

Evaluation of mechanical and water absorption properties of polypropylene/recycled poly(ethylene terephthalate) blends

Badrina DAIRI^{1,2*}, Nadira BELLILI^{1,2}, Hocine DJIDJELLI², Amar BOUKERROU²

¹ Department of Process Engineering, Faculty of Technology, Skikda University 20 August–1955 – Algeria

² Department of Process Engineering, Faculty of Technology, Laboratory of Advanced Polymer Materials (LMPA), Abderrahmane MIRA University, Béjaïa 06000, Algeria

Corresponding author*: b.dairi@univ-skikda.dz; badrina_d@yahoo.fr

Received: 12 May 2022; Accepted: 12 June; Published: 21 July 2022

Abstract

This study is part of the recovery and mechanical recycling of polyethylene terephthalate (PET) waste, which is an abundant deposit due to its use in the packaging sector. Mixtures were prepared by melting, the effect of the composition of r-PET and MAPP was followed by morphological and mechanical studies. The results were discussed in relation to base polymers. In the absence of the compatibilizing agent (MAPP), PP/r-PET mixtures at different concentrations of r-PET exhibit a clear phase separation with poor dispersion of r-PET in the PP matrix. The addition of MAPP in PP/r-PET mixtures results in a decrease in the particle size of the dispersed phase (r-PET) in the PP matrix and an improvement in the interfacial conditions. This results in an improvement of the mechanical properties at traction and bending.

Keywords Polyethylene terephthalate, compatibilizing agent, Polymer blend, Polypropylene, mechanical properties.

I. Introduction

A recent notion (which is increasingly taken into account in our daily lives) is the notion of sustainable development, depending in part on the reduction of waste and/or its management. This goes through 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, plastics, 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 may be mechanical or chemical.

Mechanical recycling involves reusing the waste to make a finished or semi-finished material. However, this type of recycling generally results in a reduction 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 in 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 CO₂ [1]. For all these reasons, PET is increasingly used as packaging material. Its widespread use generates large quantities of waste which require the implementation of recycling techniques.

Recycling PET is not easy because of its degradation during reprocessing caused by temperature, humidity and contaminants. The degradation leads to a decrease in molecular weight and loss of properties [2]. One way to improve the properties of recycled polymers is to mix them

with unmodified polymers (polyolefins) with good properties. Polypropylene (PP) is widely used in this case [3], due to its good properties (lightness, transparency, high mechanical resistance, electrical insulation, inertia 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 exhibit good mechanical characteristics and permeability.

However, PET and polyolefins have very different chemical structures, which makes them immiscible with each other. The major disadvantage resulting from this incompatibility is that the resulting mixtures have poor mechanical properties.

The most frequently used means of partially filling this performance gap is compatibilization, which consists in creating chemical affinities between the constituents of the mixture 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 compatibility between the two polymers [6,7]. Maleic anhydride grafted MAPP may be used as a compatibilizing agent in PP/PET-r mixtures [8, 9, 10]. It has been reported that the use of MAPP in PP/PET-r mixtures can improve dispersion and adhesion between the two components [8]. It has also been indicated that the use of MAPP as a compatibilizing agent improves the strength and rigidity of PP/PET-r polymer mixtures [9]. Therefore, the main objective of this study was to investigate MAPP effect on the morphology and physico-mechanical properties of PP/r-PET blends.

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 anhydride-grafted-polypropylene (MAPP) with a melt flow index of 2.63 g/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, in the presence and in the absence of the 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. Formulations of PP/r-PET blend

Sample	Table Column Head		
	PP (wt%)	r-PE T (wt %)	MA-g-PP (wt%)
PP/r-PET ₁₀			
PP/r-PET ₁₀ /2,5%MA-g-PP	90	10	0
PP/r-PET ₁₀ /5%MA-g-PP	87,5	10	2,5
PP/r-PET ₁₀ /10%MA-g-PP	85	10	5
PP/r-PET ₂₀	80	10	10
PP/r-PET ₂₀ /2,5%MA-g-PP	80	20	0
PP/r-PET ₂₀ /5%MA-g-PP	77,5	20	2,5
PP/r-PET ₂₀ /10%MA-g-PP	75	20	5
PP/r-PET ₃₀	70	20	10
PP/r-PET ₃₀ /2,5%MA-g-PP	10	30	0
PP/r-PET ₃₀ /5%MA-g-PP	67,5	30	2,5
PP/r-PET ₃₀ /10%MA-g-PP	65	30	5
PP/r-PET ₃₀ /10%MA-g-PP	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.

Tensile and flexural tests were conducted with a Universal Testing Machine (Zwick/Roell Z020) at a crosshead speed of 5mm/min and 1.1 mm/min at room temperature according to ASTM D-638 and D-790, respectively. Five samples of each type were tested and average values were reported.

Water absorption of the PP/r-PET blends with and without MAPP was determined according to ASTM D570. Samples were immersed in distilled water at 23°C. The percentage of water absorption was calculated with the following equation (1):

$$WA = \frac{w-w_0}{w_0} \times 100 \quad (1)$$

III. Results and discussion

III.1. Morphology of Blends

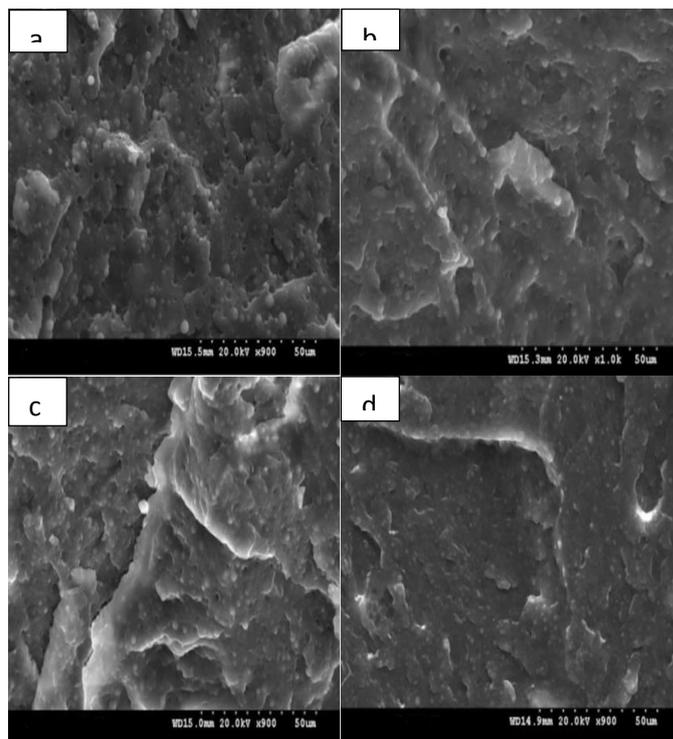


Figure 1: SEM micrograph of PP / r-PET 80/20 blend (a), SEM micrograph of the blend of PP / r-PET / 2.5% MAPP (b), SEM micrograph of the blend of PP/r-PET/ 5% MAPP, SEM micrograph of the blend of PP/r-PET /10% MAPP.

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 10.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 PP-g-MA, 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.2. Mechanical Properties

The presence of MAPP in PP/r-PET mixtures (Figure 5) increases elongation at break compared with completely incompatible PP/r-PET binary blends. This increase is more significant with the increase in the rate of MAPP. This indicates improved interfacial adhesion between the two components. Consequently, the blends can withstand tensile deformation at higher elongations.

PP/r-PET/MAPP ternary blends are relatively less rigid than PP/r-PET binary blends. Indeed, MAPP, due to its compatibilizing role, improving the interfacial interactions between r-PET and PP, also provides flexibility to the PP / r-PET blend. indicates improved interfacial adhesion between the two components. Consequently, the blends can withstand tensile deformation at higher elongations.

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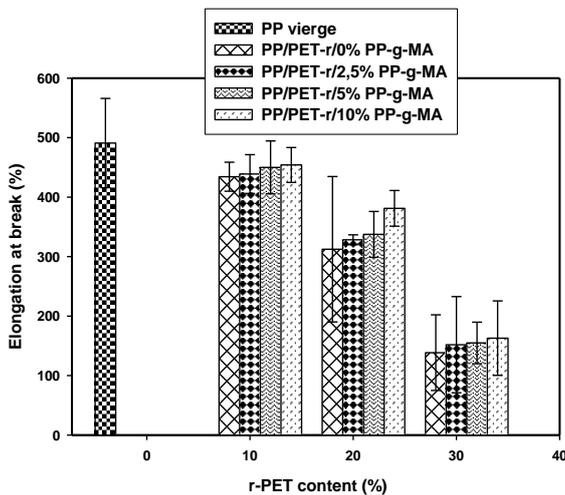


Figure. 2: Evolution of the elongation at break of PP/r-PET mixtures as a function of the rate of r-PET, in the presence of MA-g-PP.

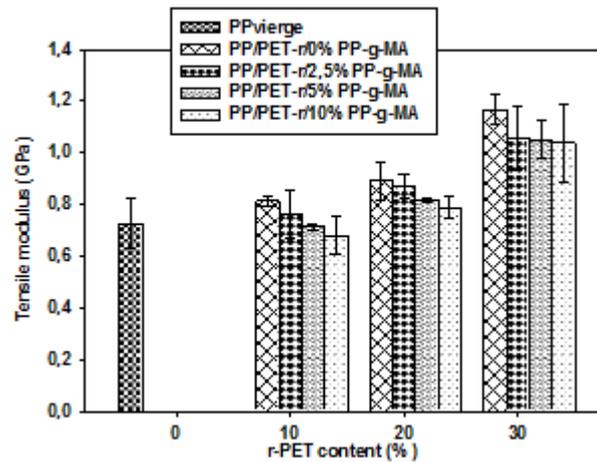


Figure. 3: Evolution of the Young's modulus of PP / r-PET blends as a function of the rate of r-PET, in the presence of MA-g-PP.

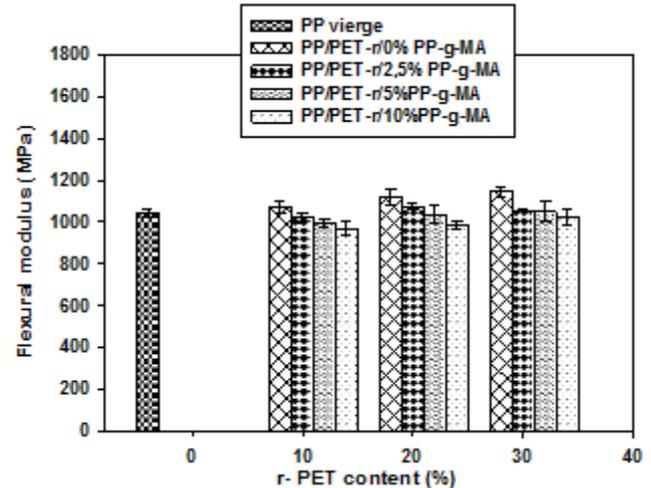


Figure. 4: Evolution of the flexural modulus of PP/r-PET blends as a function of the rate of r-PET, in the presence of MAPP.

In the presence of the MAPP copolymer, the behavior of PP/PET-r mixtures is reversed, where the modulus of traction and flexion decreases in the same range of composition which is due to an elastomeric behavior of this copolymer [11].

The transition from the brittle behavior of the PP/r-PET mixture to the ductile behavior for PP/r-PET/MAPP mixtures could be attributed to the more uniform morphology of the latter and by better adhesion in ternary mixtures compared with the PP/r-PET binary mixtures [11]. These results confirm the effectiveness of MAPP as a compatibilizer for PP / r-PET blends, causing a decrease in Young's modulus and flexural modulus.

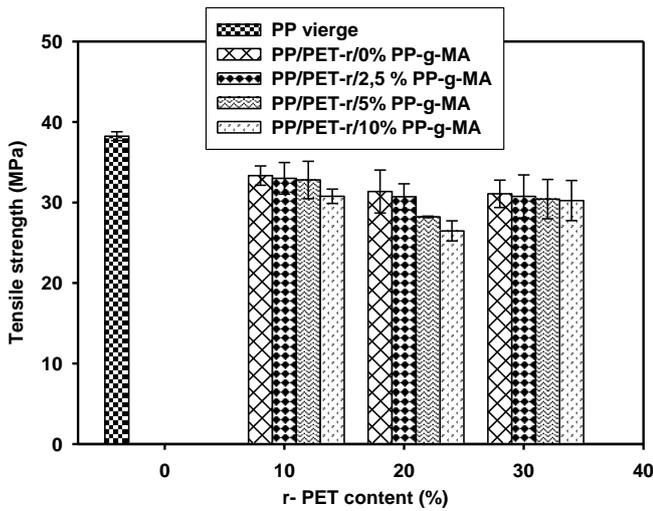


Figure 5: Evolution of the tensile stress of PP / r-PET blends as a function of the rate of r-PET, in the presence of MAPP.

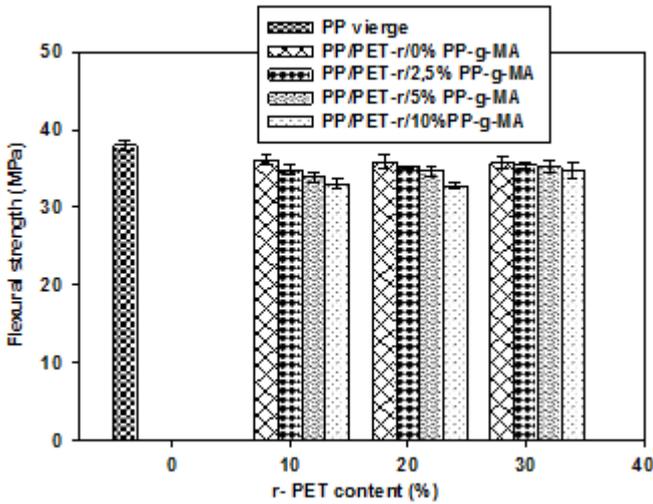


Figure 6: Evolution of the flexural stress of PP / r-PET blends as a function of the rate of r-PET, in the presence of MAPP.

We observe that the general trend of the histograms is similar for all the mixtures with different levels of r-PET, characterized by a slight decrease in tensile and flexural stress with the increase in the content of MAPP. This decrease is attributed to the elastomeric behavior of MAPP [12].

III. 3. Fourier Transforms Infrared Spectroscopy Measurements (FTIR)

Examination of the interface between the PP and the PET-r allows for further information on the effect of compatibility on polymer blends. At the same time, the analysis of the infrared spectra of the mixtures will make it possible to establish the link between the interface and the compatibilization reaction.

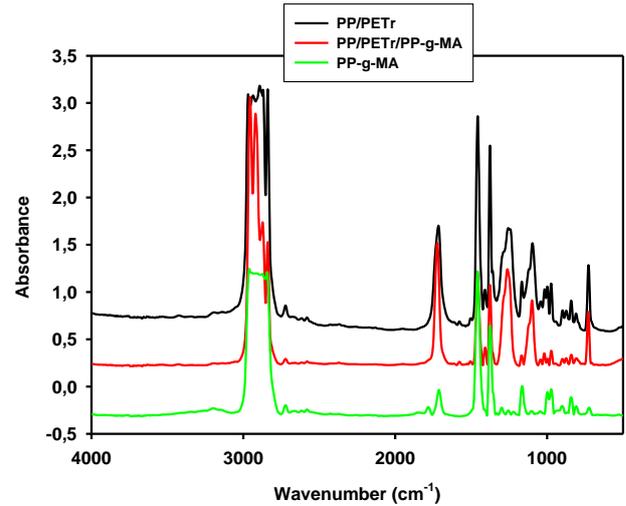


Figure 7: Infra-red spectra of PP / r-PET (80/20) blend, in the absence and in the presence of MAPP.

The spectroscopic study of the mixture to establish the chemical reaction of functional groups of MAPP with end groups of r-PET. Analysis of infrared spectra of PP / r-PET₂₀ (80/20) blend compatibilized by 10% MAPP (Figure 7) does not show a peak at 1784 cm⁻¹, characteristic of the maleic anhydride function. This means that all of the maleic anhydride functions were indeed consumed during the reaction of compatibility with the r-PET hydroxyl groups [13].

III. 4. Water absorption properties

It can be clearly seen from the experimental curves (Fig 8,9,10,11) that the water absorption rate of r-PET is higher than that of PP due to the hydrophilic group (ester groups) of r-PET.

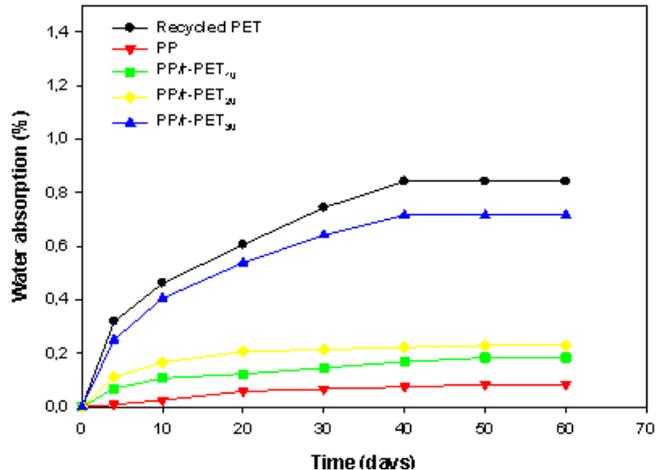


Figure 8: Evolution of the water absorption rate of PP/r-PET blends as a function of the immersion time at different rate of r-PET, in the absence of MAPP.

The increase in PET-r results in an increase in water absorption. This increase is attributed to the increase in the concentration of ester groups that have a high affinity with water. We can also attribute this phenomenon to the poor interfacial adhesion between the two phases resulting in the increase of microvoids [14]. For example, samples of PP/PET-

r_{10} and PP/PET- r_{20} blends reached their water saturations (0.18%, 0.23% respectively) after 30 days of immersion. However, the sample PP/PET- r_{30} reached a maximum absorption (0,7 %) after 60 days of immersion compared to PP/PET- r_{10} and PP/PET- r_{20} .

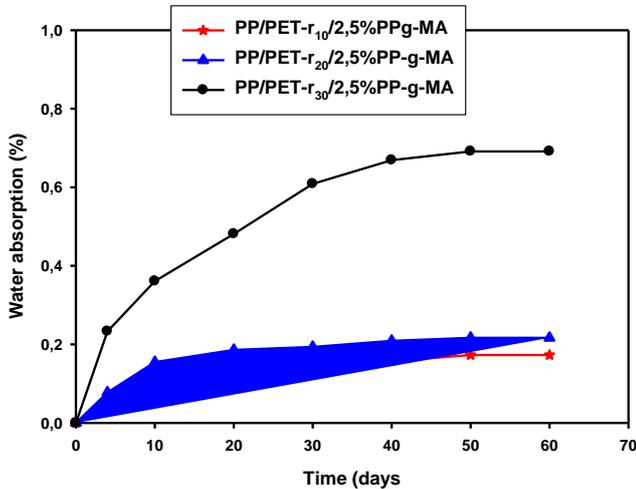


Figure. 9: Evolution of the water absorption rate of PP/r-PET blends as a function of the r-PET rate, in the presence of 2.5% MA-g-PP.

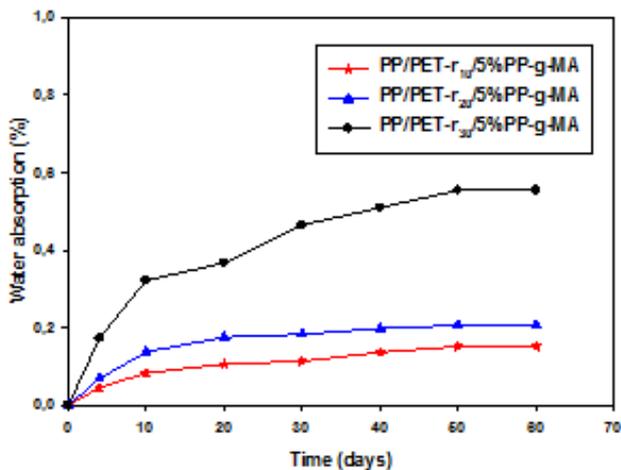


Figure. 10: Evolution of the water absorption rate of PP/r-PET mixtures as a function of the r-PET level, in the presence of 5% MA-g-PP.

The introduction of MAPP into PP/r-PET blends at different levels of r-PET reveals reduced water absorption compared to non-compatible PP/r-PET blends (Figure 1), this reduction is more significant with the increase in the rate of MAPP, this is attributed to an improvement in the interfacial adhesion between the dispersed phase and the polymer matrix and consequently a considerable decrease in the microvoids which promote water absorption [15].

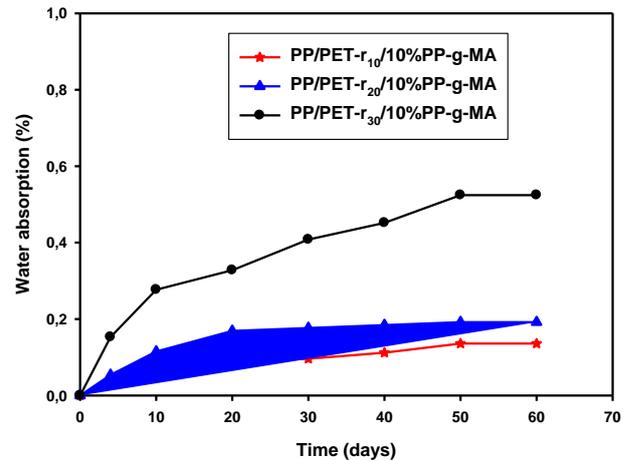


Figure. 11: Evolution of the water absorption rate of PP/r-PET blends as a function of the r-PET rate, in the presence of 10% MA-g-PP.

IV. Conclusions

During this study devoted to the study of the optimization of the rate of the compatibilizing agent PP-g-MA, we have been particularly interested in the problem of the PP/PET-r interface at different PP-g-MA rates, by varying the rate of 2.5, 5 and 10%. The demonstration of compatibility was examined by the various analytical techniques.

All the results obtained indicate that the addition of PP-g-MA as a compatibilizing agent improves the morphology of the PP/PET-r polymer blends at different rate of MAPP. These results in a reduction in the size of the particles of PET-r embedded in the PP matrix and an improvement in the interfacial adhesion between the two polymers. In addition, a decrease in Young's modulus and flexural modulus is also observed with an increase in elongation at break. The infrared spectra confirm that the reaction between the hydroxyl groups of PET-r and the maleic anhydride functions of MAPP has occurred giving a PP-g-PET copolymer. The introduction of MAPP into PP / PET-r blends at different rate of PET-r reveals reduced water absorption compared to non-compatible PP/PET-r blends. This is attributed to an improvement in the interfacial adhesion between the dispersed phase and the polymer matrix.

Disclosure of interest: The authors report no conflict of interest.

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