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Morphology, mechanical and dynamic mechanical properties of recycled high density polyethylene and poly(vinyl alcohol) blends

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Abstract

Blends of post-consumer high density polyethylene (HDPEr) and poly(vinyl alcohol) (PVA) were prepared with maleic anhydride-grafted HDPEr (HDPEr-AM), as the compatibilizer, to evaluate the effectiveness of the PVA as a modifier for polyethylene and influence of PVA concentration on the blend properties. Films of polyethylene having biodegradable polymers could be a good solution for agricultural purpose since they can degrade more easily. The blends HDPEr/HDPEr-AM/PVA were investigated by physical tests, dynamic-mechanical analysis (DMA) and scanning electron microscopy (SEM). Thermal properties were measured by means of differential scanning calorimetry (DSC). The blend HDPEr/HDPEr-AM/PVA (50/10/40) with 10wt% of compatibilizer showed the highest tensile strength (28 MPa) compared to the blends (60/40) without compatibilizer (11 MPa). On the other hand, morphologic analysis showed synergism of the polymers in the blend HDPEr/HDPEr-AM/PVA (30/10/60), with 10wt% of compatibilizer. Overall, it was observed that the blend HDPEr/HDPEr-AM/PVA with composition of (70/10/20) showed the best properties for agricultural films processing application.

Keywords

PVA, HDPE, blends, properties, crystallinity

Introduction

High density polyethylene is a ubiquitous material with versatile properties and is widely used due to its mechanical strength, low cost, easy processability and resistance to chemical and biological attack [1]. It is used extensively in many fields, including agricultural and food-packing films [2]. However, some concern has been placed on pollution, since plastic waste accumulates in the environment, leading to long-term environmental and waste management problems. There has been an increased interest in enhancing the polyethylene biodegradability and blending it with polar biodegradable polymers such as amide, poly (vinyl alcohol) (PVA) [3,4], polyhydroxylbutyrate (PHB) [5], and poly(lactic acid) (PLA) [6,7] should be overcome for successful applications. The application of biodegradable polymers is limited due to theirs poorer mechanical properties compared to the conventional polymers. In general, the difficult processability and higher cost of some restrict the biodegradable polymers applications [8].

Polyethylene has been found immiscible with various polymers, such as polypropylene [9], poly(vinyl chloride) [10], polyethylene terephtalate [11] and PVA [12]. The poor compatibility between polyolefins and polar materials is because polyolefins are non polar polymers, hydrophobic and inert, thus compatibilizer or coupling agents must be used [13]. A poor compatibility between the mixture components results in poor adhesion among it phases and consequently poor mechanical properties. There are several methods developed to improve or modify the affinity between blend components, and one of them is to use grafted functionalized compatibilizer as maleic anhydride grafted polyethylene prepared by solution or melt graft process [14]. Few studies make reference to the blend HDPE/PVA and that carried out by Wu and Shen [15] on HDPE/PVA - 85/15 fiber composite showed that tensile strength increased from 32.6 MPa to 40 MPa, respectively, when 10%wt. of HDPE irradiated for 48h UV, was used as a compatilizer agent.

In this study, the mechanical characteristics and morphology aspects of blends prepared with post-consumer high density polyethylene (HDPEr), present in high quantities in solid domestic waste in Brazil [16], and PVA, a water soluble biodegradable polymer, were investigated. Maleic anhydride grafted post-consumer polyethylene (HDPEr-AM) was used as a compatibilizer in order to obtain an HDPEr/PVA blend with good properties for agricultural film production and a more suitable material with biodegradable potential after been used in the farmlands.

Experimental

Grounded (1.2mm – 14/20 Tyler mesh) HDPE was recycled from the crates. The HDPE recycled (HDPEr) showed crystallinity index of 56%, numerical and ponderal average MW of 4.5 x 10^4 and 1.5 x 10^5 Dalton, respectively, and polidispersity of 3.3. PVA with hydrolysis degree of 88.3%, numerical and ponderal average MW of 4.060 and 85.298 Dalton, was provided by Vetec Química Fina.

The compatibilizer (HDPEr-AM) (0.5wt%)) was obtained by grafting reaction of maleic anhydride on HDPEr using dicumyl peroxide under N_2 atmosphere in a SEIBT single-screw extruder (L/D = 32, D = 35 mm, Fc = 2.5) with temperature profile of 150, 160, 170 and 190ºC, 1050 rpm during 9 min [12].

The blending process of the polymers was carried out in molten state in the same SEIBT single-screw extruder, with a temperature profile of 180, 210, 220 and 210ºC by feeding the polymers physical mixtures in the composition evaluated. The blends HDPEr/HDPEr-AM/PVA code, for example, 30/10/60 means, respectively, the quantities of HDPEr, HDPEr-AM and PVA. The PVA content in the blend varied from 20 to 80 wt% and the compatibilizer content was 5 or 10 wt%.

The differential scanning calorimetry (DSC) measurements were carried out in a Shimadzu DSC-50 Instruments. Indium was used for calibration and liquid nitrogen was used to cool the samples below room temperature. The samples for DSC analyses (~10mg) were taken in a laminar form from the internal and central part of the injection molded Izod impact specimen. The samples were heated from room temperature to 270°C at a constant heating rate of 10°C/min and held isothermally at that temperature for 1 minute to erase any thermal history in the sample and then cooled back to -30°C at the same rate. The second run from -30 to 270°C was carried out at the same heating rate. The measurements were carried out under nitrogen flow of 50mL/min. The crystallinity index of the polymers was calculated through the expression (Equation 1):

$$X_c = (\Delta H_{f\,\text{polymer}} / \Delta H_{f\,100\%}) \times 100 \qquad (1)$$

Where X_c is the crystallinity index (%), $\Delta H_{f\ \text{polymer}}$ is the fusion enthalpy of the polymer normalized to its content in the blend, and $\Delta H_{f\,100\%}$ is the fusion enthalpy of the hypothetically 100% crystalline polymer, 293 $J.g^{-1}$ [17] for the HDPEr and 156 $J.g^{-1}$ for the PVA [18]. The crystallinity index of the blend was calculated through the expression (Equation 2):

$$X_{c\ \text{mixture}} = n\,(X_{c\ \text{HDPEr}}) + m\,(X_{c\ \text{PVA}}) \qquad (2)$$

Where n and m are the HDPEr and PVA quantities in the blend, $X_{c\ \text{HDPEr}}$ and $X_{c\ \text{PVA}}$ are the crystallinity index of HDPEr and PVA.

The tensile strength of the samples were measured using an universal testing machine EMIC type DL 3000, with a crosshead speed of 50mm/min and cell load of 2000 kgf, in accordance with ASTM D638-98. The IZOD impact strength tests were carried out in a testing machine CEAST, model Resil 25, with a 4J pendulum at a speed of $3.46 m.s^{-1}$ in accordance with ASTM D256-97. The specimens for the physical tests were obtained through injection molding into a HIMACO injection machine with temperature profile of 190, 220 and 240ºC.

The Scanning electronic microscopy analysis of the fractured surface of the specimen in liquid nitrogen, before and after PVA extraction by water at 80ºC during 3 h, was carried out in a JEOL microscope, model ISM – 6200.

The dynamic mechanical analysis of the blends in traction mode was carried out with a DMA 2980 TA Instruments, from -130 to 110°C with an oscillation frequency of 1Hz and deformation of 0.1%.

Results and Discussion

The blends HDPEr/HDPEr-AM/PVA were evaluated regarding the variation in the tensile strength, elasticity modulus, elongation, impact strength and morphology as a consequence of the PVA and compatibilizer content in the mixture. The PVA, a rigid polymer since it has glass transition temperature (Tg = 65°C) above the room temperature, had a significant effect on the stress-strain curve profile as showed in Figure 1 for the blends HDPEr/HDPEr-AM/PVA with 5 and 10% of compatibilizer. The compatibilizer HDPEr-AM having polar groups (ester groups from maleic anydride) interacts with the hydroxyl of the PVA though hydrogen bonds improving the interaction between the blends components. This interaction can be responsible for the high yield point of the blends with 20 and 40% of PVA compared to the pure HDPEr. Blends of HDPEr with 60 and 80% of PVA were more rigid material due to the high amount of PVA. In the blend with only 20% of HDPEr, the PVA (80%) acts as a matrix and lower plastic deformation was observed. The use of 10% of compatibilizer in the blends did not affect the stress-strain behaviour these compared to those with 5%.

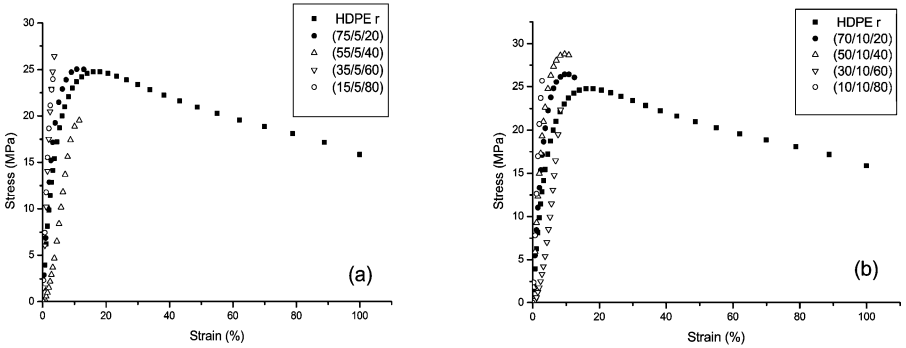


Figure 1 – Stress-strain curves of the blends HDPEr/HDPEr-AM/PVA with (a)5 and (b)10% of compatibilizer, HDPEr-AM.

Figure 2 shows tensile strength variation of the blends with 5 or 10% of compatibilizer with the increase in the PVA content. Only the blends with 40 (55/5/40) and 60% (30/10/60) of PVA showed lower tensile strength than the pure HDPEr, in which compositions a phase inversion was observed. The blends HDPEr/HDPEr-AM/PVA with the highest tensile strength were those with 60% of PVA and 5% of compatibilizer (35/5/60) and with 40% of PVA and 10% of compatibilizer (50/10/40).

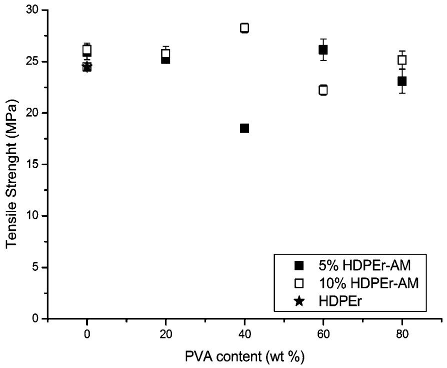


Figure 2 – Tensile strength variation *vs* PVA content, HDPEr/HDPEr-AM/PVA blends with 5 and 10% of compatibilizer (HDPEr-AM).

Figure 3 shows the SEM micrographs and Table 1 shows the tensile strength values of the HDPEr/PVA blends with 40 and 60% of PVA without compatibilizer. The polymer phase separation or the polymer domains is evident, which indicates the polymer immiscibility that results in poor mechanical properties. On the other hand, as expected, in the HDPEr/PVA blends with compatibilizer there was a better polymer interaction resulting in a better morphology and compatibility at the polymer interfaces.

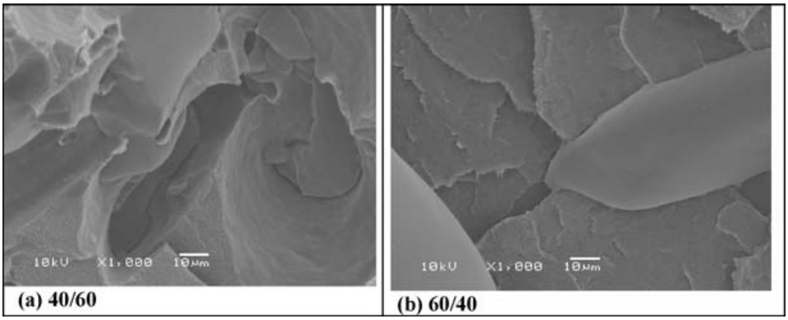


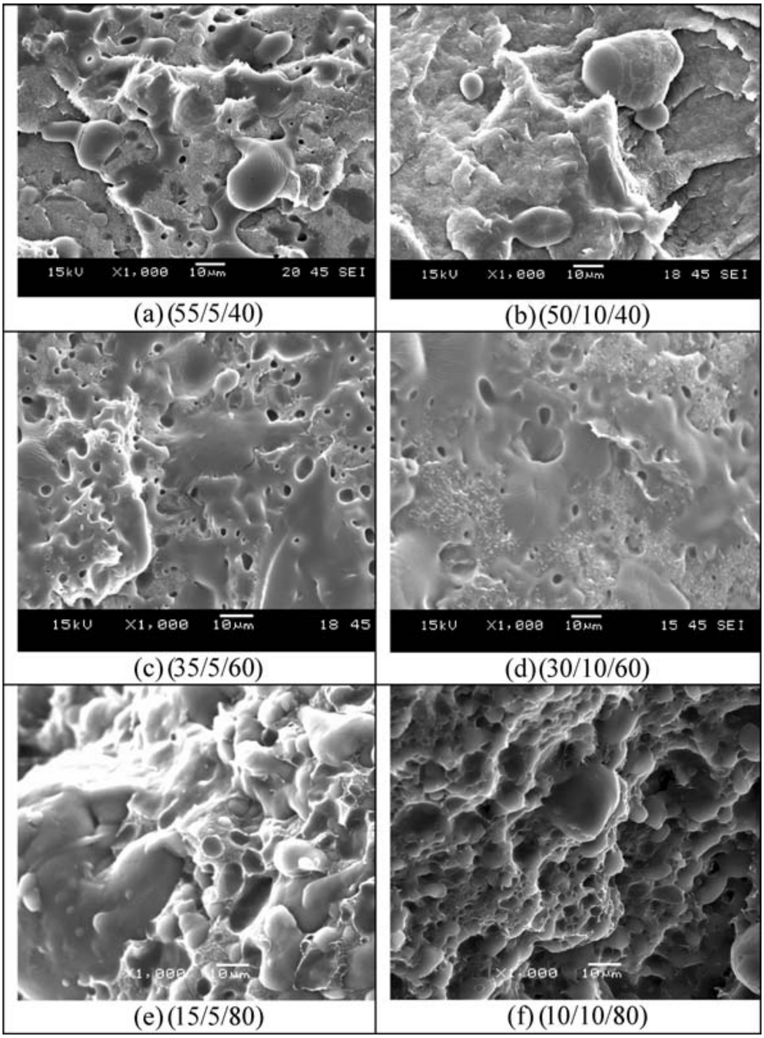
Figure 3 – SEM micrographs of HDPEr//PVA blends with (a) 60 and (b) 40% of PVA (1000X).

Table 1 – Tensile strength of the HDPEr/PVA mixtures

(HDPEr/PVA)	Tensile strength (MPa)
40/60	6,0 ± 2,5
60/40	11,04 ± 0,9

Although as expected the SEM micrographs showed the immiscibility of the polymers in all blend compositions through the evidence of domains or the blend heterogeneity as already reported [19-20], it was possible to see that the blend HDPEr/HDPEr-AM/PVA with 60% of PVA presented the best morphology and very small domains of PVA could be observed totally dispersed in the HDPEr matrix. The blend HDPEr/HDPEr-AM/PVA (55/5/40) with 40% of PVA and only 5% of compatibilizer had a significantly low tensile strength that could be corroborated with the morphology revealed in the SEM micrographs showed in Figure 4. In the blend with composition (55/5/40), having 5% of compatibilizer (Fig.4a), the PVA domains are more evident in the HDPEr matrix compared to the blend with 10% of compatibilizer (Fig.4b). A lower interaction between the two phases makes the material more fragile. The blend HDPEr/HDPEr-AM/PVA (50/10/40) with the same quantity of PVA, however, with double quantity of the compatibilizer, showed a better result indicating a more efficient synergism between the polymers, and thus a more compatible interface. When the blends had 60% of PVA (35/5/60 and 30/10/60) the morphology did not show any change or there was no evidence of HDPEr domains, Fig 4 (c) and (d), respectively, and the tensile strength of the blend with 10% of compatibilizer was a bit lower. The separation of phases was more evident in the blends with 80% of PVA, Fig 4(e) and (f), carried out only for comparison purpose since it does not achieve technological application for films. The HDPEr particles are pulled more easily from the PVA matrix during the cryogenic fracturing by essentially lack of physical or chemical interaction between the polymer phases.

Figure 5 shows the SEM micrographs of HDPEr/HDPEr-AM/PVA blends with 40 and 60% of PVA and 5 and 10% of compatibilizer after the specimens have been treated in hot water at 80ºC. The PVA during the treatment solubilized in hot water been partially extracted from the HDPEr matrix and fractured surface change to a rugged aspect showing a synergism of the polymers.



(a)(55/5/40) (b)(50/10/40)

(c)(35/5/60) (d)(30/10/60)

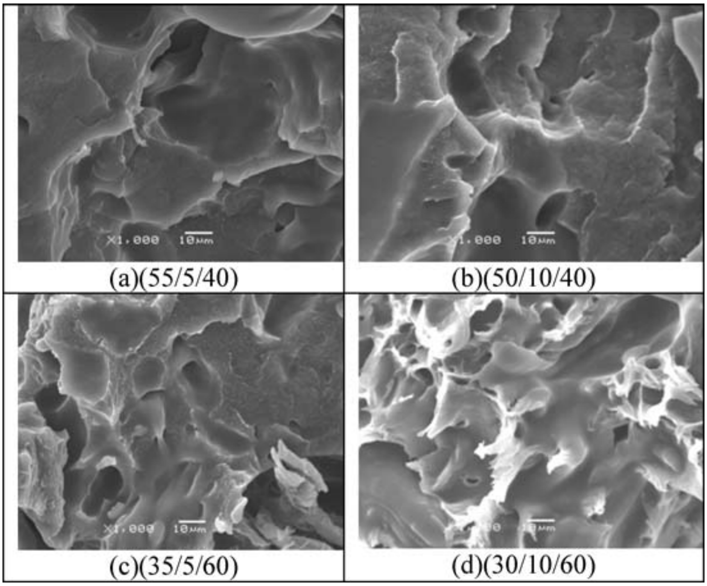
(e)(15/5/80) (f)(10/10/80)

Figure 4 – SEM micrographs of blends the HDPEr/HDPEr-AM/PVA (a) 55/5/40, (b) 50/10/40, (c) 35/5/60, (d) 30/10/60, (e) 15/5/80 and (f) 10/10/80, (1000X).

Figure 6 shows the temperature ranges of the thermal events: glass transition (Tg), crystallization (Tc) and fusion (Tm) temperatures of the polyethylene and PVA.

The crystallization of HDPE occurred within the same temperature range of the PVA, which crystallizes from 122°C, where the HDPEr is still in the melt state. Since the PVA has lower chain mobility and also crystallizes in the same temperature range of the HDPEr, the PVA can induce epitaxial crystallization of polyethylene acting as a nucleation agent [21].

The HDPEr melted in the range of 124.1 to 140.8°C with peak temperature at 133.5°C (Tm) and the PVA melted in the range of 181.9 to 203°C with peak temperature at 194.5°C. The crystallinity of both polymers HDPEr and PVA were determined in relation to their respective melting peaks in the blend. The 10% of the compatibilizer increased the blend crystallinity, with the exception for the blend with 20% of PVA. Thus, intermolecular interaction occurred preferentially between the PVA and the compatibilizer with polar groups, due to their greater chemical similarity. Although the polyethylene crystallinity increased in the blends with the content of the PVA, the crystallinity of the mixture ($X_{c\ mixture}$) decreased since the PVA has very low crystallinity. This can be associated to a high intermolecular interaction between the carbonyls of the compatibilizer HDPEr-AM and the hydroxyls groups of the PVA that could nucleate and immobilize the polyethylene chains in a more favored conformation in the crystallites environmental.



(a)(55/5/40) (b)(50/10/40)
(c)(35/5/60) (d)(30/10/60)

Figure 5 – SEM micrographs of the blends HDPEr/HDPEr-AM/PVA after hot water treatment at 80°C (a)55/5/40, (b)50/10/40, (c)35/5/60 and (d)30/10/60, (1000X).

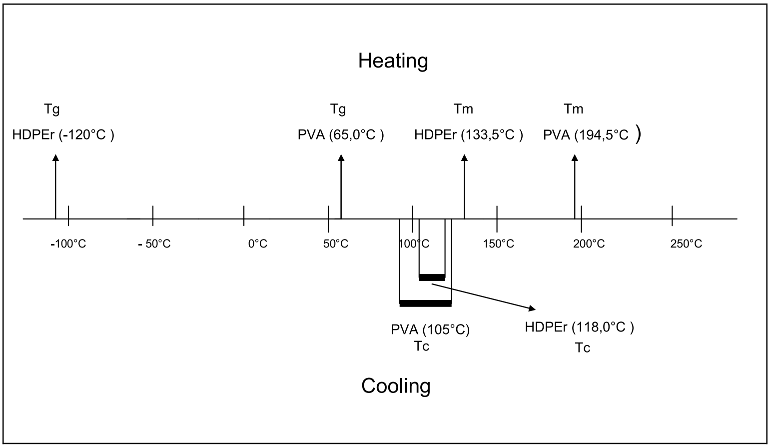


Figure 6 – Temperature range of the thermal transitions (Tg, Tc and Tm) of HDPEr and PVA.

Table 2 shows the crystallinity index of the net polymers and their crystallinity index in the blends determined by the fusion enthalpy taken from the endothermic curves obtained in the first DSC runs.

Table 2 – Crystallinity index of the polymers and HDPEr/HDPEr-AM/PVA blends by DSC

(HDPEr/HDPEr-AM/PVA) (wt %)	**Xc (1˚) HDPEr (%)**	**Xc (2˚) HDPEr (%)**	**Xc (1˚) PVA (%)**	**Xc (2˚) PVA (%)**	**Xc (1˚) blend (%)**	**Xc (2˚) blend (%)**
HDPEr	56.20	56.50	--	--	--	--
PVA	--	--	27.1	11.62	--	--
75/5/20	70.7	65.6	6.4	2.5	58	53
70/10/20	64.0	64.0	9.6	9.6	53.1	53.1
55/5/40	66.3	62.4	4.7	3.1	42	38.6
50/10/40	71.1	65.6	2.4	0.8	44	40
35/5/60	73.1	65.0	7.1	4.1	33.5	28.5
30/10/60	87.9	79.2	6.6	5.5	39.1	35
15/5/80	81.8	80.0	1.6	1.6	18	18
10/10/80	88.8	88.8	0.8	0.8	18.4	18.4

(1°) -1° Heating, (2°) - 2° Heating

The pure HDPEr presented the same crystallinity index in the first and second heating. However, the PVA showed a significant difference between the crystallinity values before and after the crystallization conditions in the DSC (cooling from the melting at 10°C/min) which shows that it is extremely sensitive to the thermal treatment.

The HDPEr/HDPEr-AM/PVA blend with 80% of PVA had the lowest crystallinity, being of the order of, or lower than, that of pure PVA ($X_c = 27\%$). Considering that this composition of HDPEr had a high X_c, and the PVA had a crystallinity lower than 2%, the crystallinity of the mixture is due only to the HDPEr.

The HDPEr crystallinity higher than 80% in the blends with 80% of PVA (15/5/80; 10/10/80) is a direct consequence of its influence on the nucleation and crystallization of polyethylene. The low amorphous fraction, due to the high crystallinity of HDPEr, explains the lack of yield point of polyethylene in the blend, which although flexible (Tg = -120°C) is insignificant.

Figure 7 shows the variation in the impact strength of the mixtures as a function of PVA and compatibilization agent contents, the values being lower than those of HDPEr for all of the compositions tested. The impact strength is due mainly to the polyethylene since the Tg value is -120°C. The insertion of PVA makes the material more rigid since it does not have chain mobility at the test temperature of 23°C. For PVA contents from 60% to 80% the decrease in this property may result from the higher crystallinity of the polyethylene induced by the PVA.

With the exception of blend with a 40% PVA composition in which a phase inversion was observed, for the other mixtures the impact strength with 10% HDPEr-AM was higher than with 5% HDPEr-AM.

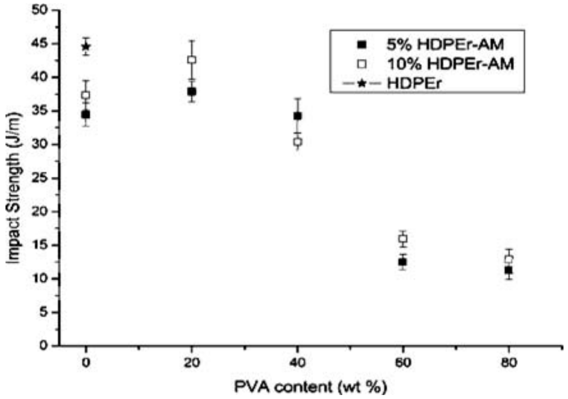


Figure 7 – Impact resistance of the HDPEr/HDPEr-AM/PVA blends and of HDPEr.

The blend which showed the best result for impact strength was with 20% of PVA (70/10/20), and 10% of HDPEr-AM, and its value is very close to the impact strength for HDPEr.

Figure 8 shows the variation in the E`, E`` and tan δ values of the mixtures and of HDPEr. In Figure 8(a) the immiscibility of the polymers, previously identified through SEM, can be verified for certain HDPEr/PVA compositions.

On analyzing Figure 8(b) it can be observed that for HDPEr there are relaxation peaks, γ, β and α, occurring, respectively, at the following temperatures: -120ºC

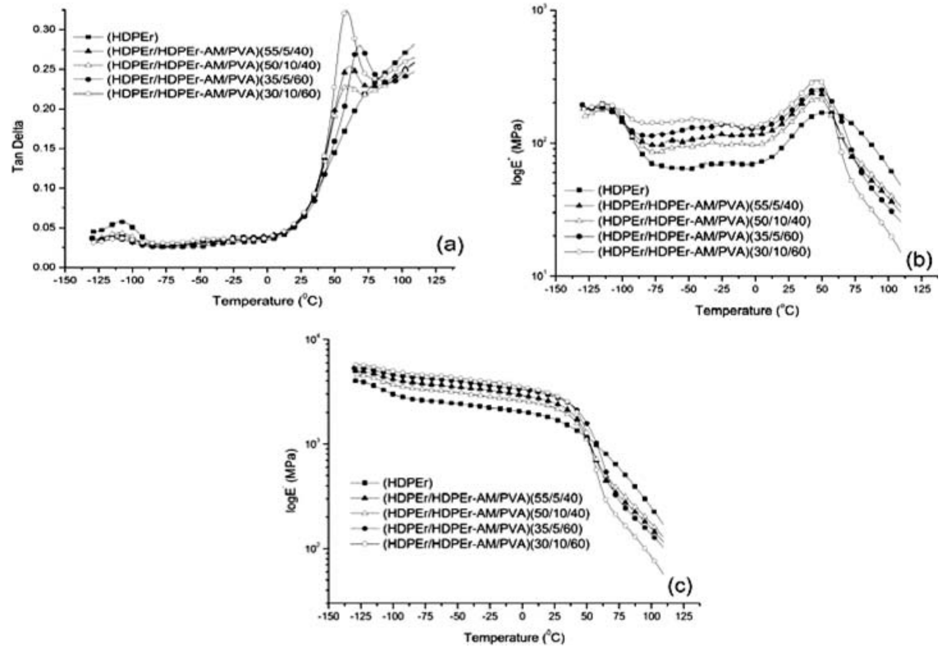


Figure 8 – Dynamic mechanical properties of HDPEr and HDPEr/HDPEr-AM/PVA blends: 55/5/40, 50/10/40, 35/5/60 and 30/10/60, (a) Tan Delta (b) Loss modulus and (c) Storage modulus.

related to the Tg, 0ºC related to chain´s free segments not stretched and 60 to 120ºC related to the HDPE fusion. In the temperature between 50ºC and 60ºC there is a relaxation which is characteristic of PVA. This PVA transition occurred at a temperature of 65ºC, in Fig. 6, and was displaced to a range of 50-60ºC due to a possible interaction with HDPEr-AM or PVA degradation, occurring during the processing. This event is characterized by the appearance of a maximum in the curve related to the Tg of PVA. It can be verified that PVA restricts the HDPE viscous deformation, which is reflected in an increase in the viscous modulus and, consequently, there is a displacement on the curves to higher values, being for the blend (30/10/60) the most significant one. The composition (30/10/60) showed a widening of the peak related to the glass transition of PVA, polymer which is passing by the transition process. This peak widening shows a possible synergism between the polymers, fact already confirmed through SEM. Increasing the amount of PVA in the blends composition has, as effect, higher values of loss modulus.

Conclusions

The use of 5 or 10% of compatibilizer agent did not allow significant changes in the mechanical properties of the blends, however, when compared to blends without compatibilizer (resulted of tensile strength), this it revealed efficient.

The blends HDPEr/HDPE-AM/PVA were immiscible, however, 40% and 60% PVA contents led to a synergism of the polymers of the blend, favored by the action of the compatibilization agent. For PVA contents of 20%, 40% and 60%, the values for the elasticity modulus and tensile strength of the blends were higher than those for polyethylene and the use of 10% compatibilization agent in the blends allowed a greater adhesion between the matrix and the dispersed phase. Blend with 20% of PVA, besides the mechanical properties (tensile strength and impact strength) being the same or better than those of pure HDPEr, are the blend with the lowest cost since they have the lowest percentage of PVA.

The HDPEr crystallization is favored by the presence of PVA in the blends, increasing its crystallinity index of 56% to values above 88%. However, the crystallinity of the blends decreased with the presence of PVA since it has a very low crystallinity.

The dynamic mechanical properties showed a reduction in the relaxation temperature of the amorphous domains of the PVA, probably due to the degradation of this material during the processing. Increasing the amount of PVA in the blends composition has, as effect, higher values of loss modulus in the blends and increasing the tan δ value. This behavior is associated with the molecular rigidity of the PVA.

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