Thermal, Flammability, and Morphological Properties of Nano-composite from Fir Wood Flour and Polypropylene

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The thermal, flammability, and morphological properties were investigated for a nano-composite made from fir wood flour and polypropylene. Polypropylene (PP), fir wood flour, maleic anhydride polypropylene (MAPP), and nanosilica at 5 different concentrations (0, 2, 4, 6, and 8 phc), were mixed using an extruder, and samples were made using a hand-press. Then, the hardness and the thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), limited oxygen index (LOI), X-ray diffraction (XRD), and scanning electron microscopy (SEM) results were studied. The results showed that increasing the nanosilica content up to 8 phc increased the hardness. Also, when the nanosilica content was increased to 8 phc, the thermal stability increased and more charcoal was retained. Increasing the nanosilica content increased the crystallization. The limited oxygen index increased. Studying the x-ray diffraction spectrum showed that the width and peak intensity decreased with the increased intake of silica nanoparticles. Scanning electron microscopy images showed that an increased concentration of nanosilica meant better connections and a more uniform bond was established between the fibers and the matrix.

Keywords: Fir wood flour; Nanosilica; Differential scanning calorimetry; Thermogravimetric analysis; Hardness

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INTRODUCTION

Wood plastic composite (WPC) is a relatively new material made from a combination of thermoplastic polymer and wood flour or wood fibers as filler and small amounts of additives (Samariha *et al.* 2015). Wood plastic composites are marketed on the basis of their low maintenance and environmental credential (lifespan and no toxic chemicals). Due to their good properties, WPC's are being used in construction industries and residential productions such as exterior decking, railing systems, roofing, and siding.

Polypropylene, $(C_3H_6)_n$ (PP) is a well-known thermoplastic. PP, as a polyolefin, is used in a variety of applications. It has low density and demonstrates excellent stress resistance and good dimensional stability. PP is increasingly being recycled using conventional equipment (Danesh *et al.* 2012).

Many problems in the field of polymer composites have been recently solved by nano science and nanotechnology (Tjong 2006). Nanotechnology can be used to improve the properties of polymer composites. Mineral nanoparticles having spherical or plate structures are scattered in polymeric matrices in nanocomposites (Njuguna *et al*. 2008; Soon *et al*. 2012). Silica nanoparticles can improve the properties of polymer composites due to their spherical and porous structure, high surface area, and their mineral nature (Xanthos 2010). In fact, because nanosilica can increase the mechanical strength and thermal properties of composites and polymer composites, nanosilica nanoparticles have many applications in the polymer composites industry (Wu *et al*. 2005). Currently, the usage of nanosilica is a topic of interest due to its hardness, tensile and flexural modulus, high strength, cheapness, chemical inertness, heat resistance, and environmentally friendly properties (De Dios and Diaz-Garcia 2010). The main characteristics of such nanoparticles are as follows: small particle size, specific gravity, porous structure, surface silanol groups, and polarity dependence on the construction method (Quercia *et al.* 2012). Compared with composites, nanosilica polymer composites have different mechanical and physical properties such as tensile and flexural modulus and higher strength (Du *et al*. 2012). Researchers believe that silica nanoparticles can improve the resistance, hardness, tensile and flexural modulus, crystallinity, and melt viscosity of polypropylene (PP) (Guyard *et al*. 2006).

There has been a lot of research on the use of silica particles in combination with different polymers (Chung *et al*. 2002; Zhang *et al*. 2003; Xu *et al.* 2008; Zhang *et al.* 2008). Researchers have found that silica particles improved the strength, hardness, tensile and flexural modulus, crystallinity, viscosity, creep resistance, and adhesion within the structure of polyethylene, polypropylene, and thermoplastic elastomers due to the surface properties of silica nanoparticles (Zhang *et al*. 2003; Rong *et al*. 2004; Guyard *et al*. 2006; Parvinzadeh *et al*. 2010). Ismaeilimoghadam *et al*. (2015) studied the effects of silica particles on the properties of PP/wood flour nanocomposites. The results showed that the mechanical properties improved as the content of nanosilica particles increased to 3%, but worsened as the nanoparticles were further increased to 5%. The results of the morphology, as observed using a scanning electron microscope, showed a good distribution of silica nanoparticles when using 3% nanosilica particles, whereas there was less accumulation of silica particles when using 5% nanosilica particles. Deka and Maji (2012) studied the effects of clay and silica nanoparticles on the properties of wood polymer composites, and their results showed that the thermal properties of nanoparticles were improved with increased nanoparticles up to 3%, whereas the addition of increased nanoparticles up to 5% was linked to worsened properties.

The morphology and thermal properties of nanocomposites, with polyethylene terephthalate containing three types of nanosilica as filler, were also examined by some researchers. The results showed that after the addition of silica nanoparticles into the composite, the modulus and tensile strengths of composites increased while the elongation to break point was reduced by the addition of silica nanoparticles. The results from differential scanning calorimetry (DSC) also showed that the silica nanoparticles function as a nucleating agent that acts on the growth of crystals, leading to increased crystallinity and heat-resistant composites (Parvinzadeh *et al*. 2010). The limited oxygen index (LOI) is an accurate and simple method for determining fire self-extinguishment and it is widely used. The index is a parameter to evaluate the combustibility and fire retardancy of polymers. This number is the minimum amount of required oxygen for burning with a stable flame in a mixture of oxygen and nitrogen gases. The aim of this study was to investigate the thermal, flammability, and morphological properties of a nano-composite made from fir wood flour polypropylene.

EXPERIMENTAL

Materials

Polymer

The thermoplastic polypropylene (PP) as a matrix with the trade name V30S was provided by Arak Petrochemical Company (Arak, Iran). Its melt flow index (MFI) was 18 g/10 min at 190 ºC. The density and molecular weight of PP were 0.952 g/cm^3, 225552 g/mol respectively.

Natural fiber

Fir (*Picea abies*) wood flour, supplied by Kian Wood Company (Gorgan, Iran.) was used as filler. It was oven dried for 24 h at 103 °C ± 2 °C and then screened. The wood flour passed through the 40-mesh sieve and retained on a 60-mesh sieve were used for composite fabrication.

Coupling agent

Maleic anhydride grafted polypropylene (MAPP, 1 wt. % maleic anhydride) from the Krangin Company, Karaj, Iran. was used as a coupling agent. The density, average molecular weight and melt flow index (MFI) of MAPP were 0.965 g/cm^3, 40000 g/mol and 7g/10 min, respectively.

Nanosilica

A commercial nanosilica product (Degussa) with a density of 2.4 g/cm^3 was ordered from Evonik Industrials, Inc. (Essen, Germany). It was used at five different concentration levels: 0, 2, 4, 6, and 8 phc. The properties of the materials used, including nanosilica, are summarized in Table 1.

Table 1. Specifications of the Nanosilica

Silicon Oxide		SiO_2
Purity		99+ %
Average Particle Size (APS) (nm)		11 to 13
Specific Surface Area (SSA)		200 m^2/g
Bulk Density		< 0.10 g/cm^3
Color		White
Moisture		< 2%
Weight Loss on Ignition		30%
Certificate of Analysis	SiO_2	< 99%
	Ti	< 120 ppm
	Ca	< 70 ppm
	Na	< 50 ppm
	Fe	< 20 ppm
*Note: According to the producer information		

Methods

Mixing

The oven-dried fir wood flour as a filler, MAPP and as a coupling agent, and poly propylene and nanosilica were weighted and bagged. The complete formulation and abbreviation of blends are given in Table 2.

Table 2. Composition of the Studied Formulations

Sample Code	Fir Wood Flour (wt.%)	PP Content (wt.%)	NS (phc*)	MAPP (phc)
PP 100	0	100	0	0
50% WF 50% PP 2%M	50	50	0	2
50% WF 50% PP 2% M 2% NS	50	50	2	2
50% WF 50% PP 2% M 4% NS	50	50	4	2
50% WF 50% PP 2% M 6% NS	50	50	6	2
50% WF 50% PP 2% M 8% NS	50	50	8	2

PP: Polypropylene; WF: Fir wood flour; M: MAPP; and NS: Nanosilica
(*) phc: parts per hundred compounds.

Compounding of materials was carried out in a co-rotating twin screw extruder (Model TSE20, Brabender Co., Germany) at the Iran Polymer and Petrochemical Research Institute (PPRI). The screw rotation speed was 60 rpm. The temperature of the extruder barrel were 165 °C, 170 °C, 175 °C, 180 °C, and 185 °C for zones 1 to 5, respectively. A granulator machine (WIESER, WGLS 200/200 model, Hamburg, Germany) was used to transform mixed molten material leaving extruder into the granules.

Then the granules were dried for 24 h at 105 °C. The differential scanning calorimetry (DSC), limiting oxygen index (LOI) and thermogravimetric analysis (TGA) samples were produced at 200 °C under 25 MPa for 4 min using a mini test press from Toyoseiki Company (Tokyo, Japan). To avoid the crack formation and bubble creation inside samples, the samples were separated using a puncher and de-aeration was repeated several times. Before each test the samples were stored under controlled conditions (50% relative humidity and 23 °C) for at least 40 h.

Measurement of hardness

The hardness of samples were determined according to ASTM D2240-05 (2010).

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were conducted with PL-150, Agilent thermal analyzer (Santa Clara, USA.). Test specimens of 7 mg were analyzed at the heating range of 15 °C/min from 25 °C to 700 °C in the nitrogen atmosphere to avoid oxidation of samples.

Differential scanning calorimetry (DSC)

DSC was carried out using DSC131 (SETARAM Co., Caluire, France) instrument with heating rate of 10 °C/min. The heating range scanned was from 25 °C to 200 °C, followed by cooling from 200 °C to 25 °C. The sample weight was 8 mg approximately. For further analysis of the results, the data obtained from the first stage cooling and second heating were used. The crystallinity (X_c) of the composite was calculated using the following equation,

$$X_c = \frac{\Delta H_m}{\Delta H^{\circ}_{m} . w} \times 100 \tag{1}$$

where ΔH_m, ΔH°_m, and w are the enthalpy of fusion of the system, the enthalpy of fusion of perfectly (100%) crystalline PP, and the percent of polymer in specimen, respectively. For ΔH°_m (PP), a value of 190 J/g was used for 100% crystalline PP

Limited oxygen index

Limited oxygen index (LOI) measurement were carried out using a FTA flammability unit, (Stanton Redcroft S/N710, Epsom, England) according to the ASTM D-2863-13 (2013) standard. In this method the minimum concentration of oxygen in an oxygen/nitrogen mixture required to support a flaming burn of test specimens were recorded. Sample dimensions were of 15 mm long, 50 mm wide, and 2 mm thick. During the test, a certain volumetric concentration of the specimen was ignited in a tube by holding a hydrogen flame on top of the sample and gradually varying the oxygen and nitrogen gas concentration at fixed rates.

X-ray diffraction

To determine the index of connection and relative intercalation for the nanosilica particles, an x-ray diffraction (XRD) analysis was applied. A Philips XPert (PANalytical Co., Eindhoven, Netherlands) apparatus was used in this research. The experiment was performed with a Co lamp at the wavelength of 1.79 Co-Kα, a step of 0.02°, speed of 0.3 °/s, and at 2θ angles of 20° to 80°. The samples were prepared in the form of 10 × 10 × 4 mm (length x width x thickness), while the electrical settings of the power source were 30 mA and 40 kV.

Morphological analysis using scanning electron microscopy

The morphology of the composites was characterized using a scanning electron microscope (SEM, Model AIS2100, Seron Technology, Gyeonggi-do, Korea) set at a 0.5 kV to 30 kV accelerating voltage. The composite samples were frozen and fractured in liquid nitrogen to ensure that microstructure of samples remained clean and undamaged and then coated with a gold layer to provide a conductive surface.

Statistical analysis

The results of the hardness tests were analyzed using a randomized statistical plan under a factorial test using the 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.

RESULTS AND DISCUSSION

Thermal Analysis

Table 3 shows the following parameters for the polymer nano-composite plastic timber: the initial degradation temperature (Ti), the maximum pyrolysis temperature (T_m), the temperature of degradation in various percentages of weight loss (T_D), and the remaining weight (RW%). The production of some composites required the mixture of fibers and the polymer matrix in high temperatures. Therefore, the thermal degradation of lignocellulose material could cause undesirable impacts on the composite's features.

The effect of the nanosilica percentage on the weight loss percentage of the polypropylene/wood flour composite has been indicated in Fig. 1 at a 50% level during the heating time (from 30 °C to 700 °C).

Initially, an initial weight loss was observed at 150 °C, which was the result of a gradual evaporation of absorbed moisture by natural compounds; this was not highlighted in the figure because of its intangible amount. As shown in Fig. 1, the temperature degradation curve of the nano-composite and composite were divided into two stages. The first stage was related to the analysis of wooden fibers and the second stages were related to the polymer analysis. The first stage, which contained the range of approximately 150 °C to 400 °C, was related to wood fibers; in fact, when the composites were faced with heat, initially the hemicelluloses, cellulose, and a bit of lignin were degraded, and the composites lost weight. Usually, cellulose and hemicellulose degrade in the range of 150 °C to 500 °C; in fact, hemicellulose degrades at 150 °C to 350 °C, cellulose degrades at 275 °C to 350 °C, and lignin degrades at 250 °C to 500 °C (Lee and Wang 2006; Han *et al*. 2008). Therefore, the addition of lignocellulose compounds to polymer composites decreased thermal stability.

The initial degradation that continued until 400 °C was related to the degradation of fir wood flour. At the first stage of degradation, it was notable that the weight loss percentage or thermal degradation coincided with the increased silica percentage. This finding demonstrated the positive influence of silica on the improvement of composites' thermal stability.

At more than 400 °C, the second stage of degradation began, which mostly was related to the matrix analysis. At this stage, the distances between graphs increased relatively, because the analysis of silica composites occurred at higher temperatures. In fact, after thermal analysis, nanosilica had created a char layer and reduced the procedure of oxidation degradation; therefore, the weight loss procedure reduced. Moreover, it could be expected that the process of the creation of char layer had quickened as a result of the increased amount of nanosilica in the composites; this phenomenon led to the reduction of ignition and weight loss. In fact, the addition of nanosilica increased thermal stability. The rate of composites weight loss has been indicated in Fig. 2 by derivative thermogravimetric (DTG) curves. As shown, the rate of composites' weight loss at the first stage (from 200 °C to 350 °C), which was due to the degradation of fir wood flour, had an intangible difference with the nanosilica composites. However, from 350 °C to 500 °C, which mostly was related to the matrix analysis, the pace of the weight loss of composites was considerably higher than the nanosilica composites. This result showed that the silica nanoparticles had a positive effect on the race of composites' thermal decomposition, especially the polymer matrix.

Deka and Maji (2010) observed that the thermal stability of the polymer compounds increased after an increase in the amounts of wood flour and the coupling agent. The initial degradation temperature increased after an addition of silica and clay nanoparticles. A higher diffusivity coefficient of nanosilica particles improved thermal dispersion in the composites and this could postpone surface ignition and the diffusion of volatile flammable particles across composites. The addition of a silicate increased the thermal stability of polymethyl methacrylate (PMMA) (Hu *et al*. 2004).

Table 3 indicates the effect of the wood flour and nanosilica content on the limited oxygen index. The limited oxygen index increased with an increased amount of wood flour compared to pure polypropylene; thus, the sample needed more oxygen for ignition. The limited oxygen index of wood-plastic composites in the samples without nanosilica was lower than that of the samples with 8 phc nanosilica.

Table 3. Thermal Analysis and Limiting Oxygen Index (LOI) Values of Polymer Blend and Wood Polymer Nano-composite

Sample	T_i (°C)	$T_m{}^a$ (°C)	$T_m{}^b$ (°C)	Temperature of Decomposition (T_D) in °C at Different Weight Loss (%) Values				RW% at 600 °C	Limiting Oxygen Index (%)
				20%	40%	60%	80%		
PP 100	387	480	498	461	470	478	485	0.6	17.5
50% WF 50% PP 2% M	318	391	511	347	432	463	478	9.7	19.1
50% WF 50% PP 2% M 2% NS	314	391	512	349	428	465	482	11.4	19.3
40% WF 60% PP 2% M 4% NS	315	390	514	346	425	466	484	12.7	19.5
40% WF 60% PP 2% M 6% NS	314	391	514	351	444	470	485	13.4	19.6
50% WF 50% PP 2% M 8% NS	310	393	515	351	442	473	489	15.8	19.7

[a] T_m value for first step.
[b] T_m value for second step.

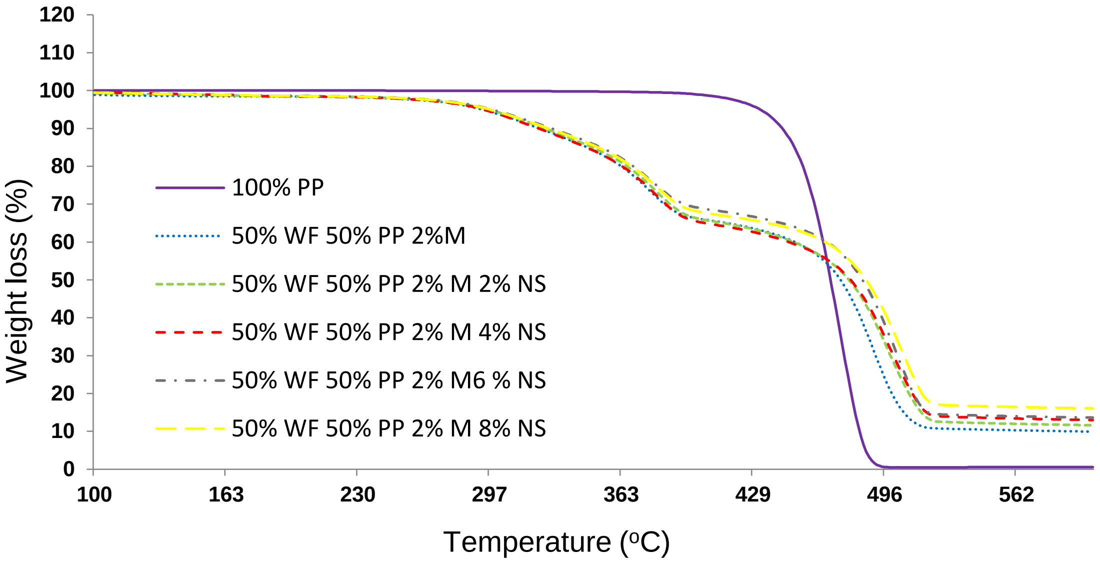


Fig. 1. TGA curves of the composites with 50 wt.% WF and 0, 2, 4, 6, and 8 phc nanosilica

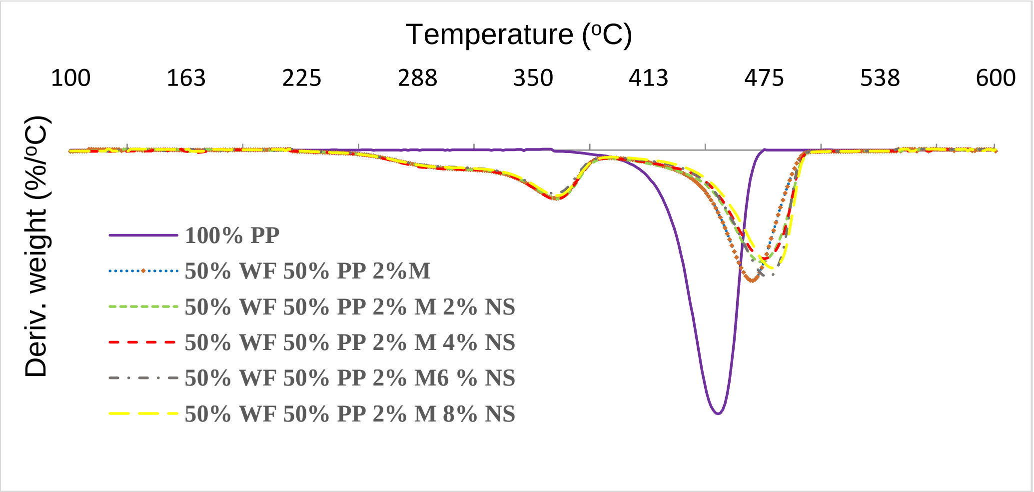


Fig. 2. DTG curves of the composites with 50 wt.% WF and 0, 2, 4, 6, and 8 phc nanosilica

Limited Oxygen Index

Table 3 demonstrates the effects of the wood flour and nanosilica content on the limited oxygen index. The limited oxygen index increased with increased wood flour content compared to pure polypropylene, such that the sample needed more oxygen for ignition. The LOI of the wood-plastic composite in the samples without nanosilica was lower than that of the sample with 8 phc nanosilica.

When a material had a higher index, it needed more oxygen for flaming and ignition. The higher index showed greater resistance to fire and higher thermal tolerance in the considered material.

It was observed that the limited oxygen index increased with increased. Higher levels of LOI may have been the result of carbonaceous-silica char on the surface. The higher silica levels meant more char formation. The char created tiny black trails of smoke that had a flame, such as a candle flame.

The silica nanoparticles created a labyrinth path that prevented the entrance of oxygen and postponed the burning capacity of the compound. Guo *et al*. (2007) observed that the flame deterrence of the wood-polymer composites increased during the increase of nano clay content. The addition of modified silica to cetyl trimethyl ammonium bromide (CTAB) increased the interaction between the wood, clay, and polymer through hydroxyl and cetyl groups. Silica nanoparticles also formed a thermal barrier against oxygen and improved the property of flame deterrence. Erdem *et al*. (2009) also reported the improvement of flame postponement under the effect of the addition of nanosilica. In addition, an enhancement of nanosilica particles could occupy part of the voids and reduce pores; therefore, the accessibility of oxygen for ignition would be more difficult.

Effect of Nanosilica Content on Hardness

Table 4 depicts the effects of wood flour and nanosilica contents on the nano-composite hardness. Increasing the nanosilica content from 0 phc to 8 phc increased the hardness of the WPC. The nanosilica particles had remarkable hardness and adding them to the WPC led to an improvement in the hardness of the composites. Thus, the hardness of the whole composite could be increased by the addition of nanosilica (Khosravian 2010). The formation of exfoliation and intercalation structures due to the addition of nanosilica led to a better distribution of these particles within the polymer matrix. This better distribution enhanced the hardness of the composites (Wang *et al*. 2006).

Table 4. Thermal Properties of Polypropylene, Wood Flour, and Nanosilica Composites

Sample	Hardness (Shore D)	T_m (ºC)	ΔH_m (J/g)	T_c (ºC)	ΔH_c (J/g)	X_c (%)
PP 100	66^{a}	168.99	62.03	114.02	81.04	32.65
50% WF 50% PP 2% M	70.9^{b}	167.93	22.57	118.72	42.72	24.2
50% WF 50% PP 2% M 2% NS	72.7^{c}	166.06	30.14	120.05	42.21	32.99
40% WF 60% PP 2% M 4% NS	73.5^{cd}	165.4	28.78	123.20	36.77	32.11
40% WF 60% PP 2% M 6% NS	74.6^{e}	167.44	32.55	123.1	41.98	37
50% WF 50% PP 2% M 8% NS	76.8^{f}	167.52	27.76	124.59	37.01	32.15
(small letters indicate the Duncan ranking of the averages at a 95% confidence interval.)						

DSC Analysis

The results of the impact of the nanosilica percentage on the melting temperature (*Tm*), crystallization temperature (*Tc*), melting enthalpy (ΔHm), crystallization enthalpy (ΔHc), and crystallization percentage have been indicated in Table 4 at a 50% level.

As shown in Table 4, the highest crystallization percentage (37%) was observed for the samples that contained 6 phc nanosilica and the lowest percentage (24.2%) was obtained in the case of the samples without nanosilica. Therefore, the higher the nanosilica percentage in the composites, the higher the crystallization percentage; this confirmed the positive role of nanosilica in the enhancement of crystallized nuclear that followed with the increased crystallization percentage (Wu *et al*. 2005).

Moreover, the addition of nanosilica increased the crystallization temperature, which confirmed that in the presence of nanosilica, crystals formed sooner. This phenomenon played a role in the enhancement of the capability of creating crystallized nuclear and the stimulation of crystal creation within the polymer matrix .

An increase of nanosilica and lignocellulose material in the polymer matrix, molecular movement, and crystals growth were postponed; therefore, the melting enthalpy was reduced in comparison with the pure polymer. In addition, a reduction in the melting temperature was observable with the addition of nanosilica particles.

In the studies of Qiu *et al*. (2006) and Hosseinaei *et al*. (2012), the role of lignocellulose fibers in the enhancement of the crystallization degree was mentioned. When melted polymer is in the vicinity of the outer surface, with the capability of creating crystallized nuclear at the surface, crystals grow in the radial direction from the surface and create the crystallized layer around the fiber (Qiu *et al*. 2006; Hosseinaei *et al*. 2012).

Cellulose fibers and their surface acted as a nucleating agent that promoted crystallization. When in contact with the semi-crystallized polymer they could create more highly crystalline layers. Various studies have been conducted about how these layers are created and their effects on the composites' properties (Qiu *et al*. 2006). The amount of these layers is related to different factors, such as the fiber percentage, chemical compounds, and parasitology of the fiber surface (Hosseinaei *et al*. 2012).

X-ray Diffraction

Figure 3 shows the pattern of intensity and the diffraction angle, 2θ, for nanosilica powders and for nanocomposites that contained 2, 4, 6, and 8 phc silica nanoparticles. Figure 3 shows the diffraction peak of the amorphous silica nanoparticles ($2\theta = 25.33^{\circ}$). In nanocomposites that contained different percentages of nanosilica, the intensity of the crystallinity decreased (Fig. 3). It was also revealed that the severity of the other crystalline peaks decreased. The reduction in the intensity of the crystalline peaks improved the amorphous section of the composite, which consisted of amorphous nanoparticles and wood flour. Figure 3 shows that the width and intensity of the peak decreased with an increased use of silica nanoparticles. This indicated that the agglomeration phenomenon of the silica particles was impacted by the use of higher percentages of nanoparticles. This could have been attributed to the formation of hydrogen bonds, because the silica particles on which these bonds depended increased the distance between the layers. Deka and Maji (2012) investigated the effect of nanosilica on the properties of wood flour and a polymer composite, and their results showed that the intensity of the peak decreased when the amount of silica increased. This showed that the silica nanoparticles were injected into the plastic timber.

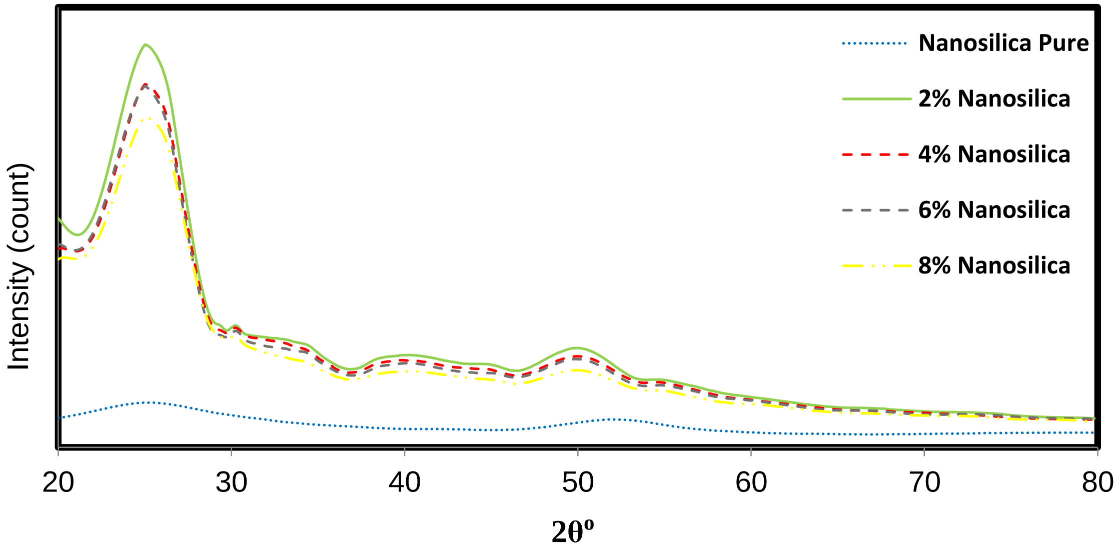
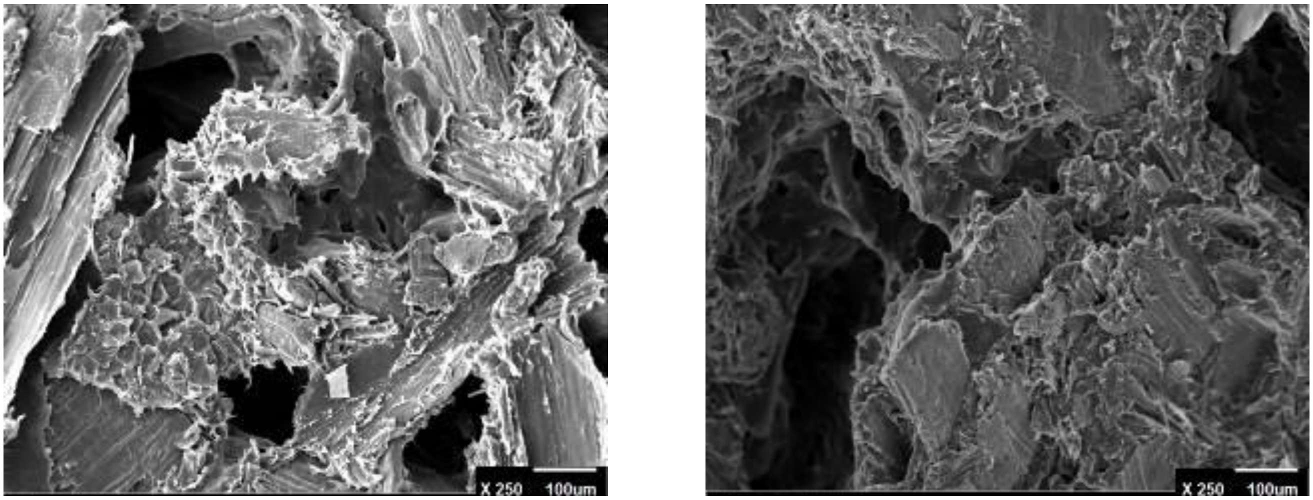


Fig. 3. X-ray spectrum of nanocomposites (50% wood flour, 2, 4, 6, and 8 phc nanosillica and pure silica nanoparticles)

SEM Morphology

Figure 4 shows the fracture of surfaces in the samples of nanocomposites containing 50% wood flour in five levels of 0, 2, 4, 6, and 8 phc silica nanoparticles. Blank spaces indicated the weak connection between the meal and the matrix. The compatibility increased when the nanosilica increased, and there was improved connection and bonding, and better and more uniform adhesion between the fibers and the matrix. The increase in the oxygen index in the samples confirmed this matter. Nanosilica increased the oxygen index and prevented the exiting of the volatile and igneous gases through the composite pores from the interior to the surface (Burnside and Giannelis 1995). The nanosilica filled these cavities and prevented oxygen from moving into the nano-composite structure, thus acting as a barrier against the diffusion of gases.



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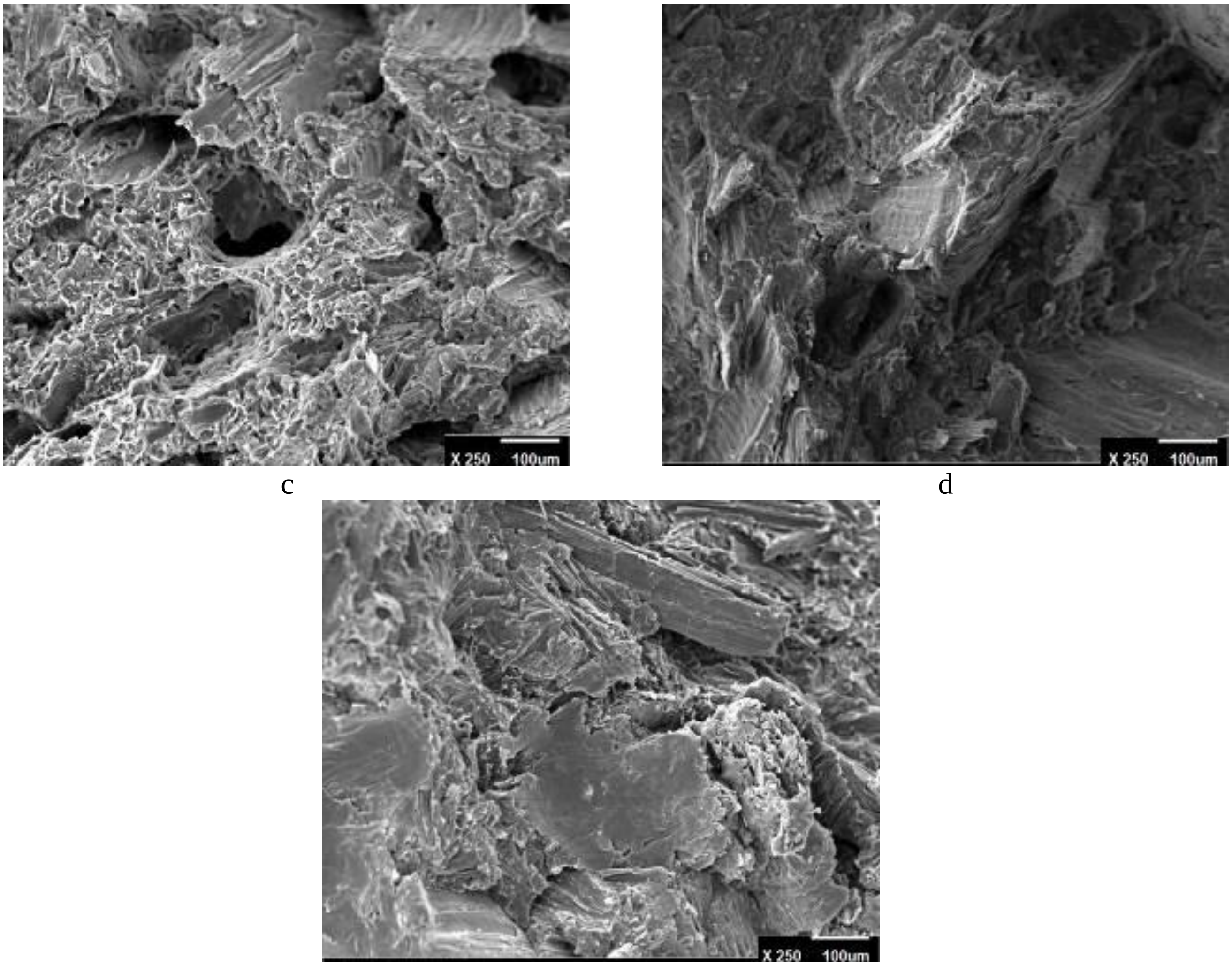

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Fig. 4. SEM image of sample containing 50% wood flour; a) 0 phc, b) 2 phc, c) 4 phc, d) 6 phc, and e) 8 phc nanosilica

CONCLUSIONS

This study investigated the thermal, flammability, and morphological properties of nano-composite made from fir wood flour polypropylene. The results were as follows:

1. By increasing the nanosilica to 8 phc, the thermal stability, charcoal residue, and LOI increased.

2. By increasing the nanosilica to 8 phc, the hardness increased.

3. The crystallization increased when the nanosilica content increased.

4. The width and intensity of the X-ray diffraction spectrum peak decreased when an increased amount of nanosilica was used.

5. Observations of the scanning electron microscopy images showed that increased nanosilica increased the compatibility, which led to more connections, more bonding, and better uniform adhesion between the fibers and matrix.

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