Poly(ethylene-co-vinyl acetate) Blends with Phenoxy

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ABSTRACT: EVA was blended with phenoxy over the whole range of composition using a twin-screw Brabender. Two-phase separation caused by EVA crystallization was observed in the EVA-rich blends and the dispersed domain of EVA was not clearly shown in the phenoxy-rich blends. Differential scanning calorimetry (DSC) showed that the glass transition temperature (T_g) of EVA was increased by 5–10°C in the EVA-rich blends but the T_g of phenoxy was superposed over the melting behavior of EVA. X-ray diffraction measurement indicated that EVA crystallization was restricted in the phenoxy-rich blends and the EVA crystal structure was influenced by incorporation of phenoxy into the EVA-rich blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 227–236, 1999

Key words: poly(ethylene-*co*-vinyl acetate); poly(hydroxy of bisphenol A); X-ray diffraction; morphology; partial miscibility

INTRODUCTION

Polymer blends and alloys have received widespread attention during the last several decades. Polymer blends are defined as a physical mixture of two or more polymers. They may be divided into different categories: so-called miscible blends in which the components exist in a simple homogeneous phase and immiscible ones in which the components exist in two distinct separated phases. Generally, the former offer various advantages over the latter. The origins of miscibility between the polymer pairs have been understood based on theoretical background and experimental results.^{1,2} Most polymers are thermodynamically immiscible. In immiscible polymer blends, morphology is affected by the composition, viscosity ratio, interfacial tension, processing conditions, and so on. $^{3-5}$

Thermoplastic blends are a commercially important class of material. Both EVA and phenoxy

are commercially useful thermoplastics. Poly(ethylene-vinyl acetate) (EVA) is a thermoplastic elastomer sysnthesized from ethylene and vinyl acetate. EVA with a low content of vinyl acetate (VA) has similar properties to those of low-density polyethylene, whereas, with a high content of VA, it has properties like rubber. With increasing VA content, EVA becomes flexible and its degree of crystallinity decreases. The change of physical properties of EVA, by adding VA, results from the depression of crystallinity.⁶⁻¹⁰

Poly(hydroxy ether of bisphenol A) (phenoxy) is a linear thermoplastic, with a hydroxy group and an ether group, that promotes wetting and bonding to polar substrates and fillers. Phenoxy is a relatively tough and ductile amorphous polymer with an excellent oxygen-barrier property, good hydrophilicity, and good mechanical properties. It is well known that phenoxy is miscible with aromatic or aliphatic polyesters and with polyethers, due to the strong hydrogen bonding.¹¹⁻¹⁵

EVA and phenoxy have functional groups, a hydroxy and ether group and an ester group, and their solubility parameters are 20.66 and 17.48 $J^{1/2}$ cm^{3/2} mol⁻¹, respectively.¹⁶ Therefore, it is

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wave number (cm⁻¹)

Figure 1 FTIR spectra of EVA/phenoxy blends.

likely that EVA and phenoxy have the possibility to form partially miscible blends. The thermal, mechanical, flow, and morphological properties of EVA/phenoxy blends prepared by melting were investigated. In addition, the effect of phenoxy on the crystalline structure of EVA was also investigated.

EXPERIMENTAL

Materials and Blending

An EVA copolymer containing 28 wt % VA supplied by DuPont-Mitsui Polychemicals Co., Ltd. (Japan) was used and has an MFI of 5 g/min. The phenoxy used was of PKHH grade ($M_n = 50,700$) supplied by Union Carbide (U.S.A.). The binary blends of EVA/phenoxy in the composition ranges 90/10, 70/30, 50/50, 30/70, and 10/90 were prepared by melt mixing the appropriate quantities of polymers in a twin-screw Brabender (PLE 331) at a screw speed of 50 rpm at 180°C for 5 min.

FTIR

For the purpose of identifying the blends prepared in this study, infrared spectroscopy was performed using a Shimadzu DR-8100 FRIR spectrometer.



Figure 2 Shear stress as a function of shear rate for EVA/phenoxy blends.

Sample	EVA	90/10	70/30	50/50	30/70	10/90	Phenoxy
n	0.40	0.39	0.37	0.38	0.37	0.37	0.36

Table IValues of Power Law Index n

Differential Scanning Calorimetry

Thermal properties were measured using a differential scanning calorimeter (DSC) (TA 2010, Du-Pont). The samples were heated at the rate of 20°C/min to 180°C and kept isothermally for 3 min and then cooled to 20°C at the rate of 20°C/ min.

X-ray Diffraction

The crystalline structure of the samples was determined by a wide-angle X-ray diffractometer (Rigaku D/max-2500) using CuK α radiation with a scan speed of 5°/min.

Mechanical Measurement

The density of the samples was measured by a floating method in a CCl_4 and *n*-heptane mixed solution. Tensile properties were determined fol-

lowing the standard procedure described in ASTM D 638. The tensile tester (Testometric micro 350) was operated at a crosshead speed of 10 m/min. Tests were made at room temperature, and at least five runs were made to report the average.

Capillary Rheometer

Melt-rheological measurements were carried out on a piston-type capillary rheometer (Rosand Precision). The capillary was of a circular cross section (diameter 1 mm) and the length/diameter ratio was 16. The apparent shear stress and shear rate obtained from the rheometer, using the conventional expressions, were corrected using Bagley and Rabinowitsch corrections.

Scanning Electron Microscopy

The morphology of the blends was observed using a scanning electron microscope (SEM, Hitachi-



Figure 3 Shear viscosity as a function of shear rate for EVA/phenoxy blends.



Figure 4 DSC heating scans of EVA/phenoxy blends.

4100). SEM micrographs were taken from cryogenically (in liquid nitrogen) fractured surfaces of the blends. The fractured surfaces were sputtered with gold before viewing.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectra of the EVA/ phenoxy blends. The virgin phenoxy was identified by the peaks of a C—H single bond at 3000 cm⁻¹, the hydrogen-bonded OH group at 3200– 3500 cm^{-1} and the ether group at 1280 cm⁻¹, and EVA by the peaks of alkane at 3000 cm⁻¹ and the ester group at 1700 cm⁻¹. In the overall blends, these characteristic peaks appeared and no new peaks were clearly observed. This suggests that phenoxy and EVA are qualitatively mixed in the melt state by physical force.

Flow Properties

Flow curves, shear rate versus shear stress plots at 180°C, of the EVA/phenoxy blends at various compositions and the individual components are shown in Figure 2. As shear rate increases, shear stress also increases in the all samples. All the flow curves are quite linear in the studied range of the shear rate, obeying the Ostwald de Waele power law.^{13,17}

Both in high and low shear rate regions, the flow curves of the blends are between the two individual components and the slopes are similar. The values of the power law exponent, "n", evaluated by regression analysis of the data, are shown in Table I. The pure components and blends are quite similar in their values of n. They all show nearly pseudoplastic behavior. The separated domains formed in the melt state do not affect the flow of EVA/phenoxy blends.

The melt viscosity varies as a function of EVA content of the blend, as shown in Figure 3. The general trend of the decrease of viscosity with increasing shear rate is obeyed by the blends at all the blending ratios, as well as by the two individual components. The slopes are similar for all samples and the slopes of the blends are between the pure components which show a composition-dependent viscosity.



Figure 5 DSC cooling scans of EVA/phenoxy blends.



Figure 6 X-ray diffraction profiles of EVA/phenoxy blends.



Figure 7 Density of EVA/phenoxy blends.

The flow curve of the 10/90 blend is nearly equal to that of virgin phenoxy. In the blend system, the dispersed-phase domains tend to deform and orient along the direction of shear due to the effect of shear force.¹⁷ Very small domains do not

modify greatly the melt viscosity. The variation of melt viscosity can be explained on the basis of the variation of the number density and size of the dispersed domains in the matrix. As will be shown below in the Morphology section, the two



Figure 8 Elongation at break versus phenoxy content for EVA/phenoxy blends.



Figure 9 Stress at break versus phenoxy content for EVA/phenoxy blends.

polymers have a strong interaction in the melt state to form a nearly single phase.

Thermal Properties

Figure 4 shows DSC thermograms of EVA/phenoxy blends obtained from the first heating run.

Phenoxy shows a point of inflection at about 90°C, corresponding to its T_g as a typical amorphous polymer.

The melting peak temperature (T_m) of pure EVA appears at 75°C and the T_g at -20°C. In all the blends, the melting point of EVA was similar



Figure 10 Tensile modulus versus phenoxy content for EVA/phenoxy blends.



Figure 11 SEM micrographs of EVA/phenoxy blends.

to that of pure EVA and the $T_{\rm g}$ of phenoxy was superposed over the EVA melting behavior.

In phenoxy-rich blends, the EVA melting behavior was not clearly observed. It is likely that EVA crystallization was significantly interfered with by the rigid phenoxy chain. The T_g of EVA was shifted to higher temperature by about 5–10°C with increasing phenoxy content up to 50 wt %. This is because the flexible amorphous region of EVA was affected by the rigid phenoxy

chain and the chain mobility was restrained.^{18,19} In the crystalline/amorphous polymer blends, the T_g values lie between the two T_g 's of the components. These T_g shifts are indicative of partial miscibility.^{20,21}

The crystallization behavior is shown in Figure 5. Virgin EVA exhibits a crystallization peak at 50°C. With increasing phenoxy content, the crystallization peak was slightly shifted to higher temperature. The 10/90 blend shows no crystallization peak. Phenoxy preferentially dissolved in the EVA phase, resulting in the improvement of viscosity.^{21,22}

X-ray Diffraction

Figure 6 shows X-ray diffraction profiles of the EVA/phenoxy blends. Phenoxy shows a broad diffraction profile from 13° to 25° as a typical amorphous structure. For the virgin EVA, the peaks at $2\Theta = 20.8^{\circ}$ and 22.5° appear but are not clear.

In the EVA-rich blends (90/10, 70/30), the peaks are clearly shown and shifted to 21.4° and 21.8°. The corresponding Bragg spacing, d, relative to the interplanar spacing of crystal of virgin EVA at 4.27 Å, decreased to 4.11 and 4.07 Å, respectively. This implies that the EVA crystal structure can be changed by phenoxy. But in the 50/50 blend, the diffraction intensity was significantly decreased and it shows a broad diffraction profile.

In the phenoxy-rich blends, the diffraction profile follows that of amorphous phenoxy and the characteristic diffraction of EVA is not observed. It is also in accord with the result of thermal properties in which there were no clear characteristic melting peaks of EVA in the phenoxy-rich phase. This indicates that in phenoxy-rich blends EVA crystals could not grow through contact with the rigid phenoxy chain, whereas in EVA-rich blends, EVA crystals become more compacted by the rigid phenoxy chain.

Mechanical Properties

The densities of the EVA/phenoxy blends are shown in Figure 7. The densities of phenoxy and EVA are 1.17 and 0.95 g/cm³, respectively. Although the trend for the blends is similar to simple additivity, there is a positive deviation for the EVA-rich blends.

The mechanical properties of the EVA/phenoxy blends are shown in Figures 8–10. They show small negative deviations from simple additivity and relatively high deviation in strength and modulus due to the poor inherent interfacial interaction. As the content of phenoxy increases the elongation at break of EVA decreases but the strength and modulus increase significantly. The effect of phenoxy on EVA is much greater than that of EVA on phenoxy as evidenced by DSC and X-ray diffraction.^{23–25}

Morphology

Scanning electron micrographs of freeze-fractured surfaces of the EVA/phenoxy blends and pure components are shown in Figure 11. Phenoxy-rich blends (10/90, 30/70) show a very tough surface without a clearly dispersed EVA phase, while EVA exhibits a smooth surface like rubber. These blends show no clear phase separation. The dispersed EVA domain is not observed clearly and the number density and size of the EVA domain are unchanged despite increasing the EVA content in the phenoxy-rich blends. On the other hand, EVA-rich blends display phase separation. Crystal regions of EVA are observed as a dispersed domain in the blended amorphous matrix and the size of dispersed domains increase with increasing phenoxy content. It is also consistent with the results of X-ray diffraction that the diffraction intensity of EVA crystals increases and the crystal interplanar spacing is shorter, with the EVA-rich phase, and EVA crystallization was interrupted by the phenoxy-rich phase.

CONCLUSIONS

Phenoxy-rich blends exhibited a tough fractured surface without a clear phase of dispersed EVA in the phenoxy matrix. Interaction between EVA and phenoxy was strong enough to form a uniform structure and typical properties of EVA were not observed. On the other hand, EVA-rich blends showed phase separation which was caused by EVA crystallization. In these blends, the crystal structure of EVA is affected by the incorporation of phenoxy. The effect of phenoxy is much greater than that of EVA. It can be deduced that phenoxy and EVA are partially miscible in EVA-rich blends.

REFERENCES

 Paul, D. R.; Newman, S. N. Polymer Blends; Academic: New York, 1978.

- Olabisi, O.; Robeson, L.; Show, M. T. Polymer– Polymer Miscibility; Academic: New York.
- 3. Han, C. D. Multiphase Flow in Polymer Processing; Academic: New York, 1981.
- Utracki, L. A.; Shi, Z. H. Polym Eng Sci 1992, 32, 1824.
- Brukhart, R. D.; Zutty, N. L. J Polym Sci Part A 1963, 1, 1137.
- 6. Mark, H. F. Encl Polym Sci 1973, 6, 403.
- 7. Wu, H. F. J Polym Sci Part A-2 1970, 8, 153.
- 8. Wu, T. K. J Polym Phys Ed 1975, 12, 901.
- 9. Han, C. D. Rheology in Polymer Processing; Academic: New York, 1978; p 169.
- Robeson, L. M.; Furtek, B. J Appl Polym Sci 1979, 23, 645.
- 11. Defieuw, G.; Groeninkx, G.; Reynaers, H. Polymer 1989, 30, 2164.
- Iriate, M.; Espi, E.; Etxeberria, A.; Fernandez-Berridi, M. J.; Iruin, J. J. Macromolecules 1991, 24, 5546.
- Jung, J. H.; Son, T. W.; Lim, S. K.; Moon, B. H.; Kim, S. S. J Kor Fiber Sci 1997, 34, 16.
- 14. Pacific Polymer Conference Preprints, Kyongju, Korea, 1997; Vol. 5, p 195.

- 15. Van Krevelen, D. W.; Properties of Polymers; Elsevier: Amsterdam, 1990.
- Gupta, A. K.; Ratnam, B. K.; Srinivasam, K. R. J Appl Polym Sci 1992, 46, 281.
- Defieuw, G.; Groeninckx, G.; Reyaners, H. Polymer 1989, 30, 2164.
- Yang, X.; Painter, P. C.; Coleman, M. M. Macromolecules 1992, 25, 4996.
- Kim, B. K.; Choi, C. H. Polym Eng Sci 1996, 36, 1495.
- Kolarik, J.; Lednicky, F. Polym Eng Sci 1992, 32, 886.
- Kim, W. N.; Burns, C. M. J Appl Polym Sci 1990, 41, 1575.
- Kim, B. K.; Choi, C. H. Polym Eng Sci 1996, 36, 1495.
- Arridge, R. G. C. In Polymer Blends and Alloys; Folkers, M. J.; Hope, P. S., Eds.; Chapman & Hall: London, 1993.
- Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum: New York, 1976.
- 25. Proceedings ATC 97: The 4th Asian Textile Conference, Taipei, Taiwan, 1997; Vol. 1, p 110.