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LOWER-COST, LIGTHER AND GREENER POLYPROPYLENE-BASED BIOCOMPOSITES FOR INDUSTRIAL APPLICATIONS

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Abstract

This paper discloses the viability of the formulation, processing, and performance of advanced biocomposites and bioblends based on polypropylene (PP) designed for industrial manufacturing. The PP was compounded with three different types of cellulosic fibers, in a bioblends with polylactide (PLA) as bio-sourced polymer, and in PP/PLA/cellulosic biocomposites. These biomaterials were characterized in terms of morphology, mechanical and thermal properties. Tensile strength, tensile modulus, and the heat deflection temperature of the bioblends and the biocomposites presented at least equivalent values comparing with virgin PP and with PP current industrial grades. The extruded biocomposites, foamed in injection molding process, presented similar properties as the unfoamed and reference counterparts while being up to 25 wt.% lighter, up to 50% less expensive, and up to 50% greener.

Introduction

The construction and automotive industries, like all the other industries, growingly orient toward the use of environmental-friendly materials and processings for the manufacturing of lighter, lower-cost and greener materials. Given these unavoidable trends, the industry looks at the replacement of heavy parts by lighter and lower-cost polymer parts, and at the replacement of 100% petroleum-based thermoplastic parts by lower-cost biocomposites containing biomass. Thermoplastic-based bioblends and biocomposites are promising materials and have high potentials to be partial or complete alternatives for 100% petroleum-based thermoplastics and composites [1].

PP, the highest used injection molding resin in 2013, had a global demand estimated at 33 M tons [2]. PP and PE, filled with minerals or fiber-reinforced, are the most used thermoplastic polymers in construction and building industries, more precisely in the fabrication of window and door frames, trims and moldings, sidings, and roofing. In addition, 180 kg of thermoplastics are used in one car, i.e. 12 % based on car mass and 50 % based on car volume. The most of these thermoplastics, as for construction industry, are used in fiberglass composites or mineral filled compounds [1, 3]. Amongst these thermoplastics, the PP represents 80 kg based on car mass, mostly used in the manufacture of dashboards, central consoles, front and end modules, IP carriers, tubs in floor, etc.

There are many studies in the literature concerning PP/cellulosic biocomposites. It was proven that mechanical properties of PP/cellulosic biocomposites depend on cellulosic source [4-8], on fiber treatment [9, 10], on fiber/polymer affinity [8, 11, 12] and on the processing conditions [13]. On the other hand, some improvements in PP/PLA blends and PP/PLA/cellulosics biocomposite mechanical properties were observed when appropriate coupling agents, formulations and processing parameters were considered [14-16].

Therefore, this paper presents developments done at National Research Council of Canada (NRC) concerning the formulation and processing of bio-based PP compounds formulated for industrial applications. Important cost and weight reductions can be achieved using these compounds in appropriate fabrication processes. When cellulosics replace up to 40 wt.% of petroleum-based PP, around 30% cost reduction is achieved. Up to 25% lighter parts were produced by adapting the injection foaming process at PP biocomposite behavior. The incorporation of cellulosics in PP/PLA bioblends allowed the fabrication of biomaterials with up to 50 wt.% renewable content. These environmental-friendly biomaterials with significant weight and cost reductions present at least equivalent tensile and thermal performances as industrial reference counterparts.

Materials

The PP used in this work was Pro-fax 6323, a general-purpose homopolymer for injection molding applications from Lyondell Basell. Properties of PP industrial grades were used as references. As mineral filled references, Accutech 20L was a PP filled with 20 wt.% talc and Accutech 40L a PP filled with 40 wt.% talc were used. Concerning industrial grades of PP/glass fiber (GF) composites, the properties of PP with 20 wt.% GF

(Polifil GFPP-20) and PP with 40 wt.% GF (Polifil GFPP-40), were used as references.

PLA 8302D, an amorphous grade from Nature Works, was selected as the bio-sourced minor phase for the production of the PP/30 wt.% bioblends. Cellulosic fibers concentration were 20 % and 40 wt.%. These cellulosic fibers were:

- Short flax supplied by Schweitzer Mauduit Canada.
- Thermo-mechanical pulp, (TMP), was supplied by a Canadian producer.
- Wood fibers (WoodForce - WF) in the form of dices were supplied by Sonae Industria.

Appropriate coupling agents (CA) were used in each case.

Processing

The extruder used to process the bioblends and the biocomposites was a Leistritz 34 mm co-rotating twin-screw having 12 mixing zones and an L/D ratio of 40. Two feeding locations, first zone for PP, PLA and additives and at mid-extruder for cellulosics, were available. A special screw configuration designed at NRC was used to preserve the cellulosic fiber lengths during the extrusion. All materials were dried before the compounding for 24 hours at an appropriate temperature for each one.

The compounded pellets were dried again and used in injection molding process to produce foamed parts. As chemical blowing agent, 1 wt.% Hydrocerol 1514 from Clariant was used to foam the biocomposites.

Characterization

Morphology

Scanning electron microscopy (SEM) was carried out on polished composite surfaces, coated or fractured. A coating of gold/palladium alloy was applied on the specimens prior to the observation. JEOL JSM-6100 SEM at a voltage of 10 kV was used to analyze the dispersion of the fibers into the matrix and the interface between fibers and matrixes.

Mechanical Properties

The samples designated for mechanical testing were first dried and then injection molded using a Boy injection molding press with a screw temperature and a mold temperature adapted for each polymer. The tensile testing was carried out according to ASTM D638 on standard type I dog-bone shaped samples with a thickness of 3 mm. The impact testing was carried out according to ASTM D259.

Heat Deflection Temperature (HDT)

Heat deflection temperature (HDT) was determined on rectangular specimens according to ASTM D648 (method B).

Results and Discussions

Morphology of PP-based biocomposites

PP with 20 and 40 wt.% cellulosics, i.e. flax, TMP and WF, without and with CA were obtained in extrusion. Figure 1 represents SEM micrographs of the surface rupture in transversal direction for PP/20 wt.% flax only. The aspects of the rupture surfaces are different for the formulation without and with CA. When CA was used, the important decrease on the pull-out of fibers and the fracture that passed throughout the fibers instead fiber/polymer interfaces, are main evidences of the excellent adhesion obtained between the PP and flax fibers. Similar SEM morphologies were obtained for PP/TMP and PP/WF biocomposites. Therefore, our CA types and concentrations used were very efficient in the achievement of an excellent adhesion between the hydrophobic PP and hydrophilic cellulosic fibers.

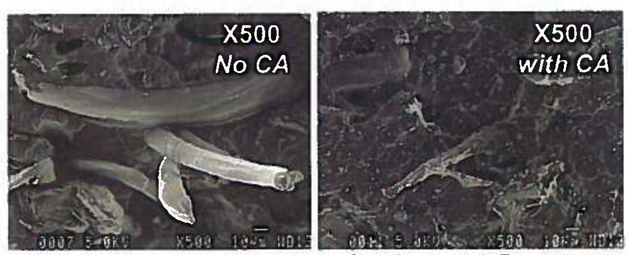

Figure 1. Morphology of PP/20 wt.% flax.

Low-cost PP-based biocomposites

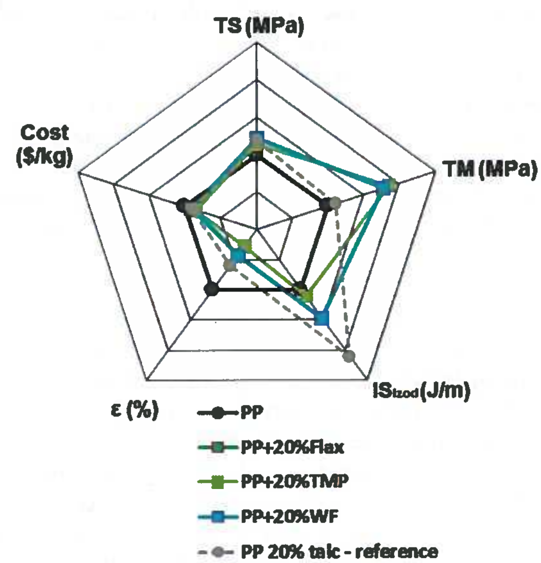

Figure 2. Properties comparison for PP, PP-based biocomposites and PP reference.

Relative costs of PP-based biocomposites studied in this work were calculated starting from the prices existing on the market for the virgin PP, for the three types of cellulosic fibers, and for the PP industrial grades used as references. A comparison of relative materials costs and of their mechanical properties is presented in the Figure 2. Tensile strength and modulus of PP/20 wt.% flax, PP/20 wt.% TMP and PP/20 wt.% WF were higher than virgin PP and reference PP. Izod impact strength and elasticity of the PP-based biocomposites decreased as expected due to the incorporation of cellulosics. Elastomers/impact additives should be used in the formulation as impact modifiers with the purpose to improve the toughness of these biocomposites obtained with cellulosic fibers. Otherwise, considering the costs of these materials, a reduction of 10 to 30% could be obtained when 20 wt.% up to 40 wt.% of pure PP was replaced by the cellulosics. This reduction is due to the lower price of the cellulosic materials comparing with the PP prices. Therefore, the PP-based biocomposites obtained in this work had up to 30% lower cost at similar tensile properties comparing to current used PP industrial grades.

Lighter PP-based biocomposites

The decrease of the weight of PP-based materials can be accomplished in two manners:

1. In the case of PP-based composites with GF, by the partially or totally replacement of heavy and expensive GF (density of 2.55 kg/m^3) by the lighter and cheaper cellulosic fibers (density of 1.4 kg/m^3);
2. In all cases, i.e. for pure PP, PP-based biocomposites, and PP/GF/cellulosic hybrids by the use an adequate foaming-injection molding process.

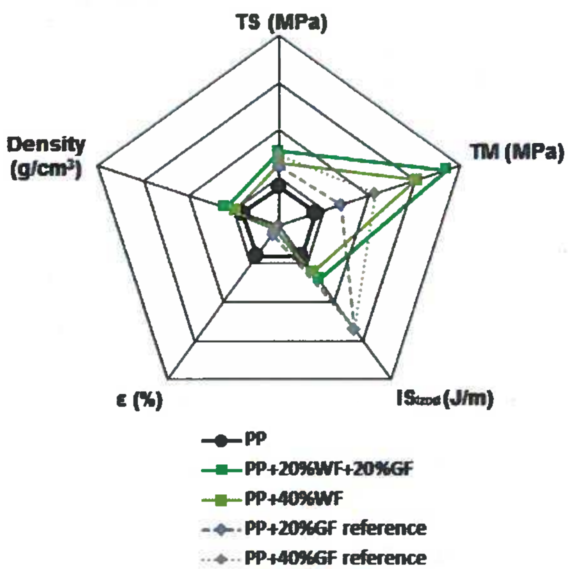

Figure 3. Properties comparison for different PP-based biomaterials.

The material properties comparison that reflects the situation 1 listed here above is disclosed in the Figure 3. The PP/40 wt.% WF and PP/20 wt.% WF/20 wt.% GF developed in this work presented at least a 50% increment in tensile strength and modulus comparing with virgin PP and, more than that, comparing with PP market references with 20 and 40 wt.%GF contents. The impact strength, as explained before, decreased as expected. In terms of costs, our PP/20 wt.% WF/20 wt.% GF demonstrated to be 10% less expensive comparing with the current industrial grade PP/40 wt.% GF. Therefore, PP-based biocomposite hybrids, at 10% lower-price, presented more important tensile properties than the corresponding industrial grades.

The situation 2 listed here above is disclosed in the Figure 4. The density and mechanical properties of virgin PP, unfoamed and foamed PP/40 wt.%WF, and unfoamed and foamed PP/20 wt.% WF/20 wt.% GF hybrid were compared in this figure. First, it can be observed that the PP-biocomposite and the PP-hybrid, foamed in injection-molding, have slightly decreased mechanical properties compared with the unfoamed samples. Moreover, a weight reduction up to 25 wt.% was observed after foaming. This will translate in a supplementary cost reduction up to 25%. In conclusion, important weight alleviations at equivalent mechanical properties can be reached using injection foaming process.

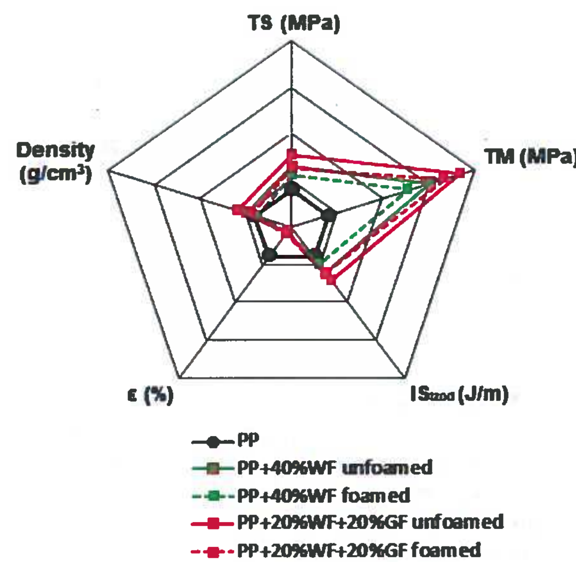

Figure 4. Properties comparison for virgin PP, unfoamed and foamed PP/40 wt.%WF, and unfoamed and foamed PP/20 wt.% WF/20 wt.% GF hybrid.

Greener PP-based bioblends and biocomposites

PP/30 wt.% PLA bioblend and the corresponding biocomposite with 20 wt.% WF were compounded and samples for mechanical testing were injection-molded. Figure 5 reveals the properties comparison between virgin PP, PP/20 wt.% WF unfoamed and foamed, the bioblend

PP/30 wt.% PLA and its biocomposite with 20 wt.% WF. The PP/30 wt.% PLA bioblend presented equivalent properties with virgin PP since excellent adhesion was reached with the addition of an appropriate CA. The biocomposite PP/30 wt.% PLA/20 wt.%WF presented more important tensile and impact properties comparing with the foamed and unfoamed biocomposites formulated without PLA. The current industrial grade, PP/ 20 wt.% talc, revealed lower performances comparing with our biocomposites, excepting the elongation at break. Furthermore, the developed PP/30 wt.% PLA/20 wt.%WF presented an HDT of 126°C that is much higher comparing with virgin PP (80°C) and with PP/ 20 wt.% talc (115°C) respectively. It is obvious that using PP/PLA bioblends as matrix in biocomposites allowed a supplementary increment in the renewable content besides the enhancement in mechanical and thermal performances.

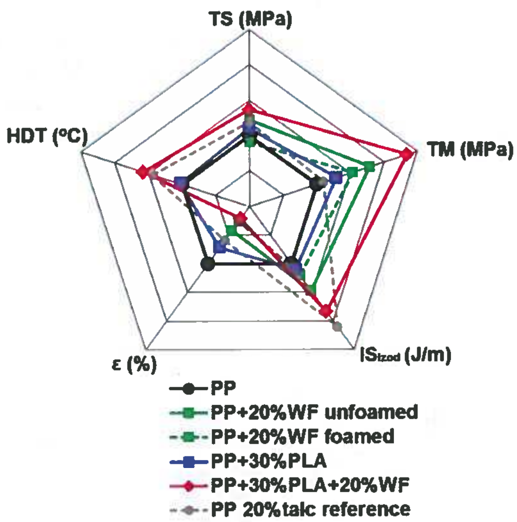

Figure 5. Properties comparison for virgin PP, unfoamed and foamed PP/40 wt.%WF, and unfoamed and foamed PP/20 wt.% WF/20 wt.% GF hybrid.

Figure 6 unveils demonstrators manufactured in our laboratory using the polyolefins (PP, HDPE) and polyolefins/PLA biocomposites developed in our laboratory. Those demonstrators are in order: injection-molded, thermoformed, and extruded parts. These biomaterials are recommended in different industrial applications, for example, in construction/building and automotive industries.

Conclusions

This paper disclosed formulation/processing solutions and properties concerning lighter, less-expensive and greener innovative PP-based formulations that have great potential applicability in construction/building and automotive industries.

The developed biocomposites based on PP and PP/PLA bioblends present at least equivalent mechanical and thermal properties comparing with conventional PP-based materials currently used in industry, while having:

- Lower-cost due to a content up to 40 wt.% of cellulosic fibers;

- Lower-weight due to the partial or complete replacement of glass fibers by cellulosic fibers and/or by using an adequate injection foaming process;

- Higher renewable content: when besides cellulosic fibers, a bio-based bioplastic is used in a bioblend with the PP matrix.

Although impact properties still need to be improved, those innovative bioblends and biocomposites enable the design of engineering thermoplastics compounds containing up to 50 wt.% renewable contents.

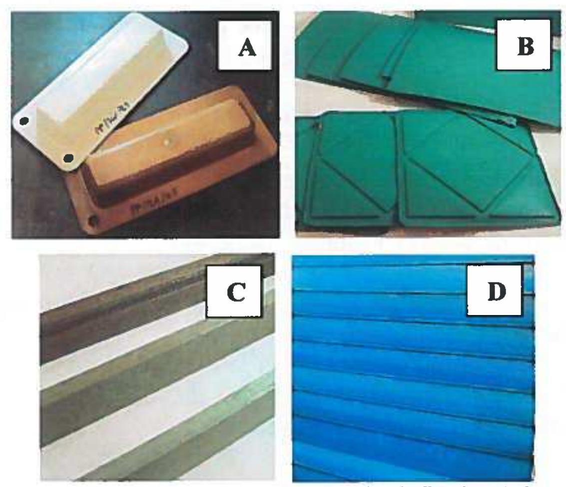

Figure 6. Polyolefins-based and polyolefins/PLA-based biocomposite demonstrators obtained by injection molding (A), thermoforming (B), and profile extrusion (C and D).

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