CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECT OF ALFA FIBER TREATMENT AND MAPP COMPATIBILIZATION ON THERMAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE/ALFA FIBER COMPOSITES

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This study investigates the behavior of a polypropylene (PP) thermoplastic reinforced with different contents of alfa fiber (10 and 20 wt%). Structural, thermal and tensile test analyses were carried out. The dynamic thermo-mechanical behavior was observed by DMA, and the vibration test was conducted as well. Two types of treatments were carried out on these composites, including the modification of alfa fiber with acetic anhydride and the addition of a compatibilizer (5 wt%). The results obtained showed the incorporation of the treated and untreated alfa fiber in the matrix improved the mechanical properties, as determined by three techniques. As for the thermal properties, apart from the onset decomposition temperature, which decreased with the addition of treated and untreated alfa fibers, it was noted that the maximum rate of decomposition decreased, thus the thermal stability improved.

Keywords: alfa, interfacial adhesion, composites, polypropylene, mechanical properties

INTRODUCTION

Plastic materials have experienced a great rise in recent decades. They invaded our daily lives both in a wide range of common household goods and in technical use through high performance applications. Thermoplastics are the most widely used, in particular polyolefin, such as PP.[1] They represent more than 50% of the world production of plastic. PP comes second after polyethylene (PE), with over 30 million tons produced each year and an annual growth of 7%.[2] The thermoplastic properties (lightness, good electrical properties, chemical resistance, barrier properties etc.), combined with a low cost and ease of processing, make these materials the best choice for various industries: construction, automotive, biomedical, packaging and many other applications.[3-4] Thermoplastic materials also have limitations, but their limitations do not preclude their usage for applications that require high performance, particularly mechanical performance. In order to overcome their shortcomings, a new class of materials called composites was born, which make a compromise between performance and cost.

The use of cellulosic materials (flax, kenaf)[5-6] as fillers or reinforcements for thermoplastic matrices, such as PP, offers many advantages compared to conventional reinforcement. Cellulosic materials present low density, less abrasion on processing equipment and good specific properties.[7-8] They come from abundant resources, which reduces their cost, are renewable and naturally biodegradable, which presents them as ecological materials.[8,4] However, the hydrophilic nature of lignocellulosic materials presents a disadvantage, when they are incorporated into hydrophobic polymers. In fact, they are poorly dispersed, which is the reason for the formation of an unsuitable interface to transfer stress and of water pockets causing cavities during processing, which leads to low mechanical properties. In addition, the degradation temperature of lignocellulosic fibers is lower than 200 °C, which is a limitation in the processing of wood-polymer composites because of the volatiles that may be achieved, and fiber degradation.[9] Therefore, the surface modification of the fiber or polymer is of paramount importance in order to achieve a material with good mechanical properties.

Several researchers have modified interfacial adhesion by acetylation[10-11] or by the addition of a compatibilizing agent.[12-13] These studies have shown the effectiveness of a load change of the interphase/matrix by surface treatment of the filler or the matrix, or by incorporation of a compatibilizing agent to improve the interactions between these two constituents. Consequently, the hydroxyl groups existing on the surface of the load reduce the surface energy, which improves compatibility.

Alfa is an herbaceous perennial of the Gramineae family. Indeed, it is an abundant resource in the arid western basin of the Mediterranean Sea.[14] It plays a vital role in the fight against erosion. Alfa was used for making mats, curtains, rugs, baskets, bins, trays, shoes, jugs, twine and links. At the end of the 19th century, alfa quality paper appeared, which would bring great economic importance to this plant.[15] Due to its many advantageous features, alfa plant fiber has a wide scope of applications.

This study aims to incorporate alfa fiber into a PP matrix, and then to investigate the modification of interfacial adhesion forces between the alfa fiber and the PP matrix in order to increase their compatibility by two different methods. The first method was based on the chemical treatment of alfa fiber by acetylation, whereas the second one consisted in using a coupling agent, maleic anhydride-grafted polypropylene (MAPP), to improve the interfacial bonding between the alfa fiber and the PP matrix. The mechanical properties of the obtained samples were determined by the tensile test, dynamic mechanical analysis (DMA) and vibration analysis. The thermogravimetric and infrared spectral analyses were performed.

EXPERIMENTAL

Materials

Isotactic polypropylene (PP500P©) was used in this study as matrix and was provided by SABIC (Saudi Arabia). It had a melt flow index (MFI) of 3 g/10 min (230 °C/2.16 kg) (ASTM D-1238) and a density of 0.9 g.cm^{-3} (values from supplier datasheets). The alfa used as reinforcing filler was collected at M'sila in Algeria and its average particle size was around 100 µm. It was previously dried in an oven at 80 °C until its weight reached a constant value.

Two methods were carried out in this paper to improve fiber/matrix interfacial adhesion. The first corresponded to the incorporation of a compatibilizing agent in PP, *i.e.* maleic anhydride-grafted polypropylene (MAPP), supplied from ARKEMA Co. (France), (MFI = 2.63 g/10 min (190 °C/2.16 kg) from supplier datasheet). The second method consisted in treating the alfa fiber surface by acetylation using acetic anhydride (98%), acetic acid (18.09 M) and sulfuric acid (18.40 M), which were provided by Sigma-Aldrich.

Fiber treatment

An amount of 15 g of alfa fiber was placed in a round bottom flask with 72.5 ml acetic acid. The reaction was performed in a thermostatic bath at 35 °C for 45 min under mechanical stirring. After that, 24 ml of acetic acid (18.09 M) was added with 0.1 ml of concentrated H_2SO_4 (18.40 M) and the bath was maintained for more than 1 h. After this step, the mixture was cooled at 18 °C for slow addition of anhydride acetic (40 ml) with 0.6 ml concentrated H_2SO_4 during 3 h under constant stirring. A temperature of 24 °C was maintained for more than 15 min and then was slowly increased to 50-55 °C and the reaction continued for 3 h. Finally, this mixture was vacuum filtered, washed with distilled water then dried in an oven at 50 °C for 24 h to obtain cellulose acetate.[16]

Composite processing

Different formulations of PP/alfa fiber were prepared by twin-screw extrusion. The formulations contained PP, PP/untreated alfa fiber and PP/alfa fiber treated by two types of treatment: acetylation and addition of a compatibilizing agent MAPP. Table 1 shows the compositions by weight of the various formulations of PP/alfa fiber.

The equipment used for the preparation of the composite PP/alfa fiber was a bi-screw extruder connected to an injection press ERINKA mark. From the injection molding machine, tensile specimens were obtained. Working conditions were as follows:

- Temperature: 180 °C;
- Pressure: pre-injection (4 bars), injection (5 bar) and the holding pressure (5 bar);
- Mold temperature: 30 °C.

Techniques

Fourier transform infrared spectroscopy

The samples were characterized by Fourier transform infrared spectroscopy (FTIR) using the KBr pellet technique. Spectra were recorded on a Shimadzu FTIR-8400, with a resolution of 4 cm^{-1} within the region from 3500 to 1000 cm^{-1}.

Thermogravimetric analysis (TGA)

TGA experiments were carried out on a Setaram TG-DTA 92-10 thermal analyzer, using a scanning rate of 10 °C.min^{-1} under nitrogen in the temperature range starting from 25 °C to 700 °C.

Tensile test

The static tensile tests were carried out using a MTS Synergie RT1000 (MTS, Eden Prairie, MN, USA) testing apparatus in a laboratory, where the temperature was 23 °C and the humidity was 48%, according to ISO 527. The loading speed was 1 mm.min^{-1}. An MTS extensometer was used with a nominal length of 25 mm.

The tests were carried out at least five times for each specimen and the results were averaged arithmetically.

Table 1
Samples used in this study

PP (wt%)	Fiber content (wt%)	MAPP (wt%)	Treated fibers (wt%)	Name
100	0	0	0	PP
80	20	0	0	FUT
75	20	5	0	FCT
80	20	0	20	FAT

Table 2
Designation of different formulations of PP/alfa fiber composites

Designation	Formulation
Virgin PP	Virgin PP: neat PP
F20UT	F20UT: alfa fiber (20 wt%) and neat PP
F20AT	F20AT: alfa fiber (20 wt%) modified by acetylation and neat PP
F20CT	F20CT: alfa fiber (20 wt%) and (5 wt% MAPP compatibilizer) and neat PP

Dynamic mechanical analysis (DMA)

The samples were also studied by dynamic mechanical analysis (DMA), using a single cantilever bending system DMA Q 800 (TA Instruments) at a frequency of 1 Hz. The dynamic storage modulus (E') and loss factor (tan δ) of the specimens were determined as a function of temperature from -50 °C to +160 °C.

Vibration analysis

The dynamic analysis methods for studying the mechanical behavior of viscoelastic materials are extensively used.[17-18] These largely developed methods identify the viscoelastic properties, such as storage modulus and damping.

The sample is placed in the "cantilever" position (built-in at one end and kept free at the other) and subjected to a drop test, that is to say by the application of mechanical impulse at the free end. The dynamic movement of the sample was measured by a SunX HL-C203F laser. Thus, to verify the linearity of the response of the system, it is not necessary to measure the impulsive force. This assumption permits to determine the first natural frequency of the system from the smoothing of the frequency response of the sample through Modan 3.0 software. Due to the complex geometry of the test piece, a finite element model is carried out using Comsol Multiphysics R software, which allows a trace back to the storage modulus by frequency recalibration.

RESULTS AND DISCUSSION

FTIR analysis

The chemical modification reaction of alfa fiber by acetylation was monitored by infrared spectral analysis in Fourier transform (FTIR). Figure 1 shows the IR spectra of the natural and acetylated alfa fibers. It shows that acetylation reduces the intensity of the peaks corresponding to the absorption bands of the hydroxyl groups at 3382 cm^{-1} substituted by acetyl groups. The intensities of the peaks at 1375 cm^{-1} and 1239 cm^{-1} assigned to the vibration of the methyl group (-CH_3) and acetyl, respectively, are greatly enhanced through the replacement of hydrogen atoms hydroxyl groups by acetyl groups. Also, the appearance of a new peak at 1751 cm^{-1} is observed and assigned to the vibration of the C=O of acetyl. These results allow us to highlight the success of the acetylation reaction of alfa fibers, and are consistent with those of Luz *et al.*, Jebrane *et al.* and Tserki *et al.*[16,19,20]

Thermogravimetric analysis

Thermogravimetric analysis was conducted to study the effects of the fiber content and of the two treatments on the thermal stability of the composites (Figs. 2 and 3). We can remark that the introduction of fibers improves the thermal stability of the composites. For unmodified fiber (Figs. 2 and 3), the literature mentions that dehydration and lignin degradation occur between 200 and 500 °C, while the cellulose is decomposed at a temperature of 350 °C.[21]

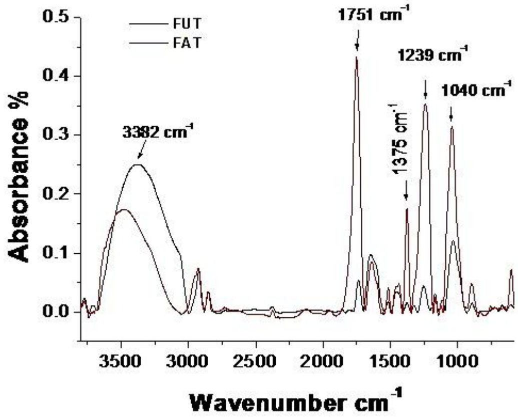

Figure 1: FTIR spectra of treated and untreated alfa fiber

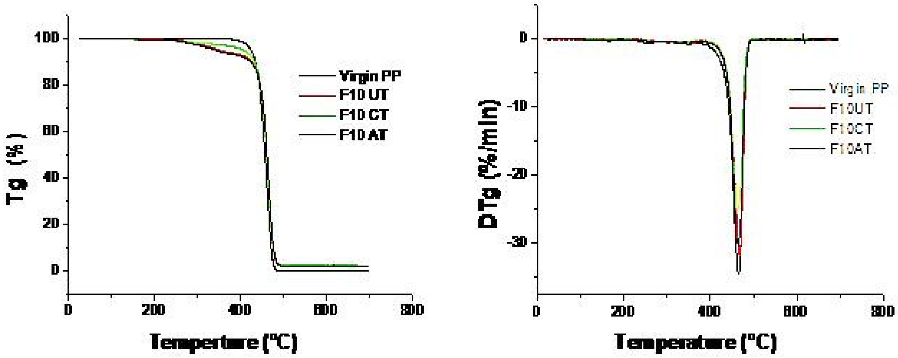

Figure 2: Thermal degradation behavior of the composites: TG and DTG curves of formulation F10

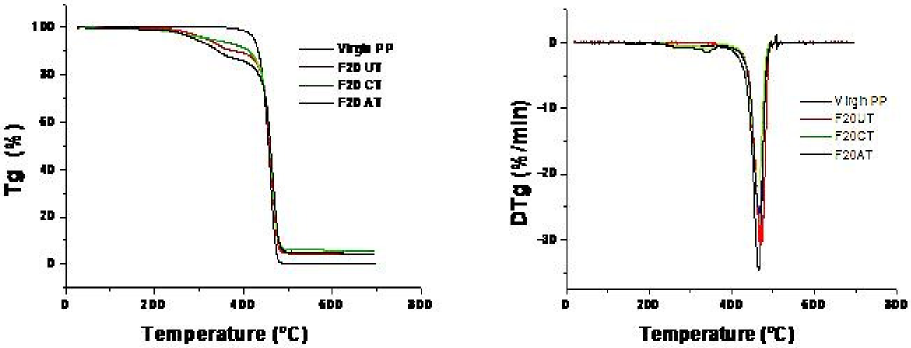

Figure 3: Thermal degradation behavior of composites: TG and DTG curves of formulation F20

Table 3
TGA data for neat PP and PP/alfa fiber composite materials

Formulation	T_{onset} (°C)	T_{max} (°C)	V_{max} (%/min)	Char (wt%)
Virgin PP	421	455	34.15	0.50
F10UT	391	474	31.48	2.54
F10AT	314	463	30.09	2.58
F10CT	412	461	25.54	2.10
F20UT	320	467	29.50	4.11
F20AT	307	466	25.77	5.54
F20CT	418	464	22.51	4.29

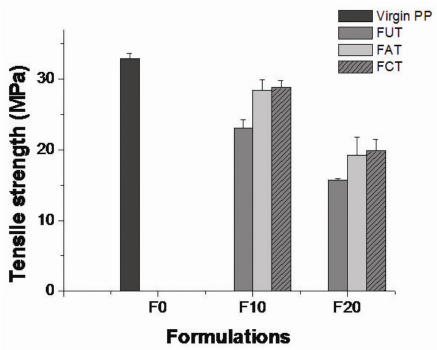

Figure 4: Tensile strength behavior

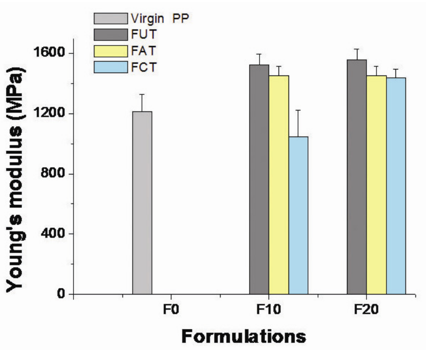

Figure 5: Young's modulus behavior

The decomposition of the PP (Figs. 2 and 3), meanwhile, starts at about 400 °C (breaking the C-C bonds of the main chain),[21,16] a higher temperature than that for fiber degradation. We recorded one stage for PP degradation, unlike composites whose degradation occurs in two steps. The first step stands for the decomposition of the fiber, and the second step corresponds to that of the PP matrix. The composites exhibit an intermediate thermal stability between that of the fibers and that of the matrix.[22] Generally, adding fiber decreases the thermal stability of composites based on PP thermal stability, because the thermal stability of fiber is lower than that of PP, and the degradation of fiber can induce the decomposition by the effect of PP contamination.[22] However, we noted that the treatment of fiber slightly limited this loss of stability, compared to untreated fibers. This can be explained by an improvement in the interfacial adhesion and the intermolecular bonds between the fibers and the matrix.[21] Also, the OH groups are replaced by more bulky groups, which results in restrictions in the segmental mobility, and increases the rigidity of cellulose. Other authors also show that the treatment of fibers, in particular by the MAPP compatibilizer, improves the thermal stability of the composite.[21-23] The detailed results of the thermogravimetric analysis are reported in Table 3.

Tensile properties

Figures 4 and 5 display the evolution of mechanical properties as a function of chemical treatment of the fiber and addition of compatibilizer. Whatever the reinforcement content, the addition of untreated alfa fiber leads to decreased mechanical performance of the composites, such as tensile strength (Fig. 4) (23.03 and 15.67 MPa for untreated formulations F10 and F20, respectively). The mechanical properties of the composites are strongly dependent on the adhesion and compatibility of the matrix with the load.

When towing the polymer/untreated alfa fiber composite, the rupture of the material is attributed to the failure of adhesion between the matrix and the dispersed and/or agglomerated fibers, which results in a stress concentration around the defects and inhomogeneities in the structure of the material. Indeed, many research studies have confirmed this result, such as those by Boukerrou *et al.*, and Nachtigall *et al.*[12,24] As for the composites treated by the addition of MAPP, they have better mechanical properties (tensile strength), compared to the matrix, and the composites PP/FUT and PP/FAT. These results confirm the capacity of MAPP to form strong interfacial bonds between the PP and the alfa fiber, therefore allowing better stress transfer between the two phases, compared to the treatment by acetylation.

As regards Young's modulus (Fig. 5), it may be noted that it increases with the introduction of the untreated fiber. This increased stiffness may be attributed to the stiffness of the fibers, which have better mechanical properties than those of the matrix. The chemical treatment of the alfa fiber led to a reduction of Young's modulus, compared to the untreated composite. Sabu *et al.*, Tihminliog *et al.* and Sapuan *et al.*[25-27] found similar results, and they explained this outcome by the phenomenon of plasticization of the alfa fiber after the treatment with MAPP, which makes the composite less rigid.

Viscoelastic properties

Dynamic mechanical properties, such as storage modulus (E'), and loss factor (tan δ) of PP and PP/alfa fiber composites were evaluated in the temperature range -50–160 °C (Fig. 6) at a frequency of one Hertz. According to the literature,[28] three temperature zones are distinguished: (1) the glass transition region, -50 to 10 °C; (2) the elastic transition zone, 10 to 80 °C; (3) the rubbery region above 80 °C.[28] In the case of the matrix (virgin PP), the storage modulus E' decreased significantly depending on the result of the progressive softening temperature of the material and the increase of segmental mobility. This phenomenon is observed only in the amorphous phase, while the crystalline region remains solid up to the melting temperature. Whatever the temperature, after the addition of the fiber (FUT), we observe an increase in the storage modulus, which can be explained by the improved stiffness of the composite and better stress transfer across the interface (from the matrix to the fiber). However, at high temperatures (over 100 °C), the gain provided by the fibers is less important. Indeed, when the softening takes effect: (1) the flow of the polymer increases, (2) the interactions between the matrix and the fiber are strongly reduced. Therefore, the transfer of stress is not sufficient to achieve high values of E'.

Regarding the loss factor tan δ of the PP/alfa fiber composite, we observe two relaxation zones. The first main relaxation (β transition) relates to the glass transition region and indicates the Tg of the amorphous portions (PP matrix). On the other hand, in the alfa fiber-reinforced composite there is a shift towards lower temperatures Tg, which may be ascribed to a nucleating effect generated by the presence of fibers.[29] The secondary relaxation (α transition) at 80 °C-100 °C is attributed to a mechanism of lamellar slip and the rotation in the crystalline phase (PP matrix),[29] as well as a decrease in chain mobility in the presence of fibers. The effect of the chemical treatment of PP/alfa fiber composite is illustrated in Figure 6. The shape of the graphs is the same as that obtained previously for the untreated composite. There are always three areas for the storage modulus and two relaxation zones (β transition and α) to the loss factor. For the systems based on treated fibers, the storage modulus is slightly lower (MAPP) compared to the materials based on non-modified fibers. This reduction can also be explained by a reduction of stiffness.

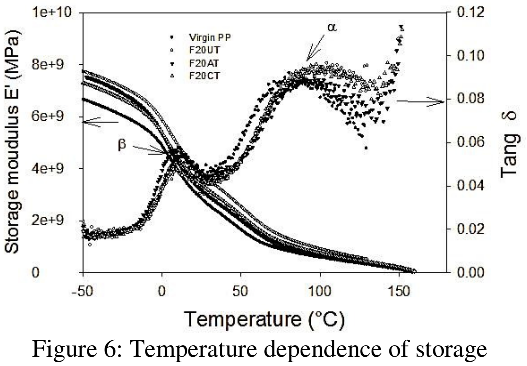

Figure 6: Temperature dependence of storage modulus and tang delta of PP/alfa fiber composites

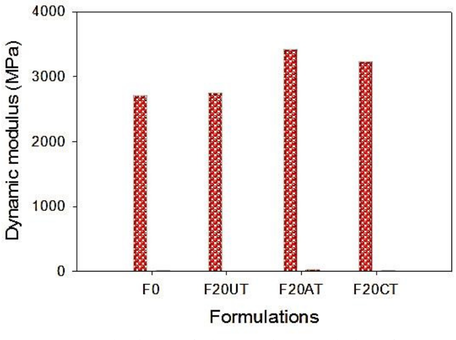

Figure 7: Evolution of dynamic modulus for PP/alfa fiber composites

This result confirms the data obtained by the tensile measurements, which show a decrease in tensile modulus for the composite treated by the addition of the compatibilizer at room temperature. This behavior is attributed to the presence of MAPP, which provides more ductility to the composite material. The modification in the loss factor in the glass transition region (β relaxation) is reduced by the addition of MAPP; this could be the result of a reduction in the mobility of macromolecular chain segments due to adhesion.[30]

Vibration analysis

Vibration analysis allows obtaining data in a fast, accurate and inexpensive way on the mechanical properties, in terms of rigidity of materials. Figure 7 shows the results of the vibration analysis on samples of PP/alfa fiber composites. In these specimens, the passage of frequency response functions (FRF) with dynamic parameter E is based on a simple analytical calculation. From these results (Fig. 7), we find that the modulus of the composites increased with the incorporation of the treated and untreated fibers, compared to modulus of PP alone.

CONCLUSION

FTIR spectroscopy characterization of alfa fiber samples showed that after acetylation, the hydrophilicity of the fiber decreased, which was attributed to the substitution of the hydroxyl groups by acetyl groups.

The incorporation of treated alfa fiber improved the thermal stability of the composites. However, the use of MAPP compatibilizer provided better thermal stability, compared to both treated and untreated alfa fiber.

The mechanical properties (tensile strength) were observed to decrease as the content of FUT increased. This is attributed to the poor dispersion of the fiber in the matrix, thereby forming aggregates, which leads to an embrittlement of the composite system. The viscoelastic properties were significantly improved by the addition of treated and untreated alfa fiber. It should also be noted that, under certain conditions, the fibers tended to act as nucleating agents and influenced the crystallization process. Therefore, the glass transition temperature Tg shifted to lower temperatures for the polypropylene matrix.

Vibration tests showed that the dynamic modulus of elasticity of the composites increased with the incorporation of the treated and untreated fibers, compared to the modulus of PP alone. Thus, the stiffness of the materials seems to suggest that the composites may have been damaged.

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