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Interaction between ethylene vinyl acetate copolymer and polyethylene

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Summary

Low density Polyethylene (LDPE) and Ethylene Vinyl Acetate (EVA) Copolymer have been processed at 170°C for 7 minutes. Dynamic mechanical analysis shows a single composition dependent glass transition temperature of the 50:50 EVA/LDPE blend. Infrared spectra of pure EVA processed at the same condition shows splitting of >C=0 stretching band of EVA while spectra of the 50:50 EVA/LDPE blend shows a well resolved single band. Thermogravimetric analysis of the blend shows greater stability than those of the pure components. A schematic mechanism ascribing to the synergistic effect observed is proposed.

Introduction

In recent years, blends containing a judicious combination of a homopolymer with its copolymer have gained considerable attraction, particularly when the components are semicrystalline. The structural similarity between the polymers may lead to some sort of compatible composition, sometimes through the co-crystallization phenomenon (1,2).

Compatibility phenomenon between Polyethylene and Ethylene Vinyl Acetate (EVA) copolymer was studied by Kovacs and Kallo (3) through electron microscopy. Recently, a detailed study on the relation between morphology of EVA/LDPE blends and their mechanical properties, dynamic mechanical properties and electrical resistivities have been communicated (4). We have also reported the stress-strain behaviour of EVA/LDPE blends and the effect of straining and process parameters on the microstructure of the blends (5,6). Grafting of EVA on PBTP has been studied by earlier researchers (7).

Experimental

Materials used

Materials used for the investigation have the following characteristics :

	Characteristics	Trade name	Producer
EVA	VA content 28% d = 0.95 gms/c.c. MFI = 6g/10 min.	PILENE 2806	PIL;INDIA
LDPE	d = 0.92 gms/c.c. MFI = 0.2g/10 min.	INDOTHENE 20CA002	IPCL;INDIA

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Preparation of the blends

Blending was carried out in a Brabender Plasticorder (PLE-330) fitted with a cam type rotor. Temperature was set at 170°C and rotor speed at 60 r.p.m. LDPE was first allowed to melt in the Plasticorder, followed by addition of EVA. Mixing carried out for about 7 minutes until the torque was stabilized. The mixed mass was then compression molded at 150°C under 10 MPa pressure.

Thermogravimetric analysis

Thermogravimetric Analysis (TGA) were carried out in a 951 Thermogravimetric Analyser fitted with Dupont Thermal Analyser-9000 in nitrogen atmosphere at a heating rate of 20°C min^{-1}

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical measurements were carried out on a dynamic mechanical analyser (Rheovibron DDV-III-EP). The experiment was performed in tension mode from -150°C to +150°C at a frequency of 3.5 Hz at 0.17% dynamic strain amplitude with a programmed heating rate of +2°C min^{-1}

Infrared Spectrophotometric study

Infrared Spectrophotometric analysis of the blend and the pure components were performed with a Perkin-Elmer 843 model. Thin films were used for analysis. The spectral resolution was kept at 2.40 cm^{-1} for all samples and the scan was taken at room temperature.

Results and Discussion

Figure 1 shows TGA traces of the 50/50 EVA : LDPE blend and the individual components. Both pure EVA and the 50/50 blend show a two - step decomposition. However, the second plateau is wider in the case of 50/50 blend revealing greater thermal stability of the blend compared to that of pure EVA.

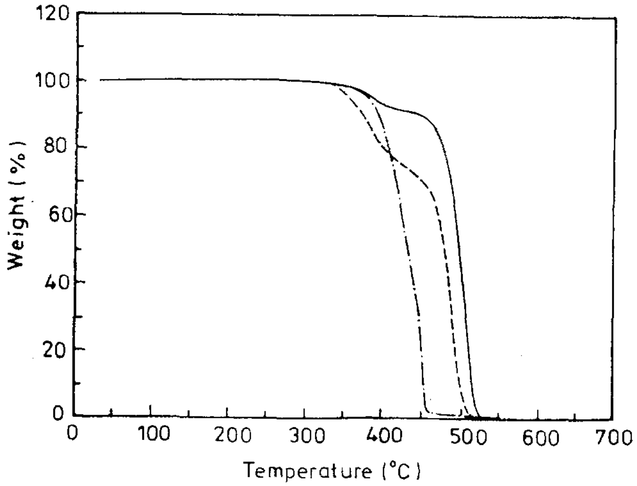


FIG. 1 TGA curves of EVA (- - -), LDPE (- · — · -) and 50:50 EVA / LDPE blend (——)

Fig.2 shows that the activation energy (E_a) of the 50:50 EVA/LDPE blend (8) calculated through Freeman Carroll's equation (9) deviates from weighted average value. This indicates the existence of some chemical interaction between the components of the blend .Similar observation have been reported by other authors(10). This may be explained by IR analysis.

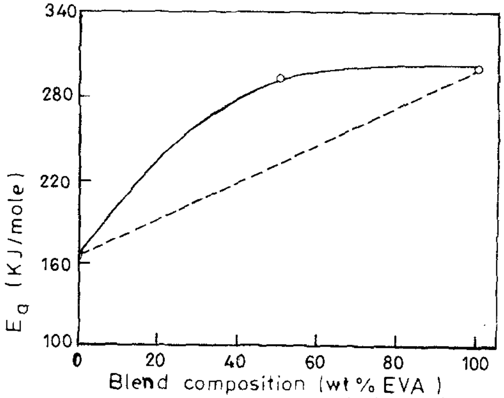


FIG.2 Plot of activation energy vs. blend composition

Figure 3 shows different relaxation peaks of pure LDPE, pure EVA and their 50/50 blend. These peaks are termed as α , β and γ in the decreasing order of temperature. The γ - peak is considered as the glass-rubber relaxation temperature (Tg) of polymethylene groups which is the main backbone of both LDPE and EVA (11). Now, theoretical Tg as predicted for comptaible blend from Gordon-Taylor and Fox equation show close agreement with that of the experimental value of 50/50 blend (4). This implies some degree of compatibility (miscibility) between LDPE and EVA copolymer. Morphological study reveals formation of interpenetrating network structure of blends. The samples were subjected to IR analysis to find the possibility of any chemical interaction between the two polymers.

Figure 3 represents the IR spectra of pure EVA and 50/50 blend of EVA and LDPE in the 1900-1600 cm^{-1} region (>C=0 stretching region).

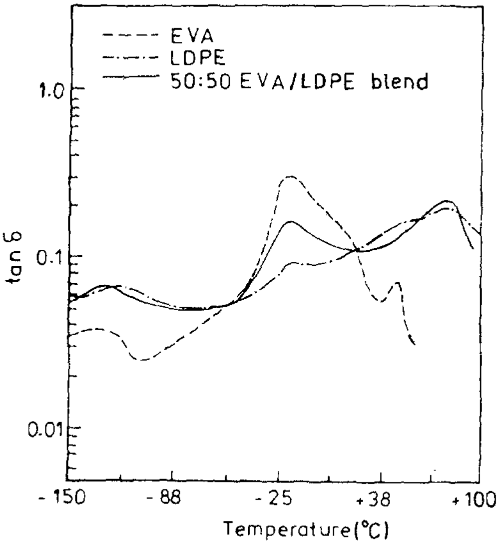


Fig.3 tan δ vs. Temperature plot of EVA, LDPE and blend

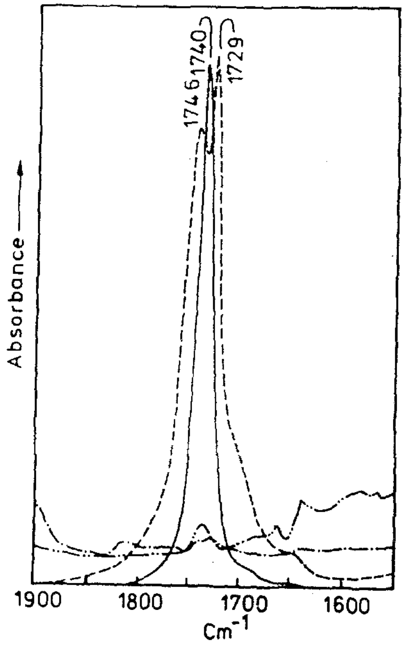
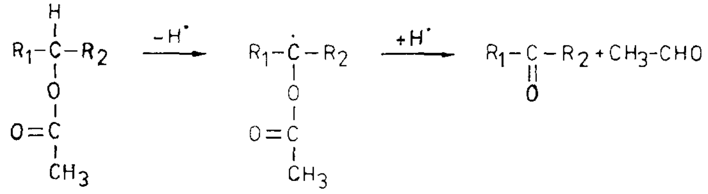


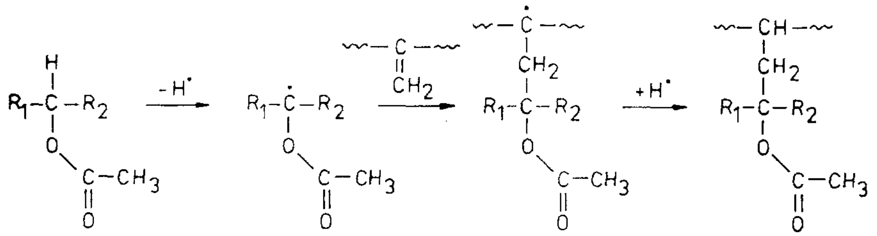
Fig.4 IR spectra of EVA (- -), LDPE(-··-), 50:50 blend (——) processed at 170°C and LDPE at 130°C(-··-).

The spectra of pure EVA shows two distinct carbonyl peaks at 1746 cm^{-1} and at 1729 cm^{-1}. The 1746 cm^{-1} peak is assigned to the >C=0 stretching vibration of the vinyl acetate group (12). The second peak at 1729 cm^{-1} may be assigned to the keto carbonyl stretching vibration (12,13). The formation of Ketone group in pure EVA during processing is schematically represented by the following reaction scheme:



Similar observation have been made and the above mechanism have been proposed by Sultan and Sörvik (13).

Interestingly, the IR spectra of the blend (processed under the same condition) in the 1900 - 1600 cm^{-1} region show a single well resolved >C=0 stretching band at 1740 cm^{-1} which implies no trace of keto-carbonyl group. The absence of keto group in the blend may be attributed to the reaction of the macroradicals (formed during processing through abstraction of the α - H - atom of EVA) with the vinylidene group of LDPE (13). The reaction may be represented schematically by the following steps:



The macroradical formed on the vinylidene C - atom of LDPE after combination with EVA macroradical may terminate in either of the following ways, (a) addition of H• radical, (b) reaction with an EVA macroradical or (c) liberation of a H• radical from adjacent methylene group. The case (b) may be ruled out due to steric factor. Possibility of liberation of a H• radical case (c) may also be eliminated, since the bond energy of C - H bond is ~ 100 kcal/mole compared to ~60 kcal/mole for >C=C<(14). So, the only possibility left for the termination of the macroradical by addition of a H• radical. Thus it may be inferred from IR analysis of pure EVA and 50/50 blend of EVA and LDPE that under the action of heat and shearing at the process condition LDPE-g-EVA is being formed.

Conclusion

Observed synergistic effect in thermal stability of the blend compared to either of the pure components supports the occurrence of grafting reaction between the two polymers as shown by IR study. The γ - transition temperature of EVA and LDPE involves the mobility of the main chain in the amorphous region. So, if the amorphous region is affected by some means, the γ - transition will shift accordingly. Here, the grafting reaction is taking place in the amorphous region of both the polymers. Hence this grafting reaction may be one of the reasons behind the shift of the γ - transition temperature indicating miscibility between the component polymers.

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