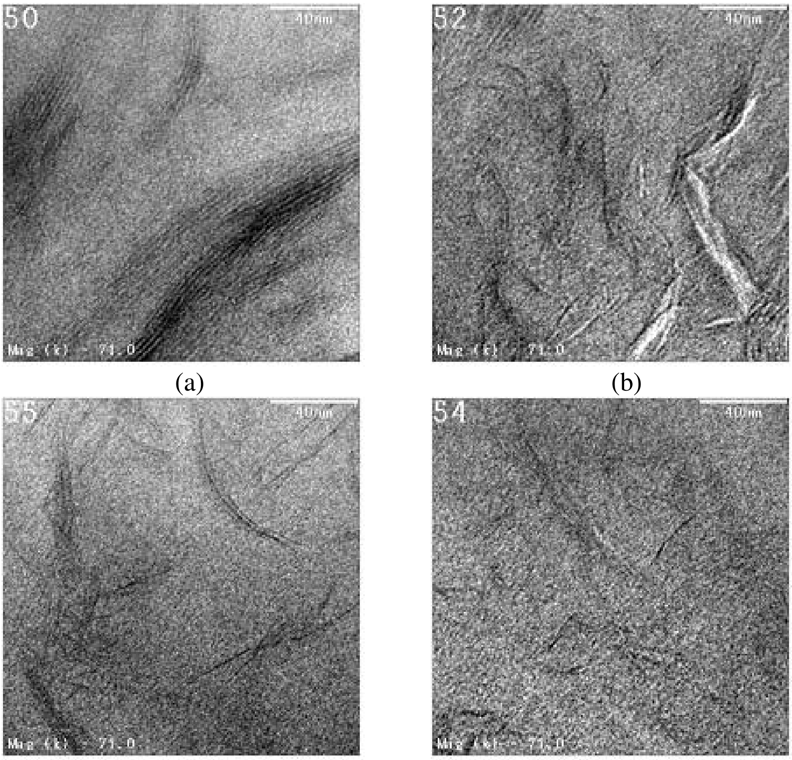


(a) (b) (c)

Figure 2. TEM micrographs of HDPE/MMT nanocomposites without compatibilizer.
MMT content is (a) 0.5phr, (b) 1 phr and (c) 2phr.

Figure 3 shows the TEM images of the master batch prepared with HDPE-g-MAH and MMT. It is clearly seen from the TEM images that the MMT aggregates have been broken down into smaller stacks and exfoliation has occurred depending on the ratio of HPDE-g-MAH and MMT. Figure 3(a) shows an indication of intercalated MMT aggregates in case of the ratio of 3:1. This means that the content of the compatibilizer is insufficient to aid the dispersion of MMT. Figure 3(b), (c) and (d) show that the MMT is partially exfoliated throughout the HDPE-g-MAH matrix. It is understood from the results of TEM images that HDPE-g-MAH is an effective compatibilizer in HDPE-g-MAH/MMT ratio of 5~20:1.

It is well known that the polymer/MMT nanocomposites have better thermal properties as compared to the original matrix owing to the hindered different volatile decomposition products within the nanocomposites [8]. Thermal stability of HDPE/MMT nanocomposites was assessed by TGA under nitrogen atmosphere at the heating rate of 20 °C/min. Figure 4 shows that the nanocomposites degrade at a higher temperature than that of HDPE. Table 3 shows the 5% weight loss temperature of the nanocomposites. The temperature of 5% weight loss is shifted up to 15 °C by the addition of as low as 1 phr of MMT. The temperatures of HDPE/MMT nanocomposites without compatibilizer are lower than those of HDPE/MMT with compatibilizer. However, higher amount of MMT is unfavorable as exemplification by a temperature shift of only 10 °C when the content of MMT is 2 phr. It seems that the effect of the dispersion of MMT. It is obvious From Table 3 and Figure 4 that the degradation of the HDPE/HDPE-g-MAH/MMT nanocomposites is retarded. This effect can be explained that MMT disturbs the diffusion of oxygen and volatile products throughout the nanocomposite materials.



(a) (b)

(c) (d)

Figure 3. TEM micrographs of HDPE-g-MAH/MMT master batch with various ratios; (a) 3:1, (b) 5:1, (c) 10:1(c) and (d) 20:1.

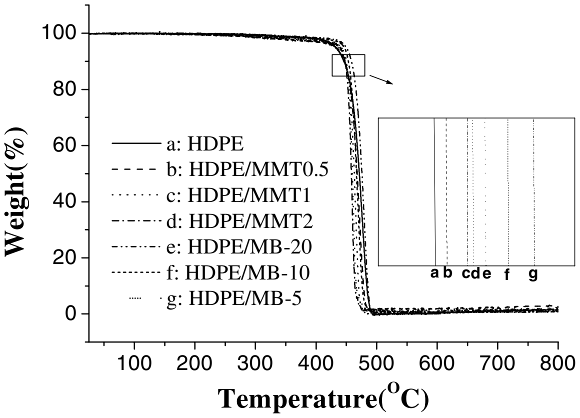


Figure 4. TGA thermograms of HDPE nanocomposites with various compositions.

Table 3. Thermal Properties of HDPE/MMT Nanocomposites

Sample	5% weight loss temperature(°C)
HDPE	432
HDPE/MMT0.5	433
HDPE/MMT1	440
HDPE/MMT2	438
HDPE/ MB-20	450
HDPE/ MB-10	446
HDPE/ MB-5	442

The crystallization behaviour and crystal forms in the HDPE and HDPE/MMT nanocomposites were evaluated using DSC and XRD.

Figure 5 shows the percentage crystallinity of HDPE and HDPE/MMT composites blown films. As the MMT content is increased, the crystallinity is decreased. Furthermore, the crystallinity was considerably decreased with an increase in the compatibilizer content.

The MMT have a significant effect on crystallinity of HDPE/HDPE-g-MA/MMT nanocomposites. It seems that the degree of crystallinity is dependent on the MMT content.

The reduction in the crystallite size is shown through Table 4 and Figure 6. It seems that the increase in the MMT contents increases the amount of the oriented lamellar in the SEM images and decreases the crystallite size.

Furthermore, the MMT acts as a nucleation agent and contributes to increase in the crystallization temperature and reduction in the crystallite size [8].

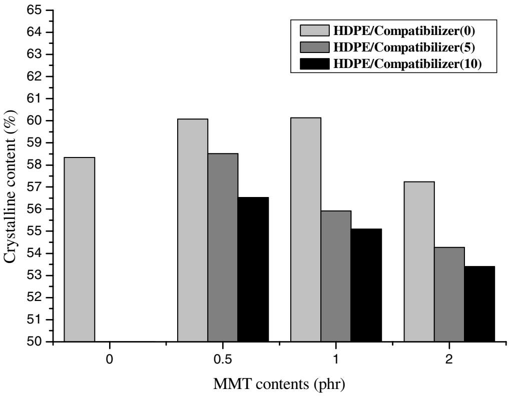
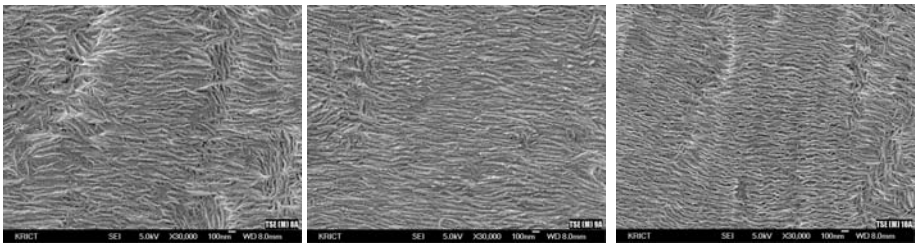


Figure 5. Crystallinity content of HDPE/MMT nanocomposites films.

Table 4. Crystal Dimension (nm) in (110) Planes Direction

MMT	0 phr	0.5 phr	1.0 phr	2.0 phr
HDPE/MMT	4.83	4.75	4.6	4.38
HDPE/MB		4.95	4.67	4.25



(a) (b) (c)

Figure 6. SEM micrographs of HDPE/MMT nanocomposites films.
MMT content = 0.5phr (a), 1phr (b), 2phr (c).

The addition of the sufficient amounts of HDPE-g-MAH into conventional HDPE/MMT nanocomposite gives rise to the exfoliated nanocomposite structure in which individual MMT platelets are exfoliated very well in the HDPE matrix, resulting in a corresponding increase in mechanical properties. Moreover, the tensile strength of nanocomposites is enhanced, due to improved interfacial adhesion [9-10]. It leads to better stress transfer at the other words the improvement of interfacial adhesion by HDPE-g-MAH can prevent separation between HDPE and MMT during tensile deformation. The tensile strength of HDPE/MMT nanocomposites was compared with the different MMT contents. Figure 7 represents the tensile strength of HDPE/MMT nanocomposites with and without HDPE-g-MAH as a function of MMT content. It shows that the samples prepared by MMT with compatibilizer have higher tensile strength. The tensile strength increased in the machine direction (MD) up to 70% for HDPE/MMT nanocomposite films in comparison to pure HDPE film. It seems that the increase in the MMT contents increased the tensile strength. At the same MMT content, the tensile strength was increased by the addition of compatibilizer.

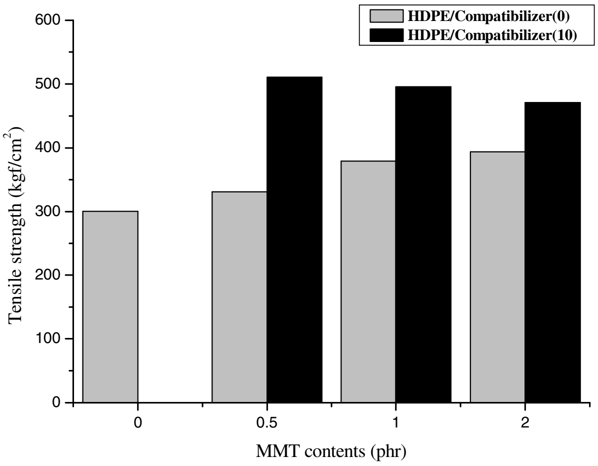


Figure 7. Tensile strength of HDPE/MMT nanocomposites with various compositions.

Conclusion

HDPE/MMT nanocomposites with and without compatibilizer were prepared by melt mixing. And their films were prepared by the blown film process. HDPE-g-MAH acts as compatibilizer between HDPE and MMT and makes it feasible to achieve the exfoliated structure. XRD and TEM micrographs suggest an exfoliated structure for HDPE/MMT nanocomposites with compatibilizer. Increasing the MMT content, the crystallinity and crystallite size decreases. The thermal stability and mechanical properties of HDPE/MMT nanocomposites were affected by MMT content and the degree of exfoliation of MMT.

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