Abstract
Impact behavior of recycled polyethylene (PE) / polypropylene (PP) blends and wood plastic composites (WPC) based on recycled blends (as matrix) was performed via structural modifications with maleated polyethylene (MAPE) / ground tire rubber (GTR) compounds. Double layer structures (one layer of PE/PP or WPC and one layer of MAPE/GTR) were characterized through scanning electron microscopy, flexion and high speed puncture tests with different directions of applied load. Structural modification of both PE/PP blends and WPC (containing 40% wood flour) led to significant improvement in their deformability and ductility. The results show that direction of applied load (in both flexion and impact tests) played an important role on strength and deformability of these structures. Flexural modulus, on the other hand, was independent of load direction.

1 Introduction

In the past, life cycle of polymeric materials only included one use. After their service life, these products were discarded as wasted to landfills which ultimately led to legislation pressures caused by severe environmental impacts [1]. Inclusion of different recycling processes to the traditional life cycle of polymeric materials is the current strategy to alleviate the problems related to landfill disposal [2].

The origin of plastic waste streams is a crucial concept in determining the recycling challenges. The most difficult recylates are post-consumer plastics, especially of municipal solid waste streams, since a mixture of several commodity polymers and contaminants is obtained. This waste stream is typically composed of polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) [3]. Mechanical recycling of such a heterogeneous waste needs some preliminary separation steps to improve resin quality and processability. But a complete sorting of these materials is still not economically viable and in some cases impossible. However, the easiest sorting method proposed for this waste stream is based on density segregation (floatation in sink-float water tanks). In this technique, the materials are separated in two fractions, in which the light fraction (floating on water surface) mainly includes polyethylene and polypropylene with some possibility of impurities [4, 5].

Although the chemical structure of the plastics in the light fraction is considered relatively similar, the mechanical properties of the recycled blend (PE and PP) are still lower than those of neat plastics [6]. This behavior is related to the fact that most polymers are basically immiscible (or have limited miscibility) which is caused by differences in their chain configuration [7]. It is reported that even different grades of polyethylene do not show complete miscibility when blended [8]. Lednicky et al. reported that introduction of 20% PP in low density polyethylene led to high phase separation in the blend [9].

Inclusion of particulate reinforcement can lead to increased mechanical properties (especially stiffness) in blends of polyethylene and polypropylene. Over the last decades, natural fibers have attracted a growing attention as reinforcement in polymer based composites instead of conventional materials such as glass fibers. Several investigations were also devoted to reinforce thermosets or
thermoplastics using natural fibers such as wood flour, flax, banana, oil palm, jute, etc. [10-17]. Composites containing natural fibers and polyolefins as matrix, however, were shown to suffer from poor compatibility between both phases. Hydrophilic nature of natural fibers (due to presence of hydroxyl groups on cellulose and hemi-cellulose) is responsible for such defects. Incorporation of compatibilizers, such as maleated polyolefins, is known to improve compatibility between natural fibers and thermoplastic matrices.

Incorporation of particles to a thermoplastic matrix can also lead to significant reduction in impact strength due to stress concentration caused by the presence of the filler. To solve this problem, virgin elastomers such as ethylene propylene diene monomer (EPDM) and styrene butadiene rubber (SBR) have been extensively proposed. For instance, Oksman and Clemons [18] investigated impact modification of polypropylene / wood flour composites using EPDM, maleic anhydride grafted EPDM (MA-g-EPDM) and maleic anhydride grafted styrene ethylene butylene styrene tri-block copolymer (MA-g-SEBS). They concluded that maleated EPDM and SEBS acted as both impact modifier and compatibilizer as they had greater effect on Izod impact strength than EPDM itself. It was also suggested that the elastomer phase domain size must be smaller than one micron in order to have good impact modification effect.

However, inclusion of virgin rubber into natural fiber composites leads to increased cost (especially in composites with recycled origin). It also leads to a significant decrease in modulus due to the uncrosslinked structure of the rubber phase. One approach to overcome this problem is via introduction of recycled rubbers in the form of ground tire rubber (GTR) to polymer composites. Adding GTR to polymer composites should noticeably decrease the costs of raw material and, on the other hand, help reduce environmental concerns related to waste tires [19-23]. Nevertheless, the main drawback to introduce GTR as impact modifier in such composites is low compatibility between the rubber particles and the thermoplastic phase. The crosslinked structure of GTR is reported to be responsible for this behavior. Since rubber molecules are crosslinked, they do not have enough freedom to entangle with the thermoplastic matrix molecules resulting in poor interfacial adhesion [24-27].

Previous investigations performed by the authors, showed that maleated polyethylene is an excellent choice as thermoplastic matrix for GTR filled compounds [28]. MAPE is assumed to create strong chemical bonds with vulcanized rubber through reaction of maleic anhydride groups with unsaturated (C=C) bonds of rubber molecules. It was shown that compounds with GTR concentrations up to 90% by weight can be successfully produced using MAPE.

Lamination designs offer many advantages over conventional monolithic structures, particularly when flexural loadings are predominant [29,30]. In this technique, distinct composite layers are bonded together to form an efficient load bearing assembly. These structures are designed to use the benefits of each separate layer and therefore optimize the structural properties of the whole assembly.

Therefore, addition of MAPE/GTR compound to PE/PP/wood composites via development of a multilayered structure can potentially improve impact strength of composites with minimum negative effect on other characteristics.

In this work, impact modification of recycled PE/PP blends and wood plastic composites based on recycled PE/PP blends as matrix was performed via structural modifications with maleated polyethylene / ground tire rubber compounds. Double layer structures (one layer of WPC and one layer of MAPE/GTR) were produced via compression molding. Characterization of the structures was performed through scanning electron microscopy, as well as flexural and high speed puncture tests using different directions of applied load.

2 Experimental

2.1 Materials

Flakes of post-consumer plastics were received from RECYC RPM (Quebec, Canada). These materials were collected from municipal solid waste. Using density segregation, i.e. flotation in water,
polyethylene and polypropylene were separated as the light fraction.

For additional insight, Fourier transform infrared (FTIR) spectroscopy of the light fraction is presented in Figure 1. The FTIR spectra were recorded using a Nicolet Magna 850 spectrometer (Thermo Scientific, Madison, WI) equipped with a liquid-nitrogen-cooled narrow-band MCT detector with Golden-Gate (diamond IRE) ATR accessories (Specac Ltd., London, U.K.). The spectrum was obtained from the acquisition of 128 scans at 4 cm\(^{-1}\) resolution, from 4000 to 750 cm\(^{-1}\) using a Happ-Genzel apodization. From FTIR investigations, the analysis revealed the presence of only two components (PE and PP) in the light fraction of recycled plastics (contaminant materials are assumed to be less than 1% which is about the detection limit of the method).

The wood flour was a blend of sawdust from different species (sieved between 125 µm and 1 mm, with an average size of 330 µm) and kindly supplied by the Department of Wood and Forest Sciences of Université Laval.

Ground tire rubber, with particle size distribution between 50 and 850 µm (average particle size of around 300 µm) was obtained from Recyc-RPM inc. Canada and used as received.

In addition, maleated polyethylene, Epolene C-26, and maleated polypropylene (MAPP), Epolene E-43, were supplied by Westlake Chemical Corporation.

2.2 Processing

First, flakes of the light fraction part of recycled polymer were extruded to produce PE/PP blends. Extrusion was performed using a co-rotating twin-screw extruder, (Leistritz ZSE-27, L/D=40) with a screw speed of 110 rpm and a temperature profile from the hopper to the die (10 zones) of: 170/185/200/215/230/230/230/215/210/205˚C.

To produce wood plastic composites containing 40% wood flour, WPC(40), blends of recycled plastics (PE/PP) along with the compatibilizers (MAPE/MAPP), were fed into the main feeder (first zone) of the extruder, while wood flour was added at the fourth zone through a side-stuffer to prevent thermo-mechanical degradation. Screw speed was 115 rpm with a temperature profile of 170/180/185/185/185/185/190/190/195˚C.

In a separate extrusion process, MAPE/GTR compounds were produced via extrusion with a flat temperature profile (170˚C) and a screw speed of 120 rpm. Two compounds, containing 50 and 70% GTR, were produced and coded as GTR(50) and GTR(70), respectively.

Plates of all materials (PE/PP blend, WPC(40) and MAPE/GTR compounds) were first produced through compression molding (3 mm in thickness) at 200˚C. To obtain the final products (two layered structures), PE/PP blend and WPC(40) were compression molded along with MAPE/GTR compounds, GTR(50) and GTR(70), to create plates with 6 mm thickness as shown in Figure 2. Specimens for flexion (6×12.7×140 mm\(^3\)) and high speed puncture test (6×90×90 mm\(^3\)) were cut from the plates using a band saw.

2.3 Morphological observations

Scanning electron micrographs (SEM) were used to investigate the interface quality between the components. A JEOL model JSM-840A was used to take SEM micrographs. Samples were fractured in liquid nitrogen, coated with a thin layer of gold/palladium alloy and then examined at 15 kV.

2.4 Mechanical testing

Flexural properties of the composites were evaluated according to ASTM D790 using an Instron (model 5565) universal testing machine with a 500 N load cell and crosshead speed of 4 mm/min. The span was 60 mm for single layer and 120 mm for double layered structures.

High speed puncture tests were performed using a CEAST 9340 drop tower at a velocity of 200 m/min on the samples (3 and 6 mm thick) according to ASTM D3763.

3 Results and discussions

3.1 Morphological observations

SEM micrographs of the interface between WPC(40) layer and MAPE/GTR compounds with 50 and 70% GTR are presented in Figure 3. Figure 3a shows that although few gaps between GTR(50) and WPC(40) layers exist, the overall quality of surface interaction between both layers is good.
between the layers occurs due to entanglement of MAPE macromolecules with macromolecules from the PE/PP blend. Figure 3b, on the other hand, shows that increasing GTR concentration to 70% led to lower compatibility between both layers. This behavior can be related to the negative effect of the filler content on surface interactions. In case of layer with high GTR concentrations, the matrices (PE/PP and MAPE) have lower ability to interact through physical entanglement of their macromolecules.

3.2 Mechanical properties
Effects of impact modification of recycled PE/PP blends and WPC using GTR(50) and GTR(70) layers are shown in Table 1. It is observed that two layered structures (with both 50 and 70% GTR) have higher impact energy (per unit of thickness) and deformability in comparison with unmodified WPC. Impact energy per unit of thickness and deformability of PE/PP blends increased by around 30% and 90%, respectively, after structural modification using MAPE/GTR: 50/50 (MAPE/GTR layer was on top under the impactor). Increasing GTR concentration for the MAPE/GTR layer also led to higher impact energy and deformability of these structures. Structure WPC(40)-GTR(70) has an impact energy of 5.4 kJ/m compared to 4.8 kJ/m for WPC(40)-GTR(50) (in both cases the MAPE/GTR compound was the top layer under impactor). It is also shown that when the MAPE/GTR layer was the top layer under the impactor (samples marked by *), the structures had higher deformability and were able to absorb more energy. For instance, for the WPC(40)-GTR(70) structure, the absorbed energy and deformability during impact were respectively 29% and 27% higher when the MAPE/GTR compound was the top layer under the impactor. In these structures, the MAPE/GTR layer is believed to absorb most of the initial impact energy and protect the WPC layer. But when the WPC is the top layer (samples marked by **), the samples break instantly by catastrophic damage to the structure at the initial point of impact.

Flexural properties of the composites are also included in Table 1. It is observed that production of two layered composites via introduction of MAPE/GTR blends resulted in lower flexural modulus of PE/PP blends and WPC(40). Flexural modulus of WPC(40) was 2186 MPa compared to almost 560 MPa for the structure containing WPC(40) and GTR(50) layers. It is also shown in Table 1 that changing the direction of applied flexural load produced no significant effects on the flexural modulus of sandwich composites. Flexural modulus of structure PE/PP-GTR(70) was 241 MPa when MAPE/GTR(70) was in extrados and 247 MPa when the PE/PP blend was in extrados.

Interesting results are achieved via comparison between strains at yield of the different composite structures. It is observed that structures with MAPE/GTR compounds in the extrados of the beams show higher deformability compared to structures with WPC in extrados layer. In the structure WPC(40)-GTR(50) for instance, strain at break was 7.3% when the MAPE/GTR compound was in extrados and only 3.5% when the WPC was in extrados. Under flexural load, the layer in the extrados is known to be subjected to tensile load. Thus, the observed behavior in structure’s deformability is due to the fact that MAPE/GTR compounds have tensile elongation at breaks higher than 400% [25], while the values are much lower for PE/PP blends or WPC [31].

Comparison between flexural strength of the structures with the MAPE/GTR layer in extrados or the WPC layer in extrados also reveals that the former can sustain much higher flexural loads than the latter. Changing the MAPE/GTR layer from intrados to extrados in structure WPC(40)-GTR(50) led to 53% increase in flexural strength. This is also due to higher deformability of these structures. Increase of GTR concentration in MAPE/GTR compounds (from 50 to 70%) seems to decrease the ability of the MAPE/GTR layer to enhance the deformability of the structure under flexural load. For instance, deformability of structures WPC(40)-GTR(50) and WPC(40)-GTR(70) (in both cases MAPE/GTR was in extrados) were 97% and 50% higher than deformability of WPC(40) alone. This observation is linked to poor interactions between the MAPE/GTR: 30/70 and WPC layers (Figure 4b). Weak interface between both layers leads to poor load transfer from one layer to the other and, eventually, delamination (due to shear stress at the interface). This behavior was not observed in our impact tests. During impact tests, the interface is subjected to compressive loads which do not produced layer separation (delamination).
Conclusions
Structural modification of recycled PE/PP blends and WPC with 40% wood content was performed through addition of MAPE/GTR compound layers. SEM micrographs revealed that increase in GTR concentration from 50 to 70% resulted in decreased surface interaction between the layers. It was shown that impact energy and deformability of PE/PP and WPC increased via production of two layered structures. Flexural modulus of sandwich structures, on the other hand, was lower compared to WPC. Flexural strengths of structures with WPC(40) and 50% GTR were comparable to WPC due to its high deformability. It was also shown that the direction of load (in both impact and flexion tests) played an important role on the behavior of the structures. Structures with the MAPE/GTR layer as extrados (in flexion tests) or as the top layer under impactor (in impact tests) showed higher deformability and strength. Positive effects of including MAPE/GTR compounds to WPC and PE/PP blends was less significant for GTR(70) compared to GTR(50) due to decreased interaction (adhesion) between the layers.

References


Fig. 1. FTIR spectrogram of the municipal plastic waste light fraction.

Fig. 2. Two layer structure with WPC containing 40% wood (top layer) and MAPE/GTR:30/70 (bottom layer).
Table 1. Impact and flexural properties of single layered and two layered structures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Puncture test</th>
<th>Flexion test</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Absorbed energy (kJ/m)</td>
<td>Deflection at break (mm)</td>
</tr>
<tr>
<td>PE/PP blend</td>
<td>4.3</td>
<td>14.8</td>
</tr>
<tr>
<td>WPC(40)</td>
<td>3.5</td>
<td>7.9</td>
</tr>
<tr>
<td>PE/PP - GTR(50)</td>
<td>5.6*</td>
<td>27.8*</td>
</tr>
<tr>
<td></td>
<td>4.6**</td>
<td>23.4**</td>
</tr>
<tr>
<td>PE/PP - GTR(70)</td>
<td>5.5*</td>
<td>30.6*</td>
</tr>
<tr>
<td></td>
<td>4.7**</td>
<td>26.2**</td>
</tr>
<tr>
<td>WPC(40) - GTR(50)</td>
<td>4.8*</td>
<td>25.7*</td>
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<tr>
<td></td>
<td>4.2**</td>
<td>22.3**</td>
</tr>
<tr>
<td>WPC(40) - GTR(70)</td>
<td>5.4*</td>
<td>30.8*</td>
</tr>
<tr>
<td></td>
<td>4.2**</td>
<td>24.3**</td>
</tr>
</tbody>
</table>

*MAPE/GTR is the top layer under impactor. ** PE/PP blend or WPC are the top layer under impactor.
A) MAPE/GTR is in extrados. B) PE/PP blend or WPC are in extrados.