

Studying the Intercalation of Low Density Polyethylene/Clay Nanocomposites after Different UV Exposures

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Abstract---This study attempts to understand the effect of different UV irradiation methods on the intercalation of LDPE/MMT nanocomposites, and its molecular behavior at certain isothermal crystallization temperature. Three different methods of UV exposure were employed using single composition of LDPE/MMT nanocomposites. All samples were annealed for 5 hours at a crystallization temperature of 100°C. The crystallization temperature was chosen to be at large supercooling temperature to ensure quick and complete crystallization. The raw material of LDPE consisted of two stable monoclinic and orthorhombic phases according to XRD results. The thermal behavior of both phases acted differently when UV exposure method was changed. The monoclinic phase was more dependent on the method used compared to the orthorhombic phase. The intercalation of clay, as well as, the non-isothermal crystallization temperature, has also shown a clear dependency on the type of UV exposure. A third phase that is thermally less stable was also observed. Its respond to UV irradiation was greater since it contains low molecular weight entities which make it more vulnerable to any UV exposure.

Keywords---LDPE/MMT nanocomposites, crystallization, UV irradiation, intercalation.

I. INTRODUCTION

THE most common layered silicates used in preparing polymer/layered silicate nanocomposites are Montmorillonite (MMT). It is one of the typical natural minerals in the smectite clay family. The stacked layers of MMT are of about 1 nm in thickness and are separated from each other by a weak dipolar force. They form interlayers or galleries that are usually occupied by exchangeable Na^+ , K^+ , Ca^{+2} and Mg^{+2} cations. In order to improve the ion exchangeability of the layered silicates, MMT is usually modified organically by exchanging the alkali counter ions with cationic-organic surfactants, such as alkylammoniums [1], [2].

The organic modification of MMT allows the polymer molecules to intercalate within the galleries. Depending on the strength of the interfacial interactions between the polymer matrix and layered silicates, polymer/layered silicate can form either intercalated nanocomposites, where few molecular layers of polymer are intercalated, or exfoliated nanocomposites where the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on the clay loadings [3]. Well exfoliated

nanocomposites show better mechanical properties compared to its pure polymer. However, the interfacial interaction between LDPE and MMT is generally weak and require an intermediate agent like Maleic anhydride.

The importance of LDPE in the different fields of industry is well-known. Based on recent statistics [4], 17.5% of the total consumption of plastic industries in Europe is of LDPE. Its application varies from food packaging and shopping bags to electrical applications, auto parts, construction sites, and many other important and crucial applications. LDPE/layered silicates composites have shown improvement in their mechanical properties, flame retarding and thermal stability.

Radiation effect on the properties of LDPE and LDPE/MMT nanocomposites has extensively been studied in literature. High energy ion beam irradiation [4]-[7], γ radiation [8]-[11] and electron beam irradiation [12]-[16] are examples to the methods used to affect the molecular structure of certain polymers, including LDPE, and hence study its influence on the different properties of these polymers. Photo-oxidation using UV irradiation has also gained a wide interest in literature [17], [18]. Studying the rheological behavior of LDPE at temperatures exceeding their melting temperature and under UV irradiation was the goal of Marek and Verney [19] where they concluded that LDPE has shown less chain-scission compared to HDPE and PP. On the other hand, UV irradiation of LDPE/montmorillonite nanocomposites did not gain similar attentiveness in literature. Sánchez-Valdés et al. [20] studied the effect of photo-oxidation on two groups of LDPE/clay nanocomposites where they concluded that clay has enhanced the degradation rate of the nanocomposites compared to the raw PE material.

In this study, we irradiated an arbitrary selected composition of LDPE/MMT composite using short wavelength UV source. UV irradiation conducted at different stages of the crystallization process in order to investigate its effect on the molecular and crystalline structure of these composites.

II. EXPERIMENTAL PROCEDURE

A. Materials

A commercially available grade of low density polyethylene (LDPE) produced by SABIC (HP4023W) company was used in this study. The melt flow rate of this product is 4.0 g/10min. according to ASTM D1238. The nano-clay nanomer 1.44P is a montmorillonite clay surface

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modified with 35-45 wt. % dimethyl dialkyl (C14-C18) amine and is a product of Sigma Aldrich. The Maleic Anhydride grafted polyethylene (MA-g-PE) was used as a compatibilizer and is also a product of Sigma Aldrich.

B. Sample Preparation

The raw material was melt mixed using a Dynisco laboratory mixer. The composition of the mixture was arbitrarily selected to be of a 93 wt. % LDPE, 3 wt. % MA-g-PE and 4 w. % nano-clay. The barrel temperature was set at 140°C, while the orifice temperature was set at 130°C. The homogeneous compound was directly quenched in water at room temperature. The compound was then slightly pressed at 140°C to form homogeneous films of 0.1 mm thickness.

Samples were divided into four groups based on the method of UV treatment. A short UV wavelength of 254 nm at a distance of 13 cm was used for all samples.

- Sample A: was exposed to UV radiation during the 5 hours crystallization time.
- Sample B: was exposed to UV radiation for 3 days before melting.
- Sample C: was exposed to UV radiation for 10 minutes during melting.
- Sample D: was not exposed to any UV radiation.

Using Linkam T95-HS hot stage, the heating profile used to crystallize the samples was as follow: melting the sample at 130°C for 10 minutes to remove any thermal history; then rapidly cooling down to an arbitrary selected crystallization temperature of $T_c = 100^\circ\text{C}$; the sample is left for 5 hours to allow sufficient time for crystallization.

C. Testing Methods

The wide angle x-ray diffraction patterns were obtained for all samples using Bruker D8 advance X-ray diffractometer with Cu K_α radiation of wavelength $\lambda = 0.154$ nm and a running voltage and current of 40.0 (kV) and 40.0 (mA), respectively.

DSC endotherms were taken using Perkin Elmer DSC 8000. All samples were heated at the rate of $10^\circ\text{C}/\text{min}$, then cooled down to room temperature at the same rate.

III. DATA AND RESULTS

The melting behavior of raw LDPE material, see Fig. 1, shows a single broad endotherm peak at about 109.4°C indicates a relatively wide molecular weight distribution. The two second order transitions at around 59°C and 73°C are believed to be due to the presence of the slip and anti-block additives that were added to the raw material, as specified in its data sheet. The melting behavior of samples A - D that were isothermally crystallized at 100°C is shown in Fig. 2. All samples show three distinct peaks. At lower temperature, in the range between $93.0 - 95.0^\circ\text{C}$, a broad melting peak (peak 1) with small heat flow appears; while a peak with smaller FWHM and higher heat flow values (peak 2) appears in the range $104.0 - 106.0^\circ\text{C}$. At around 109.0°C peak 3 is observed; it has sharper and larger heat flow values. The absence of the multi-peak behavior in the raw material suggests that the

addition of MMT and PE-g-MA is the reason behind this action.

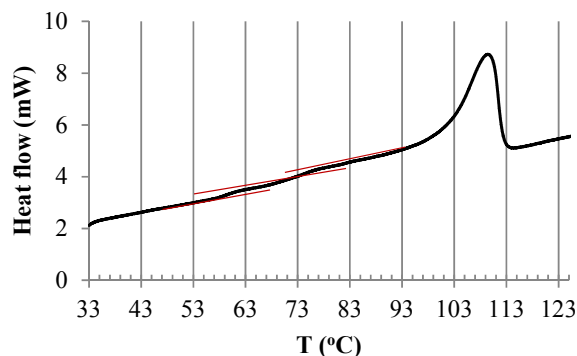


Fig. 1 DSC endotherm of raw LDPE

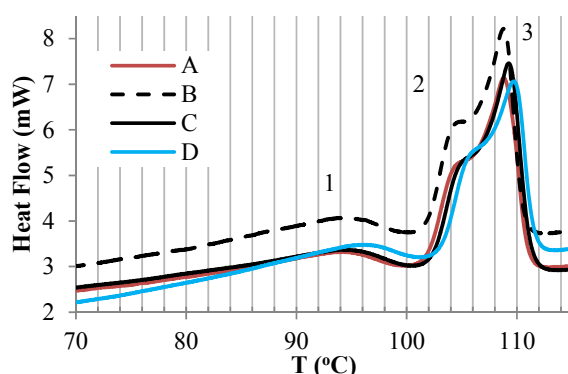


Fig. 2 DSC endotherms of all samples

Multi-peak behavior in DSC thermographs could be attributed to the presence of either different crystalline structures or different molecular weight population. In this work, it is thought that both interpretations are valid. Peak 1 is believed to be due to the melting of crystals that were formed by relatively low molecular weight chains [21]. These chains start to segregate producing some form of organized entities during the cooling process from melting to the crystallization temperature [22]. While the other two peaks are believed to be due to the formation of two different crystalline phases: the monoclinic and orthorhombic phases [23]. Since peak 3 coincides with the melting point of the raw material, it is believed that this peak refers to the orthorhombic phase of LDPE. Peak 2, on the other hand, should reflect the melting of the monoclinic phase. The existence of both phases is clear from XRD results as will be discussed later.

Fig. 3 shows the exotherms of all samples studied. The non-isothermal crystallization temperature of sample D has increased compared to the raw material; while temperatures of samples A, B and C fall in between them. In order to understand this behavior, raw material needs to be excluded from this analysis since it is not a composite and was not processed similar to the other samples. The large value of the non-isothermal crystallization temperature of sample D is

believed to be due to the less mobility of its relatively larger molecular chains since no chain cession has occurred. Other samples however, have shown lower non-isothermal crystallization temperatures. Chain cessions that occurred for these samples, because of UV exposure, produced shorter molecular chains which provided them with more mobility. This as a result delayed the crystallization process to lower values. Although the differences between the values of the non-isothermal crystallization temperatures of samples A, B and C are small, one can observe that sample A has the lowest value among them.

By comparing the temperatures of the three peaks of all samples, it can be noticed that sample D is more thermally stable (Fig. 2). Peak 1, however, shows almost similar values for samples A, B, and C. This behavior is expected since this peak represents small molecular chain entities which will have limited chain cession effect. In general, the thermal behavior of samples A and B are very similar. This suggests that the effect of crystallizing the material at 100°C for 5 hours under UV is equivalent to the effect of 3 days exposure of UV at room temperature. This conclusion, on the other hand, requires further studies in order to understand the time effect of UV exposure on the thermal stability of these phases.

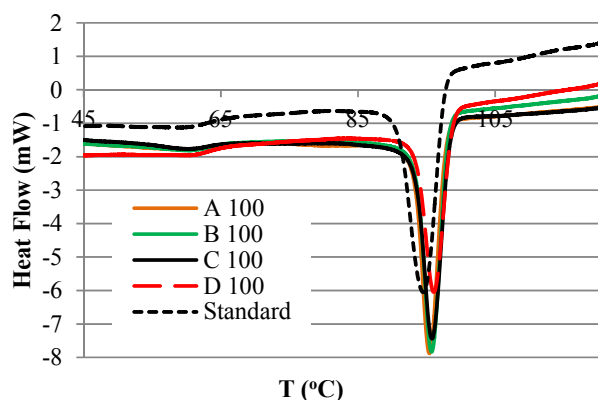


Fig. 3 A comparison between the DSC exotherms of all samples

Sample C, on the other hand, shows more thermal stability in the orthorhombic and monoclinic phases compared with samples A and B. Although the effect of UV radiation on the molten phase is supposed to be larger due to the large energy of free radicals, the time of exposure was not enough to allow more chain cessions. This explains the smaller shift in melting temperature towards lower values where smaller size crystals might have been generated compared with the size of crystals of the unexposed sample.

The results of XRD shown in Fig. 4 and 5 coincide with what was suggested by DSC. The two (110) and (200) orthorhombic peaks appear at angles $2\theta \approx 21.7^\circ$ and 24.0° respectively, while the monoclinic (010) appears at $2\theta \approx 19.6^\circ$ [23]. The appearance of both crystalline phases could not be referred to the addition of MMT or MA since these phases appear in the spectrum of the raw material too (Fig. 4). However, the two peaks formed at lower scattering angles 2θ

$\approx 2.5^\circ$ and 4.9° are referred to the basal spacing (001) and (002) of MMT clay in which an intercalated nanocomposites are formed [24], [25]. Comparing XRD results with DSC thermal behavior we can conclude that the endotherm peaks formed at larger temperatures ($\sim 109.5^\circ\text{C}$) in Fig. 2 are due to the melting of the orthorhombic crystals while those formed at temperature near 104°C represent the melting of the monoclinic crystals.

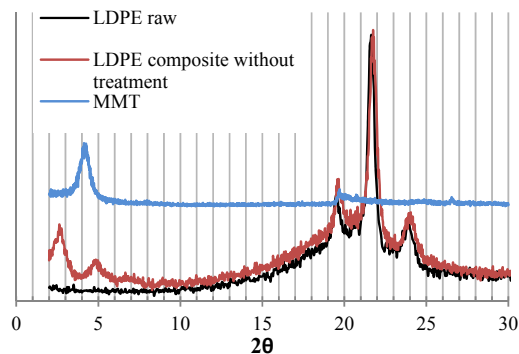


Fig. 4 X-ray spectra of raw LDPE, LDPE composite without treatment and clay

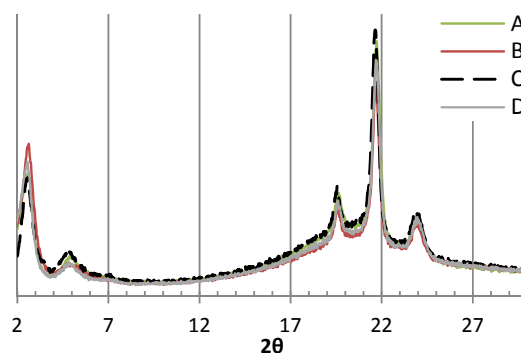


Fig. 5 X-ray spectra of samples A, B, C and D

XRD spectra of all samples A – D shown in Fig. 5 did not show any change in the type or size of crystals formed. This could be concluded from the absence of any new peaks or any shift in the peak positions. Crystallinity values listed in Table I were calculated for $2\theta = 10\text{--}30^\circ$, where sample C has the largest crystallinity value. Although the crystalline structure of sample C is similar to sample D, the melting temperatures suggested a smaller crystalline size of D due to limited chain cession. This, on the other hand, increased the possibility of forming more perfect crystals. Another possible reason for the large crystallinity could be attributed to the ability of the molecules located in between the silicate layers to crystallize or form a certain ordered structure. The fact that the d spacing of the (002) increases for sample C, as seen in Fig. 6 and listed in Table I, gave the LDPE molecules an extra degree of freedom to organize itself and hence improved the crystallinity of this sample [26].

TABLE I
LIST OF D SPACINGS OF THE TWO PEAKS GENERATED DUE TO THE EXISTENCE
OF MMT

Sample	Crystallinity %	2θ	$d_{(001)}$ (Å)	2θ	$d_{(002)}$ (Å)
A	56.8	2.53	34.85	4.93	17.92
B	50.7	2.58	34.18	4.85	18.19
C	82.2	2.54	34.76	4.81	18.36
D	52.5	2.49	35.51	4.86	18.16

Sample D, showed the largest d_{001} spacing indicating a better intercalated composite. Apparently, UV exposure during crystallization process depressed the intercalation process. This could be due to the effect that MA molecules were largely affected by free radicals causing some chain-cission to occur. This will eventually affect the compatibility between the clay and polymer. This observation is in agreement with the depression of the non-isothermal crystallization temperature listed in Table I. This depression is believed to occur when certain structure hinders the crystallization process. In this study, the formation of free radicals, as a result of UV exposure, and the possibility that it might interact with some branches of the LDPE is believed to be the reason for this cause. This conclusion agrees with the fact that the non-isothermal crystallization temperature of sample D, where no UV treatment has occurred, has the largest value.

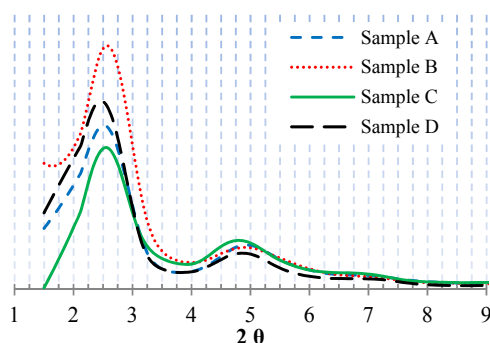


Fig. 6 X-ray spectra of the peaks formed by MMT clay

IV. CONCLUSION

LDPE/MMT nanocomposites compose of two stable crystalline structures, orthorhombic and monoclinic. UV exposure has a clear effect on the thermal stability of LDPE/MMT nanocomposites. However, the effect of UV exposure was not the same on both crystalline structures when sample was exposed according to method A. Sample behavior and chain-cission is dependent on the method of exposure. The effect of UV irradiation on the molten phase has significant effect on thermal stability even for relatively short times.

Intercalation process was affected by the method of UV exposure. Better intercalation was observed when exposing UV during the crystallization process (method A), while least intercalation occurred when UV exposure was before the crystallization process (method B).

Non-isothermal crystallization temperature is affected by the method of exposure, since each method generates different amount of free radicals. This eventually has an influence on the branches of LDPE and hides the non-isothermal crystallization process.

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