Study of In-situ Hybrid Composites of Poly(ethylene terephthalate)/Liquid Crystalline Polymer Filled with Microwave-synthesized Zinc Oxide Powder

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ABSTRACT

This work aims to investigate the system called “in-situ hybrid composites” normally consisting of a thermoplastic, a liquid crystalline polymer, and an inorganic filler. Blends of poly(ethylene terephthalate) (PET) with 10 wt% liquid crystalline polymer (LCP) were filled with zinc oxide powder (ZnO) at 0.5 and 1.0 phr loadings. The ZnO powder was synthesized from zinc nitrate in an aqueous system via microwave irradiation. Melt-blending was conducted in a twin-screw extruder and the compounds obtained were then injection-molded. It was hypothesized that transesterification between the LCP and PET might be promoted by the catalytic activity of ZnO, yielding a composite with better mechanical performance. A reduction in the LCP fibril fraction in the PET matrix, along with a lower shear viscosity, was observed with increasing ZnO loadings. Tensile strength results for the samples filled with ZnO indicated no improvement of the interfacial adhesion between LCP and PET suggesting that the transesterification is not evident. ZnO was found to increase the tensile modulus of the PET/LCP blend. The isothermal and non-isothermal crystallization kinetics of PET were enhanced in the presence of LCP but retarded in the presence of ZnO.

Keywords: in-situ hybrid composites, liquid crystalline polymer, microwave, zinc oxide

1. INTRODUCTION

It is widely accepted that the use of short glass fibers as a reinforcing agent can considerably improve the mechanical strength and stiffness of polymers. However, conventional polymer composites usually require a high load of glass fibers making them more difficult to process because of the rise in melt viscosity. Other difficulties encountered include wear to processing machinery caused by abrasion and fiber breakage. To overcome these problems, blending of a thermoplastic (TP) with a highly rigid, non-abrasive component which did not hinder the polymer flow would offer clear advantages. A potential candidate as a substitute for glass fibers is the liquid crystalline polymer (LCP). Under optimized flow conditions, the LCPs can align themselves...
to and elongate with the direction of flow, resulting in a reduction in melt viscosity and improved mechanical properties. Thus the LCP/TP blends are usually termed ‘in-situ composites’. Blending of an LCP with a thermoplastic also helps reduce the cost as an LCP alone is too expensive to be used in domestic and some engineering applications.

There are many studies dealing with systems containing an LCP and various inorganic solid reinforcements, such as glass fiber [1,2], carbon black [3,4], whisker [5,6], and silica [7,8]. The final properties of the systems depend critically not only on the blend morphology but also on the interfacial properties between the thermoplastic matrix and the reinforcing LCP domains. Improving mechanical performance sometimes requires additional enhancement of interfacial adhesion, commonly by the use of polymeric compatibilizing agents. A compatibilizing agent may be added to the blend as a third component or may be generated during reactive mixing of the blend. The latter (also referred to as in-situ compatibilization) may involve transesterification provided that the system contains ester exchange reactive groups. The resulting copolymers will be located at the polymer interfaces providing lower interfacial tension and better adhesion leading to effective stress transfer at the interface. An example of such an approach was demonstrated by blending polycarbonate with Vectra A950, both of which contain ester linkages that can be inter-exchangeable. Tovar et al. [9] observed better dispersion as well as improved mechanical properties of PC/Vectra A 950 as transesterification increased. Exchange reactions have also been seen between Vectra B950 and PET [10]. In some cases, adding a nano-sized inorganic filler can improve compatibility of blends such as nano-clay [11] in Polyamide6/LCP blends and carbon nanotube in PC/LCP blends [12]. However, up to now there has been no research that investigated metal oxides in the system of in-situ composites. Among the metal oxides, zinc oxide (ZnO) is an inorganic material that has been widely used as an additive in numerous materials including plastics, ceramics, glass, cement, rubber, lubricants, paints, adhesives, pigments, retardants, etc. Polymer composites of various forms of ZnO have demonstrated improved properties, for example the use of ZnO of pigmented grade (150-200 nm mean particle size) can give protection in UV absorbing acrylic composites [13]. Nano-sized ZnO particles (53 nm) have been reported to increase hardness and reduce the wear rate compared to the neat PC [14]. Also, ZnO coatings can protect PC films against UV radiation [15]. It is known that the alteration of the resulting composite properties depends on the type of matrix polymer and the characteristics of the ZnO used (size, distribution, dispersion, surface properties) together with the interfacial adhesion [14]. Recently, S. Wacharawichanant et al. investigated the polyoxymethylene (POM)/ZnO composites with different ZnO particle sizes. They found that the smaller ZnO particles rendered composites with better mechanical properties than the larger ones. However, larger ZnO particles dispersed better at high loadings [16]. Coltelli et. al. [17] compared ZnO and a stronger nucleophilic zinc derivative, the zinc acetate (ZnAc2) on their catalytic reactivity for a tranesterfication reaction between dibutyl maleate functionalized poly(ethylene) (POF) and PET. The nucleophilic character of the zinc derivatives plays a key role in PET degradation; i.e. the stronger the catalyst nucleophilicity, the greater the tendency for PET to undergo nucleophilic substitution with the catalysts, leading to its degradation. Based on this criterion, ZnO was expected to
contribute to reduced PET degradation compared to ZnAc₂. The same authors report that ZnO is able to produce a certain amount of PET-POF copolymer without leading to PET degradation. In this research, we prepared the composites of PET/LCP with well-dispersed ZnO particles. ZnO particles were synthesized by eco-friendly water-based, microwave radiation. The rheological, morphological, thermal and mechanical properties will be discussed.

2. MATERIALS AND METHODS

2.1 Materials

The poly(ethylene terephthalate) (PET) used was RAMAPET N1, purchased from Indorama Polymers Public Company Limited, Thailand. The LCP used was Vectra A950 (labeled VA hereafter), kindly supplied by Hoechst-Celanese. VA is a copolyester of 73 mol% p-hydroxybenzoic acid (HBA) and 27 mol% 2-hydroxy-6-naphthoic acid (HNA). All the materials were dried in a vacuum oven at 120°C for at least 12 h prior to use.

2.2 Microwave-Assisted Synthesis of ZnO Powder

Zn(NO₃)₂·6H₂O (99.5 mol%, Carlo Erba) and solid NaOH (Labscan) were separately dissolved in 50 ml of deionized water and stirred using a magnetic stirrer for 30 min at room temperature. Then the two solutions were mixed together with an additional 100 ml of deionized water to yield a final 200 ml solution. The solution was then immediately irradiated by a microwave in a domestic microwave oven (Samsung, M-183GN, 2.45 GHz, 850W) in air for 5 min. The products were separated by centrifugation, then washed with deionized water three times, and dried at 70°C under atmospheric pressure. The ZnO nanoparticles were characterized by XRD (Model D8 Discover, Bruker AXS) using VANTEC-1 detector at atmospheric pressure and room temperature. The ZnO sample was analyzed using a double-crystal goniometer. The XRD pattern of the sample was obtained with a 2θ range of 20°-80° at a scan speed of 5°/min using CuKα radiation (λ = 0.154 nm).

2.3 Preparation of Blends

PET, VA resins and ZnO powder were premixed in a dry mixer to prepare PET/VA blends with a VA content of 10 wt% and ZnO of 0, 0.5, and 1.0 phr with respect to the total polymer weight. The compounds were designated as shown in Table 1. The dry-mixed blends were melt-mixed in a self-wiping, co-rotating twin-screw extruder (Collin, ZX-25). The temperature of the barrel section from the feeding zone to the die was set at 95, 250, 260, 270, 275, 265°C. The rotor was operated at a speed of 20 rpm. The extrudates were cooled by water and then pelletized.

The neat PET and the blends, with or without ZnO, were injected into dumbbell-shaped specimens 2.5 mm thick on an AP-90 (Asian Plastic) injection molding machine for the tensile tests. The injection molding conditions are provided in Table 2.
2.4 Rheological Measurement

The shear viscosity of the blends was measured using a CEAST Rheologic 5000 twin-bore capillary rheometer with an inner diameter and barrel length of 15 and 250 mm, respectively, and the inner diameter and the length of the die were 1 and 20 mm (i.e. L/D ratio = 20), respectively. The temperature tolerance was set at ±0.5°C. Measurement was done at 260°C and a shear rate range of 200-6,400 s⁻¹. The rheometer extrudates were quenched at room temperature and collected for further SEM analysis.

2.5 Morphological Observation

The morphological study was conducted using a JEOL JSM5200 scanning electron microscope (SEM). The polymeric specimens were cryogenically fractured in liquid nitrogen to provide a cross-sectional view. The rheometer extrudates were also immersed in 2-chlorophenol at 80°C for 2 h to dissolve the PET matrix as the first step, followed by repeated washing of the VA residue. The fractured surfaces, the VA residue, and the ZnO powder were sputtered with a thin layer of gold prior to observation. Energy dispersive X-ray (EDX) analysis was also performed to evaluate the dispersion of the Zn element in the composites.

2.6 DSC Characterization

The differential scanning calorimeter measurements were carried out using a Perkin-Elmer DSC7 differential scanning calorimeter (DSC). All measurements were performed under a dry nitrogen atmosphere at a flow rate of 20 ml/min. The standard sample used was indium. Each sample holder was loaded with samples of comparable quantity (7±0.5 mg). All the experiments started with heating the sample from 25°C to a fusion temperature of 310°C at a heating rate of 200°C min⁻¹ for a melt-annealing period of 5 min in order to remove previous thermal histories, after which the samples were cooled at a rate of 10°C/min to 25°C. The sample was then heated to 300°C at a heating rate of 10°C min⁻¹ and the melting endotherms were recorded. To study of isothermal crystallization behavior after the melt-annealing, the sample was cooled from 310°C to the predetermined crystallization temperature of 200°C and maintained until the crystallization of the PET matrix was complete. The non-isothermal crystallization
experiment was done by cooling the sample from 310°C to 25°C at different cooling rates ranging from 2.5-30°C/min.

2.7 Investigation of Mechanical Performance

To measure the mechanical properties of the samples, tensile testing was conducted using an Instron 4206 tensile tester at room temperature with an extension speed of 5 mm/min and an initial gauge length of 25 mm. The mechanical properties (tensile modulus, tensile strength, and percent elongation at break) were averaged from at least five samples.

3. RESULTS AND DISCUSSION

3.1 Characterization of ZnO Powder

Figure 1 displays the X-ray diffraction patterns of the obtained powders, corresponding to the hexagonal wurtzite structure of ZnO. The sharp diffraction peaks indicated high crystallinity of the synthesized ZnO powder. The crystallite size, D, can be calculated using the Debye-Scherrer formula:

$$D = \frac{0.89\lambda}{B\cos\theta_B}$$

where $\lambda$ is the X-ray wavelength (1.54 Å), $\theta_B$ is the Bragg diffraction angle, and B is the full width at half maximum of the peak located at $2\theta_B = 36.26^\circ$. The crystallite size (D) was found to be approximately 26.6 nm.

From the SEM image shown in Figure 2, the synthesized ZnO powder consisted of fairly uniform spherical particles with an agglomerate size of 170±0.03 nm (calculated using the SemAfore program). Each ZnO agglomerate was therefore the combination of 6-7 crystallites.

![Figure 1. XRD spectra of the synthesized ZnO particles.](image-url)
3.2 Rheological Results

Figure 3 displays the viscosity data as a function of shear rate for the pure polymers (PET and VA), the neat blends (PET/VA) and the composites (PET/VA/ZnO). VA shows the strongest non-Newtonian behavior implying that the VA molecules can most readily be oriented under the shear flow. The shear viscosity of the neat VA is the greatest at shear rate up to 1000 s\(^{-1}\), and then becomes comparable to that of PET. The PET/VA blend shows a viscosity reduction as compared to the pristine PET. This reduction originates partly from the chain alignment of VA and partly from the interfacial slip between the LCP and the matrix. Further viscosity reduction is found with increasing ZnO loading. One may think of a viscosity reduction as an indicator of a decreased molecular weight as a consequence of polymeric decomposition.

Zinc derivatives such as zinc acetate, zinc chloride and zinc oxide can serve as a transesterification catalyst. In the chemical recycling of PET, a small molecule ester exchange reagent such as methanol is introduced into the system at elevated pressure and temperature to recover the acid and alcohol components, where the catalyst used may be ZnO\(^{[18]}\). In our experiment, the only ester exchange reactive agents are PET and VA, and consequently it is expected that the most likely chemical reaction to occur would be the transesterification between reactive end-groups of these two polymers. Also, as supported by Coltelli\textit{ et al.} \textit{[17]}, the degradation of PET induced by ZnO is negligible. The viscosity reduction is therefore ascribed to the lubricating effect as the spherical ZnO particles facilitate the flow of the molten polymer.

Figure 2. SEM image of the synthesized ZnO particles.
3.3 SEM Analysis

Figure 4 shows the SEM images of the VA residue taken from injection-molded samples. Both short microfibrils and droplets are obtained in the PET/VA blend. Only sufficiently large VA domains can undergo deformation during injection-molding. Therefore, the observed droplets that were too small to fibrillate in an injection molding machine retained their spherical shape. The addition of 0.5 phr ZnO, however, resulted in a loss of fibril fraction. At 1 phr ZnO loading, none of VA fibrils could be found. The EDX element map showing the distribution of zinc is constructed from the fractured surface of PVA 1 ZnO [Figure 5]. Good distribution is observed on the PET matrix and the VA domains. Another EDX map in Figure 5 and Figure 6 displays the distribution of Zn on the VA residue, confirming the existence of Zn adhering on VA domains despite the removal of PET matrix and vigorous washing of the VA residue.

Figure 3. Rheological curves of PET, VA, and their blends with ZnO extruded through a capillary die (L/D = 20) at 260°C.

Figure 4. SEM images of the capillary rheometer extrudate after extrusion at 260°C, 1600 s⁻¹ of (a) PVA, (b) PVA 0.5 ZnO, and (C) PVA 1 ZnO.
3.4 DSC Analysis

As displayed in Figure 7, the neat PET shows a single melting peak belonging to the PET phase whereas those of the blends either with or without ZnO particles exhibit double melting peaks. VA shows a small endothermic peak due to the crystalline-to-nematic transition at around 280°C. From the peak positions, it can be assumed that peak I and peak II belong to the crystallization fraction of PET. In other words, PET and VA crystallize separately. The bimodal shape of the melting peaks could be a result of the melting-recrystallization process. According to the literature, the multiple melting phenomenon observed in PET and PET-based composites mostly arises from the melting-recrystallization process of the materials [19,20]. In this case, it is possible that peak I is the first melting of the crystallites formed during a cooling scan while peak II is the melting of the recrystallized materials. However, it is well known that introducing a foreign material into a semi-crystalline polymer can disrupt the crystallization process, thus rendering imperfect crystallites. These imperfect crystallites can appear as another melting peak on a lower temperature side [21-23]. Therefore, there are two possibilities that explain the origin of double melting endotherms: the two different crystal qualities or the melting-recrystallization process. To evaluate the origin of double melting endotherms observed in the sample containing VA, the PET/VA blend was crystallized from melt under varied cooling rates ranging from 5 to 30°C/min and then reheated under the same heating rate of 10°C/min. Since the heating rate was kept constant, its effects on melting-recrystallization behavior (if any), and thermal lag could be eliminated. The heating scans shown in
Figure 8 display the double melting endotherms for PET/VA at every cooling rate. Peak I and peak II are assigned to the lower temperature and the higher temperature melting peak, respectively. It is obvious that, in contrast to peak I, peak II becomes more distinct with increasing cooling rate. Generally, a less perfect crystallite melts prior to a more perfect one. If peak I was taken as the melting of a less perfect crystalite population as compared to peak II, the sample crystallized at the lowest cooling rate would have the most perfect crystallites and yield the largest peak II. But the results are found to be the opposite. Based on this finding, the double melting temperature should have originated from the melting-recrystallization process. Peak I represents the melting of the original crystallites generated during cooling while peak II represents the melting of the recrystallized crystallites. The concave region between the two peaks is then assigned to the recrystallization exotherm. Based on this assumption, the largest peak II can be found for the sample with the greatest cooling rate, and VA promotes the recrystallization process during the heating scan. We also carried out the DSC experiment on the samples where the cooling rate was kept constant (10°C/min) and the heating rate was varied from 5 to 20°C/min. It was found that PET exhibited only monomodal peaks whereas PC/VA showed wholly bimodal peaks (results not shown here) which agrees with our assumption.

Figure 7. DSC heating scans (heating rate of 10°C/min).
Data shown in Table 3 are extracted from the thermograms in Figure 9. The initiation temperature of the non-isothermal melt crystallization process (see $T_{nc,m}$) of PET is lower than PVA but higher than those observed from ZnO-containing samples. However, when filled with ZnO, the crystallization process is found to start slightly sooner for a composite with a higher ZnO content. This suggests that VA exhibits a nucleation effect on the PET non-isothermal melt crystallization process. ZnO, on the contrary impedes the PET crystallization probably by impeding polymer chain mobility. A greater ZnO content might lead to a more agglomeration, thus the retardation effect on PET crystallization for the blend with 1 phr ZnO is less pronounced than with 0.5 phr ZnO. Melt crystallization under isothermal conditions was also investigated (see Figure 10). The crystallization half-time $t_{1/2}$, defined as the time the polymer takes to reach 50% of its equilibrium crystallinity, is a useful parameter to qualitatively compare the crystallization rate. The values of $t_{1/2}$ tabulated in Table 4 suggest that the bulk crystallization kinetics are in the following order: PVA > PVA 1 ZnO > PVA 0.5ZnO > PET. The crystallization enthalpy normalized by the weight fraction of PET component (ignoring the weight of ZnO since only a small amount is used) suggests that the degree of crystallinity of PET obtained during the isothermal crystallization is ranked as follows: PVA > PVA 1 ZnO > PVA 0.5 ZnO > PET. It can be concluded that VA has positive effects on PET crystallization, while ZnO has negative effects. Junrong et al. [24] studied the role of different sizes of ZnO, from nano- to micrometer-size, on the crystalline structure and crystallization kinetics of nylon-6. They claim that the ZnO particles induce nylon-6 crystallization from the melt through the nucleation effect. They believe that ZnO can provide an ordered surface suitable for the hydrogen bonding formation with nylon-6 and thus facilitate the heterogeneous nucleation process. However, the nucleation effect of ZnO is inverse to its size. The crystallization rate is enhanced by this nucleation effect, but
can also be retarded by the restriction in polymer chain mobility as a result of polymer-filler interactions. According to the study of crystallization behavior of PET/ZnO nanocomposites done by Junqing et al. [25], silane coupling-treated ZnO nanoparticles can accelerate PET crystallization. With the determination of crystallization kinetics via the Ozawa model approach [26], they claimed that adding ZnO nanoparticles results in an increase in the crystallization growth point. However, it is believed that ZnO in this work did not act as a nucleating agent. This is because the hydrogen bonding formation between the polymer and the filler is not significant in the PET/ZnO system and the ZnO used in this study was unmodified. Another reason may be the lattice mismatch between the hexagonal ZnO and the triclinic PET crystallite [27]. Based on these facts, ZnO would not provide a suitable surface for the PET crystal growth. Instead, the restricted mobility of PET chains by the presence of ZnO retards the crystallization rate. However, introducing VA improves the crystallization process of PET by accelerating the overall crystallization rate of PC/VA/ZnO along with increasing the normalized degree of crystallinity. Similar observations have been reported in Ref. [28, 29] for the blends of PET with an LCP.

Table 3. Thermal characteristics of neat PET, PET/VA blends, and PET/VA/ZnO composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating scans</th>
<th>Cooling scans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm,I</td>
<td>Tm,II</td>
</tr>
<tr>
<td>PET</td>
<td>-</td>
<td>236.7</td>
</tr>
<tr>
<td>PVA</td>
<td>235.2</td>
<td>248.4</td>
</tr>
<tr>
<td>PVA 0.5ZnO</td>
<td>236.7</td>
<td>248.4</td>
</tr>
<tr>
<td>PVA 1ZnO</td>
<td>234.9</td>
<td>247.8</td>
</tr>
</tbody>
</table>

Figure 9. DSC cooling scans at a cooling rate of 10°C.
3.5 Mechanical Performance

The mechanical properties of all samples are reported in Table 5. VA provides mechanical reinforcement in the blend as reflected in improved modulus and tensile strength. ZnO promotes only the tensile modulus. The addition of 1 phr ZnO and 10 wt% VA to PET increases the tensile modulus by 29%. The loss of LCP fibrils in the system with ZnO does not have a negative influence on the tensile modulus because the small elongation at which the modulus is measured would prevent filler-matrix debonding. On the other hand, the tensile strength is affected by such loss as this property relies greatly on the interface properties, a key factor that determines the stress transfer. A reduction in the filler aspect ratio leads to a decreased interfacial area necessary for the stress transfer, thus in our system, no improvement in the tensile strength is found. However, the tensile strength of the PET/VA/ZnO composite is retained at a very low ZnO content of 0.5 phr. At 1 phr ZnO loading, the tensile strength is drastically reduced. A decrease in the percent elongation at break is not surprising for the composites filled with either inorganic particles or LCP. Up to this point, the role of ZnO as a catalyst for the transesterification between PET and

Table 4. Isothermal crystallization data of neat PET, PET/VA blends, and PET/VA/ZnO composites measured at 200°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$t_{1/2}$ (s)</th>
<th>Normalized $\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>120</td>
<td>34.23</td>
</tr>
<tr>
<td>PVA</td>
<td>76</td>
<td>39.95</td>
</tr>
<tr>
<td>PVA 0.5ZnO</td>
<td>84</td>
<td>36.04</td>
</tr>
<tr>
<td>PVA 1ZnO</td>
<td>81</td>
<td>39.18</td>
</tr>
</tbody>
</table>
VA is not evident. The results from tensile properties and the phase morphology imply that there is no improvement in the interfacial properties between PET and VA. Thus, the transesterification products, if present at all, are insufficient to alter the composite properties.

Table 5. The static mechanical properties of neat PET, PET/VA blends, and PET/VA/ZnO composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1144(9)</td>
<td>65.0(0.2)</td>
<td>398(75)</td>
</tr>
<tr>
<td>PVA</td>
<td>1329(16)</td>
<td>71.4(1.1)</td>
<td>7(1)</td>
</tr>
<tr>
<td>PVA 0.5ZnO</td>
<td>1354(47)</td>
<td>70.5(2.0)</td>
<td>6(1)</td>
</tr>
<tr>
<td>PVA 1ZnO</td>
<td>1471(47)</td>
<td>34.7(6.7)</td>
<td>3(1)</td>
</tr>
</tbody>
</table>

Note: Numbers in the parentheses represent the values of standard deviation.

4. CONCLUSIONS
A liquid crystalline copolyester, Vectra A950 (VA), and a thermoplastic polyester, poly(ethylene terephthalate) (PET), were melt-blended and filled with small loadings of ZnO particles. It was hypothesized that a transesterification reaction and a subsequent improvement in interfacial properties might be achieved through a catalytic role of ZnO. Results from the rheology indicated that the apparent shear viscosity decreased by the addition of VA and decreased further with ZnO. The loss of VA microfibrils was ascribed to the lubricating effect of ZnO spherical particles; these suppressed the stress which PET would have exerted upon VA domains in the absence of ZnO. Molten PET and VA are immiscible and crystallized separately. VA played a nucleating role for PET crystallization while ZnO retarded PET crystallization by restricting PET chain mobility. At a very small ZnO loading of 0.5 phr, the composite was able to retain its tensile strength but this value dropped drastically at a greater ZnO loading, providing evidence that there is of no enhancement in interfacial adhesion. In other words, the unmodified ZnO used in this study did not promote the transesterification reaction between PET and VA to a significant extent. The tensile modulus of the composite with 1 phr ZnO increased by 29%.

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