OPTIMIZING WOOD FLOUR AND NANOCLAY CONTENT OF BIO-BASED NANO POLYMER COMPOSITES (APPROACH TO THERMAL STABILITY)

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The effects of nanoclay and wood flour contents on the notched impact and hardness properties, thermal gravimetric analysis (TGA), limited oxygen index (LOI), and morphological characteristics of poplar flour/polypropylene (PP)/nanoclay composites were investigated. To prepare the composites, poplar wood flour was mixed with polypropylene and nanoclay (Cloisite 30B) and maleic anhydride polypropylene (MAPP). All the components were mixed in an extruder and the test specimens were made by injection molding. Then, the notched impact and hardness properties, thermal stability and LOI, as well as scanning electron microscopy (SEM) images and X-ray diffraction (XRD) spectra were examined. The results showed that the hardness was improved and notched impact strength was reduced when increasing the wood flour content from 40% to 60%. Increasing the nanoclay content up to 4 wt% increased the notched impact strength, but decreased the hardness. The LOI improved with increasing content of wood flour and nanoclay. Increasing the amount of nanoclay led to higher ash content and improved stability. An analysis of the obtained XRD patterns led to the conclusion that an intercalation structure developed in the composite. SEM showed the composite pores and voids decreased by adding nanoclay, which determined an increase in the oxygen index.

Keywords: nanoclay, notched impact, hardness, intercalation structure, thermal gravimetric analysis

INTRODUCTION

The popularity and expansion of wood-plastic composites (WPCs) into construction materials markets and the construction industry, including siding, exterior decking, railing materials, are due to the products' perceived low maintenance and environmental performance (lifespan and non-toxicity) relative to wood.[1] Polypropylene (n-C_3H_6) (PP) is a thermoplastic with a wide variety of applications, it has excellent resistance to stress, possesses low specific gravity, and is readily recyclable using conventional equipment. Endeavors have been made to reuse such waste plastics so as to diminish the environmental and the utilization of virgin plastics.[2] The desired properties of WPCs can be also enhanced by utilizing added substances, for example, lubricants, coupling agents, antioxidants, and antimicrobial agents.[3] A poor capacity to transfer stress from the polymer framework to the wood filler leads to a prompt decline or reduction of mechanical properties. Therefore, coupling agents are a good choice for improving the compatibility.[4] Maleated polypropylene (MAPP) is regularly utilized as a part of WPCs and is widely viewed as primary coupling agent.[4-6]

Thermal analysis of WPCs helps to determine the maximum temperature that can be used during the production process. In fact, low thermal stability of wood restricts the number of polymers that are processed below 200 °C. Also, the high flammability of WPCs limits their application in various fields.[7] Thus, prediction by thermal analysis would be useful for selection among a wide range of polymers.[8] Thermal stability of pp-nanoclay composites has been studied by means of DSC and TGA. Results showed that oxygen penetration into composites significantly decreased as the nanoclay was used. Also due to addition of nanoclay particles, the thermal decomposition of polymer composites was

reduced. The release of oxygen and gas escaping from polymer were decreased as well.[9] The most important factor in the thermal stability caused by nanoclays is the formation of a coal layer, which is crucially important in the thermal analysis.[10] Compared with a virgin polymer, the creation of an intercalation morphology at the polymer matrix by using a silicate material, improved the dissolution temperature up to 40 to 50 °C.[11] Measuring the weight loss of a composite, caused by heating, is an acknowledged method for studying the thermal behavior of composites. This technique was applied to investigate the thermal stability and degradability of polymers under different conditions. Molecular weight changes are strongly depended on the nature and mass of the sample, atmospheric pressure and the rate of thermal scanning of the samples.[12]

The conventional system for decreasing the combustibility of composites is the utilization of flame retardants (FRs). The amount of FR usually employed is so high that the mechanical properties of composites are diminished.[8] Limited oxygen index (LOI) analysis is one of the most important methods to examine the flammability of different materials and is applied where the materials under examination can burn in contact with oxygen.[13] Among the variables that affect the flammability of the composites, the rate of heat release is more significant.[14] The consumption of oxygen is the main parameter determined during thermal analysis. It means that there is direct relationship between this parameter and the content of heat released during polymer testing. Guo *et al*. tried to reduce the flammability of wood flour reinforced plastics by adding nanoclay to the plastic matrix. They successfully reduced the burning rate of wood flour composites filled with nanoclay up to 18% in comparison with the composites without nanoclay.[15]

The main aim of this study has been to investigate the influence of the amounts of nanoclay and poplar wood flour in wood flour polypropylene composites on their properties, such as notched impact, hardness, thermal stability and flammability behavior, as well as morphology.

EXPERIMENTAL

Materials

Polymer

The polymer matrix polypropylene (PP) with the trade name V30S was supplied by Arak Petrochemical Company in Iran, and had a density of 0.952 g/cm^3 and melt flow index (MFI) (190 ºC/2.16 Kg) of 18 g/10 min.

Natural flour

Poplar wood flour was purchased from Aria Cellulose Company, Tehran, Iran. It was oven dried at 103±2 °C for 24 h. Particles that passed through a 40 mesh (400 µm) screen and were retained on a 60 mesh (250 µm) screen were selected.

Coupling agent

Polypropylene modified with maleic anhydride (MAPP) with a density of 0.965 g/cm^3 (MFI of 7 g/10 min, 1 wt% maleic anhydride) was used as the coupling agent. It was obtained from Solvay Company, Belgium.

Nanoclay

A commercial nanoclay product (Cloisite-30B), with a density of 1.98 g/cm^3 was ordered from Southern Clay, Inc. (Texas, USA). It was used at three different levels: 0%, 2%, and 4%. Cloisite-30B is a natural montmorillonite clay modified with a quaternary ammonium salt, having a d-spacing of 18.5 Å and modifier concentration of 90 meq/100 g clay.

Methods

Mixing

The PP, oven dried poplar wood flour, nanoclay and MAPP were then weighed and mixed according to the formulations given in Table 1.

The materials were mixed in a co-rotating twin-screw extruder (Model T20, Germany), at the Iran Polymer and Petrochemical Research Institute. The rotation speed of the screw was set to 60 rpm. The temperatures of its barrel zone (1 through 5) were adjusted to 165, 170, 175, 180, and 185 °C, respectively. The mixed molten materials were transformed into granules in a granulator machine (WIESER, WGLS 200/200 model, Germany) after leaving the extruder. The resulting granules were dried at 105 °C for 24 h. The obtained granule particles were prepared using an injection molding machine at a temperature of 185 °C and pressure of 3 MPa in accordance with the ASTM D 3641-12 standard, to make test samples for impact and hardness tests, as well as TGA analyses.

To make the LOI samples, a mini test press from Toyoseiki Company (Japan) was utilized. These samples were produced at a temperature of 200 °C under 25 MPa for 4 min. To avoid the creation of bubbles inside the samples, deaeration was repeated several times. Using a puncher, the samples were separated to avoid the formation of cracks. The specimens were stored under controlled conditions (50% relative humidity and 23 °C) for at least 40 h prior to testing.

Table 1
Composition of the studied formulations

Sample label	Poplar wood flour (wt%)	PP content (wt%)	Nanoclay (wt%)	MAPP (wt%)
100%PP	0	100	0	0
40%WF 60%PP 2%M	40	60	0	2
40%WF 60% PP 2%M 2%NC	40	60	2	2
40%WF 60% PP 2%M 4%NC	40	60	4	2
50%WF 50% PP 2%M	50	50	0	2
50%WF 50% PP 2%M 2%NC	50	50	2	2
50%WF 50% PP 2%M 4%NC	50	50	4	2
60%WF 40% PP 2%M	60	40	0	2
60%WF 40% PP 2%M 2%NC	60	40	2	2
60%WF 40% PP 2%M 4%NC	60	40	4	2

PP: polypropylene; WF: poplar flour; M: MAPP; NC: nanoclay

Measurement of mechanical properties

The test specimens were examined according to the regulations of the ASTM D256-10 standard for the notched impact properties, and ASTM D2240-05 for the hardness test. The reported results come from the average of a minimum of five samples for each treatment.

Thermal analysis

TGA measurements were carried out using a thermal analyzer (PL-150, Agilent, USA) for 7 mg of test specimen in the range of 25 to 700 °C at the heating rate of 15 °C/min. This analysis was performed in nitrogen gas to avoid oxidation of the materials.

Limited oxygen index

LOI testing was performed using a Stanton Redcroft apparatus (model: S/N710, England). The LOI was derived according to the ASTM D2863-13 standard. ASTM D2863 is a method to determine the minimum concentration of oxygen in an oxygen/nitrogen mixture that will support a flaming burn in a testing specimen. The composites of standard size were subjected to burning tests, after preparing specimens of each composition with the dimensions of 15 mm length, 5 mm width, and 1.2 mm thickness. During the test, a certain volumetric concentration of specimen was ignited in a tube with a hydrogen flame on top of the sample by gradually varying the oxygen and nitrogen gas concentration at fixed rates.

Scanning electron microscope

The morphology of the composites was characterized using scanning electron microscopy (SEM, Model JXA-840, JEOL (Japan)) at 25-kV accelerating voltage.

X-ray diffraction

X-ray diffraction analysis was utilized to determine the index of connection and relative intercalation for the nanoclay particles. This analysis was done using a Philips XPert (Netherlands) apparatus. The experiment was performed with a Co lamp at the wavelength of 1.79 Co-Kα, step of 0.02°, speed of 0.3 °/s, and 2d angles of 1° to 9°. The samples were prepared in the form of 10×1×1 mm sheets, while the electrical settings of the power source were 30 mA and 40 kV.

Statistical analysis

The results of the notched impact and hardness tests were analyzed using a randomized statistical plan under a factorial test using statistical package for social science (SPSS) software (IBM Software, Armonk, New York; version 11.5). The post-hoc Duncan test was used at a 95% reliability level for comparison of the averages.

Table 2
Variance analysis results (F and Sig. values) of the nanocomposites made from poplar flour, polypropylene and nanoclay

Variable properties	Notched impact strength	Hardness
Poplar flour content	7.997*	0.6^{ns}
Nanoclay	1.140^{ns}	157.05*
Poplar flour content × nanoclay	0.791^{ns}	62.7*

*Significance level = 95%; ns = non-significant

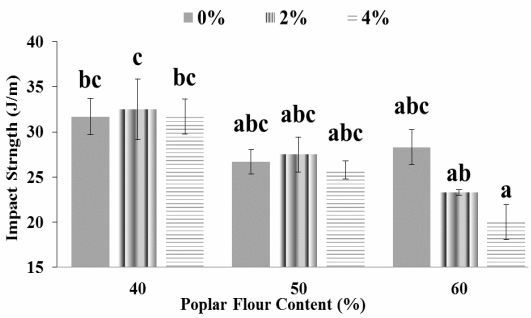

Figure 1: Effect of nanoclay and wood flour content on impact strength of wood flour/PP/nanoclay composites (small letters indicate the Duncan test averages at a 95% confidence interval)

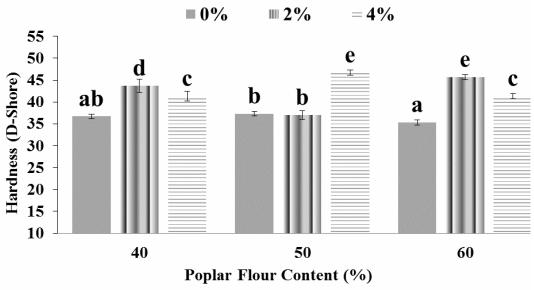

Figure 2: Effect of nanoclay and wood flour wood flour content on hardness of wood flour/PP/nanoclay composites (small letters indicate the Duncan test averages at a 95% confidence interval)

RESULTS AND DISCUSSION

Formulations with amounts of poplar wood flour at three different levels (40%, 50% and 60%) and nanoclay at three different levels (0%, 2% and 4%) were investigated in this study. The F values and Significance (Sig.) level values are listed in Table 2.

Mechanical properties

Figures 1 and 2 depict the effects of wood flour and nanoclay contents on mechanical properties of the nanocomposites.

Effect of wood flour content on notched impact strength

The notched impact strength of a material conveys its hardness and toughness, which indicates the strength of the material against failure.[16] Increasing the wood flour up to 60 wt% caused a reduction in the notched impact strength. The inconsistency between the wood flour and matrix was intensified by the further addition of wood flour, and the product became much weaker against the impact. In fact, the notched impact strength decreases because of the decreased ductility and greater brittleness of the samples.[8,17] Moreover, the addition of wood flour increases the agglomeration probability of the cellulose fibers and causes stress concentration, thus necessitating a smaller amount of energy to reach failure.[18-19] These results are consistent with the results of Wang, Yang *et al*., and Cui *et al*.[5,20-21]

Effect of wood flour content on hardness

Increasing the wood flour content from 40 to 60 wt% increased the hardness of the WPC, but not significantly. The presence of lignocellulose materials in the WPC will reduce toughness, so that the hardness of the WPC increases.[22]

Effect of nanoclay content on notched impact strength

Adding a further amount of the nanoclay reduced the notched impact strength of the composite, which is consistent with the results of Han *et al*., Lei *et al*. and Nozari *et al*.[23-25] The nanoclay particles create stress concentration areas and crack initiation points. Since the polymer chains became hard, their mobility was reduced. A higher amount of absorbed energy and the development of stressful points in the composite, besides the hardening matrix, led to the appearance of suitable sites for crack development.[23]

Effect of nanoclay content on hardness

Increasing the nanoclay content from 0 to 4 wt% increased the hardness of the WPC. The nanoclay particles have significant hardness and adding them to WPC led to improved hardness of the composites. Thus, the hardness of the whole composite can be increased by the addition of nanoclay.[10] The formation of exfoliation and of an intercalation structure due to the addition of nanoclay led to better distribution of these particles within the polymer matrix. This better distribution enhanced the hardness of the composites.[26]

Limited Oxygen Index

Table 3 illustrates the effect of wood flour content on LOI.

Effect of wood flour content on flammability behavior

Compared with the samples with lower wood content, the LOI of higher wood content samples was increased. These samples will no longer need

a great amount of oxygen for burning and also the burning process will take more time. These findings are in agreement with the results of Stark *et al*.[27] Usually, some porosities form in composite materials during their production. These porosities are interconnected in a network. Oxygen can pass through these voids and add to the flammability. The porosity of a composite will decrease as the weight percent of fiber is increased. This reduction of porosity inhibits the movement of oxygen through the matrix.[10]

Effect of nanoclay content on flammability behavior

Increasing the nanoclay content led to a higher LOI. In other words, a larger amount of nanoclay will require more oxygen to burn, and, in fact, the flammability of the sample is reduced by increasing the nanoclay content (Table 3). The nanoclay can act as a barrier to prevent penetration and movement of the oxygen into the nanocomposite structure, and against the penetration of gases to fill the voids.[10] The most important factor for achieving higher thermal stability by the addition of nanoclay is the formation of a coal-like layer. The higher specific surface area and proper coating by nanoclay at this inflammable layer made the structure more thermally stable.[10] The use of nanoclays has been reported to improve thermal properties and reduce flammability.[28-29]

Scanning Electron Microscopy (SEM)

SEM micrographs of the composites made with 50 wt% wood flour and 0, 2 and 4 wt% nanoclay are shown in Figures 3 to 5, respectively. It is obvious that increasing the nanoclay content decreased the porosity of the composites. In fact, the nanoclay filled the pores in the composites and, consequently, their thermal stability and ignition potential reduced. Furthermore, nanoclay prevented the escaping of volatile gases from the pores to the surface of the composites. Thus, the oxygen index of the composites increased.

Table3
Effect of composition on LOI of wood flour/nanoclay composites

Sample labelling	LOI (%)
100%PP	17.3
40%WF 60%PP 2%M	17.8
40%WF 60%PP 2%M 2%NC	18.1
40%WF 60%PP 2%M 4%NC	18.2
50%WF 50%PP 2%M	19.5
50%WF 50%PP 2%M 2%NC	19.6
50%WF 50%PP 2%M 4%NC	19.9
60%WF 40%PP 2%M	19.9
60%WF 40%PP 2%M 2%NC	20
60%WF 40%PP 2%M 4%NC	20.2

PP: polypropylene; WF: poplar flour; M: MAPP; NC: nanoclay

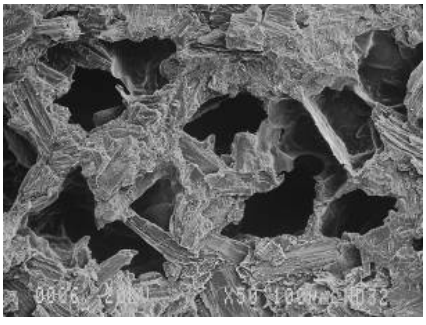

Figure 3: SEM micrograph of the composite with 0 wt% nanoclay

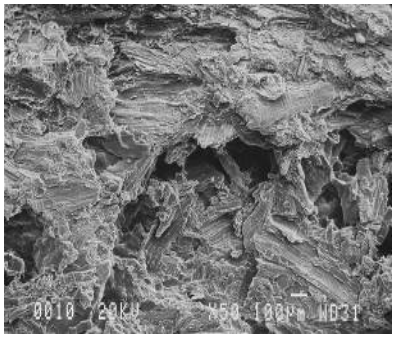

Figure 4: SEM micrograph of the composite with 2 wt% nanoclay

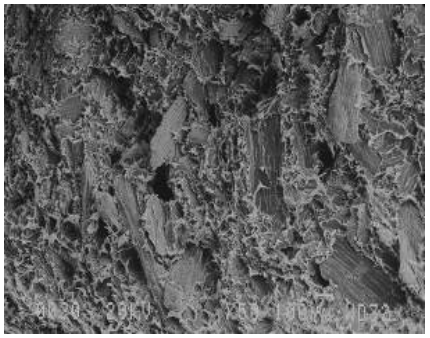

Figure 5: SEM micrograph of the composite with 4 wt% nanoclay

Table 4
Thermal analysis values of the polymer and wood polymer nanocomposites

Sample	T_i	T_m [a]	T_m [b]	Temperature of decomposition (T_D) in ºC at different weight loss (%)				RW% at 650 ºC
				20%	40%	60%	80%	
100% PP	388	480	498	461	470	478	485	0.6
50%WF 50%PP 2%M	302	485	518	385	469	482	494	9.4
50%WF 50%PP 2%M 2%NC	300	486	520	350	465	482	496	11.2
40%WF 60%PP 2%M 4%NC	299	487	521	362	469	485	498	11.6

[a] T_m value for the first stage; [b] T_m value for the second stage

Thermal Gravimetric Analysis (TGA)

The initial degradation temperature (T_i), the maximum pyrolysis temperature, decomposition temperature at different weight loss (TD) and the remaining weight (RW) of the wood-polymer nanocomposites are shown in Table 4. Due to the inherent heat stability properties of nanoclay, the temperature of the second stage of decomposition was increased.

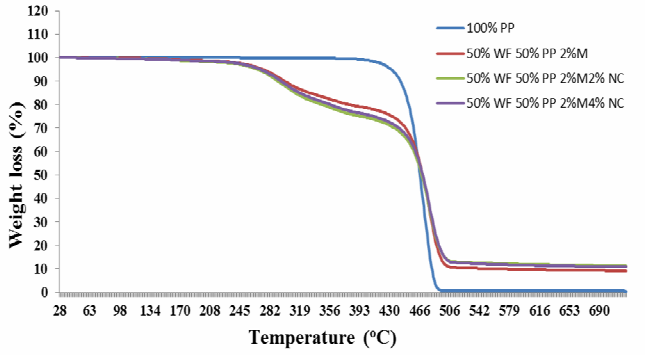

Figure 6: Thermal analysis of nanoclay and polypropylene samples

The results of TGA showed that the thermal stability of the samples was increased by adding nanoclays and the nanocomposites were decomposed at higher temperatures with weight losses (Table 4).

Meanwhile, the amount of residual ash also increased (Fig. 6), which is consistent with the results of Zhu *et al.* and Gilman *et al.*[29-30] Possibly, the release of compounds that are used for modifying nanoclays led to this increment. The greater amount of ash is also due to the presence of mineral compounds in the nanoclay. The layered silicate structure acts as a super insulator and slows down the release of the

volatile materials produced during the burning of the polymer.[14] This structure decreased the accessibility of volatile materials needed for burning.[14]

Structural analysis by XRD

Increasing the nanoclay content from 0 to 4 wt% in the composition with 40% wood flour reduced the 2θ angle. The peak XRD of pure nanoclay is at the angle of 2θ=5.53° and the layer distance of 18.5° (Fig. 7). Increasing the nanoclay up to 2 wt% shifted the XRD peak to 2θ=2.09° and the layer distance to 49.07 Å. At the same time, increasing the nanoclay up to maximum 4 wt% shifted the XRD peak forward and the distance between the silicate layers decreased (d = 47.7 Å and 2θ = 2.15°).

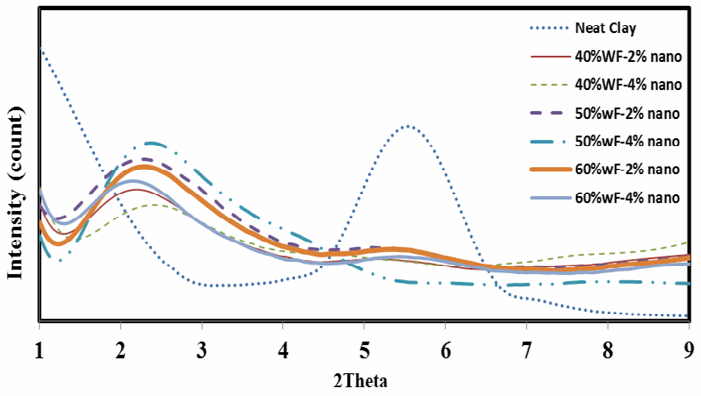

Figure 7: XRD patterns of nanocomposites made from 40%, 50% and 60% wood flour with 2% and 4% nanoclay

In the formulation containing 50% wood flour, increasing the nanoclay up to 2 wt% shifted the XRD peak toward smaller angles (d = 44.4 Å and 2θ = 2.31°).

In the formulation with 60% wood flour, increasing the nanoclay up to 2 wt% shifted the XRD peak toward smaller angles (d = 45.58 Å and 2θ = 2.25°). Increasing the nanoclay content up to 4 wt% moved the XRD peak backward and increased the distance between the silicate layers (d = 48.61 Å and 2θ = 2.11°). As observed, the morphological structure is of the intercalation type. In the intercalation structure, some peaks are evident in the patterns that are related to the crystalline region of the nanoclay that was not completely removed and just moved toward angles smaller than 2θ or larger than 2θ.[31] In other words, in the intercalation structure, the distance between the silicate layers of nanoclay increased or decreased as a result of the penetration of the polymer chains, but without complete disintegration of the clay layers. Therefore, the intercalation structure of the nanocomposite may contribute to better distribution of the nanoclay in the polypropylene structure.[32] The results of this section of research are found to be in agreement with the results of Danesh *et al*. and Samariha *et al.*[2,33]

CONCLUSION

The present research work has allowed drawing a number of conclusions, as detailed below.

- The addition of wood flour from 40 to 60 wt% determined an improvement of the hardness of the composites by 0.5%, while the notched impact strength decreased as much as 32.2%.
- Increasing the nanoclay content from 0 to 4 wt% led to improving the hardness of the composites by 18.3%, while the notched impact strength decreased as much as 11.5%.
- The addition of nanoclay and wood flour determined an increase of the limited oxygen index by 1.9 and 11.1, respectively.
- Composite pores and voids were decreased by adding nanoclay, which contributed to increasing the oxygen index.
- Increasing the nanoclay amount contributed to a higher amount of remaining ash and higher thermal stability.
- XRD analysis revealed the formation of an intercalation structure, which indicated proper

distribution of the nanoclay particles in the polymer matrix.

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