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Biodegradable aliphatic polyester-poly (epichlorohydrin) blend/organoclay nanocomposites; synthesis and rheological characterization

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Polymer/organoclay nanocomposite systems were prepared from biodegradable aliphatic polyester (BAP)-poly(epichlorohydrin) (PECH) blends via the solvent casting method. From X-ray diffraction analysis, it was confirmed that the increased interlayer distance of the clay was solely affected by the BAP, implying that the BAP has better affinity to clay than PECH in a competitive intercalation mechanism. To clarify the sole effect of clay on polymer blend nanocomposite systems, we fixed the clay content at 3 wt%. The mechanical properties and rheological characteristics in steady and oscillatory shear modes of BAP-PECH/clay nanocomposites were investigated and compared with those of BAP-PECH blends without clay.

1. Introduction

As one way to improve properties of polymeric materials, polymer blending has been investigated extensively since this allows a beneficial balance of properties by combining the best characteristics of the constituents with relative ease. Specifically, the mixing among miscible polymers, which forms a homogenous mixing state and shows better properties, has become more popular than that of immiscible polymers in the polymer industries. Concurrently, as a new method to enhance physical properties of the polymers, polymer/clay nanocomposite systems are being adopted in various fields of the usages of polymer, since they exhibit excellent hybrid characteristics in physical and mechanical properties over a simple mixing method of the two components. A nanoscale dispersion of clay platelets in the polymer matrix caused by the strong interaction between polymer and clay is known to be responsible for the enhancement, such as solvent resistance, ionic conductivity, optical properties, heat resistance, decreased gas permeability and flammability, when compared with pristine commercial polymers or conventional polymer composites [1–8]. Based on these features, we combined the manufacturing methods of polymer blends and polymer/clay nanocomposites to create and investigate new candidates as alternative composite materials [9], especially for biodegradable polymers. Additionally, we chose the solvent casting method to utilize the simplicity in manufacturing the polymer blends/clay nanocomposites without introducing additional equipment.

Layered silicates, mainly consisting of silicon, oxygen, and small amounts of aluminum, magnesium, and other metal ions, can be regarded as rigid inorganic materials, and they can swell in polar solvents, such as water due to alkali metals between the silicate sheets. Especially, mica-type silicates with 2:1 structure of tetrahedral sheet and octahedral sheet including montmorillonite (MMT) and hectorite, have received much attention recently as reinforcing additives for polymers owing to their large aspect ratio and unique intercalation/exfoliation characteristics. To improve the affinity between MMT with hydrophilic surface and polymers with hydrophobicity, it is necessary to modify the surface of MMT into organophilicity (organophilically modified montmorillonite, OMMT) by replacing the metal cations within interlayer galleries of silicates with various cationic organic surfactants.

Biodegradable aliphatic polyester (BAP), as used in this study, is a thermoplastic polyester with only ester bonds and no aromatic component, which decelerates the rate of biodegradation. BAP also has similar physical properties to polyethylene or polypropylene with excellent processability and no odor in either

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the molten state or the solid state, and shows less heat of combustion than that of polyethylene on incineration. However, some difficulties for applications exist due to its low melting temperature, low thermal stability, and low molecular weight. Therefore, by blending this biodegradable material with conventional thermoplastics such as linear low-density polyethylene (LLDPE) [10], poly(vinyl acetate) (PVAc) [11], and poly (epichlorohydrin) (PECH) [12], low-cost materials with enhanced physical properties can be obtainable. Kim *et al.* [12] reported the miscibility of the BAP-PECH blend system via differential scanning calorimetry and dynamic mechanical thermal analysis. Furthermore, various biodegradable polymers/clay nanocomposites [13–17] were recently investigated.

In this paper, we prepared polymer blends (BAP-PECH) based clay reinforced nanocomposites via a solvent casting method and investigated their characteristics on the basis of rheology together with other characterizations, such as X-ray diffraction and mechanical tests. The internal structure of the nanocomposites was elucidated by X-ray diffraction (XRD) and the mechanical properties of these polymer blend/clay nanocomposites were characterized by elongation at break and other tensile test measurements. Moreover, we examined viscoelastic properties of the polymer blend/clay nanocomposites from both rotational and oscillatory modes to systematically study and compare the rheological characteristics of BAP-PECH blends and their nanocomposites.

2. Experimental

2.1. Materials

The BAP ($M_w = 60{,}000$ g/mol, SK Chemical, Korea) used in this study is a copolymer, synthesized through polycondensation reaction of aliphatic glycols (ethylene glycol and 1,4-butanediol) and dicarboxylic acids (succinic acid and adipic acid). The PECH ($M_w = 700{,}000$ g/mol) was purchased from Scientific Polymer Products, Inc. (Ontario, NY, USA). The organoclay (Cloisite 25A) was obtained from Southern Clay Products (Gonzales, TX, USA), in which the pristine Na^+ MMT was treated by the manufacturer by a cation exchange reaction with a dimethyl, hydrogenated tallow (~65 wt% C18; ~30 wt% C16; ~5 wt% C14), 2-ethyhexyl, quaternary ammonium [18]. The cationic exchange capacity of the clay was 0.95 meq/g.

2.2. Preparation of BAP-PECH blends and polymer blend/clay nanocomposites

Two series of BAP-PECH systems were constructed: one, a simple polymer blend system; the other, a polymer blend/clay nanocomposite system. In the simple blend system case, we varied the PECH content up to 20 wt% (BP05, BP10, BP15, and BP20). The last two digits of the sample code represent the PECH content in wt%. To prepare the blend systems, both BAP and PECH were dissolved using methylene chloride as a cosolvent. The solvent was then evaporated, and the prepared blend samples in a film form, were stored for two days in a vacuum oven to complete the removal of residual traces of solvent prior to testing. Finally, the films were cut into small pieces, and compression moulded in a hot press at 140°C for 2 min under the pressure of 9.8 kN/m^2.

TABLE I The BAP-PECH/OMMT nanocomposite systems

System	Sample code	BAP content (wt%)	PECH content (wt%)	OMMT content (wt%)
BAP Homopolymer	BAP	100	0	0
BAP-PECH blend system	BP05	95	5	0
	BP10	90	10	
	BP20	80	20	
BAP-PECH/Clay nanocomposite	NBP05	92.15	4.85	3
	NBP10	87.30	9.7	
	NBP20	77.60	19.4	

To investigate the effect of PECH on the BAP-PECH/OMMT nanocomposites, we varied the PECH content (sample codes; NBP05, NBP10, NBP15, and NBP20) at a fixed clay content (3 wt%). Each BAP-PECH blend having a different composition was initially dissolved in methylene chloride. These solutions were mixed with clay in methylene chloride using a magnetic stirring bar. Following the same procedure for a simple blend system, the compression molded samples were prepared for characterization. The composition and sample code prepared in this study are summarized in Table I.

2.3. Characterization

The change of OMMT interlayer distance was confirmed by the wide-angle X-ray diffraction (WAXD) method. The WAXD was conducted at ambient temperature on a Philips PW-1874 X-ray crystallographic unit with CuKα radiation generated at 40 mA and 50 kV. Diffraction spectra were collected for a 2 θ range of 1.5–10° at a scan rate of 3°/min.

2.4. Measurements

The mechanical properties of elongation at break and tensile strength were analyzed with a Universal Test Machine (UTM, Hounsfield, H25K-S Chamber system, England) at a speed of 30 mm/min at room temperature.

The viscoelastic properties of BAP-PECH/OMMT nanocomposites were determined with a rotational rheometer (Physica MCR300, Stuttgart, Germany), using a 25 mm diameter parallel plate geometry (PP-25) with 1 mm gap between two plates. The measuring temperature was held constant at 160°C. Two types of test modes of steady shear and oscillatory shear measurements were employed. In the steady shear mode, we examined the relation of shear rate vs. shear stress. From these flow curves, we obtained the steady shear viscosity and other characteristic parameters for BAP-PECH/OMMT nanocomposites. Dynamic mechanical properties of the systems were collected from a frequency sweep mode. The oscillatory test was performed at the fixed 3% strain, which was determined by the amplitude sweep test to ensure the validity of the viscoelastic properties.

3. Results and discussion

3.1. Characterization of nanocomposites

The XRD spectra of OMMT and BAP-PECH/OMMT nanocomposites having different composition ratios are shown in Fig. 1. The interlayer spacing was calculated using Bragg's equation ($n\lambda = 2d\sin\theta$, Cu-K$_\alpha$ ($\lambda = 0.154$ nm)). The characteristic peak of pristine OMMT occurred at 4.68° (2θ) which corresponds to the basal spacing of 1.88 nm for pristine OMMT. The shifted peak values to lower angle of 2.84 and 1.50° indicated the polymers intercalated into the OMMT layers for NBP series and PECH, respectively. These peak positions corresponded to the interlayer spacing of 3.11 nm (for NBP series) and 5.89 nm (for PECH and clay). In other words, polymer intercalation into OMMT layers gave rise to the increase of interlayer gallery spacing of about 1.23 nm (NBP series) and 4.01 nm (PECH), when compared to OMMT itself. Moreover, Fig. 1 also shows that interlayer gallery distance for NBP nanocomposites series is independent of the PECH loading. Based on the homopolymers/clay nanocomposites of BAP and PECH, respectively, we deduce that the insertion of polymer chains in the BAP-PECH blend system has a selective nature between the two competitive components. In other words, the overall chain insertion into the layer structure is dominantly achieved by the BAP chains in the BAP-PECH/OMMT system. As shown in Fig. 1, the characteristic peak positions of NBP series are identical to those of BAP/OMMT nanocomposites. This selective nature can be explained by the better affinity of BAP chains to OMMT interlayer characteristics [9].

From these results, we can derive an interesting intercalation process in the polymer blend/clay nanocomposites system. To begin with, we first examined the morphological or internal structural changes of the polymer blend based nanocomposite system. Conjecturing the distinct differences of an intercalation process from other simple polymer/clay nanocomposites is not difficult due to the factors affecting the affinity between polymer and clay. Although BAP and PECH are thermodynamically miscible, the intercalating process accompanying structural changes for them is different. As shown in Fig. 1, each polymer can intercalate into the interlayer spacings. However, the increase of the interlayer spacing is significantly different (3.11 and 5.89 nm). In the blend, these differences created the selective intercalation. From our result, the structural difference, degree of affinity on the clay surface, and kinematic differences in the intercalation process enabled the BAP/clay to have better affinity with the organophilic surfaces of OMMT, as opposed to PECH.

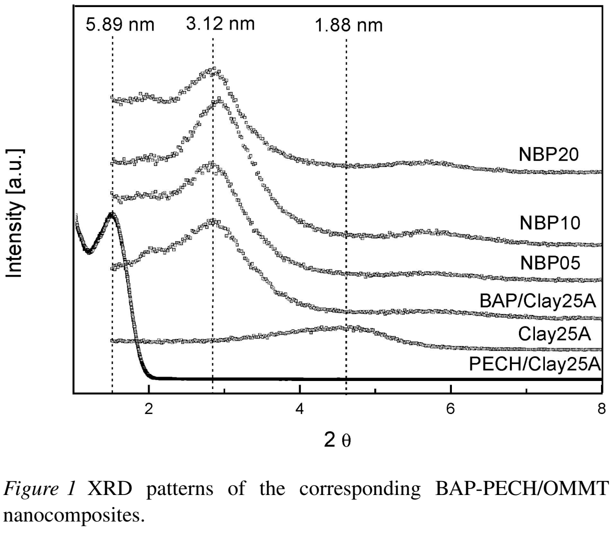
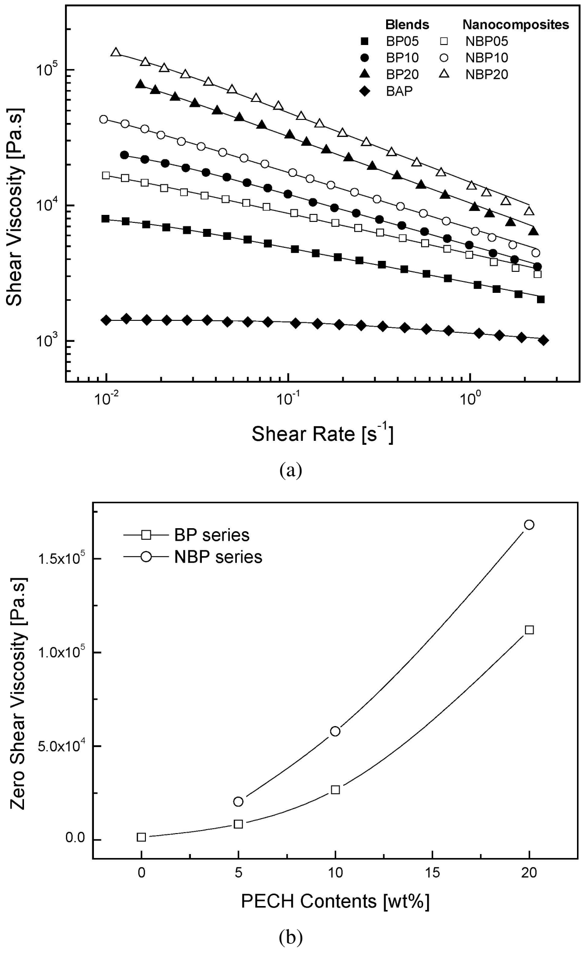


Figure 1 XRD patterns of the corresponding BAP-PECH/OMMT nanocomposites.

3.2. Rheological characterization

The rheological properties of polymer/OMMT nanocomposite provide useful information in material processing [19–22], including structural analysis and theoretical prediction of polymer dynamics [23, 24]. Thereby, the viscoelastic properties of polymer/clay nanocomposites have been widely investigated [19, 20, 25, 26]. It has been reported that in exfoliated nanocomposites developed via tethering the chains to the layered-silicate based on nylon-6 and poly (ε-caprolactone), the low-frequency storage and loss modulus gradually changed from liquid-like to pseudo-solid-like behavior for nanocomposites with as little as 3 wt% layered-silicates [19]. Fig. 2a shows steady shear response and curve fits obtained from the Carreau model for BAP-PECH/OMMT nanocomposite. To examine the relationship between shear viscosity (η) and shear rate ($\dot{\gamma}$), we fitted the



(a)

(b)

Figure 2 (a) Shear viscosity vs. shear rate with various PECH contents. (b) Zero shear viscosity obtained from Carreau model.

TABLE II Parameters in Carreau model (Equation 1) for BAP-PECH/OMMT nanocomposite

Sample	η_0[Pa·s]	$t_1[S]$	n
BAP	1.42×10^3	8.84×10^0	0.90
BAP05	8.41×10^3	8.38×10^1	0.74
BP10	2.67×10^4	8.17×10^1	0.62
BP20	1.12×10^5	1.26×10^2	0.51
NBP05	2.04×10^3	1.72×10^2	0.70
NBP10	5.79×10^4	1.82×10^2	0.59
NBP20	1.68×10^5	1.12×10^2	0.49

data using the Carreau model [27, 28] given by:

$$\eta = \frac{\eta_0}{[1 + (t_1\dot{\gamma})^2]^{\frac{(1-n)}{2}}}. \qquad (1)$$

Here, η_0 is the zero shear rate viscosity which can be obtained directly from the plateau at extremely low shear rates, as shown in Fig. 2a. The t_1 is a characteristic time, and "n" is a dimensionless parameter, and the slope in the power-law region is given by $(n - 1)$. Equation 1 reduces to the Newtonian fluid for $n = 1$, and describes shear-thinning or pseudoplastic materials for $n < 1$.

The model parameters obtained from a nonlinear regression are summarized in Table II. At a low shear rate, the shear viscosity increases monotonically with PECH loading. In Fig. 2b, we re-plot the obtained zero shear viscosities using the Carreau model as a function of PECH content. The zero shear viscosities of the polymer blend and the polymer blend/OMMT nanocomposites dramatically increase with the PECH contents. Moreover, the zero shear viscosities of a clay loaded system (NBP series) are higher than those of a simple blend system (BP series). On the other hand, the values of "n" decrease with PECH content in both NBP and BP series, indicating that in both BP and NBP systems the pseudoplasticity showing shear-thinning behavior increases with PECH loading. From the fact that the value of "n" in the NBP system is lower than that in the BP system at a fixed value of PECH, the OMMT is also found to affect the pseudoplastic behavior of a BAP-PECH/clay nanocomposite system.

Fig. 3 shows viscosities of BAP-PECH/OMMT nanocomposites obtained from both oscillatory shear and steady shear modes. Cox and Merz [29] reported that the complex viscosity ($\eta^* \equiv \eta' - i\eta'' = G^*/(i\omega)$) in oscillatory mode is equal to the steady shear viscosity at $\dot{\gamma} = \omega$;

$$\eta(\dot{\gamma})|_{\dot{\gamma}=\omega} = |\eta^*(\omega)| = \sqrt{\eta'^2(\omega) + \eta''^2(\omega)}. \qquad (2)$$

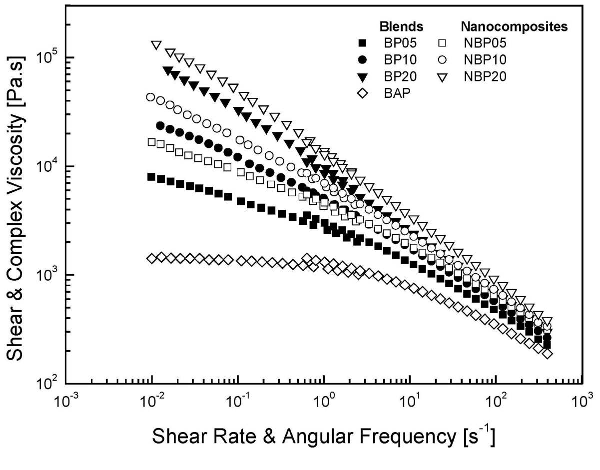
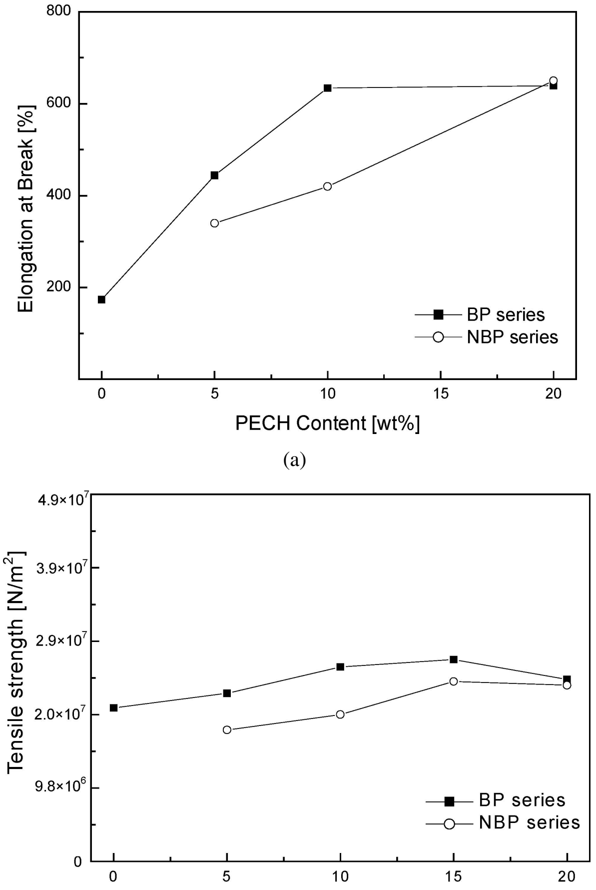


Figure 3 Cox-Merz relationship of shear and complex viscosities.

For highly elastic fluids and polymer melts, measuring the steady shear viscosity at high shear rates via a parallel plates geometry is very difficult, because the melt usually fractures, coming out of the gap during the measurement. Thereby, the shear viscosities at high shear rates can be estimated from an oscillatory test via the Cox-Merz relation (Equation 2). Generally, for the cone and plate device, the maximum shear rate applied is approximately 10 s^{-1}. Slightly higher values of shear rate are possible with the parallel plate device [30]. Therefore, we selected the shear rate range from 10^{-2} to 10 s^{-1}. Complex viscosity obtained from oscillatory measurements and shear viscosity obtained from rotation measurements agree well in BAP-PECH blends and blends/clay nanocomposites, indicating that BAP, BP series, and NBP series preserve the homogeneous internal structure in their melt state. In other words, this demonstrates that BAP and PECH are miscible and the organoclays are well dispersed in polymer blend matrix, forming a homogeneous melt structure in NBP series. Further, it is possible to obtain the viscosity in a wide range of shear rate or angular frequency (0.001–600 s^{-1}; approximately five decades). Thereby, we are able to obtain η_o and power-law shear thinning behavior in a broad range of shear rates.

3.3. Mechanical properties

We also investigated mechanical properties of elongation at break and tensile strength for both BP and NBP series. Figs 4a and b show the elongation at break and the tensile strength, respectively. For both BP and NBP systems the elongation at break and the tensile strength showed an increasing trend with PECH content (Fig. 4), which is consistent with our previous study [12]. This suggests better compatibility and adhesion of the rubber part with the matrix polymer (BAP), due to the interactions between BAP and PECH [11]. In addition, when we compared the two blend systems, with and without OMMT, the clay filled blend system showed lower values of elongation at break and tensile strength. This means that the BAP-PECH/OMMT nanocomposites may have anisotropically (or nonhomogeneously) aggregated structures of clay associated with polymers, although nanoscopic interactions exist between the polymer chains and the layered silicates [31–33]. On the other hand, the results of higher PECH content (20 wt%) are nearly the same in both BAP and NBP series. This is due to the rubber part (PECH), which affects in the elongation at break and the tensile strength, becoming more dominant in the blend matrix as the PECH content increases. As a result, the negative effect of particle aggregation on the elongation at break and the tensile strength can be screened via the contribution of PECH at approximately 20 wt%.



(a)

(b)

Figure 4 (a) Elongation at break of BP and NBP series. (b) Tensile strength of BP and NBP series.

4. Conclusions

Biodegradable aliphatic polyester (BAP)-poly(epichlorohydrin) (PECH) blend and their blend/organically modified montmorillonite (OMMT) nanocomposites were prepared via a solvent casting method, and their viscoelastic and mechanical characteristics were examined. Since BAP has higher affinity to the OMMT interlayer surface than PECH, BAP chains were intercalated dominantly into the OMMT interlayers. As for the role of clay in the blend system, we observed considerable viscosity increase even with a small clay addition (3 wt%), in all NBP series, due to a nanoscopic interaction between clay and matrix polymer. The linear viscoelastic properties obtained from a steady shear and dynamic oscillation can be closely correlated to each other through the Cox-Merz relationship, revealing the homogeneous internal structure in the BAP-PECH blend and BAP-PECH/OMMT nanocomposite systems.

Concerning mechanical properties, the clay addition in the blend system gave rise to the decrease in the elongation at break and the tensile strength, implying that insufficient nanoscopic dispersion of clay could restrict the enhancement of material properties, forming particle agglomerated structure.

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