JMPE

Characterization of blendes (PET/PEHD) basis recycled materials: Study of the effects of chains extension and compatibilization.

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Abstract ▬ Poly(ethylene terephtalate) (PET) and polyethylene (PE) are widely used as packaging materials such as containers, bottles and films. Their annual rates of growth of production and consumption steadily increase. So, their recycling can reduce the resources needed for manufacturing, conserve energy and decrease the impact of their wastes on the environment. Triphenylphosphite (TPP) has been used as a chain extender to regenerate PET and high density polyethylene (HDPE) wastes and to improve the properties of PET/HDPE system based on recycled materials. Also, the blend has been compatibilized using the copolymer styrene/ethylene-butadiene/styrene (SEBS-g-MA). TPP incorporation in PET and HDPE showed a noticeable increase of the torque as a function of the mixing time and proved that degradation reactions rates are considerably decreased. In the case of PET/ HDPE blends, the increase of the torque was strongly dependent on the composition of the homopolymers. Furthermore, TPP and SEBS-g-MA incorporation contributed to significant variations of the structural and thermal properties of the regenerated PET and HDPE and their blends

Keywords: *Recycling, Chain extender, Hydrolysis, Phosphites.*

Introduction

Due to their good mechanical and barrier properties, poly (ethylene terephtalate) (PET) and high density polyethylene (HDPE) are widely used in packaging materials. These types of articles are routinely used which inevitably creates serious resource waste and pollution. So, face to the increased awareness of the environmental protection, post-consumed plastics recycling is actually the most adapted solution to recover material, conserve energy and reduce wastes and pollution [1, 2].

Mechanical recycling of post-consumed (R-PET) is a complicated process because it is generally associated to a series of degradation mechanisms like thermal, mechanical, hydrolytic and oxidative reactions which reduce drastically its molecular weight and intrinsic viscosity.

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So actually, the main challenge in R-PET reuse is to overcome the consequences of the retained moisture and contaminants that decrease its quality and processing performances [3-4]. In this purpose, adding chain extenders is an effective way to regenerate the melt viscosity of R-PET. Chain extenders are multifunctional molecules that can react with at least two PET chain ends which increase significantly the molecular weight of the polymer and reduce the concentration of the carboxyl and hydroxyl groups that can be involved in degradation reactions **[5-6]**. Chain extenders can be classified into two principal sorts depending on whether the extending process is associated to the release of by-products or not. The second class which is particularly the most attractive, proceeds according to an irreversible reaction and includes oxazolines, isocyanates and anhydrides compounds. In the other hand, the bridging reactions involved between the first class of chain extenders and R-PET groups are accompanied by undesirable by-products especially phenol, like it is the case when

triphenylphosphite (TPP) is used [5-7]. Despite this disadvantage, TPP has proven its effectiveness in the regeneration of R-PET viscosity by connecting PET chains after reacting with carboxyl and hydroxyl ends groups [8-9]. Organic phosphorous compounds as TPP are also used for the processing stabilization of polyolefins, like HDPE because they can act as antioxidants. The stabilizing action of phosphites is mainly attributed to three principal reactions: the decomposition of hydroperoxides by their reduction to alcohols and the reactions with alkoxy and peroxy radicals. By these mechanisms, the concentrations of the groups responsible of the degradation of HDPE are reduced, which provides a more safe melt processing [10-11].

The investigation of recycled PET/polyolefins blends has pointed out the necessity of compatibilizers to promote the adhesion between these components and also, PET chain extenders to enhance R-PET viscosity [2, 7, 12-13]. The aim of the present work is to use triphenylphosphite concurrently as an antioxidant for R-HDPE and a chain extender for R-PET and to investigate its effects on the rheological, mechanical and thermal properties of R-PET, R-HDPE and R(PET/HDPE) blends before and after compatibilization with maleic anhydride–grafted poly(styrene-ethylene/butadiene-styrene) (SEBS-g-MA).

Expérimental
1-Materials

PET wastes were received from a post-consumer beverage disposal, and then they have been washed, dried and pelletized to prepare R-PET flakes. High density polyethylene (HDPE) is Marlex HHM 5502 BN manufactured by Qatar Chemical Company. HDPE has been subjected to two extrusion cycles in a Controlab single screw extruder at a speed of 45 rpm and according to the following temperatures program: 170, 180 et 190°C. The obtained R-HDPE was then cooled and pelletized. Triphenylphosphite (TPP)(($C_6H_5O)P$) was purchased from Fluka. Maleic anhydride-grafted poly(styrene-ethylene/ butadiene -styrene) (SEBS-g-MA) incorporated as a compatibilizer was Kraton FGX 1901X from Shell Chemical Company, containing 70% of

ethylene–butadiene block and 30% of styrene and grafted with 1.84 w% maleic anhydride.

2-Processing

After drying neat materials, the elaboration of recycled polymers formulations and blends with and without TPP and SEBS-g-MA was performed in a Brabender internal mixer at 270°C for R-PET and R(PET/HDPE) blends and at 190°C for R-HDPE formulation, at a mixing speed of 30 rpm and during 15 minutes. The loading levels of TPP and SEBS-g-MA were, respectively, 1% and 10% based on the total weight of the mixed formulation. R (PET/HDPE) weight ratios were 30/70, 50/50 and 70/30.

3-Characterization
3-1Fourier Transform Infrared analysis (FTIR)

To point out the occurrence of reactions between TPP and/or SEBS-g-MA and the two polymers, Fourier transform infrared (FTIR) spectra were obtained between 500 and 4000 cm^{-1} on a Perkin Elmer 1000 apparatus. Ten scans were averaged at a resolution of 4 cm^{-1} for compressed films of R-PET, R-HDPE and R(PET/HDPE) mixed with and without TPP and SEBS-g-MA.

3-2Differential Scanning Calorimetry (DSC)

The values of the blends crystallinity were evaluated on the basis of thermograms of the first scanning of samples obtained on a DSC 200 Netzsch, under the following conditions (temperature range: 25 to 300°C, heating rate of 10°C). Values of the melting enthalpy of pure PET and HDPE crystals equal to 117 J/g and 276 J/g, respectively, were used [13].

3-3Thermogravimetry analysis (TGA)

The thermal stability of R-PET, R-HDPE and R(PET/HDPE) mixed with and without TPP and SEBS-g-MA have been studied by thermogravimetric analysis using a Perkin Elmer TGA apparatus, by heating the samples from 30 to 650°C at a heating rate of 10°C/min. Degradation parameters have determined from TG and DTG thermograms giving, respectively, the variations of the weight loss and its derivative as a function of temperature.

Results and discussions
1-Infrared analysis

Infrared spectra of R-HDPE melt mixed without then with TPP represented in **figure 1** are practically identical and reveal the symmetric and asymmetric stretching vibrations of the C-H bond at 2980 and 2830 cm^{-1} and the deformation vibration of –CH$_2$ group at 1470 cm^{-1}. Also, FTIR spectra of R-PET melt mixed without and with TPP show the stretching vibrations of aromatic C-H between 3100 and 3000 cm^{-1} and the symmetric and asymmetric vibrations of the C-H bond belonging to the –CH$_2$ group at 2970 and 2830 cm^{-1}. The strong band observed at 1720 cm^{-1} is characteristic of the C=O group whereas the bands indicated by the wave numbers 1577, 1504 and 1470 cm^{-1} are attributed to the aromatic ring vibrations. The zone comprised between 1400 and 1000 cm^{-1} is particularly complex, which do not allow the detection of new bands characteristic of the products generated after the reactions between R-PET and TPP. Indeed, all the expected phosphorous products vibrations frequencies are included in the gap of wave numbers where the R-PET spectra is particularly rich in bands. This same interpretation is valid for the 50/50 R(PET/HDPE) blends melt mixed without and with TPP which spectra is similar to R-PET one.
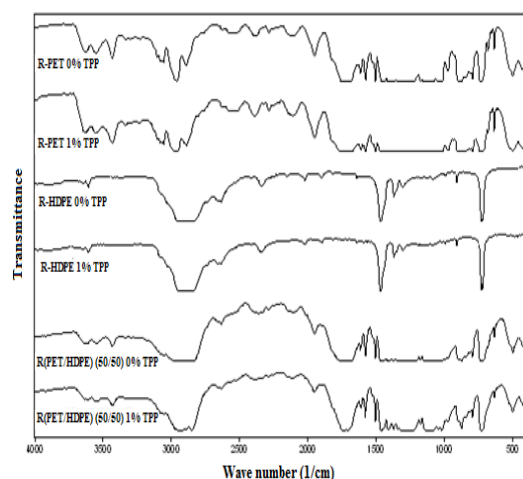

Fig. 1 FTIR spectra of R-PET, R-HDPE and R-(PET/HDPE) (50/50) melt mixed without and with TPP **[14].**

In the other hand, the SEBS-g-MA spectra reveal clearly the stretching vibrations of the unsaturated –C-H groups of butadiene and aromatic groups between 3100 et 3000 cm^{-1} as well as those of the C-H bonds of the saturated part of the molecule. The carbonyl group of the anhydride is observed at 1790 cm^{-1}, as it is reported in the **figure 2**. FTIR spectra of R (PET/HDPE)/SEBS-g-MA (50/50/10) melt mixed without and with TPP assemble SEBS-g-MA, PET and HDPE bands and reveal the occurrence of the reaction between SEBS-g-MA and the hydroxyl group of R-PET. Indeed, we have noticed that the carbonyl band of the anhydride group of the compatibilizer situated at 1790 cm^{-1} disappeared from the spectra of the blend, which state that it has completely reacted with R-PET to generate R-PET-block-SEBS-g-MA copolymer.
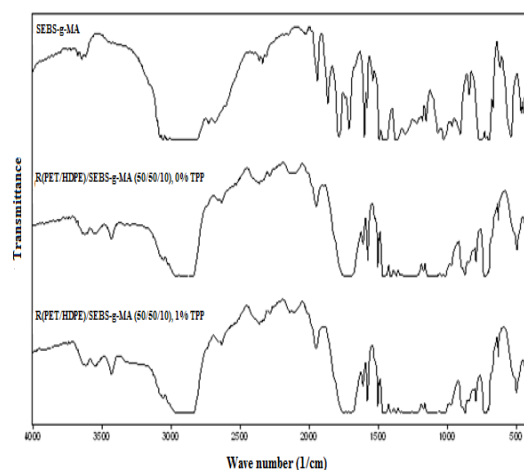

Fig. 2 FTIR spectra of SEBS-g-MA and compatibilized R(PET/HDPE)/SEBS-g-MA (50/50/10) melt mixed without and with TPP.

2-Thermal properties
2-1Thermal properties of the formulations prepared without SEBS-g-MA

According to the thermograms giving the variations of the heat flow with temperature, R-HDPE presents a melting peak equivalent to a crystallinity of approximately 42% and a melting temperature of 150°C, which do not vary when TPP is added. R-PET has also revealed only one melting endotherm which maximum is situated at 265°C and which area is equivalent to a crystallinity of 26%. R(PET/HDPE) thermograms show two endotherms, which maximum are situated at 150°C for the first and around 265°C for the second and that are not

affected by TPP and after blending, contrary to the crystallinity which is totally controlled by the composition. Indeed, it was noticed that blending reduces the crystallinity of the two polymers and particularly R-PET, which melting endotherm disappears completely when R-HDPE constitutes the majority in the blend. This result is attributed to the fact that when HDPE crystallization is achieved, the organization of R-PET chains that are present in a small amount relatively to HDPE ones, is not allowed, which decreases drastically its crystallinity, as it is showed by **table 1**.

Table 1. Thermal properties of R(PET/HDPE) melt mixed with and without TPP.

R(PET/ HDPE)	TPP (%)	R-PET		R-HDPE	
		T_m (°C)	X_c (%)	T_m (°C)	X_c (%)
0 /100	0	-	-	151	42
	1	-	-	152	43
30/70	0	-	-	151	22
	1	265	8	151	36
50/50	0	266	22	144	23
	1	265	24	146	19
70/30	0	264	31	144	13
	1	265	30	145	13
100/0	0	265	26	-	-
	1	266	27	-	-

2-2 Thermal properties of the compatibilized formulations

After SEBS-g-MA incorporation, R-PET and R-HDPE crystallinity decreased drastically proportionally to their rates in the blends, as it is reported in **table 2.**

Table2. Thermal properties of compatibilized R(PET/HDPE) melt mixed with and without TPP in presence of SEBS-g-MA.

R(PET/H DPE)	TPP (%)	SEBS-g-MA (%)	R-PET		R-HDPE	
			T_m (°C)	X_c (%)	T_m (°C)	X_c (%)
30/70	0	10	263	4	149	26
	1		262	3,5	149	23
50/50	0	10	274	3	150	10
	1		271	10	150	16
70/30	0	10	271	11	151	7
	1		262	32	149	13

This result is considered as a proof of the blend compatibilization after the reaction of R-PET with maleic anhydride and the penetration of the SEBS segment into the R- HDPE phase. So, the presence of the SEBS-g-MA copolymer in the two blends phases prevent their crystallization.

3-Thermal stability of recycled materials and blends Recycled polymers and uncompatibilized blends

As revealed by **figure 3**, R-PET and R-HDPE possess different thermal stabilities that are strongly related to the chemical structure of the polymers. R-HDPE exhibits a higher thermal stability because it starts its decomposition, after R-PET at, approximately, 415°C. The temperature corresponding to the maximum weight loss equal to 63% is attained at 487°C, then R-HDPE finishes its decomposition at 507°C without any residual mass. In the other hand, R- PET starts to waste mass at 360°C and finishes around 500°C with a residual mass of 18%. The incorporation of TPP had no effect on the thermal stability of R-HDPE.

For R-PET melt blended without TPP, DTG thermogram reveals only one maxima corresponding to the maximum weight loss of 50% at a temperature of 447°C. But, for R-PET melt mixed with 1% TPP, it appears two maxima, one at 442°C characterizing a new structure resulting from the reaction between R-PET and TPP, and the other at 447°C and which can be assigned to the same structure that is revealed by the single maxima observed for R-PET without TPP
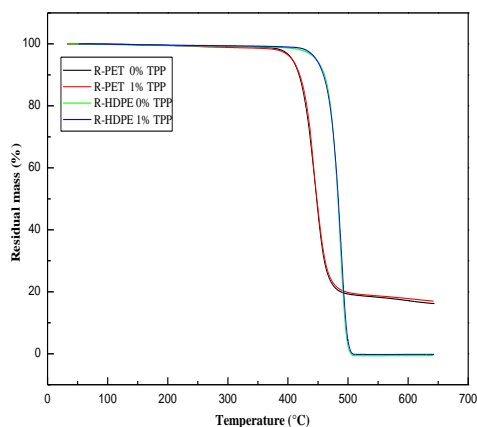
Fig. 3 TG thermograms of R-PET and R-HDPE melt blended without and with phosphites.

Uncompatibilized R(PET/HDPE) mixtures melt blended without and with TPP exhibit a thermal stability that is situated between those of the two recycled polymers. So, R-HDPE has contributed to the promotion of R-PET thermal stability. Indeed, whether TPP has been added or not during mixing, it appears from TG and DTG thermograms that the blends start to waste weight from 370°C, and finish around 510°C with a residual mass of approximately 10%. The temperature corresponding to the maximum weight loss which is around 40%, is of 450°C.
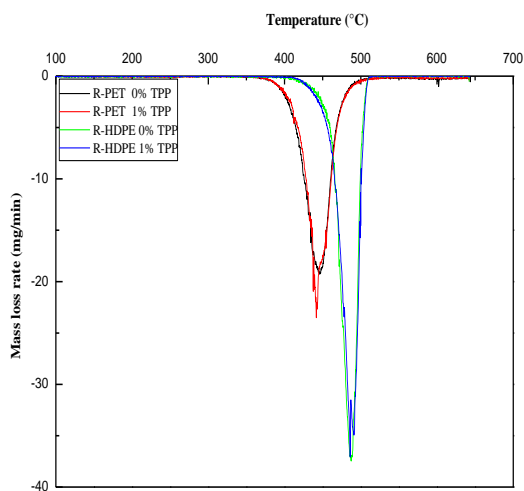

Fig. 4 DTG thermograms of R-PET and R-HDPE melt blended without and with phosphites

Conclusions

This paper reports the results of an investigation on the effects of incorporation of triphenylphosphites as a chain extender for R-PET and an antioxidant for R-HDPE and SEBS-g-MA as a compatibilizer on the properties of R(PET/HDPE). Infrared results have not permitted to reveal the products of the reactions between TPP and R-PET and HDPE but have confirmed the occurrence of the reaction between the anhydride group of SEBS-g-MA and the hydroxyl group of R-PET.

. Also, blending and SEBS-g-MA incorporation decrease drastically the cristallinity of HDPE and R-PET in the blend, whereas the melting temperatures are not affected.

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