

A study of strength and thermal stability of Low-density polyethylene grafted maleic anhydride/montmorillonite nanocomposites

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Abstract

In the field of polymer materials at present, polymer/layered silicate (PLS) nanocomposites are very prevailing in basic research or development for industries, among them montmorillonite (MMT) has the most significant applied value. In this study, various contents of organic/inorganic nanocomposites of low-density polyethylene (LDPE) matrix which was filled with MMT nano-filler (low-density polyethylene/montmorillonite (LDPE/MMT), and low-density polyethylene grafted maleic anhydride/montmorillonite (LDPE-g-MA/MMT)) were investigated experimentally. Properties of strength and thermal stability of LDPE/MMT and LDPE-g-MA/MMT nanocomposites research were carried out. Firstly, different raw materials LDPE/MMT and LDPE-g-MA/MMT nanocomposites were fabricated via twin-screw extruder, and then the test specimens were produced by an injection machine in accordance with the test norms. Furthermore, the main analytical tests were tensile test, impact test, bending test, hardness test, DSC analysis, TGA analysis and SEM microstructure observed. The increasing mechanical properties were found to have certainly improved after the proper MMT and MA grafted were added. In addition, in DSC test, the T_m and enthalpy of LDPE-g-MA group was also lower relatively. In TGA test, it is apparent that dispersion degree and thermal stability are increased because the presence of the MA grafted. Finally, in SEM microstructure observation, it was showed that the structure of LDPE-g-MA group appears looser structure than the structure of LDPE group so it is easy for MMT to embed and disperse uniformly in the structure of LDPE-g-MA group.

keywords: montmorillonite (MMT), low-density polyethylene (LDPE), low-density polyethylene grafted maleic anhydride (LDPE-g-MA), strength, thermal stability

1. INTRODUCTION

Polymer-layered silicate nanocomposites are a new class of materials with improved barrier properties, thermal stability [1-2], mechanical properties [3-4] and reduced flammability [5-7] modified as compared to those of neat polymers. Supong Arunvisut et al. prepared LDPE/MMT nanocomposites with LDPE, organo-clay, PE-g-MA as the compatibilizer, result showed presence of PE-g-MA improved dispersion of exfoliation, tensile modulus, yield strength as the MMT content increased [8].

In the field of polymer materials at present, polymer/layered silicate (PLS) nanocomposites are very prevailing in basic research or development for industries. Among them montmorillonite (MMT) has the most significant applied value [9]. Polyethylene (PE) based nanocomposites with o-MMT were also obtained by different methods including polymerization of PE in the presence of layered silicate and application of polyethylene-grafted-maleic anhydride (PE-g-MA) as a matrix [10-11].

In this study various components of organic/inorganic nanocomposites of low-density polyethylene (LDPE) matrix which was filled with MMT nano-filler (low-density polyethylene/montmorillonite (LDPE/MMT), low-density polyethylene grafted maleic anhydride/montmorillonite (LDPE-g-MA/MMT) were investigated experimentally.

2. EXPERIMENTAL METHODS

2.1. Materials and preparation

Low-density polyethylene (LDPE203) and polyethylene grafted with maleic anhydride (PE-g-MA, GN1703) as matrix from USI Corporation (Taiwan). Montmorillonite from Long Chain International Corporation (LCIC). In the case, LDPE, PE-g-MA and nanoclay were melt-mixed by twin-screw extruder (ZPT-32HT) with a temperature profile of 160 °C and a screw speed of 150 rpm, 20 min to obtain nanocomposite. The samples and compositions prepared are listed in Table 1.

2.2 Testing methods

Tension tests were performed using a mechanical testing machine at a speed of 10 mm/min using at least 3 specimens of each material was according to ASTM D638 [12]. Impact tests were performed using Izod impact testing machine, the specimens were according to ASTM D256 [13] and CNS 13334 [14]. Bending test was using a three-point bending machine at a speed of 0.5 mm/min, 200 second. Hardness tests were using the Shore tester. Thermal properties of materials were determined by DSC, samples were heated from 30 to 300 °C at the rate of 4°C/min. Thermal stability was determined by TGA thermogravimetric analyzer during heating at the rate of 10 °C/min from 30 to 800 °C, under the N₂. Morphology of sample surfaces were examined by scanning electron microscope (SEM). The dispersibility of samples was evaluated using by transmission electron microscope (TEM), Hitachi H-7100.

Table 1: Compositions of PE/Clay Nanocomposites Prepared

Composition	LDPE-g-MA (wt %)	LDPE (wt %)	MMT (wt %)
LDPE	100	-	0
LDPE/MMT-1	99	-	1
LDPE/MMT-2	98	-	2
LDPE/MMT-3	97	-	3
LDPE/MMT-4	96	-	4
LDPE/MMT-5	95	-	5
LDPE-g-MA	-	100	0
LDPE-g-MA/MMT-1	-	99	1
LDPE-g-MA/MMT-2	-	98	2
LDPE-g-MA/MMT-3	-	97	3
LDPE-g-MA/MMT-4	-	96	4
LDPE-g-MA/MMT-5	-	95	5

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

3.1.1 Tensile test

The Young's modulus plots of samples are shown in figure 1. Young's modulus of the samples was determined from the slope of the initial elastic region (plot not shown). It can be observed that the Young's modulus of pure LDPE is 80 MPa, and Young's modulus increases when clay was added. The maximum Young's modulus was 121 MPa in LDPE group (increased 51.25% to pure LDPE); the maximum Young's modulus is 129.83 MPa in LDPE-g-MA group (increased 62.1% to pure LDPE). In the literature [15], it also can be seen that Young's modulus improved when org-clay added.

3.1.2. Impact test

From figure 2 shown that the impact strength improved since the MMT was added to LDPE group and LDPE-g-MA group. In the LDPE/MMT group, the maximum impact strength (increased toughness 60.62% to pure LDPE) was obtained at 5 wt% clay content; in the LDPE-g-MA/MMT group, the maximum impact strength (increased toughness 67.88% to pure LDPE) was obtained at 4 wt% clay content.

3.1.3 Bending test

The flexural modulus in each group was all less than the flexural modulus of pure LDPE from figure 3. It meant that the composite materials became more difficult to bend; that was, there was increased in rigidity. The least flexural modulus occurred at 5 wt% clay content in the LDPE-g-MA/MMT group (increased about 8.5% rigidity).

3.1.4 Hardness test

Figure 4 shown that hardness in LDPE-g-MA group was increased significantly. It meant the reinforcement in the LDPE-g-MA group was better then LDPE group. The maximum hardness value in LDPE group occurred at 5 wt% clay content (increased 0.60% to pure LDPE); the maximum hardness value of the LDPE-g-MA group occurred at 3 wt% clay content (increased 2.58% to pure LDPE).

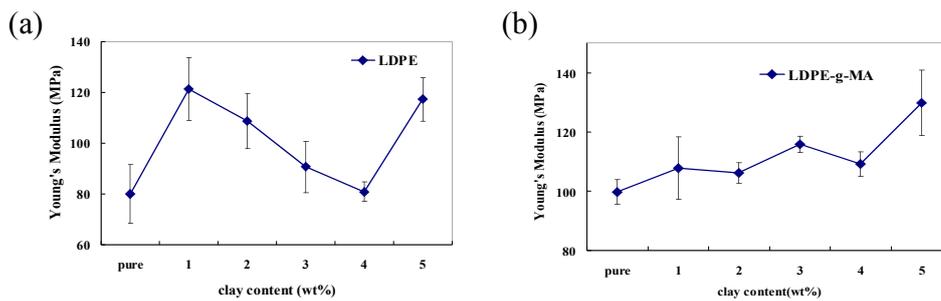


Figure 1: (a) Young's modulus for LDPE/MMT group. (b) Young's modulus for LDPE-g-MA/MMT group

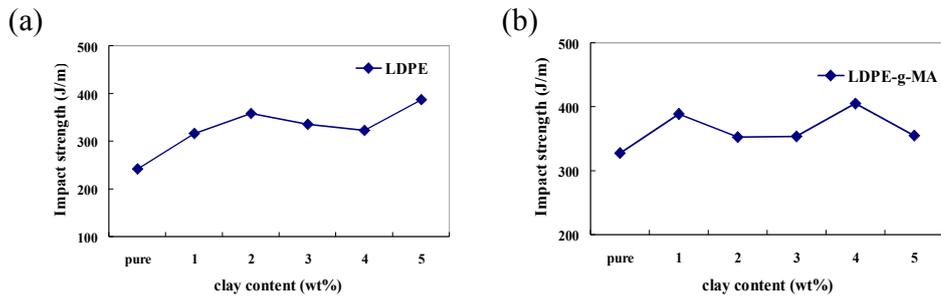


Figure 2: (a) Impact resistance strength for LDPE group. (b). Impact resistance strength for LDPE-g-MA group

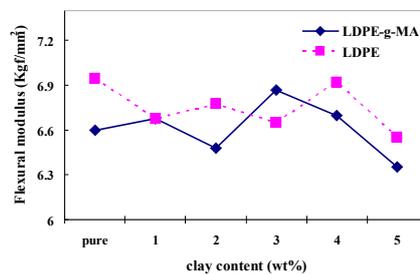


Figure 3: The flexural modulus for LDPE and LDPE-g-MA group

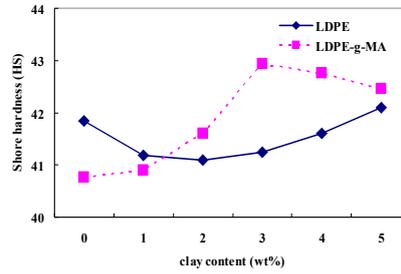


Figure 4: Shore hardness for LDPE and LDPE-g-MA group

3.2. Thermal analysis

3.2.1 DSC analysis

The melting point (T_m) and enthalpy of LDPE and LDPE-g-MA group are showed in Figure 5 and Figure 6. In twin-screw melt extrusion process, the polymers were impeded by the clay to produce an aggregative phenomenon of crystallization as a result of the endothermic areas of crystallization decreasing and a declining enthalpy because the clay dispersed evenly in polymer. In addition, the enthalpy of LDPE-g-MA group was also lower relatively. It is indicated that MMT would be made easier to embed in polymer by MA grafted so that clay dispersion was better. There was no difference in melt temperature between samples as it is visible in figure 5. This behaviour thermal was similar to the previous literature [16].

3.2.2 TGA analysis

In the TGA plots of composites (Figure 7) shown that LDPE group, only clay content at 2 wt% appeared thermal decomposition temperature (T_d) (444.6 °C) higher than the pure LDPE. In LDPE-g-MA group; only when clay content at 1 wt% content is T_d (455.09 °C) higher than the pure LDPE. By comparison, the T_d of LDPE-g-MA group was almost higher 10 °C than of LDPE group, and the other T_d points at different clay contents were no significant different, it corresponded with previous literature [17-19]. It is appeared that dispersion degree and thermal stability were increased because of the presence of the MA grafted.

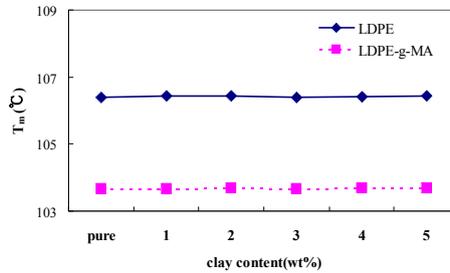


Figure 5: Melting point for LDPE and LDPE-g-MA group

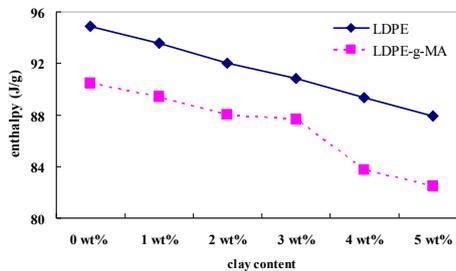


Figure 6: Enthalpy for LDPE and LDPE-g-MA group

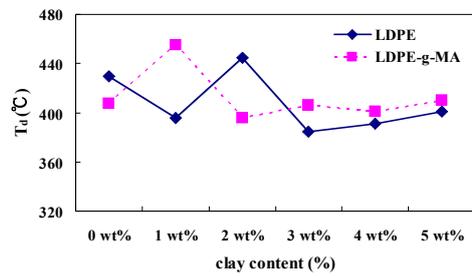


Figure 7: Thermal decomposition temperature for LDPE and LDPE-g-MA group

3.3 SEM Microstructure observed

The SEM studies of surface of samples are shown in figure 8 and figure 9. Figure 8 shown that although MMT embed to polymer improved with increasing MMT content, but MMT particles were dispersed un-uniformly. The large particles of MMT were about 30 μm in diameter and the small particle less than 1 μm in diameter in which two types of composite materials with 5 wt% content of clay observed from figure 8 (e) and (f). It meant that a part of MMT had a coalescence phenomenon, so that it could not be dispersed well. Compared figure 9 (a) and figure 9 (b), the structure observation of LDPE-g-MA group (b) appears looser structure than the structure of LDPE group (a). So it was easier for MMT to disperse and embed uniformly in the structure of LDPE-g-MA group.

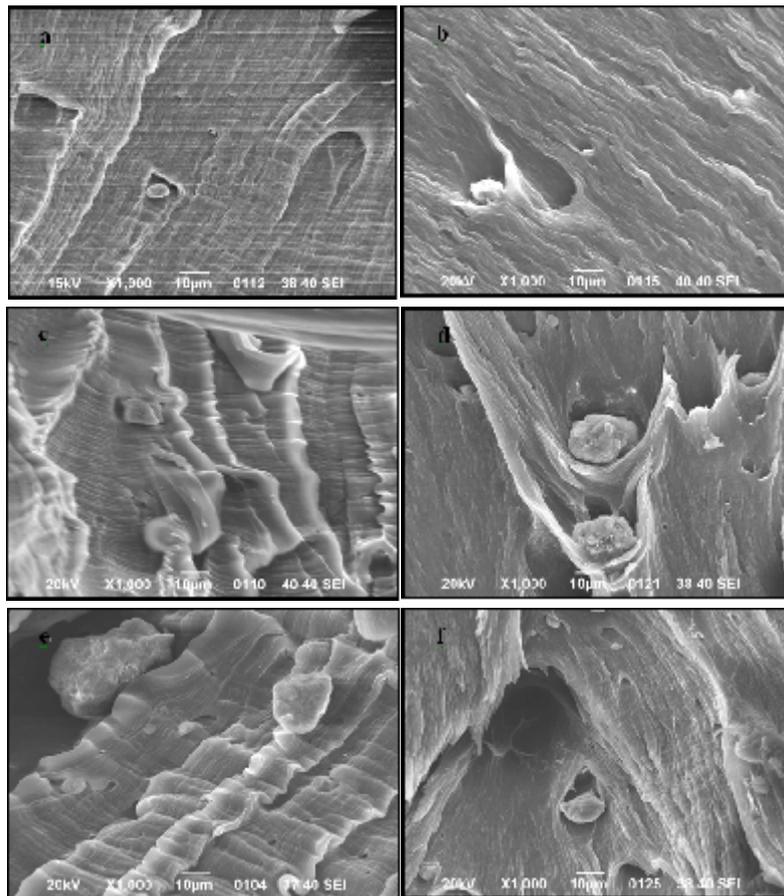


Figure 8: (a) SEM of LDPE/MMT-1 wt%. (b) SEM of LDPE-g-MA/MMT-1 wt% ($\times 1000$) (c) SEM of LDPE/MMT-3 wt%. (d) SEM of LDPE-g-MA/MMT-3 wt% (e) SEM of LDPE/MMT-5 wt%. (f) SEM of LDPE-g-MA/MMT-5 wt%

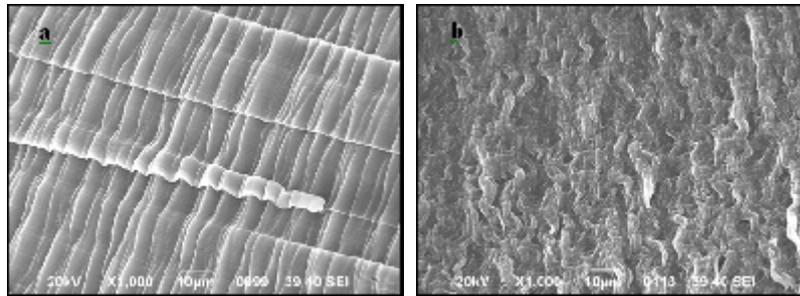


Figure 9: (a) SEM of pure LDPE. (b)SEM of pure LDPE-g-MA ($\times 1000$)

3.4 Characterization of samples by Transmission electron microscopy (TEM)

The TEM micrographs of LDPE/MMT-1wt%, LDPE/MMT-5wt%, LDPE-g-MA/MMT-1wt% and LDPE-g-MA/MMT-5wt% nanocomposites are shown in Figure 10 and 11. From the low magnification images (Figure 10, 5K), we can see that the clay is not homogeneously distributed for LDPE group and LDPE-g-MA group. The dispersibility of 1wt% content of clay was better than 5wt% for both groups. But it can be seen that no matter clay content is for both groups, all appear agglomeration (from Figure 11, high magnification, 20K). The clay actually maybe well-dispersion in some location but congregated in others [17]. This behaviour due to there is without compatibilizer between polymer and clay [16], exactly as seen by SEM.

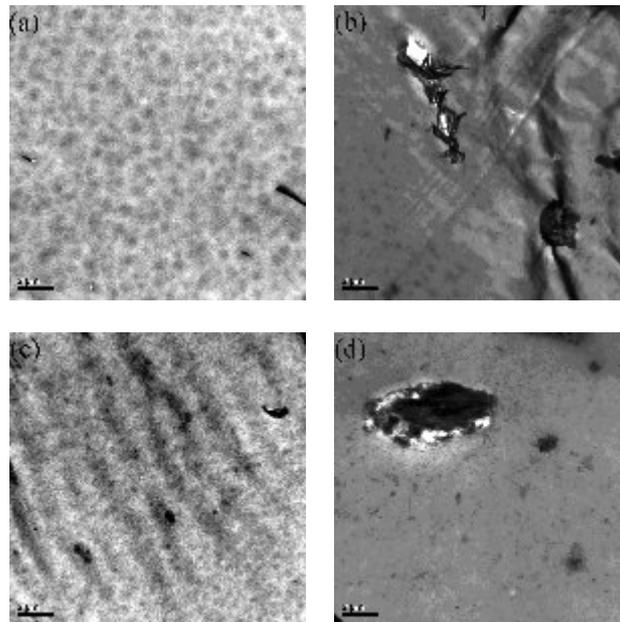


Figure 10: TEM images of samples (5K) (a) LDPE/MMT-1wt% (b) LDPE/MMT-5wt%
(c) LDPE-g-MA/MMT-1wt% (d) LDPE-g-MA-5wt%

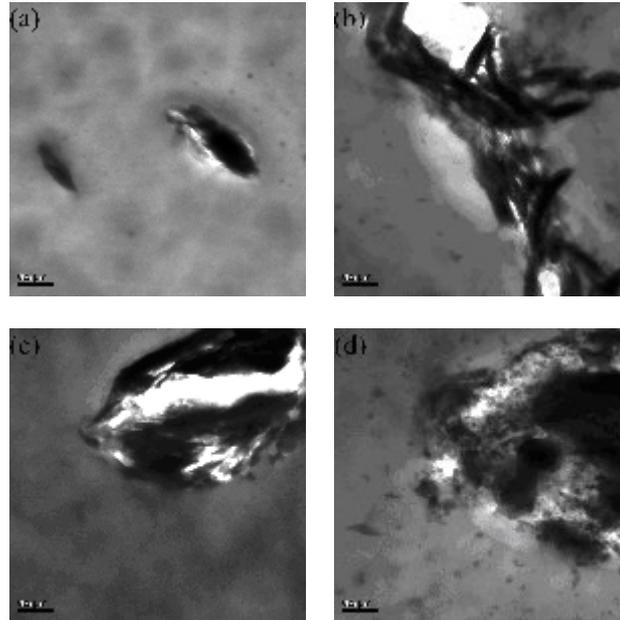


Figure 11: TEM images of samples (20K) (a) LDPE/MMT-1wt% (b) LDPE/MMT-5wt% (c) LDPE-g-MA/MMT-1wt% (d) LDPE-g-MA-5wt%

4. CONCLUSION

These experiments demonstrated four mechanical properties, two thermal properties, and SEM microstructure observation analysis by comparison in the pure LDPE, LDPE, LDPE-g-MA group. The increasing mechanical properties were found to have certainly improved after the proper MMT and MA grafted were added. In the tensile test, the greatest Young's modulus of LDPE group is increase 51.25 % than pure LDPE; the greatest Young's modulus of LDPE-g-MA group is increase 62.1 % than pure LDPE. In the impact test, the highest impact resistance strength of LDPE-g-MA group more than LDPE group. In bending test, the least rate of bending elasticity occurred at 5 wt% clay content in the LDPE-g-MA/MMT group (increased 8.5 % rigidity). In the hardness test, it was found to have had a significantly increase in LDPE-g-MA group. In addition, in DSC test, the T_m and enthalpy of LDPE-g-MA group was also lower relatively. It is indicated that MMT would be made easier to embed in polymer by MA grafted. In TGA test, it is apparent that dispersion degree and thermal stability are increased because the presence of the MA grafted.

Finally, in SEM microstructure observation, it was showed that the structure of LDPE-g-MA group appears looser structure than the structure of LDPE group so it is easy for MMT to embed and disperse uniformly in the structure of LDPE-g-MA group. However, there was a coalescence phenomenon to be found that MMT particles were dispersed un-uniformly with increasing MMT content. In TEM micrographs, it can be seen the dispersibility was poor, as it was not compatible between polymer and MMT. This research demonstrated the significant potential efficiency and reliability of LDPE-g-MA/MMT nanocomposites to employ in the development of personal protect equipment for the labors.

5. Future

MMT added in polyethylene and maleic anhydride certainly demonstrated an effect of reinforcement. This experiment was based on LDPE-g-MA as matrix. In addition, used LDPE-g-MA as a compatibilizer [16], another method would be tried to fabricate PE/LDPE-g-MA/MMT composites or MMT would be modified in order to obtain a high degree of bond a result of increasing the interface strength between polyethylene and MMT. It will be believed that the characteristics of composite materials will be a great deal of demonstration.

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