INVESTIGATION OF THE MORPHOLOGICAL AND THERMAL PROPERTIES OF WASTE NEWSPRINT/ RECYCLED POLYPROPYLENE/ NANOCLAY COMPOSITE

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The main objective of this research was to study the potential of waste polypropylene and waste newsprint fiber for making wood-plastic nanocomposites. We used 30 wt.% waste newsprint fiber and 10 wt.% compatilizer in this study. Nanoclay was used at two levels: 2.5 and 5% by wt. Materials were mixed with either recycled or virgin polypropylene. The effects of nanoclay (NC) on the mechanical and thermal properties were also studied. The improvements in tensile properties of the blended composites with the addition of NC were further supported by Scanning Electron Microscope (SEM) micrographs and X-Ray Diffraction (XRD) data. Thermal degradation behavior of the composites showed that the degradation temperatures shifted to higher values after addition of nanoclay. The XRD data showed that the relative intercalation of composites with 2.5% nanoclay was higher than 5% nanoclay. The experimental results demonstrated that the waste materials could be used as appropriate alternative raw materials for making low cost wood-plastic composites (WPCs).

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INTRODUCTION

Many research organizations and institutes have or are currently conducting research on wood-plastic composites that will provide more durable and cost-competitive products by using waste materials. The reutilization of waste materials in the production of wood-plastic composites (WPCs) can have advantages to the economy, environment, and technology.

The largest component of municipal solid wastes generated each year consists of paper and paper products that are reused by the paper industry. Recycling of waste paper into other useful paper products has important environmental implications. Usually the recycling process in the paper mills involves fiber sorting, removing inks, dyes, clay, sizing agents and binders, and for some uses, rebleaching (Ashori 2008). One of the good options for using waste paper is in the preparation of wood-plastic composites. These

fibers constitute a largely unutilized resource, and in this case no extensive cleaning and refinement arerequired. Moreover, the processing cost of these fibers is lower than other recyclable wood particles and fibers.

Polypropylene (C_3H_6) (PP) is a thermoplastic with a semi-crystalline polymer structure, and it is used in a wide assortment of applications. PP has an excellent resistance to stress and a low specific gravity. PP is readily able to be mechanically recycled several times using conventional equipment. Attempts have been made to reuse these waste plastics in order to reduce the environmental impact and consumption of the virgin plastics (Hannequart 2004). Past studies have demonstrated that the recycled plastics possess similar mechanical properties but are much cheaper than their virgin counterparts (Panthapulakkal et al. 1991).

The desired properties of WPCs can be improved by using additives such as lubricants, coupling agents, antioxidants, and antimicrobial agents (Jayamol et al. 2001). The hydrophilic nature of wood or natural fibers and hydrophobic nature of polymers cause the weak chemical bonding between these two phases. Therefore, the poor ability to transfer stress from the polymer matrix to wood fillers leads to a decrease in mechanical properties. Thus, coupling agents should be incorporated to improve the compatibility (Li et al. 2001). Maleated polypropylene (MAPP) is commonly used in WPCs and is highly regarded as the effective coupling agent (Wang et al. 2003; Li et al. 2001; Jacob et al. 2005).

In recent years, natural, inorganic fillers like clay with wood fibers are being added to thermoplastic polymers to produce wood polymer composite because they are naturally occurring minerals that are commercially available, exhibit a layered morphology with high aspect ratio, have large specific surface areas, and have substantial cation exchange capacities (Advani 2007). This natural inorganic filler is useful for the modification of certain characteristics of composites such as physical and mechanical properties, thermal stability, and their resistance against biological deterioration for outdoor applications (Smith and Wolcott 2006; Youngquist et al. 1994; Panthapulakkal et al. 1991). The use of small amounts of montmorillonite-based clays is enough to improve the overall properties of a polymer matrix at a relatively low cost (Pascual et al. 2009; Ratnayake and Haworth 2006). They belong to the aluminosilicate group, having 2 to 1 type layers in which exchangeable cations, such as Na^+ and Ca^{2+}, can fill spaces between the layers. The exchangeable cations can be replaced by organic cationssuch as quaternary ammonium salts by chemical treatments, producing organophilic clay (generally called organoclay), which have a much higher compatibility with the polymer (Ramos et al. 2005).

The main aim of this study was to investigate the potential of municipal solid waste materials for the conversion of recycled wood fiber and plastics into durable products that are recyclable and environmentally friendly. The reasons for focusing on these specific fibers and polymers are their high volumes and inherent ease of (easy) collection. The effect of nanoclay on the mechanical, thermal, and morphological properties of manufactured WPCs was also characterized.

EXPERIMENTAL

Materials

Waste newsprint was collected from Mazandaran Wood and Paper Industry, Iran. It was dried in an oven at 65±2 °C for 24 hours to decrease moisture content, and then ground to a finer flour by using a plate grinder. The industrial grade of virgin poly-propylene (PP) V30S was purchased from Arak Petrochemical Co. (Iran) with 18g/10min melt flow index and a density of 0.92 g/cm^3. The recycled PP granules were prepared from a local loom factory in Chalous, Iran. The recycled PP was washed with water, then ground to small granules. The coupling agent used was MAPP, having the trade name of Priex 20070, provided by Solvey. A commercial nanoclay product with trade name of Cloisite 15A was purchased from Southern Clay (Southern Clay Products Inc., Texas, USA). Cloisite-15A is a natural montmorillonite modified with dimethyl-dehydrogenated tallow–ammonium chloride salt, having a d-spacing of 31.5Å and modifier concentration of 125meq/100g clay. The formulations of composites are shown in Table 1.

Table 1. Composition of the Studied Formulations

Sample code PP/NF/C/N	Polypropylene (wt%)		Newsprint fiber (wt%)	Compati-bilizer (wt%)	Nanoclay (wt%)
	Virgin	Recycled			
60RPP/30NF/10C	-	60	30	10	0
57.5RPP/30NF/10C/2.5N	-	57.5	30	10	2.5
55RPP/30NF/10C/5N	-	55	30	10	5
60VPP/30NF/10C	60	-	30	10	0
57.5VPP/30NF/10C/2.5N	57.5	-	30	10	2.5
55VPP/30NF/10C/5N	55	-	30	10	5

Nanocomposite Fabrication

All the nanocomposites were prepared with a HAAKE device (Model HBI System 90, USA). First, the PP was put in the mixer rotating at 60 rpm with a temperature of 180 °C; the nano-filler and MAPP were added after the PP had reached its melting temperature. In the next step, fibers were added into the mixture and rotated; the mixing process took 13 min on average. Each blend was removed from mixing chamber, cooled, and cut into smaller pieces, then milled to produce granules. The resulting granules were subsequently injection-molded at 180°C to produce standard specimens.

Thermal Analysis

The thermal characterization of nanocomposites was carried out using a thermo-gravimetric analyzer (TGA). TGA was used to investigate the thermal decomposition behavior of the nanocomposites. Tests were done under a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere at a scan rate of 10°C/min in a programmed temperature range of 30 to 600°C. A sample of 8±1 mg was used for each test. The weight change was recorded as a function of temperature.

Mechanical Testing

Mechanical properties (tensile strength and tensile modulus) were measured according to the ASTM D 638 standard using an Instron Universal Testing Machine (model 1186) at speeds of 2 mm/min. The dimensions of the specimens for the tensile tests were 149 x 19 x 4 mm^3 (length x width x thickness). For each treatment level, five replicated were measured for each property and the average values were reported.

X-ray Diffraction

The wide-angle X-ray equipment was from Seifert-3003 PTS (Germany). The radiation wavelength was kCu= 1.54 nm, and the test conditions used were: voltage= 50 kV and current intensity= 50 mA. The X-ray images were used to investigate the intercalation, or exfoliation, behavior of the nanoclay by estimating the distance between the silicate platelets (by considering the Bragg's Law). The samples were scanned over the range of 2θ= 2° to 10°.

Scanning Electron Microscopy

The morphological properties of the nanocomposites were studied with a Philips XL 30 scanning electron microscope (SEM). The thin sections of the specimens after a tensile test were cut to observe their fracture surfaces. The specimens were coated with thin layer of gold before analysis.

RESULTS AND DISCUSSION

Tensile Properties

The mechanical properties of composites are dependent on the interface and interphase interactions between the wood flour and polymer matrix. The effects of the nanoclay content on the tensile modulus and strength of recycled and virgin nanocomposites are shown in Fig. 1 (a and b). The virgin-based composites had higher tensile properties than the recycled based composites. These reductions could be related to the presence of chemical impurities such as pigments, lubricants, antioxidants, and antimicrobial agents that weakened the interfacial bonding between the wood flour and the polymer matrix. In both types of composites, the tensile strength and modulus increased with increase of nanoclay up to 2.5% wt. and then decreased up to 5% wt. The high aspect ratio and huge interfacial contact area of nano-scale filler can improve the mechanical properties (Ramos et al. 2005; Advani 2007). These enhancements at 2.5% wt. of nanoclay are attributed to the lower percolation points created by the high aspect ratio nanoclay. The increase in properties may also be related to the formation of intercalated and exfoliated nanocomposite structures formed at these nanoclay levels (Kord et al. 2011; ZiaeiTabari et al. 2011; Lei et al. 2007; Wu et al. 2007; Han et al. 2008). The increment of the modulus depends on the dispersion of nanoclay on the composites that could be a positive effect. The decrease in tensile properties at 5% wt. of nanoclay may be related to the formation of agglomerated clay tactoids (Chen et al. 2007; Mohanty and Nayak 2007; Samal et al. 2008).
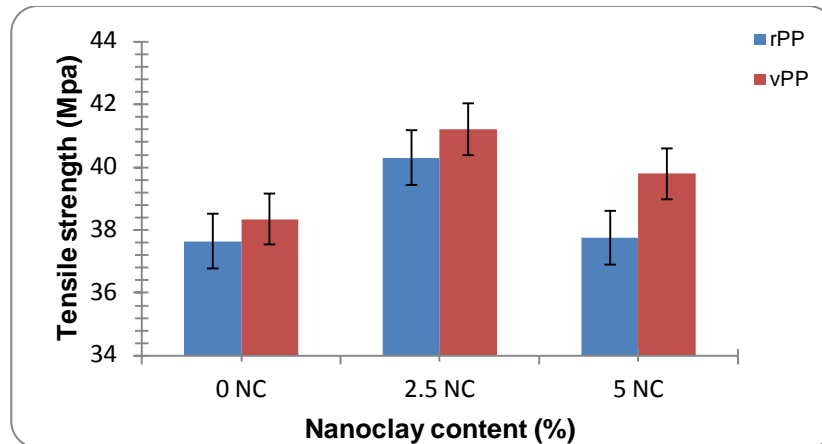
Fig. 1. a) Tensile strength of recycle and virgin polypropylene composites with different content of nanoclay
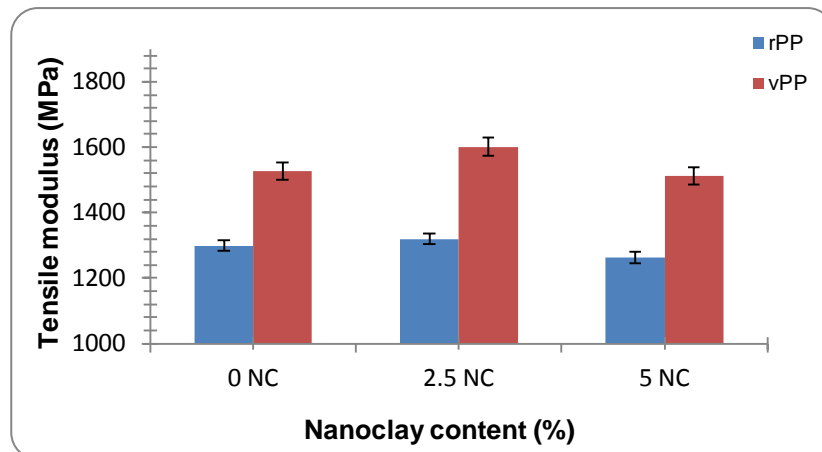
**Fig. 1. b)** Tensile modulus of recycle and virgin polypropylene composites with different content of nanoclay

Characterization of Fracture Surfaces

The fractured surfaces of the virgin and recycle-based nanocomposites were analyzed by SEM imaging (Figs. 2 and 3). According to Fig. 2, dispersion of the newsprint fibers in the rPP matrix (Fig. 2 (a)) was uniform as compared to vPP matrix (Fig. 2(b)) at the same concentration of nanoclay. This may be due to the different grade of plastic and other impurities (such as pigments, lubricants, antioxidants, and antimicrobial agents) in the rPP. In some cases, the part of the wood lumen was filled with plastic that could increase the strength of the composites because of mechanical interlocking. However, by comparison between Fig. 2 (a) and (b), it was observed that rPP composite samples had a weak interfacial region, and damage mainly occurred along the loose and weak interface between the newsprint fiber and PP matrix under loading. From micrographs of Fig. 2 (b), less gaps can be seen between the newsprint fibers and the virgin PP matrix, which indicates good interfacial bonding. Very few protruding newsprint fibers were observed in Fig. 2 (b); therefore, it was demonstrated that suitable adhesion between waste fiber and virgin polymer matrix in one side and appropriate distribution of nanoclay on the other side can improve the composite tensile properties.
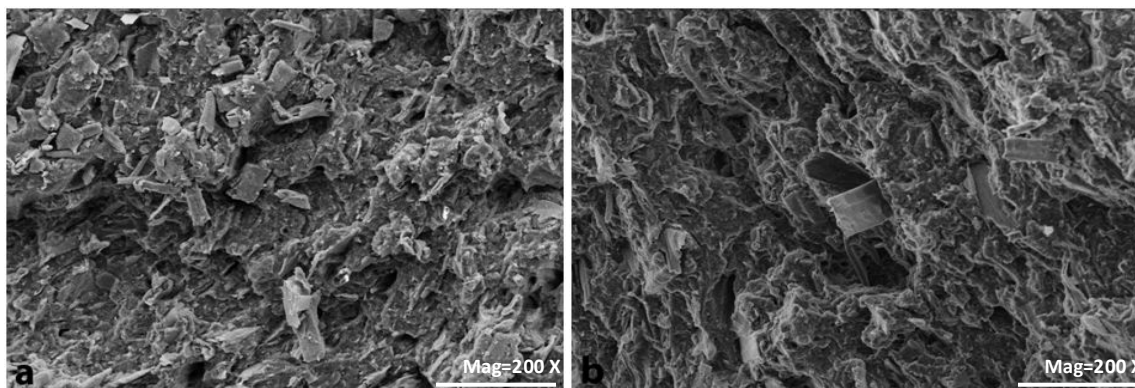
Fig. 2. SEM images of fractured surface of the waste newsprint/PP based nanocomposites, (a) recycle, and, (b) virgin samples incorporation of 2.5% nanoclay

According to Figs. 3 (a) and (b), the presence of these cavities and pulled-out fibres confirms that the interfacial bonding between the filler and the matrix polymer was weak. This phenomenon could relate to inappropriate dispersion of nanoclay in compareson with 2.5% nanoclay (according to the XRD data), caused mostly by heterogeneous parts in the matrix, which decreases the composite strength. Also, based on Fig. 3 (b), it is clearly observed that there were distinct clusters and gaps between polymer matrix and waste fiber. This is maybe related to the patterns from the waste fibers, which were so weakly bonded to the matrix and had been released from the matrix during fracture. The failure surface was undulated with clear wood flour surfaces with visible tracheids and lumens, indicating the path of weakness through the wood-wood interface and weakest polymer matrix.
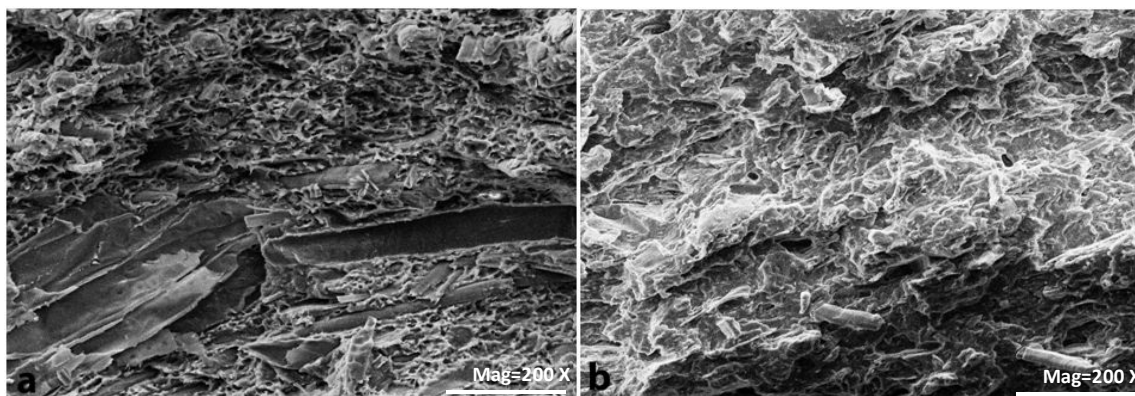
Fig. 3. SEM images of fractured surface of the waste newsprint/PP/ based nanocomposites, (a) recycle, and, (b) virgin samples incorporation of 5% nanoclay

X-ray Diffraction

The clay dispersion processes were studied by X-ray diffractometry (XRD). Table1 shows the summary of the X-ray diffraction of the samples with different amounts of nanoclay. By considering the Bragg's law, we have estimated the distance between silicate platelets and compared it with the basal plane distance of Cloisite 15A to determine whether intercalation or exfoliation occurs,

$$2d \sin \theta = \lambda n \tag{1}$$

where d is the distance between crystallographic planes, θ is half of the angle of diffraction, n is an integer, and λ is the wavelength of the X-ray.

The relative intercalation (*RI*) of the polymer in the nanoclay was calculated by the following equation:

$$RI = \frac{(d-d_0)}{d_0} \cdot 100 \tag{2}$$

where d_0 is the d-spacing of the clay in the pristine clay.

The XRD patterns for composites with different amount of nanoclay show a decrease in the peak intensity; the $2\theta = 2.8^o$ is related to neat clay with $d_{001} = 31.5$ nm. The peak was displaced to a lower angle ($2\theta = 2.37^o$, $d_{001} = 37.3$ nm) for composites with 2.5% nanoclay and ($2\theta = 2.46^o$, $d_{001} = 35.8$ nm) for composites with 5% nanoclay, which implies the formation of intercalation morphology. These data show that the order of intercalation and relative intercalation was higher at 2.5% nanoclay than it was at 5% nanoclay (the tensile properties confirmed this fact). These decreases in peak intensities could be related to the high amount of coupling agent that causes the good interaction between the polymer chains and nanoclay (ZiaeiTabari et al. 2011; Pascual et al. 2009). In other words, the presence of compatibilizer causes the good dispersion of nanoclay in the polymer matrix.

Table 1. Summary of XRD Data of Nanocomposites

Nanoclay Content (%)	Pure nanoclay	2.5	5
2θ (o)	2.8	2.37	2.46
d-spacing (nm)	31.5	37.3	35.8
Relative Intercalation (%)	-	18.41	13.65

Thermal Properties

TGA results of nanocomposites based on recycled and virgin polypropylene are shown in Fig. 4. In this study, only one weight loss graph of TGA was presented as a function of temperature. There are two degradation stages for the composites based on wood fiber. The first stage is related to the natural fibers degradation that involves two different processes, a low-temperature stage and a high-temperature stage. The second stage results from the decomposition of polymer matrix and other inorganic substances (Xu et al. 2008; Liu et al. 2009). According to the curves, the degradation of natural fibers are started at 240°C, which is related to low-temperature stage from degradation of cellulose and hemicellulose and the high-temperature stage from degradation of lignin. The presence of a high amount of compatibilizer agent causes strong interactions between polymer matrix, waste newsprint fiber, and organic modifier of the clay; this has a positive internal reinforcement effect, so the material needs higher temperature values to displace and separate chains (Pascual et al. 2009).

There was no significant difference between the curves of composites based on virgin polypropylene with 2.5% and 5% nanoclay; that can be attributed to the good

dispersion of nanoclay in the polymer matrix (the XRD results confirms this fact). From Fig.4 it is obvious that the thermal stability of the nanocomposites, based on virgin polypropylene, was higher than nanocomposites based on recycled polypropylene, and it was improved by the addition of nanoclay. By increasing the nanoclay percentage, the thermal stability was enhanced. The inorganic material can prevent the heat from being conducted quickly and limits further degradation (Barick and Tripathy 2010).
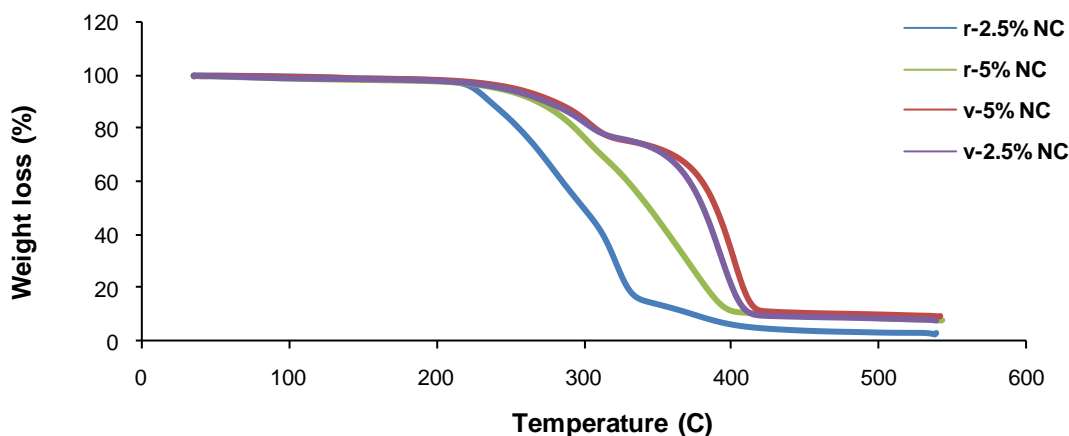

Fig. 4. TGA results of nanocomposites based on recycled and virgin polypropylene

CONCLUSIONS

1. The results show that the reinforcement with nanoclay is an efficient way to obtain an overall improvement on mechanical and thermal properties of the nanocomposites (by increasing from 1299 to 1601 (MPa) in tensile modulus, from 37 to 41 (Mpa) in tensile strength and increasing the temperature of decomposition at 90% weight loss from 418 ^{o}C to 551 ^{o}C). Tensile strength and modulus of composites based on virgin poly-propylene were higher than those of composites based on recycle polypropylene, and, in both cases, the tensile properties were improved by the addition of nanoclay.

2. The XRD data show that the order of intercalation and relative intercalation was higher in the case of composites with 2.5% nanoclay than 5% nanoclay.

3. The SEM images show no clear gaps between the newsprint fibers and the virgin PP matrix, which indicates good interfacial bonding. The images of recycle-based nano-composites show some extent of weak interfacial bonding, but there was a uniform dispersion of newsprint fibers in the polymer matrix.

4. The thermal degradation behavior of the composites was characterized with TGA. In all cases, the degradation temperatures was shifted to higher values after addition of nanoclay.

5. The recycled PP-based composites had lower physical and mechanical properties than that of virgin PP-based composites, but no significant differences were found between these two types of composites. Thus, it can be concluded that recycled wood fiber and plastics composites have the potential to serve as durable and environmentally friendly products.

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