Effect of Hemp Fiber on PET/Hemp Composites

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ABSTRACT: The properties of polyethylene terephthalate (PET) reinforced with 1, 5, 10, 15 and 20% (w/w) alkaline-treated hemp fibers were investigated following a series of processing stages. The fiber concentration significantly impacts the compounding process, yielding thermostable composites below 300°C. Their elastic moduli varied logarithmically with fiber concentration, and were increased by up to 20% with respect to the nonreinforced formulation. Such reinforcement was, however, followed by a drastic decrease in the elongation at break, from more than 20 mm for the unreinforced PET to as low as 2.5 mm. Other properties showed closer observations to the variations of the elastic moduli. An appreciably good fiber-matrix interface was also observed; however the actual processing method could not take advantage of the fiber's length. This work has a major impact in the development of composite biomaterials, as it extends their application range to the subexploited area of high-melting thermoplastic matrices reinforced with natural fibers.

KEYWORDS: Polyethylene terephthalate (PET), hemp fibers, thermal, composites, properties

1 INTRODUCTION

The past decades have witnessed the emergence of natural fibers-reinforced composites as an important class of engineering material [1]. The features of natural fibers-reinforced composites have been under intensive investigation, with the objective of achieving their optimal application. An important challenge which is also investigated in this work consists in increasing the melting range of thermoplastic polymers that can be reinforced with natural fibers. In fact, due to the potential thermal degradation of natural fibers during processing with high-melting thermoplastic, there is currently a numerical imbalance between the composite applications with low and high-melting thermoplastics reinforced with natural fibers. Such potential degradation is due to the low onset of thermal degradation of natural fibers, which is around 190°C [2], as compared to the melting points (T_m) of high-melting thermoplastics, which by definition are found above 200°C [3].

Consequently, limited works have been reported about composites of high-melting thermoplastics with natural fibers by Caulfield *et al.* [3], Field *et al.* [4], and Bo Madsen [5] respectively. Each of these works presents a strategy to hinder the thermal degradation of natural fibers during processing. Caulfield *et al.* have thus processed polyamide 6 (PA 6) and polyamide 6-6 (PA 6,6) with high purity woodpulp fibers by extrusion, followed by cooling; Field *et al.* have blended PET and cellulose using a mixture of trifluoroacetic acid (TFA) and methylene chloride; and Bo Madsen has processed PET fibers reinforced with hemp fibers through the winding of both filament yarns followed by thermo-compression molding.

There are numerous advantages in reinforcing PET with hemp fibers. They include their high availability, their recyclability, and the toughness provided by PET's aromatic rings. Moreover, the solid state of its applications at room temperature is guaranteed by the high glass transition temperature (Tg) of PET, which is 60°C.

The processing effects on the fiber quality and the fiber's effect on the composite's mechanical, thermophysical, and structural properties have been investigated.

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2 MATERIALS AND METHODOLOGY

2.1 Materials

PET grade AA-48 (Eastman, Montreal, QC, Canada), polycaprolactone (PCL) from Sigma Aldrich (Oakville, ON, Canada), and hemp fibers of composite grade, having an average initial length of 6 cm (Lanaupôle, Berthierville, QC, Canada) were used in this work.

2.2 Methodology

PET/Hemp fibers composite was processed through many steps including a 5N alkaline treatment of hemp fibers, followed by compounding of PET, treated hemp fibers, and 5% PCL with a torque-based internal batch mixer (Haake Rheomix, PolyLab OS system, USA). The tests coupons were finally injection molded with a Haake Minijet. Five formulations reinforced with 1, 5, 10, 15, and 20% hemp fibers, compounded with the mixing chamber's temperature of 240, 250, and 260°C respectively were processed. The thermophysical, mechanical, and structural properties of the various composite formulations were tested respectively with a differential scanning calorimetry (DSC) model Q20 from TA Instruments (New Castle, DE, USA), Zwick Roell mechanical testing equipment, and a scanning electron microscope (SEM) model XL 30 from Philips (USA).

3 RESULTS

The individual properties of hemp fibers were found to affect various aspects of the investigated PET/Hemp composites, as well as their processes. The fibers' surface-to-volume ratio was, for example, found to affect the compounding processes, while their modified surfaces and thermophysical and mechanical properties showed a significant impact on the composite's mechanical, structural, and thermophysical properties. Based on these observations, there is further anticipation of potential impacts of hemp fibers on the applications of PET/Hemp fibers composite formulations. The specific properties are further developed in the following sections.

3.1 Effect of Fibers' Surface-to-Volume Ratio

The differences between untreated and alkaline-treated fibers are shown in Figure 1.

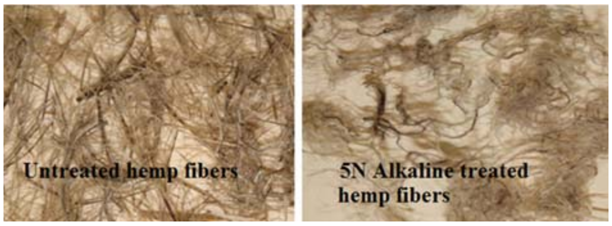

Figure 1 Contrasting aspect of untreated and alkaline-treated hemp fibers.

It can be observed that alkaline treatment results in the structural modification of hemp fibers, yielding more microfilaments, increasing their surface-to-volume ratio, which results in a higher fiber-matrix interface. Overall, such a modification has a significant positive impact on most composite parameters; however an increase of the surface-to-volume ratio also limits the reinforcement concentration, leading to another level of processing challenges. Consequently, a maximum of 20% hemp fibers was applied for the reinforcement of PET in this work, based on being compounded in a torque-based Rheomix. Reinforcements with a higher fiber volume could, however, be expected when processing with equipments of industrial size.

Figure 2 also shows the challenges of compounding in the variations of PET/Hemp fibers. In fact the compounding challenges increase with the fiber concentration. Moreover, the composite's melting time was found to vary with the fiber concentration.

3.2 Fiber-Matrix Interface

All the studied composite formulations showed similar and appreciably good fiber-matrix interface, which can be attributed to the hydrogen bonding between the carbonyl groups of PET and the hydroxyl groups of the modified hemp fibers. An example of such an interface is the scanning electron micrograph of PET reinforced with 20% hemp fibers shown in Figure 3. It shows good fiber wetting by the matrix, and attests to the fibers' limited thermal degradation during processing following the formulated strategy. The micrographs of all the other formulations showed similar structural patterns among which the negligible fiber degradation both during melt compounding and granulation is critical for high-melting thermoplastics reinforced with natural fibers.

3.3 Mechanical Properties

A summary of the mechanical properties of the studied PET/Hemp fibers composite formulations is given in Table 1. The elastic modulus, the load at yield and the elongation at break, were found to vary with the fiber concentration. Moreover, there is an increase of the elastic modulus with respect to the fiber concentration

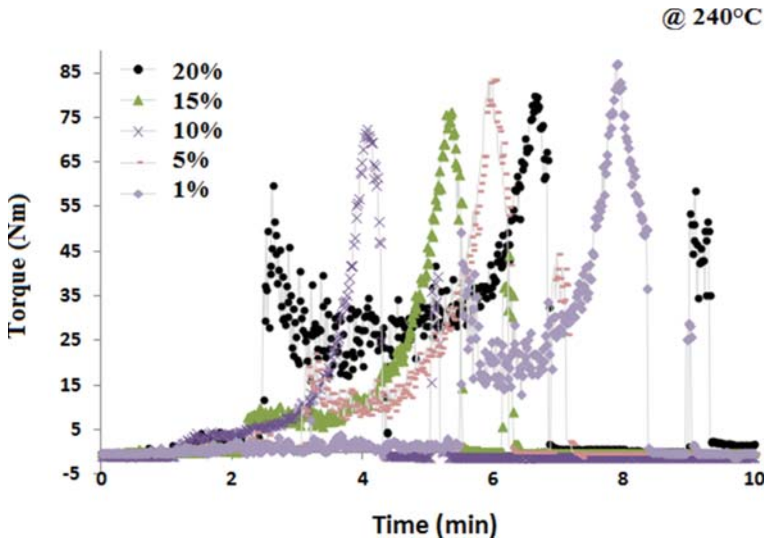

Figure 2 Torque data variations for the compounding of PET/Hemp fibers composite formulations.

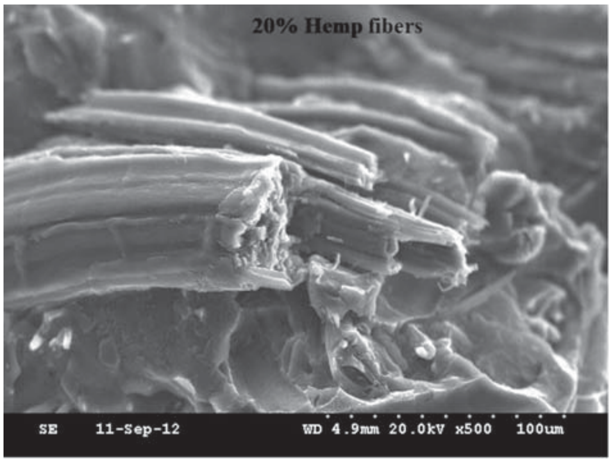

Figure 3 SEM micrograph showing the structure of PET-20% Hemp fibers.

Table 1 Mechanical properties of PET/Hemp fibers composite formulations.

Fiber concentration	Young's modulus [MPa]	Load at yield [N]	Elongation break [mm]
1 %	1434	399.76	3.41
5 %	1553	334.31	2.64
10 %	1509	450.08	3.73
15 %	1638	323.34	2.5
20 %	1853	473.28	3.29

until a threshold is reached around 15%, followed by a plateau. Although similar variation patterns were described in previous works [8,9], they were mostly based on the use of coupling agents, contrary to the focus on hydrogen bonding in this work. A focus on the fiber's structure indicates that the observed mechanical properties are mostly in agreement with previous processes with coarse wood particles reported by Godard *et al.* [10]. In this regard, better results could be anticipated both with more homogeneous fibers and with the use of long woven fibers. The insignificant difference between the mechanical properties of the composites reinforced with 15 and 20% hemp fibers is another indication of the processing challenges with a higher surface-to-volume ratio reported in the previous section. We presume that the loading challenges associated with processing with high fiber concentration, while increasing the process cycle, may have resulted in the partial thermal degradation of hemp fibers.

3.4 Thermophysical Properties

The DSC and heat capacities of Figures 4–7 describe the thermophysical properties of the studied PET/Hemp fibers composite formulations. The first two graphs are direct DSC curves, while the others are heat capacity variations which were derived from in-built TA software. The applied software was previously validated with virgin PET data and its literature values [11]. Still, for the heat capacity analysis, Sapphire's data were used for references in each stage. Furthermore, Figure 4 and Figure 6 are the results of the first experimental run, while Figure 5 and Figure 7 refer to the second. A second experimental run was necessary to avoid any

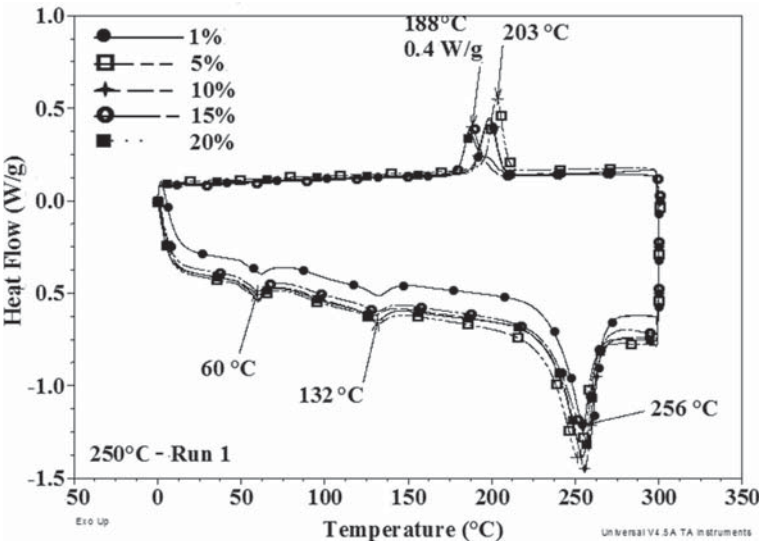

Figure 4 PET/Hemp fibers composite formulations compounded at 250°C. Thermal transitions from the first DSC experimental run.

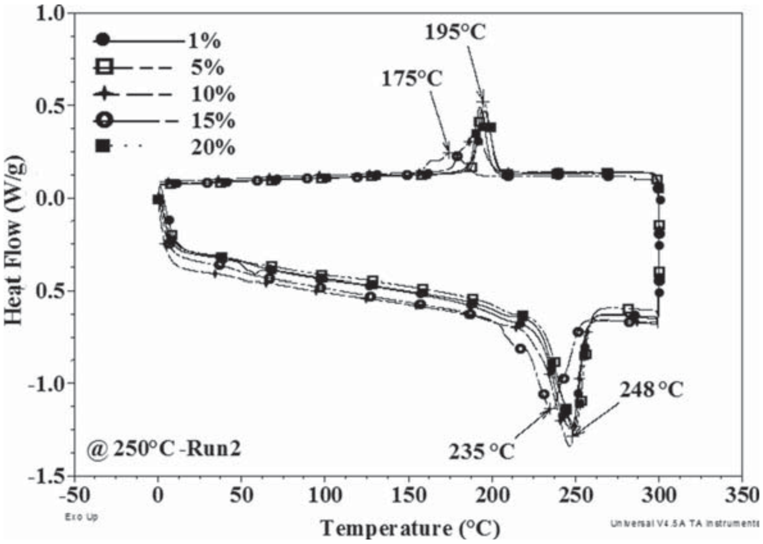

Figure 5 PET/Hemp fibers composite formulations compounded at 250°C. Thermal transitions from the second DSC experimental run.

interference of thermal histories; however, it was found that three major areas of the first experimental runs were not easily noticeable on the second ones. By respectively contrasting Figure 4 to Figure 6 and Figure 5 to Figure 7, the peaks' onsets of these areas were 60, 125, and 240°C. They are respectively related to either the melting point of PCL or the glass transition temperature of PET, the crystallization or the melting point of PET [12,3]. The high intensity of the first peak may suggest the presence of free PCL chains in the formulation, thus the need to improve on PET-Hemp-PCL interface.

There was no difference in the onset of melting and crystallization; however, the amount of heat transfer associated with these transitions varied with the fiber concentration. A predictable variation trend could not be found, contrary to man-made fibers which present consistent and repetitive properties. Such behavior further limits the application of natural fibers-reinforced composites in different industries.

The heat capacities of all formulations were found to vary with temperature during the first DSC experimental run, with a range of 0.5–1.5 [J/g/°C] at room

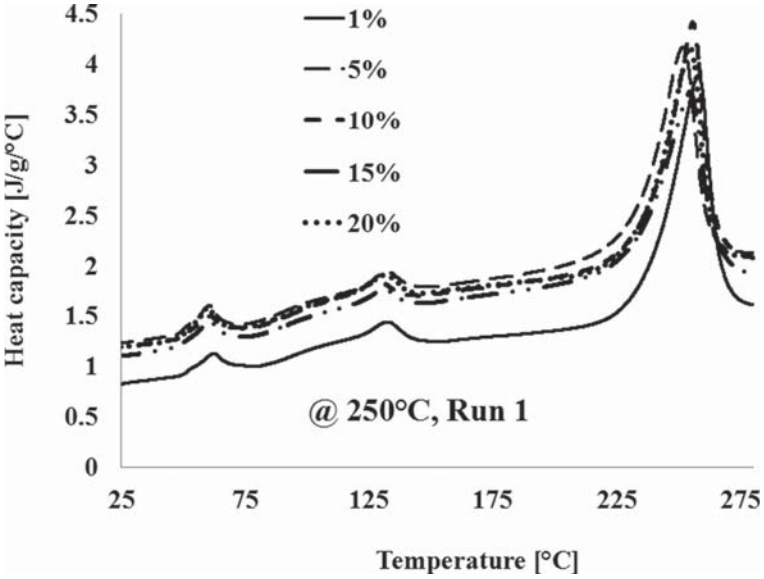

Figure 6 PET/Hemp fibers composite formulations compounded at 250°C. First experimental run heat capacities.

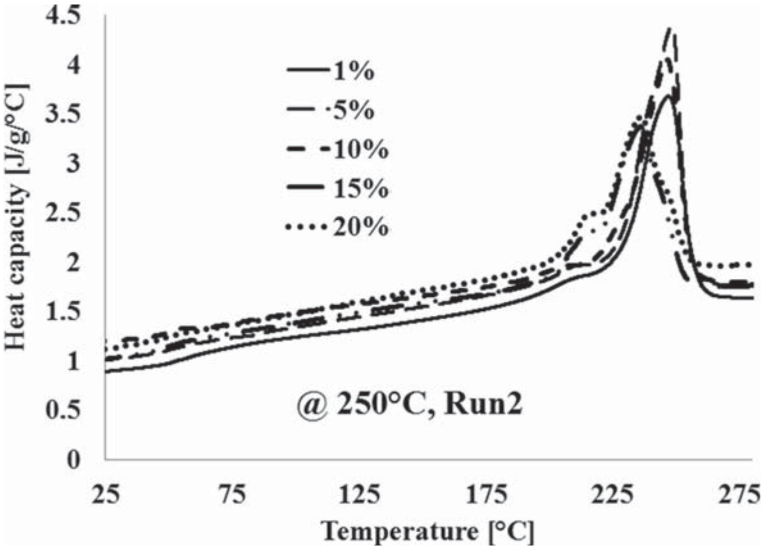

Figure 7 PET/Hemp fibers composite formulations compounded at 250°C. Second experimental run heat capacities.

temperature, and a maximum of 5 [J/g/°C] at the PET's melting peak. This represents more than a 50% increase, which can either be explained by the limited polymeric chain mobility, or the limited fiber-matrix interaction, both caused by the presence of a high fiber volume. In fact, fiber-matrix interaction has been reported by some authors to affect both the polymeric chain mobility and the composite material's crystallinity [14,15].

The observed difference between the first and the second DSC experimental runs may either be attributed to the sample's annealing or crystallization. In fact, a possible partial thermal degradation of hemp fibers during the 10 minute isotherm at 300°C may have led to even further crystallization. A similar observation had earlier been made by Nabar [12]. Moreover, the observed concentration of the heat capacities was found around 1 [J/g/°C] for the second experimental run, contrary to more dispersed values in the first. The disappearance of the first peak between the first and the second experimental runs could either indicate the absence of free PCL chains or just the effect of the insulating properties of hemp fiber [16,17].

4. CONCLUSION

Many effects of hemp fibers were studied on five formulations of PET/Hemp fiber composites. The mechanical, structural, and thermophysical properties of the processed composite material were improved under specific processing conditions. The effects on the mechanical properties varied with the fiber concentration, however, closely similar effects on both the structural and thermophysical properties were shown by almost all the formulations. A high fiber surface-to-volume ratio has a limited effect on the compounding process and needs to be carefully considered in an eventual industrial process, alongside other important parameters such as the quality optimization through the standardization of the fiber's particles.

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