Research Article

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Studies On Compatibilization Of Recycled Polyethylene/Thermoplastic Starch Blends By Using Different Compatibilizer

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Abstract: In this study, the aim was to examine the effects of three different compatibilizers on the recycled polyethylene/ thermoplastic starch (r-LDPE/TPS) blends which are used in producing garbage bags. Polyethylene-Grafted-Maleic Anhydride (PEgMAH), maleic-anhydride modified ethylene propylene rubber (EPMgMAH) and ethylene maleic anhydride copolymer (PEMAH) were selected as the compatibilizers. r-LDPE/TPS blends with or without compatibilizer were prepared by using a twin screw extruder and characterized by means of mechanical, thermal, structural and morphological analyses. It was found that tensile strength values increased with the addition of PEgMAH but decreased with the addition of EPMgMAH. Elongations at break values of the r-LDPE/TPS blends were significantly improved by using PEgMAH and EPMgMAH. T_m and T_c values have slightly affected by the compatibilizer usage in the DSC analysis. In addition, the better interfacial interaction was observed for the compatibilized blend with the PEgMAH and EPMgMAH during the SEM analysis. It was concluded that PEgMAH and EPMgMAH showed mainly changed results in elongation at break values and this is the important parameter in the packaging industry.

Keywords: Biopolymer, thermoplastic starch (TPS), recycled polyethylene, compatibilizer

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1 Introduction

In recent years, plastic material consumption increased rapidly worldwide. Every year tons of plastics go to the landfill. In the European Union, some measures have been taken and the amount of materials that goes to the landfill has decreased but still tons of material go to landfill. Recycling is the most commonly used method to tackle this issue and to protect the environment from the plastic pollution [1-2]. The mechanical recycling process is a physical method and the new product forms from the plastic wastes by cutting, shredding or washing into granulates, flakes or pellets of appropriate quality for manufacturing, and then melted to make items by extrusion. The reproduced material can also be blended with neat material to obtain superior results [3]. Many scientists have tried to use other methods to reduce synthetic polymer waste after usage. In one method, to produce an environmentally friendly polymer, synthetic polymers such as polyolefins and vinyl polymers, are blended with cheap biopolymers such as cellulose and starch [4]. Thus, the polymeric materials which are degradable and/or biodegradable have been obtained since the 1970s [3]. Biopolymer can degrade in the soil much faster than synthetic polymers. But, their mechanical properties are weak when used alone. That is the reason for why natural biopolymers often used with other synthetic based polymers [5].

Starch is a bio polymer that is cheap and very easy to find. It is not a thermoplastic but in the presence of plasticizer at high temperature and under shear rate, it can be easily melted and flow, similar to most of the synthetic thermoplastic polymers [6]. It plasticized with the glycerol-like plasticizer to make thermoplastic starch (TPS). TPS has wide range of properties due to the plasticizer type and loading level. Its low oxygen permeability is an interesting property for packaging industry [7]. TPS is often used with other polymers such as polyethylene (PE) for packaging applications. Various studies have reported the blending PE and TPS [8, 11].

However, the necessary mechanical properties have not been obtained for packaging applications owing to incompatibility between PE and TPS. Deterioration was reported in the transparency, tensile elongation, tensile strength, tear strength, and gas barrier properties of the PE/TPS blends [12-13]. The compatibilizers, which are containing reactive groups and nanofillers were used to overcome this drawback. [8]. A few compatibilizers such as polyethylene-co-vinyl alcohol (EVOH), polyethylene-co-acrylic acid (EAA), polyethylene-co-glycidyl methacrylate (PEgMA) and polyethylene-g-maleic anhydride (PEgMAH) have been studied for the PE/TPS blends [9]. PEgMAH as a compatibilizer has been used in a few studies and the good efficiency of PEgMAH was shown by the esterification reaction between maleic anhydride groups of PEgMAH and hydroxyl groups of starch, as well as good interaction of its non-polar chain with the PE matrix [9-14]. To the author's knowledge, recycled PE have not been used in the reported compatibilizing studies. In addition, a comparison study of the effects of PEgMAH, maleic-anhydride modified ethylene propylene rubber (EPMgMAH) and ethylene maleic anhydride copolymer (PEMAH) on the TPS/PE blends has not been studied.

Thermoplastic polymers are used many times until eventually, they lose their properties. However, they can be recycled from wastes and used as garbage bag before to sending to landfill. In this study, the effects of three different type of compatibilizer on the properties of r-LDPE/TPS blends that are used in producing garbage bags were investigated. r-LDPE/TPS and compatibilized r-LDPE/TPS blends were prepared by using a twin screw extruder and characterized by means of mechanical, structural, thermal and morphological analyses.

2 Material and method

2.1 Materials and Preparations of the Blends

Recycled polyethylene (rPE) was used in study and it was provided from Polipro Plastic Recycling Company in Turkey. rPE has a melting temperature at 123.4°C and a crystallization temperature at 110.9°C. Thermoplastic starch was obtained from Sunar Starch Company with 28 wt.% glycerol content (Adana, Turkey).

Samples were prepared by using a twin screw extruder Poex T-27, with the screw diameter 27 mm and L/D ratio 48:1. Compounds were produced with 140 to 160°C barrel temperature with screw speed 400 rpm. The compositions of the prepared blends were given in Table

Table 1: Compositions of the Prepared Blends.

Samples	RLDPE	TPS	PEgMAH	PEMAH	EPMgMAH
rPE40T	60	40			
rPE40T5P	55	40	5		
rPE40T10P	50	40	10		
rPE40T5PM	55	40		5	
rPE40T10PM	50	40		10	
rPE40T5E	55	40			5
rPE40T10E	50	40			10

Figure 1: The chemical structure of the using compatibilizers.

1. TPS content fixed at 40 wt.% in the r-LDPE/TPS blend. rPE40T was produced to use for the control sample. Three different types of compatibilizer were used. The chemical structures of using compatibilizer are shown in Figure 1. Two different loading levels were used for compatibilizer, 5wt. % and 10wt.%.

2.2 Characterization of LDPE/TPS Blends

2.2.1 Mechanical Properties of the Blends

Tensile properties of specimens were measured by using Lloyd LC universal tensile testing machine equipped with 5 kN load cell as a load indicator and long stroke extensometer as extension indicator. Testing speed was set to 50 mm/min and gauge length (Lo) was set to 100 mm. Izod impact strength of specimens was measured by using Ceast 9050 Izod impact machine which could operate between 0.5 and 25 Joule energy range.

2.2.2 Thermal Properties of the Blends

The thermal properties of the samples were obtained by TA Instruments (Model Q20) differential scanning

calorimeter (DSC). DSC analysis was performed according to ISO 11357-1. All of the blends were heated between 25°C and 300°C at 10°C/min heating rate. The samples were then cooled to room temperature at a cooling rate of 10°C/min to determine their crystalline characteristics. The sample weights were in the range of 8–10 mg. All measurements were made under a nitrogen atmosphere. The percentage crystallinity of the produced sample was determined using the following equation;

$$X_c (\% \text{crystallinity}) = \Delta H_c / w_f * \Delta H_m^0 * 100$$

Where ΔH_c is the crystalline enthalpy for each sample, obtained from the DSC curve, w_f is the weight fraction of r-LDPE, and ΔH_m^0 is the enthalpy heat of 100% crystalline LDPE. ΔH_m^0 was used as 279 J/g [15].

2.2.3 Determination of Chemical Interaction

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed to determine the compatibility between the matrix material and compatibilizer. A structural analysis of the blends was also undertaken. Samples were measured with a Bruker Alpha model FTIR-ATR Spectrometer over a range of 400–4000 cm^{-1} with ISO 10640:2011 standard.

2.2.4 Morphological Study by Scanning Electron Microscopy (SEM)

Samples were prepared by the fraction surface of the impact test samples. Small pieces were coated with pre-gold and characterized by QUANTA 400F Field Emission scanning electron microscope at an operating voltage of 20 kV.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Mechanical Properties

Tensile strength and elongation at break values of the prepared blends were given in Figure 2-3. Tensile strength values increased with the addition of PEGMAH but decreased with the addition of EPMgMAH. The drop in tensile strength is an expected result for the maleic anhydride modified EPM rubber. EPDM can be

easily blended with PE in all ratios. If the elastomer is predominant, the blends showed elastomeric properties and can be used in the uncured state in many applications. At the adverse condition, interesting modifications of plastic are obtained such as impact resistance [16-17]. Sadek et al. studied the blends of ethylene propylene diene terpolymer (EPDM) rubber with thermoplastic polyolefins such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), high molecular weight polypropylene (PP), and polypropylene random copolymer grade (PP-R) [17]. They showed that the tensile strength value of the EPDM/LDPE blend decreased by the increasing loading level of EPDM in the LDPE matrix. They arranged them according to their values of tensile strength as PP-R > PP > HDPE > LDPE > EPDM

PEGMAH has slightly increased the tensile strength value for the r-LDPE/TPS blends in this study. PEGMAH compatibilizer has increased tensile strength value up to 9.5 MPa by using 5wt.% but this value decreased using the 10wt.% PEGMAH. It can be concluded that PEGMAH should be used under the 5wt.% loading for the 40% TPS included blends when it is used as the compatibilizer. Bikiaris et al. studied the different loading level of polyethylene/plasticized starch blends by using a poly(ethylene-g-maleic anhydride) copolymer as a reactive compatibilizer [10]. They reported a better dispersion of TPS within the LDPE matrix by using compatibilizer, due to the significant reduction in the phase size, indicating an increased adhesion between the two polymers. This case also enhanced the tensile strength values of the blends with a high plasticized starch (20 and 30wt%).

Elongations at break values of the r-LDPE/TPS blends were significantly improved by using PEGMAH and EPMgMAH. The highest elongation at break value was obtained by including 10wt.% PEGMAH sample. PEGMAH however, showed a negative effect on the elongation at break value and it decreased this value when it was used as 10 wt.% in the blend. The low elongation value for the r-LDPE/TPS blends is an important limitation for the production of blown films from these materials [11].

Impact strength values of the prepared r-LDPE/TPS based blends were depicted from Figure 4. This value was increased with the addition of the EPMgMAH. This increase can be contributed to the rubber or elastic properties of the EPM. It was also observed that this significant improvement was with the addition of the PEGMAH. PEGMAH has decreased the impact strength values at the studied range as so the tensile properties.

Figure 2: Tensile strength values of the prepared r-LDPE/TPS based blends.

Figure 3: Elongation at break values of prepared r-LDPE/TPS based blends.

Figure 4: Impact strength values of prepared r-LDPE/TPS based blends.

3.2 Thermal Properties

DSC measurements were undertaken to characterize the thermal behavior of the prepared samples. Melting temperatures (T_m), crystallization temperatures (T_c), the enthalpy of melting and the enthalpy of crystallization values of the compounds were obtained from the DSC analysis. DSC analysis parameters and the thermal diagrams were given in Table 2 and Figure 5 respectively. According to DSC curves, T_m and T_c values were not

Table 2: DSC results of the control sample and compatibilized blends.

Samples	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$	ΔH_m (j/g)	ΔH_c (j/g)	X (%)
rPE	123.4	110.9	144.8	131.5	47.1
rPE40T	124.2	109.2	50.2	48.4	28.9
rPE40T5P	123.8	110.1	71.6	69.9	45.6
rPE40T10P	123.2	110.7	62.2	59.7	42.8
rPE40T5PM	123.7	109.4	63.8	63.2	41.1
rPE40T10PM	123.4	109.4	61.1	59.9	42.9
rPE40T5E	123.1	110.0	66.2	62.9	41.0
rPE40T10E	123.7	109.7	69.4	64.6	46.3

significantly affected by the compatibilizer type and loading level in the usage range in r-LDPE/TPS blend. T_m values diminished in the range of 1.0-1.7°C. Crystallinity value of the r-LDPE decreased with the addition 40% TPS to the r-LDPE. % crystallinity values were increased with the addition of compatibilizers to the rPE40T compared to the control sample % crystallinity value. The decrease of the crystallinity of rPE with the addition of TPS can be explained by two ways in the literature [18]. The first one is that the addition of starch obstructed the molecular chain motion of rPE in the cooling stage. The other one is that the interfacial tension between starch and LDPE limited the migration and diffusion of long-chain branched PE to the crystal form and therefore hindered the crystallization during the cooling.

The T_c in the compatibilized blends with the PEGMA begins close to that of pure rPE, it shows that PEGMA diminishes the effects of starch on crystallization of LDPE [18]. This case was observed for PEGMAH and EPMgMAH in this study. It is supposed that these two compatibilizers decrease the interface tension between the TPS and rPE. SEM micrograph showed this to be the case.

3.3 Morphological Study

SEM microphotographs of the control sample and compatibilized blends were given in Figure 5. A lot of empty spots and rough surface for incompatibilized blend or control sample were observed due to the incompatibility between rPE and TPS. In addition to this, it was observed to be very smooth with better interfacial interaction for the compatibilized blend with the PEGMAH and EPMgMAH. There was also no determined phase separation for these blends. We can say that these compatibilizers improve the

Figure 5: DSC curves of prepared r-LDPE/TPS based blends.

Figure 5: SEM Photographs of prepared r-LDPE/TPS based blends.

compatibility between rPE and TPS. On the other hand, when it was compared with the control sample with the PEMAH compatibilized blend, a similar structure was observed for these blends. Therefore, addition of PEMAH

did not significantly change the structure of the r-LDPE/TPS blend.

Figure 6: FTIR Spectrums of prepared r-LDPE/TPS based blends.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

The compatibilizers effect on the r-LDPE/TPS blends was evaluated by FTIR analysis. FTIR spectra of the blends with or without compatibilizer were shown in Figure 6. According to starch spectrum, the bands at the region of 3200–3400 and 2850–2900 cm^{-1} are attributed to OH stretching and CH_2 stretching vibrations [6]. TPS has peaks at 1150 and 1078 wavenumbers attributed to C-OH stretching vibration. These peaks shape and intensity changed with the addition of compatibilizers [19]. The increments were observed at this peaks intensity for PEgMAH and EPMgMAH. When the PEMAH as the compatibilizer, the peak intensity decreased at 1150 and 1078 wavenumber. The better compatibility of the polymer blend meant the correlative peaks shifted and the peak shapes altered owing to the mechanism of compatibility [19]. The FTIR spectra showed PEgMAH and EPMgMAH successful interacted with TPS. However, PEMAH didn't affect any interaction between PE and TPS. Besides, FTIR spectra confirmed tensile strength results and SEM analysis.

4 Conclusion

The effects of three type of compatibilizer on the properties of r-LDPE/TPS blends were investigated. r-LDPE/TPS and compatibilized r-LDPE/TPS blends were prepared by using a twin screw extruder and characterized by means

of mechanical, thermal tests and morphological analyses. PEgMAH showed better tensile results as compatibilizer among the others in this study. Elongation at break values of the r-LDPE/TPS blends were significantly improved by using PEgMAH and EPMgMAH. It is also concluded that PEMAH did not show a good effect on the elongation at break value in the used loading level. Elongation at break values is more important for garbage bags, therefore PEgMAH is more suitable than EPMgMAH. EPMgMAH showed better impact values in LDPE/TPS blends. PEgMAH and EPMgMAH can be suggested for r-LDPE/TPS blends for different applications. For applications which require better impact resistance, EPMgMAH can be evaluated within the LDPE/TPS blends.

Conflict of interest: Authors declare no conflict of interest.

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