Study of the reprocessing effects on the behavior of the PVC/alfa composites compatibilized with PVC-g-MA

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1 Introduction

Composite materials provide design engineers with superior quality and long life span. Higher strength, lower weight and less maintenance have led to many engineering applications [1]. Further fore, one major advantage of natural fiber plastic composites is the capability to recycle the product either during the manufacturing process (internal recycling) or later at the end of the service life (external recycling) [2].

It is important to bear in mind that the utilization of resources sparingly to their utmost benefits is an important strategy for conservation of natural resources. One such route is to recycle wood polymer composites (WPC) waste. Recycling reduces the raw material cost, it can help WPC manufacturers to gain competitive advantage on cost of raw materials while also conserving environment [3]. Hence, recycling of WPC waste is deemed appropriate in terms of economy, utilization and management of natural resource and environment. The survey of literature shows that available studies on the recycle-ability of WPC composites are so rare and only a few papers published up-to-date. Effect of recycling on properties of rice husk-filled-polypropylene was studied which indicated slight decrease in tensile, flexural, impact properties, and water absorption [4]. Bourmaud and Baley [5] investigated the recycle ability of hemp and sisal fibers reinforced polypropylene composites. Their results showed that the mechanical properties are well conserved. Beg et al [6] also investigated the effect of reprocessing of the wood fiber-PP composites in injection molding process and reported both decrease in tensile strength and Young’s modulus because of the fiber damage.

As far as recycling of PVC-based WPC is concerned, no information is available. Investigations have, however, been carried out on composites based on polypropylene, polyethylene and other thermoplastics. Most of these studies have considered composites made with recycled post-consumer polymers and “fresh” vegetable fillers [7].

At the end of the service life of PVC-containing products, several options are available for disposal and waste management. Of course, the first option is recycling and/or reuse into different useful products. The problem associated with the above solutions is the number or recycling cycles acceptable and with limited damage on PVC [8].

This work examines the impact of reprocessing on the structure and mechanical properties of PVC/alfa composites in with and without PVC-g-MA used as the compatibiliser by melt-processing in an internal mixer (Brabender plasticorder). Neat PVC was also reprocessed as a reference material. The effects of structural changes on the mechanical properties were determined by tensile tests. The morphology of the composites was studied by scanning electron microscopy (SEM). Dynamic-mechanical analysis (DMA) was used to analyse possible changes in the physical structure.

2 Experimental

2.1 Materials

All the PVC/alfa formulations used in this work were based on PVC type SE-1200 provided by CABEL “Cablierie Electrique” located in Algiers (Algeria). The polymer has the following physical characteristics: Kwert (parameter that characterizes the viscosity of a material), 70.2–72.0; powder density, 0.521. The additives used in the preparation of the various formulations were dioctyl phthalate as a plasticizer, a thermal stabilizer system based on Ca/Zn, and stearic acid as a lubricant. The alfa used as reinforcing filler was collected at M’Sila in Algeria and its average particle size is around 125 µm. The compatibilizer was the maleic anhydride-grafted-polyvinyl chloride (PVC-g-MA). It was synthesized at the laboratory of organic materials,
University A. Mira of Bejaia, Algeria [9]. The grafting content of maleic anhydride was 3.8%.

2.2 Preparation of the Composites

PVC powder and the various additives were placed in a high-speed twin steel-wall mixer and processed at a speed of 3000 rpm at 70 °C, below the glass transition temperature of PVC. A Brabender Plasticorder mixing chamber (model W 50 EHT) was used for the melt blending of PVC with alfa fiber and compatibilizer. Mixing was performed with 50 rpm at 170°C for a time period of 5 min. Prior mixing, the PVC-g-MA compatibiliser and the fiber were dried at 80 °C for 24 h. The processed material was granulated and then subjected to four repeated cycles under the same operating conditions. For each cycle, a part of resulting material was compressed with the aid of hydraulic press after 5 min heating at 170°C with a pressure of 30 bars. The sheets were allowed to cool to room temperature. The 1.5 mm thick plates obtained were then removed to be used in various characterizations. Sample compositions are listed in Table 1.

Table 1 Formulation codes of PVC/alfa composites used

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Composition wt.%</th>
</tr>
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<tbody>
<tr>
<td>PVC</td>
<td>100 0 0</td>
</tr>
<tr>
<td>PVC/alfa</td>
<td>80 20 0</td>
</tr>
<tr>
<td>PVC/alfa/PVC-g-MA</td>
<td>75 20 5</td>
</tr>
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</table>

3 Techniques

3.1 Scanning electron microscopy (SEM)

The morphologies of the fracture surfaces were observed by using a scanning electron microscopy (SEM) (Jeol JSM 6460LV). The specimens were fractured after immersion in liquid nitrogen. The fractured surfaces of specimen were coated with a thin layer of gold–palladium before SEM examination.

3.2 Tensile test

The tensile test for the composites was conducted using a MTS Synergie RT1000 (MTS, Eden Prairie, MN, USA) testing machine with a crosshead rate maintained at 2 mm min⁻¹. Five measurements were conducted and average for the final result was considered. The dimensions of the calibrated part have a width = 4 mm and a length = 45 mm

3.3 Steric exclusion chromatography (SEC)

Samples before and after recycling were analysed by Sterical Exclusion Chromatography (SEC). For SEC experiments, a Shimadzu LC10AD system was used in combination with a Shimadzu RID10A differential refractometer and a Shimadzu SPD 10Avp UV dual wavelength detector. The column set was constituted of five 30 cm PL Gel columns. The solvent was analytical grade THF.

3.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was conducted in a tension mode using a DMA 50 N (METRAVIB, ACOEM,). Temperature scans were run from -20 to 120°C at a heating rate of 2°C/min using an elongation mode and the data presented in this study were run at 1Hz. The amplitude deformation was 10 mm, the loss factor (tanδ) were measured as a function of temperature. Sample dimensions were about 20 mm length, 5mm width and 2mm thickness. The main relaxation temperature $T_g$ can be defined as the temperature at which the maximum of tanδ is reached.

3.5 Thermogravimetric analysis (TGA)

TG and DTG were carried out using Setaram TG-DTA 92-10 instrument, in an inert atmosphere at a heating rate of 20 °C/min. The weights of samples were in the range of 10-20 mg and they were scanned in the temperature range starting from 25 °C to 700 °C.

4 Results and discussion

4.1 Scanning Electron Microscopy (SEM)

The effect of reprocessing on the dispersion of alfa fiber in the PVC matrix and the interfacial adhesion between the alfa fiber and PVC matrix were investigated by using scanning electron microscopy (SEM) technique. Fig. 1(a) shown that after the addition of 20 wt.% of alfa fiber particles to PVC matrix, a pull out fiber can be seen clearly. In addition, there was some fiber debonding as indicated by the circular as well as the longitudinal voids indicating poor adhesion for composites without compatibilizer. Moreover, aggregates of various sizes are formed at the PVC surface. However, no clear gap is seen in the rough interfacial region between the PVC matrix and alfa fiber for compatibilised systems (Fig. 1(b)). The compatibilizer used in the PVC/alfa composite improve the interfacial interaction in the interface, which results in an enhancement of tensile strength.
Fig. 1(c) and (d) show the SEM micrographs of the fracture surface for both PVC/alfa and PVC/alfa/PVC-g-MA composites after four extrusion cycles, respectively. In both figures, it was obvious that alfa fiber was more compatible with PVC as indicated by rare pulled-out trace. Fig. 1(f) also show the reduction in diameter of the fibers to the micrometer scale after four cycles, in comparison to the pristine fiber shown in Fig. 1(e) confirming fibrillation. Fibers are not well observed on the composite surface, clearly evidencing their shortening as a consequence of the successive reprocessing of the composite. The pictures highlight the presence of bundles and long fibres after the first cycle (Fig. 1(e)). These bundles have nearly disappeared; only short and well separated fibres remain after reprocessing (Fig. 1(f)). The fibrillation created a better interfacial adhesion in the composites as a result of reprocessing. Other authors have also reported a severe shortening of the cellulose fibers length as the factor responsible for the increase observed for the mechanical properties of short-cellulosic fiber reinforced composites upon reprocessing [7,18].

4.2 Mechanical properties
Mechanical performance of WPC products was of major importance. To investigate the effect of reprocessing process on the mechanical properties, tensile test was carried out.

Fig. 2 shows the evolution of Young’s modulus with the number of recycling for both neat PVC and PVC/alfa composites. The Young’s modulus for all composites with and without compatibilizer was higher than the value for neat matrix, as a consequence of the high modulus of lignocellulosic filler. After the first cycle, we can notice a considerable improvement of Young’s modulus with the addition of alfa fibers by almost 175 MPa passing from 246 MPa for the neat PVC to 421 MPa for PVC/alfa. The Young’s modulus of the composites containing PVC-g-MA is superior to the value observed for composites without compatibilizer.

Recycling of pure PVC induces a slight increase in Young’s modulus; it is probably a consequence of the increase in molecular weight induced by reprocessing.

![Fig. 2 Young modulus of PVC, PVC/alfa and PVC/alfa/PVC-g-MA as a function of number of reprocessing cycles](image)

The degradation of poly (vinyl chloride) is a complex chain dehydrochlorination that consists of an initiation process to generate an active intermediate and a series of chain reactions that generates additional active intermediates with progressively increased numbers of double bonds.
The elimination of hydrogen chloride is one of the fundamental aspects of PVC decomposition. In the first stage, this reaction starts by the formation of one double bond followed by a very fast unzipping reaction, which leads to a polyene sequences in the backbone [12] (Fig. 3). If the levels of degradation are high, secondary processes are also observed during degradation. For example, the polyene sequences can react with one another, leading to a crosslinked network by Diels Alder process as explained in Fig. 4 [12-14].

Fig. 3 Scheme of dehydrochlorination of PVC

Fig. 4 Scheme of crosslink of PVC

It can be seen from Fig. 2 that up to 4 reprocessing cycles, the Young’s modulus seems to be relatively changed for both PVC/alfa and PVC/alfa/PVC-g-MA. For the PVC/alfa composites, the increase between the first and fourth cycle is very substantial, the values indicate that the Young’s modulus of PVC/alfa in the fourth cycle is 125% higher than that of the initial one. The same tendency is shown by young’s modulus of composites with compatibilizers. The better dispersion of particles inside the matrix could justify this effect.

Variation of the tensile strength as a function of reprocessing cycles for neat PVC and PVC composite samples is shown in Fig. 5. The tensile strength of the neat PVC was 19.5 MPa against 9.5 MPa for the composites at 20% fiber content.

On the other hand PVC/alfa composites showed 51% lower tensile properties in compare with PVC. Due to addition of compatibilizer, tensile strength improved 43% for those fibers composites which is because of ester linkage formation via PVC-g-MA between alfa fiber and polyvinylchloride matrix. Reprocessing seems to have no significant influence on tensile strength of the neat PVC. The average improvement was about 15 % after the second cycle, but after 3 cycles the polymer strength decreased by 5.7%. The increase in tensile strength was highly significant for reprocessed composites. This appreciate change is due to the decrease in particle size of fiber induced by reprocessing. To explain differences between the mechanical properties of composites virgin and reprocessed samples, the main factors to be considered are as follows: wood particles size, wood particles dispersion, changes in molecular architecture of polymeric matrix and in the interfacial bonding between the two components. It has been reported that the smaller particle size results in a higher strength of the composite. It could be due to the better dispersion of fine particles in the matrix [15].

Fig. 5 Tensile strength and Elongation at break of PVC, PVC/alfa and PVC/alfa /PVC-g-MA as a function of number of reprocessing cycles

The values of elongation at break for virgin and reprocessed PVC and their composites with and without compatibilizer are shown in Fig. 6. It is evident from the data that the ultimate elongation decreases with the number of processing cycles. That is, the material becomes progressively stronger, stiffer and less ductile. These observations can be explained by the formation of an increasing number of crosslink. According to Kaci et al [16] it is due to increased adhesion which leads to reduced deformability. Improved adhesion hinders the formation of large voids, thus preventing catastrophic failure. Moreover, the location of the compatibilizer at the interface between the two phases enhances the stress transfer and reduces particle size because of the emulsifying effect. Balatinecz et al [17] investigated the effects of repeated recycling on the properties of wood fiber-
polyolefin composites. The results indicate a slight decrease in tensile strength for PP and PE composites. This was probably due to the reduction in the fiber aspect ratio as a consequence of reprocessing cycles. The changes in the modulus of PP and PE composites were minor in relation to repeated recycling. Due to the differing structures of polypropylene and polyethylene, different degradations are characteristic of each. In polyethylene, crosslinking is the primary degradation. In polypropylene, the primary mechanism is chain scission.

4.3 Molecular weights

Results summarized in Table 2 show that molecular weights of PVC and PVC/alfa composites increase strongly after reprocessing and this confirms the formation of a crosslinked network induced by reprocessing.

Table 2: Molecular weight of PVC samples and PVC/alfa composites with and without PVC-g-MA before and after reprocessing

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
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<tbody>
<tr>
<td>PVC cycle 1</td>
<td>185 700</td>
<td>02,13</td>
</tr>
<tr>
<td>PVC cycle 3</td>
<td>214 700</td>
<td>03,04</td>
</tr>
<tr>
<td>PVC/alfa cycle 1</td>
<td>220 900</td>
<td>03,55</td>
</tr>
<tr>
<td>PVC/alfa cycle 3</td>
<td>425 400</td>
<td>11,55</td>
</tr>
<tr>
<td>PVC/alfa/PVC-g-MA cycle 1</td>
<td>274 200</td>
<td>03,10</td>
</tr>
<tr>
<td>PVC/alfa/PVC-g-MA cycle 3</td>
<td>652 500</td>
<td>10,00</td>
</tr>
</tbody>
</table>

4.4 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is a reliable approach to examine the relaxation behavior of the materials. In order to evaluate the effect of the reprocessing thermomechanical properties were measured. The result of DMA analysis shown in Fig. 7(a) and (b) are exemplified by the loss tangent (tan δ) data for PVC, unmodified PVC/alfa composites and modified with PVC-g-MA at a loading of 5 wt.% before and after three cycles. The loss tangent for all composites reached a maximum in a temperature range of 40-60 °C; this relaxation corresponds to the Tg of PVC. The measurement can give knowledge about the interfacial behavior of composites. The peak position shifts if there are strong interactions between the matrix polymer and filler/reinforcement [19]. Fig. 7(a) illustrates the tan δ curves after first cycle, clearly showing the reduction of the tan δ peak height with fiber incorporation. As respect Tg one can see that fiber incorporation caused the increase of the values. This is expected because the addition of alfa fiber in PVC increases the stiffness of the composites.

Fig. 6 Elongation at break of PVC, PVC/alfa and PVC/alfa /PVC-g-MA as a function of number of reprocessing cycles

Fig. 7 Tan δ as a function of temperature at 1 Hz stress frequency obtained by using DMA experiments for PVC, PVC/alfa and PVC/alfa/PVC-g-MA. a: cycle 1 and b: cycle 3.
The peak amplitude is decreased with the addition of compatibilizer, which indicates that the number of molecular segments involved has decreased due to improved adhesion between fiber and matrix.

According Gajender Saini et al [20] the presence of rigid filler together with an excellent adhesion between the filler and the matrix resulted in restriction of the molecular mobility of the polymer and thereby resulted in enhancement of Tg. A slight improvement in the tan δ values with recycling is shown (Fig. 7(b)). However, the Tg of composites with and without compatibilizer is shifted a lot toward a higher temperature. The shift in the tan δ peak position also shows that the molecular motion is restricted, and this confirms the strong interaction between alfa fiber and PVC matrix after reprocessing.

4.5 Thermogravimetric analysis

The thermal stability and degradation behavior of PVC and its composites with and without compatibilizer in a nitrogen environment were also investigated by TGA before and after three cycles. The results are shown in Fig. 8(a) and (b). Similar to PVC, its composites exhibited two-stage degradation. The first stage was attributed to dehydrochlorination followed by the formation of the conjugated polyene sequences, whereas the second stage corresponded to the thermal cracking of the carbonaceous conjugated polyene sequences. [21] From the TGA curves, the temperature at 5% weight loss (T5%) and the temperature at 50% weight loss (T50%) were collected and are summarized in Table 2. T5% and T50% corresponded to the course of dehydrochlorination and backbone degradation, respectively. It can be seen in Fig. 8(a) the incorporation of the alfa fiber in PVC matrix decreases the onset decomposition temperature (T5%). This reduction can be attributed to the decomposition of the hemicellulose, which is less stable than cellulose and lignin. The addition of compatibilizer to the composites presents little influence on the thermal stability of the material. However, T50% of the composites shifted toward higher temperatures 7°C passing from 314 °C for neat PVC to 321°C for PVC/alfa with and without compatibilizer. The results indicate that the backbone degradation of PVC were delayed with the addition of alfa fiber and PVC-g-MA. Weight loss and the residues percentage of PVC/alfa composites with and without PVC-g-MA are lower than that of PVC.

Furthermore, the DTG results indicate that the temperature of maximum rate of weight loss of the composites is improved and its value is around 252 °C which is higher than the corresponding neat PVC (249 °C). All these due to the alfa fiber involved in PVC, and it also leads to reactions between alfa and PVC [9]. Therefore, by analyzing the thermograms of DTG, it was verified that the maximum degradation rate recorded during the first phase of degradation are definitely higher than the maximum temperature of the PVC. The reduction of the maximum decomposition rate is attributed to alfa fiber which hinders the diffusion of the volatile decomposition products.

Fig.8 TGA/DTG thermograms of PVC, PVC and PVC/Alfa/PVC-g-MA composites recorded at a heating rate of 20 °C/min under N2 atmosphere. (a): cycle 1 and (b): cycle 4.

Fig. 8(b) shows the TGA curves obtained for the third cycle reprocessed PVC and PVC/alfa treated and untreated composites. After three cycles, the TG results indicate that the T50% of the PVC and composites is increased 3°C, they are shifted towards higher temperatures comparing with the
ones obtained in the first reprocessing cycle. When discussing the reason of the increase observed for the three cycle reprocessed composites, it was indicated that the fiber is well dispersed and is surrounded by the matrix. By consequently the cellulosic reinforcement contained in the reprocessed composites is less prone to degradation than that contained in the original ones.

5. Conclusion

In this study, the effects of reprocessing on properties of PVC and PVC/alfa composites were investigated. Mechanical, dynamical and thermal tests were performed on the samples of composites with and without compatibilizer before and after four cycles.

The results of the present study confirmed that generally the recycling process enhanced tensile strength and Young modulus in the studied formulations. This is mainly due to better fiber dispersion, lower amounts of voids, better interface quality. These are clearly revealed through an SEM analysis. After reprocessing, the morphology of the composite materials indicates that the alfa fiber particles are uniformly dispersed and embedded in the polymer matrix. The bundles have nearly disappeared after the four cycles.

The change in the structure of PVC after reprocessing which yields large crosslink evidenced by molecular weight measurements.

Another interesting result from this work is that obtained about a dynamical properties. Our result demonstrate that the incorporation of alfa fiber and PVC-g-MA produce a decrease of the tan δ peak height. This behavior was attributed to the presence of the fibers themselves, to macromolecular chain mobility restrictions at the neighborhood of the fibers and to the development of better fiber/matrix adhesion specifically when compatibilizer are used. In addition, it is found that the reprocessing cycles increase in Tg of PVC and PVC/alfa composite . The shift in the tan δ peak position shows that the molecular motion is restricted, and this confirms the strong interaction between alfa fiber and PVC matrix after reprocessing.

The thermal stability of PVC and PVC/alfa composites with and without compatibilizer before and after reprocessing has been studied. It is also observed that the maximum degradation rate is shifted to a slightly higher region in the case of composites than that of PVC, due to the higher thermal stability of the composites. The alfa fiber takes an important protective role in the PVC degradation by slowing down its decomposition rate. The reduction of the maximum decomposition rate is attributed to alfa fiber which hinders the diffusion of the volatile decomposition products.

In short, this study indicate that PVC/alfa composites may represent good potential for utilization after multiple recycling specially with compatibilizer.

References


