

Evaluation of the Role of Ethylene Vinyl Acetate on the Thermo-Mechanical Properties of PET/HDPE Blends

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Abstract-In this paper, blends of recycled polyethylene terephthalate (r-PET) and high-density polyethylene (HDPE) with and without a compatibilizer were prepared using a Brabender Haake Rheocord at 270°C and 32rpm. Ethylene vinyl acetate was chosen as the compatibilizer and its proportion was set to 5, 7, and 10 wt%. The thermal properties and crystallization behavior were determined by Differential Scanning Calorimetry (DSC). Micromechanical properties were also investigated using a Vickers microindentation tester. The DSC analysis indicates that the melting temperature of r-PET and HDPE in all the blends, compatibilized and uncompatibilized, remains constant and almost the same as those of the pure component. On the other hand, it is shown that the degree of crystallinity of HDPE in the blends calculated by DSC depends on the composition of the polymeric mixture. However, the Hardness (H) decreases with increasing r-PET content until 50/50 composition of r-PET/HDPE is reached, whereas for larger r-PET content values, H increases. The same trend was obtained with the addition of the compatibilizer.

Keywords-recycled polyethelene terephthalate; DSC; hardness; compatibilization

I. INTRODUCTION

Recycling plastic waste not only preserves energy and raw resources but also provides an option of plastic waste disposal [1-3]. For both economic and environmental reasons, the interest in recycling polymeric materials has significantly increased over the last few decades [4]. Recycled polymers, however, are subjected throughout thermal and mechanical processes that result in structural and morphological changes, which in turn have an impact on the material qualities. Blending recycled polymers with unmodified polymers could be an approach to enhance their properties. In practice, formulating polymer blends is a viable method for developing materials with relatively new combinations of specified features. An important portion of post-consumer waste is made up of high density polyethylene (HDPE) and polyethylene terephthalate (PET), which are widely utilized in the packaging of consumer and industrial items.

Due to the unique combination of its physical and mechanical properties, which include great thermal resistance, strong fatigue resistance, and good solvent resistance, PET has revolutionized the globe with its use [5, 6]. On the other hand, HDPE, due to its wide use in the packaging industry, contributes greatly to environmental degradation [7], in the light of the structural considerations by the absence of specific interactions and according to [8-10] affirming the non-compatibility of PET with polyolefins. Due to the poor mechanical characteristics of PET/PE blends, compatibilizers must be used in order to decrease interfacial tension, which in turn increases morphological stability and interfacial adhesion. The study of the binary PET/HDPE polymeric system with the use of compatibilizing agents has been the subject of several research works. Among the most commonly used compatibilizers in HDPE/PET blending systems are graft copolymers containing reactive Maleic Anhydride (MA), functional groups such as MA-grafted polyethylene (PE-g-MA) [11, 12], HDPE-g-MA [13], and Maleic Anhydride-grafted Styrene-Ethylene-Butene copolymer (SEBS-g-MA) [14]. Another group of compatibilizers often used in research are the random copolymers containing GMA, such as HDPE-g-GMA [15], ethylene-glycidyl methacrylate copolymer (E-GMA) [16], Ethylene Ethyl-Glycidyl Methacrylate (E-EA-GMA) [15], and Ethylene Butyl Acrylate-Glycidyl Methacrylate (EBA-GMA) [17]. Other possibilities that are also promising have been investigated, such as compatibilizing the PET/HDPE system with an epoxy chain extender [18].

The indentation test is one of the easiest methods of determining a material's micromechanical characteristics [19, 20]. This method has been successfully used in a wide range of systems and is extremely sensitive to changes in the morphology and microstructure of polymers. In one of our previous research works [21], we investigated how combining clay and a compatibilizer SEBS-MAH affected the microindentation hardness (H) of PET/HDPE.

The objective of the current study is to investigate the rheological, thermal, and mechanical properties of recycled

PET (r-PET) and HDPE blends as a function of their composition, compatibilized with Ethylene Vinyl Acetate (EVA).

II. MATERIALS AND METHODS

The following materials were used in this investigation: recycled r-PET bottles from Bangkok Polyester Public Co., Bangkok (Thailand), commercial grade HDPE ALCUDIA 6006 (REPSOL) with Melt Flow Index (MFI): 0.56g/10 Min. The EVA used is UL00218CCN from EXON CHEMICALS with an MFI of 1.5g/10 Min. Before blending, the r-PET pellets were dried in vacuum at 105°C for 16h. The dried r-PET pellets were dry-mixed with the HDPE pellets in the following weight ratios: 25/75, 50/50, and 75/25. The blends were prepared in a Brabender Haake Rheocord type M, at 270°C and 32rpm in two steps. At first, the r-PET was fed into the chamber, and once it was melted, the HDPE and the EVA compatibilizer were added. From the preceding blends, films were prepared by compression molding in a 7102 Zwick machine (Ulm, Germany), at a pressure of 150kg/cm². The compression was performed at 275°C for a duration of 6min (4min for preheating and 2min for compression). A Zwick Universal Testing Machine (UTM) was used to study the tensile properties of the blends as per ASTM D 638 standard. The crosshead speed was 50mm/min.

The thermal study was performed with the help of a Perkin Elmer (Norwalk, Connecticut, USA) DSC-7 Differential Scanning Calorimetry (DSC) instrument in an inert N₂ atmosphere. The weights of the samples were 5–10mg. The studied temperature range was 50–300°C. The heating rate was 10°C/min. The crystallinity measured by DSC (α_{DSC}) was derived from the melting enthalpy obtained by DSC with the following expression:

$$\alpha_{DSC} = \Delta H_m / \Delta H_m^\infty \quad (1)$$

where ΔH_m and ΔH_m^∞ are the experimental melting enthalpy and the melting enthalpy for an infinitely thick crystal, respectively. For PET, the ΔH_m^∞ used was 140.1J/g [21] and for HDPE 293.86J/g [22].

Microhardness H was determined at room temperature with a Leitz (Wetzlar, Germany) microindentation tester with a square-based diamond indenter. The H value was derived from the residual projected area of indentation according to the following expression [23]:

$$H = kP/d^2 \quad (2)$$

where d is the length of the impression diagonal (m), P is the contact load applied (N), and k is a geometrical factor equal to 1.854. Loads of 0.5 and 1N were applied. The loading cycle was 0.1min. Ten indentations were performed on the surface of each sample, and the results were averaged.

III. RESULTS AND DISCUSSION

Figure 1 shows the variation of the equilibrium torque as a function of the % r-PET in the blends. It was found that the torque of the blends without EVA decreases for up to a 50% increase of the amount of r-PET. Beyond this threshold, the

torque values stabilize. The same trend was observed with the addition of EVA to the different blends. It was observed that the r-PET/HDPE (50/50) blends show the lowest torque values for all formulations with and without EVA. This can be explained by the large contact area at equivolume percentage between the two polymers, thus reducing the transformation energy of the blends.

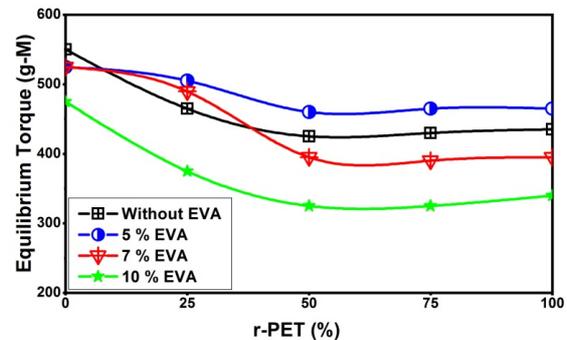


Fig. 1. Variation of the equilibrium torque as a function r-PET percentage.

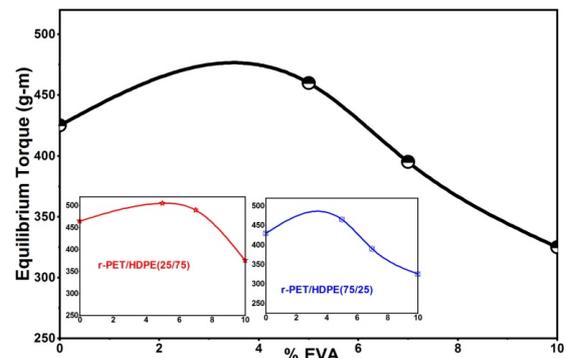


Fig. 2. Effect of % EVA on the equilibrium torque.

The change in equilibrium torque was displayed as a function of % EVA in order to visualize the impact of the addition of EVA on the r-PET/HDPE (50/50) blends (see Figure 2). It was found that the torque increases with the addition of EVA up to 5% indicating that there may have been interactions between the polymers, which increase the flow resistance. Further, the torque decreases with increasing EVA content, which is probably due to the increase in the free volume created by the EVA. It was also noted from the results of the MFI (not shown here) that the MFI increases with the increasing percentage of the r-PET in the blends. This increase is not too significant at low concentrations of r-PET, but it is noticeable at high concentrations. It was also noted that the addition of EVA affects both polymers in a significant degree, slightly decreasing the MFI of HDPE and acting as a plasticizer for r-PET, while the blend values remain very complex. However, the values of the blends of r-PET/HDPE 50/50 concentration are the lowest for all formulations with EVA compared to the MFI values without EVA, showing a resistance to flow, confirming the equilibrium torque results. Figure 3 shows the variation of stress at break as a function of the incorporation rate of R-PET with and without the addition of EVA.

The stress at break values of r-PET are higher than that of HDPE while their blends show lower values than those of homopolymers. This can be explained by the dimixture between these two polymeric phases due to their incompatibility. It should be also noted that the stress values of the r-PET/HDPE 75/25 blends are very close to those of the greater amount of component, i.e. r-PET, while the r-PET/HDPE 25/75 blend has a stress value close to that of HDPE. Thus, the minor component has a dispersed spherical morphology in the major part and therefore the properties of the blends are those of the high concentration polymer as it absorbs all the stresses when subjected to a load or force. With the addition of EVA, the results are better. An addition of 5% EVA improves the stress at break of the blends up to 10%. This rise is caused by a decrease in interfacial tension, which in turn improves the adhesion between the two phases of the individual polymers. As a result, EVA has reduced the phase border energy, increasing the phase boundary area. The greater the phase boundary area, the more effectively energy can be transferred from one phase to another, improving the mechanical characteristics.

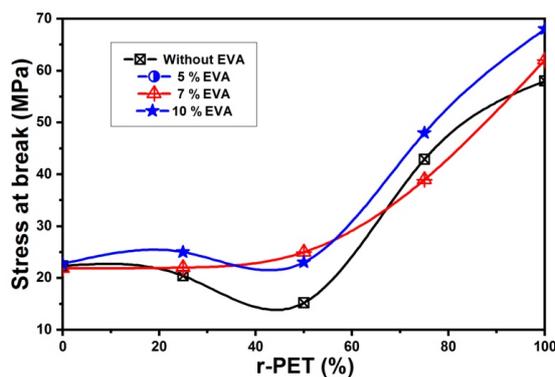


Fig. 3. Effect of the concentration of the EVA on the stress at break of the r-PET/HDPE blends.

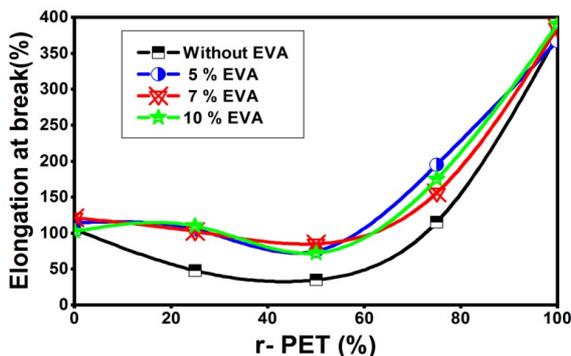


Fig. 4. Effect of the concentration of the EVA on the elongation at break of the r-PET/HDPE blends.

The incompatibility of the r-PET blends with the HDPE of the binary blends without EVA is reflected much more in the elongation at break (Figure 4), where the values obtained are significantly lower than those of the homopolymers for all compositions. The calorimeters limit such resolutions and the T_g of one of the components of the mixture (HDPE) is below

0°C. On the other hand, the glass transition temperature of r-PET, which is around 70-80°C, was not detected in some thermograms, perhaps due to the presence of HDPE in the compositions and the melting temperature T_m of the HDPE. Authors in [24] were able to detect the T_g of r-PET in r-PET/PP blends of 75/25 composition and this temperature was almost the same as that of pure r-PET. Therefore, we limited ourselves to the study of the melting temperature and the determination of the crystallinity. The thermograms in Figures 5, 6 reveal that the T_m values of both components were nearly constant throughout all of the compositions and were the same as those of the pure polymers. $T_m = 122-131^\circ\text{C}$ for HDPE and $241-249^\circ\text{C}$ for PET. As a result, the blending method had little effect on the crystal thickness (l_c) of the components.

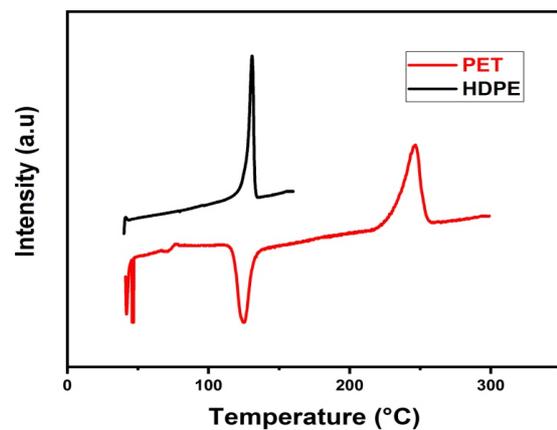


Fig. 5. DSC thermograms of neat polymers.

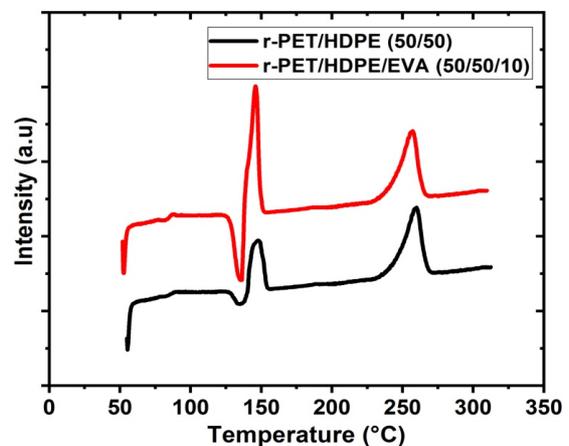


Fig. 6. DSC thermograms of the r-PET/HDPE (50/50) blends with and without EVA.

The Thomson-Gibbs equation was employed to determine the l_c value of each component. Consequently, the l_c value calculated was 25nm and 14nm for PET and HDPE respectively. The crystallization temperatures for the r-PET component were found to have somewhat decreased values. The crystallinity decreased as the r-PET level increased for all compositions (pure blends and blends with compatibilizer).

Figure 7 shows the H of the various blends as a function of the r-PET content. The H 's additivity behavior is depicted as a straight line. It is evident from the plot that neither the uncompatibilized nor compatibilized blends with EVA respect the additivity law of a binary blend as a function of composition. With increasing PET content, the blends became harder and deviated from linearity. EVA caused a reduction in H , which was more evident as the compatibilizer concentration increased. According to the two-phase model, the H of a semicrystalline polymer can be described by [22]:

$$H = H^{r-PET} \phi_1 + [H_c^{HDPE} \alpha^{HDPE} + H_a^{HDPE} (1 - \alpha)](1 - \phi) \quad (3)$$

Equation (3) considers the compositions of the blends as well as the crystalline H_c and amorphous H_a hardness of each individual component. The H values for the blends with EVA were noticeably lower than those obtained from the additivity law in accordance with (3). It is evident that the compatibilizer's two primary effects on these blends were a decrease in their crystallinity and a concurrent decrease in their hardness.

TABLE I. PURE r-PET/HDPE BLENDS AND BLENDS WITH EVA

Composition	HDPE crystallinity (%)	T_m (°C) r-PET	T_m (°C) HDPE
r-PET.HDPE (100/0)	0	249	129
r-PET.HDPE (75/25)	0.15	248	130
r-PET.HDPE (50/50)	0.23	249	127
r-PET.HDPE (25/75)	0.49	247	130
r-PET.HDPE (0/100)	0.53	247	129
r-PET.HDPE/EVA(100/0/5)	0	248	126
r-PET.HDPE/EVA (75/25/5)	0.09	249	128
r-PET.HDPE/EVA (50/50/5)	0.08	248	129
r-PET.HDPE/EVA (25/75/5)	0.12	246	129
r-PET.HDPE/EVA (0/100/5)	0.23	249	130
r-PET.HDPE/EVA(100/0/7)	0	248	129
r-PET.HDPE/EVA(75/25/7)	0.09	248	127
r-PET.HDPE/EVA (50/50/7)	0.03	249	128
r-PET.HDPE/EVA (25/75/7)	0.09	246	130
r-PET.HDPE/EVA (0/100/7)	0.10	248	129
r-PET.HDPE/EVA(100/0/10)	0	246	127
r-PET.HDPE/EVA(75/25/10)	0.10	249	129
r-PET.HDPE/EVA (50/50/10)	0.18	248	127
r-PET.HDPE/EVA (25/75/10)	0.10	247	129
r-PET.HDPE/EVA (0/100/10)	0.12	249	128

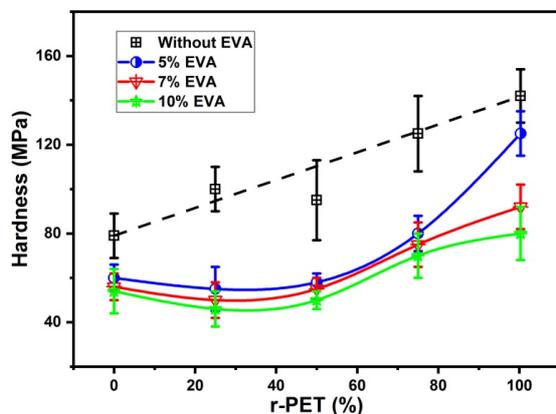


Fig. 7. Hardness dependence on the r-PET content with and without EVA.

IV. CONCLUSION

It is evident from the obtained results that PET was incompatible with HDPE, but the presence of EVA as a compatibilizer allowed combinations of these polymers. The compatibilization of blends with additional small quantities of EVA in one processing step is an interesting proposal, particularly for recycled blends, because it does not require prior expensive synthesis and leads to better results. The r-PET/HDPE 50/50 blends show the lowest torque values for all formulations with and without EVA caused by the large contact area at equivolume percentage between the two polymers. The T_m values of both components were nearly constant for all compositions and were the same as those of the pure polymers. The composition was the only factor influencing the crystallinity of the r-PET/HDPE blends (pure blends and blends with compatibilizer), whereas the PET affects the crystallizability of the HDPE component. The blending method had little effect on the crystal thickness of the components and the calculated values for PET and HDPE were 25nm and 14nm respectively. Moreover, the presence of the EVA strongly induced a hardness decrease in the blends.

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