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Study of the effect of MAPP rate on the morphology and thermal properties of PP/r-PET blends

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Abstract

The morphological and thermal study of the blends based on polypropylene (PP) and poly (ethylene terephthalate) recycled (r-PET) without and with a compatibilizer MAPP. PP/r-PET /MAPP Melt blending, the effect of blend composition of (r-PET) and MAPP was followed by morphological and thermal studies. The results obtained were discussed compared to the base polymer. In the absence of the compatibilizing agent (MAPP), PP/r-PET blends at different concentrations of r-PET exhibit clear phase separation with poor dispersion of r-PET in the PP matrix. The addition of MAPP in the blends PP/r-PET leads to a reduction of the particle size of the dispersed phase (r-PET) in the PP matrix, as well as improved interfacial conditions.

Keywords *: Polypropylene, poly(ethylene terephthalate) recycled, compatibilizer, blend, thermal proprieties*

I. Introduction

A recent concept (which is increasingly taken into account in our daily lives) is the concept of sustainable development, which depends in part on the reduction of waste and/or its management. This involves their treatment with a view to their recovery or recycling. A large part of the waste is made up of plastic materials used in convenience products, household appliances, construction, transport, etc. Unfortunately, plastic materials, in general, have a major drawback which is their resistance to biodegradation. One of the possible solutions to reduce or eliminate them is recycling. This can be mechanical or chemical. Mechanical recycling consists of reusing waste for the manufacture of a finished or semi-finished material. However, this type of recycling generally results in a decrease in the properties of the polymer. Among these plastics, poly(ethylene terephthalate) (PET) is considered one of the most important technical polymers. PET is mainly used for the manufacture of films, fibers and containers (bottles). PET has very good characteristics for its use in packaging: high transparency in blown containers, good mechanical properties for a minimum thickness, dimensional stability during handling (even at high temperatures), relatively low cost (price per container) and low permeability to gases such as CO_2 [1]. For all these reasons, PET is increasingly used as a packaging material. Its widespread use generates large quantities of waste that require the implementation of recycling techniques.

PET recycling is not easy because of its degradation during reprocessing, caused by temperature, moisture and contaminants. The degradation leads to the decrease of molecular weight and loss of properties [2]. One way to improve the properties of recycled polymers is to blend them with unmodified polymers (polyolefins) with good properties. Polypropylene (PP) is widely used in this case [3], because of its good properties (lightness, transparency, high mechanical strength, electrical insulation, inertness to chemical aggression and use at high temperatures) [4]. It has been reported that blends of polyolefins (especially polyethylene (PE) and PP) and PET can display good mechanical and permeability characteristics. However, PET and polyolefins have very different chemical structures, making them immiscible with each other. The major drawback resulting from this incompatibility is that the resulting blends exhibit poor mechanical properties. The most frequently used means to partially overcome this performance deficit is compatibilizing, which consists of creating chemical affinities between the constituents of the blend in order to reduce interfacial tensions, improve adhesion between the phases and stabilize the morphology [5]. Some of these studies have focused on techniques to improve the compatibility between the two polymers [6, 7]. Maleic anhydride-grafted PP (MAPP) can be used as a

compatibilizing agent in PP/PET-r blends [8-10]. It has been reported that the use of MAPP in PP/PET-r blends can improve the dispersion and adhesion between the two components [8]. It has also been indicated that the use of MAPP as a compatibilizing agent can improve the strength and stiffness of PP/PET-r polymer blends [9].

II. Material and methods

PP 500P polypropylene with a melt flow index of 3.00 g/10min was provided by SABIC Basic Industries Corporation (Saudi Arabia). Poly(ethylene-terephthalate) (r-PET), or waste r-PET, was recovered from waste mineral water bottles. The size of r-PET pieces ranged from 2 to 5 mm. Maleic anhydridegrafted-polypropylene (MAPP) with a melt flow index of 2.63g/10 min was provided by Arkema (Insa de Lyon, France).

II.1. Blend preparation

Several formulations based on a PP/PET-r mixture were prepared with and without compatibilizing agent MAPP according to the compositions indicated in Table PET-r flakes were dried at 120 °C for 24 h to remove any trace of water that may cause hydrolytic degradation of the material during use.
The PP/r-PET blend (matrix) was extruded at the melting temperature of PET at 265°C and 120 rpm for 2 min using a laboratory scale co-rotating twin-screw mini extruder (15mL Micro compounder, DSM Xplore, University A. Mira of Bejaia, Algeria). The compounds were subsequently injection molded using a laboratory scale injection-molding machine (12mL Micro injection Molder, DSM Xplore, University A. Mira of Bejaia, Algeria) at 180°C barrel temperature, 90°C mold temperature, and 10 bars injection and holding pressure. Samples were molded for mechanical and physical characterization.

Table 1: Composition of PP/PET-r blend formulations.

The blends	PP(unite)	r-PET	MAPP
PP/PET-r_{10}	90	10	0
PP/r-PET_{10}/2,5%MAPP	87,5	10	2,5
PP/r-PET_{10}/5% MAPP	85	10	5
PP/r-PET_{10}/10%MAPP	80	10	10
PP/PET-r_{20}	80	20	0
PP/r-PET_{20}/2,5%MAPP	77,5	20	2,5
PP/r-PET_{20}/5% MAPP	75	20	5
PP/r-PET_{20}/10%MAPP	70	20	10
PP/PET-r_{30}	70	30	0
PP/r-PET_{30}/2,5%MAPP	67,5	30	2,5
PP/r-PET_{30}/5% MAPP	65	30	5
PP/r-PET_{30}/10%MAPP	60	30	10

II.2. Characterizations

Sample morphology was performed on Hitachi S- 3500N Variable Pressure Scanning Electron Microscope (Hitachi High Technologies Canada) with an accelerating voltage of 20.0 kV. Specimens were freeze-fractured in liquid nitrogen and then coated with a thin layer of carbon for characterization.
In thermogravimetric analysis (TGA), the mass of a sample, maintained in controlled atmosphere, is recorded as a function of the temperature (rise, fall orisothermal) or time. Saved thermograms provide informationmainly on the physical phenomena of vaporization, sublimation or desorption, but also on decomposition or oxidation reactions, particularly in the case of polymers.
In this study we used a TGA Q500 type device from TA instruments. He is composed of a sample boat driven by a high
precision microbalance. The basket is introduced into an oven allowing the sample to be subjected to a ramp in temperature from 20 to 600 °C with a speed of 10 °C/ min, under a flow of inert gas (N_2).
X-ray diffraction is a non-destructive analysis method generally used to determine the mineralogical composition of a sample. The spectra of the X-ray diffraction analysis were recorded using a “PANalytical Expert-Pro” type apparatus equipped with a copper anticathode tube and a monochromator using a Kα1 line of wavelength λKα1=1.5405 Aº. For crystallinity measurements, the diffracted intensity as a function of the angle 2θ between 5 and 45° is measured in reflection.

III. Results and discussion

III.1. Morphology of Blends

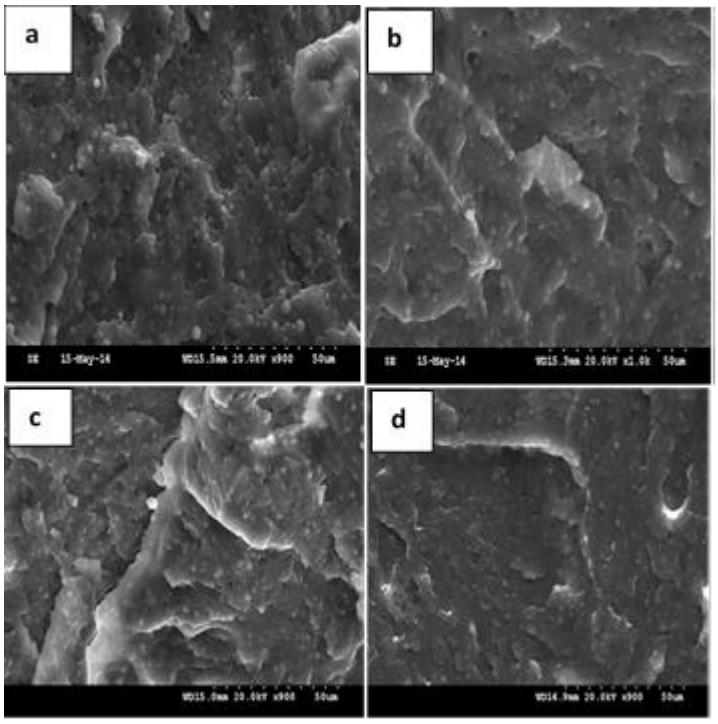

Figure 1: SEM micrograph of PP / r-PET 80/20 blend (a), PP / r-PET / 2.5% MAPP (b), PP/r-PET/ 5% MAP(c) P, PP/r-PET /10% MAPP (d).

Analysis of the surface morphology of the three samples, shows the presence of a homogeneous surface characterized by a reduction in the size of the particles of r-PET embedded in the PP matrix in comparison with the non-compatible PP/r-PET mixture micrograph (Figure 1.a). This reduction in the size of the dispersed phase is significant with the increase in the content of MAPP. The morphology change is the result of interfacial interactions between the r-PET particles and the PP matrix. The addition of 10% MAPP significantly reduces the size of r-PET particles: the PET-r particle size is changed from 2,88 µm for the non-compatible PP/r-PET20 mixture to 2,02 µm, 1,75 and 0,77 µm for PP/r-PET 20 /2,5% MAPP mixtures, PP/r-PET/5% MAPP and PP/r-PET/10% MAPP, respectively. In addition, the PET-r particles appear to be "included" in the PP matrix, this can be explained by the chemical bonds created between PET-r and MAPP, thus forming anchor points between phases, and on the other hand, the absence of voids as well as the homogeneity of the structure, which suggests the existence of a certain cohesion between the matrix and the dispersed phase.

III.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed under inert atmosphere for all blends to study the thermal degradation of these samples.

The TGA and DTG thermograms are presented in Figures 2, 3 and 4. The temperatures corresponding to the decomposition steps (5, 10 and 50%) and the temperatures corresponding to the maximum degradation rate are essential to evaluate the thermal stability of a polymer (Table 2).

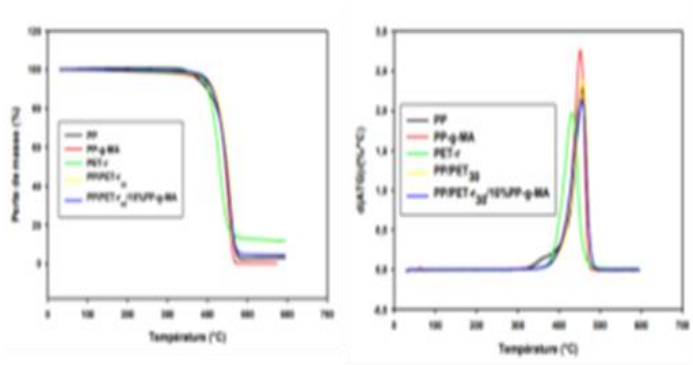

Figure 2: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 10 blends in the presence of 10% MAPP.

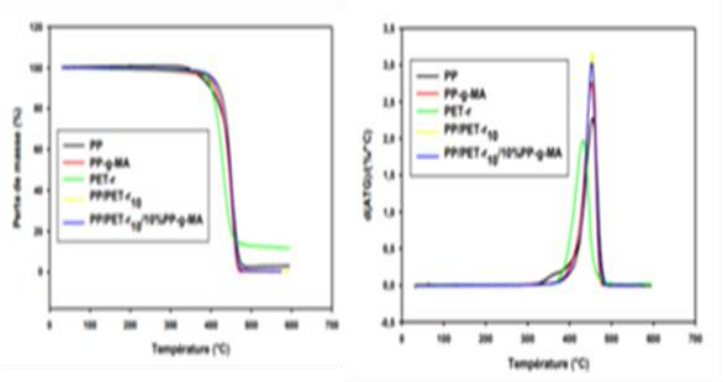

Figure 3: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 20 blends in the presence of 10% MAPP.

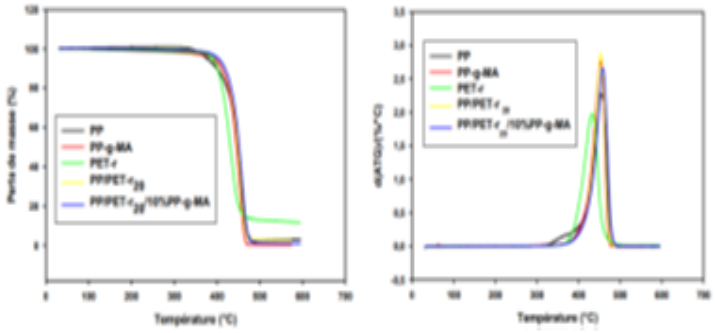

Figure 4: ATG/DTG thermograms of PP, PET-r, MAPP and PP/PET-r 30 blends in the presence of 10% MAPP.

Table 2: Results of thermal properties determined by ATG.

Formulations	Tdégradation 5% (°C)	Tdégradation 10% (°C)	Tdégradation 50% (°C)	T at Vmax (°C)	Résidue at 600°C (%)
PP	377,68	399,75	447,99	452,36	3,02
PP/rPET10	405,47	422,38	448,28	452,48	0,48
PP/rPET10C	403,17	419,66	448,75	453,20	0,35
PP/rPET-20	402,55	418,00	449,87	454,36	2,49
PP/rPET-20C	402,93	418,42	451,92	457,61	1,075
PP/rPETr 30	400,09	416,00	447,60	456,18	4,50
PP/rPET-30C	397,52	412,10	450,84	457,61	4,36
r-PET	389,46	400,71	430,87	433,29	11,60
PP-g-MA	391,91	410,97	445,36	525,52	0,17

The ATG thermograms show that PET-r undergoes a single-step mass loss in the temperature range 370-465 °C. The maximum of the DTG thermogram, which corresponds to the temperature at which the maximum mass loss rate is recorded, gives a value of 433 °C (Table 2), which is due to the thermal degradation of the PET-r chain [11]. The residual mass at 600 °C is 11.6% (Table 2).

Polypropylene also degrades in a single step in the region 346-482°C. The temperature corresponding to the maximum rate of degradation of PP is 454°C.

Binary PP/PET-r blends (PP/PET-r10, PP/PET-r20, PP/PET-r30) in the absence of PP-g MA as well as ternary blends (PP/PET-r10/10%PP-g-MA, PP/PET-r20/10% MAPP and PP/PET-r30/10%PP-g-MA) compatibilized with 10% MAPP show the same thermal behavior. According to Table 2, the

temperature values corresponding to the maximum degradation rates of binary mixtures (in the absence of MAPP) are lower than those corresponding to ternary mixtures (in the presence of MAPP), which implies a faster degradation of the latter. This part allows us to conclude that the presence of MAPP in binary mixtures has an influence on the thermal stability of the corresponding mixtures [12,13].

III.4. X-ray diffraction (XRD) analysis

The changes that can occur in the microstructure of PP/r-PET blends after addition of the polypropylene-maleic anhydride graft copolymer (MAPP) were monitored by X-ray diffraction (WAXD). Figures 5, 6 and 7 show the diffractograms of the PP/PET-r10, PP/PET-r20 and PP/PET-r30 blends in the presence of the compatibilizing agent MAPP

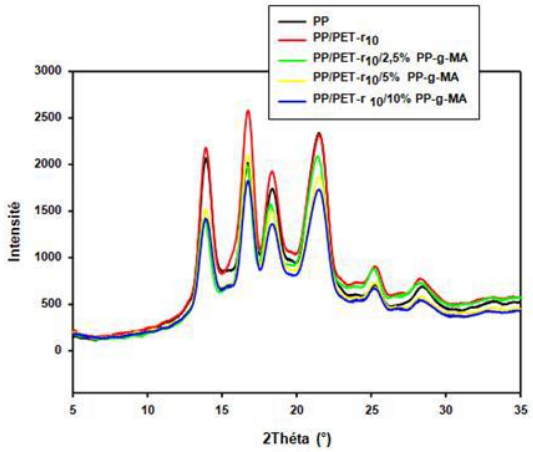

Figure 5: X-ray diffraction of PP/PET-r10 blends at different PP-g-MA rates.

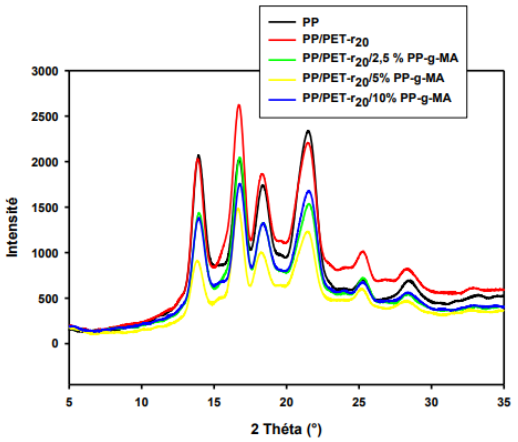

Figure 6: X-ray diffraction of PP/PET-r 20 blends at different MAPP rates.

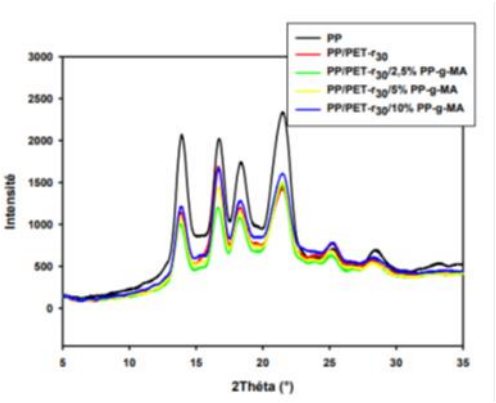

Figure 7: X-ray diffraction of PP/PET-r30 blends at different MAPP rates.

The diffractogram profiles of PP/PET-r blends at different PET-r contents (10, 20 and 30%) containing the polypropylene-maleic anhydride graft copolymer are similar to those of the non-compatibilized blends. However, it can be noted that with the increase in the compatibilizer content, the peaks tend to shift slightly towards lower diffraction angles. This shift may be due to the interactions between PP and PET-r with MAPP.

IV. Conclusions

In this study devoted to the study of the optimization of the rate of the MAPP compatibilizing agent, we were particularly interested in the problem of adhesion to the interface of PP/r-PET blends at different rates of MAPP, by varying the rate of 2.5, 5 and 10%. The highlighting of the compatibilizing was examined by the different analysis techniques.
All the results obtained indicate that the addition of MAPP as a compatibilizing agent improves the morphology of PP/r-PETpolymer blends at different MAPP levels. This results in a decrease in the size of the PET-r particles embedded in the PP matrix and an improvement in the interfacial adhesion between the two polymers. The presence of MAPP in the PP/r-PET binary blends has an influence on the thermal stability of the corresponding blends.

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