Effect of Carbon Nanotubes on Physical, Mechanical and Morphological Properties of Baggase Fiber-recycled Polypropylene Composites

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Abstract: In this study, the effect of multi-wall carbon nanotube (MWCNT) on physical, mechanical and morphological properties of baggase fiber- recycled polypropylene composites was investigated. Recycled polypropylene (rPP) was obtained from pass virgin polypropylene to twin-screw extruder under controlled condition. Composites with different contents of CNTs (0, 0.5, 1 and 1.5 phc) and maleic anhydride polypropylene (MAPP) (0 and 2 phc) were mixed by melt compounding in an internal mixer and then the nanocomposites were manufactured by injection molding. The mass ratio of bagasse fiber to polymer was 40/60 (w/w) in all compounds. Water absorption, flexural modulus, flexural strength, tensile modulus, tensile strength and morphological properties of the prepared nanocomposites were evaluated. From the results, WPCs made from recycled polymers exhibited weaker physical and mechanical properties compared to those made from virgin polymers. The physical and mechanical properties of baggase fiber- rPP composites could be significantly improved with increasing the content of MWCNTs (from 0.5 to 1.5 phc) and using 2 phc MAPP in the panels. Based on the findings in this work, addition of 0.5 phc MWCNTs dramatically improved the properties of the composites made from recycled PP; as their mechanical strength was higher than those made from virgin polymers. Also Scanning Electron Microscope (SEM) micrographs indicated that the microcracks of baggase fiber- rPP composites can fill by CNTs. The addition of MAPP has a positive effect on the performance of carbon nanotubes in the nanocomposites.

Key words: Carbon nanotubes • Polymer recycling • Wood-plastic composites • Physical and mechanical properties

INTRODUCTION

One of the major components of global municipal solid waste (MSW) is plastic wastes (such as PP, PE, PS and PVC). Annually, thousands of tons of post-consumed polymeric material wastes are generated all over the world. It is clearly obvious that high costs annually should be paid by governments for disposal or reducing environmental impacts of the polymeric wastes.

On the other hand, agricultural wastes (such as flax, jute, wheat straw, sisal, etc.) make up another important category of the solid wastes. Bagasse is one of the agricultural wastes that are widely generated in high proportions in the agro-industry. Shibata et al. (2005) reported that the worldwide production of bagasse fiber is ~7 times larger than that of jute, kenaf and hemp combined [1]. Baggase is the residue after sugarcane stalks are crushed for sap extraction. It is a typical practice to burn these lignocellulosic wastes, allow it to decay or bury it in a landfill, resulting in significant environmental problems including air pollution and emission of greenhouse gases. Hence finding a way to reduce these wastes is very necessary. So far several methods have been suggested to reduce the negative impacts of agricultural and polymeric wastes [2-4]; one of the best suggested methods is the use of them in Wood- Plastic Composites (WPCs) [5-6].

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Traditionally, WPCs are made from virgin polymers and wood fibers. One of the most important advantages of WPCs is the possibility of using the agriculture wastes and recycled thermoplastics in their composition. Nowadays because of environmental and economical reasons, use of low value materials in WPCs is growing [7-8]. Several researchers have indicated that WPCs manufactured from agricultural and wood fibers do not have significant differences [9]. However, according to previous studies, the composites made from recycled polymers exhibited lower physical, mechanical and thermal properties rather than those made from virgin polymers [10-11]. In recent years, there have been considerable efforts to develop WPCs based on recycled polymers [8, 12-13].

Use of nano-materials such as Multi-Wall Carbon Nanotubes (MWCNTs) is one of the best methods to overcome the negative effects of the engineering composites. MWCNTs have high specific strength, resistance against water and chemicals, excellent electrical and thermal conductivity and high mechanical properties (Flexural modulus: 1 TPa, Flexural strength: 200 MPa) [14-15]. The excellent properties of carbon nanotubes make this resource very attractive for use as reinforcement agent in various composites [16-18]. So far several researchers have focused on improvement of mechanical and thermal properties of virgin-based polymer composites by CNTs [19-20]. Our previous studies indicated that carbon nanotubes have significantly positive effects on physical and mechanical properties of the wood flour-virgin polyethylene composites [21]. However, currently there is no information about the effect of carbon nanotubes on properties of WPCs based on recycled polymers. Hence the aim of this research was the improvement of physical and mechanical properties of bagasse fiber-recycled polypropylene composites by carbon nanotubes.

**MATERIALS AND METHODS**

**Materials:** Recycled polypropylene (rPP) was obtained from pass polypropylene to co-rotating twin-screw extruder at a rotor speed of 100 rpm and a temperature of 190°C. Melt flow index of rPP was 10 g/10 min (190°C). Maleated Polypropylene (MAPP) produced by Kimia Javid Factory (Isfehan, Iran) with melt flow index (MFI) 100g/10min (T= 230°C, load=2.16kg) and 1.1 percent coupled maleic anhydride was used as compatibilizer. Bagasse fiber supplied by a local company was used to produce experimental panels. According to Younesi Kordkhili et al. (2012) method, bagasse fibers were initially soaked into water for two days to enhance the overall disintegration quality of the material before they were dried in a laboratory type oven at a temperature of 80°C for three days [22]. Average dimensions and tensile strength of the bagasse fibers are shown in Table 1. Multi-wall carbon nanotubes (MWCNT) with an average diameter and length of 50 nm and 500 nm, respectively were provided by the Research Institute of Petroleum Industry Company (RIPIC), Iran. The CNTs were prepared using a chemical vapor deposition (CVD) process. Raman spectra and Scanning Electron Microscope (SEM) micrographs of the used MWCNTs are presented in Fig. 1 and 2, respectively.

**Composite Preparation:** Polypropylene (PP), Recycled Polypropylene (rPP), maleated polypropylene (MAPP), Bagasse fiber and multi-wall carbon nanotubes were chemically compounded in internal mixer (HBI System 90, USA) according to Table 2 and then the nanocomposites were manufactured by injection molding (Imen machine, Iran). Details of sample manufacturing were presented elsewhere by Younesi Kordkheili et al. [21].

**Measurements**

**Short-term Water Absorption:** Short-term water absorption tests of the nanocomposites were performed according to ASTM D-7031-04 standard. Three specimens from each combination were taken and dried in an oven for 24 h at 100±3°C. The weight of dried specimens was measured at an accuracy of 0.001 g. The specimens were...
then immersed in distilled water for 24 hours and kept at a temperature of 22 ± 2°C. Weight of the specimens was measured after excessive water was removed from their surface. The value of the water absorption in percentage was calculated using the following Equation:

\[ W_A(t) = \frac{W(t) - W_0}{W_0} \times 100 \]

where \( W_A(t) \) is the water absorption (%) at time \( t \), \( W_0 \) is the oven dried weight and \( W(t) \) is the weight of specimen at a given immersion time \( t \).

**Mechanical Tests:** The flexural and tensile tests were measured according to ASTM D790-03, using an Instron machine (Model 1186, England). The tests were performed at crosshead speeds of 5mm/min.

**Scanning Electron Microscopy (SEM):** The morphology of the composites was examined using a scanning electron microscope (XL 30) supplied by Philips Company Limited. The fracture surfaces of the specimens after impact test were sputter-coated with gold before analysis. All images were taken at an accelerating voltage of 17 kV.

**RESULTS AND DISCUSSION**

**Short-term Water Absorption:** Figure 3 shows the short-term water absorption content of the nanocomposites after 24 h immersion in distilled water. Because of constant baggase fiber content (40wt %) in all compounds, the different water absorption can be attributed to the role of coupling agent (MAPP) and multi-wall carbon nanotubes (MWCNTs). Fig. 3 indicated that the composites without CNTs and MAPP exhibited higher short-term water absorption values rather than those containing them. Addition of MAPP increases the ester linkages between the hydroxyl groups of natural fiber and the anhydride part of MAPP [23]. Therefore, the amount of free OH in the natural cellulose is reduced because some of them are interacting with maleic anhydride. Due to these changes, the water absorption
Fig. 3: Effect of MWCNTs and MAPP content on water absorption of bagasse fiber-recycled PP composites

increment is rather less, compared to the composite formulations without MAPP. Also the composites with MAPP have higher crystallinity than those without it. The crystalline regions are resistant to water penetration [24]. So far several papers have been reported about the positive effect of MAPP on water absorption properties of WPCs [21, 25, 26]. Also, Fig. 3 indicated that at the presence and absence of MAPP, the composites made from recycled PP exhibited higher water absorption content than those made from virgin polymer (control). During the recycling process, the crystalline structure of plastics decreases [27-28]. Regard to positive effect of crystalline structure in reduction of water absorption, higher water absorption of the composites based on recycled plastic compared to those made from virgin polymers is expectable. In constant level of coupling agent, the natural fiber- recycled PP composites containing MWCNs exhibited lower water absorption contents as compared with those made without them and control samples (bagasse fiber-virgin polymer composite). In the wood-based composites, initially, water saturates the cell wall of the fiber and then it occupies the void spaces. Kazemi Najafi et al. (2009) indicated that some microcracks and voids are created by recycling of polymers [28]. Fig. 4a corresponds to SEM photomicrographs of the fractured samples of composites made from recycled PP without presence of CNT. Fig. 4a is showing the cavities which are available in composites made from recycled polymer. Also Figure 4.b is showing the position of CNTs in composites containing 1 phc carbon nanotubes and 2 phc MAPP. Figure 4.b reveals that CNTs fill the voids of wood plastic composites. As the composite cracks and voids were filled with CNs, water penetration into the deeper parts of composite due

Fig. 4: SEM Photomicrographs of fractured samples of the manufactured composites: (a): baggase fiber-recycled polypropylene composites, (b): baggase fiber/ MWCNT/recycled polypropylene nanocomposites
to capillary action was prevented [16]. Another reason for less water absorption of the nanocomposites could be explained by the hydrophobic nature of the CNTs surface. Tavassoli Farsheh et al. [29] and Younesi Kordkheili et al. [21] indicated that addition of CNTs to natural fiber-virgin polymer composites decrease water absorption and thickness swelling of samples. Also, Fig. 3 indicated that the nanocomposites containing recycled polymer and 0.5 phc carbon nanotubes exhibited lower water absorption than control samples. Generally, water absorption test results indicated that addition of CNTs and MAPP had a positive effect on decreasing the water absorption of WPCs based on recycled PP.

**Flexural Properties:** Flexural modulus of the manufactured nanocomposites is presented in Fig. 5. It is clearly seen that addition of CNTs and coupling agent (MAPP) increased flexural modulus of the manufactured WPCs. In absence of CNTs and MAPP, composites made from virgin PP exhibited higher flexural modulus (2650 MPa) than those made from recycled PP (2052 MPa). This behavior is expected because polymer chains become shorter with recycling, causing an increase in the plasticity. So far several papers have reported higher flexural modulus of WPCs made from virgin PP compared to those made from recycled PP [11]. As shown in Fig. 5, maximum flexural modulus of nanocomposite was 3957 MPa for nanocomposites with 1.5 phc MWCNTs and 2 phc maleic anhydride polypropylene, while minimum flexural modulus is approximately 2200 MPa for bagasse fiber-recycled PP samples. In absence of MAPP, flexural modulus of the samples with 0.5, 1 and 1.5 phc MWCNTs were 11, 28 and 52 % higher than the control ones, respectively. Also the bending test results indicated that the composites made with 2 phc MAPP and 0.5, 1 and 1.5 phc carbon nanotubes had flexural modulus of 25, 41 and 50 % higher than the composites made from virgin polymers and without CNTs. Flexural modulus in composites is mainly the function of the modulus of individual components [21]. Flexural modulus of CNTs (about 1Tpa) was considerably higher than that of bagasse fiber and PP. Hence it was expected that the composites with CNTs exhibited higher flexural modulus values. Also CNTs could fill most of the microcracks in the polymer matrix and natural fiber-PP interface which were produced by recycling process.

On the other hand, Figure 5 indicates that MAPP had a positive effect on flexural modulus of the nanocomposites. The greater flexural modulus can be attributed to the efficient stress transfer between natural fiber and polymer [25]. In addition, the good dispersion also contributes to the dramatic increase in modulus (Fig.4). Also MAPP helps to dispersion of carbon nanotubes in polymer matrix leading to the increase of flexural modulus of the nanocomposites (Fig 4b).

Figure 6 indicates flexural strength of the manufactured nanocomposites. Generally similar to flexural modulus, the composite made from virgin PP exhibited higher flexural strength than those made from recycled PP. Greater flexural strength was achieved in the WPCs based on recycled polymer when the content of carbon nanotubes and coupling agent used in the manufacture of the composites increased. Addition of CNTs up to 1.5 phc dramatically enhanced flexural strength of the composites based on recycled PP. Composite strength depends on the properties of constituents and the interfacial interaction [30]. Because of carbon nanotube size, aspect ratios (length to diameter
ratio) and high mechanical properties, CNTs can be well distributed in the WPCs and improve adhesion between the elements. Jia et al. [31] found that the interface adhesion between nanotubes and matrix is quite good. Also the results indicated that adding coupling agent (MAPP) could enhance the interface adhesion. This interfacial adhesion improvement was associated with the formation of covalent bonds (ester linkages) between the bagasse fiber and polymer. Maleic anhydride caused uniform dispersion and better wetting of the bagasse fiber in the PP matrix, which led to efficient stress transfer from the matrix to the fiber. Also Scanning electron microscopy (SEM) micrograph test such type of samples was evaluated by Prashantha et al. [32] and it was found that better dispersion and good adhesion between the nanotubes and the PP matrix is caused by wrapping of MAPP on MWCNTs. When MAPP is added, dynamic moduli and viscosity further increase compared to PP/MWNT nanocomposites.

The samples containing 1.5 phc CNTs and 2 phc MAPP showed the highest flexural strength (138 MPa) in among the studied composites. Several researchers have reported significant improvements in polymer based composites by adding carbon nanotubes [29].

**Tensile Properties:** Tensile modulus and strength of manufactured nanocomposites are shown in Fig. 7 and 8, respectively. Similar to flexural properties, it can be observed that tensile modulus and strength of the WPCs based on recycled PP were weaker than those made from virgin PP. This behavior was expected as a result of polymer chain degradation because of severe thermal and stress exerted during the extrusion process, which led to a molecular weight reduction [10]. This reduction led to a decreased stress transfer via covalent linkages and an increased crack initiation and propagation in the polymer matrix [28]. Fig. 7 and 8 indicated that the positive effect of coupling agent and carbon nanotube on tensile properties of bagasse fiber- recycled PP composites. The highest tensile modulus (3500 Mpa) and strength (26 MPa) related to the nanocomposites with 1.5 phc MWCNTs and 2 phc MAPP. Also the composites made from recycled PP (without MWCNTs and MAPP) exhibited the lowest tensile properties. The presence of maleic anhydride as coupling agent enhances the interface adhesion between bagasse fiber and polymer matrix bringing about better encapsulation of bagasse particles by the plastic which consequently results in higher tensile properties. Also the adhesion of MAPP on the nanotube surfaces modifies the wettability of the nanotubes and promotes the disentanglement in the PP matrix leading to a better dispersion during melt processing [32]. It can be seen that tensile modulus and strength of the nanocomposites increase with the increase in CNTs content from 0 to 1.5 phc. In absence of MAPP, tensile modulus of nanocomposites containing recycled polymers and 0.5, 1 and 2 phc CNTs were 11, 78 and 91% higher than control sample (bagasse fiber- virgin PP composites), respectively. The composites made with 2 phc MAPP and 0.5, 1 and 1.5 phc CNTs had tensile modulus of 67, 72 and 83 % higher than the control samples. From the results, addition of CNTs up to 1.5 phc significantly increased tensile properties of composites based on recycled PP. This phenomenon can be related to high stiffness of carbon nanotubes (1 TPa) and good bonding between polymer and nanoparticles. The orientation of reinforcing fiber as well as its aspect ratio in the composites influences the tensile strength of

Fig. 7: Effect of MWCNTs and MAPP content on tensile modulus of bagasse fiber-recycled PP composites

Fig. 8: Effect of MWCNTs and MAPP content on tensile strength of bagasse fiber-recycled PP composites

fiber reinforced composites [33]. Bagasse fiber and MWCNTs have high aspect ratios (200 and 2000, respectively) which result in significant increase in tensile strength of the studied wood-plastic composites.

Long et al. [34] indicated that thermal degradation of the recycled PP-carbon nanotube composites shifts toward higher temperatures as the concentration of CNTs is increased. Also they showed that with increase in CNTs content, tensile strength and elongation at break increase firstly and then decrease.

CONCLUSION

In this study, the effect of multi-wall carbon nanotube (MWCNT) on physical, mechanical and morphological properties of experimental bagasse fiber-recycled polypropylene (PP) panels was investigated. The results show that compared to WPCs based on virgin polymer, the composites containing recycled PP exhibited higher water absorption value and lower tensile modulus, tensile strength, flexural modulus and flexural strength. The results also indicated that MWCNTs as well as the coupling agent (MAPP) had significant effect on physical and mechanical properties of the composites based on recycled polymers. From the results, Addition of CNTs content up to 1.5 phc increased physical and mechanical properties of bagasse fiber-recycled PP composites. High aspect ratio and large surface area of CNTs resulted in the enhancement of composites mechanical strength. Recycled composites with 0.5 phc CNTs exhibited lower water absorption value and higher flexural and tensile properties than the WPCs made from virgin polymers. When MAPP was added to bagasse fiber/recycled PP/carbon nanotubes nanocomposites, all the measured properties increased compared to those made without
MAPP. Scanning Electron Microscope (SEM) micrographs indicated that the microcracks of bagasse fiber-rPP composites can fill by CNTs.

REFERENCES


