# Effect of Nano Clay on Properties of Nanocomposites Based on EVA for Film Packaging Applications

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*Abstract-* The concept of nanoscale reinforcement provides opportunity for synthesis of polymer materials with unique properties. Behaviors of EVA nanocomposites containing nanofillers, such as nanoclay (Cloisite<sup>®</sup>30B) were investigated. Samples were prepared with the nanoclay content 1, 3 and 5 wt % and their mechanical properties such as tensile strength, tensile modulus have been considered. So  $O_2$  permeablity and optical transparency test have also been done.

Wide Angle X-Ray Diffraction (WAXD) and Transmission Electron Microscopy (TEM) were in support of the formation of partially delaminated nanocomposite material. TEM images confirmed that the nanocomposites possessed a high level homogeneity resulted from a sufficient dispersion of nanoparticles in the resin matrix.

The results also indicated that tensile test of the nanocomposites was significantly influenced by the VA content.

 $O_2$  Permeability decreases with increasing clay. Also optical transparency is seen that one sample has the maximum haze and minimum gloss.

Keywords- Nanocomposites; EVA; Clay, Mechanical Properties; Gas Permeablity; Optical Transparency

#### I. INTRODUCTION

The promise of hybrid composites engineered from polymers and nanoscale components (such as carbon nanotubes, nanoclays, and nanofibres) presents a challenge to researchers in applied materials science [1]. The EVA (ethylene vinyl acetate) copolymer is synthesized through the copolymerization of ethylene and vinyl acetate by a high pressure, high temperature, bulk polymerization process just like low density polyethylene; it possesses various properties when changing the initial concentration of vinyl acetate. Especially, the crystallinity of the EVA, controlled by the vinyl acetate contents, affects the properties of the obtained EVA. As the VA (vinyl acetate) content increases, the copolymer presents less crystallinity, more polarity and different physical behaviors [2].

The increasing polarity with increasing VA content is apparently useful in imparting a high degree of polymer–clay surface interaction, and it has been reported that there is a significant rise in the young's modulus and the yield strength of the EVAPCNs (ethylene vinyl acetate base of polymer clay nanocomposites), in tune with the behavior of other polymeric nanocomposites [3].

Reported results on EVA based nanocomposites as a function of organoclay concentration by Zanetti et al have been done [3]. The combination of ethylene vinyl acetate (EVA) with nanoclay has wide commercial applications (such as packaging films, cables and adhesives), and these applications depend on the vinyl acetate (VA) contained in the main chain [3].

In this paper, we prepared exfoliated EVA/organoclay nanocomposite with different (wt%) VA content compared to those previously reported and characterized their tensile properties.

Since the VA content dictates the polarity of the matrix – thus dictating the level of organoclay–polymer interaction – morphologies of EVA nanocomposites would differ based on VA content and their interaction with its nanoclay content. For example, some authors have reported how the structure–mobility properties of EVA polymer are influenced by the VA content and this chain mobility in and around clay galleries could significantly modify the level of interaction in clay nanocomposites [3].

Also, it is well known that inclusion of filler provides a suitable pathway for increased crystallinity and consequently higher crystallization temperatures in polymeric samples because of the nucleation effects of the fillers (by providing active surface structures).

Main emphasis has been put on both tensile strength and tensile modulus properties of exfoliated EVA/clay nanocomposites with different clay loadings. So,  $O_2$  permeability and optical transparency are discussed.

#### II. EXPERIMENTAL

### A. Materials

The clay material is Cloisite<sup>®</sup>30B from Southern clay products. It is a natural montmorillonite organically modified with a methyl tallow bis-2-hydroxyethyl quaternary ammonium. The as-received clay (montmorillonite) particles were disk-like stacks of thin silicate layeres, 1 nm thick and ranging from 100 nm to several micrometers in diameter (with an aspect ratio ranging between 200 and 1000).

The ethylene vinyl acetate (EVA) copolymer was obtained with the following characteristics in Table I.

TABLE II PROPERTIES OF EVA

Property	Value
density	0.948 g/ mL at 25 $^\circ \!\! \mathbb{C}$
number-average molecular weight(Mn)	22,460 g/mol
weight-average molecular weight (Mw)	137,550 g/mol
polydispersity index (PI)	6.1
melt flow index (MFI)	8.0 dg/min

# B. Sample Preparation

EVA and Clay were melt-mixed by twin-screw (ZPT-32HT) with " $160^{\circ}$ C" temperature. The speed of rotor 150 rpm for 20 minutes were prepared with 1, 3 and 5 wt% clay.

# C. Techniques

X-ray diffraction patterns were obtained in a Siemens D-500 diffractometer using a Ni-filtered CuK- $\alpha$  radiation generator with an intensity of 25 mA and a voltage of 35 kV. The diffraction patterns were collected within the range 0.5-30 ° using a scanning rate of 0.6  $\gamma$ min.

Tensile tests were performed at room temperature according to ASTM D-882. Results are an average of at least five specimens for tensile.

Gas permeability tests of EVA/clay nanocomposites with various clay contents were performed with an Oxygen Permeation Analyzer (Illinois Instruments, Model 8501) according to ASTM D-3985 at 25°C. Samples before measurement were kept for 3 days at 50% relative humidity.

Optical transparency test includes gloss and haze measuring. Gloss of plastic in this plastic test standard is ASTM D2457. ASTM Method D1003-95 describes the type of instrument to be used for measuring transmission haze.

TEM Micrographs were taken with a Philips CM12 TEM at an acceleration voltage of 110 kV.

# III. RESULT

# A. Materials Structure and Morphology Characterization

XRD is a useful screening tool for determining if any sort of nanocomposite was prepared. XRD gives the distance between clay layers, thus revealing the relationship of the clay layers to themselves, not of the clay layers to the polymer. XRD does not reveal how well dispersed the clay is throughout the polymer, nor does it define the degree of intercalation or exfoliation. Fig. 1 presents the WAXDs of EVAPCNs as well as clay nanoparticles.

X-ray diffraction confirmed the formation of exfoliated nanocomposite in all cases with disappearance of the characteristic peak corresponding to the d-spacing of the pristine organoclay [3].

WAXS data shown in Fig. 1 to Fig. 3 have been discussed in detail.

Fig. 1 does not show any sharp crystalline diffraction peaks in this nanocomposie and we can find clay to dispersed in EVA matrix well.

In Fig. 1 clay was found to have  $d_{001}$  3.54 nm as compared to the swelled EVA10 PCNs in Fig. 2 with 4.64 nm (1%), 4.41 nm (3%) and 3.92 nm (5%).



Fig. 1 XRD-Spectra for Cloisite<sup>®</sup>30B and EVA nanocomposite



Fig. 2 WAXS patterns comparing the nature of intensity and *d*-spacing of clay as well as EVA10-Clay nanocomposites at clay loading of 1, 3 and 5 wt.%

The WAXS data show that the peak intensity of 1% clay has been significantly reduced and shifted towards lower angles, but the peak is not as broad as 3% or 5% indicating that in 1%, the tactoids separate into platelets with comparatively larger gallery space and maintain their ordered structure in the smaller scale. However, the peak intensities in 1% is insignificant as compared to 3% or 5% indicating that in PCNs with the latter different concentrations, the comparatively higher concentration of clay could not be exfoliated but in general, small groups of layered silicates in a tactoidwould have become more disordered and randomly oriented, while maintaining a periodicity within the platelets giving a highly diffused band at higher angles. Such characteristics have been dealt similarly in other's interpretation [4].

Fig. 3 shows that all EVA30 PCNs have a low intensity shoulder at ( $d_{001} = 6.3$  nm) indicating a high degree of platelet incoherence or a 'highly exfoliated system' [3].



Fig. 3 WAXS patterns comparing the nature of intensity and d-spacing of Clay as well as EVA30-Clay nanocomposites at clay loading of 1, 3 and 5 wt.%

Compared to pristine clay, it is thought that the increased polarity of the polymer chains could have facilitated polymeric chain stabilization within the clay galleries.

Similar effects are also seen for EVA20 PCNs, and the stabilization could be due to the higher amorphous content (due to the increased VA groups) that prevents it from re-crystallizing during annealing and allows the polymeric chains to remain diffused within clay platelets.

WAXS data displayed in Fig. 2 have been discussed in detail before. Primitive clay was found to have  $d_{001} \sim 3.5$  nm as compared to the expanded EVA10 PCNs with 4.72 nm (1wt%), 4.64 nm (3wt%) and 4.41 nm (5wt%). The WAXS data show that the peak intensity of 3wt% clay has been reduced and shifted towards lower angles, but the peak is not as broad as 3wt% or 5wt% indicating that in 3%, the tactoids separate into platelets with comparatively larger gallery space and maintain their ordered structure in the smaller scale.

In general, small groups of layered silicates in a tactoid would have become more disordered and randomly oriented, while maintaining a periodicity within the platelets giving a highly diffused band at higher angles. Such characteristics have been dealt similarly in other's interpretation [4].

Fig. 3 exhibits that all EVA30 PCNs have a low intensity shoulder at  $2\theta = 1.4^{\circ}$  ( $d_{001} \sim 6.5$  nm) indicating a high degree of platelet confusion or a 'highly exfoliated system' when compared to pure clay. It is thought that the increased polarity of the polymer chains could have promoted polymeric chain stabilization within the clay sets.

Transmission electron microscopy (TEM) analysis was used to provide a 'visual' confirmation of the morphological information obtained on the platelet dispersion and distribution from the WAXS data as the latter lacks the ability to characterize the disordered-intercalated or the exfoliated structures due to the absence of scattered intensity peaks for those morphologies [6].

Fig. 4 (a,c,e) indicates that nanocomposite based on nano clay is a prepar homogeneous mixture and nanoparticles were dispersed sufficiently too. Forther more, this low level of homogenity can be also seen in Fig. 2 (b,d,f).



Fig. 4 TEM micrograph (with scale 200nm ) of matrix amorphicity EVAPCN

### B. Tensile Test

Fig. 5 exhibits behavior of the stress-strain in a sample of EVA and EVA/Clay with 3% clay.

As indicated in Fig. 5, EVA nanocomposite based on nano clay shows an increase of 50% in strain by adding just 3 wt% of nano clay, indicating nanoparticles possess a significant effect on properties of EVA nanocomposite.



Fig. 5 Behavior of the stress-strain in a sample of EVA and EVA/Clay with 3% clay

Fig. 6 exhibits the tensile modulus of EVA nanocomposites with nanofiller. Nanocomposite with 5% clay had the highest percentage of modulus in 10 % EVA at nearly 73 Mpa, followed by nanocomposite with 3% clay at about 63 Mpa and nanocomposite with 1% clay at 50 Mpa. Neat EVA (no clay) examined the most startling decrease.

As a result, the tensile modulus increased progressively with increase of nanofiller loading. This is due to the fact that the typical nanofunctionality of the samples reveals superior reinforcement due to an interaction of highly surface area of clay with polymer's matrix.



Fig.6 Tensile modulus variation at different clay concentrations and with increasing matrix amorphicity for EVAPCN

Fig. 7 shows the tensile strength data for EVAPCNs. The extent to which clay incorporation modifies the PCN morphology can be studied by considering the influence of clay (wt%) and the effect of increasing VA content concurrently.



Fig. 7 Tensile strength at different clay concentrations and with increasing matrix amorphicity for EVAPCN

Neat EVA's strength remained low. The patterns in neat EVA (no clay) and nanocomposite with 5% clay were rather different. The number of strength per different % EVA in nanocomposites with 1 and 3% clay increases sharply between 0 and ~20 % EVA from around 7 Mpa in nanocomposite with 1% clay to about 12 in ~20% EVA and from nearly 9 to 15 in nanocomposite with 3% clay. Thereafter both patterns strength decline steadily to around 6 Mpa in nanocomposite with 1% clay and 7 Mpa in nanocomposite with 3% clay.

The extent of suppression is significantly influenced by the VA content. The reduction in EVAPCNs strength could be explained by considering that nanoclay increases the spatial hindrance for polymeric chain movement and this is most evident for EVA with 5% clay, possibly because of the rigidity imparted by the randomly oriented cluster of tactoids that were dispersed in the matrix. However, if the clay wt.% is increased in the matrix, EVA PCNs show the interesting results [4].

Fig.7 shows that EVA10 PCNs have an increasing trend with increasing clay concentration, whereas, EVA20 and EVA30 PCNs show an increasing–decreasing trend. The possibility of a flexible clay network structure in the EVA PCNs was mentioned before now, and this allows the polymeric chain to absorb higher deformational energy by increased alignment and partial transfer due to an intercalation before the chain rupture.

The probability of a flexible clay network structure in the EVAPCNs was mentioned at an earlier time, and this allows the polymeric chain to absorb higher deformational energy by increased alignment and partial transfer as a result of the intercalation before the chain bursts.

### C. Gas Permeability Test

Gas permeability is one of the physical properties that Table II shows O<sub>2</sub> permeability of the EVAPCNs.

Materials	Materials O2 permeability (cc mm/[m.sup.2] 24 hr at tam	
EVA	145.8 [±] 20.2	
Clay/EVA 1/99	106.8[±] 8.8	
Clay/EVA 3/97	76.6 [±] 7.2	
Clay/EVA 5/95	81.0 [±] 6.2	

TABLE II  $\mathrm{O}_2$  PERMEABILITY AT DIFFERENT CLAY CONCENTRATION FOR EVA NANOCOMPOSITES

Specific drinks such as beer for several years were not supplied in polyethylene bottles. These high oxygen permeability materials will reduce the shelf life of the drink.

Silica layer can extremely decrease the influence of oxygen. EVAPCNs is compared to pure EVA that permeability decreased with increasing clay.

#### D. Optical Transparency

Many drinks such as milk are very sensitive to the effects of light. When they are exposed to light, they look like that we provide the corruption of all the products. In addition to adding to the beauty of transparent packaging products, further ensuring the quality of its contents are the customer. This condition can be treated to improve the type and colour of materials used in packaging.

Angel is 45 ° for exhibiting properties of gloss test. Gloss is a measure of how shiny, or reflective a material is at a specified angle based on refractive index. Comparison of gloss data can only be made between similar materials and test procedures. Gloss values for transparent and opaque materials are not comparable. Gloss varies with smoothness and flatness and is sometimes used to compare these attributes [5].



Fig. 8 Gloss at different clay concentrations and with increasing matrix amorphicity for EVAPCN

Figure 8 shows gloss data for EVAPCNs and Figure 9 displays haze of EVAPCNs with different percents of EVA content. It can be clearly seen that the rate of gloss is currently declining in Fig. 8. The graff decreased gradually to 61 by 15% EVA content and continued to decrease but more steeply to 57 in 30% EVA content. The number of haze in nanocomposites increased sharply between 0 to 20 % EVA content from around 2.5 to 5 % in Fig. 9. Thereafter pattern declined to around 4.5 in 30 % EVA.

In Figure 8 and Figure 9 it is seen that sample (with 30% EVA) has approximately the maximum haze and minimum gloss.



Fig. 9 Haze at different clay concentrations and with increasing matrix amorphicity for EVAPCN

### IV. CONCLUSIONS

Exfoliated EVA nanocomposites were synthesized by using nanofillers while intercalated nanocomposites were obtained with nanofillers. The morpholog of nanocomposites were investigated with various techniques such as XRD and TEM.

Final results showed that EVA-Clay was compared to EVA and some mechanical properties such as tensile modulus and tensile strength of EVAPCNs, with better performance. The extent to which clay incorporation modifies the PCN morphology can be studied by considering the influence of clay (wt%) and the effect of increasing VA content concurrently.

The tensile modulus increased gradually with increase of nanofiller loading in 10 % EVA..The number of strength per different % EVA in nanocomposites with 1 and 3% clay increased attentively between 0 and ~20 % EVA in nanocomposite. Thereafter patterns strength declined steadily in nanocomposite with 1 wt% clay and 3 wt%.

 $O_2$  permeability decreases with increasing clay. Also optical transparency is seen that one sample has the maximum haze and minimum gloss.

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