PA/EVOH 블렌드의 물성 및 산소 투과 특성

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Properties and Oxygen Permeability of Polyamide/Ethylene-Vinyl alcohol Copolymer Blends

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Introduction

Plastic packaging materials having excellent barrier properties with respect to gas and organic solvent possess many advantages such as light weight, flexibility, transparency, strength and ease of processing in comparison to metal or glass.[1,2]

In general, plastic films with high barrier properties have been produced with multilayered structure. In a typical three-layer film, ethylene-vinyl alcohol copolymer(EVOH) or polyamide(PA) with high barrier property is positioned as a middle layer to exclude the effect of humid in the atmosphere. However, this multiple films require high manufacturing cost and present a limitation of recyclability. Thus, polymer blending of polyolefin resin and small quantity of a barrier resin such as EVOH or PA has been attempted to produce packaging films with improved barrier property by generating laminar mophology of the dispersed phase.[3,4]

EVOH has some drawbacks of high cost, low toughness, and difficult processing, although it exhibits excellent gas barrier property and transparency. Meanwhile, PA that is inexpensive relative to EVOH exhibits high resistance to the permeation of hydrocarbons as well as good toughness. In this study, therefore, blending of PA and EVOH was attempted to produce new material systems with attractive characteristics. Ultimately, this blend system will be utilized in the future work by incorporating with polyolefin(PO) resin to produce ternary blend system of PO/(PA+EVOH) with high barrier property with respect to gas as well as organic compound. It has been well known that blends of PA and EVOH are fairly compatible and show a single homogeneous phase at appropriate concentration due to hydrogen bonding interactions between hydroxyl group of EVOH and amide group of PA.[5,6]

In this study, the relationships between composition and properties of PA/EVOH blends were analyzed using various techniques and the results were investigated in terms of level of compatibility. Rheological, morphological, thermal, and mechanical analysis and oxygen permeability measurement were carried out.

Experimental

The polymers used for the study were PA(2835TF, a copolymer of Nylon 6 and Nylon 66, T_m=191.5℃, T_c=143.9℃), which was obtained from Hyosung Co., and EVOH(ethylene-vinyl alcohol copolymer; EP-F101A, ethylene content=44mol%, M.I.=1.3g/10min, T_m=185.41℃, T_c=157.87℃) supplied from Kurray Co. was used. Thin films for infra-red analysis were prepared by casting from diluted solutions obtained by dissolving melt prepared blends in Dimethylacetate/lithium chloridel. The FT-IR spectra were obtained by Perkin-Elmer 1725 FT-IR spectrometer. Before processing, the resins were pre-dried over night at 60℃ in a vacuum oven and dry blended before extrusion. The weight ratio of PA/EVOH was 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100, respectively. PA/EVOH melt blends with various compositions were obtained using a twin screw co-rotating extruder(Brabender, L/D=20) operating at a screw speed of 60 rpm. A processing temperature profile of 190-205-220-230 ^{o}C from hopper to the head was fixed.

The compatibility of the blends were evaluated by thermal, morphological, FT-IR analysis, and measurements of tensile properties. The oxygen permeability of the samples was examined according to the method based on ASTM D3985. Tensile strength and elongation at break were measured using an Instron testing machine(Model : IX series 6.05) with a cross head speed of 200 mm/min. A minimum of five samples were tested in each case, and the standard deviation was less than 20%. The specimen dimensions were in accordance with ASTM-D638 at room temperature.

Result and Discussion

FT-IR analysis

FT-IR analysis was carried out to evaluate the miscibility and to identify the specific interactions between the components in PA/EVOH blends with varying blend composition. PA and EVOH have the functional groups drawn to each other by hydrogen bonding as seen Figure 1. FT-IR analysis on the PA/EVOH blend indicates that the peak intensity of NH bending mode(1550cm-1) and overtone peak intensity of NH bending mode(3100cm-1) noticeably decreases at the ratio of PA/EVOH (80/20 wt%) compared to that of pure PA. As the EVOH content increased, the peak intensity decreased gradually up to 60wt% of the EVOH content, and then nearly disappeared at more than 80 wt%. From this result, interactions between -NH group and -OH group were thought to be almost achieved at the ratio of PA/EVOH (20/80 wt%). According to the theory of vibrational spectroscopy,(3,4) the peak intensity can be related to molecular motion. So increase of interactions of the functional groups means the decrease of that of mobility. Therefore, we can conclude that the interactions between OH group of EVOH and NH group of PA is stronger than self associated interactions of PA and the miscibility between PA and EVOH may be strongly dependent on the strength of the attraction between the -OH group and -NH group.

Rheological property

The effect of EVOH content on the rheological properties of the PA/EVOH blends was investigated. Figure 2 shows the viscosity as a function of composition at three different shear rates. The viscosity of PA is always lower than that of EVOH on the range of shear rate from 0.1 to 100 s^{-1}. Comparing the experimental data with the values of the straight line calculated by additive rule, it was seen that at a certain blend ratio the bulk viscosity went through a maximum and showed positive deviation in complex viscosities over entire range of shear rate. When the content of EVOH is about 40 wt%, the degree of the positive deviation becomes greater as the shear rate decreases because the interfacial hydrogen bonding interactions may dominate over at low shear rates. It is well known that the positive deviation in viscosities occurs when interfacial interactions exist among components or the component polymers are intimately mixed. Their miscibility and strong intermolecular interaction may be responsible for the positive deviation in complex viscosities.

Tensile property

The tensile properties of the PA/EVOH blends were shown in Figure 3. Tensile strength and elongation of the blend exhibited positive deviation from simple additive rule. These results were well consistent with that of rheological properties. The significant positive deviation in the elongation is remarkably important. Similar to the results observed in the complex viscosity, the positive deviation in the tensile properties is probably related to the miscibility and strong intermolecular interaction between PA and EVOH.

Oxygen permeability

In Figure 4., the measured oxygen permeabilities as a function EVOH content indicate that EVOH exhibits much better oxygen barrier property than PA, and the logarithm of permeability of PA/EVOH blend was correlated linearly with the weight fraction of EVOH component exhibiting slight positive deviations of experimental results from additive rule.

References

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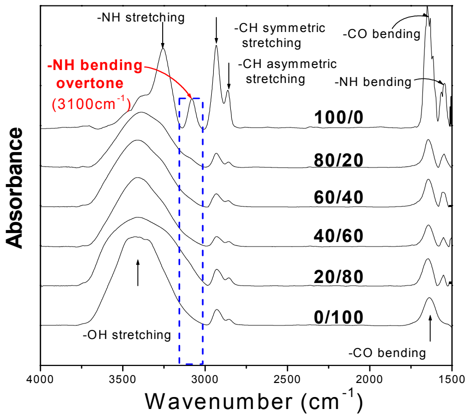

Fig.1 FT-IR absorbance spectra of PA/EVOH blends in the range of 4000 – 1500cm^{-1}.

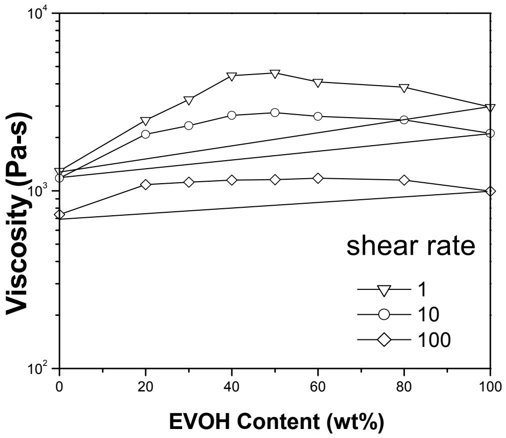

Fig.2 Shear viscosity of PA/EVOH blends as a function of EVOH content(wt%) and shear rate.

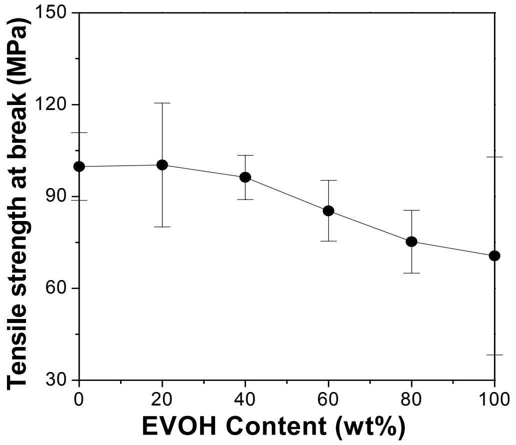

Fig.3 Tensile strength at break of PA/EVOH as a function of EVOH content(wt%).

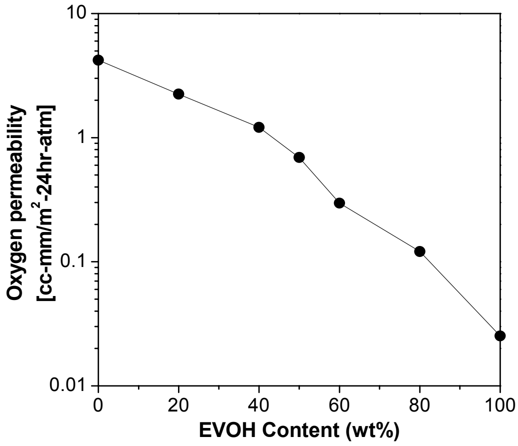

Fig.4 Oxygen permeability of PA/EVOH blends with varying EVOH content (wt%).