

Preparation and characterization of Polypropylene /Polyethylenterephthalate/wood Fibers composites in the presence of compatibilizer

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Abstract

This work consists in studying the structure-property relationships of polymer blends based on recycled polypropylene (PP) and poly (ethylene terephthalate). This research reports the results of incorporating a vegetable filler into the PP / r-PET blend. A synergistic effect is observed during the simultaneous incorporation of the wood flour and the agent compatibilizing MAPP in the polymer mixture. Composites based on PP / r -PET was prepared in two steps. Scanning electron microscopy (SEM) analysis of the fractured surface samples revealed a better interaction between the WF and the polymer mixture. The thermogravimetric analysis (ATG / DTG) of the sample showed that the presence of the filler decreases the thermal stability of the composites compared to the PP / r -PET mixture, but does not accelerate the degradation process. The DSC allows showing that the incorporation of wood flour in the mixture of polymer PP / PET-r has an influence on the values of T_f of the two polymers (PP and r -PET), with an increase in the degree of crystallinity was observed.

Keywords: Polypropylene, Polyethylene terephthalate, Wood flour, Composite materials, Thermal properties.

I. Introduction

A recent notion (which is taken more and more into account in our daily life) is the notion of sustainable development, depending in part on waste reduction and / or their management. This involves their treatment with a view to their recovery or their recycling. A large part of the waste consists of plastics 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 them or eliminating 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 the decrease in polymer properties. 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 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 significant quantities of waste that require the implementation of recycling techniques.

Recycling PET is not easy because of its degradation during reprocessing, caused by temperature, humidity and contaminants. Degradation, leads to decrease in molecular weight and loss of properties [2]. A way to improve the properties of recycled polymers is to mix them with polymers not modified (polyolefin) with good properties.

Polypropylene (PP) is widely used in this case [3], because of 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 mixtures of polyolefin (especially polyethylene (PE) and PP) and PET can display good mechanical characteristics and of permeability.

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

mediocre. The most frequently used means of partially filling this deficit performance is the compatibilization, which consists in, creating chemical affinities between constituents of the mixture in order to reduce interfacial tensions, improve adhesion between phases and stabilize morphology [5]. Some of these studies have focused on the techniques to improve the compatibility between the two polymers [6, 7]. PP grafted with anhydride maleic (MAPP) can be used as a compatibilizer in mixtures of PP / PET-r [8- 11]. The strengthening of polymeric materials is expressed by the improvement of certain processing and end-use properties.

The last few decades have seen an interest growing for the use of renewable resources as back-ups in systems composite polymers. This is due to the growth of environmental regulations and increased interest in the proper use of renewable natural resources for develop environmentally friendly materials. In this way, the incorporation of natural fibers, especially wood flour as a reinforcing filler, can produce composites which often exhibit a remarkable improvement in their properties, for example compared to the pure polymer. Indeed, the addition of wood flour as a natural filler renewable in polymer blends aims to produce a unique combination of high performance, lightness, recyclability, biodegradability and the advantages of low cost processing.

The incorporation of wood flour in such a matrix polymer blend can lead to the development of a new group of materials composites. These advantages have led to the use of natural fillers such as, potential replacement for traditional reinforcement materials such as fiberglass, calcium carbonate and silica in composite systems [12]. However, there are certain limits to their use for structural applications. The main problem stems from the inherent incompatibility of most polymer matrices due to the high cellulose content of natural fibers.

The presence of polar hydroxyl groups (-OH) on lignocellulosic material leads to a hydrophilic character of these fibers, which weakens the interfacial bond with the hydrophobic organic matrices [13]. The poor compatibility between the two phases leads to poor interaction and therefore low capacity of the matrix to transfer charges applied to the reinforcing fibers. To solve the problem, the maleated polyolefins are commonly used as coupling agents to establish a good interaction between each phase in the composite [14]. Several studies have been carried out on the production of composites of natural fibers based on polyolefin blends (PP / PE) [15-20], however, little work has focused on polyolefin / recycled PET as a matrix [21, 22].

II. Material and methods

PP 500P polypropylene with a melt flow index of 3.00 g/10 min 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). The WF was extracted from Aleppo pine trees growing in the Djelfa region in southern Algeria. Average particle size was approximately 50 μ m.

Table 1: Formulations of PP/r-PET/WF composites

Sample	PP (wt %)	r -PET (wt%)	MAPP (wt%)	Wood flour (wt%)
PP/r-PET/WF10	70	20	0	10
PP/r-PET/WF20	60	20	0	20
PP/r-PET/WF30	50	20	0	30
PP/r-PET/WF10C	60	20	10	10
PP/r-PET/WF20C	50	20	10	20
PP/r-PET/WF30C	40	20	10	30

The r-PET was dried at 120°C, WF at 105°C, and PP and MAPP at 90°C. The composites were produced in a two-stage process: (i) extrusion for pelletizing and (ii) injection molding. In the first stage, 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 (15 mL Micro compounder, DSM Xplore, University A. Mira of Bejaia, Algeria). After air cooling, the extrudates were cut into pellets. In the second stage, composites were produced in the presence or absence of MAPP at 10%, 20%, and 30% WF content. The PP/r-PET pellets, WF and 10% MAPP compatibilizer [23–25] were mixed and fed into the same twin screw extruder at 180°C and 100 rpm for 10 min to prevent degradation of the cellulose fibers. Compounding ratios of the prepared composites are presented in Table 1. The compounds were subsequently injection molded using a laboratory scale injection molding machine (12 mL 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.

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 isothermal) or time. Saved thermograms provide information mainly on the physical phenomena of vaporization, sublimation or desorption, but also on decomposition or oxidation reactions, particularly in the case of polymers [26].

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 (N₂).

The characterization of crystallization and melting of polymers can be carried out by considering the thermal exchanges linked to these processes. In fact, heat is released when the polymer crystallizes as it absorbs heat as it melts. Analysis Differential Scanning Calorimetry (DSC) is used to measure the amounts of heat released or absorbed during these steps, by applying the same temperature program to, the tested sample and an inert reference. A signal proportional to the power difference, supplied to the sample and to the reference (dw / dt) is recorded [27].

This method is widely used for the characterization of polymers. It provides information on the glass transition of amorphous polymers, temperature and enthalpies melting and crystallization of semi- crystalline polymers .She permits, in particular, to follow the evolution of crystallinity through the estimation of the crystallinity rate [28].

III. Results and discussion

Figure 1 shows the SEM micrograph of the rupture surface of the PP / PET-r mixture (80/20). It can be seen that PET-r is dispersed in the continuous phase of PP, in the form of globular particles. The fractured surface has many voids, and the interface between the r-PET particles and the continuous phase of PP can be clearly distinguished, indicating the immiscibility of both r-PET and PP polymers.

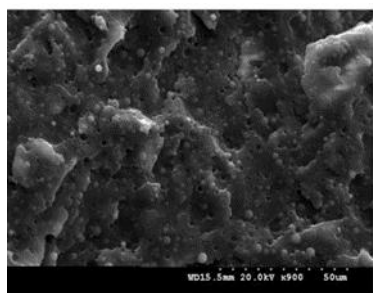


Figure 1: SEM micrograph of the mixture of PP/r-PET (80/20).

Adding 10, 20 and 30% of the cellulosic filler to the PP / r-PET mixture causes the onset of distinct phases, as shown in Figure 2. It seems that no interaction has developed between the phases, which reveal a weak affinity between wood flour and polymer blend (PP / r-PET). The morphology of surface shows a rough, irregular and heterogeneous surface as well as the presence of micro vides and cavities on the surface due to the release of the load from the matrix PP / r -PET during fracture. These micro vides become more pronounced as the rate of load increases (Figures B and C), highlighting the incompatibility of the phases due to the poor interfacial adhesion between the WF and the PP /r- PET mixture.

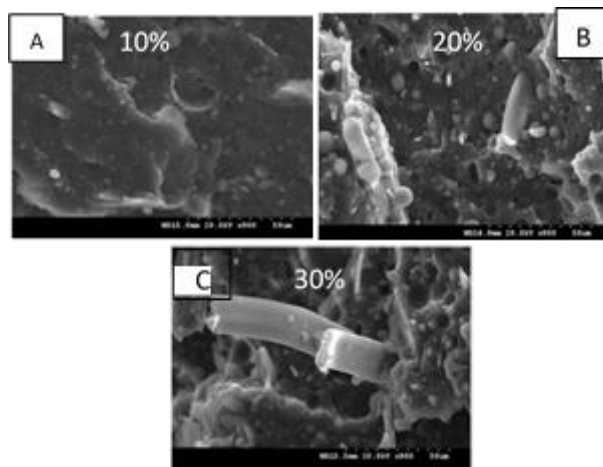


Figure 2: SEM micrograph of the composite of PP/r-PET/ WF, in the absence of MAPP.

Figure 3 show the micrographs, respectively, of composites PP /r -PET/ WF10C, PP/r -PET/WF20C and PP /r -PET / WF30C.

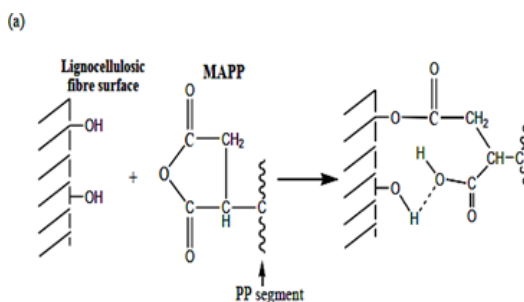
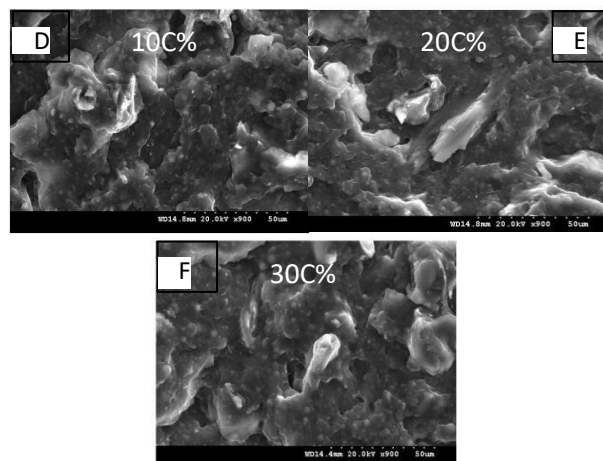


Figure 3: SEM micrograph of the composite of PP / r -PET / WF10C/20C/30C, in the presence of MAPP.

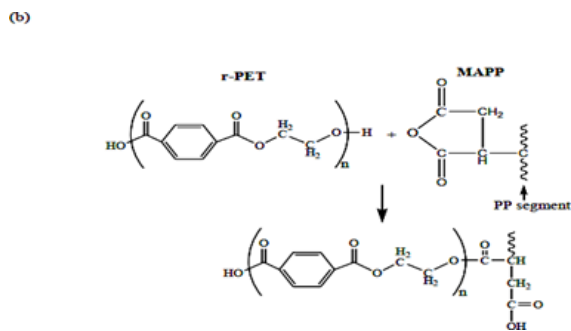


Figure 4: Chemical reactions between: Lignocellulosic loads and MAPP r -PET and MAPP.

The presence of a compatibilizer considerably modifies the morphology of the composite. The incorporation of the copolymer of MAPP (at 10%) as a compatibilizer, results in a more homogeneous and smooth surface with less cavities and microvoids, in comparison with that of non- compatibilized composites. Indeed, the micrographs show better adhesion between the cellulosic filler and the mixture of polymer resulting from the reduction of the interfacial tension between the components. This is attributed to the ability of MAPP to interact with both polypropylene, poly (ethylene terephthalate) and wood flour. The proposed coupling mechanism is a binding hydrogen and the covalent bond of the ester produced by the chemical reaction of anhydride groups of MAPP and hydroxyl groups on the surface of fibers [29, 30] and also the chemical reaction between maleic anhydride and terminal functional groups PET-r as shown in Figure 4. The chemical reaction between the anhydride maleic (AM) and the -OH groups of PET-r resulted in a PP-g-PET copolymer during melting the mixture [31]. The use of MAPP in the composite has a pronounced effect on the creation of interactions between the components present in the composites [32].

Thermal properties:

Thermogravimetric analysis (TGA)

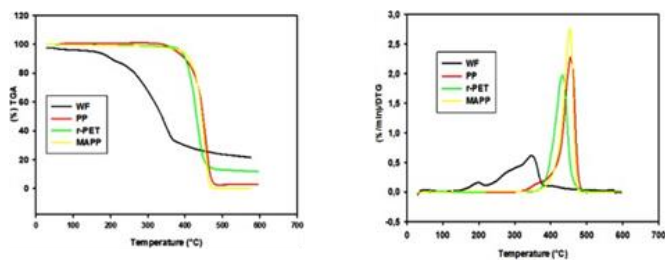


Figure 5: ATG/DTG thermograms of Wood Flour (WF), PP, r-PET and MAPP.

From the ATG thermograms (Figure 5), it can be seen that PP, PET-r and MAPP decompose in a single step, and that the temperatures at the start of degradation ($T_{\text{degradation 5\%}}$) are 377.68°C, 389.46 °C and 391.91 °C, respectively. The latter (MAPP) exhibits high thermal stability compared to that of PP, PET-r and cellulosic filler. Conversely, wood flour has three stages of decomposition. The first at 100 °C is attributed to the gradual evaporation of the absorbed water. From 200 °C to 350 °C, there is degradation of hemicellulose and above 350 °C; it is associated with decomposition and condensation of aromatic rings in lignin [33].

Figure 6 represent the ATG and DTG thermograms of the composites not compatible with PP / r -PET / WF at different loading rates (10, 20 and 30%).

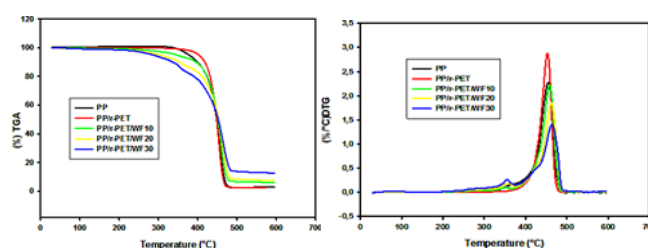


Figure 6: ATG/ DTG thermograms of PP / r -PET and PP / PET-r / WF composites, in absence of MAPP.

From the ATG thermograms shown in Figure 6, we observe that the Thermal degradation profiles of incompatible composites are similar. Indeed, we record three stages of degradation for composites, while we observe that a single decomposition stage for the polypropylene /poly (ethylene terephthalate) recycled. We note that the incorporation of wood flour in the PP / PET-r mixture decreases the temperature of the onset of decomposition and this decrease is greater than the charge rate increases. It is estimated at 402.55 °C for PP / r -PET, 347.25 °C, 301.78 °C and 285.61 °C for non-compatibilized composites PP/r-PET / WF10, PP / r -PET / WF20 and PP / r - PET / WF30, respectively. This decrease can be attributed to the presence of the three main constituents (cellulose, hemicellulose and lignin) of the cellulose filler [34]. The cellulosic filler degrades between 200 °C and 350 °C. While our polymer blend PP/r-PET degrades at temperatures above 400 °C. Therefore the thermal behavior of the composite represents the sum of the individual behaviors of these constituents, lignocellulosic filler and mixture of PP / r -PET. Around of 485 °C, a level of stability is recorded, attributed to the formation of ash However, looking at the peaks of the DTG thermograms shown in Figure 6,

It is noted that the temperatures corresponding to the maximum speeds of degradation recorded are : 458.33 °C, 461.25 °C and 464.70 °C for the non- compatibilized PP/r-PET/WF composites at different loading rates, 10%, 20% and 30%, respectively, which are

significantly higher than that of the PP / r -PET mixture which is 454.36 °C. Apart from the initial decomposition temperature, it can be clearly seen that the charge Lignocellulosic significantly retards the degradation of the PP / r - PET mixture. In other words, it acts as an inhibitor of thermal degradation.

The effect of the compatibilizer on the thermal behavior of composites PP / r -PET / WF is shown in Figure 7.

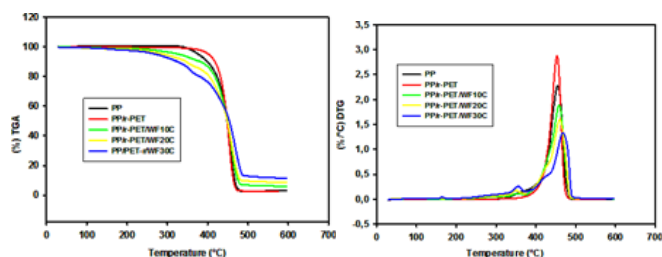


Figure 7: ATG/DTG thermograms of PP / r - PET and PP / PET-r / WF composites, in presence of MAPP.

In the presence of MAPP in PP / PET-r / WF composites at different loading rates (10%, 20% and 30% by weight), the temperatures corresponding to the maximum speeds of degradations ($T_{\text{to Vmax}}$) are shifted to higher temperatures compared to those of non- compatibilized composites.

The improvement in the thermal stability of compatibilized composites is due to better interfacial adhesion and over intermolecular bonds which produces a reaction esterification between the hydroxyl groups of the lignocellulosic charge and the maleic anhydride functional group of MAPP [35, 36].

This result indicated that the use of a compatibilizer in composite systems improves the thermal stability of composites [37-40]. However, composites not compatibilized were easily thermally degraded by the increase in temperature which is due to poor interfacial adhesion between the polymer mixtures PP / r-PET and wood flour which degrades the thermal properties of the materials of composites [41, 42].

Differential Scanning Calorimetry (DSC):

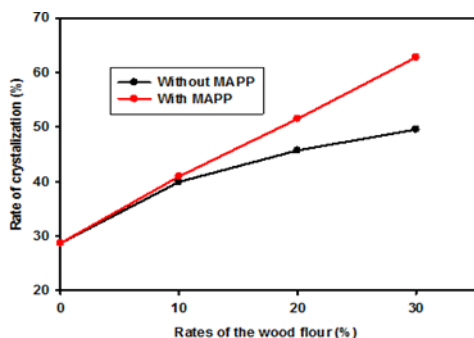


Figure 8: Evolution of the crystallinity rate of PP / r-PET

/ WF composites, in the absence and in the presence of MAPP.

From the results obtained, it can be seen that the introduction of WF into the mixture of PP/r-PET increases the crystallinity rate (Figure 8), the latter increase as the flour rate increases. It goes from 28.70% for the; mixture (matrix) PP / r- PET pure at 39.93% for the composite PP / r-PET / WF10 at 10% and 45.70% for the PP / r-PET / WF20 composite at 20% and 49.54% for the PP / r- PET composite at 30%, respectively. Generally, the incorporation of the cellulosic filler into the matrix polymeric occurs in the amorphous zone of the material and the surface of the filler acts as nucleation sites which modify the crystallization kinetics of polymers [48, 49]. The presence of wood flour in the PP / r -PET mixture decreases the T_f of PP and PET-r by compared to the pure PP / PET-r mixture, there is therefore the formation of crystals of smaller size or with more flaws. For compatibilized composites, the DSC data reported in Table 3 determine that the degree of crystallinity is higher than that of non-composite composites compatible with different charge rates. According to the literature, this could be due to stronger interactions between the lignocellulosic charges (WF) and the polymer mixture. PP /r-PET is affected by maleic anhydride moieties containing agent-compatibilizing MAPP. The influence of charge on the crystallization of PP and r-PET would then be larger. A similar effect was observed by Luz et al. [44].

I. Conclusions

An innovative composite material based on wood flour and a polymer blend PP /r-PET was developed using two extrusion cycles, followed by molding by injection. The effect of the addition of wood flour (WF) as well as the compatibilizer MAPP on the morphology and thermal properties of PP / r -PET / WF composites was studied. Scanning electron microscopy (SEM) of PP / r-PET / WF composites has indicated that the addition of MAPP had beneficial effects on the compatibilized PP / r-PET / WFC composites, resulting in a homogeneous load distribution (WF) and a strong adhesion between the filler and the PP / r- PET mixture.

Thermogravimetric analysis (ATG / DTG) of the samples reveals that the presence of the load at different contents (10, 20 and 30%), decreases the thermal stability of composites compared to PP / r- PET blend, but does not accelerate the degradation process. However, with the addition of MAPP an improvement in the thermal stability of composites is recorded.

The differential calorimetric analysis shows that the incorporation of the wood flour in the polymer mixture PP / r-PET has an influence on the values of melting temperatures of the two polymers (PP and r-PET), with an increase in the rate of crystallinity is observed. The surface of the flour acts as nucleation sites which modifies the crystallization kinetics of PP and r -PET.

All these results obtained allow us to conclude that the presence of wood and the compatibilizer MAPP has a strengthening effect of the PP / r-PET mixture. This technology offers a way to use engineering plastics (r-PET) for applications of WPC (Wood Plastic Composite).

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