

EFFECT OF WOOD FLOUR AND NANO-CaCO₃ CONTENT ON THE PROPERTIES OF NANO-CaCO₃/WOOD FLOUR/POLYPROPYLENE INJECTION MOLDED COMPOSITES

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This study evaluated the effect of wood flour and nano-CaCO₃ contents on some properties of nano-CaCO₃/wood flour/polypropylene injection molded composites. The poplar flour content was set at three different levels: 30%, 40% and 50%, the maleic anhydride polypropylene (MAPP) content was constant at 2%, and the nano-calcium carbonate content was set at four different levels: 0%, 1.5%, 3.0% and 4.5%. The materials were mixed in a co-rotating twin-screw extruder. Test samples were made by injection molding. The physical and mechanical properties were studied using X-ray diffraction and scanning electron microscopy. The results showed that the notched impact strength decreased, while the tensile and flexural strength, tensile and flexural moduli, hardness, water absorption and thickness swelling increased when the wood flour content increased from 30 to 50% and the nano-calcium carbonate level was 4.5% after 24 h. The X-ray diffraction spectra showed that an intercalation structure was created in the composite. The scanning electron microscopy images showed that the bonding surface between the matrix and the filler material increased with increasing nano-calcium carbonate and wood flour contents, resulting in stronger connections within the matrixes.

Keywords: composites, wood flour, polypropylene, nano-calcium carbonate, injection molding, tensile strength, tensile modulus, hardness

INTRODUCTION

A composite refers to a material that is made of one or more discontinuous phases inside a continuous phase. The continuous phase is a background material or matrix, while the discontinuous phase is a harder and stronger reinforcement of the continuous phase.¹ The reinforcement phase improves the mechanical properties of the composite, and the matrix phase transfers the power to the reinforcement phase and increases the resistance to chemical agents and heat treatment. In general, natural fibers are appropriate for reinforcing plastics (*e.g.*, thermoset and thermoplastic). Biomass fibers are lightweight, non-abrasive, non-hazardous, abundant and inexpensive.² Plastic materials have experienced increased popularity in recent

decades. They invaded our daily lives both in a wide range of common household goods and in technical use through high performance applications. Thermoplastics are the most widely used, in particular polyolefin, such as polypropylene (PP).³ Polypropylene possesses favorable characteristics with regard to hardness, chemical resistance, thermal and mechanical properties, impermeability and food safety. In addition, polypropylene has been applied in high temperature processing. Due to its properties, polypropylene has many advantages as a polymer in various industries, such as industrial packaging, car manufacturing, as well as in the agricultural and pharmaceutical sectors. It is a good alternative to acrylonitrile butadiene styrene

(ABS), polyvinyl chloride and polystyrene.⁴ The mechanical properties and performance of a composite are increased by the enhanced interface between the matrix and the reinforcement in a smaller reinforcement phase.⁵ The field of natural fiber/fabric, wood, and agro-based waste materials is now rapidly growing both in terms of industrial applications and fundamental research as their usage is diversified.⁶

Chen *et al.* investigated the effect of temperature on the mechanical and surface properties of calcium carbonate-filled bamboo fibers and polypropylene composites and discovered that the treatments improved the compatibility between fibers and the polypropylene matrix. Consequently, the tensile strength and modulus of the composites were increased.⁷

Nano-powder is a collection of particles (spherical in diameter and aspherical in length, width and height) with each diameter in the 1 to 100 nm range.⁸ Calcite is one of the oldest natural powders, and precipitated calcium carbonate was produced for the first time over 100 years ago.⁹ Its low price, high availability, lightness, ease of coating and production, as well as high load-bearing capacity, are the factors that have led to the widespread application of this reinforcement material.¹⁰ Previous studies on the mechanical properties of nano-composites with polypropylene/inorganic materials showed an increase in tensile strength and modulus as the amount of nano-particles increased.¹¹⁻¹² Likewise, adding calcium carbonate nano-particles can reduce the mechanical properties of polypropylene, such as Young's modulus.¹³⁻¹⁴ This study investigated the effect of calcium carbonate on the nano-mechanical and morphological properties of nano-composites made from poplar flour and recycled polypropylene.

EXPERIMENTAL

Materials

Poplar (*Populus*) flour (for reinforcement), with dimensions of 200 μm , was obtained from Arya Cellulose Co. (Tehran, Iran). The poplar flour was dried (0%) in an oven for 24 h at 100 ± 3 °C.

Polypropylene (PP) (polymer matrix), with V30S trade name, was supplied by Arak Petrochemical Company (Arak, Iran). It had a density of 0.952 g/cm³ and a melt flow index (MFI) (190 °C/2.16 kg) of 18 g/10 min. PP was recovered twice, using a twin-screw

extruder at a temperature of 180 °C and speed of 100 rpm.

Polypropylene grafted with maleic anhydride (coupling agent), with MDL number MFCD00212584, was provided by Priex Co. (Aldrich, Germany), with a density of 0.65 g/cm³, melt flow index of 64 g/10 min and a grafted anhydride concentration of 1%.

Nano-calcium carbonate obtained from Neutrino Co. (Tehran, Iran) had a particle size of 80 nm and purity of 99%.

Methods

Material mixture

The polymer matrix (PP), poplar flour, coupling agent (MAPP) and nano-calcium carbonate were mixed together in various ratios (Table 1).

The compounds were mixed using a two-screw, co-rotating extruder (Model T20, Germany). The extruding thermal zones were 165, 170, 175 and 180 °C for 1 to 4 allocated areas, respectively. The rotational speed of the spiral was set at 60 rpm. After the extrusion, the mixed melt materials were converted into granules using a granulator machine (WIESER, WGLS 200/200 model, Germany). To avoid any negative effects of moisture, the granular particles were dried at 85 °C for 24 h. The obtained granule particles were prepared by injection molding at 170 °C with a speed of 60 rpm and a pressure of 100 MPa, in accordance with ASTM D3641 (2012)¹⁵ standard for impact, flexural, tensile and hardness testing. After formation of the samples, the following tests were conducted: tensile strength and modulus testing (dumbbell-shaped samples); flexural strength and modulus testing (simple-shaped samples); notched impact strength testing; and hardness and physical property analysis, *i.e.*, water absorption and thickness swelling after 7 weeks. The specimens were then placed in distilled water and kept at room temperature. The previously mentioned tests were run in accordance with ASTM D 638 (2010),¹⁶ ASTM D 790 (2010),¹⁷ ASTM D 256 (2010),¹⁸ ASTM D 2240 (2005)¹⁹ and ASTM D 7031 (2010)²⁰ testing standards. The results are presented as the mean of 5 samples per treatment level.

X-ray diffraction

X-ray diffraction (XRD) was performed on a 3003 PTS diffractometer (Seifert Co., Germany) to determine the connection and relative intercalation of nano-calcium carbonate particles. Radiation tests using a cobalt lamp were performed with a wavelength of 1.59, step of 0.02°, velocity of 0.3°/s, a 2 θ angle in the range of 10 to 40°, and an electric current of 30 mA and 40 kV. The samples were formed into laminar shapes of 10 × 10 × 4 mm (length x width x thickness). The tensile strength specimens were used for X-ray diffraction tests.

Scanning electron microscopy

The morphology of the composites was characterized using a scanning electron microscope (Model 440i, Leo Oxford, England) at a 25 kV accelerating voltage. The samples were initially frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact. Ten layers of gold provided electrical conductivity. Notched impact strength specimens were used for SEM tests.

Statistical analysis

The statistical analysis was performed using the analysis of variance (ANOVA) model for completely randomized designs (SPSS software, IBM software, Armonk, New York, version 11.5), and the means were separated using Duncan's multiple range tests when the overall ANOVA model was significant. Significance was accepted at $P < 0.05$.

Table 1
Weight percentage of various components in wood plastic composites

Poplar flour (%)	PP (%)	MAPP (%)	Nano-calcium carbonate (%)
30	70	2	0
30	70	2	1.5
30	70	2	3
30	70	2	4.5
40	60	2	0
40	60	2	1.5
40	60	2	3
40	60	2	4.5
50	50	2	0
50	50	2	1.5
50	50	2	3
50	50	2	4.5

Table 2
Analysis of variance results for poplar flour/recycled polypropylene/nano-calcium carbonate nano-composite

Properties	Poplar flour content	Nano-calcium carbonate	Wood flour content * nano-calcium carbonate
Tensile strength	27.355*	5.423*	0.512
Tensile modulus	24.365*	0.185	0.038
Flexural strength	42.679*	3.944*	0.603
Flexural modulus	209.487*	31.994*	2.207
Impact strength	1222.367*	0.024	0.002
Hardness	34.995*	11.841*	0.780
Water absorption	92.142*	7.017*	5.452*
Thickness swelling	6.874*	0.906	0.338

*significance was accepted at 95% significant level; Values represent the mean of 5 samples

RESULTS AND DISCUSSION

In this study, the amount of poplar flour was divided into three treatment levels (30%, 40% and 50%), and the nano-calcium carbonate was used in four concentrations (0%, 1.5%, 3.0% and 4.5%). The F -value and significance are shown in Table 2. The effect of poplar flour on the physical and mechanical properties of the composite was significant at the 95% confidence level.

The effect of nano-calcium carbonate on the tensile and flexural strength, flexural modulus, hardness and water absorption was significant at

the 95% confidence level, while the flexural modulus, notched impact strength and thickness swelling were not significant. The interaction between nano-calcium carbonate and poplar flour on the strength properties of the nano-composite was significant at the 95% confidence level, with the exception of water absorption. Samples 1 through 8 showed positive effects of the addition of poplar flour and nano-calcium carbonate on the mechanical and physical properties of the nano-composite.

Effect of poplar flour on nano-composite properties

Tensile and flexural strength

The tensile and flexural strength increased with increasing concentration of poplar flour (from 30 to 50%; Figs. 1 and 3). The mechanical strength of the composite is strongly dependent on the quality of the interface between the two phases; thus, transferring tension from the matrix to the reinforcement phase is done by the interface region. Because of the tension in the matrix phase, the filling material and the reinforcement are required to transfer the power to the second phase, reinforcing the matrix. Therefore, the allowable stress on the composite was increased by increasing the content of reinforcement.²¹ Consequently, the tensile and flexural strength increased with increasing wood flour concentration. These results are in accordance with the results reported by other researchers.²²⁻²³ The shear load transfer between the matrix and the filler particles was created during the tensile stress; thus, the interface between the filler particles and the matrix should be able to properly perform the transfer.²⁴

Tensile and flexural moduli

The results showed that the flexural and tensile moduli increased with increasing concentration of poplar flour (from 30 to 50%; Figs. 2 and 4). Because a direct relationship exists between the elasticity modulus and the components' modulus, an increase in the content of lignocellulosic material will result in a higher elasticity modulus.²⁵⁻²⁷ Cellulosic material creates a higher tensile modulus;²⁸ thus, the tensile modulus will increase as a result of the increasing wood flour

content. In fact, one of the main reasons of adding lignocellulosic material to plastic is to increase the tensile modulus and the reinforcing capabilities. The results were in accordance with Yang *et al.*²³

Notched impact strength

The notched impact strength expresses the stiffness and toughness of a composite, and it also refers to the strength against breakage.²⁹ The notched impact strength was reduced by the addition of wood flour (up to 50%; Fig. 5). The presence of lignocellulosic material increased the absorption energy of the composite, and the additional reinforcement created areas in the polymer matrix that were predisposed to tension-related failure and cracking.³⁰ The notched impact strength decreased with increasing poplar flour concentration because of the lack of compatibility between the fibers and the matrix. Consequently, a reduction in the impact strength alludes to vulnerability and brittleness.^{27,31} These results were in accordance with the results of Cui *et al.*, Wang, and Yang *et al.*^{22,32,23}

Hardness

Adding cellulosic filler to the matrix causes the polymer chain mobility to decline and increases the hardness of the composite.³³ The hardness value of the composite increased with increasing wood flour concentration (from 30 to 50%; Fig. 6). Previous research has also found that adding lignocellulosic material to the matrix reduces polymer toughness and increases the hardness of composites.³⁴

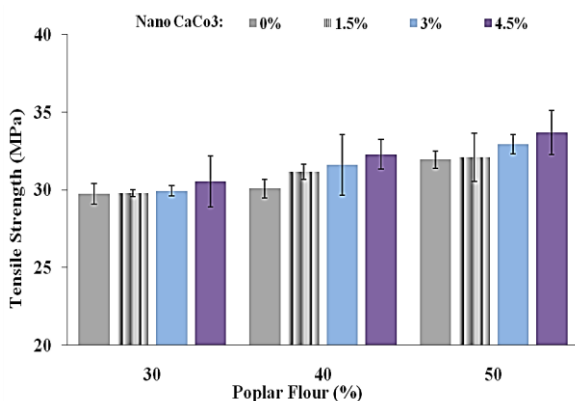


Figure 1: Effect of poplar flour concentration on the tensile strength of poplar flour/recycled polypropylene/nano-calcium carbonate composites

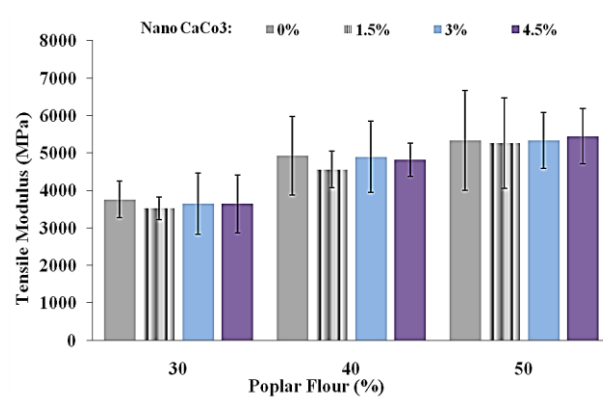


Figure 2: Effect of poplar flour concentration on the tensile modulus of poplar flour/recycled polypropylene/nano-calcium carbonate composites

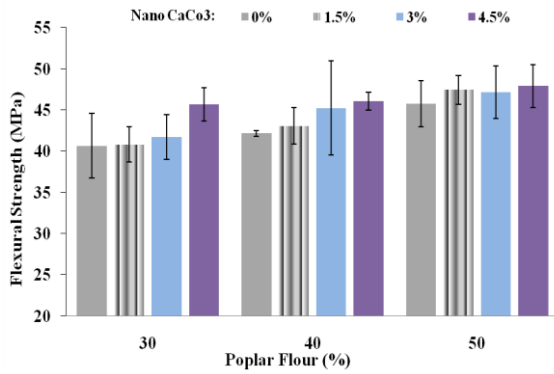


Figure 3: Effect of poplar flour concentration on the flexural strength of poplar flour/recycled polypropylene/nano-calcium carbonate composites

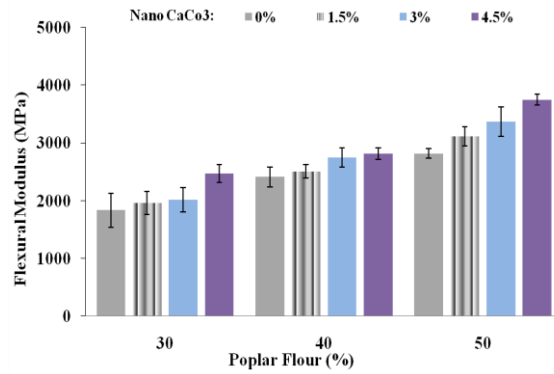


Figure 4: Effect of poplar flour concentration on the flexural modulus of poplar flour/recycled polypropylene/nano-calcium carbonate composites

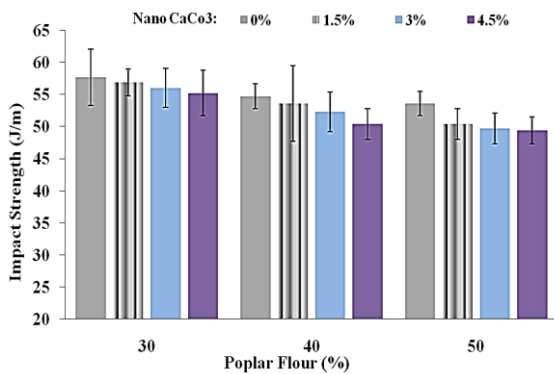


Figure 5: Effect of poplar flour concentration on the notched impact strength of poplar flour/recycled polypropylene/nano-calcium carbonate composites

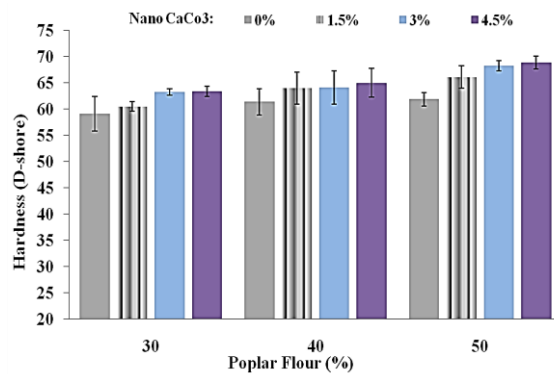


Figure 6: Effect of poplar flour concentration on the hardness of poplar flour/recycled polypropylene/nano-calcium carbonate composites

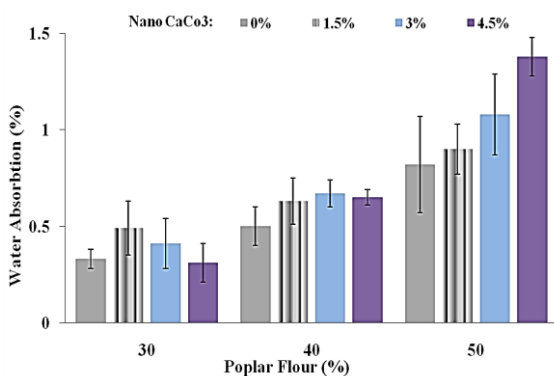


Figure 7: Effect of poplar flour concentration on the water absorption of poplar flour/recycled polypropylene/nano-calcium carbonate composites

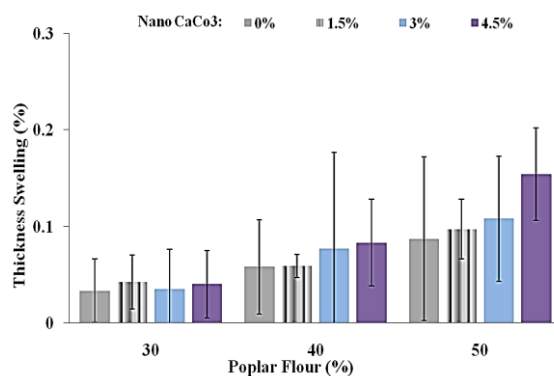


Figure 8: Effect of poplar flour concentration on the thickness swelling of poplar flour/recycled polypropylene/nano-calcium carbonate composites

Water absorption and thickness swelling

In this study, water absorption and thickness swelling of the composite increased with increasing amounts of wood flour (from 30 to 50%; Figs. 7 and 8). In fact, the amount of free hydroxyl group-linked hybrid molecules increased the water absorption and thickness swelling as a result of the lignocellulosic material content. Because of the nature of the hygroscopic lignocellulosic material, water absorption is enhanced in wood-based plastics. Thus, the water absorption and thickness swelling of the wood-plastic composites increased with increasing wood flour (hydrophilic material) to plastic (hydrophobic material) concentration. The water absorption and movement of water molecules between filler molecules was enhanced by the increase in filler content. The results were in accordance with those reported in other studies.³⁵⁻³⁶

Effect of nano-calcium carbonate on nano-composite properties***Tensile and flexural strength***

Tensile and flexural strength of the composites increased with increasing nano-calcium carbonate concentration (Figs. 1 and 3). The nano-calcium carbonate particles exhibited a tendency for filling the mesoporous area and cracks on the surface of the fibers, reducing the empty spaces on the surface of the wood-plastic composite.³⁷ The flexural strength increased upon adding nano-calcium carbonate, and it created strong surface adhesion with the polymer.³⁸ In addition, the nano-calcium carbonate created strong chemical bonds and multiple hydrogen bonds, which increased the resistance of the material by reducing the hydrophilic nature of the fiber. The nano-particles of calcium carbonate, along with the hydrogen and covalent bonds, improve the performance of the interface through reactions with hydroxyl groups at the interface between the fibers and polypropylene. An increasing strength of the interface can effectively transfer the tensile stress from the matrix to the reinforcement phase. Therefore, the flexural and tensile strength increased upon the addition of calcium carbonate nano-particles.

Tensile and flexural moduli

The effect of nano-particle concentration on the mechanical properties of the polymer nano-composites depends on factors, such as the size,

shape, form, appearance, crystallization, quantity and quality of the distribution of nano-particles, and the way they connect with the polymer.³⁹ Because of the high number of influencing factors related to the nano-particles, the flexural and tensile moduli increased with the use of 4.5% nano-calcium carbonate and the interface between the two phases also increased (Figs. 2 and 4). The strength property increased with increasing nano-calcium carbonate concentration. Clay nano-particles have been also reported to increase the interface between the two phases of reinforcement.⁴⁰

Notched impact strength

The notched impact strength declined as the concentration of nano-calcium carbonate increased (Fig. 5). The addition of nano-particles to the composites leads to the following effects: the creation of tension in the polymer matrix, the creation of starting points for failure and cracks, hardening of the polymer chains, reduction in the mobility of chains, and increased absorption energy of the composite.⁴¹

Hardness

The hardness of the nano-composite increased with increasing concentration of nano-calcium carbonate (Fig. 6). Because considerable stiffness was achieved by addition of the nano-calcium carbonate, the hardness of the composite increased when the amount of nano-particles increased.³³

Water absorption and thickness swelling

The hydrophilic property of nano-calcium carbonate on the water absorption and thickness swelling were studied. It was found that the water absorption and thickness swelling of the nano-composite increased with increasing nano-particle concentration (Figs. 7 and 8).

X-ray diffraction

The 2θ peak angle increased when the composites were prepared with 50% poplar flour and 4.5% nano-calcium carbonate (Fig. 9). The XRD peak of pure calcium carbonate nano-particles was created at the angle of $2\theta = 29.5^\circ$, and the distance between the layers was 18.5 Å. In the case of the composite, the XRD peak was transferred to a larger angle and the distance between the layers was 49.07 Å, with increasing calcium carbonate nano-particle concentration.

The morphological study revealed the intercalation structure of the composite. The peaks for this type of arrangement were visible in the spectra. These points are related to the crystalline area of the calcium carbonate nano-particles, which were not totally eliminated, and their peaks only shifted to lower and higher 2θ .⁴² In other words, the distance between the silicate layers of the calcium carbonate nano-particles

decreased or increased upon penetration into the polymer chain in the intercalation structure; however, a perfect fragmentation has not occurred. Therefore, one of the most important conditions to fulfill in order to create a nano-composite interlayer is to ensure better dispersion of nano-calcium carbonate into the polypropylene structure.⁴³ These results were in accordance with those reported in other research.⁴⁴⁻⁴⁵

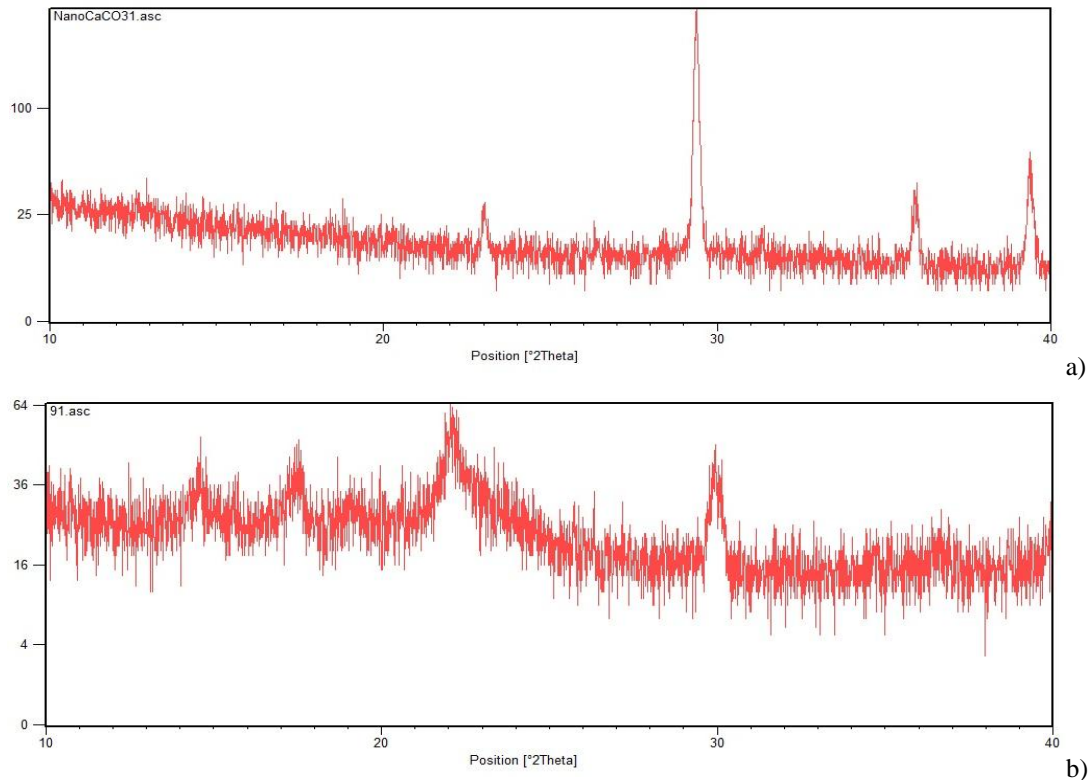


Figure 9: X-ray diffraction patterns of (a) neat nano-calcium carbonate and (b) nano-composites made from 50% poplar flour and 4.5% nano-calcium carbonate

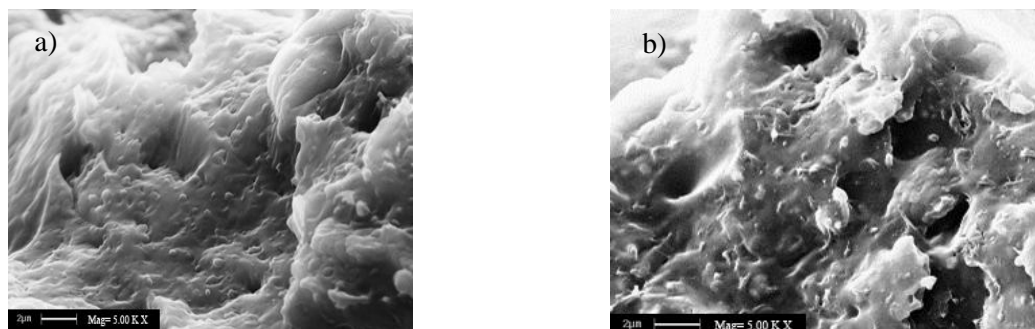


Figure 10: Scanning electron micrographs of the fracture surface of samples: (a) the composite with 50% poplar flour, and (b) the composite with 50% poplar flour and 4.5% nano-calcium carbonate

Scanning electron microscopy

Figure 10 shows the fracture surface of different samples. Figure 10a exhibits the samples containing 50% poplar flour, while Figure 10b –

those comprising 50% poplar flour and 4.5% nano-particles of calcium carbonate. The calcium carbonate nano-particles partially filled the pores of the composite. The distribution of nano-

particles was almost uniform in terms of size and quantity. Many nano-calcium carbonate fillers are distributed in the polymer matrix due to the appropriate connection through the resin network. This connection limits the movement of the polymer chains and changes the polymer structure. Because of the low distance among the nano-particles, this creates a sturdy network between the polymer and the filler. Additionally, aggregation of nano-particles and the formation of pores in the matrix were observed in some areas. The results are in agreement with others reported in earlier research.^{37,46}

CONCLUSION

1. By increasing the amount of poplar flour from 30 to 50%, the notched impact strength decreased, while the tensile and flexural strength, tensile and flexural moduli, hardness, water absorption and thickness swelling increased.
2. By increasing the amount of nano-calcium carbonate to 4.5%, the notched impact strength decreased, while the tensile and flexural strength, tensile and flexural moduli, hardness and water absorption increased.
3. X-ray diffraction analysis indicated that an intercalation structure was created, and there was also an appropriate distribution of nano-calcium carbonate in the polymer matrix.
4. Scanning electron microscopy images revealed that the commissure of the material was strengthened by increasing nano-calcium carbonate and poplar flour concentrations. In addition, stronger connections were created between the matrix and the filler.
5. The optimal content of wood flour and nano-calcium carbonate was found to be 50% and 3%, respectively, which allowed obtaining composites with optimal properties.

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