THE INFLUENCE OF EVA AND PE-g-AM COMPATIBILIZERS ON THE PROCESSABILITY, MECHANICAL AND STRUCTURAL PROPERTIES OF RECYCLED PET / HDPE MIX

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Protecting the environment by reducing PET waste has become a global priority. Recycling is considered one of the simplest and most environmentally friendly ways to reduce PET waste. However, during recycling, PET undergoes thermal / hydrolytic degradation, which leads to reduced molecular weights and low physical, mechanical, chemical, etc. properties. Thus, in order to prevent the degradation processes and to improve the mechanical and processing properties, various blends based on PETr / HDPE (60: 40 mass ratio) will be processed on a Brabender mixer in the presence / absence of the compatibilizers, EVA and PE-g-AM. The diagrams of torque versus time, recorded during processing demonstrate that PETr suffers degradation processes, which leads to a decrease in torque due to reduced viscosity /molecular weight and reduced physical-mechanical and processing properties. Instead, with the addition of EVA or PE-g-AM, in varying amounts, degradation processes are largely avoided. These observations are also supported by the values obtained from the Izod impact resistance tests, namely the higher the amount of compatibilizer, the higher the shock resistance due to the higher phase adhesion. The hardness of the blends progressively decreases, relative to the PETr control sample value, from 83 to at least 61°Sh D for the compatibilized blends. FTIR microscopy, performed on the obtained samples, shows higher homogeneity between PETr / HDPE if the addition of EVA or PE-g-AM is higher (20%). Melt flow index is improved for compatibilized blends compared to PETr and PETr / HDPE.

Keywords: polymer blends, compatibilisers, characterization.

INTRODUCTION

Polyethylene terephthalate (PET) is one of the most common thermoplastic polyesters used in various products such as carbonated beverage bottles, packaging foils, synthetic fibers used in the textile industry, electronics, and other applications due to its superior chemical, physical, mechanical and barrier (oxygen, carbon dioxide) properties. Due to the high consumption of PET products and its non-biodegradable nature, it raises many environmental problems, with a high interest in recycling and re-use. However, during recycling, PET suffers thermal and hydrolytic degradation, which leads to a lower molecular weight and, implicitly, to poor mechanical, thermal properties (Guessoum *et al.*, 2013). In this regard, to improve these properties, many research studies have focused either on mixing with one or more polymers or on the addition of reinforcing agents. The most common polymers used in PET blends are polypropylene-PP (Chen *et al.*, 2018), high density polyethylene - HDPE (Krehula *et al.*, 2015), and low density polyethylene-LDPE, etc.

A problem in the processing of these two classes of polymers (polyesters and polyolefins) is related to the thermodynamic incompatibility between the phases

(separation, lack of adhesion, weak dispersion) leading to poor mechanical and barrier properties. Thus, compatibility is fundamental to obtaining optimal properties for both PET and recycled / virgin polyolefin. Because of its structure, PET has the ability to chemically react with polar polymers and form polar-specific interactions such as hydrogen bonding (Dobrowszky and Ronkay, 2016). Improving the compatibility of these heterogeneous systems can be achieved by various methods including reactive mixing and injection molding processes. Thus, the improvement of phase compatibility is favored by the presence of block copolymers or graft copolymers because they have the ability to reduce interfacial tension, improve dispersion and adhesion between phases through interpenetration and entanglements at the polymer / polymer interface (Pracella *et al.*, 2004). The most common block or grafted copolymers used to improve the compatibility between PET and polyolefin are maleic anhydride polyethylene (PE-g-MA), maleic anhydride-grafted styrene-ethylene/butylene-styrene (SEBS-g-MA), maleic anhydride-grafted EVA copolymer (EVA-g-MA), amino-telechelic polyethylene (ATPE), and ethylene vinyl acetate copolymer resins etc. (Todd *et al.*, 2016; Taghavi *et al.*, 2017).

MATERIALS AND METHODS

Materials

Polyethylene terephthalate in the form of flakes was obtained by the industrial partner SC MONOFIL SRL by recycling of municipal waste bottles using a knife mill; ethylene vinyl acetate copolymer resins (EVA), Elvax, vinyl acetate content: 9wt%, anti-oxidant - butylated hydroxytoluene, DuPont; maleic anhydride modified mLLDPE (PE-g-AM) - Bondyram TL4109E, MFI 190°C/2.16 Kg: 2, density g/cm³: 0.905, melting point °C/°F: 117/243, VICAT softening point °C/°F: 85/185, maleic anhydride %: high, from Polyram, Israel; high density polyethylene, SIDPEC EGYPTENE® HD 6070 UA HDPE Injection Molding, Sidi Kerir Petrochemicals Co, Egypt.

Method

Before pelleting, PETr flakes were subjected to an advanced pre-drying process at 150°C in a hot air oven for a minimum of 24 hours to remove the adsorbed physical water. After flakes drying, binary (PETr / HDPE in 60:40 wt) or ternary (PETr / HDPE / PE-g-AM or EVA) mixtures formulations were processed in a Brabender mixer at 240°C with screws speed ranging from 30 rpm for about 2 minutes to 110 rpm for 5 minutes. The total mixing time in the Brabender mixer, from loading with the raw materials until all components were homogenized, was 7 minutes for all the processed blends. As Table 1 shows, the PETr / HDPE ratio was 60: 40 wt% for all samples and the amount of compatibilizers used (PE-g-AM or EVA) was 10 or 20 wt% relative to the total amount of PETr and HDPE present in the blend. Figure 1 shows a sudden drop in torque (from 220 to 145 Nm and subsequently to 30 Nm) for PETr melt mixing - sample 0, depending on time and screws speed (30 or 110 rpm), indicating that degradation processes occur. The reduction of intrinsic viscosity / molecular mass is especially evident in case of sample 0, which undergoes hydrolytic / thermal degradation to a much higher extent compared to sample 1 - torque increases from ~ 45 Nm (screws speed at loading - t_0 , 30 rpm) to 75 Nm after a mixing time of 60 seconds at 110 rpm, and decreases progressively, although to a much lower extent than sample 0.

For samples 2 and 3, a torque increase from 60 Nm (t_0) to ~ 110 Nm after 70 seconds is observed, which indicates that the viscosity of the mixture increases. Viscosity also increases in samples 4 and 5, however, to a lesser extent than samples 2 and 3, indicating that the type of compatibilizer used influences the viscosity of the mixture and prevents degradation processes. Figure 2 shows that for sample 0 a higher mixing energy (90 kJ) is required in the first 240 sec. (4 min) compared to samples 1-5. However, for samples 2-5 containing compatibilizers, the energy required for mixing is much higher compared to samples 0 and 1 after a mixing period of 180 seconds, due to the increase and maintenance of a higher viscosity in the melt. These results demonstrate that degradation reactions responsible for viscosity reduction are significantly avoided by the addition of compatibilizers, observations confirmed by impact resistance tests. From the processed blends, test specimens with a length of 100 mm and a thickness of 4 mm were obtained in an electric press at a temperature of 243°C, pressing time of 7 minutes, pressure force 300 kN. The obtained specimens were used to determine Izod impact resistance and hardness. The morpho-structural analyses were performed in fracture, on the specimens obtained after Izod impact resistance tests.

Table 1. Formulations based on PETr / HDPE with / without compatibility

Samples/ Raw materials	0	1	2	3	4	5
PETr, g	280	168	168	168	168	168
HDPE, g	-	112	112	112	112	112
PE-g-AM, g	-	-	28	56	-	-
EVA, g	-	-	-	-	28	56
TOTAL, g	280	280	308	336	308	336

Figure 1. Variation of torque vs. time for samples 0-5, processed in Brabender

Figure 2. Variation of mixing required energy vs. time for samples 0-5, processed in Brabender

RESULTS AND DISCUSSION

Physico-Mechanical Tests

Izod Impact resistance recorded for samples 0-5 shows significant changes, induced by the type and amount of compatibility agents. Thus, for sample 0, impact resistance shows an extremely low value of only 1.2 kJ/m². Practically, these specimens are so

friable that they break when the notch is made. An improvement in friability can be seen in the case of the addition of HDPE - sample 1, although due to the incompatibility between the phases, impact resistance records a low value of only 1.83 kJ/m^2 . Significant improvements could be seen with the addition of 10% PE-g-AM (Sample 2) and 20% PE-g-AM (Sample 3), the impact resistance being 7.93 and 12.91 kJ/m^2 respectively. This can be attributed to the fact that the addition of a higher amount of PE-g-AM improves the compatibility between the phases due to the reactions taking place between the various phase components, and prevents the degradation processes. In the case of 10% and 20% EVA addition, the impact resistance improves compared to samples 0 and 1 but to a much lower extent than samples 2 and 3. The obtained results are in very good concordance with the FTIR microscopy, which shows that the higher the compatibilizer quantity (20%), the more the degree of homogeneity of mixtures increases.

Figure 3. Physical-mechanical determinations and melt flow index of samples 0-5

Hardness of the mixtures decreases from 83°ShD for sample 0 to 72°ShD for sample 1 (PETr / HDPE). For mixtures containing EVA or PE-g-AM, a hardness drop is observed as the amount of compatibility increases.

Melt flow index was determined on samples 0-5 at 254°C and a 5 kg force. As can be seen from Figure 3, sample 0 - PETr has the lowest fluidity index of all the mixtures tested. This was to be expected because the higher the torque and the hardness the lower the fluidity index. Significant improvement in the indexes could be seen in samples 4 and 5, which shows that EVA improves flow properties. The samples containing 10 and 20% PE-g-AM (samples 2 and 3) shows a decrease of melt flow index up to 90.1 and 89.1 due to the increase in viscosity in the polymer melt (also highlighted by the torque / hardness tests). However, samples 2 and 3 did not raise processability issues, and the results obtained from physico-mechanical / morpho-structural tests showed that these mixtures have superior properties compared to other mixtures.

FTIR Microscopy

The FTIR microscopy was recorded on the fracture surface of the samples, and the maps recorded at the specific wavelengths of the components are presented in Figure 4.

Figure 4. FTIR maps recorded at the specific wavelengths of the components

All the obtained samples were analyzed by FTIR microscopy and for all samples, good homogeneity was observed, being similar with the two examples provided in Figure 4. Based on the FTIR spectra of the samples it can conclude that the best peaks to monitor the distribution of PETr, HDPE and EVA are those centered at 1740, 1460 and 1261 cm^{-1} while for the PETr, HDPE and PE-g-AM the best peaks are 1737, 1104

and 730cm^{-1} (even if some peaks are overlapped, the distribution of the three components can be evaluated because the contribution of the overlapped peaks can be subtracted according to the intensity of other peaks) (Bui *et al.*, 2016).

CONCLUSIONS

Improving the adhesion, processability and physico-mechanical properties of the PETr / HDPE mixture is possible by the addition of suitable compatibilizers to limit the thermal or hydrolytic degradation processes, and the creation of optimal bonding at the polymer / polymer interfaces. The obtained results show that the PE-g-AM compatibilizer induces better properties to mixtures compared to EVA. Based on the FTIR data, it can be concluded that the use of PE-g-AM and EVA induces a very good compatibility between PETr and HDPE and this can be also highlighted in the fracture area.

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