A Study on the Morphology and Properties of PP/(Nylon–EVOH) Blends

Seong Woo Kim and Gyoung Soon Huang

Department of Chemical Engineering, Kyonggi University
Department of Chemical Engineering, University of Texas at Austin

Introduction

Polypropylene (PP) with a good processability, low cost, and high resistant property to moisture has been widely used as a field of the packaging applications. However, it shows poor barrier property to organic solvents and oxygen.[1] On the other hand, ethylene–vinyl alcohol copolymer (EVOH) is highly resistant to the permeation of oxygen, carbon dioxide, but EVOH has a few shortcomings such as relative high brittleness, high cost, and difficulty of processing. Incorporation of nylon into PP/EVOH blend may not only compensate the inferior properties of EVOH, but also give additional functionality. Nylon is more advantageous in cost relative to EVOH, and it exhibits high resistance to the permeation of organic solvents and high impact strength. Previous studies have shown that compatibility in Nylon/EVOH blend system was assured due to inherent chemical structure of these two polymeric components, resulting in occurrence of hydrogen bonding interactions between amide group of nylon and hydroxyl groups of EVOH copolymers.

Plastic films with high barrier properties are usually produced with a multilayered structures using coextrusion or lamination process. Currently, an alternative approach to these multilayer films has been proposed by blending a small quantity of a barrier material with a lower cost polyolefin resin. In this polymer blend system, the improvement in barrier properties is accomplished through the formation of a laminar morphology of the dispersed phase resulting in increase of the tortuous path. EVOH or nylon has been chosen as the barrier material to obtain blend system with developed laminar morphology and barrier properties. However, most studies on the barrier blends have been performed using single barrier polymers as a dispersed phase.

In this work, ternary blend films of PP/(Nylon–EVOH) were prepared, in which barrier polymers of Nylon and EVOH were used as the dispersed
phase, and PP was used as the continuous phase. In this blend, the barrier polymers were dispersed in two forms, distinguished double phase from dry blending and hybrid single phase from melt blending. The effects of blending sequence (three methods in this study) on the morphology, oxygen barrier properties, and tensile properties of the blends were investigated.

**Experimental**

The polymer used as a continuous phase were a polypropylene supplied from Samsung General Chemicals (HF21AGT; M.I. (g/10 min, 190°C, 2160g) = 2.0, density (g/ml) = 0.751). EVOH and nylon with high barrier property were chosen for a dispersed phase. EVOH (EP-F101A, ethylene content=44mol%, M.I.=5.5g/10min, Tm=164°C, Tc=142°C) was obtained from Kurray Co. Nylon (2835TF; a copolymer of nylon 6 and nylon 66, Tm = 191.5°C, Tc = 143.9°C), was obtained from Hyosung Co. The molar ratio of nylon 6/nylon 66 was 17/83, and the melting temperature of the resin was much lower than original nylon 6 and nylon 66. Since PP and (EVOH-nylon) are incompatible, PP resin with 0.3 wt% grafted maleic anhydride (PP-g-MAH) as a compatibilizer was used to improve the interfacial adhesion between continuous and dispersed phase. This is a PO1015 resin provided by Exxon Co. Melt blends of nylon/EVOH 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 was 190-205-220-230°C.

Three different blending preparation methods were used for obtaining blend films of PP/(Nylon-EVOH)/PP-g-MAH. In step-A, all blend components in pellet form were dry mixed mechanically, and then melt blended using Hakke Rheomix 252 single screw extruder. Step-B process consists in melt blending of the nylon and EVOH resin in twin screw extruder prior to dry blending with PP and compatibilizer. In step-C, nylon, EVOH, and compatibilizer were melt blended, and then this blend was dry blended with PP to obtain blend films through melt blending. The weight ratio of the nylon-EVOH blend was 80/20, 50/50, and 20/80. The weight ratio of the PP/(Nylon-EVOH) blend was 80/20 with a fixed compatibilizer content of 7 phr in all cases.

The oxygen permeability of the sample was measured using method of 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**

In the blend system, viscosity ratio of the dispersed phase to the continuous phase ($\lambda = \eta_d/\eta_m$) is an important factor in controlling the blend morphology. The viscosity ratio close to unity induces easier deformation and breakup of the minor phase domains because of effective stress transfer from
the continuous phase to the dispersed phase. Whereas, the extent of deformation is diminished as the deviation of the viscosity ratio from unity increases. To examine the range of viscosity ratio for pure component and melt blend of nylon and EVOH, the melt shear viscosities as a function of shear rate was measured at 230°C as shown in Fig. 2. It can be seen that viscosity ratio of PA-EVOH melt blend is higher than that of pure component, resulting in more difficult deformation during film processing.

In this study, the compatibilizer (PP-g-MAH) was used to enhance the interfacial adhesion between dispersed and continuous phase and to obtain stable morphology in immiscible binary blends of PP and (Nylon+EVOH). Furthermore, it has been known that addition of compatibilizer into immiscible blends can prevent coalescence of the dispersed particles during melt flow through die after dispersed domains are crushed by high shear stress induced from screw rotation in the extruder. Fig. 1 shows the morphology of the compatibilized PP/(Nylon-EVOH) (80/20) blend films observed for the different blending methods. As shown in the figure, blending by step-C produced well-developed layer morphology in the MD direction with a larger number of thinner (Nylon-EVOH) layers in comparison with step-A or step-B blending. In addition, step-A method was found to be more effective than step-C method to obtain well-developed layer morphology of the dispersed phase. These morphological results can be explained by the rheological results shown in Fig. 2. Therefore, step-C blending provides a longer path to travel through the blends and thus yields a lower oxygen permeability.

Fig. 3 shows the effect of blending methods and composition in Nylon/EVOH blend on the oxygen permeability of the PP/(Nylon-EVOH) blend films. Oxygen permeability decreases as EVOH content in Nylon/EVOH dispersed phase increases because of high barrier property of EVOH itself. Blend film produced by step-C method has a lowest permeability. This is consistent with the morphological observations represented in Fig. 1. The blending sequence in preparation of PP/(Nylon-EVOH) blend was found to be a significant processing parameter to control the morphological structure of the dispersed phase and to obtain high barrier blends.

Acknowledgement

This research was supported by faculty exchange program(2004) with foreign university from Kyonggi University.

References

2. S. Y. Lee and S. C. Kim, "Laminar Morphology Development Using

Applied Chemistry, Vol. 9, No. 2, 2005

**STEP-A**  **STEP-B**  **STEP-C**

**TD**

**MD**

Fig.1 SEM micrographs of cross sections of fractured films of PP/Nylon/EVOH/PP-g-MAH(80/16/4/7) blends. (×3,000;—10μm)

**Fig.2** Viscosity of Nylon/EVOH blend and pure resins as a function of shear rate at 230°C.

**Fig.3** The effect of blending sequence and composition of PA/EVOH on the oxygen permeability.