Biocomposites and bioblends based on engineering thermoplastics for automotive applications

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BIOCOMPOSITES AND BIOBLENDS BASED ON ENGINEERING THERMOPLASTICS FOR AUTOMOTIVE APPLICATIONS

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Abstract

This paper presents innovative solutions concerning the utilization of engineering polymers in bioblends and biocomposites designated for automotive applications. The studied biomaterials have lower-cost, lower-weight, and at least same performance comparing with the current engineering thermoplastics used in automotive parts. Polyamide (PA6) and acrylonitrile-butadiene-styrene (ABS) were formulated using different types and concentrations of cellulosics, polylactic acid (PLA) as a bio-sourced polymer, and in a combination of cellulosics and PLA. These biomaterials were characterized in terms of morphology, mechanical properties, and heat deflection temperature. The extruded biocomposites, foamed in injection molding process, presented similar properties as the unfoamed and reference counterparts while being around 25-30% greener, lighter and less expensive.

Introduction

The current needs and trends of the automotive industry are, definitively, environmentally oriented. The driving forces for the greener implementations in the automotive industry are to decrease the part weight, the material cost, the fuel consumption and the use of eco-friendlier materials and processing methods. Given these imperative needs, the automotive industry looks to the replacements of metal by lighter and less expensive polymer parts, and the replacement of petroleum-based thermoplastics parts by lower-cost biocomposites containing biomass. Thermoplastic bioblends and biocomposites have high potentials to be partial or complete substitutes for petroleum-based thermoplastics and composites [1].

180 kg of thermoplastics are used in one car, i.e. 12 % from the car weight and 50 % from the car volume. Most of these thermoplastics are used as fiberglass composites or mineral filled compounds [1, 2]. Amongst these thermoplastics, the polypropylene (PP), the nylons (PA6, PA66) and styrenics (such ABS) are the most used in the fabrication of thermoplastic automotive parts. PA-based parts represent 36 pounds from the car weight. PA6 or PA66 are used in engine shrouds, engine covers, gearshifts, front-end grills, oil pan modules, manifolds, funs, etc. Typically, the nylons are formulated with fiberglass or minerals that are heavy and expensive. It was shown in the literature that the replacement of a part PA6 or PA66 matrix with cellulosic fibers increased the mechanical properties compared with the unreinforced matrix [3, 4, 5]. Therefore, the natural fibers have considerable reinforcement potential and offer many possibilities for the industrial applications once incorporated in PA-based biocomposites. On the other hand, the addition of PLA in PA seems to have as result the preservation or a slightly increase of mechanical properties when adequate coupling agents are used [6, 7]. Similarly, ABS-based parts represent 30 pounds from the car weight. ABS filled with minerals, ABS reinforced with glass fibers, and ABS/PC are utilized in the fabrication of overhead consoles, grills, spoilers, B/C pillars, fascia and instrument panels, door and setting assemblies, dashboards etc. Almost no work exists in the literature on ABS/cellulosics or ABS/biopolymer formulations and processing.

The automotive green vision for PA and ABS should orient toward:

- Replacement of those engineering polymers filled with minerals or reinforced with fiberglass with their biocomposites counterparts containing cellulosic fibers, which allow weight and cost reductions.
- The use of injection foaming process, which further allows supplementary weight and cost reductions of PA and ABS parts.
- The substitution of a part of PA or ABS by a bioplastic that is a way to increase the renewable content.

Therefore, this paper presents the work done at National Research Council of Canada (NRC) concerning the formulation and processing of bio-based PA6 and bio-based ABS compounds formulated for automotive applications. Important cost and weight reductions can be achieved using these compounds in appropriate fabrication processes. When cellulosic materials replace 20 wt.% of petroleum-based PA6 and ABS, around 30 % cost reduction is achieved. Up to 25 % lighter parts were produced by adapting the injection foaming process at biocomposite behavior. The combination of PA6 or ABS with cellulosics and PLA allowed the fabrication of biomaterials with up to 50 % renewable content. These environmentally friendly biomaterials with important weight and cost reductions present at least equivalent tensile and thermal performances as reference counterparts.

Materials

The PA6 Ultramid B27 from BASF was an injection molding grade. Industrial PA6 grades used as references were PA6 Ultramid B3M6 a 30 wt.% mineral filler grade (high impact) and PA6 Ultramid B3WG a 30 wt.% glass fibers grade. The ABS Lustran Elite HH 1827 is an injection-molding grade for high-heat automotive applications. The ABS automotive grade used as industrial reference was STAT-LOY AX06484, a talc filled grade. The PA6 and ABS references represent usual materials employed currently in automotive parts manufacture.

The PLA 8302D, an amorphous grade from Nature Works, was selected as the bio-sourced minor phase for the production of the bioblends based on PA6 and ABS. Cellulosic fiber concentrations used in both engineering thermoplastics were 20 % and 40 wt.%. These cellulosic fibers were (Figure 1):

- 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 were used in each case.

Figure 1. Flax, TMP and WF fibers as used in compounding process

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 location were available: first zone for polymers and additives and at mid-extruder for cellulosics. A special screw configuration designed at NRC was used to preserve the cellulosic fiber lengths. All materials were dried before extrusion 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 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 matrices.

Mechanical Properties

The samples designated for mechanical testing were first dried and then injection molded using a Boy molding press with a screw temperature and a mold temperature adapted for each biomaterial. 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 Discussion

PA6-based bioblends and biocomposites

Morphology of PA6-based biocomposites

PA6/flax, PA6/TMP and PA6/WF biocomposites were obtained in extrusion at 20 and 40 wt.% for each cellulosic type. The selected screw configuration and extrusion parameters gave a very good dispersion of fibers, no matter the fiber type and fiber concentrations. Figure 2 presents only the morphological features of transversal polished surfaces of PA6/flax biocomposites at two different magnifications. The lack of fiber pull out and the fracture type, that passed throughout the fibers instead fiber/polymer interface, are main evidences of the excellent adhesion between the PA6 and cellulosic fibers.

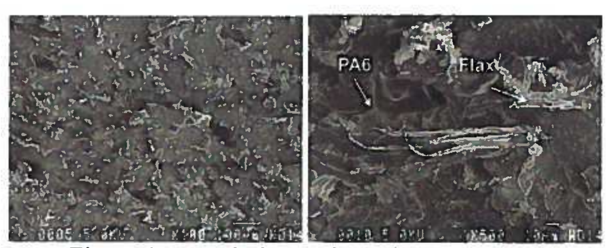

Figure 2. Morphology of PA6/20 wt.% flax.

Low-cost PA6-based biocomposites

Figure 2 discloses the tensile modulus and strength of PA6, PA6 with 20 and 40 wt.% of each cellulosic type compared with the reference, 30 wt.% minerals filled PA6. Is obvious that when replacing 20 to 40 wt.% of the PA6 matrix with cellulosic fibers, the mechanical properties are preserved and the cost of the material is reduced due to lower price of the cellulosics comparing with the PA6 price.

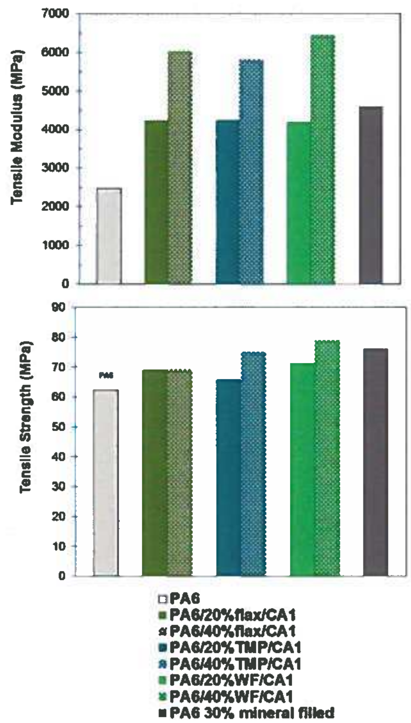

Figure 3. Tensile properties of PA6, PA6 with 20 wt.% cellulosics and PA6/30 wt.% minerals reference.

Figure 4 discloses a comparison of mechanical properties, densities and costs of pure PA6, PA6 reinforced with 20 and 40 wt.% WF and the reference PA6 filled with 30 wt.% minerals. While the biocomposites density is roughly equivalent with reference materials, the calculated costs based on market values demonstrated that the PA6-based biocomposites could be 20 to 35% less expensive.

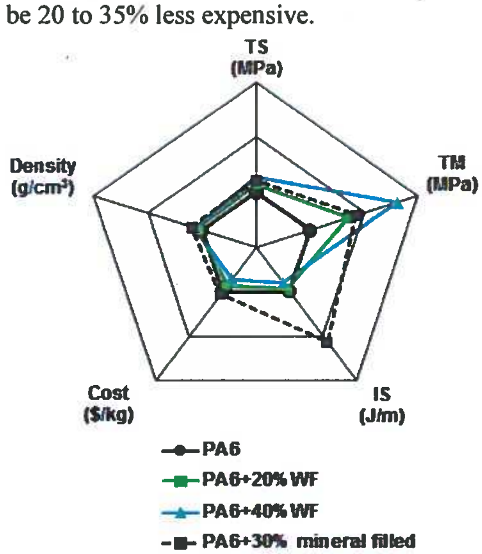

Figure 4. Properties comparison of PA6 materials.

Lighter PA6-based biocomposites

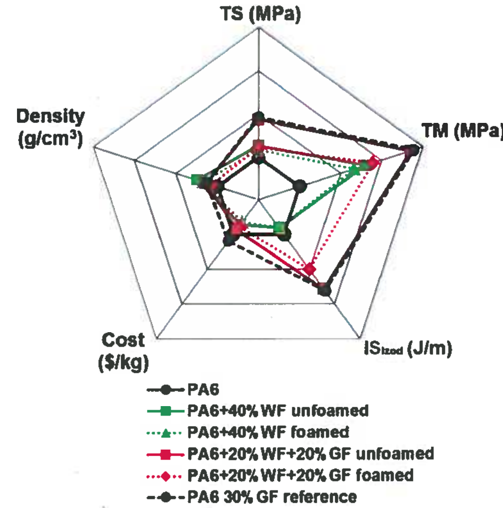

Figure 5. Properties and cost comparison of PA6-based biocomposites, glass fibers/WF hybrids and the reference PA6/30 wt.% mineral filled.

PA6 reinforced with glass fibers (GF) are used frequently in automotive part fabrication due to their key mechanical properties and thermal resistance (HDT). Nevertheless, the GF are heavy with a density of 2.55 kg/m^3. Hybrid biocomposites of PA6/20 wt.% cellulosic fibers/ 20 wt.% GF were also obtained by extrusion with the purpose to alleviate the weight by replacing a part of GF with cellulosics (densities around 1.4 kg/m^3). Moreover, supplementary weight alleviation was obtained by foaming in injection molding of biocomposite and hybrid parts. Figure 5 discloses a comparison of mechanical properties, densities and costs for PA6, PA6/40 wt.% WF (unfoamed and foamed), PA6/20 wt.%. WF/20 wt.% GF (unfoamed and foamed) and the reference PA6/30 wt.% GF. In terms of mechanical properties, the PA6/40 wt.% WF performances are increased comparing with PA6 alone and slightly lower comparing with the reference. The hybrid biocomposites PA6/20 wt%. WF/20 wt.% GF have equal mechanical properties when unfoamed and slightly decreased when foamed comparing with the reference. Replacing 40 wt.% of PA6 with cellulosics results in up to 35% cost reduction. In addition, the PA6 biocomposites foaming allows a supplementary 10% weight reduction, which translates in additional 10% material cost reduction.

Greener PA6-based bioblends and biocomposites

PA6/20 wt.% PLA bioblends and PA6/20 wt.% PLA/20 wt.% WF biocomposites were prepared by compounding and then injection-molded to obtain samples for mechanical testing. A comparison of mechanical and thermal properties of these biomaterials with the PA6/30 wt.% reference is disclosed in the Figure 6. The HDT of virgin PA6 was increased from 160°C to

190°C in the case of PA6/20 wt.%PLA/20 wt.%WF. The mechanical properties of bioblends and biocomposites are similar or higher than for PA6 alone and the reference excepting, the strain elongation (ε%) that is an usual behavior for biocomposites.

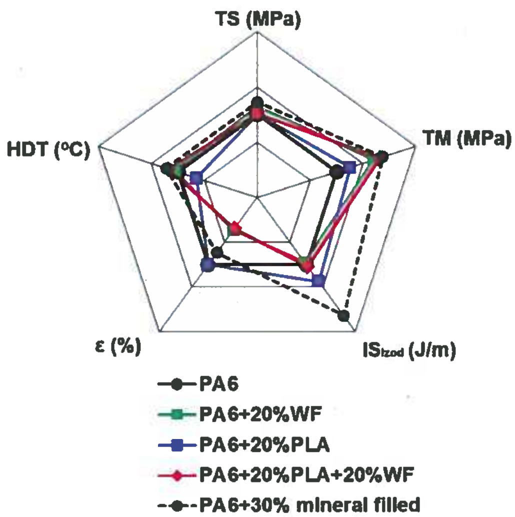

Figure 6. Properties comparison of PA6-based biocomposites, bioblends and reference PA6/30 wt.% mineral filled.

ABS-based bioblends and biocomposites

Morphology of ABS-based biocomposites

ABS/flax, ABS/TMP and ABS/WF biocomposites with 20 and 40 wt.% contents for each cellulosic type were also obtained in extrusion in a similar way as for PA6-based biocomposites. Figure 7 presents, at the same magnifications, the morphological structures of transversal polished surfaces for only ABS with 20 wt.% WF, with and without coupling agent. The SEM morphologies were identical for all ABS-based biocomposites. It is obvious that significant differences can be seen between the morphological aspects of the two ruptures. When the coupling agent was present in the biocomposite formulations, the lack of fiber pull-out and the rupture throughout the fibers instead fiber/polymer interface, are the key evidences of the excellent adhesion between the ABS and cellulosic fibers.

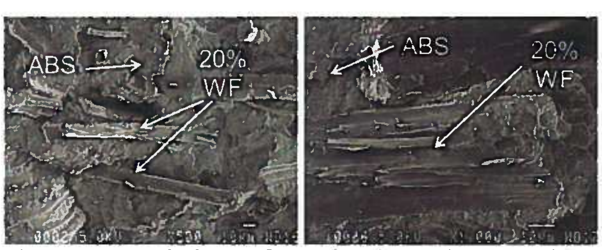

Figure 7. Morphology of ABS/20%WF biocomposites, without and with coupling agent.

Low-cost ABS-based biocomposites

The Figure 8 unveils a comparison of mechanical and thermal properties of virgin ABS, ABS/WF biocomposites and the 2 references, an industrial grades of ABS. Tensile properties increased when WF was incorporated in the ABS comparing with the references. An increase of HDT from 85°C to 95°C for ABS-based biocomposites was also observed. This value is similar with the one of industrial grades of ABS filled with minerals or reinforced with glass fibers. Our cost evaluations based on market values of polymers and fibers demonstrate that the ABS-based biocomposites could be 20 to 35% less expensive that existing industrial grades.

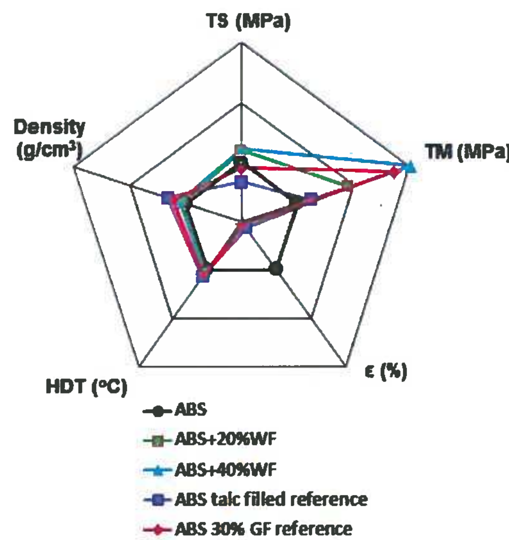

Figure 8. Properties comparison of pure ABS, ABS-based biocomposites and the 2 ABS references.

Lighter ABS-based biocomposites

As for PA6-based biocomposites, weight reductions were achieved for ABS-based biocomposites by replacing a part of GF with WF in ABS/GF composites and by foaming the biocomposite hybrids parts in injection molding. The comparison results are presented in the Figure 9. The foamed and unfoamed ABS/40 wt.%WF and ABS/20 wt.%WF/20 wt.%GF presented higher tensile properties comparing with virgin reference and industrial grade reference as well. The impact properties decreased at the additions of fibers in ABS formulations as expected. The ABS uses in the automotive parts subsists in its important impact properties. Therefore, impact additives are further recommended in ABS-based biocomposites to upgrade the impact performance. In relation to ABS-based biocomposites cost, replacing 20 to 40 wt.% of ABS with cellulosics resulted is a 12-25% cost reduction. Furthermore, conform to foaming tests done in our laboratory, a 8 wt.% reduction was obtained which translates in a supplementary material cost reduction.

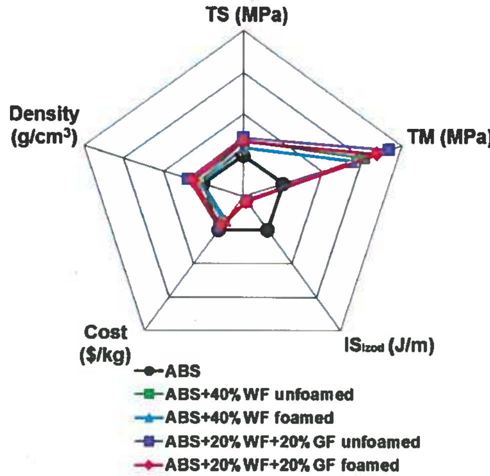

Figure 9. Properties and cost comparison of unfoamed and foamed ABS-based biocomposites.

Greener ABS-based bioblends and biocomposites

Figure 10 reveals the properties comparison of virgin ABS, ABS/20 wt.% WF unfoamed and foamed, the bioblend ABS/10 wt.% PLA and the corresponding biocomposite with 20 wt.% WF content. The bioblend ABS/10 wt.% PLA presents equivalent properties with virgin ABS excepting the impact properties. The biocomposite ABS/10 wt.% PLA/20 wt.%WF presented very similar properties as the foamed and unfoamed biocomposites formulated without PLA. Using PLA in bioblends and as minor phase in biocomposite matrix allowed a further increment of the renewable content of ABS-based parts for automotive applications.

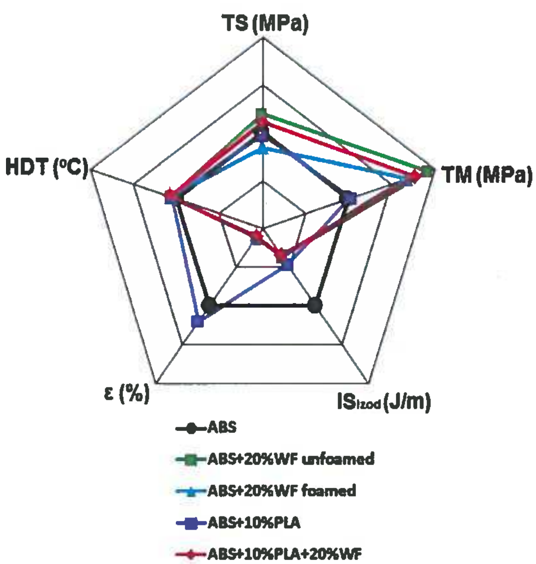

Figure 10. Properties comparison ofABS, ABS-based biocomposites, ABS/PLA bioblend, ABS/PLA-based biocomposites.

Conclusions

This work proved the development feasibility of novel PA6 and ABS-based bioblends and biocomposites for automotive applications. Beyond this feasibility, the lower-cost, lower-weight and the greener content are capital characteristics for these innovative biomaterials.

35% less expensive PA6-based biocomposites and 25% less expensive ABS-based biocomposites were obtained incorporating up to 40 wt.% cellulosic fibers in the matrices while mechanical and thermal properties were preserved. The injection foaming process enabled 10% and 8% weight reductions for PA6-based and ABS-based biomaterials respectively. This further translates in more cost reductions for each type of biocomposite. Adding a PLA content as minor phase, permitted to obtain bioblends and biocomposites with equivalent properties but with an increased renewable content.

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

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