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Preparation and Rheological Characteristics of Ethylene-Vinyl Acetate Copolymer / Organoclay Nanocomposites

Hyung Min Lee^a, Bong Jun Park^a, Rahul Kumar Gupta^b, Sati N. Bhattachary^b and Hyoung Jin Choi^{a,*}

^a Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

^b Rheology and Materials Processing Centre, School of Civil and Chemical Engineering, RMIT University, Melbourne, Victoria 3000, Australia

E-mail: hjchoi@inha.ac.kr

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Abstract

Ethylene-vinyl acetate copolymer (EVA) with 40 wt% vinyl acetate content (EVA40)/organoclay nanocomposites were prepared via a melt intercalation method with several different clay concentrations (2.5, 5.0, 7.5, and 10.0 wt%). 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. Transmission electron microscopy studies also revealed an exfoliated morphology of the nanocomposites. Morphology and thermal properties of the nanocomposites were further examined by means of scanning electron microscopy (SEM) and thermogravimetric analysis (TGA), respectively. Rheological properties of the EVA40/organoclay nanocomposites were investigated using a rotational rheometer with parallel-plate geometry in both steady shear and dynamic modes, demonstrating remarkable differences with the clay contents in comparison to that of pure EVA40 copolymer.

INTRODUCTION

Polymer/clay nanocomposites are a new emerging class of organic-inorganic hybrid materials. With nanoscopic dispersion of a tiny amount of inorganic clay (montmorillonite, saponite, kaolinite, etc.) with platelet-like structures in a polymeric matrix [1, 2], they often exhibit remarkable improvement of material properties when compared with those for pure polymer or conventional polymer composites (micro- or macro-composites) with such fillers as glass fiber and carbon fiber. These improvements include enhanced physical and mechanical properties of high tensile moduli and strength [3, 4], increased dimensional stability [5, 6], decreased gas permeability and flammability [7], improved solvent and UV resistance [8], improved electrical property and increased biodegradability of biodegradable polymers [9]. The main reason for these enhanced properties in the nanocomposites is caused by the very high aspect ratios (10-1000) and/or large surface area of exfoliated clay particles and the strong interfacial interaction between the silicate platelets of 1nm layer thickness and the polymer matrix [1-9]. Furthermore, the clay is naturally abundant, cheap, and environmentally friendly.

On the basis of the strength of the polymer /clay interactions, intercalated, exfoliated, and tactoid nanocomposite systems are generally known. Among these, the intercalated structure is a form where one or more extended polymer chains are inserted into the clay gallery with fixed interlayer spacing, while the exfoliated structure is

obtained when the silicate clay layers are completely dispersed in a polymer matrix. To achieve full exfoliation of clay in a polymer matrix, the clay particles must be premodified with an organic ammonium cationic surfactant. Among various polymeric materials for polymer/clay nanocomposites, ethylene vinyl acetate copolymer (EVA), a random copolymer consisting of ethylene and vinyl acetate (VA) as a repeating unit, has been recently adopted for its nanocomposite system due to its potential engineering application in the fields of packaging films and adhesives [10, 11]. The EVA 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 content increases, the copolymer presents less crystallinity, more polarity and different physical behaviors [12, 13]. Common grades have vinyl acetate contents ranging from 1%~50% by weight depending upon the application [14]. Recently, several groups have extensively studied EVA copolymer nanocomposites with various vinyl acetate (VA) contents [15-18].

In this paper, we prepared exfoliated EVA/organoclay nanocomposite with rather high (40 wt%) VA content compared to those previously reported and characterized their physical and rheological properties [19]. Since the vinyl acetate group is polar, it is well known that increasing the VA content in the EVA increases the polarity of EVA [20] and thus affects characteristics of EVA40/clay nanocomposite. Main emphasis has been put on both steady shear and dynamic rheological properties of exfoliated EVA40/clay nanocomposites with different clay loadings.

EXPERIMENTAL

Materials

Organo-modified montmorillonite (MMT) clay, Cloisite® 30B (C30B) by Southern Clay Products (Gonzales, USA), was used as received. The pristine Na⁺-MMT has been treated with a quaternary ammonium salt of methyl, tallow, bis-2-hydroxyethyl (with a cation exchange capacity (CEC) of 90meq/100g clay). EVA copolymer with 40wt% of vinyl acetate (EVA40), supplied by Dupont Inc., (Melbourne, Australia) was used without any purification.

Nanocomposite preparation

All nanocomposites were prepared using the melt blending technique. Prior to feeding the samples into an extruder, both the polymer and the organoclay were dry-mixed for about 1 minute and then fed into an intermeshing counter-rotating twin-screw extruder (Brabender, Duisburg, Germany). Composites with varying filler level (2.5, 5, 7.5 and 10% w/w) were prepared and the relevant processing conditions are shown in Table 1 below. The nanofiller, C30B for EVA40 was chosen according to the manufacturer's recommendations.

Characterization

Immediately after the sample preparation, various methods were used for the characterization of the EVA40/organoclay nanocomposites. Change of interlayer distance of the organoclay in the EVA40 matrix was checked via wide angle X-ray diffraction (WAXD); a Rigaku X-ray diffractometer (the wavelength of 0.154 nm: a rotating anode type (Cu-K α)) with 40kV accelerating voltage and 40mA current for

recording data within a range of $2\theta=1.0\sim30^\circ$. In addition, to examine the X-ray diffraction of the nanocomposites more accurately, especially at a low angle, small angle X-ray scattering (SAXS) experiments were adopted using a rotating anode type (Cu-K α) of Rigaku X-ray diffractometer (DMAX-2500) with 40kV accelerating voltage and 120mA current [21, 22]. Intensities in the range of $2\theta=0.06\sim3^\circ$ were recorded. Transmission electron microscopy (TEM) images were obtained with a Phillips CM200 operated at an acceleration voltage of 120kV. The samples were ultramicrotomed using a RMC ultramicrotome with a CR-X Cryosection attachment at -160°C . Note that preparing TEM sample by cutting both pristine EVA and nanocomposite samples at room temperature was extremely difficult due to the rubbery nature of the EVA. The morphology of a cross-sectional surface fractured after dipping into a liquid N₂ was observed by scanning electron microscopy (SEM) (Hitachi S-4300, Japan) under the condition of 3K magnification and 10KV. The thermal properties were examined using a thermogravimetric analyzer (TGA) (Q50 thermogravimetric analyzer, TA Instrument, USA). The measurement was carried out under a nitrogen environment by purging nitrogen gas at 20 ml/min and heating from room temperature to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$. Both steady shear and linear viscoelastic properties of the neat EVA40 and its nanocomposites were measured by using a rotational rheometer (Physica MCR300, Germany) with a parallel-plate geometry (25mm diameter). The stress relaxation measurements were also performed for both neat EVA40 and EVA40/clay nanocomposites at a fixed 5% strain. All the measurements were carried out in the molten state of the samples at 130°C with 1mm gap distance.

RESULTS AND DISCUSSION

The nanocomposite structure was characterized using both XRD and TEM, in

which these analyses were sensitive enough to detect a crystalline structure of the clay in the polymer/clay nanocomposites. Especially, the WAXD and SAXS of the XRD offer a convenient method to determine the interlayer spacing of the clay layers, while the TEM allows a qualitative understanding of the internal structure through direct visualization.

XRD patterns for the pure organoclay (C30B) powder and EVA40/ clay nanocomposites with different clay loadings are presented in Figure 1. The d -spacing (001) of the clay interlayer of the nanocomposites was calculated based on the observed peaks by using the Bragg equation: $\lambda = 2d \sin \theta$ ($\lambda = 0.154 \text{ nm}$). In the scattering curve for the pure clay as shown in Fig. 1(a), the salient peak (d_{001}) corresponding to the basal spacing of Cloisite 30B occurs at 1.85 nm . However, this reflection peak disappears in the scattering curves for all the EVA40/clay nanocomposites in the WAXS without showing any corresponding Bragg peaks. On the other hand, the shoulder peaks of all the EVA40/clay nanocomposites at about $2\theta = 6^\circ$ can be regarded to be the d_{001} peak of C30B shifted toward a higher angle of almost 2° , because some parts of the C30B will shrink due to the detachment of cationic quaternary ammonium surfactant during melt processing at 130°C . In addition, the lack of order at higher d -spacing (under $2\theta = 3^\circ$) can be confirmed from SAXS data (Figure 1(b)). This SAXS plot did not show any characteristic diffraction peak of the dispersed clay layers, demonstrating successful exfoliated formation of the EVA40/clay nanocomposites.

This observation can also be confirmed by the TEM images for the internal structure of EVA40/clay nanocomposites as shown in Figure 2 for 2.5 wt% (a), 5.0wt% (c), 7.5wt% and 10 wt% (d). Even though XRD analyses are useful in examining interlayer d -spacing of ordered layered silicate structures, they may fall short when no

scattered intensity peaks are observed and such lack of peaks could be interpreted as exfoliation. Therefore, TEM has been regarded to be essential as it gives a direct evidence of what structure exists in the nanocomposite [23]. All the EVA40/clay nanocomposites were found to indicate individual dispersion of completely delaminated clay sheets in the EVA40 matrix from the TEM. The clay platelets were dispersed well, possibly due to the high matrix polarity. The increased number of clay platelets can be observed as the clay contents increased. Note that the vinyl acetate (VA) is a polar functional group that is attached to the ethylene backbone, and the higher the VA content, the higher the polarity. Prasad et al. [23] has already reported that besides the ethylene backbone providing a point of contact between the EVA chain and clay layers via the surface modifier, the VA group can help by attaching itself to an unmodified region of the clay layers that is virtually hydrophilic. Therefore, EVAs with higher VA of 40 wt% will be able to have a greater degree of interaction with layered silicates compared with previously studied ones with 9, 18 and 28% VA contents, thus producing a much greater enhancement of melt properties. The strong interaction between EVA40 and clay might occur to such extent that the pure clay of dense layered structure was shown to be broken apart and dispersed with individual platelets in the matrix polymer. From the study of nanocomposites of EVA with different VA content, Pasanovic-Zujo et al. [10] reported that EVA28 and EVA18 were predominantly exfoliated while EVA9 was mostly intercalated.

Figure 3 shows the morphology of the fractured surface of pure EVA40 and EVA40 / clay nanocomposites observed by SEM. We can examine the morphological changes of EVA40/clay nanocomposite. The SEM micrograph of pure EVA40 (Fig. 3 (a)) does not show any interesting morphological information; however, distinct morphological

changes with two different domains appear in which the bright portions in the SEM image were thought to be fractured boundary induced due to the influence of clay presence [17]. The structural evolution of the EVA40/clay nanocomposites system with increasing clay content showed rougher surfaces.

The thermogravimetric curves (Figure 4) demonstrated that the incorporation of clay in the EVA affects its thermal stability. Thermal degradation characteristics of EVA40 and EVA40/clay nanocomposites in nitrogen gas surroundings showed two distinct regions. At the first step, the degradation of EVA40/clay nanocomposites became faster than that of the pure EVA. This can be assigned to the loss of acetic acid which was accelerated as a function of clay loading, possibly due to catalytic effect of the acidic sites of the clay [24-26]. Such increase in degradation rate with increasing amount of dispersed clay was observed in the TGA results for synthetic biodegradable aliphatic polyester/clay nanocomposite [27]. Lim et al. [27] explained such findings indicating that the clay acts as a heat barrier. Although it could enhance the overall thermal stability of the system, as well as assisting in the formation of char after thermal decomposition, the heat barrier effect would result in a reverse thermal stability in the first step. Since the clay also acts as a heat reservoir with higher heat conductivity than polymer matrix, local heating at the boundary of the clay layers enhances thermal degradation of the EVA40. The second step of degradation is the main-chain

degradation. At temperature, beyond about 400°C we found that the EVA40/clay nanocomposites have a higher thermal stability. That is, OMMT can enhance the thermal stability of the main chain of EVA. In general, clay possesses an excellent barrier property and prevents against the permeation of gas or liquid, because nanometer-sized silicate platelets are impenetrable to diffusing gas/liquid molecules. The effect on the barrier property of polymer/clay nanocomposites mainly depend on the degree of exfoliation. Furthermore, it has been also reported that the thermal performance of nanocomposites could be enhanced by hindering the volatile products generated during thermal decomposition process [28].

Since the viscoelastic properties of a particle suspension depend on the structure, particle size and shape, the rheology can be used to provide a tool to examine the structural evolution and the dispersion quality of polymer/clay nanocomposites in a melt state. Figure 5 shows the plot of the shear viscosity as a function of the shear rate for the pure EVA40 and EVA40/clay nanocomposites system at 130°C in the molten state. The systems displayed shear thinning behavior with increasing clay contents [29-31]. The appearance of shear thinning means the existence of a structure formed by either intercalation or exfoliation between polymer and clay. The higher the clay content, the higher the degree of shear thinning observed. The increase of the degree of shear thinning also means the nanocomposites became more solid-like. Furthermore, the pure EVA40 shows a Newtonian plateau behavior at around 0.02 /s shear rate. In addition to the increase of shear viscosity, increasing clay concentration shifts Newtonian plateau to

lower shear rates, leading to an earlier onset of shear thinning. Those with clay contents of 7.5% and 10% hardly indicated any sign of a Newtonian plateau with a zero shear viscosity possibly due to the presence of a three-dimensional network structure within the shear rate range tested [23]. Such a behavior can be analyzed quantitatively via a Carreau model curve fitting parameter as follows:

$$\eta = \frac{\eta_0 - \eta_\infty}{[1 + (\gamma t_1)^2]^{(1-n)/2}} + \eta_\infty \quad (1)$$

Where η is an apparent shear viscosity, η_0 is a zero shear viscosity, η_∞ is an infinitive shear viscosity, t_1 is a relaxation time and n is a power law index. The power law index (n) is just a criterion of the degree of shear thinning. If $n=1$, the fluid flows like a Newtonian fluid. If $n<1$, the fluid complies with shear thinning are pseudo-plastic behavior. The zero-shear viscosity (η_0) can be obtained from the Carreau model. Zero-shear viscosity, power law index and relaxation time are listed in Table 2. The shear viscosities of EVA40/clay nanocomposites are higher than that of pure EVA40 at a low shear rate. The enhancement arises from the interaction and dispersion of the clay in the polymer matrix. Although the shear viscosity of EVA40 at 10 wt% clay is larger than that of the others, all of these nanocomposites have similar shear viscosity at high shear rates due to the alignment and orientation of clay particles. Prasad et al. [23] also reported that at high shear rates, the shear viscosity of EVA18 nanocomposites was independent of clay loadings. These results are due to polymer chain conformation changes and reorientation of clay particles under shear, leading to preferential orientation and alignment of clay layers and polymer chains in the flow direction. The

EVA40/clay nanocomposites can be melt-processed due to this shear thinning property, thus manufacturing can be simplified [32]. Furthermore, a yield stress, which is characterized with a shear viscosity slope of -1 in the low shear rate region, is another rheological property we can deduce from this steady shear rheological measurement especially for higher clay contents. The presence of a yield stress implies a network structure which is related to the concentration and strength of a material formed as a result of polymer matrix-clay and clay-clay interactions [23].

The viscoelastic properties measured at 130°C for EVA40 and EVA40/clay nanocomposites are plotted as a function of angular frequency in Figure 6. With an oscillatory measurement, the viscoelastic response of materials can be investigated without any destruction of the internal structure of the samples if the experiment is performed within the linear viscoelastic region [33, 34]. In order to assure this condition, a test was performed to verify the linear correlation between amplitude and material function such as storage or loss modulus prior to the angular frequency sweep measurements. In the case of EVA40, the amplitude deformation was fixed at 1% in the dynamic measurement. In Figure 6(a) and 6(b), storage (G') and loss (G'') moduli were obtained simultaneously as a function of an applied frequency, showing that both storage and loss moduli increased monotonously with angular frequency. Depending on the material characteristics, the resultant response represents solid-like or liquid-like behavior. The materials behave like a solid for $G' > G''$, while like a fluid for $G' < G''$ (see Fig. 6c). With the increase of clay loading, the nanocomposites exhibited more solid-like behavior [35, 36]. In addition, a shift of the crossover point towards the lower frequency region of G' and G'' was observed. However, the crossover points for more than 5wt% clay loadings nanocomposites were not seen, even at very low angular

frequency as presented in Figure 6(c). In other words, the storage modulus (G'), which is the index of elasticity, can increase remarkably with clay loadings, due to a strong interaction between EVA40 and clay.

Figure 7 shows stress relaxation behaviors of EVA40 and EVA40/clay nanocomposites at a fixed strain of 5%, measured using a rotational rheometer. $G(t)$, in general, describes the time behavior of a material system. In short and medium timescales up to 5 seconds, the relaxation behavior is qualitatively similar for all nanocomposites and pure EVA40. However, for long timescales, neat EVA40 relaxes like a liquid, whereas the nanocomposites with increasing clay contents behave more like solid materials. On the basis of $G(t)$, it is clear that the addition of clay has a profound effect on the longtime relaxation of the nanocomposites. By increasing the loading of clay, the higher relaxation modulus $G(t)$ is observed for all time ranges, which may be caused by the enhanced elasticity (more solid-like) resulting from the increased clay loading. These changes of stress relaxation behavior of the EVA40/clay systems in the long time region were considered to be due to restricted stress relaxation of the confined polymer chains occupied by the meso-structure generated due to a strong interaction between clay platelets.

Conclusion

EVA40/organoclay nanocomposites were prepared using a melt blending technique. The change in the clay interlayer spacing as a function of the clay loading was examined; exfoliation of the clay in the polymer matrix was confirmed by X-ray diffraction investigation. TEM images also showed the exfoliated silicate layers. Microstructure and surface morphology of the nanocomposite systems were examined

by SEM. The pure EVA40 was featureless; however, distinct morphological changes with different two domains in the nanocomposites appear in which the bright portions in the SEM image were thought to be fractured boundary induced due to the influence of clay presence. The structural evolution of the EVA40/organoclay nanocomposite systems with increasing clay content showed rougher fracture surfaces.

The structural change and the effect of interfacial interaction on the extent of exfoliation as well as on the rheological properties of EVA40/clay nanocomposites with the clay contents were further investigated. A dramatic increase in elasticity was found with the addition of clay, which was confirmed by the storage modulus measurements. The solid-like behavior appeared to be due to good dispersion of clay in the EVA40 matrix.

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Figure 1. (a)WAXD peaks of EVA40/clay nanocomposites and pure clay.
(b)SAXS peaks of EVA40/clay nanocomposites.

Figure 2. TEM image of exfoliated EVA40 / clay nanocomposite samples.

Figure 3. SEM micrographs of (a) pure EVA40 and (b) 2.5wt%, (c) 10wt% nanocomposites.

Figure 4. TGA curves of EVA and EVA / clay nanocomposites.

Figure 5. Steady shear viscosity with Carreau model fitting as a function of shear rate at 130°C for pure EVA40 and EVA40 / clay nanocomposites.

Figure 6. (a) Storage modulus and (b)loss modulus as a function of angular frequency at 130°C for pure EVA40 and EVA40 / clay nanocomposites (c)Plot of storage modulus and loss modulus together.

Figure 7. Stress relaxation test at 130°C for pure EVA40 and EVA40/clay nanocomposites.

Table 1: The processing conditions employed for EVA40 organoclay-polymer system

Processing Conditions	EVA40 – C30B
<i>Residence time, min</i>	25
Barrel temperature, °C	110
Screw speed, rpm	70

Table 2. Zero shear viscosity, relaxation time and power law index of EVA40/clay nanocomposites.

Clay contents (wt%)	Zero shear viscosity η_0 [Pa.s]	Power-law index, n	Relaxation time, t
0	55,760	0.62	25.4
2.5	178,220	0.49	53.2
5.0	402,070	0.34	68.2
7.5	1,421,800	0.25	166.0
10	4,643,900	0.22	430.4

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.