

비상용성 고분자 블렌드(BAP-PVAc)의 모폴로지와 열적, 유변학적 특성에 대한  
유기화 접도의 영향

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**Effect of Organoclay on Morphological, Thermal and Rheological Properties of  
Immiscible Polymer Blend (BAP-PVAc)**

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**Introduction**

Neat plastics are often not rigid or strong enough to meet the requirements of some applications. The addition of a variety of reinforcing fillers is routinely used to improve these properties enough for certain plastics to be useful in these structural end uses. Thermoplastic composites with various fillers and reinforcements are well established for a variety of applications. It is, however, less well known that the matrix of a number of these composites is a polymer blend itself. We can utilize a polymer blend to improve polymeric material properties since they allow a synergistic balance of properties by combining the best properties of the constituents, with relative ease. For this reason, miscible polymer blends have become popular within the polymer industry. As a new method to control the polymer properties, polymer/clay nanocomposite systems are being adopted in various fields, since they exhibit hybrid properties of the two components, showing superior physical and mechanical properties, 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. Based on these features, we combined the manufacturing methods of polymer blends and polymer/clay nanocomposites to create and investigate new candidates to be successful composite materials. Therefore it is important to enhance the compatibility of an immiscible polymer blend system. However, the use of nano clay as a compatibilizer in incompatible polymer blend system is limited.

In this paper, we prepared blend (BAP-PVAc) and polymer/clay nanocomposites with biodegradable polymers via the solvent casting method with chloroform ( $\text{CHCl}_3$ ) as a cosolvent. We examined effects of nano clay as a compatibilizer in incompatible polymer blend (BAP-PVAc) by various characterizations. The morphology of the nanocomposites was elucidated by SEM. And thermal property of these polymer blend (BAP-PVAc)/clay nanocomposites was characterized by TGA. Moreover, we examined the viscoelastic properties of polymer blend/clay nanocomposites in various test modes, including rotational and oscillatory modes. Thus, we could systematically study and compare the rheological characteristics of BAP-PVAc blends and these nanocomposites.

**Experimental**

Synthetic BAP (Skygreen 2109, SK Chemical, Korea) was the copolymer obtained from

polycondensation of diols and dicarboxylic acids with a weight-averaged molecular weight of  $6.0 \times 10^4$  g/mole. PVAc sample was purchased from Aldrich Chemical Co. (USA) in pellet form. The weight-average molecular weight of the PVAc measured from GPC was  $1.67 \times 10^5$  g/mole. Cloisite 20A (Southern Clay Products, USA) was the organophilic clay, modified with cationic surfactant.

BAP/PVAc blend and polymer/clay nanocomposite samples were then prepared from the solvent casting method using chloroform ( $\text{CHCl}_3$ ) as a co-solvent. We designated our samples as BAP05, PVAc05, BPVAc7300 and BPVAc7305. The first two digits represented the polymer blend ratio and the last two digits represented the weight percent of organophilic clay in polymer matrix.

The BAP/PVAc solutions were mixed by stirring for about 2 days at room temperature and dried to constant weight in a vacuum oven at  $30^\circ\text{C}$ . Both film and disk types of BAP/PVAc samples were prepared using hot press at  $130^\circ\text{C}$ . We identified the intercalated layered structure by X-ray diffraction (XRD) and directly observed the internal structure by transmission electronic microscopy (TEM). In addition, the degree of dispersion and phase separation between domains were investigated using scanning electron microscopy (SEM) at various magnifications at 10kV. TGA was also used to investigate the thermal decomposition characteristics. Rheological properties of the immiscible blend were investigated using a rotational rheometer (MCR300, Physica, Stuttgart, Germany).

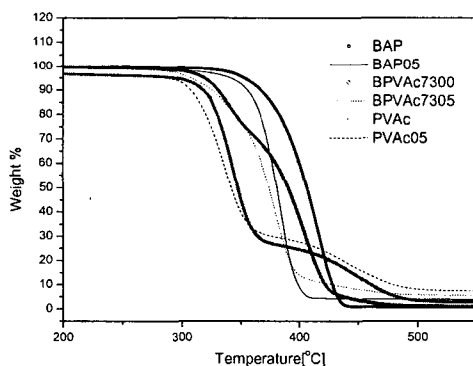


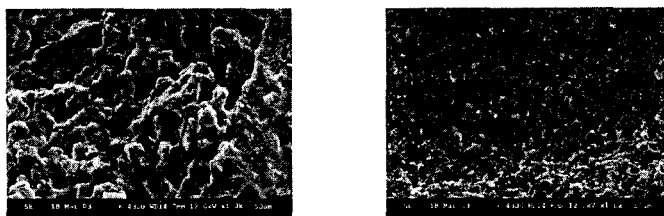
Fig. 1. TGA curves for various polymer/clay nanocomposites and simple blend system.

## Results and Discussion

Figure 1 shows the characteristic weight loss of single polymers (BAP, PVAc) and its blend accompanying the curves of their counterparts; nanocomposites. In the case of BAP, it follows the single decomposition process from about  $350^\circ\text{C}$ . On the other hand, pure PVAc shows both inferior thermal stability and two step decomposition process. The resultant characteristics of BPVAc7300 contain these two distinctly different thermal decomposition processes. As we can see in the figure, the curve positioned in-between two curves of BAP and PVAc. It means that the blend system still have each characteristics not disturbed by each other, implying the existence of immiscible and separate domains; BAP and PVAc. When these simple polymer and blend system were processed to polymer/clay nanocomposites, we can find some interesting thermal properties such as the disappearance of two step decomposition process in

BPVAc, and reduced thermal stabilities in both BAP05 and PVAc05. As far as simple polymer systems (BAP and PVAc) and their nanocomposites (BAP05 and PVAc05) concerned, it is noticeable that the thermal stability was reduced, but the characteristic decomposition was not changed in polymer clay nanocomposites. Contrary to these features, BPVAc7305 shows the change of thermal decomposition process from two-step to single step process. It means that the immiscible blend characteristics distinctively reduced, and followed the homogeneous or single polymer characters in thermal properties. As a result, we can conclude from TGA curves that the addition of organically treated clay can successfully improve the compatibility in immiscible polymer blend systems. These features will be further discussed in conjunction with other experimental result in later part of this work.

Figure 2 shows SEM micrographs of the fractured surface of the BAP/PVAc blend and its nanocomposite. The SEM studies were performed on ethanol-extracted samples to discern the macrostructure of BAP in the blend. Being a good solvent to PVAc, but a relatively poor solvent to BAP, ethanol can selectively remove PVAc component from BAP/PVAc blend. Thus, the SEM micrographs in Figure 2 may clearly represent the phase behavior of BAP/PVAc. The presence of clay affect the morphological structure of the blend. As shown in Figure 2, in the blend pellets extracted with ethanol at a constant time, the PVAc domains are uniformly distributed in the BAP phase and the distributive size of the PVAc component become smaller by clay effect. The original blend system (Fig. 2(a)) distinctively shows the immiscible character, which contains phase-separation morphology. As we anticipated, two different polymeric phases have each affinity to make nano-level incorporation with organoclay. As a result, the immiscible phase boundary can be associated with each other. These morphological observations also show the compatibility between BAP and PVAc increases.



**Fig. 2** SEM micrographs of the fracture surface of BAP/PVAc blend and its nanocomposite:  
(a) BPVAc7300 (left), (b) BPVAc7305 (right).

In Figure 3, the direct visualization of the internal structure in BPVAc7305 blend was also performed using TEM, clearly demonstrating an intercalated layer structure. And also, the image from pristine blend helps the understanding of TEM result containing dark and grey portions. In addition, we also confirm that the intercalated structure also partially includes the exfoliated structure. On the other hand, PVAc has a higher complex viscosity than BAP due to its higher molecular weight-PVAc is more viscoelastic than BAP. In general, it can be said that when the dispersed phase is less viscous than the continuous phase, the droplets may be elongated by the shear stress and form fibrils parallel to the flow direction. When the dispersed phase is more viscous, it is difficult to deform the suspended droplets except with very large stresses. Because BAP, which is less viscous than PVAc, is a rich phase, the frequency sweep

result for BAP/PVAc blend shows that loss modulus ( $G''$ ) is large than storage modulus ( $G'$ ) in total frequency. By adding organoclay as compatibilizer, Figure 2 clearly shows that PVAc domain size decreases. That is to say, as viscous PVAc phase decreases, storage modulus ( $G'$ ) increases. This may be evidence that BAP/PVAc immiscible blend become miscible by organoclay effect.

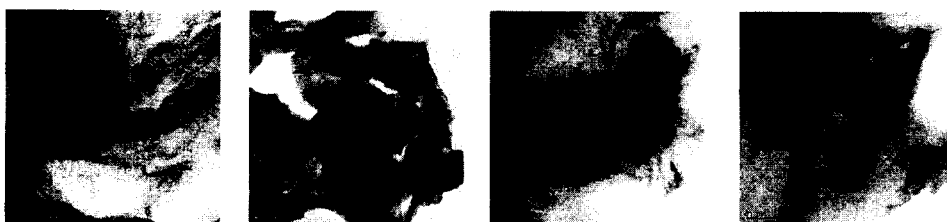


Fig. 3. TEM images of BAP/PVAc blend and various nanocomposites: (a) BPVAc7305, (b) BPVAc7300, (c) BAP05, and (d) PVAc05 (from left to right in order).

### Conclusion

We examined the compatibility, morphological and rheological properties for BAP/PVAc blend and its nanocomposite. TGA curve for BPVAc7305 showed the disappearance of two step decomposition process of immiscible blend (BPVAc7300), implying the enhancement of compatibility due to the addition of organoclay. In addition, the reduced drop size and its morphologies also support the increase of miscibility in BPVAc7305. Due to the presence of organoclay in incompatible polymer blend system, we can find various experimental evidences for reduced incompatibility. These results will be further examined by other parameters in different experiments, which are underway.

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