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Ultrasound assisted batch-processing of EVA-organoclay nanocomposites

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Abstract−The aim of this study was to investigate the effect of ultrasound on the properties of a poly[ethylene-co-(vinyl acetate)] (EVA)-organoclay nanocomposite. By using a torque rheometer, in-situ rheological behaviors of various EVA resins with varying VA content were examined. It was found that the effect of ultrasound was most significant for EVA 31 (31 wt% VA). EVA31/organoclay nanocomposites were prepared in batch mixer with and without irradiation of ultrasound. The characterization of the nanocomposite was performed using XRD, TEM, rheometry, and universal testing machine. XRD and TEM results revealed that the produced EVA31/organoclay nanocomposite with ultrasonic irradiation possessed intercalated structure. Rheometry result indicated that EVA31/organoclay nanocomposite processed with ultrasound had a highly disordered or delaminated structure. A considerable increase in stiffness and Young's modulus for the sonicated nanocomposite compared to those for unsonicated one was obtained. This study demonstrated the possibility of producing EVA-organoclay nanocomposites with enhanced dispersion of nanoclays using ultrasound assisted processing.

Key words: EVA, Ultrasound, Melt Intercalation, Nanocomposite, Dispersion

INTRODUCTION

Polymer-clay nanocomposites have attracted extensive interest due to their superior chemical, physical and mechanical properties [1-3]. The structure of the polymer-clay nanocomposite can be classified to intercalated, exfoliated, or mixed intercalated/exfoliated structures. In intercalated structure, the polymeric molecules reside in the galleries between the silicate layers of the clay and the ordering of the clay layer still exists. In the exfoliated structure, the regularity of the silicate layer ordering is destroyed and the individual clay layers are finely dispersed in the polymeric matrix [4]. In the mixed structure the two structures exist within the nanocomposite system. The structure of the polymer-clay nanocomposite depends on the thermodynamic interactions between polymer and layered silicates. The main production methods are in-situ polymerization and melt blending. Melt blending is the preferred method because of simplicity, low environmental impact and compatibility with conventional polymer processing machines.

The most critical technology in the shaping of polymer-clay nanocomposite is how to disperse clay layers in polymeric matrix. Among various processing methods to improve the dispersion, ultrasonic irradiation has attracted much interest. Especially, the applications of powerful ultrasound in the polymer processing field have been an attractive field of study. When ultrasound is applied, chain scission occurs, generating reactive macro-radicals. Also, there is a direct mutual coupling between different macromolecules. It was demonstrated that successful compatibilization of immiscible polymer blends based on various polymers was achieved [5,6]. Isayev et al. studied the effect of ultrasound on extrusion. The ultrasound was imposed on the die boundary during the flow of polymeric materials. A permanent decrease of molecular weight and viscosity was observed due to the imposition of ultrasound. However, there was no deterioration of the mechanical properties [7]. Isayev and Mandelbaum investigated the effect of ultrasound on foam extrusion [8]. The density of the foam was found to increase with an increase of the amplitude and a decrease of the flow rate. Ultrasound also influenced cell sizes and their distribution in extruded samples. These effects were caused by break up of large cells or by disruption of coalescence of small cells. The mechanical properties were found to increase with ultrasound.

Ethylene vinyl acetate copolymer (EVA) is a polyolefin bearing polar vinyl acetate (VA) that can be synthesized with various VA contents. EVA has applications in footwear, hot melt adhesives and flexible packaging due to the properties such as heat-seal strength, flexibility, low strength and high permeability.

In this study, EVA/organoclay nanocomposites were prepared by melt intercalation using an intensive mixer with ultrasound irradiation. For the effective mixing, a special extruder equipped with power ultrasound generator was employed. It is expected that ultrasound-assisted melt processing would enable effective dispersion of clay platelets in EVA matrix.

EXPERIMENTAL

1. Materials

To investigate the effect of VA content, three EVA resins containing 15, 31, 60 wt% VA content were used. Their characteristics are summarized in Table 1. The organo-modified montmorillonite (Cloisite

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Table 1. EVA resins used in this study

Property	VA content (%)	Density (g/cc)	Melt index (g/10 min)	Product name	Manufacturer
EVA15	15	0.938	1.8	EVA1318	Hanwah Chemical
EVA31	31	0.95	24	UE638-35	USI Chemical
EVA60	60	1.02	0.15	EY SP004	Millennuim Petrochem

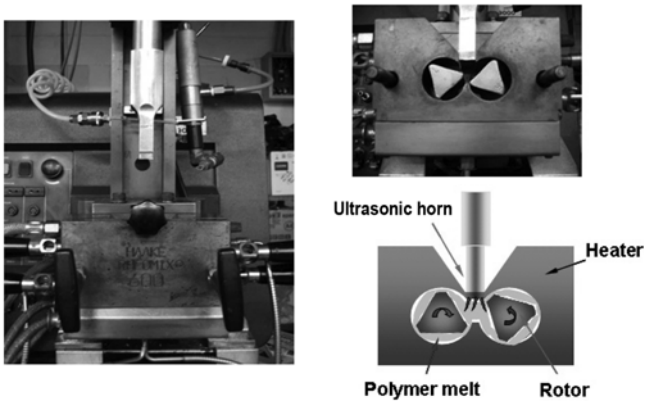

Fig. 1. Sonicated intensive mixer.

15A) was obtained from Southern Clay Products. The Cloisite 15A is the montmorillonite ion-exchanged with dimethyl dehydrogenated tallow ammonium ions, where tallow is composed predominantly of octadecyl chains with smaller amount of lower homologues. The approximate composition is C18 (65%), C16 (30%) and C14 (5%).

2. Melt Mixing with Ultrasonic Irradiation

For the irradiation of ultrasound during batch mixing, a specially designed ultrasonic horn was affixed Haake Rheomix 600 (Fig. 1). For a prolonged ultrasonic sonic operation, the horn was air cooled. The horn vibrated longitudinally at a frequency of 20 kHz with an amplitude of 15 μm. A 1.5 kW power supply with a piezoelectric converter was used. Each sample was loaded into the mixer on a fixed volume basis of 100% of the mixer volume. This full loading was necessary to have large enough torque values when the EVA resins were irradiated in the mixer. The mixer was operated at a constant rotor speed of 60 rpm and at 100 °C, and total mixing time including sonication was 15 min. The on/off ratio of ultrasound irradiation was fixed continually. The content of the clay was kept at 5 wt%. After the melt mixing, specimens required for subsequent characterization were prepared by compression molding in Carver press.

3. Structural Characterization

Structural characterization (degree of delamination and dispersion) was performed by X-ray diffraction (XRD). The X-ray diffraction experiments were performed with a Rigaku D/Max-A diffractometer (Cu Kα radiation with λ=1.5406 Å) at room temperature. The 2θ angles were varied between 1.5 and 10° at a scanning rate of 1°/min in order to measure the d_{001}-spacing between silicate layers. The generator was operated at 40 kV and 40 mA.

Transmission electron microscope (TEM), Carl Zeiss LEO 912AB, was used to observe the dispersion of silicate in nanocomposites at an acceleration voltage of 160 kV. Nanometer sections were prepared from the pellets via melt compounded on the twin-screw extruder. Ultrathin sections of 100 nm in thickness, mounted on a 200 mesh copper grid, were cut using a microtome (Leica EM FCS) procedure with a diamond knife where the sample was held at room temperature to produce the uniform thin sections required to obtain clear reproducible images.

4. Rheological Properties

Rheometrics ARES plate-plate rheometer was used to measure the dynamic viscosity, the storage modulus and stress relaxation of the pure resins and the nanocomposites. The specimens were prepared by compression molding machine (CARVER laboratory press) under 20,000 lb_f for 2 minutes. The dimension of specimen was 2 mm thickness and 20 mm diameter. The frequency range was 0.1-400 rad/sec and the temperature was 120 °C. Measurements of dynamic frequency sweep mode were operated with a parallel plate type fixture (D=25 mm), gap distance of 1.5 mm and strain rate was kept 10% to ensure linear viscoelasticity.

5. Mechanical Characterization

Tensile test of nanocomposites was carried out according to ASTM D638 (sample type V) in a universal testing machine (UTM, LR-5K from Lloyd Co.). 500 Kg_f load cell was used and the crosshead speed was 50 mm/min.

RESULTS AND DISCUSSION

1. Effect of Ultrasound on EVA Polymer Melt in Internal Mixer

A procedure to find the in-situ effect of ultrasonic irradiation on the rheological behavior of virgin EVA melt is described below. To estimate the effect of the sonication on neat EVA melt, the intensive mixer equipped with the sonification unit was employed. After solid EVA pellets were introduced into the mixing head running at 60 rpm and 100 °C, the torque change was monitored. When the torque value was stabilized, the sonification was applied for a given time. Fig. 2 shows the patterns of torque evolutions for neat EVA melts with and without the sonification. For a comparison purpose, the torque behaviors of the neat EVA resins were included. It was observed that upon imposing the ultrasound the torque value of the melt was decreased and upon cessation of the ultrasound the torque value was gradually restored toward that of the unsonicated melt. It seems that EVA molecular chains are mainly broken into small chains containing free radicals upon irradiation of ultrasound, and the small chains recombine upon cessation of the irradiation. This torque behavior demonstrates an ultrasonic effect on polymer melt qualitatively. Further, this phenomenon strongly supports the possibility of the "in-situ" controlled degradation and restoration of the polymeric melt's rheology during the melt processing via ultrasound irradiation. The degradation level of EVA31 is the largest, and it seems that the ultrasonic effect is most significant for EVA31 among the EVA resins examined.

2. Effect of Ultrasound on Melt Intercalation of EVA/Organoclay Nanocomposite

The XRD patterns of EVA nanocomposites are shown in Fig. 3.

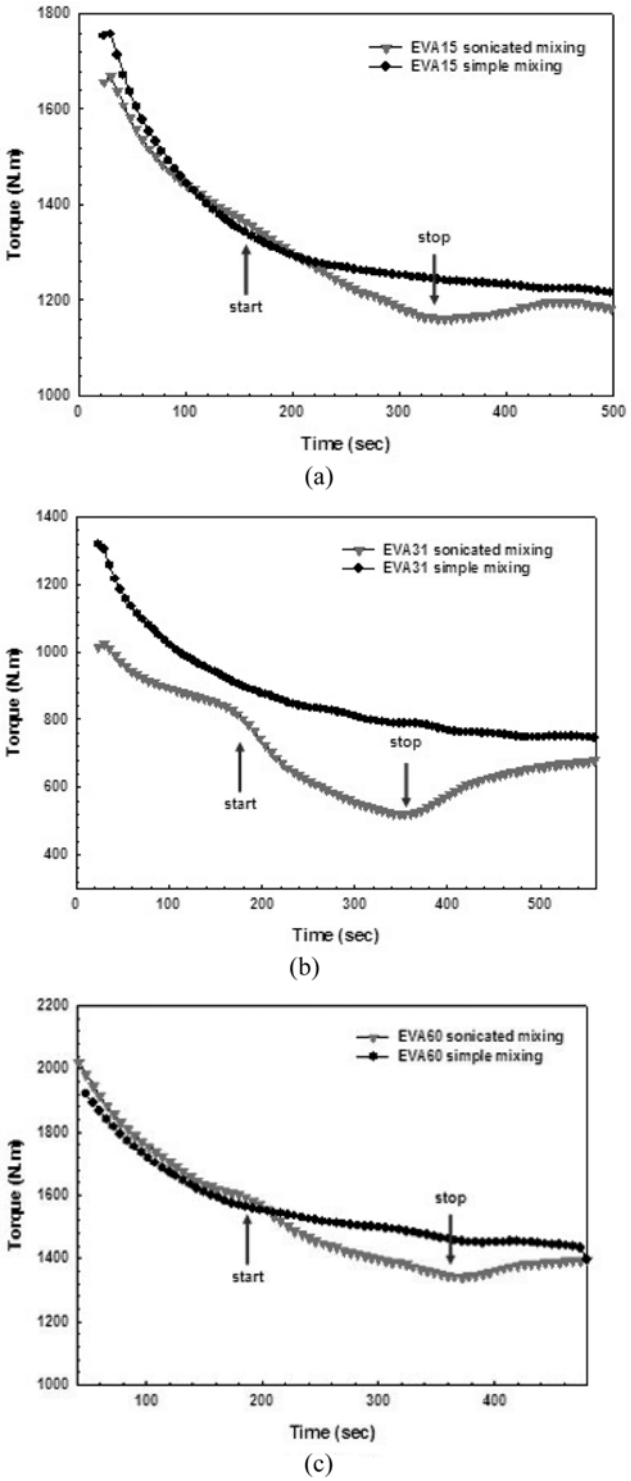

Fig. 2. Torque changes of EVA polymer melts in the intensive mixer with and without sonication (a) EVA15, (b) EVA31, (c) EVA60.

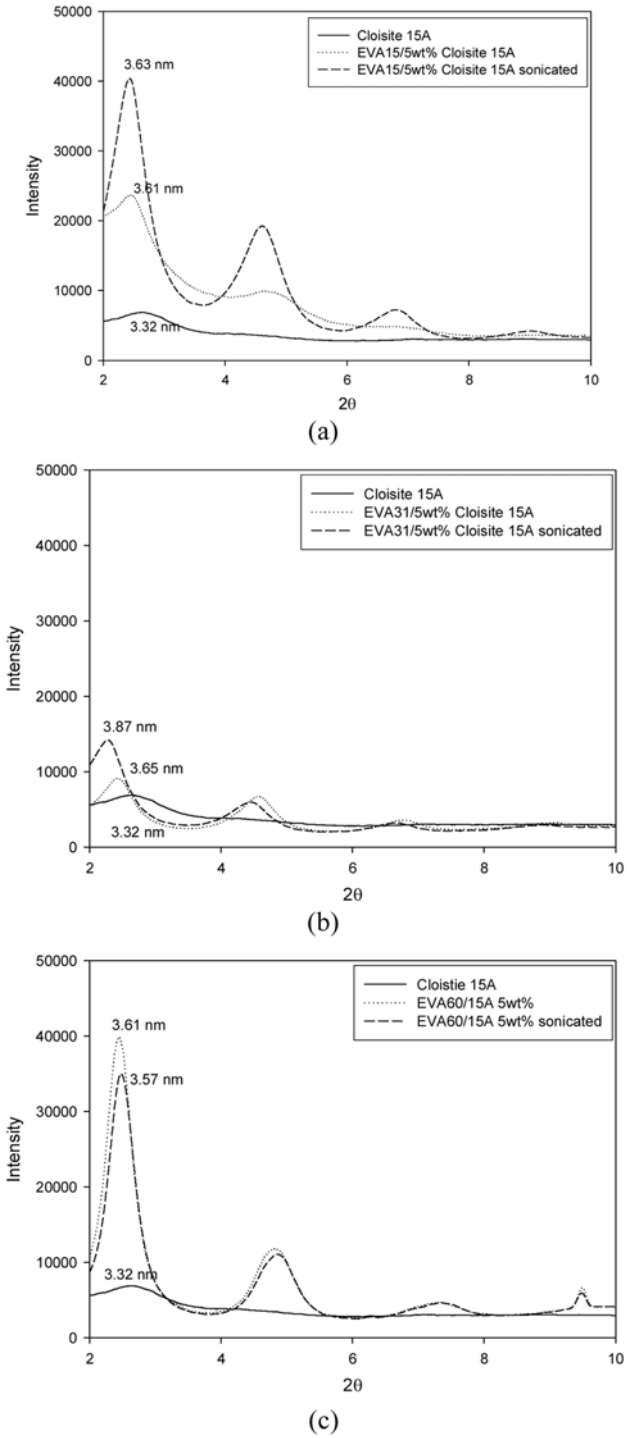

Fig. 3. XRD patterns of EVA/Cloisite 15A nanocomposites with and without ultrasound irradiation. (a) EVA15/Cloisite 15A, (b) EVA31/Cloisite 15A, (c) EVA60/Cloisite 15A.

It is seen that the EVA nanocomposites have intercalated structures. While EVA15/Cloisite 15A and EVA60/Cloisite 15A nanocomposites show almost no changes in interlayer spacing, EVA31/Cloisite 15A shows subtle increase in the interlayer spacing. The small increase of the interlayer spacing of EVA31/Cloisite 15A may be related to the effective sonic degradation of EVA31 observed in the previous section. From the result of the mixer experiment, it was surmised that EVA molecular chains are broken into small chains containing free radicals upon irradiation of ultrasound, and the small chains recombine upon cessation of the irradiation. The small chains can easily diffuse into the gallery spacings of the organoclay layers during the melt processing of EVA/organoclay composites. From the torque data for the internal mixer it was estimated that the level

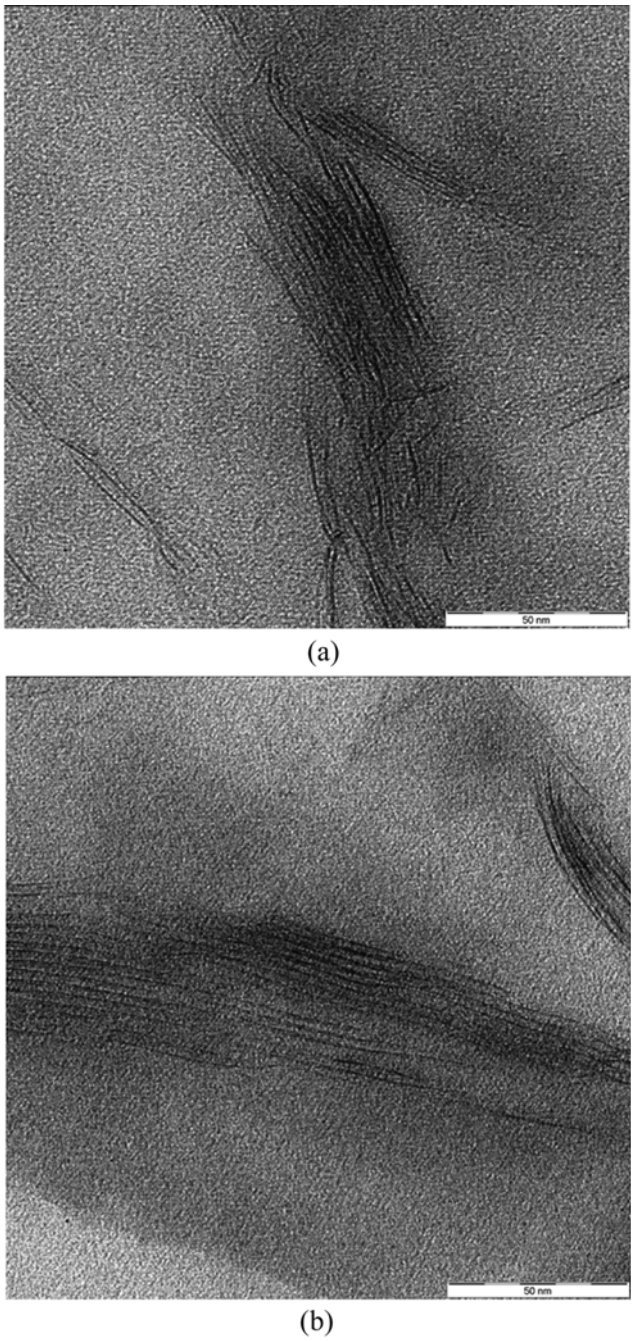

Fig. 4. TEM micrographs of EVA31/5 wt% Cloisite 15A nanocomposites (a) unsonicated (b) sonicated.

of chain scission was highest for EVA31, which explains the more intercalated structure of EVA31/Cloisite 15A nanocomposite compared with other EVA/Closite 15A nanocomposites. TEM images of EVA31/5 wt% Cloisite 15A nanocomposites with and without sonification are shown in Fig. 4. These images again confirm the intercalated structures of the nanocomposites. It seems that the silicate layer spacing for the sonicated nanocomposite is slightly increased compared with that for unsonicated nanocomposite.

3. Effect of Ultrasound on Rheology EVA/Organoclay Nanocomposite

Since the viscoelastic properties of particulate suspensions are

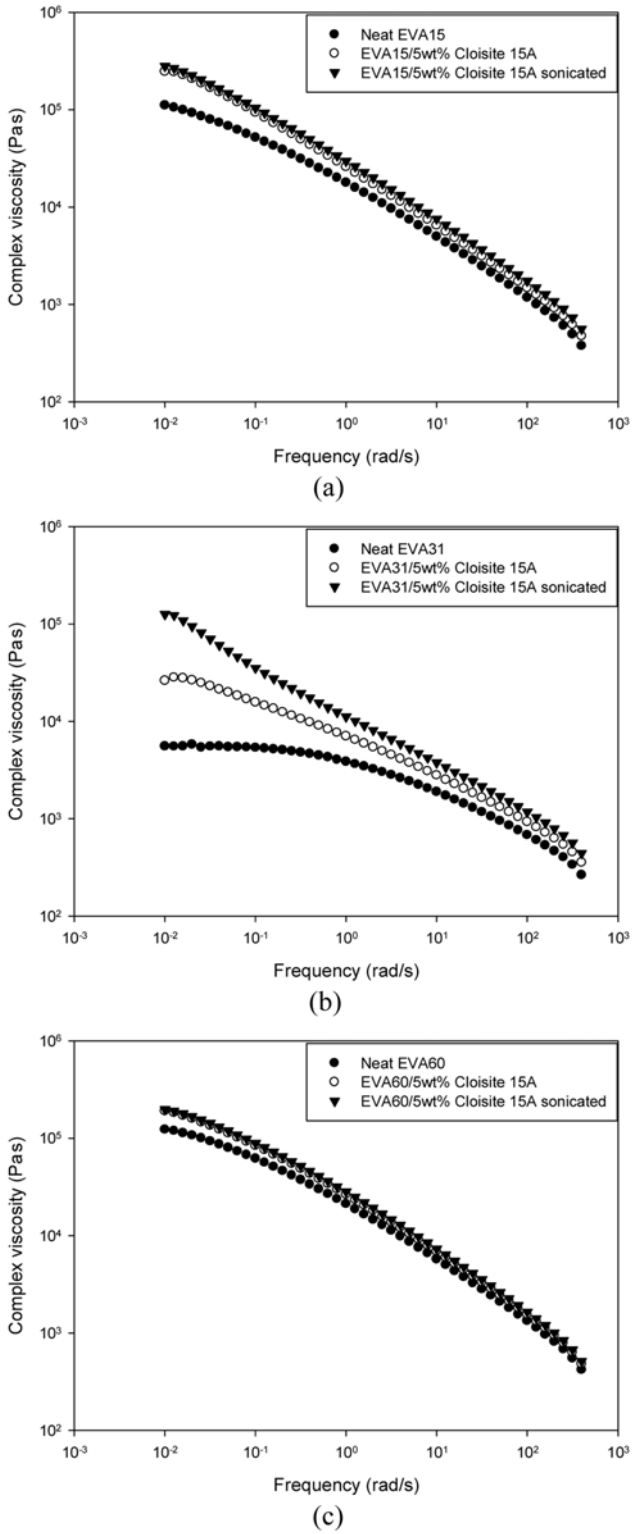

Fig. 5. Complex viscosities of various EVA nanocomposites. (a) EVA15 nanocomposites, (b) EVA31 nanocomposites, (c) EVA60 nanocomposites.

sensitive to the structure and dispersion state in melt state, rheological measurement has been used as an effective tool to indirectly but globally probe the structure of EVA-clay nanocomposites along with other spectroscopic methods. To demonstrate the effect of sonica-

tion on the melt rheology of the composites, viscosity measurements were performed in rotational rheometer with a plate-plate geometry. Fig. 5 shows the effect of ultrasound on complex shear viscosities of various EVA nanocomposites. The complex viscosities of sonicated EVA15/Cloisite 15A, EVA60/Cloisite 15A nanocomposites are almost the same as those of the unsonicated corresponding nanocomposites; the viscosity of sonicated EVA31/Cloisite 15A nanocomposite is substantially increased in low shear rate range compared with that of the unsonicated EVA31 nanocomposite. It is seen that while the effect of sonification is minimal for the EVA15/Cloisite 15A and EVA60/Cloisite 15A composites, the effect is significant for EVA31/Cloisite 15A composite.

A steep increase of viscosity in low shear rate region is commonly attributed to an indication of yielding phenomena resulting from network structure of highly delaminated or disordered nanocomposites. Wagener et al. [9] proposed the value of shear thinning exponent at low shear rate range as a semi-qualitative measure of nanodispersion of the nanocomposites. Clearly, the shear thinning exponent of the sonicated EVA31/Cloisite 15A composite is higher than those for unsonicated ones. This result demonstrates the effectiveness of the ultrasound on the enhancement of dispersion of clay layers in polymeric nanocomposite, especially in the EVA31/Cloisite 15A system. From the result of the mixer experiment for neat EVA resins, it was surmised that EVA molecular chains are broken into small chains containing free radicals upon irradiation of ultrasound and the small chains recombine upon cessation of the irradiation. The small chains can easily diffuse into the gallery spacings of the organoclay layers during the melt processing of EVA/organoclay composites. In addition, the reactive macroradicals formed by the chain scission may promote the adhesion with silicate surfaces. From the torque data for the internal mixer it was estimated that the level of chain scission was highest for EVA31, which means that more reactive macroradicals were formed for the EVA31 melt compared to other EVA resins. The reactive macroradicals may adhere to the surface of the organoclay, resulting in the enhanced load transfer from melt to clay layers during the mixing process. The more enhanced load transfer capability improved the dispersion of clay particles in the EVA31/Cloisite 15A nanocomposite.

Lertwimolnun et al. [10] studied the effect of processing conditions on the dispersion state in the polypropylene/organoclay nanocomposite and found that the intercalated structure obtained by X-ray diffraction was globally unaffected by processing parameters, but the exfoliation portion estimated by rheological measurements did depend on the operating conditions. In our case the intercalated structure was not affected but dispersion structure was affected by the irradiation ultrasound. It seems that upon sonication clay agglomerate composed of numerous stacks of silicate layers is transformed to individual stacks and this is reflected in the rheological properties of EVA31/Cloisite 15A nanocomposites.

Fig. 6 shows stress relaxation behaviors of EVA31 and EVA31/clay nanocomposites. It is observed that in short time scales, where $t<10^{-1}$ s, the relaxation behavior is qualitatively similar for neat EVA31 and EVA31/clay nanocomposites. In long time scales, where $t>10^{0}$ s, neat EVA31 relaxes like a liquid, but the nanocomposites relax much like solid materials. This solid-like behavior of the nanocomposites at long time scales corresponds to the solid-like behavior at low frequency range in small amplitude oscillatory shear result (data not shown). The sonificated EVA31/clay nanocomposites show higher relaxation modulus G(t) than the sonicated one, which may be attributed to the enhanced elasticity caused by strong interactions between clay platelets and between polymer and silicate layers.

Young's modulus and stiffness for neat EVA and EVA/clay nanocomposites are compared in Fig. 7. The storage modulus and stiff-

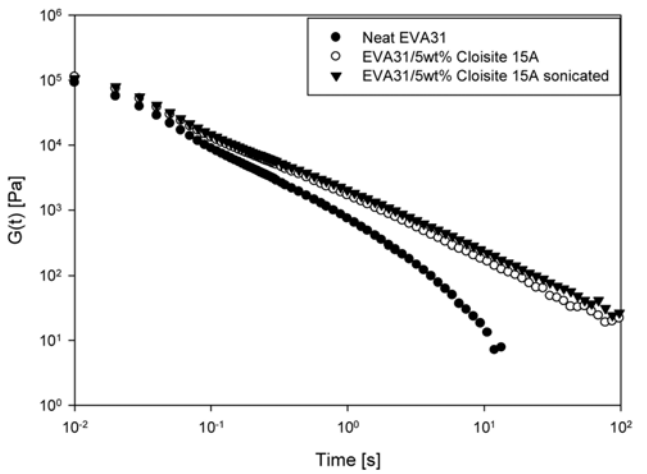

Fig. 6. Stress relaxation of EVA31 and its nanocomposites.

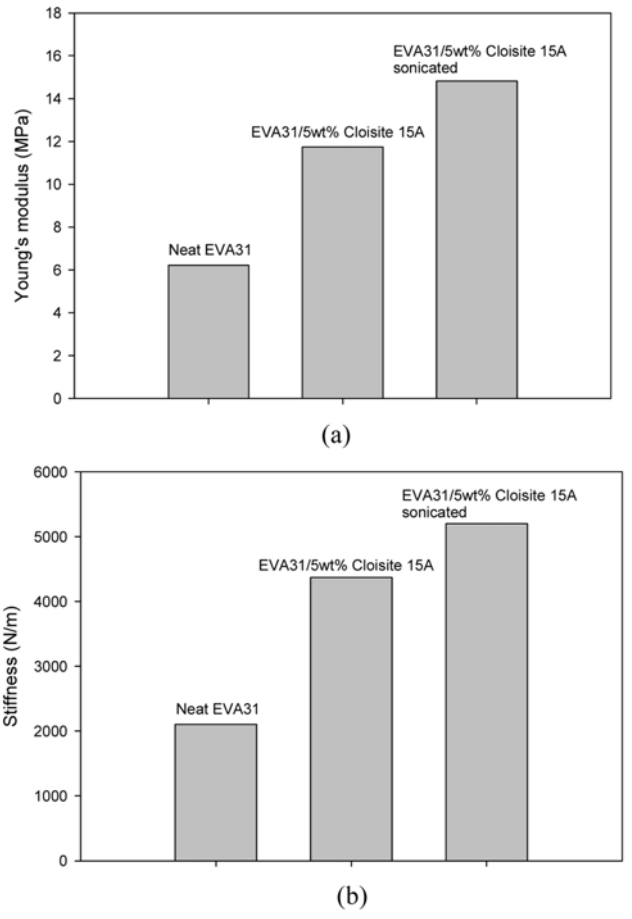

Fig. 7. Tensile properties of EVA31 and its nanocomposites. (a) Young's modulus (b) stiffness.

ness of EVA31/15A nanocomposites are substantially increased, indicating the possibilities of highly disordered structure due to the high aspect ratio of finely divided silicate layers and enhanced interaction between polymer and clay layers. Since the exfoliation morphology is the most influential for the increased elastic modulus, these results indicate the presence of a larger portion of exfoliation in sonicated nanocomposite compared to the unsonicated one.

CONCLUSIONS

By using a torque rheometer, in-situ rheological behaviors of various EVA resins with varying VA content were examined. It was found that the effect of ultrasound was most significant for EVA31. XRD and TEM results revealed that the produced EVA31/organoclay nanocomposite with ultrasonic irradiation possessed intercalated structure. Rheometry result indicated that EVA31/organoclay nanocomposite processed with ultrasound had a highly disordered or delaminated structure. It seems that upon the ultrasound irradiation, the enhancement in the intercalated structure of EVA nanocomposite is not much pronounced, but the enhancement in the exfoliated structure of the composite is significant. A considerable increase in stiffness and Young's modulus for the sonicated nanocomposite compared to those for unsonicated one was attained. This study demonstrated the possibility of producing EVA-organoclay nanocomposites with enhanced dispersion of the organoclays using ultrasound assisted processing.

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