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Effects of nano-clay particles and oxidized polypropylene polymers on improvement of the practical properties of wood-polypropylene composite

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In this article, effects of nano-clay particles and compatibilization effect of the molten phase oxidized polypropylene were studied on the composites produced by wood fibers, polypropylene polymer, and nano-clay particles. To produce samples, wood fibers, and polypropylene polymer were mixed in an extruder in presence of 0, 2, and 4% nano-clay particles and 3% oxidized polypropylene (OPP), and then these samples were hot pressed in specific dimensions. Then the mechanical and physical properties, such as flexural strength, tensile strength, impact strength, and water absorption values were evaluated according to the ASTM Standards. The results showed that increment in amount of nano-clay particles and also, the usage of oxidized polypropylene, improved mechanical and physical properties of the composites. However, the impact strength and water absorption values were reduced. Also, X-ray diffraction analysis and electron microscopes images showed that the distribution of nano-clay particles in the matrix of polymer has intercalation structure.

Keywords: wood-plastic composite; nano-clay particles; physical and mechanical properties; oxidized polypropylene

1. Introduction

From a long time ago, human has combined different materials to obtain a new product with better properties. One of these products is the wood-plastic composite. This product results from a combination of a portion of synthesized polymer (Thermoplastic) and a portion of natural polymer (wood and cellulose fibers).[1] After a relative increment in the global cost of plastics, and legislation of new bioenvironmental laws, usage of inorganic materials as a filler in composites faced a lot of restrictions. Thus, the researchers are using other materials, such as wood flour,[2] cellulose fibers, and other lignocellulose materials [3] to produce these types of composites. Despite the interesting attributes of this type of fillers, the incompatibility between natural filler (polar) and thermoplastic polymer (none-polar) is the greatest defect of these materials. In general, the common structure and attributes between the filler and the polymer interface play an important role in the definition of physical and mechanical attributes of the produced composite. Lots of efforts to improve the compatibility between

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polymer and natural fillers, and thus improving the strength of the commissure between them have been done which these materials often call as compatibilizer or coupling agent. Compatibilizers are chemical factors that make the connection between polymers and natural fibers by using mechanisms, such as covalent bonds, mechanical involvements, secondary interactions, and creating Hydrogen bonds.[4] The main application and role of compatibilizers is to improve the compatibilization and develop the bonding between cellulose and plastic materials.

Despite of the considerable developments in the compatibility between polymer and natural fillers, finding new materials which can create more compatibility with low cost between wood and plastic is a main goal of the researchers and wood-plastic industries. Oxidization of the polymers is one of the methods that can be used to adapt polymers with natural fillers which can be done through different ways. Oxidation forms polar groups on polymer surface resulting on the modification of the chemical and mechanical attributes of the polymers, such as surface polarity, gravity, and stickiness.[5,6] Lu et al. [7] used oxidized polyethylene(OPE) as a coupling agent in wood fiber high-density polyethylene composite and concluded that maleated polyethylene (MAPE) coupling agents is more effective in improving interfacial adhesion in comparison to OPE coupling agent. Recently, application of oxidized polypropylene as a compatibilizer was studied in wood flour-polypropylene composites. The results showed that usage of oxidized polypropylene has a better function than maleic anhydride grafted polypropylene (MAPP) in increasing the mechanical attributes, decreasing water absorption, and redrawing thickness.[8]

One of the mostly used nano-particles to improve the attributes of composites, is clay nano-particles in very low amounts(4–5%) which causes to improve the physical, mechanical and thermal attributes, inflammability, and insulation in wood-plastic composites due to their special dimensions and high slenderness ratio. Han et al. [9] analyzed the effect of using nano-clay and the compatibilizer material on the mechanical and thermal attributes of the composites produced by bamboo fibers high-density polyethylene. Results of their studies showed that addition of 1% nano-clay, results in the increment of the bending elasticity module, dynamic elasticity module, and crystality degree of samples, while the impact strength was decreased. Wu et al. [10] understood that by adding just 2% of nano-clay to pine flour high-density polyethylene composite, bending strength raises from 19.6 to 24% and tensile strength raises from 11.8 to 13%.

With the above description, it is recognizable that selection and utilization of the various compatibilizers and reinforcements (like nano-particles) are highly effective on resultant mechanical properties of wood-plastic composites. Although researches in this subject are increasingly growing, their findings are not enough to achieve inexpensive wood-plastic composites with highly improved properties and more researches are necessary in this way. Low costs of clay nano-particles and oxidization processes of polypropylene polymer and also separately proven positive effects of their addition to wood-plastic composites conducted this study to evaluate effects of their simultaneous addition on the resultant mechanical properties of the composite.

2. Materials and methods

2.1. Materials

Wood fibers were obtained as a mixture of forest species form the starter section of Khazar MDF Co (Mazandaran, Iran). Wood fibers were dried in an oven for 24 h at 100 ± 2 °C. The polypropylene polymer (PP) was provided with grade SI060 from

Tabriz petrochemistry Co (East Azarbaijan, Iran), and a melt flow index (MFI) 6 g/10 min ($T = 190$ °C, load = 2.164 kg). nano-clay particles used in this study were on the bases of montmorillonite DK (trade mark) which were obtained from Asia Technology Pioneers Co (Tehran, Iran) with specifications mentioned in Table 1. Also 1-Dodecanol alcohol as a catalyst was obtained from Afshar Co (Tehran, Iran).

2.2. Methods and instrumentation

2.2.1. Oxidation of polypropylene in the molten phase

Due to the less expense and environmental pollution, method of oxidation in the molten phase in the presence of air oxygen was used to produce oxidized polypropylene.[4] In this method, polypropylene and 1-Dodecanol alcohol were mixed in an Internal Mixer (Brabender) under the temperature range of 180–220 °C with the speed of 60 rpm for 2 h. Then the air oxygen was used for oxidation of this material. The achieved material after oxidation is brittle and white cream.

2.2.2. Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction

In order to verify formation of polar groups in oxidized polymer, polypropylene and oxidized polypropylene were hot pressed into polypropylene films which were cooled under pressure and then, FTIR spectra of these films were recorded using Nicolet FTIR-10 equipment in the region of 400–5000 cm^{-1}.

In this investigation, x-rays diffraction was done by XRD device with Co kα lamp radiation, $\lambda = 1/78{,}897$ A°, gum 0.02° s^{-1}, rate 1° per minute, and diffraction angle (2θ) in the range of 1–12°. The samples were prepared for this exam in laminated forms with the dimensions of $10 \times 10 \times 1$ mm^3. In addition, the XRD device used in this study was X′ Pert MPD of Philips company, Netherlands.

2.2.3. Material mixing process and sample preparation

First, materials (polypropylene, wood fibers, oxidized polypropylene, and nano-clay particles) were weighed for each formulation according to Table 2. Then, the materials were mixed in Brabender Plasticorder (Duisburg, Germany) with the speed of 50 rpm and at a temperature of 190 °C. Each mixing took about 6 min.

After the mixing process, materials were crushed by a laboratory mill and were pressed into plates with a nominal thickness of 2 mm and dimensions of 15×15 cm^2 using a laboratory hydraulic hot press at temperature of 190 °C and pressure of 10 bars for 8 min. The plates were conditioned for at least two weeks at 20 ± 2 °C and 60 ± 5% RH. Then according to planned experiments and considered standards, these plates were cut to prepare experimental samples.

Table 1. Physical and chemical characterization of nano-clay particles.

Bulk density	0.45 g/cm^3
Humidity	1%<
Average dimensions of the layers	25–100 nm
Density	1.8 g/cm^3
Color	White light-milky white

Table 2. Composition of evaluated formulations (% weight).

Treatment code	Wood fiber (%)	Polypropylene (%)	Compatibilizer (%)	nano-clay (%)
WP	50	50	–	–
WP 4%	50	46	–	4
OPP2h 3%	50	47	3	–
OPP2h[a] 3%, 2% nano	50	45	3	2
OPP2h 3%, 4% nano	50	43	3	4

[a]OPP2h: oxidized polypropylene in the molten phase.

2.2.4. Measuring physical and mechanical attributes

Water absorption test was performed according to D7031-04 regulation of ASTM standard.[11] For weighing the samples, a digital scale was used with an accuracy of 0.001gr. Samples were drowned in distilled water until they reached the highest water absorption state, and then weighed. Water absorption values were calculated using Equation (1).

$$WA(t) = \frac{W(t) - W_0}{W_0} \times 100 \quad (1)$$

$WA(t)$, water absorption (%) at immersion time of t; W_0 oven dried weight (gr) of the samples before immersion; $W(t)$, weight of the samples (gr) at a given immersion time t.

The mechanical attributes of the composites were assessed through flexural, tensile, and impact properties. Flexural properties of composites were determined according to ASTM D7031–04 specifications [11] using GOTECH machine with calibration of 1000 N cells, while the crosshead speed was set to 5 mm/min. The tensile properties of composites were determined according to ASTM D638-03 specifications [12]. For measuring the Module of Elasticity (MOE), GOTECH machine with 1000 N cells' calibration was used, while the crosshead speed was set to 2 mm/min. Un-notched impact tests were also carried out according to ASTM D256–90 specification using a Santam Izod testing machine (Tehran, Iran). Each test was replicated six times and the mean value was used.

2.2.5. Transmission electron microscopy

Transmission electron microscopy (TEM) was used for better analysis of the achieved results, and also to study morphology of the composite and additionally the polymer and fillers interface, and finally to confirm XRD results of the device which was manufactured by Philips CM 10, Netherland.

3. Results and discussion

3.1. FTIR spectrum of the oxidized PP

FTIR spectra of raw and oxidized polypropylene are presented in Figure 1. According to this figure, during oxidation process categories of polar groups, such as ketones, carboxylic acids, and esteric groups are created on the polymer surface as literature confirms too.[4] In the spectrum b, which is related to oxidize PP, appeared peaks at 1164, 1700–1780, and 3470 cm^{-1} confirm the progress of the oxidation reaction. The

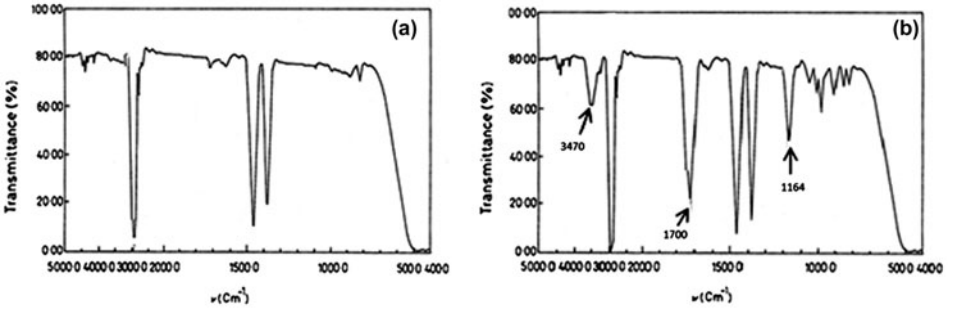

Figure 1. FTIR spectra of raw polypropylene (a) and oxidized polypropylene (b).

absorbance peak in 1700–1780 cm^{-1} is related to the stretching mode of carbonyl group, which exists in ketone, aldehyde, and anhydride groups, the peak at 3470 cm^{-1} is attributed to the stretching mode of OH groups in alcohols and the peak at 1164 cm^{-1} is related to the stretching of esteric groups.[13] So, interpretation of FTIR spectra concluded that the oxidation reaction proceeds through the formation of carbonyl and also alcohol functional groups.

3.2. Mechanical properties of samples

Figure 2 illustrates the flexural and tensile strength, and modulus of elasticity of the composites. Accordingly, it can be observed that the composites containing compatibilizer (OPP) exhibited higher flexural and tensile strength, and modulus of elasticity than composites without OPP. On the other hand, addition of nano-clay particles introduces better performances of the composites and increasing nano-clay particle amounts from 0 to 4%, results in the increment of these attributes considerably. In treatments that include compatibilizer and exclude nano-clay particles, increment in the elasticity modulus can be related to the improvement of cohesion power and coupling between wood fibers (polar phase) and polypropylene chains (non-polar phase) due to the presence of compatibilizer. Generally increment of modulus depends on the amount of bonding and coupling strength which is provided with the compatibilizer. In the samples containing compatibilizer and nano-clay particles, besides the influence of the compatibilizer on increasing the strength and modulus of elasticity of composites, furthermore, we can mention to the high slenderness ratio of nano-clay particles and the formation of intercalation structure in the composite. This characteristic of nano-particles strengthens the composite and increases the interface between the two phases. On the other hand, Silica of the nano-particles increases the compatibility between nano-particles and wood fibers and results in better bonds and subsequent improvements of the composite properties. So it can be concluded that oxidized polypropylene as a compatibilizer with nano-clay particles properly can improve Flexural and tensile properties of composites, can be confirmed by other literatures too.[11,14]

Impact strength of the composites is shown in Figure 2(e). Comparing the samples in this figure shows that application of compatibilizer caused a significant increment in the impact strength. In general, impact strength is defined as a measure for the composites ability against a sudden burst of powerful energy. The splits start from the points where the stress concentration is high, such as faulty areas or the points in which the connections between two phases are too weak. Application of compatibilizer reduces the tension

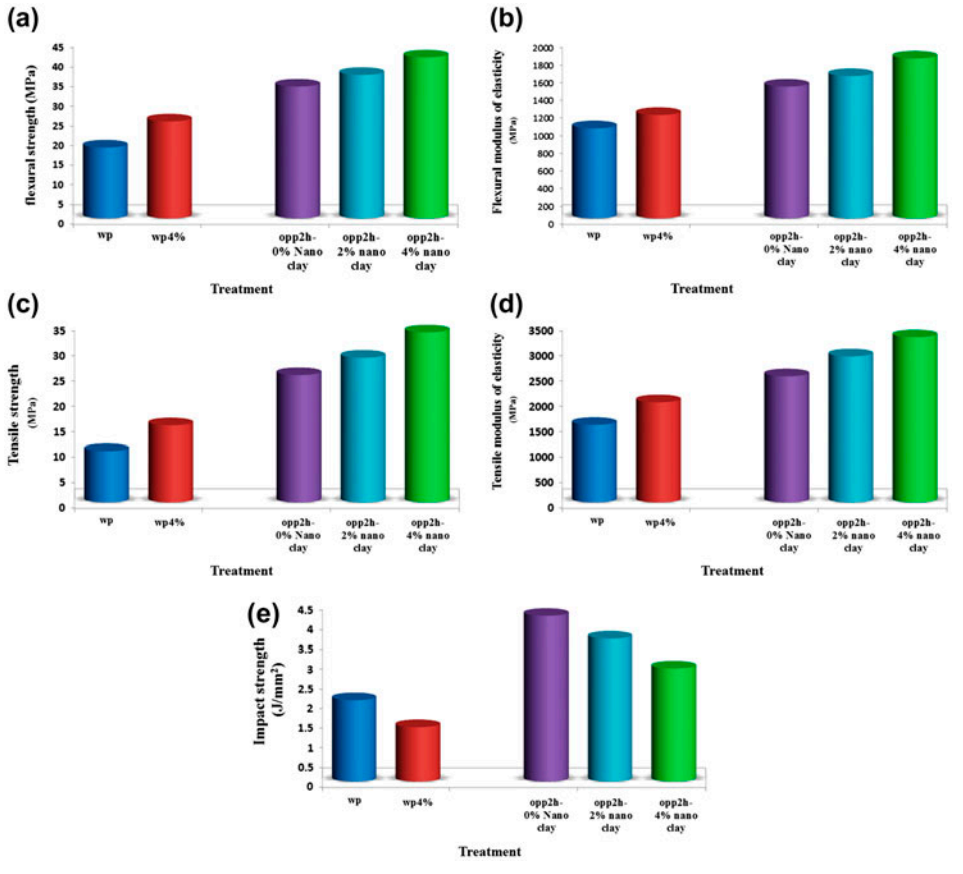

Figure 2. Flexural strength (a), flexural modulus of elasticity (b), tensile strength (c), tensile modulus of elasticity (d), and impact strength (e), values of samples with different treatments.

concentration and also increases the required energy to make a fraction as concluded in Ref. [15]. One of the reasons for the increment of impact strength by addition of compatibilizer can be related to the improvement of cohesion between polypropylene and wood fibers. In the samples containing compatibilizer and nano-clay particles, according to Figure 2(e), increasing nano-clay particle amounts from 0 to 4%, reduces the impact strengths in comparison with the samples without nano-clay particles. This phenomenon is related to the increment in crystallity structures.[5,12,16, and 17].

However, it seems that gathering and accumulation of clay aggregates in the polymer matrix results in the high stressful points in the resultant composite. Stress centralization in these points introduces initial cracks in the composite structure. Furthermore, tightening of the polymer chains due to the addition of nano-clay particles and absence of exfoliation structures are additional reasons for the observed phenomenon (decrement of impact strength).

3.3. Water absorption studies

Figure 3 shows the typical water absorption curves of wood fiber-PP composites with different types and content of compatibilizer. All composites show a similar pattern of

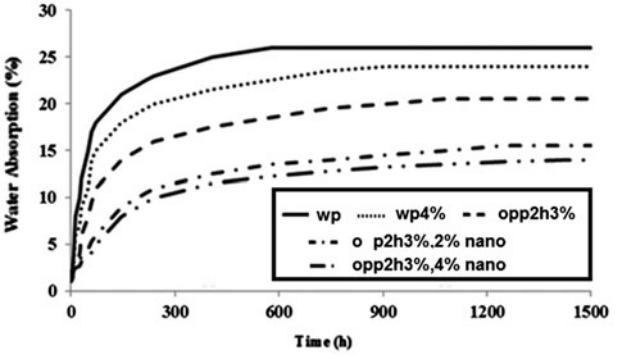

Figure 3. Water absorption curves of the composites.

water absorption that is, initial sharp water uptake followed by gradual increase until reaching a certain value at saturation point (after about 1350 h) where no more water was absorbed. Also, according to the results, it's distinguishable that the composites without compatibilizer show higher water absorption values than the composites containing compatibilizer. This observation can be related to better the interaction between OPP and wood fiber-PP composites. Furthermore, the compatibilizer, by forming polar groups and deletion of accessible OH groups, changed the hydrophile attribute of the fibers to hydrophobia and reduced water absorption. Generally it is necessary to use compatibilizers or coupling agents in order to improve the polymer/fiber bonding and in turn to enhance water resistance. With further increase in nano-clay particle content from 0 to 4%, water absorption considerably reduced and this result may be due to the hydrophobic properties of nano-particles [18].

It seems that the barrier properties of nano-scale fillers inhibit the water permeation in the polymer matrix. Two mechanisms have been reported for this phenomenon. The first is based on the hydrophobic nature of the clay surface that tends to immobilize some of the moisture and the second is that surfactant-covered clay layers form tortuous paths for water molecules transport. This barrier-like structure hinders water from penetrating into the inner parts of the composite.

3.4. X-ray diffraction analysis

Figure 4 illustrates the X-ray diffraction profile of wood fiber-PP composites including different amounts of nano-clay particle at the angles 1–12°. The results demonstrate that increasing the amount of nano-clay particles from 0 to 4% expands the distance between silicate layers.

According to Figure 4 and Bragg's equation, X-ray diffraction peak of nano-clay particle at $2\theta = 4/9$, results in the intercalation distance of $d_{001} = 20.8$ nm. However, addition of nano-clay particles to the composite and increasing their amounts from 0 to 4% caused the peak of the nano-composites to alter and pull it backwards. The backward moved peak is situated at $2\theta = 3/9$ and intercalation distance of $d_{001} = 26/17$. As it is detectable in Figure 4, the formed nano-composite is of intercalation type, because the peak related to crystalline region of nano-clay is not completely removed and is only reduced backwards and to lower 2θs. It can be reasonably related to the effect of polymer chains which due to this effect, distances between nano-clay silicate layers are

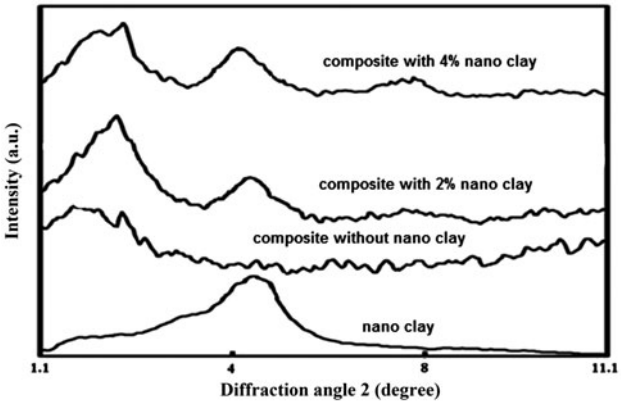

Figure 4. X-ray diffraction of different samples.

increased but the complete fragmentation of nano-clay has not occurred. Moreover, it is observable from structural study of samples by X-ray diffraction that application of a compatibilizer increased the distance between nano-clay silicate layers from 20 nm in a non-adapted state to 26 nm in the adapted state.[14]

Generally, in the X-ray diffraction pattern of the samples with constant OPP amounts and different levels of nano-clay particles, d_{001} is increasing with increment of nano-particle amounts. This can be related to the strong interactions between clay layers and compatibilizer chains in which these strong interactions originated from the penetration of the OPP chains into the clay layers' medial space during the mixing process.

3.5. Transmission electron microscopy (TEM)

To observe more detailed structure of nano-clay particles in composites and to confirm the X-ray test results, TEM images are used. Figure 5 shows TEM images related to composites produced from polypropylene and wood fibers including 2 and 4% nano-clay particles that filamentary dark lines are related to nano-clay layers and light regions are related to polymer matrix. As it is observable in this figure, filament-like regions are not completely separated from each other. Accordingly, it is the proof of incomplete separation of layers and formation of intercalation structure in the nano-composites. In the Figure 5(b), intercalation structures can be seen with more focus and better quality. The accuracy of these images has been also confirmed by XRD results. Similar conclusions are obtained by other researchers too.[12,14]

Generally, the evaluation of electron microscopy images suggests that the addition of the compatibilizer and nano-particles leads to the better connectivity at the internal phase of the composite, which results in the fewer empty spaces and also more uniform surface.

4. Conclusion

In this study, the effect of molten phase-oxidized polypropylene as a compatibilizer on the composites produced by wood fiber-PP–nano-clay composites was analyzed. Also, effects of nano-clay addition on the improvement of practical attributes of this composite were evaluated. It can be inferred from the above discussion that:

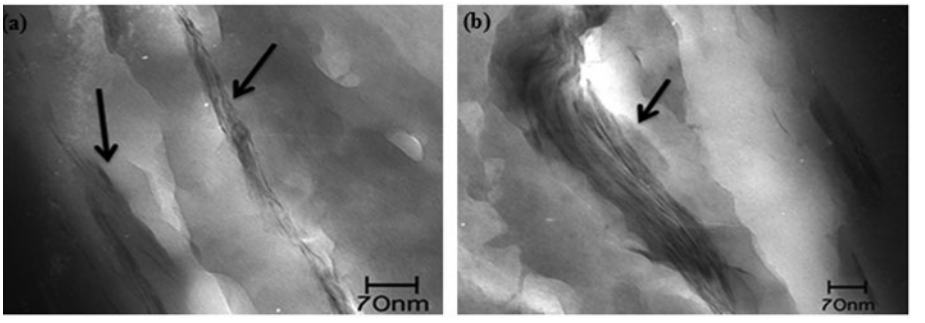

Figure 5. TEM images of wood fiber-PP-nano-clay composites. (a) Composite containing OPP and 2% nano-clay (b) Composite containing OPP and 4% nano-clay.

- Usage of compatibilizer improved the mechanical properties, such as flexural strength, tensile strength modulus of elasticity, and impact strength of the composites and decreased the water absorption values of them, so that the samples containing compatibilizer in contrast with the control samples (without compatibilizer) absorbed less amount of water in a longer time.
- The samples containing nano-clay particles, in contrast to the control samples (without nano-clay particles), have shown better and higher attributes, in a way that increment in nano-clay particle amounts decreased water absorption values and improved flexural and tensile strength of the composites. However, impact strength in the composites decreased by the addition of nano-clay particles.
- According to the obtained results, it can be concluded that molten phase oxidized polypropylene with a determined amount can perform the compatibility role in wood fiber-polypropylene-nano-clay composites. On the other hand, it can be concluded that the addition of nano-clay to the composites can improve the physical and mechanical attributes.

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