

# The Effects of Clay Platelets Orientation Achieved *via* a Dry Lamination Process on the Barrier Properties of Clay Polymer Nanocomposites

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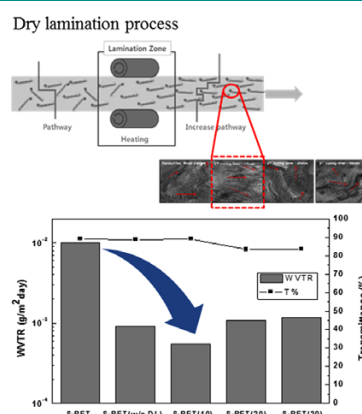
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**Abstract:** Clay platelets have been used to make clay polymer nanocomposite (CPN) in order to enhance the barrier properties of plastic substrates and sputtered barrier films. Clay platelets tend to be randomly dispersed and should be oriented in the film direction to achieve effective barrier properties. In this work, well-oriented nanocomposites were prepared on substrates by adopting a dry lamination process between two heated rubber rolls during the curing step. Dry lamination enabled the clay platelets to be oriented upon application before the sample was completely cured, and the final curing step froze the structure to maintain the orientation. The dry lamination time was optimized at a maximum peak of isothermal curing reaction using DSC. Through characterization *via* XRD and TEM, it was confirmed that clay platelets are well dispersed and exfoliated in the CPN. The CPN with highly oriented clay platelets enhanced the barrier properties to reach a water vapor transmittance rate of  $5.5 \times 10^{-4}$  g/m<sup>2</sup>/day, while maintaining optical properties.

**Keywords:** clay polymer nanocomposites, clay, barrier, dry lamination, polymer substrates, WVTR.



## 1. Introduction

Flexible and transparent ultrathin coating layers with high barrier properties are key components for adapting polymeric films to food packaging and flexible electronics. Inorganic layers formed *via* deposition processes such as chemical vapor deposition, sputtering, and atomic layer deposition have achieved excellent barrier properties. However, the deposition processes of inorganic layers are complicated batch processes requiring high levels of vacuum and temperature, while also having limited applicability as flexible barrier layers due to their mechanical fragility.

Organic and inorganic nanocomposites are promising candidates that overcome the many problems of inorganic barrier layers. Recently, polymer nanocomposite coatings with layered silicate fillers have gained attention as effective alternatives to inorganic barrier layers, improving the water vapor<sup>1-3</sup> and oxygen barrier properties<sup>4,5</sup> of polymeric films. Among these fillers, individual clay platelets with high aspect ratios are widely used for the formation of clay polymer nanocomposites (CPN's).<sup>6,7</sup> With the introduction of clay platelets, CPN can provide good mechanical properties, high thermal stability and flame retardancy, as well as good barrier properties. The improvement of

mechanical properties with the incorporation of 5 wt% clay platelets to the epoxy matrix was reported.<sup>8</sup> They concluded that nanoclusters can enhance mechanical interlocking inside CPN. The incorporation of 3 wt% of organically modified clay in the epoxy polymer increased the  $T_g$  of CPN by approximately 15 °C due to the improved exfoliation of clay platelets in the polymer matrix, while maintaining optical properties superior to polymer nanocomposites with unmodified clay platelets.<sup>9</sup> Also, the addition of 5 wt% clay platelets to PVA yields a significant decrease in oxygen and water permeability.

The clay platelets in composites play the roles of impermeable barriers to diffusing molecules such as water vapor and oxygen.<sup>10</sup> When these platelets are aligned perpendicular to the diffusion pathway, a longer difficult path can be obtained; as a result, the transmission rate of water vapor and oxygen can be significantly reduced.<sup>11</sup> Clay platelets with their dispersion and orientation in a polymer matrix remain an active and intensive area of research in CPN; however, the effects of clay platelet orientation on the barrier properties of the polymer nanocomposite coating layer have not been adequately addressed.

In this article, the CPN's were formed on PEN substrate and SiOx/SiNy sputtered PET (S-PET) substrate for characterizations. The dry-lamination process was demonstrated to induce the orientation of clay platelets incorporated inside the CPN. The orientation effect on the enhancement of barrier properties is also addressed.

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## 2. Experimental

### 2.1. Materials

Nanomer I.28E, which was organically modified using quaternary trimethyl stearyl ammonium with 140 mEq/100 g of cation exchange capacity (CEC), was supplied by Nanocor Inc., USA. Meta-xylenediamine (MXDA, Mitsubishi gas chemical company, Inc.) was used as a curing agent. Bisphenol A type liquid epoxy resin (EpA, Kukdo Chemical Co., Korea) was used as an oligomer, and *n,n*-dimethylformamide (DMF, Daejung Chemicals and Metals Co., Korea.) was used as a polar solvent for a coating solution. A polyethylene naphthalate (PEN) (Q65) substrate of 0.2 mm in thickness was provided by Teijin DuPont Films, Japan.

SiO<sub>x</sub> layer is transparent under visible wavelength range with poor barrier property, and SiN<sub>x</sub> layer could reduce the level of WVTR by increasing the layer thickness at the expense of transparency loss. Therefore, the multilayer structure with SiO<sub>x</sub>/SiN<sub>y</sub> had better optical and barrier properties than the single SiO<sub>x</sub> or SiN<sub>y</sub> layer. The SiO<sub>x</sub>/SiN<sub>y</sub> multilayer with thickness of 150 nm was deposited on PET substrate using sputtering system with RF magnetron source. A base pressure was below 2 mtorr prior to sputtering. The sputtered SiO<sub>x</sub>/SiN<sub>y</sub> PET films (S-PET films) have the water vapor transmission rate of 10<sup>-2</sup> g/m<sup>2</sup>/day.

### 2.2. Sample preparation

Nanomer I.28E was added to the flask preloaded with DMF and mixed using a mechanical stirrer at 400 rpm and room temperature for 1 h. The organically modified clay platelets were dried at 80 °C for 24 h in a vacuum oven. This solution was treated using a microtip probe sonicator for 10 min to enhance the dispersion of clay platelets in the solution. The epoxy resin was added to the clay solution and mixed in nitrogen at 75 °C for 6 h. Additionally, a stoichiometric quantity of the curing agent was added and stirred for another 30 min at 75 °C to form the coating solution. The PEN substrate was cleaned in methanol for 10 min *via* a bath-type ultra-sonicator and dried at 80 °C.

Oxygen plasma treatment was conducted on the surface of the PEN substrate to enhance the adhesion property between the substrate and coating layer using a plasma cleaner (Plasmatic system, U.S.A.) with 650 watts of power for 10 s. The CPN solution was coated on the PEN substrate and sputter-coated PET films using the bar coating system with a speed of 50 mm/s. The coating layers were cured in three steps: the CPN were first cured under optimum conditions that were confirmed *via* DSC analysis, dry lamination was conducted as a second step, and finally, the CPN were post-cured for 2 h at 75 °C in an IR oven.

### 2.3. Characterizations

The orientation of clay platelets in the CPN was confirmed using a field emission transmission electron microscope (FE-TEM) (JEM-2100F model, JEOL Ltd., Japan). The X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D8 Advance, Bruker Co., USA) equipped with a Cu K $\alpha$  tube and Ni filter

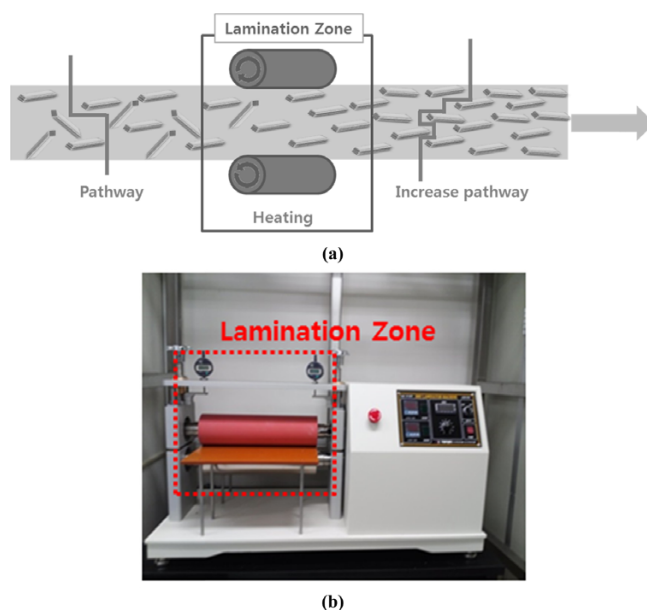
( $k=0.1542$  nm). The first curing condition of the CPN prior to the dry lamination process was optimized using a differential scanning calorimeter (DSC, Diamond DSC, PerkinElmer, USA), following a standard procedure per ASTM D3895. The specimens were heated from room temperature to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The gas flow rate was maintained at 50 mL/min at a gauge pressure of 0.035 MPa. The cell was maintained at 200 °C under a nitrogen gas atmosphere for 5 min.

The barrier property of the coating layer was characterized by measuring the water vapor transmission rate (WVTR) using a Permatran-W model 3/33 (Mocon Inc., USA). The light transmittance of the sample was measured using a color filter spectral multi-channels spectrophotometer (MCPD-3000 of Otsuka Co., Japan).

## 3. Results and discussion

The barrier properties of CPN can be enhanced by requiring a difficult pathway that retards the permeation of water vapor and oxygen molecules. The layered silicates in CPN play an important role in the formation of more difficult pathways. This tortuosity is maximized when the layered silicates are aligned perpendicular to the permeation direction. A simple permeability model for the regular arrangement of platelets has been proposed for the polymer-layered silicate nanocomposites system.<sup>12</sup> Three options were considered during the cross linking of CPN, including phase-separated composite results, intercalation, and exfoliation. The layered silicates in the composites may have non-uniform orientation due to this variability. In this sense, controlling the orientation of clay platelets in CPN and revealing their influences on barrier, thermal, and mechanical properties is highly useful.<sup>13,14</sup>

In order to study the effects of clay platelets oriented along the substrate on barrier properties, the orientation of clay platelets in the CPN can be induced using the dry lamination process



**Figure 1.** (a) Schematic of the dry lamination process and (b) equipment.

shown here. A schematic of our dry lamination process is shown in Figure 1. CPN's were partly cured during the first curing step and orientation of clay platelets is possible by dry lamination process. If they were fully cured during the first curing step, it would be difficult to control the orientation of clay platelets via the dry lamination process. Consequently, optimization of the curing conditions is required prior to the formation of CPN layers on the substrate. The first cured CPN on the substrate progress through into the dry lamination zone consisting of two

heating rolls. The roll speed was maintained in 3 rpm at 75 °C. The lamination force was controlled by adjusting the gap between the two rolls.

An onset temperature ( $T_i$ ) of 76.88 °C and peak temperature ( $T_p$ ) of 106.95 °C can be derived from the non-isothermal DSC results shown in Figure 2(a). In order to induce the high orientation effect from dry lamination, the temperature of the first curing step was maintained below the onset temperature ( $T_i$ ). The clay platelets in the CPN could be easily relocated during the dry lamination process for the first cured layer maintaining its integrity. The curing time was determined from the isothermal test while maintaining an isothermal condition of 75 °C, near the onset temperature ( $T_i$ ), as shown in Figure 2(b). Based on these results, the first curing reaction of the CPN was terminated at 7.283 min. In contrast, the curing reaction was quickly terminated at the peak temperature ( $T_p$ ) of 105 °C (Figure 2(c)), and the clay platelets could hardly be controlled in the CPN by dry lamination.

Generally, the curing reaction of epoxy resins proceeds from the liquid state into the rubbery state; the resins are then converted into the glassy state.<sup>15</sup> The following equation was obtained according to this kinetic scheme:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)^2$$

where  $\alpha$  denotes the conversion of epoxy groups and the corresponding rate constants,  $k_1$  and  $k_2$ . These rate constants depend on temperature, as shown with the Arrhenius-type expression:

$$k_i = A_i \exp(-E_i/RT)$$

where  $A_i$  denotes the frequency factor of the  $k_i$  rate constant and  $E_i$  its corresponding activation energy. When the epoxy resins are polymerized at temperatures below the glass transition temperature, the reaction cannot achieve complete conversion.<sup>16</sup> Therefore, if dry lamination proceeds around this temperature, we found that the orientation of clay platelets can be controlled in the CPN.

The TEM images of CPN's for three durations of pre-curing after terminating all procedures are shown in Figure 3. As shown, the clay platelets are dispersed randomly in the CPN without the first curing step (Figure 3(a)). After the first curing the onset temperature was maintained for around 10 min to gain optimum curing. It was then confirmed that the clay platelets exhibit clear orientation morphology. This indicate that the orientation of clay platelets is related to the dry-lamination process. Due to lower degree of curing after the first curing step, the lamination force applied on the first cured samples can induce orientation of clay platelets (Figure 3(b)). However, as shown in Figure 3(c) and Figure 3(d), the first long curing in optimum conditions does not significantly affect the orientation of clay platelets. Generally, when the curing time increases, the mobility of the epoxy polymer and hardener molecules decreases, and as a result they can hinder the orientation of clay platelets in the CPN layers.<sup>17</sup> The first curing time was optimized at 10 min for the best orientation of clay platelets before the dry lamination process.

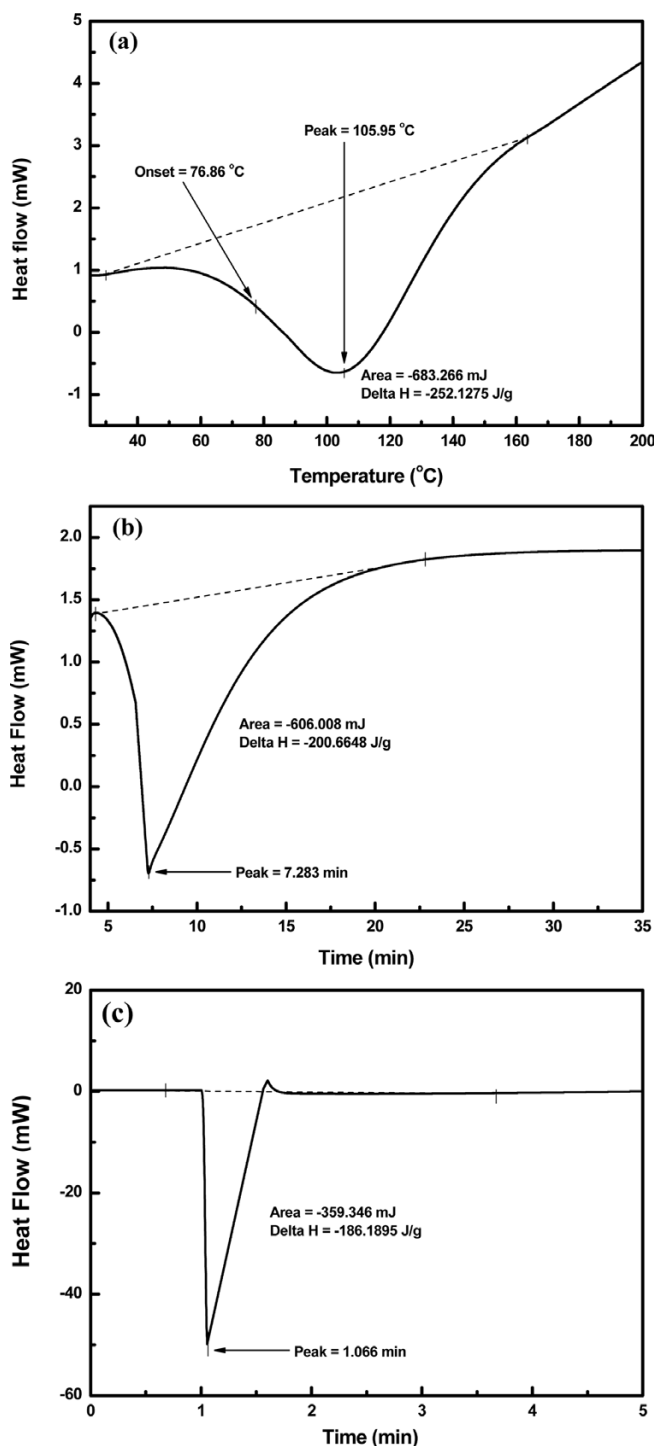
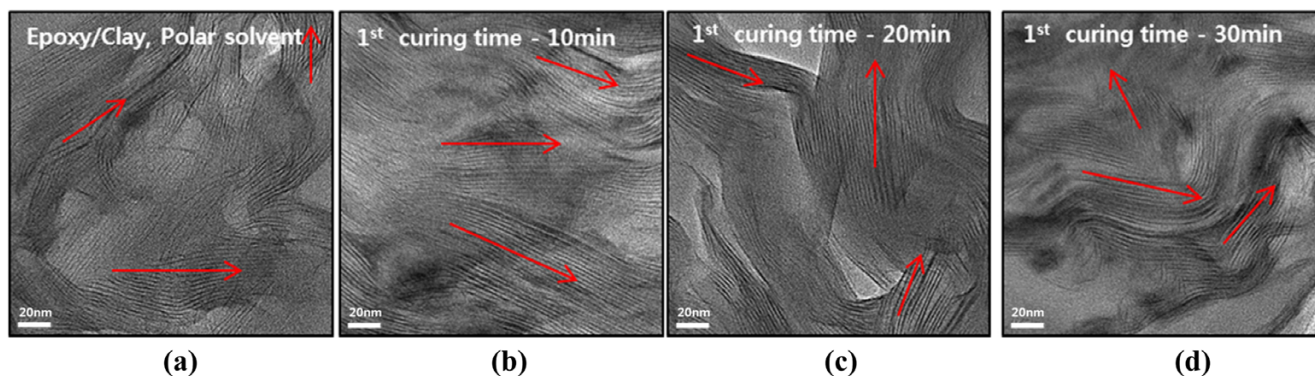
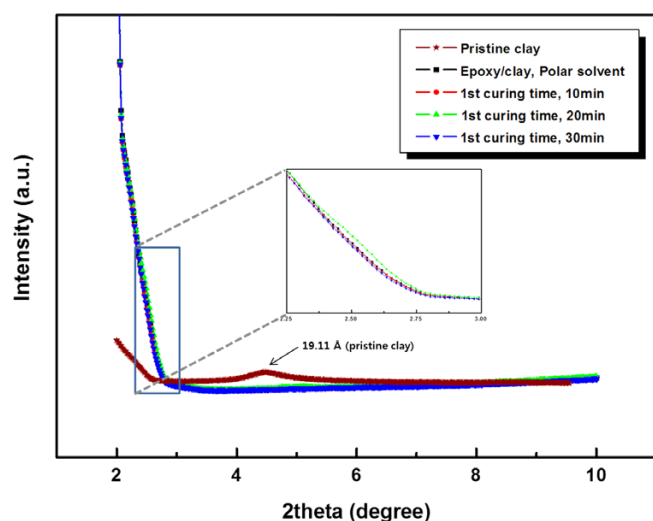


Figure 2. DSC curves of the CPN: (a) In non-isothermal condition and in isothermal conditions with temperatures of (b) 75 °C and (c) 105 °C, respectively.



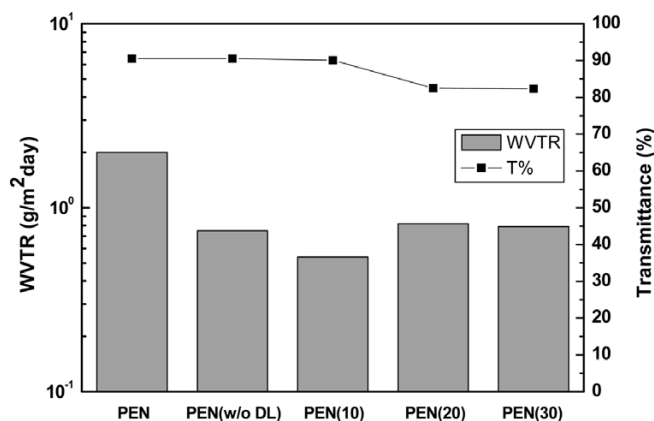
**Figure 3.** TEM images of a cross section of the CPN (a) without the first curing step and with the first curing step for (b) 10, (c) 20, and (d) 30 min.



**Figure 4.** XRD patterns of the CPN.

Figure 4 presents X-ray diffraction curves in CPN without the first curing step and with three durations of first curing before the dry lamination process. The clay platelets were well exfoliated in the CPN without the pre-curing step compared to the peak of the raw clay platelets (approximately  $3.7\sim 3.8^\circ$ ). We can also confirm that there are no significant changes in the XRD curves for the CPN with the first curing step at three durations. Although the first curing step was carried out for the formation of CPN, we also found that the first curing step does not cause reduced intercalation and dispersion of the clay platelets during the curing process. Therefore, the clay platelets in the CPN can be oriented uniaxially during dry lamination with a smaller decrease in the  $d$ -spacing.

The effects of clay platelets orientation on WVTR and light transmittance are shown in Figure 5. The WVTR of the CPN was reduced after dry lamination when compared to the sample without a dry lamination process (PEN(w/o DL)). When the first curing was conducted for 10 min at optimum conditions prior to the dry lamination, WVTR was reduced to  $0.54 \text{ g/m}^2/\text{day}$  without degradation of the optical transmittance (PEN(10)). These results confirm that the uniaxial orientation of clay platelets induced from dry lamination after the optimum first curing process enhanced the barrier properties while maintaining optical properties. However, the WVTR increased when the duration of the first curing time increased to 20 min (PEN(20))

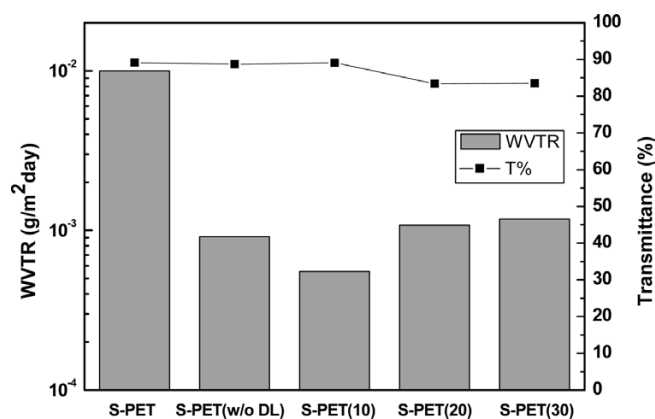


**Figure 5.** WVTR and optical transmittance of the CPN coating on the PEN substrate.

and 30 min (PEN(30)), which is due to a reduction in the clay platelets orientation at longer curing times. This is also confirmed in the TEM results. It is obvious that the increase of clay platelets orientation in the direction parallel to the surface of the substrate results in increased pathway difficulty for permeating water vapor and oxygen.

To investigate the effects of CPN coatings with highly oriented clay platelets on the enhancement of the barrier properties of sputter-coated films, five different samples were tested. These are denoted S-PET film (sputtered SiO<sub>x</sub>/SiO<sub>y</sub> PET film), S-PET(w/o DL) (CPN without dry lamination/S-PET film), S-PET(10) (CPN with first curing in 10 min/S-PET film), S-PET(20) (CPN with first curing in 20 min/S-PET film), and S-PET(30) (CPN with first curing in 30 min/S-PET film). The WVTR values of each sample are presented in Figure 6. The WVTR of the S-PET films decreased from  $1 \times 10^{-2} \text{ g/m}^2/\text{day}$  to  $9.1 \times 10^{-4} \text{ g/m}^2/\text{day}$  for S-PET(w/o DL) samples. These results indicate that the CPN layer could effectively protect the inorganic layer from defects, which caused a reduction in barrier performance. The WVTR of the S-PET films decreased drastically to  $5.5 \times 10^{-4} \text{ g/m}^2/\text{day}$  for S-PET(10). This result can also be interpreted as the effect of the uniaxial orientation of clay platelets induced by dry lamination after the optimum first curing process. This is consistent with expectations for PEN substrates. These results indicate that the clay platelets were aligned perpendicularly to the diffusion pathway, increasing the path tortuosity and enhancing the barrier properties.

However, the WVTR of S-PET(20) and S-PET(30) was not as



**Figure 6.** WVTR and optical transmittance of the CPN coating on S-PET films.

significantly decreased as S-PET(10), because the first long curing time did not significantly affect the orientation of clay platelets. As also shown in Figure 6, there are no significant changes in optical transmittance after the CPN coating on S-PET films. Consequently, it could be deduced that the uniaxial orientation of clay platelets induced from dry lamination after the optimum first curing process affected the enhancement of barrier properties in both PEN substrates and S-PET films.

#### 4. Conclusions

Clay platelets orientation induced by a dry lamination process affected the barrier properties of CPN. After an initial curing procedure with optimum conditions, dry lamination was conducted to induce the desired orientation of the clay platelets. In the first curing step, we confirmed that the curing temperature and time significantly affected the rearrangement of clay platelets in the lamination process. The CPN with clay platelets aligned

in a direction parallel to the surface of the substrate showed enhanced barrier properties of the PEN substrate and S-PET films. The water vapor transmittance rate reached its lowest level of  $5.5 \times 10^{-4}$  g/m<sup>2</sup>/day while maintaining the optical properties. It was concluded that the orientation of clay platelets in CPN leads to an increase in path difficulty, which decreased permeation of the water vapor through the layers.

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