Crystallization Kinetics of Ethylene Vinyl Acetate with Modified Clay Nanocomposites

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The interaction of nanoclays with polar polymers is receiving greater interest because the nanoclay significantly improves the thermal stability of the composites; however, since most polar polymers are bio-based, their mechanical properties and processing are of relatively lower standard than the oil-based polymers. We investigated a commercially relevant polymer with varying degree of polarity (poly(ethylene vinyl acetate) copolymer (EVA)) with varying polarity due to varying vinyl acetate content (9, 18 and 28%) and its interaction with organo-modified nanoclay filler (CloisiteR C15A and C30B). Specifically, we studied the crystallization kinetics and the relative dispersion of the nanoclays within the composites using modulated differential scanning calorimetry (DSC) and X-ray Diffraction techniques. Transmission Electron Microscopy results show that clay platelets have increasing tendency to be dispersed as the polarity of the matrix is increased; however, the overall matrix crystallinity remains largely unmodified due to nanoclays but the overall morphology was significantly modified in a way that there was an increase in the ‘rigid-amorphous’ phase. Using Avrami kinetics, we demonstrate that nanoclays play a significant role in the mechanism of growth of crystals and crystalline distribution for EVA polymer and the analysis could be used to compare processing of composites for optimizing mechanical properties for a range of applications in the flexible packaging industry. [DOI: 10.1380/ejssnt.2012.79]

Keywords: Structure-property relationship; EVA nanocomposites; Nanostructures; Crystallization

I. INTRODUCTION

EVA is a commercially attractive polymer for the use in barrier and flexible packaging applications, but it inherently suffers from very poor mechanical properties. With EVA copolymers, as the VA content increases, the polarity of the polymer increases but the ‘softer’ vinyl component reduces the mechanical strength and modulus properties [1]. One way of improving polymer’s physical properties is by increasing the crystalline content and distribution. It is well known that inclusion of nanoclays provides a suitable pathway for increased crystallinity and greater nucleation effects of the fillers [2]. Previous studies have reported increased modulus and yield strength of the EVA nanocomposites [1] and other nanocomposites [3]. On the other hand, increasing polarity with increasing vinyl acetate content also imparts a high degree of polymer-clay surface interaction, such as greater polymer mobility around clay platelets, which would modify the overall crystallinity [4]. However, the mechanism behind the evolution of matrix crystallinity due to small quantity of nanoclays has not been well-studied. For example, nanoclays maybe ‘rejected’ during molecular crystallization as impurity and may result in a significant increase in the amorphous ‘bulk’. However, such changes in nanocomposite morphology would increase their mechanical properties by providing a well dispersed clay platelet network in the amorphous bulk.

This investigation analyses the development of EVA nanocomposites morphology due to the inclusion of nanoclay and due to the influence of polar interactions based on their crystallization kinetics as found from their thermal behavior. Previously reported work in the area of crystallization kinetics of polymers includes an early work by Ozawa [5], who derived a non-isothermal kinetics equation from the basic Evans theory by considering the process of nucleation and its growth, and Harnisch and Muschik [6], who used the Avrami theory [7] to derive isothermal crystallization exponents by using calorimetric methods. Jeziorny [8] and Privalko et al. [9] extended the Avrami equation to non-isothermal crystallization situations by treating non-isothermal crystallization kinetics from calorimetric studies as an isothermal one to calculate crystallization rate constant and Avrami exponent. More recently, Liu and co-workers [10] proposed another non-isothermal equation by combining the Ozawa and the Avrami equations, from which the ratio of the Avrami exponent to the Ozawa exponent and another parameter can be obtained. This investigation applies the earlier work [7–10] to analyze clay-polymer interaction of respective EVA nanocomposites and their influence on matrix crystallinity.

II. EXPERIMENTAL

A. Nanocomposite Preparation

EVA copolymer with 9%, 18% and 28% VA was supplied by Dupont, Australia. Their molecular weights are 67320, 72600 and 58300, respectively with polydispersity of 4.6, 8.7 and 6.2, respectively. Cloisite nanoclay (C15A and C30B) by Southern Clay Products (Gonzales, USA) were used as the nanoclays. These clays are organo-modified but have different gallery spacing. C15A is more suitable for EVA9 because of its larger gallery spacing and organo-modification facilitating greater polymer-clay interaction, similar to what would be observed in C30B.
TABLE I: The processing conditions employed for different clay-polymer system.

<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>EVA9–C30B</th>
<th>EVA18–C30B</th>
<th>EVA28–C30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time (min)</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Barrel temperature (°C)</td>
<td>110</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Screw speed (rpm)</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
</tbody>
</table>

TABLE II: The characteristic basal spacing for all the EVA nanocomposites. For EVA18–C30B nanocomposites, the WAXS showed no peak intensity indicating that all samples were exfoliated.

<table>
<thead>
<tr>
<th>Amount of clay (%)</th>
<th>EVA9–C15A</th>
<th>EVA18–C30B</th>
<th>EVA28–C30B</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.42</td>
<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>2.5</td>
<td>4.64</td>
<td>6.4</td>
<td>6.3</td>
</tr>
<tr>
<td>5.0</td>
<td>4.41</td>
<td>–</td>
<td>6.3</td>
</tr>
<tr>
<td>7.5</td>
<td>3.92</td>
<td>–</td>
<td>6.2</td>
</tr>
</tbody>
</table>

with EVA18 and EVA28. Even though the clay type was varied in this investigation, the step ensured that the level of interaction was maximized for understanding the crystallization kinetics. Nanocomposites with varying clay level (2.5, 5 and 7.5% w/w) were prepared using the melt blending technique [2] using an intermeshing counter-rotating twin-screw extruder (Brabender, Duisburg, Germany). Conditions of the blending techniques are shown in Table I.

B. Modulated Differential Scanning Calorimetry (MDSC)

Samples for DSC (DSC 2920 Modulated DSC with Thermal Analyst 3100 software, TA Instruments, USA) were prepared from each nanocomposites specimen by compression molding into thin films (thickness < 1 mm). DSC tests were conducted using helium as purge gas (30 ml/min flowrate) and nitrogen as environment gas (100 ml/min flowrate) with at least two specimens for each sample, to ensure repeatability. The heating and cooling rate was constant at 2°C/min using 0.5°C modulation amplitude and a 30 sec modulation period. The results were analyzed from the second heating and cooling curves. The stability of any particular clay-polymer system was determined after comparing the crystallization enthalpy and the temperatures of the first and second cooling curves. Enthalpies of melting and crystallization, along with the respective temperatures, were obtained using the peak integration method. Non-isothermal crystallization kinetics for various EVA nanocomposites was studied using modified Avrami equation [7–9].

C. Transmission Electron Microscopy (TEM)

TEM analysis was used in provide a ‘visual’ confirmation of the morphological information obtained on the platelet dispersion and distribution. The TEM equipment used in this study was the JEOL 1010 with an accelerating voltage of 100-kV and high vacuum. The samples were ultra-microtomed to approximately 70 nm using a diamond knife on a Leica Ultracut S with a liquid nitrogen-cooling (LNC) device. Operation of the LNC device at approximately (−)165°C was necessary as cutting EVA samples at room temperature was difficult due to the rubbery nature of these composites. Table II gives the characteristic basal spacing (or interlayer d-spacing) of the nanocomposites as found from WAXS (PW 1830 XRD, Philips, The Netherlands) with 30-kV accelerating voltage and 30-mA current. Intensities from 2θ = 1.2° to 30° were recorded using Ni filtered Cu-K radiation λ = 0.154 nm).

III. RESULTS AND DISCUSSION

A. TEM Morphology

The different clays were chosen based on the polarity of each matrix to produce highly intercalated/exfoliated nanocomposites. It is well known that matrix polarity dominates the final matrix morphology partly due to interaction between the nanoclay and EVA polymer chains and partly due to intermolecular thermodynamic stability. Figures 1, 2 and 3 illustrate TEM micrographs for
EVA9, EVA18 and EVA28 nanocomposites, respectively. The higher electron density of the silicates relative to the EVA matrix gives them a much darker appearance. TEM images for EVA9 nanocomposites show the presence of tactoids that are approximately 200 nm thick. It can be seen from Fig. 1 that increasing the clay concentration increases the thickness of tactoids suggesting that for EVA9–C15A system, the clay platelets are not dispersed by the low matrix polarity. However, the tactoids themselves gain some degree of disorderness, which is strongly affected by the clay concentration.

The absence of Bragg peaks in EVA18 nanocomposites WAXS (Table II) suggested that it exhibits exfoliated or disordered intercalated morphologies. This is strongly supported by the TEM images shown in Figs. 2(a)-(c). All the EVA18 nanocomposites exhibited disordered intercalated/exfoliated morphologies. The presence of stacks of silicate layers at higher concentration shows the presence of intercalation, where few platelets are grouped together but possess random orientations whereas at lower concentrations (2.5 and 5%), the clay platelets are scattered individually, while some tactiod-structural orderness is preserved suggesting mixed exfoliation. Larger particles could also be observed and these may be tactoids that have not been dispersed well enough. Similar morphologies for EVA18-based nanocomposites were reported by Gilman et al. [11].

Figure 3 reveals that EVA28 nanocomposites have the highest degree of mixed intercalated/exfoliated morphologies. In Fig. 3, exfoliated individual layers could be seen interspersed with silicate stacks that are a few layers thick. The TEM images also show that with increased polarity of the matrix (28% VA), there is greater clay-polymer interaction which is not significantly affected by increasing silicate loading from 2.5 wt% to 7.5 wt%, as opposed to EVA9 or EVA18. The increase in the surface area of contact of silicates with the polymer matrix is expected to have a direct bearing on their nucleation and crystallization properties and therefore, the final mechanical properties.

B. MDSC Analysis

In theory of crystallization, it is well known that diffusion-controlled interface growth is dominant for filled systems such as nanocomposites. Further, since nanoclays provide excellent surface to volume ratio, presence of distributed nanoclay can cause the spherulites to have a large distribution. Further, smaller imperfections in crystall organization can be removed during heating to cause greater chain coalescence (recrystallize) and rearrangement to form larger crystals from smaller spherulites. The clay is known to increase the crystallization rate and has a strong hetero-phase nucleation effect on Nylon 6, for example [12]; however, it has been reported that the total crystallinity may not be significantly affected [13]. In this study, non-isothermal crystallization kinetics
were studied using the modified Avrami equation assuming that the crystallization process is a combination of several infinitesimally small isothermal steps such that the development of relative crystallinity can be expressed as \[8, 10\]

\[X_t = \int_{t_0}^{t} \frac{dH_c}{dt} dt\]  \hspace{1cm} (1)

and

\[X_t = 1 - \exp(-kt^n)\]  \hspace{1cm} (2)

Using the second equation, we can analyze the development of relative crystallinity with temperature. A plot of \(\log[-\ln(1 - X_t)]\) versus \(\log(t)\) can then provide slope \(n\), the parameter outlining nucleation mechanism; and \(\log(k)\), a rate constant containing the growth parameter. The Avrami plots for EVA9, 18 and 28 nanocomposites are shown in Figs. 4, 5 and 6, respectively. For EVA 18 and 28, the plots have significant linearity over a relatively wide crystalline range, with EVA28 nanocomposites showing the most linearity. The general non-linearity at higher values of \(\log(t)\) in the plots could be attributed to the presence of secondary crystallization phenomenon as reported for other nanocomposites system \[14\]. This indicates that modified Avrami equation can describe the non-isothermal crystallization process of the EVA nanocomposites with relatively higher VA content (viz., 18 and 28%), but with EVA9 the plots have two significant linear regions and suggests that there are complex mechanisms in nucleation and growth. The exponent ‘\(n\)’ is tabulated in Table III for EVA9, 18 and 28 nanocomposites, respectively and the rate constant ‘\(k\)’ is discussed later.

For EVA9 (Fig. 4), the difference in the slope of the first and the second region indicates the onset of a typical heterogeneous nucleation with melting of recently formed smaller imperfect crystals. Progressive re-crystallization leads to slow one-dimensional growth as the fractional crystallinity increases in the sample. This may be due to the presence of smaller clay tactoids that can cause apparent rapid crystallization during cooling process (by restricting the polymer motion due to obstructive influence of clay platelets), but slow platelet reorganization cause some polymeric chains to chains to orients towards the bulk and reorganize more uniformly and allow larger crystal growth. TEM pictures support this because Fig. 1 showed large regions of clay tactoids. In Fig. 4, the slower rate (second linear region) of organization enables greater stable crystallinity in the bulk and is an equally dominant process for crystallization, when compared to the second stages in EVA18 or EVA 28 (Figs. 5 and 6). Due to the complex interplay of the two dominant crystallization events, EVA9 nanocomposites do not completely conform to Avrami equation.

However, as the matrix polarity is increased (from EVA9 to EVA28), there is a larger initial heterogeneous-nucleation dominant crystallization process, and a smaller secondary crystallization phenomenon (as seen in EVA9). When the matrix polarity is very high, as in EVA28 samples, the nucleation mechanism and the rate of crystalline growth is relatively unchanged due to the different nanoclay concentration (as seen by the similar slope of the initial linear region). This when compared to EVA9 samples in Fig. 4 indicates the importance of matrix polarity in controlling the extent of matrix-nanoclay interaction.

Table III shows the calculated values of \(n\) and the most prominent observation is that for the EVA9 system, the presence of nanoclay has very little influence in suppression of the total crystallinity as compared to the EVA18 and EVA28 as the value of \(n\) for these latter nanocomposites are lower than their virgin polymer. The higher \(n\) value for EVA9–5 and EVA9–7.5 indicates that nanoclays do not hinder lamella growth, whereas for EVA18 or EVA28 nanocomposites, the \(n\) values are always lower than virgin polymer indicating that the clay platelets have strong interaction with the polymers and suppress the molecular crystallization. The TEM pictures further explain this because the larger tactoids present in EVA9 have much lower interaction and mobility compared to the well exfoliated nanoclays in EVA18 or EVA28 and therefore, molecular crystallinity is not greatly affected by the presence of large tactoids in EVA9.

The above argument was further corroborated by measuring the sample crystallinity from the total enthalpy data for all EVA nanocomposites. As shown in Table IV, the fractional crystalline morphology does not change significantly for EVA9 nanocomposites—all samples have similar degree of total crystalline fraction ~33% crystallinity— whereas, there is ~40% reduction in total crystalline morphology for EVA28 nanocomposites and ~30% reduction in EVA18-2.5 and EVA18-5 with EVA18-7.5 showing the highest reduction at ~60%. The results strongly suggest that clay exfoliation is a dominant force in controlling the polymer morphology and these results are different from previously mentioned reports because our nanocomposites show large variation in crystallinity with variable matrix polarity \[14\].

The significant finding with polar EVA nanocomposites is shown in Table IV in the form of % rigid-amorphous

Table III: Parameter \(n\) determined using modified Avrami equation for all EVA nanocomposites.

<table>
<thead>
<tr>
<th>Clay wt%</th>
<th>Vinyl acetate content 9 wt%</th>
<th>18 wt%</th>
<th>28 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.8</td>
<td>4.6</td>
<td>4.5</td>
</tr>
<tr>
<td>2.5</td>
<td>3.9</td>
<td>1.3</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>4.1</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>7.5</td>
<td>4.8</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table IV: The % crystalline morphologies and calculated % rigid-amorphous phase of the pure polymer and the EVA nanocomposites. Numbers in the bracket represent the rigid-amorphous phase.

<table>
<thead>
<tr>
<th>Clay wt%</th>
<th>% Crystallinity and the rigid-amorphous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA9</td>
<td>EVA18</td>
</tr>
<tr>
<td>0</td>
<td>30.55 (3.56)</td>
</tr>
<tr>
<td>2.5</td>
<td>31.87 (4.67)</td>
</tr>
<tr>
<td>5</td>
<td>28.24 (3.12)</td>
</tr>
<tr>
<td>7.5</td>
<td>31.54 (5.30)</td>
</tr>
</tbody>
</table>

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phase. This phase is well known, having being identified in other filled systems [2]. This phase was calculated from the WAXS data using a standard deconvolution method using commercial software available from Philips. The data in Table IV highlights that the crystallinity growth is significantly affected by the organization of the nanoclays and by the level of interaction between the polymer and the nanoclays. On average, for EVA9 nanocomposite samples, the ratio of % crystallinity to % rigid-amorphous phase is ~7, compared to EVA18 and EVA 28, both of which have ~1, indicating that exfoliated nanoclays significantly reduced the extent of molecular crystallinity. As seen from the respective TEM graphs, the clay dispersion was excellent for EVA18 and EVA28, and its effect can be quantified from the % rigid-amorphous phase. This phase is well known, having being identified in other filled systems [2].

Moreover, to understand the physical significance of the rate constant ‘k’, we consider the exotherm slope of the various nanocomposites. From the ‘slope’ values shown in Fig. 7, it is clear that the addition of clays significantly reduce the crystal growth rate for all EVA nanocomposites. The extent of reduction is significant in all nanocomposites samples as seen by more than 50% reduction in the slope value of virgin compared to 2.5% clay sample. However, it is also interesting to note that as nanoclay wt% is increased to 5% and 7.5%, the crystal growth rate does not alter significantly.

This can be explained by considering that clays platelets have the ability to suppress molecular association [2, 10] and retard the rate of spherulitic growth, but if the polymer-nanoclay interaction is poor, then the polymer matrix is able to re-organize and the smaller spherulites can grow into larger crystals using a secondary crystallization process [15]. Thus, the overall crystallinity is not altered, for example in EVA9. However, with greater extent of exfoliation, it is likely that there is formation of a ‘rigid-amorphous’ structure of platelets with increasing clay content — a network structure involving platelet-platelet interaction apart from the platelet-polymer interaction — and this structure increases the total entanglement of nanoclay-polymer volume, which reduces the total crystalline structure and the rate of crystal growth. The onset of such structure could also be seen in light of percolation threshold — a threshold where a certain fraction of polymer chains are entangled and stabilized within platelet structures— forming a non-mobile amorphous phase, which reduces the crystalline morphology [16]. This is suggested for EVA18 and 28, due to their greater degree of exfoliation leading to slow crystallization.

IV. CONCLUSIONS

This study demonstrates that the degree of exfoliation of the nanoclay greatly influences the extent of rate of crystal growth; however, the molecular crystallinity is relatively unaffected by the variation in interaction between the polymer and the nanoclays. This led to the suggestion that polar interactions are important for formation of intercalated/exfoliated nanocomposites with EVA and it is further shown that parameter n that could be used to compare morphologies within nanocomposites of varying clay content. TEM confirm that degree of dispersion is significantly related to the matrix polarity and the data support the MDSC analysis showing strong nucleating effects of the well dispersed clay platelets indicating strong heterogeneous nucleation. Avrami analysis fit EVA18 and EVA28 where there is greater polymer-clay interaction, but not for EVA9 (variation in average n was large —from 4 for EVA9 to 2.7 for EVA28). From the ‘slope’ value, there are indications that EVA9 has least polymer-clay ‘network’ formation — the reduction in the slope between the unfilled and the filled system denoting the mobility and association of polymeric chains with clay platelets— followed by EVA28 and finally, EVA18 had the best ‘network’ structure.

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