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Properties of the Blends of Ethylene-Vinyl Acetate and Ethylene-α-Olefins Copolymers

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Abstract: The effect of the vinyl acetate (VA) content on the thermal, viscoelastic, rheological, morphological and mechanical behaviors in various blends of ethylene-vinyl acetate (EVA)/ethylene-α-olefin copolymers was investigated using 28, 22 and 15 mol% of VA in EVA. In the DSC melting and crystallization thermograms of all of the EVA systems blended with ethylene-α-olefin copolymers, discrete peaks were observed which were related to the constituents. In the dynamic mechanical thermal analysis, the storage modulus increased with increasing content of ethylene-α-olefin copolymers. In addition, the transition regions relating to the tan δ peaks varied with the VA content. The crossover point between G' and G'' varied depending on the VA contents, and shear-thinning was more prominent in the EVA/EtBC system. In the SEM investigation, a discrete phase morphology was observed in both the EVA/EtBC and EVA/EtOC blends, but the contrast improved with decreasing VA content. However, the tensile strength and modulus improved, but the elongation at break reduced with decreasing VA content, implying that the ethylene-α-olefin copolymers play the role of reinforcing materials. Thus, the EVA and ethylene-α-olefin components in the copolymers are immiscible in the molten and solid states, but are nevertheless mechanically compatible.

Keywords: ethylene vinyl-acetate copolymer, ethylene-α-olefin copolymer, compatibility.

Introduction

Polymer blending is one of the most effective and economical methods in developing new materials that have distinctive properties from those of each constituent.[1,2] However, most polymer blends are immiscible in nature by presenting poor properties, thus compatibilization is one of the methods to enhance the properties or compatibility. A common way of compatibilization is an addition of a block or grafting copolymers.[3,4] In general, functional polymers carrying anhydride groups along the backbone exhibit enhanced adhesion properties to polar materials, are extensively employed as compatibilizing agents for polymer blends. For technological and commercial purposes, the functionalization of polyolefins with maleic anhydride (MA) is better achieved in the melt process where the molten polymer is mixed with MA and an initiator in an extruder or mixing chamber at elevated temperature.[5]

EVA for midsole application is accepted due to the easiness for injection molding, excellent in whiteness, low density, resistance in color change and low cost, but poor in shrinkability upon compression. In particular, EVA with high content of VA is used for expanded shoe sole.[6] The characteristics of EVA having low content of VA is similar to those of low density polyethylene (LDPE), while those of EVA having high content of VA is close to those of rubber. Recently, blends of EVA copolymer with polyolefins are widely studied. Extensive studies on rheology, thermal, mechanical, and adhesive properties of EVA/metallocene-catalized ethylene-α-olefin copolymers blends were carried out.[7] In addition, extensive studies on processability, phase morphology, and melt viscoelastic properties in the blends of EVA copolymer and metallocene-catalysed low density polyethylene[7-9] have been reported. Some technical properties, such as static and dynamic mechanical properties, creep recovery behavior, thermal expansion, and thermal conductivity of extruded foam profiles of LDPE and EVA blends, were also studied.[10]

We have extensively studied the compatibility of the blends using various EVA having 28, 22, and 15% of VA content with ethylene-α-olefin copolymers, where α belongs to 1-butene and 1-octene. Since EVA is used for shoe-midsole, the possibility of compatibility or enhancement in thermal, viscoelastic, rheological, morphological and mechanical properties is interested in, particularly with up to 30 wt% ethylene-α-olefin copolymers.

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Experimental

Base Resins. Ethylene-vinyl acetate (EVA) copolymers, EVA28, EVA22, and EVA15 consisting of 28, 22, and 15% of VA, respectively, were purchased from Dupont, Welmington, DE, USA, and Hyundai Petro Chemicals, Korea, respectively. Two different ethylene-α-olefin copolymers used for dispersive material are composed of comonomers, ethylene-1-butene copolymer (EtBC) and ethylene-1-octene copolymer (EtOC) and provided from SK Corporation and Hanhwa Corporation, Korea, respectively. 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 EVA/ethylene-α-olefin copolymer were prepared 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. 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, and for 6 min of reaction time.

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 and the specimens were used for viscoelastic measurements.

Measurements. The thermal properties of the blends of EVA/ethylene-α-olefin copolymer were measured using a DSC (differential scanning calorimeter: Perkin-Elmer DSC7). The melting temperature and the thermal behavior were measured using 5 mg of specimens by heating from 30 to 180 °C at a heating rate of 20 °C/min under atmospheric pressure. In order 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 same heating rate. The melting temperature (T_m), crystallization temperature (T_c), and glass transition temperature (T_g) were obtained in the second heating.

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

The storage modulus (G'), loss modulus (G''), and complex melt viscosity (η^*) were measured using a Torsion Rheometer Mk III, Polymer Lab, UK. Prior to the measurement, strain sweep was performed, 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%.

Morphology of the cryogenically fractured surfaces in liquid nitrogen, then coated with gold, was studied using scanning electron microscopy (SEM: Hitachi S-4300) in a magnitude of 3000.

The tensile property was measured with an universal test machine UTM (Instron 4465) at room temperature with 30% humidity according to ASTM D412 and the tensile strength, 100 and 300% modulus, and elongation at break were measured using the distance between the grip of 35 mm and crosshead speed of 50 mm/min. Hardness of the samples was measured by a dial guage using Shore A hardness tester (Durometer) after the specimen's surface was indented by a needle type indentor according to ASTM D2240.

Table I. Characteristics of the Materials Used in This Study

Material	Characteristics	Source
EVA 28	MI 3.0 g/10 min VA content 28.0 wt% Density 0.951 g/cm^3	Dupont. U.S.A
EVA 22	MI 1.8 g/10min. VA content 22.0 wt% Density 0.945 g/cm^3	Hyundai Petrochem Korea
EVA 15	MI 1.8 g/10min. VA content 15.0 wt% Density 0.945 g/cm^3	Hyundai Petrochem Korea
EtBC (ethylene-1-butene copolymer)	MI 1.0 g/10min (ethylene-1-butene) Density 0.919 g/cm^3 T_m. 117 °C	SK corporation, Korea
EtOC (ethylene-1-octene copolymer)	MI 0.9 g/10min (ethylene-1-octene) Density 0.919 g/cm^3 T_m. 123 °C	Hanhwa corporation, Korea

Results and Discussion

Thermal Properties. The effect of vinyl acetate (VA) contents in the thermal properties of the blends of EVA/ethylene-α-olefin copolymers was studied using EVA28, EVA22, EVA15, EtBC, and EtOC (the content of ethylene-α-olefin copolymer is included 10, 20, 30%). Figure 1 show the DSC melting and crystallization thermograms of EVA28/EtBC and EVA28/EtOC blends. In Figure 1(a) and 1(b), the melting temperatures (T_m) of pure EtBC and EtOC are 119 and 124 °C, respectively, however, the melting peak of EVA28 is very broad between 60 and 75 °C. As the content of ethylene-α-olefin copolymer increased from 10 to 30%, the T_m of the constituent remains constant with slightly broadened and decreased peak shape.

The crystallization temperatures (T_c) of EVA28, EtBC, and EtOC in Figure 1(c) and 1(d) showed 47, 93 and 98 °C, respectively. On the other hand, T_c of EVA28/EtBC and EVA28/EtOC blends shifted slightly from 70 to 72 °C and from 71 to 75 °C for 10 to 30% of ethylene-α-olefin copolymer, respectively. In addition, for EVA28 /EtBC (30%), very small peak representing T_c of EtBC is observed near 94 °C.

In Figure 2(a) and 2(b) representing the melting thermograms of EVA22/EtBC and EVA22/EtOC, respectively, the

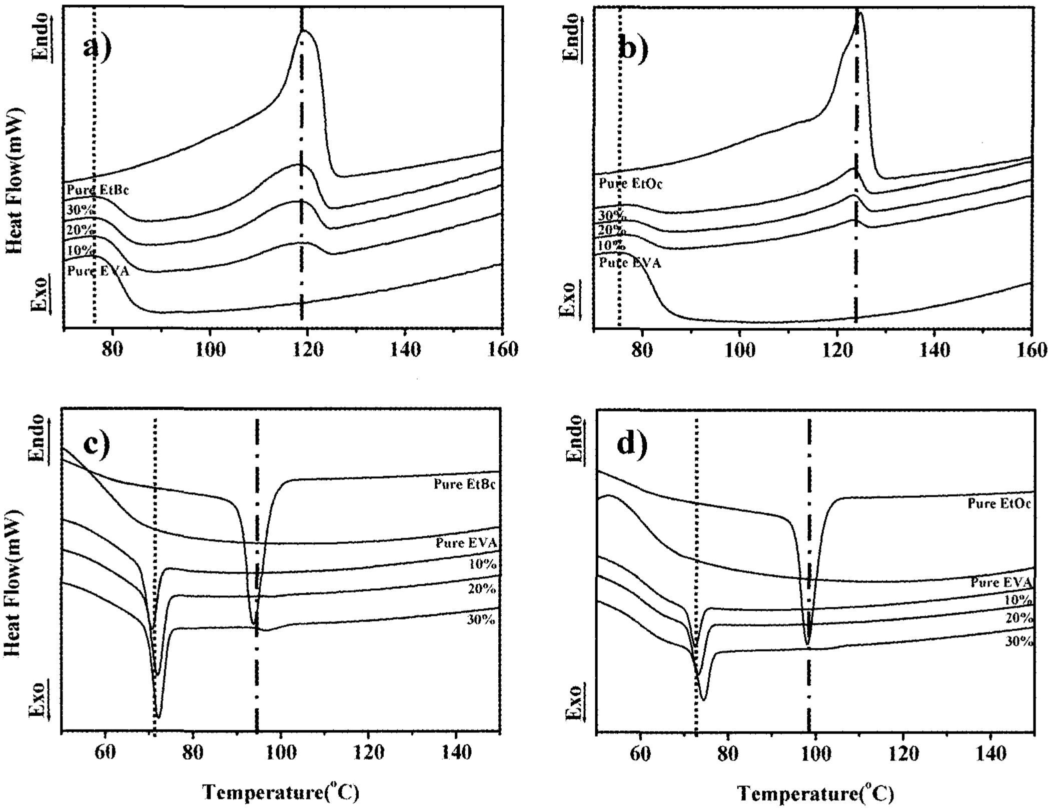

Figure 1. (a) Melting thermograms of the EVA28/EtBC blends, (b) melting thermograms of the EVA28/EtOC blends, (c) crystallization thermograms of the EVA28/EtBC blends, and (d) crystallization thermograms of the EVA28/EtOC blends.

broad melting peak of pure EVA22 is observed at 85 °C, which is slightly higher than that of EVA28 due to higher content of ethylene moiety. Then, the T_m of the rest of EtBC and EtOC are the same as observed in system EVA28 (Figure 1). In crystallization thermograms, T_c of EVA22 showed at 60 °C and the T_c of EVA22/EtBC and EVA22/EtOC blends showed rather complicated behavior. For EVA22/EtBC (10%) blend, there are two crystallization peaks observed at 62 and 70 °C. But, for EVA22/EtBC(20%), three crystallization peaks appeared at 62, 70, and 79 °C, then four crystallization peaks at 62, 70, 80, and 96 °C were observed for EVA22/EtBC (30%) blend. The first and last T_c would represent that of EVA22 and EtOC, respectively, but the rest of the crystallization peaks are not designable, yet. In addition for EVA22/EtOC (10%) blend, there are two crystallization peaks observed at 61 and 71 °C. But, for EVA22/EtOC (20%), there are three crystallization peaks appeared, then four peaks at 61, 72, 80 and 98 °C were observed for EVA22/EtOC (30%). These several crystallization peaks may be due to the reorientation of different crystal structures upon quench cooling.

The same trend was observed in Figure 3 representing the melting and crystallization thermograms of the EVA15/EtBC and EVA15/EtOC blends. The T_m and T_c of EVA15 is 90 and 68 °C, respectively, and T_m of the blends remains constant with lowering the peak intensity. On the other hand, T_c of the blends is quite different from that of EVA28 or EVA22 system. For EVA15/EtBC and EVA15/EtOC with 10-30% of ethylene-α-olefin copolymer, T_c of EVA15 does not change at all, but undesignated small peak between 80 and 85 °C and the T_c of ethylene-α-olefin copolymer were observed at 94 and 98 °C, respectively.

There is a report that cocrystallization is occurring independent of crystallization rate in commercial HDPE and LLDPE.[11] This may happen during crystallization between the chain in EVA or HDPE and that of ethylene-α-olefins copolymers. Each crystal throughout the crystallization process represents the possibility of the structural possibility of the reorientation of heterogeneous crystals.

Viscoelastic Behavior. The viscoelastic behavior of pure EVA28, EVA22, EVA15, EtBC, and EtOC in terms of log E' and tan δ is shown in Figure 4. As the VA content increased, the storage modulus (E') decreases, but the tan δ, which represents the damping factor, increases as usual. The tan δ melting peaks near 82 and 88 °C for EtBC and EtOC, respectively, were observed. In general, there are three transitions, called by α, β, and γ relaxations in polymers. Regarding on crystalline polyethylene (PE), α transition is related with crystalline phase such as melting temperature; the T_m of PE is reported near 120 °C by DSC, and the high-

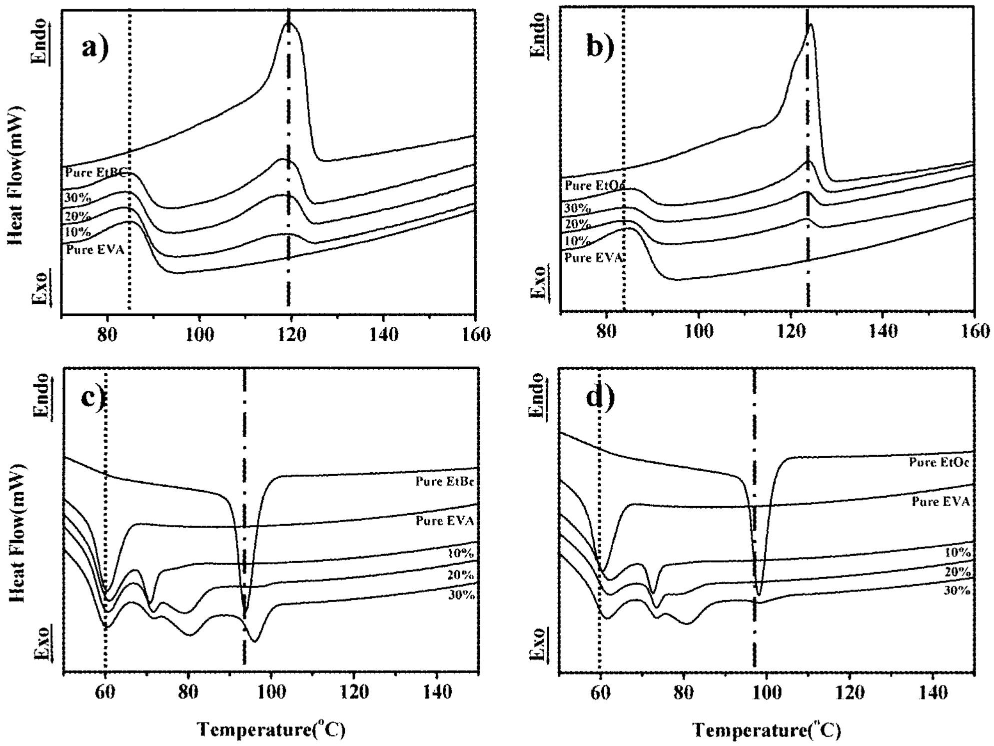

Figure 2. (a) Melting thermograms of the EVA22/EtBC blends, (b) melting thermograms of the EVA22/EtOC blends, (c) crystallization thermograms of the EVA22/EtBC blends, and (d) crystallization thermograms of the EVA22/EtOC blends.

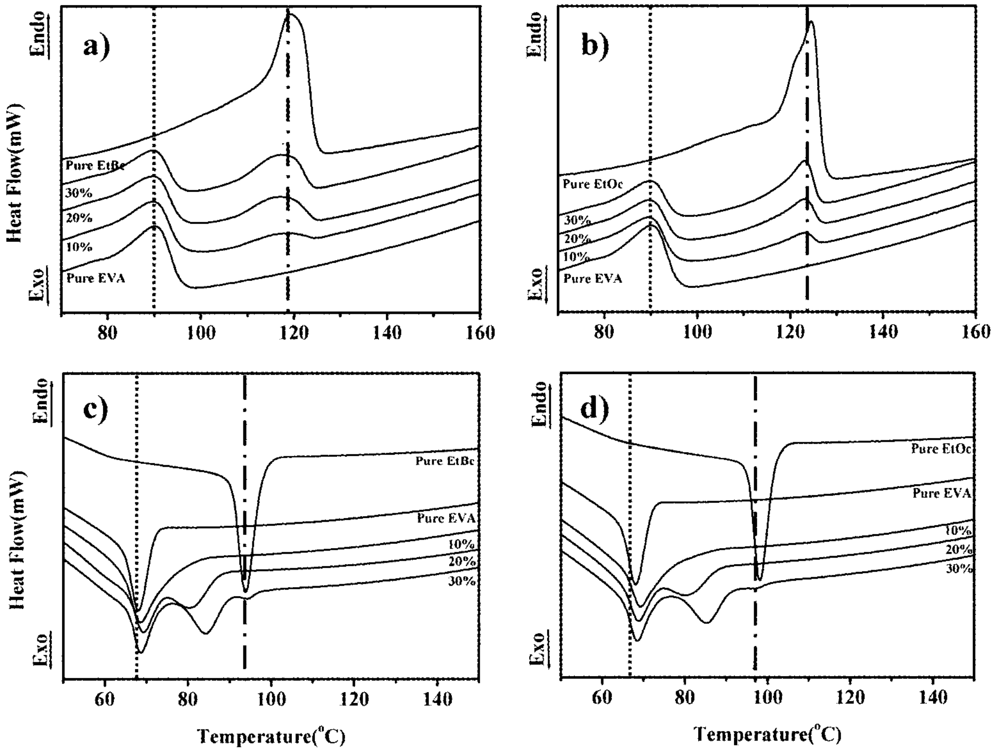

Figure 3. (a) Melting thermograms of the EVA15/EtBC blends, (b) melting thermograms of the EVA15/EtOC blends, (c) crystallization thermograms of the EVA15/EtBC blends, and (d) crystallization thermograms of the EVA15/EtOC blends.

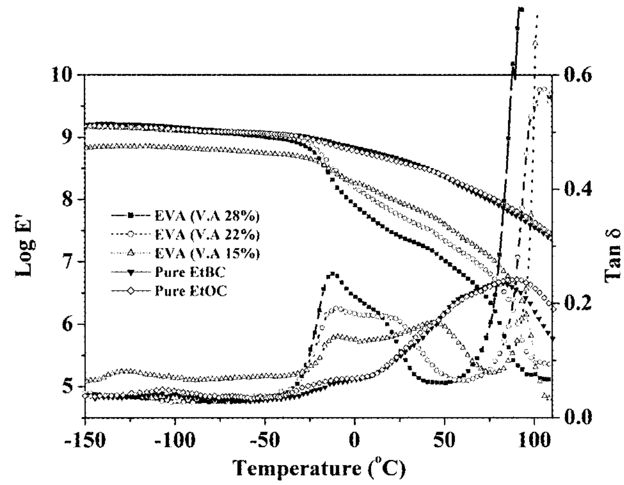

Figure 4. Comparison of DMTA thermograms of EVA blends with various contents of VA, EtBC, and EtOC.

est peak near 100 °C in tan δ would be related to the melting temperatures of EVA copolymer and ethylene-α-ethylene in this figure. In addition, the T_m and the peak height are lowered with increase of VA content because of large content of rubbery phase.

In addition to tan δ of EVA, there are two different transitions; one is at -13 °C and the other is between 20 and 43 °C. The former transition remains constant regardless of the VA content, but the latter transition shifts from 20 to 43 °C as the VA content decreases. The β transition near -20 °C is reported as the relaxation of amorphous phase of branching or side chain of PE or as the T_g of vinyl acetate group which is reported at 35 °C. Thus, we believe that the former transition corresponds to the β transition of PE and the latter transition is related to the β transition of VA. It is reported that the β transition or T_g of EVA does not change when less than 40% of VA involved.[12] Reding *et al.*[13,14] also reported that the transition at -20 °C would not be changed because the amorphous phase remains constant although the content of VA increases. Nielson reported that the constancy of the T_g of PE at -20 °C rather related with the relaxation of side chain group than with amorphous phase, which is related to the β transition.[15]

In addition, a weak and broad peak near -130 °C was observed for EVA15. The transition at -130 °C is reported to the glass transition temperature of ethylene-α-olefin copolymer, which is the relaxation of the main chain related to CH_2 repeating unit, thus it is accepted to the γ transition by McCrum[16] and Choe group.[17]

Figure 5(a) and 5(b) represent the tan δ thermograms for EVA28/EtBC and EVA28/EtOC blend, respectively. The characteristic peaks at -15 and 82 °C in Figure 5(a) are comprised from EVA28 and EtBC, respectively. As the EtBC content increased from 10 to 30%, intensity of EVA related peak decreased without the highest peak position, while the

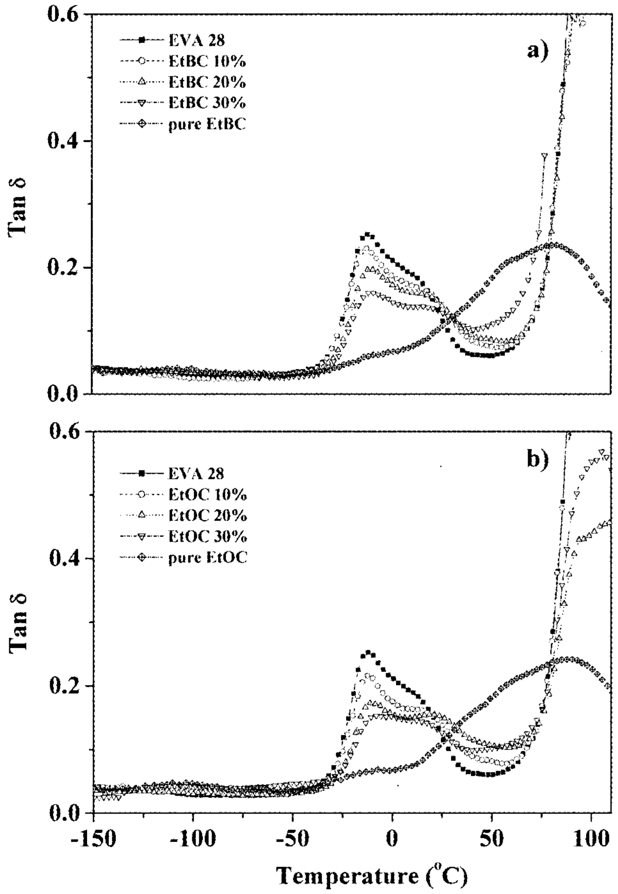

Figure 5. DMTA thermograms of tan δ. (a) EVA28/EtBC system and (b) EVA28/EtOC system.

peak height near 82 °C increased relatively. In Figure 5(b), representing the tan δ thermogram for EVA28/EtOC, the similarity was observed as seen in the EVA28/EtBC system.

Figure 6(a) and 6(b) show the tan δ thermograms for the EVA22/EtBC and EVA22/EtOC blend, respectively. Two peaks representing the characteristics of EVA22 and ethylene-α-olefin copolymer remain in same position with linearly decreased or increased peak intensity along to that of the constituent. In Figure 6(c) and 6(d) representing the EVA15/ethylene-α-olefin system, the tan δ thermogram is similar to that of EVA22 system except the broad peak near -130 °C, which is the T_g of polyethylene. In overall, since the peak at -13 °C is related with EVA, the peak intensity decreased with EVA content.

Rheological Property. Although we have not added common features of melt viscosity in the text, higher complex melt viscosity was observed with increasing content of ethylene-α-olefin copolymer and shear-thinning phenomenon was more prominent in EVA/EtBC blend system. After obtaining the strain sweep at the whole ranges of frequency (ω) at 4% strain and 175 °C, the storage modulus (G') and loss modulus (G'') were measured and plotted as a function

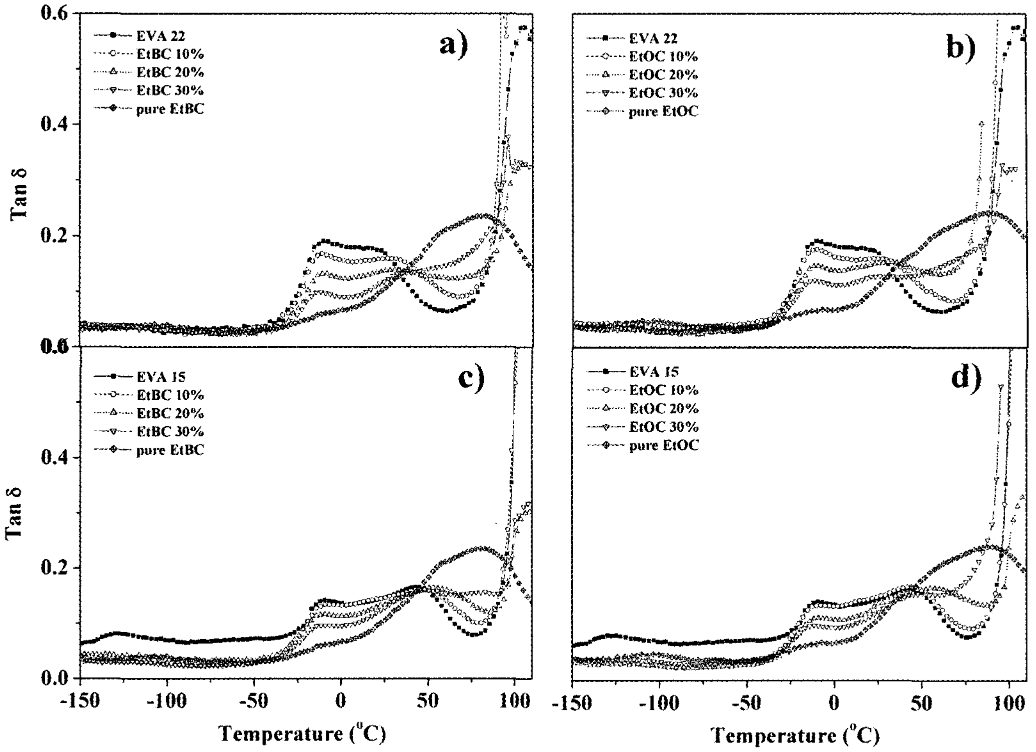

Figure 6. DMTA thermograms of tan δ. (a) EVA22/EtBC system, (b) EVA22/EtOC system, (c) EVA15/EtBC system, and (d) EVA15/EtOC system.

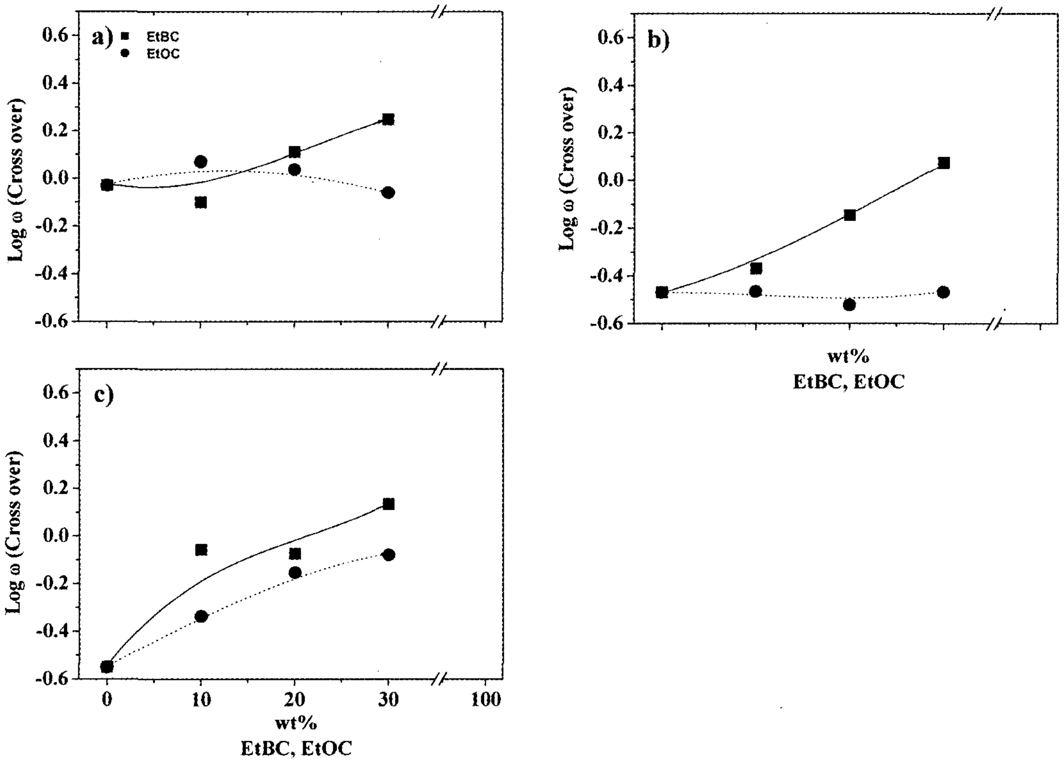

Figure 7. Comparison on the storage modulus (G') and loss modulus (G'') cross-over for EVA/EtBC and EtOC blends at 175 °C. (a) EVA28, (b) EVA22, and (c) EVA15.

of log G' and log G''. Then, the cross-over point (log ω) between log G' and log G'' in two blend systems was plotted as a function of the wt% of ethylene-α-olefin in Figure 7. Log ω (cross-over) lowers with decrease of VA content with same amount of EtBC and EtOC, and these values of EtOC system are lower than those of EtBC one. Since the cross-over point generally occurs between the plateau and terminal region, the lower value of the cross-over point implies relatively high molecular weight of the system. Thus, the lower values of the cross-over point in EtOC system than those of EtBC one may be the result of high molecular weight of the former system or the low molecular weight distribution.

Morphology. Figure 8 represents the dispersion of EtBC in EVA matrix from the cryogenically fractured surface upon nitrogen purge. The white particles representing EtBC are well dispersed in the EVA matrix and the portion of white particles increases with EtBC contents. In particular, 10 and 20 wt% of EtBC in the blends exhibit relatively small domain particles and fair dispersion. Whereas, Figure 9 shows the dispersion of EtOC in EVA matrix and very clear domain particles are observed, which means poor compatibility between the EVA matrix and ethylene-α-olefin copolymer. In addition, the more the EtOC content, the more aggregated dispersions with enlarged particles were observed. This behavior is presumably attributed to the interference of good dispersions due to longer side chain of EtOC than EtBC. In both blend systems, these blends are not apparently compatible. Since EVA is hydrophilic and ethylene-α-olefin copolymers are hydrophobic chemically, it is not surprising that these are not compatible each other.

Mechanical Properties. The mechanical properties were measured for the blends of EVA/EtBC and EVA/EtOC upon VA contents using stress-strain curve and the tensile strength, ultimate elongation at break, 100 and 300% modulus, and hardness were obtained. Figure 10 shows the tensile strength at break as a function of EtBC or EtOC. The highest value of the tensile strength was observed in EVA28/EtBC blend; this is interpreted to the higher content of VA, of which similar characteristics to rubbery material shows elastomeric property. On the other hand, EVA22/EtOC and EVA15/ EtOC blend exhibit slightly higher tensile strength

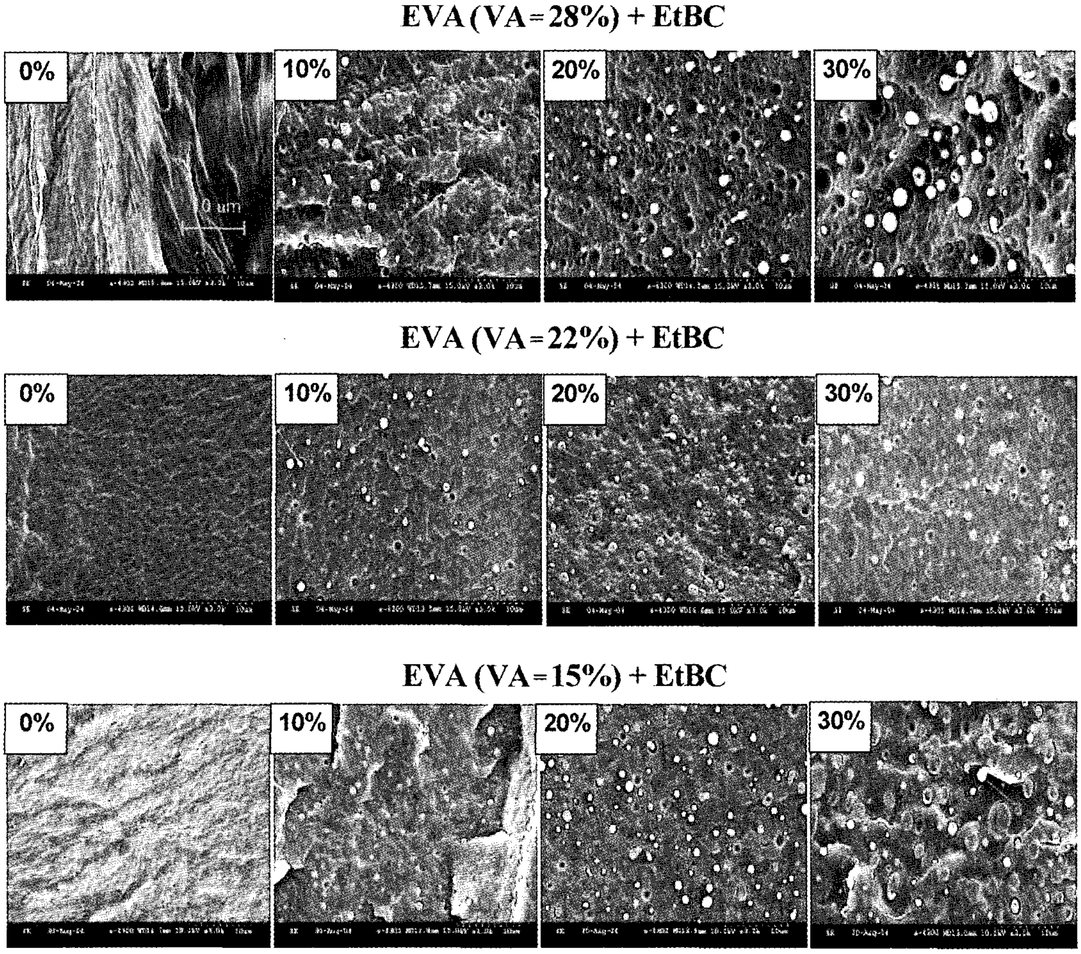

Figure 8. Comparison of SEM photographs on EVA (28, 22, and 15%) /EtBC blends.

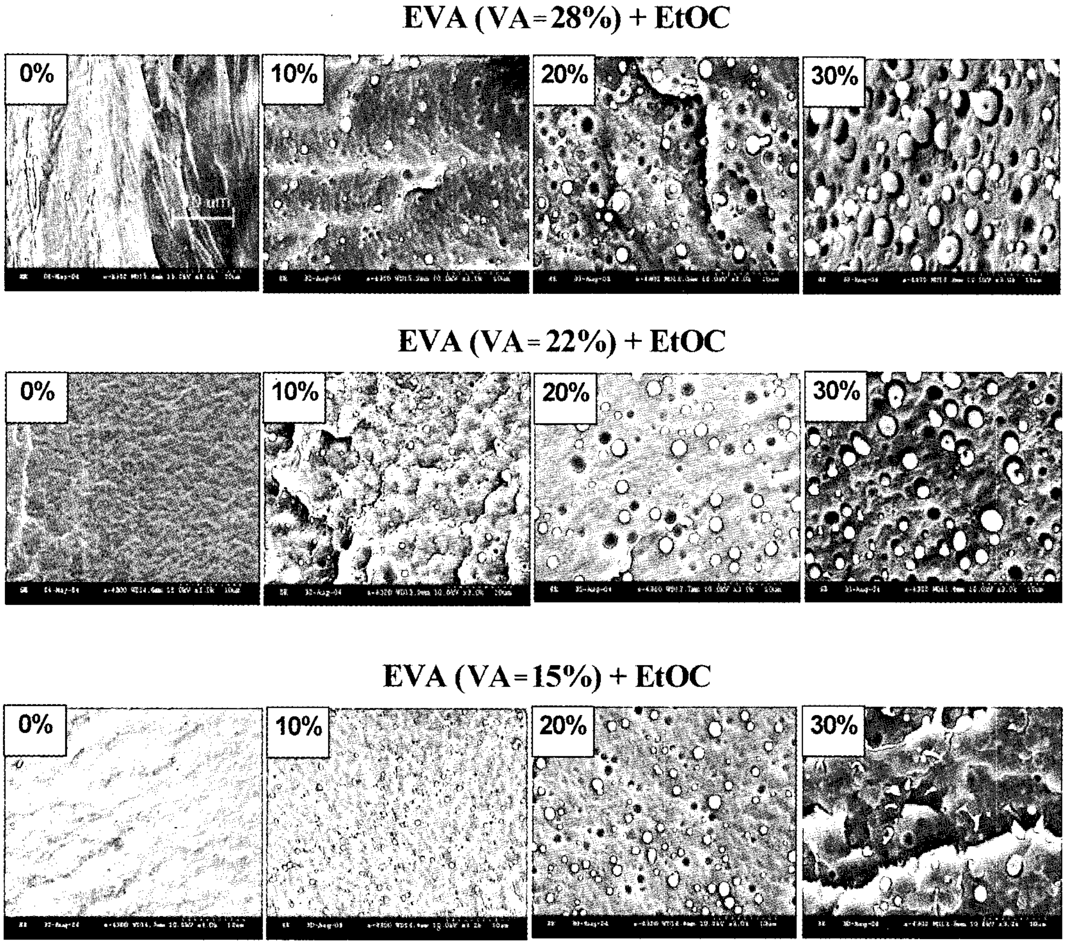

Figure 9. Comparison of SEM photographs on EVA (28, 22, and 15%) /EtOC blends.

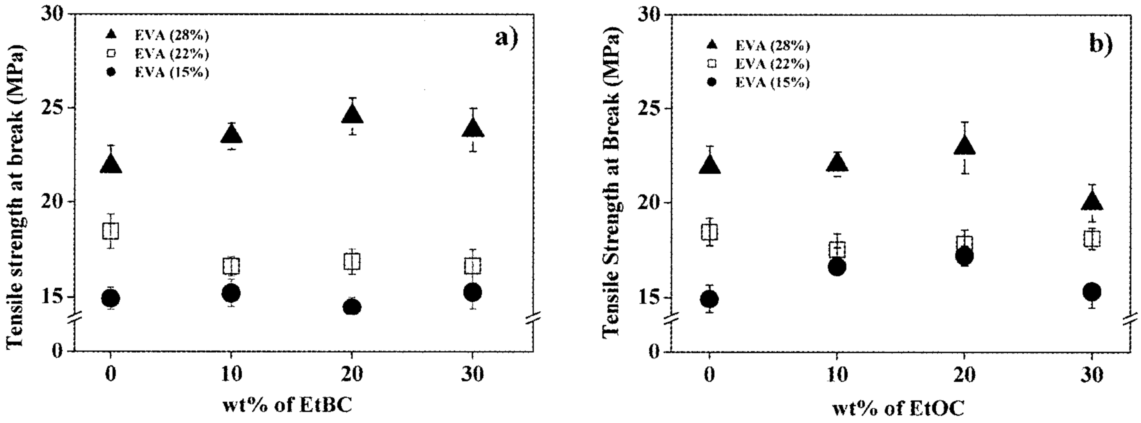

Figure 10. Tensile strength at break of EVA blends with various contents of (a) EtBC and (b) EtOC.

than that of EtBC system. From these observations, it is proposed that EVA28 blend would influence by rubbery EtBC, but EVA22 and EVA15 blends are rather dominated by stiff EtOC.

Figure 11 represents the ultimate elongation of EVA/ethylene-α-olefin copolymer blends. For EVA/EtBC blend, the ultimate elongation up to 30% of EtBC linearly decreases (from 1430 to 1300%) followed by the rule of mixtures. On the other hand, the ultimate elongation of EVA28/EtOC blend decreases linearly (1430 to 1150%), but for EVA22/

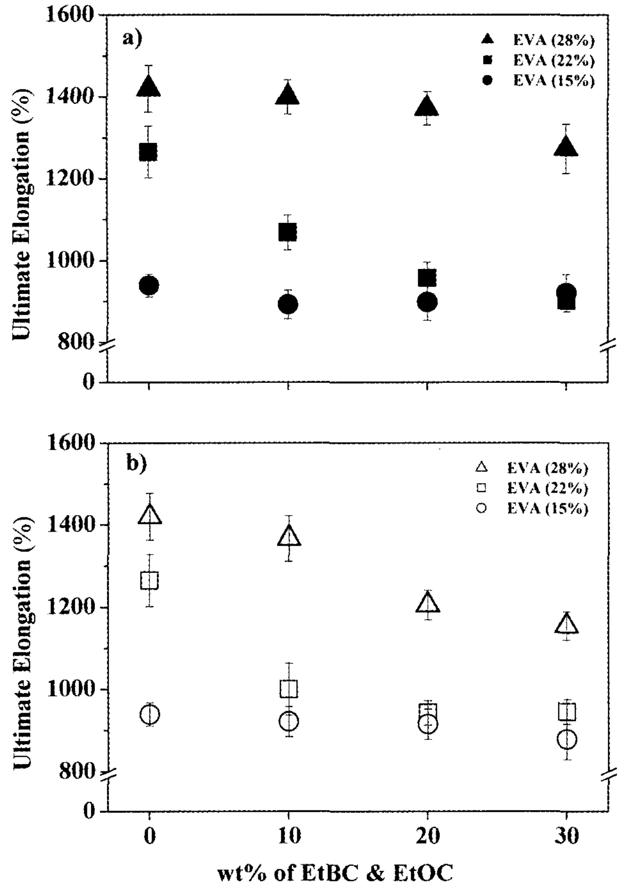

Figure 11. Ultimate elongation of EVA blends with various contents of EtBC & EtOC. (a) solid symbol : EtBC and (b) open symbol : EtOC system).

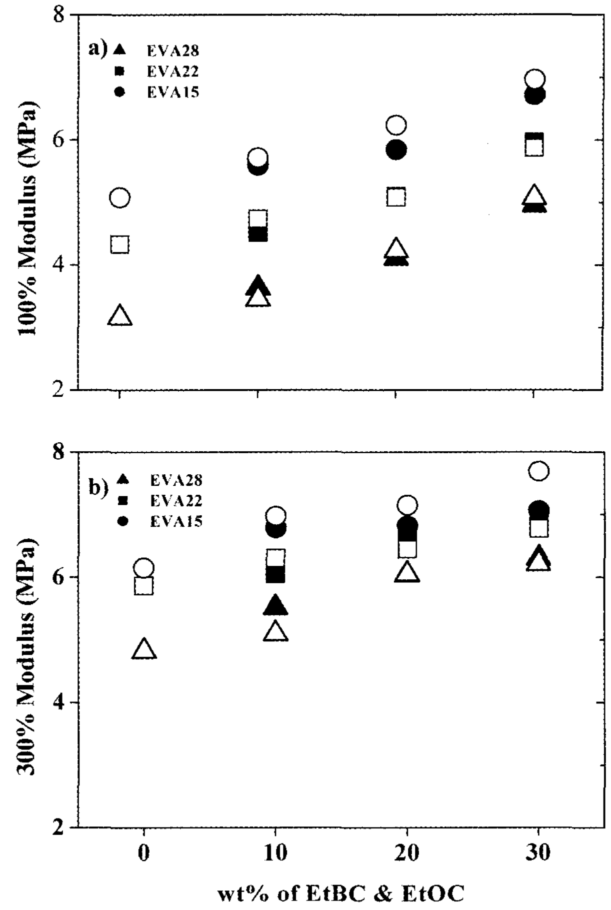

Figure 12. (a) 100% and (b) 300% modulus of EVA blends with various contents of EtBC (solid symbol) & EtOC (open symbol).

EtOC and EVA15/EtOC blends, this value depresses to 920-930% with EtOC. Thus, 22 and 15% of VA content is not enough to overcome the influence of the stiff structure of EtOC in the blends.

Since EVA/ethylene-α-olefin copolymers blend is applicable to shoe midsole, rubbery characteristics of the blends are interesting. Thus, 100 and 300% modulus is measured and the results are plotted in Figure 12. The common feature is that the 100 and 300% modulus increases with the content of ethylene-α-olefin copolymers. 100% modulus in EVA/EtOC blend is slightly higher than that of EVA/EtBC. For 300% modulus, all the modulus values augmented and the same trend as shown in 100% modulus is observed. Thus, the blend of EVA with ethylene-α-olefin copolymers may be applicable to be used for shoemid-sole without adding any further material.

In order to study the impact property, the hardness of the blends was measured and drawn in Figure 13. For all the compositions of EVA/EtBC and EVA/EtOC systems, the hardness linearly increased with ethylene-α-olefin copolymer under acceptable experimental error range. Since the structural geometry of EtBC or EtOC is stiffer than EVA, and the side chain of EtOC is longer than that of EtBC, the hardness of the blends is expected to increase with ethylene-α-olefin copolymers.[18] As a consequence, EVA/EtBC and EVA/EtOC blends are immiscible in the melt and solid state, but mechanically compatible, implying that the mechanical properties follow the rule of mixtures with experimental errors. In addition, although these blends are not miscible, the addition of ethylene-α-olefin copolymers into EVA matrix is working as a reinforcing material.

Conclusions

Thermal, viscoelastic, rheological, morphological, and mechanical behaviors of EVA/ethylene-α-olefin copolymers in the absence of compatibilizer were investigated using different VA contents in EVA matrix. In melting and crystallization thermograms on DSC, discrete melting and crystalline temperatures representing that of each constituent were observed, implying these blend systems are immiscible in the solid state. In dynamic mechanical thermal analysis, as

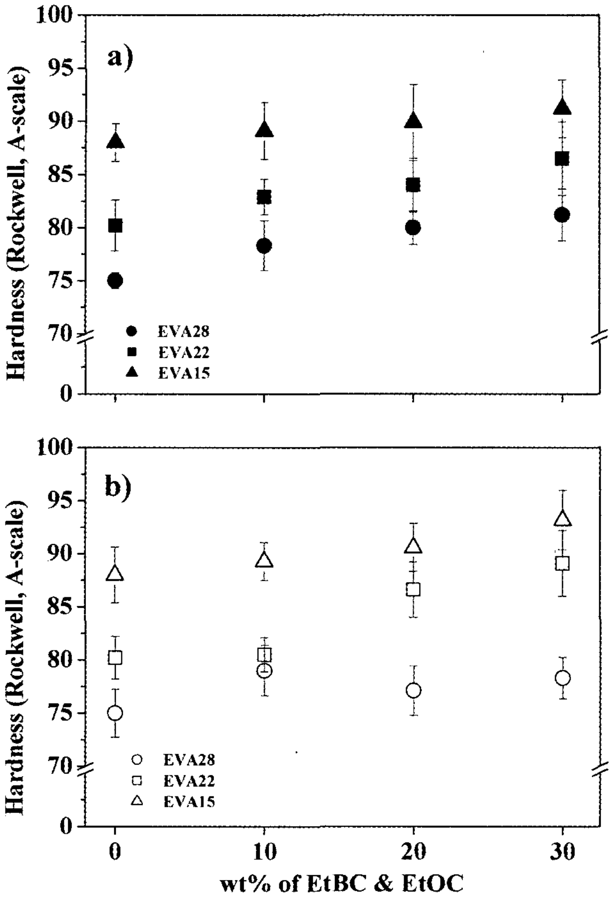

Figure 13. Hardness of EVA blends with various contents of EtBC & EtOC. (a) solid symbol (EtBC) and (b) open symbol (EtOC).

the content of ethylene-α-olefin copolymer increased, the storage modulus increased. In addition, the transition regions relating to tan δ peaks were varied with the content of VA. In complex melt viscosity, non-Newtonian behavior at almost all shear rates (ω) with respect to most of compositions was shown. In SEM investigation, the discrete phase morphology is observed in both EVA/EtBC and EVA/EtOC blend systems, but the contrast between the matrix and domain improved with less content of VA. In mechanical property, the tensile strength improved with 10~20 wt% of ethylene-α-olefin copolymers, and 100 and 300% modulus was also enhanced, but the elongation at break decreased with ethylene-α-olefin copolymers. In addition, the hardness increased with up to 30 wt% ethylene-α-olefin copolymers. Although EVA/ethylene-α-olefin copolymers are not miscible in the melt and solid state, they are mechanically compatible and it is worth while to show synergy effect for the application in shoemid sole.

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