

The Compatibilizing Effect of Maleic Anhydride in Ethylene-Vinyl Acetate (EVA)/Ethylene- α -Olefin Copolymers Blends

Soochul Park and Soonja Choe*

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea

Received February 22, 2005; Revised July 29, 2005

Abstract: The compatibilizing effect of maleic anhydride (MA) in the immiscible blends of EVA22 (vinyl acetate content 22%)/ethylene- α -olefin copolymers with 1-butene (EtBC) and 1-octene (EtOC) comonomers was studied. By adding 1, 2, and 3 phr of MA in the presence of dicumylperoxide, the morphology, tensile strength at break, and 100 and 300 % modulus of EVA22/EtBC and EVA22/EtOC blends were significantly enhanced. The melting point and crystallization point depression were observed upon the addition of MA. The changes in the β transition and glass transition temperature of ethylene- α -olefin copolymers and ethylene-vinyl acetate copolymers, respectively, indicate that MA plays a role of compatibilizer for these immiscible blends. The TGA thermograms, measured from the blends with MA, show that thermal stability is slightly enhanced with MA, indicating that MA acts as a reinforcing agent either by grafting or crosslinking with other copolymers.

Keywords: ethylene-vinyl acetate/ethylene- α -olefin copolymers, maleic anhydride, compatibility.

Introduction

Most polymers are thermodynamically immiscible or incompatible. Most incompatible polymer pairs require the use of compatibilizers to improve the compatibility and weak physical properties of polymer blends.^{1,2} Functional polymers carrying anhydride groups along the backbone exhibit enhanced adhesion properties to polar materials like polyamide, metals, and glass.³ Maleic anhydride (MA) is one of the compatibilizers in the melting process where the molten polymer is mixed with MA and an initiator in the extruder or mixing chamber at elevated temperatures.

Ethylene-vinyl acetate copolymers are thermoplastic and are synthesized by the copolymerization of ethylene and vinyl acetate. The thermal and rheological properties vary substantially as a function of the vinyl acetate content.^{4,5} Ethylene-vinyl acetate (EVA) provides a good balance of processability during extrusion, heat sealability, attack performance, and is easily blended with LLDPE. EVA for mid-sole application is well accepted due to its excellent whiteness, low density, resistance of color change, low cost, and easiness of injection molding, but it is poor in shrinkability upon compression. The mechanism proposed for the functionalization and crosslinking of EVA copolymers suggests radical reactions on the methyl groups of the acetate moiety. Ethylene- α -olefin copolymers are used as impact

modifiers or elastomers for polyolefins.⁶ Recently, blends of EVA copolymer with polyolefins have been widely studied. Some technical properties (static and dynamic mechanical properties, creep recovery behavior, thermal expansion, and thermal conductivity) of extruded foam profiles of LDPE and EVA blends are also being studied.⁷ Extensive studies on rheological behavior, processability, phase morphology, and melt viscoelasticity in the blends of EVA copolymer and metallocene-catalysed linear polyethylene were carried out by the Martinez-Salazar group.⁸ Film properties of the blends of EVA copolymer with a metallocene catalyzed elastomeric ethylene- α -olefin copolymer⁹ are also reported. In addition, rheology, morphology, thermal, mechanical, and adhesive properties of blends of EVA/metallocene-catalyzed ethylene- α -olefin copolymers containing 25, 50, and 75% EVA are thoroughly studied.¹⁰

In the previous studies, we investigated the blends of EVA with various contents of vinyl acetate (28, 22, and 15% of vinyl acetate) and ethylene- α -olefin copolymers, and reported that the blends of three EVAs (EVA28, EVA22, and EVA15) with ethylene- α -olefin copolymers are all immiscible in the solid and melt state, but mechanically comparable.¹¹ Thus, the objective of this work is to investigate the compatibilization of the immiscible blends of EVA22 with ethylene- α -olefin copolymers in the presence of MA and dicumyl peroxide (DCP) in terms of mechanical, thermal, rheological and morphological behavior.

*Corresponding Author. E-mail: sjchoe@inha.ac.kr

Experimental

Materials. The EVA copolymer, which is EVA22 with 22 % of vinyl acetate (VA), was purchased from Dupont, Wilmington, DE, USA. Two different ethylene- α -olefin copolymers, used as dispersion agents having comonomers, 1-butene (EtBC) and 1-octene (EtOC), were provided by the SK Corporation and Hanhwa Corporation, Korea, respectively. Maleic anhydride (MA) was purchased from Shinyo Pure Chemical (Gunma, Japan) and used without further purification. Dicumyl peroxide (DCP: 99% purity) was used as an initiator and purchased from Aldrich (St. Louis, MO). Its half-lifetime at the melting grafting temperature (175 °C) is about 1.45 min. Table I lists the characteristics of the materials used in this study.

Melt Blending and Sample Preparation. EVA was dried prior to use in an oven for 5 hrs at 70 °C. Blends of EVA22/ethylene- α -olefin copolymer were mixed in the weight ratio of 100/0, 90/10, 80/20, and 70/30% using a counter rotor type of Brabender plasticoder (PL-2000) internal mixer, Germany. EVA22/EtBC(20%) means that 20% EtBC and 80% EVA22 are involved in this blend composition. The mixing temperature and rotating velocity (rpm) are various upon each specimens and the mixing condition is determined upon empirical results; at 175 °C, 30 rpm of rotor speed, and for 6 min of reaction time. Once the EVA22/EtBC and EVA22/EtOC blends are prepared, 1, 2,

and 3 phr of MA with 0.3 phr of DCP are added at 175 °C and 30 rpm is set as the rotor speed in the internal mixer.^{12,13}

The pure polymers and blends were compression molded into a dumbbell bar according to ASTM D412 using a Carver laboratory hot press at 2×10^4 Pa and 175 °C.

Measurements. The morphology of the cryogenically fractured surfaces in liquid nitrogen was examined by a scanning electron microscopy (SEM: Hitachi S-4300) with a magnitude of 3000. The fractured surface of the specimens was coated with gold prior to the SEM examination.

The thermal properties of the blends of EVA22/EtBC and EVA22/EtOC copolymers were measured using a DSC (differential scanning calorimeter: Perkin-Elmer DSC7). The melting and crystallization temperatures were measured using 5 mg of specimens by heating them 30 to 180 °C at a heating rate of 20 °C/min under atmospheric pressure. In addition, to minimize the thermal history, all specimens were annealed for 3 min at 180 °C and cooled to 30 °C at 20 °C/min, then reheated up to 180 °C using the same heating rate. The melting temperature (T_m), crystallization temperature (T_c), and glass transition temperature (T_g) were obtained from the second heating.

The tensile property was measured with a universal test machine UTM (Instron 4465) at a room temperature of 30 % humidity according to ASTM D412 and the tensile strength, modulus, and elongation at break were calculated. 100 and 300% modulus, often measured in rubbery mate-

Table I. Characteristics of the Materials Used in This Study

Material	Characteristics	Source
EVA 22	MI 3.0 g/10 min, VA content 28.0 wt%, Density 0.951 g/cm ³	Dupont. U.S.A
EtBC (ethylene-1-butene copolymer)	MI 1.0 g/10 min, (ethylene-1-butene) comonomer, Density 0.919 g/cm ³ , T_m : 117 °C	SK corporation, Korea
EtOC (ethylene-1-octene copolymer)	MI 0.9 g/10 min, (ethylene-1-octene) comonomer Density 0.919 g/cm ³ , T_m : 123 °C	Hanhwa corporation, Korea
MA (maleic anhydride)	-	Shinyo Pure Chemical, Japan
DCP (dicumyl peroxide)	99% purity the melting grafting temperature: 175 °C half-lifetime: 1.45 min	Aldrich, U. S. A

Table II. Characteristic Melting and Crystallization Temperatures of the Homopolymers and Blends

	T_m (°C)		T_c (°C)		T_m (°C)		T_c (°C)	
EVA22	84.9		60.4		84.9		60.4	
EtBC	119.2		93.8		124.5		98.2	
EVA22 / EtBC 10%	84.0	118.9	60.9		84.9	124.0	62.4	
/ EtBC 20%	84.2	118.4	60.5		85.4	123.6	62.0	
/ EtBC 30%	84.3	118.0	60.4		85.6	123.5	61.5	
EVA22 / EtBC 10% / MA 2 phr	75.8	108.1	57.3	89.6	75.7	111.7	56.5	93.4
/ EtBC 20% / MA 2 phr	75.8	108.4	57.8	90.7	74.4	110	56.2	92.6
/ EtBC 30% / MA 2 phr	75.4	107.6	57.8	90.0	74.4	111.4	57.9	94.4

rial, were measured using the distance between the grip of 35 mm and crosshead speed of 50 mm/min.

The complex melt viscosity (η^*) was measured using a Torsion Rheometer Mk III, Polymer Lab, UK. Prior to the measurement, a strain sweep was performed, and a cycle type plate specimen of 38 mm diameter was scanned at a frequency range of 0.01~200 (rad/sec) with the strain range at 4%.

For the viscoelastic property, the prepared specimens were dried at 90°C in a vacuum oven, placed in a desiccator at room temperature, and then the characteristics were measured at 1 Hz with 0.1% of strain under tensile mode at a heating rate of 4°C/min between -150 and 120°C using a DMTA (Dynamic Mechanical Thermal Analyzer: Polymer Lab MK III, UK).

Results and Discussion

The effect of the addition of maleic anhydride (MA) into the EVA22 system is studied in the presence of dicumyl peroxide (DCP). Figure 1(a)~(d) represent the SEM photographs of EVA22/EtBC blend in the absence and presence of 3, 2, and 1 phr of MA, respectively. As seen in this figure, the incorporation of MA significantly improves the phase morphology of the blend compared to the use of no MA. In particular, 1 and 2 phr of MA incorporation shows better phase morphology. In addition, Figure 2 exhibits the SEM photographs of the EVA22/EtOC system in the absence and presence of MA. Since the phase contrast between EVA22 and EtOC (20 and 30%) is discrete compared to the EVA22/EtBC system without using MA, EtOC seems to

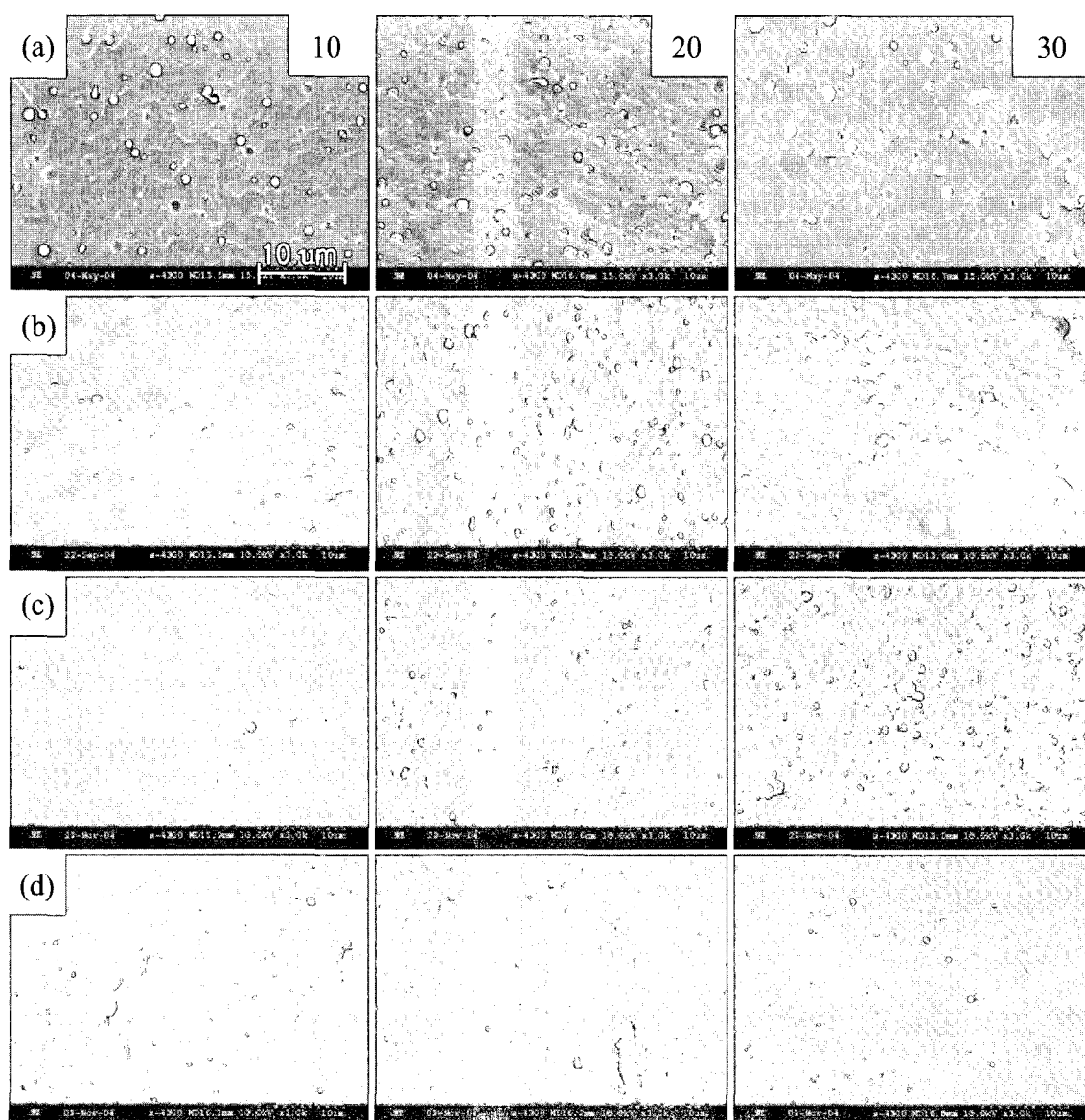


Figure 1. Comparison of SEM photographs of EVA22/EtBC blends in the absence and presence of MA.

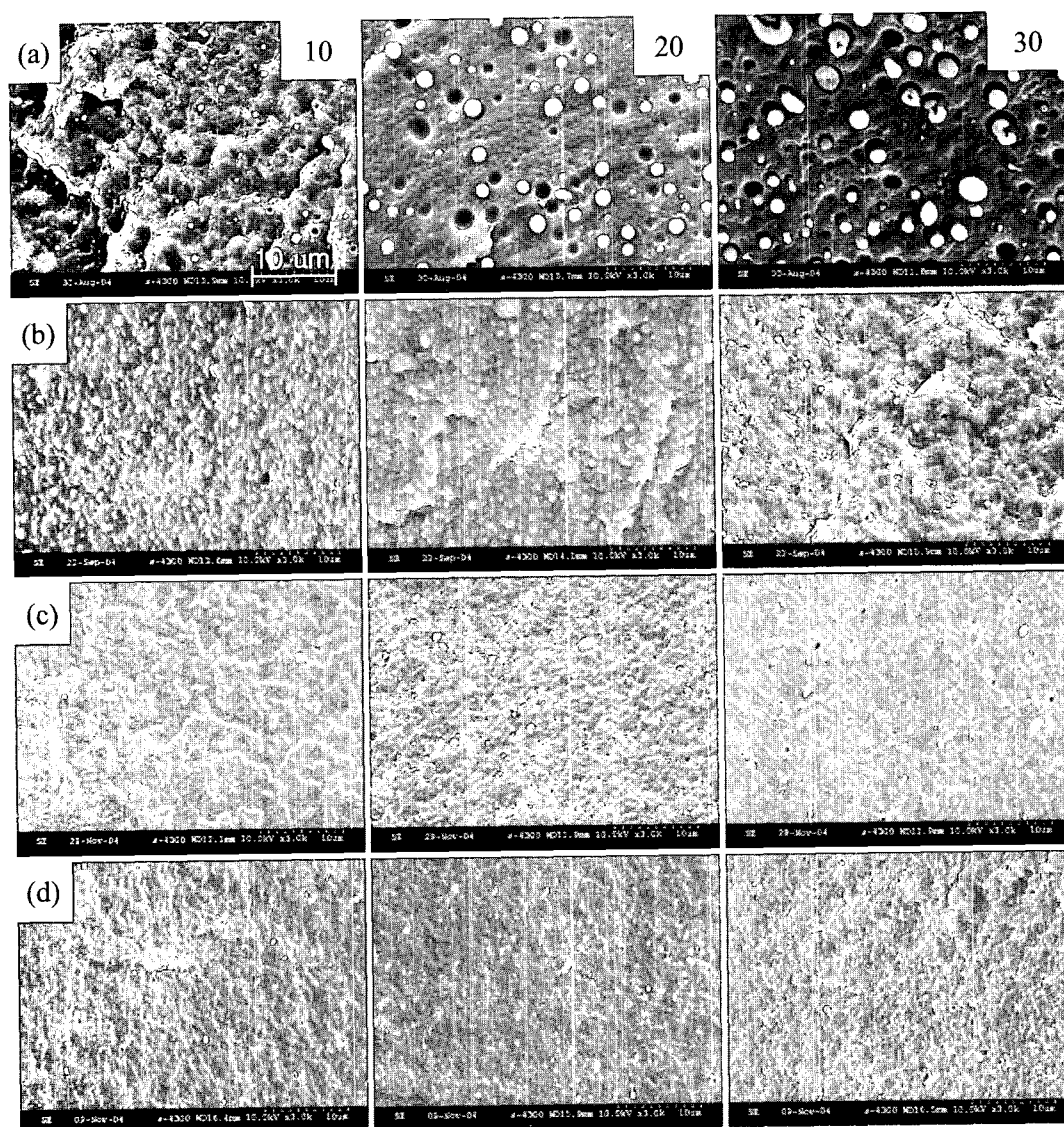


Figure 2. Comparison of SEM photographs of EVA22/EtOC blends in the absence and presence of MA.

enhance the phase morphology better. In addition, the trend of the phase behavior is similar to that in the EVA22/EtBC system, implying that 1 and 2 phr of MA clearly improves the phase morphology of EVA22/EtOC, too. Thus, MA is definitely working as an efficient compatibilizer.

Mechanical properties of the MA incorporated EVA22/ethylene- α -olefin copolymers blends were studied based on the tensile strength and ultimate elongation at break as a function of MA content by measuring the stress-strain curve. From this curve, the tensile strength and ultimate elongation at break are plotted as a function of MA content in Figure 3. As the amount of MA increased, the tensile strength of EVA22/EtBC blend linearly increased with EtBC content, while the EVA22/EtOC blend showed the highest value with 10% EtOC, then, slightly decreased with 20 and 30% of EtOC. However, incorporation of MA decreased the ultimate

elongation with ethylene- α -olefin copolymers (Figure 3(c) and 3(d)). In addition, the higher the EtBC content, the poorer the elongation property was observed, whereas no specific difference between EtOC contents was obtained. This behavior suggests that MA work as a reinforcing agent by improving the tensile strength, but reducing the ultimate elongation due to grafting or crosslinking.

Figure 4 represents the 100 and 300% modulus of EVA22/EtBC and EVA22/EtOC blend system. In general, 100 or 300% modulus, which is defined as the stress at 100 or 300% strain, respectively, is a measure of elasticity for rubbery material. The modulus increased slightly with the content of dispersive part, which is EtBC or EtOC. In addition, for the both systems, the 100 and 300% modulus improved up to 3 phr of MA, but showed the maximum with 2 phr of MA. This indicates that the incorporation of

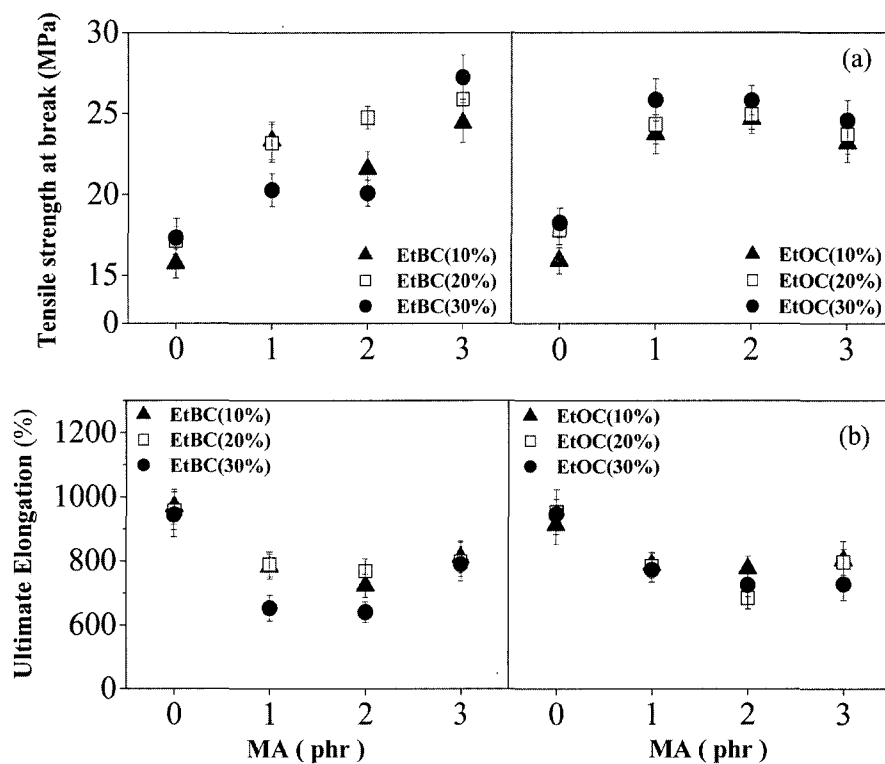


Figure 3. (a) tensile strength and (b) ultimate elongation at break of EVA22/EtBC & EVA22/EtOC blends upon an addition of MA.

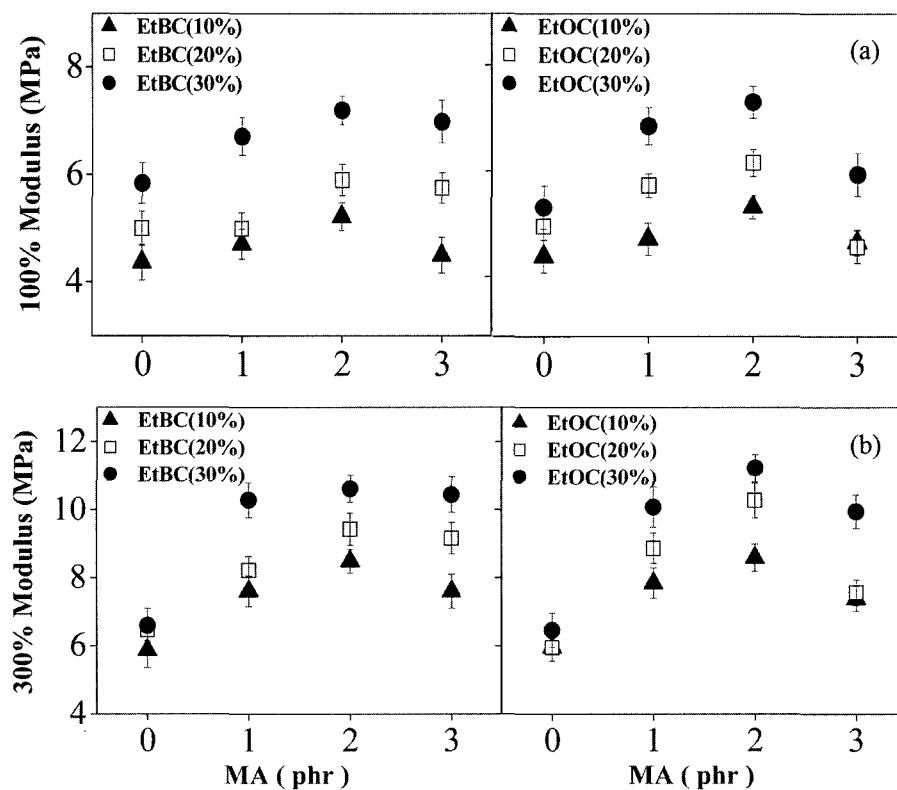


Figure 4. (a) 100% and (b) 300% modulus of EVA22/EtBC & EVA22/EtOC blends with MA.

MA enhances the mechanical properties significantly and MA is working as a reinforcing agent.

The effect of MA contents on thermal properties of EVA22/ethylene- α -olefin copolymers was studied and the representative DSC melting and crystallization thermograms in the absence and presence of 2 phr are shown in Figure 5. In Figure 5(a), representing the melting thermograms of EVA22/EtBC, the broad melting peak of pure EVA22 and pure EtBC is observed at 85 and 124°C, respectively. In addition, T_m of the blends is observed at the same position of the constituents with a reduced peak magnitude, implying no change on the melting behavior upon blending with EtBC. In the crystallization thermograms of EVA22/EtBC in the absence of MA as seen in Figure 5(b), T_c of pure EVA22 and EtBC showed at 60 and 97°C, respectively, but the T_c of EVA22/EtBC blends showed rather complicated behavior. For EVA22/EtBC(10%), there are two crystallization peaks observed at 62 and 71°C, but, for EVA22/EtBC(20%), three crystallization peaks appeared at 62, 72, and 79°C, then four crystallization peaks at 62, 72, 80, and 96°C were observed for the EVA22/EtBC (30%) blend. The first and last T_c would represent those of EVA22 and EtBC, respectively, but the rest of the crystallization peaks are not designable at this point. These multiple crys-

tallization peaks may be due to the reorientation of different crystal structures.

However, the melting behavior of the EVA22/EtBC blend in the presence of 2 phr of MA is different from the system without MA as seen in Figure 5(c). In this figure, the solid and dotted line represents the results in the absence and presence of MA, respectively. The melting peak of pure EVA22 and EtBC is shifted from 84 to 77°C and from 119 to 109°C, respectively. This behavior may be the result of melting point depression upon MA. Additionally, in the crystallization peak as seen in Figure 5(d), the complicated crystallization peaks between 70 and 80°C are completely disappeared by expect very clear two peaks at 57 and 90°C and these two are lowered upon the addition of MA simultaneously.

In the EVA22/EtOC blend system in Figure 6, the melting and crystallization behavior is similar to that shown in the EVA22/EtBC system. T_m of EVA and pure EtOC is observed at 85 and 125°C, respectively, and that of the blend according to different composition of EtOC is also observed at the same position of the constituent as shown in Figure 6(a). Crystallization behavior of pure components and that of the blends is also similar to the EtBC system; T_c of EVA22 and EtOC is 60 and 98°C, respectively, and for the blend, two to

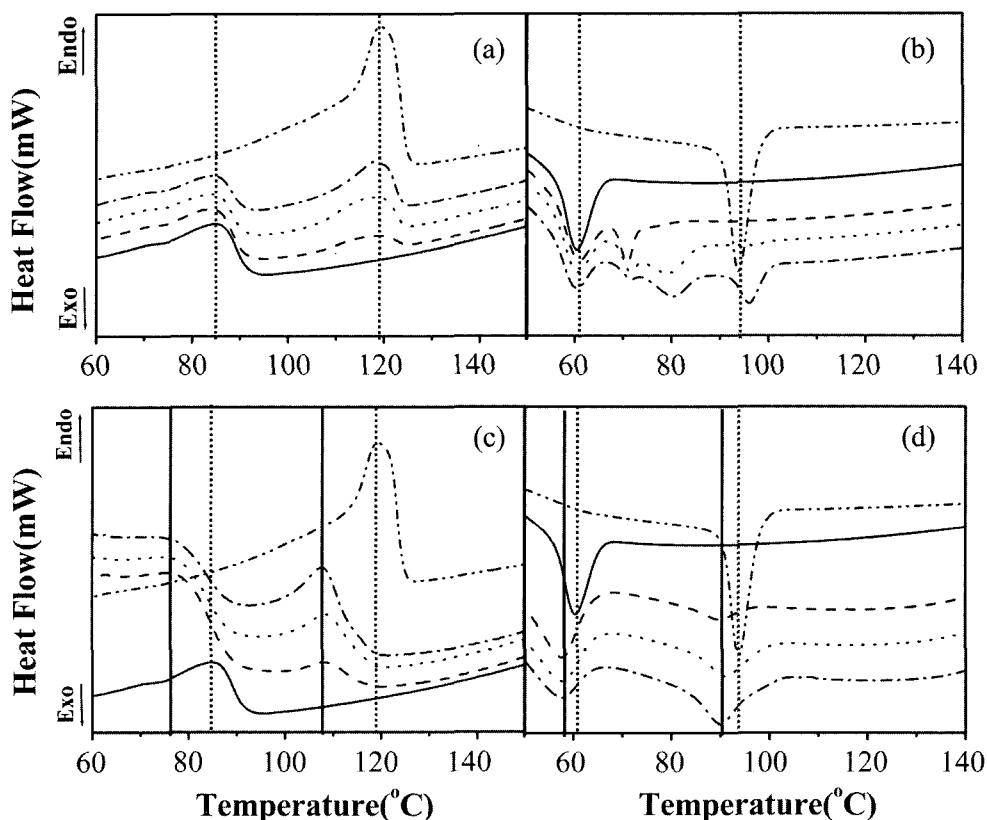


Figure 5. (a) melting thermograms of the EVA22/EtBC blend without MA, (b) crystallization thermograms of the EVA22/EtBC blend without MA, (c) melting thermograms of 2 phr of MA incorporated EVA22/EtBC blend, and (d) crystallization thermograms of 2 phr of MA incorporated EVA22/EtBC blend.

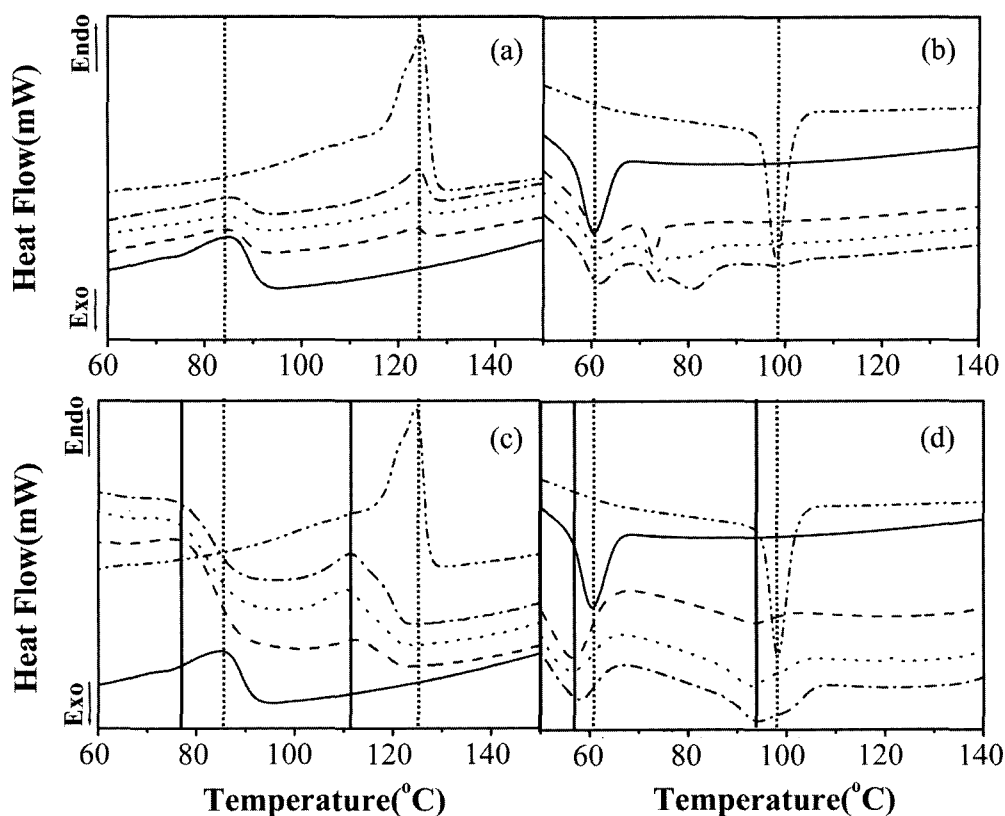


Figure 6. (a) melting thermograms of the EVA22/EtOC blend without MA, (b) crystallization thermograms of the EVA22/EtOC blend without MA, (c) melting thermograms of 2 phr of MA incorporated EVA22/EtOC blend, and (d) crystallization thermograms of 2 phr of MA incorporated EVA22/EtOC blend.

four crystallization peaks are observed in Figure 6(b). When MA is incorporated, the melting peak of the blends of EVA22/EtOC is shifted to a lower bound to 76 and 111 °C for EVA22 and EtOC, respectively, as seen in Figure 6(c). This is about 9 and 13 °C melting point depression from the system without MA addition, whereas for EVA22 and EtBC, the melting point depression is 7 and 10 °C, respectively. As seen in Figure 6(d), the crystallization peak of EVA22 and EtOC with MA is 56 and 93 °C, respectively, thus the crystallization point depression is 4 and 8 °C. This is comparable to EVA22/EtBC blend, where the crystallization depression of the constituent is 3 and 6 °C, respectively. The use of MA in the blends of EVA22 with ethylene- α -olefin copolymers displays various degree of melting and crystallization depression and may be the result of a chemical structure difference between ethylene-1-butene and ethylene-1-octene copolymer. In over all, the melting and crystallization point depression in the presence of MA in these two blend systems is suggested due to a plasticization effect of MA. There is no evidence of thermal degradation or chain scission upon process of sample preparation in the extruder and this will be discussed with melt viscosity and TGA measurements.

The complex melt viscosity ($\log \eta^*$) of EVA22/EtBC and EVA22/EtOC blends is plotted in Figure 7(a) and 7(b),

respectively. In the absence of MA, the complex melt viscosity ($\log \eta^*$) decreased with frequency, showing a non-Newtonian behavior in Figure 7(a). A higher melt viscosity of EtBC at high frequency than that of EVA22, but the intermediate value for the EVA/EtBC (20%) were observed. However, when MA is incorporated, the complex melt viscosity increased in log-log plot, implying that MA induces higher viscosity due to grafting or crosslinking effect of MA.

In order to investigate the possibility of thermal degradation or other chemical reaction during the sample preparation of the EVA22/poly(ethylene- α -olefin) copolymers with MA and DCP at 175 °C, 30 rpm of rotor speed, and for 6 min, the thermal gravimetric analysis has been carried out. The representative thermograms for the EVA22/EtBC and EVA22/EtOC blends are shown in Figure 8(a) and 8(b). No evidence of thermal degradation upon an incorporation of MA with DCP between 350 and 500 °C was observed, rather a slight enhancement in thermal property between these temperatures seems to be a consequence of grafting or a slight crosslinking.

Figure 9(a)-(b) and 9(c)-(d) represents the storage modulus ($\log E'$) and loss modulus ($\log E''$) for the EVA22/EtBC and EVA22/EtOC blends, respectively. In Figure 9(a) and

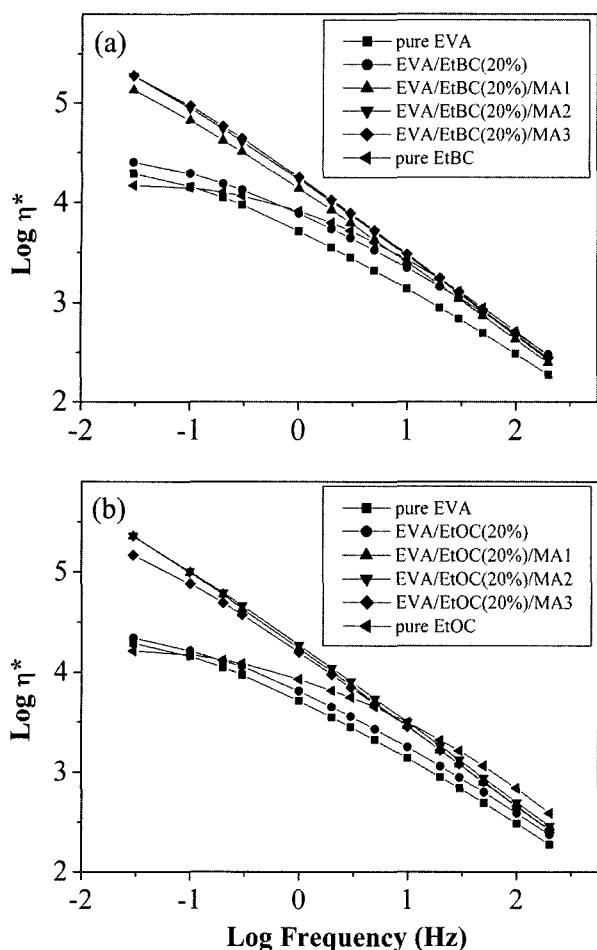


Figure 7. Comparison of the $\log \eta^*$ vs $\log \omega$ of the blends with and without MA. (a) EVA22/EtBC blends and (b) EVA22/EtOC blends.

9(b), the $\log E'$ of EVA22/ethylene- α -olefin copolymer without MA is slightly higher than that with 2 phr of MA. An interesting phenomenon is observed in loss modulus between -150 and 110°C . For the EVA22/EtBC system, the two transitions at -9.6 and 32°C in the absence of MA merged into one broad transition near -5°C with 2 phr of MA. In our previous report, the β transition of polyethylene related with EVA and EtBC is occurring at -20°C and the T_g of vinyl acetate is 35°C .¹¹ This tells us that incorporation of MA affects the β transition or T_g of EtBC or EVA. Also, for the EVA22/EtOC system, similar behavior is observed; two transitions of -10.5 and 33°C merged into one at -9°C upon the addition of 2 phr of MA. Thus, it is suggested that incorporation of MA may interfere at the molecular level, resulting the variation in due to varying the β transition or T_g of EtBC or EVA.

Conclusions

Compatibilization by MA in the blends of EVA/ethylene-

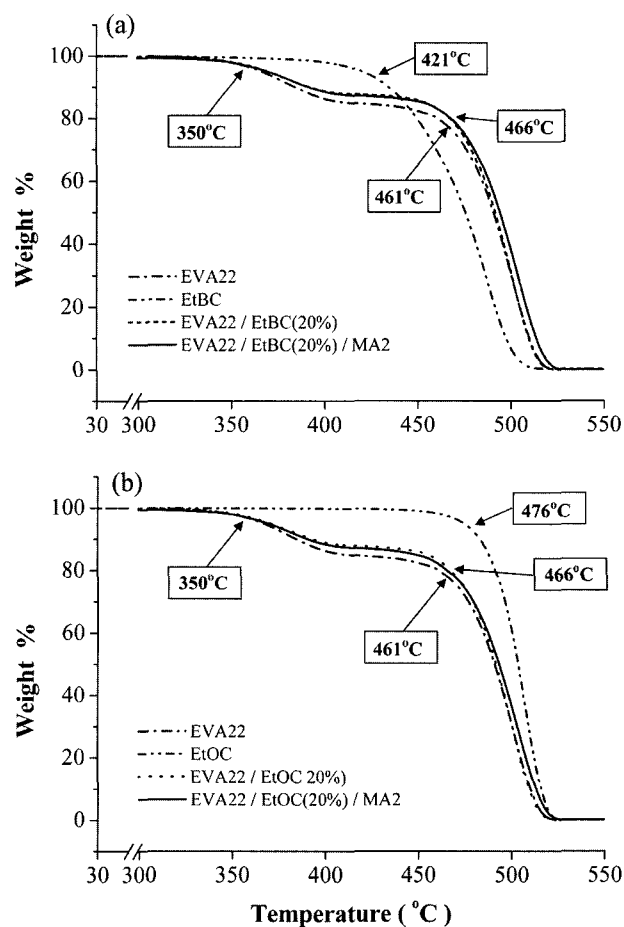


Figure 8. Comparison of TGA data of EVA22/EtBC and EVA22/EtOC blends in the absence and presence of MA. The temperature scale is same in Figure (a) and (b).

α -olefin copolymers with 1-butene and 1-octene are studied using 22 mol% of VA in terms of morphology, mechanical, rheological, and viscoelastic properties. The effect of MA in the immiscible blends of EVA22/EtBC and EVA22/EtOC was studied by addition of 1, 2, and 3 phr of MA in the presence of dicumylperoxide (DCP). The morphology was significantly improved upon incorporation of MA, in particular, 2 phr of MA is the most effective. The tensile strength at break, and 100 and 300% modulus of the EVA22/EtBC and EVA22/EtOC blends were significantly enhanced, but the elongation at break decreased with EtBC or EtOC; the best properties were obtained with 2 phr of MA. In thermal behavior, the melting point depression and crystallization point depression was observed upon the addition of MA. For the EVA22/ethylene- α -olefin copolymers blend system, the melting point depression of EVA22 and EtBC was 7 and 10°C , whereas that of EVA22 and EtOC was 9 and 13°C . In addition, the crystallization point depression of EVA22 and EtBC is 3 and 6°C , and that of EVA22 and EtOC is 4 and 8°C . This behavior tells us that the melting and crystallization point depression upon incorporation of MA is more effective.

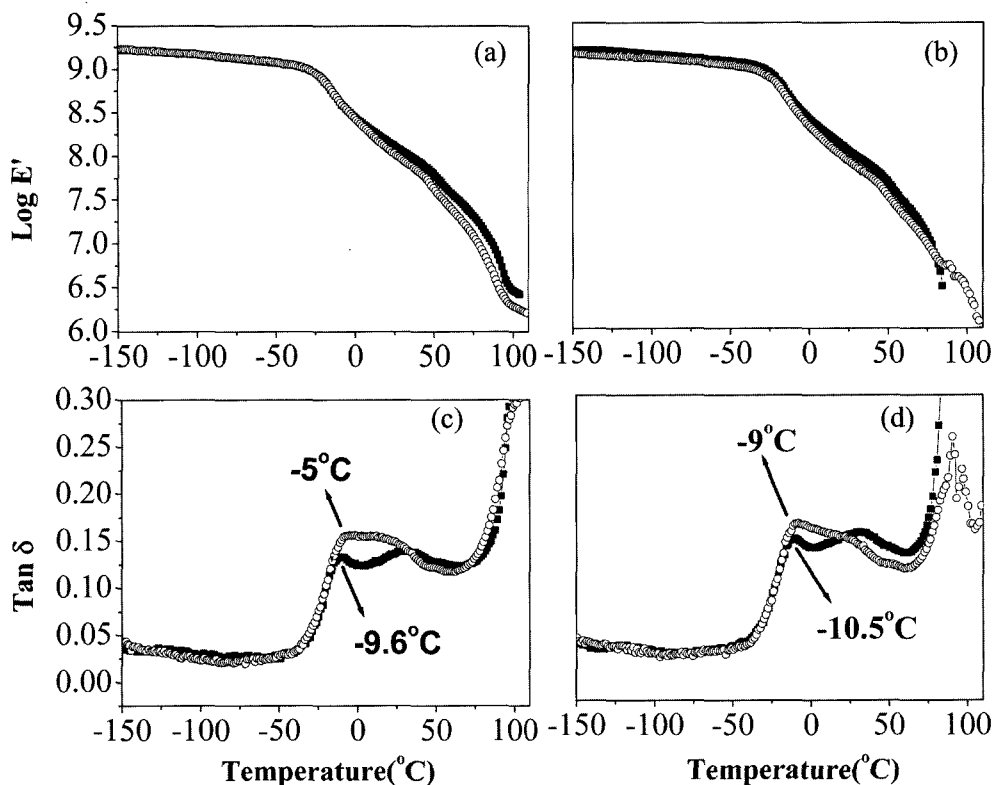


Figure 9. Comparison of storage(E') and $\text{Tan } \delta$ in the absence and presence of MA. (a), (c) EVA22/EtBC(20%) blend. (b),(d) EVA22/EtOC(20%) blend(—■— without MA, —○— MA 2 phr).

tive in the EtOC system than in the EtBC system. In TGA thermo gravimetric analysis, no evidence in thermal degradation is observed, instead, a slightly enhanced thermal properties were observed as a result of grafting or a possibility of crosslinking. In viscoelastic property, the storage modulus (E') of MA incorporated system was slightly lower than that without MA. The loss modulus ($\log E''$) is influenced with MA in both blends resulting in the change of the β transition and T_g of ethylene- α -olefin copolymers and vinyl acetate, respectively. This indicates that MA influences the molecular level of the blends by grafting between EVA and MA. In overall, MA is effective not only in improving the compatibility and mechanical properties, but also in influencing the molecular level of the constituents.

Acknowledgements. This work is supported by Inha University for the Wolchon Research Funds of Dongsung Chemicals during the year of 2003-2004.

References

- (1) L. A. Utraki, in *Polymer Alloys and Blends*, New York, Hanser Pub., 1989.
- (2) U. Sundararaj and C. W. Macosko, *Macromolecules*, **12**, 517 (1995).
- (3) A. Arzac, C. Carrot, and J. Guillet, *J. Appl. Polym. Sci.*, **74**, 625 (1999).
- (4) M. Shimoyama, S. Hayano, K. Matsukawa, H. Innoue, T. Ninomiya, and Y. Ozaki, *J. Polym. Sci., Polym. Phys.*, **36**, 1529 (1998).
- (5) M. Xanthos and S. S. Dagli, *Polym. Eng. Sci.*, **31**, 929 (1991).
- (6) M. A. Lopez-Manchado, M. Valle, R. Sapunar, and R. Quijada, *J. Appl. Polym. Sci.*, **92**, 3008 (2004).
- (7) M. A. Rodriguez-Perez, A. Duijsens, and J. A. de Saja, *J. Appl. Polym. Sci.*, **68**, 1237(1998).
- (8) J. Peon, J. F. Vega, M. Aroca, and J. Martinez-Salaza, *Polymer*, **44**, 8093 (2001); J. Peon, M. Aguilar, J. F. Vega, B. Del Amo, and J. Martinez-Salazar, *Polymer*, **44**, 1589 (2001); J. Peon, J. F. Vega, B. Del Amo, and J. Martinez-Salazar, *Polymer*, **44**, 2911 (2003).
- (9) M. Kontopoulou, L. C. Huang, and J. A. Lee, *Adv. Polym. Tech.*, **22**, 209 (2003).
- (10) M. Kontopoulou and L. C. Huang, *J. Appl. Polym. Sci.*, **94**, 881 (2004).
- (11) S. Park, C. Yim, B. H. Lee, and S. Choe, *Macromole. Res.*, **13**, 243 (2005).
- (12) S. J. Kim, C. J. Kang, S. R. Chowdhur, W. J. Cho, and C. S. Ha, *J. Appl. Polym. Sci.*, **89**, 1305 (2003).
- (13) S. J. Kim, B. S. Shin, J. L. Hong, W. J. Cho, and C. S. Ha, *Polymer*, **42**, 4073 (2001).