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Effect of Nanoclay Particles on the Properties of Particleboards

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ABSTRACT

We investigated the effect of adding nanoclay particles to resin on the properties of particleboards. Sodium montmorillonite (Na^+MMT) was used at three concentration levels:0, 3 and 6% based on dry weight of two resins: urea formaldehyde (UF) and isocyanate (MDI). Modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding (IB), thickness swelling (TS) over 24 hours and water absorption (WA) of the boards were measured. Results showed that an increasing percentage of nanoclayincreased MOR and MOE of particleboard samples. More specifically, in samples bonded with UF a 39% rise was observed in MOR with 6% of nanoclay particles, WA decreased by adding small amounts of nanoclay to UF-bonded boards, but remained unchanged for MDI boards. TS were 36% lower in UF-bonded boards with 3%nanoclay, whereas TS was increased for MDI boards.

KEYWORDS: Nano clay, particleboard, sodium montmorillonite, physical properties, mechanical properties

1 INTRODUCTION

The advent of nanotechnology has accelerated scientific development in many fields as many researchers have focused on this technology. The smaller the size of nano-particles is, the higher the ratio of their effective surface to their volume will be; this amplifies surface effects and improves catalytic properties [1]. The high concentration of atoms on the surface of nano-particles alters their physical properties and can lead to improvements in the manufactured composites[2].

There has been much research on nanoclays due to their availability and low cost compared to other nano-particles and their high specific surface area: 500-1000 m^2/g [1]. One of the most common nanoclays is montmorillonite or layered alumino-silicate.

Hong *et al.*(2008) showed that adding a small quantity of sodium montmorillonite to UF resin significantly improved its bonding performance. Addition of nanoclay had a noticeable impact on water absorption and thickness swelling of particleboards bonded with UF; and internal bonding also increased. Hong *et al*. (2008) also stated that sodium montmorillonite accelerated the curing of UF resin and its bond strength[3].

Jinshu *et al* (2007) studied the changes in water absorption and fire resistance of spruce wood after treatment with UF resin and nano-particles of silica. Water absorption decreased and fire resistance and hardness of samples improved[4]. Qiaojia *et al* added nano-silica to UF resin and found out that when nano-silica is used together with a coupling agent and also when added to UF resin using ultrasonic mixing, properties increase. Additionally, when the percentage of nano-silica was below 1.5, the amount of free formaldehyde decreased and viscosity and internal bonding increased accordingly[5]. Dong Ho and Arthur (2004) claimed that nanoclay enhances all adherence properties and physical properties of composites that are manufactured with UF resin; they specifically mentioned improved water absorption and thickness swelling of the boards[6].

Taghiyari *et al* (2011) tested the effect of nano-silver on the properties of particleboards. Hot-press time as well as heat gradient in the mats was reduced in almost every case,resulting in improved physical and mechanical properties of boards[7].Gholamiyan*et al*(2011) investigated the effect of clear paints containing nanoparticles, nanozycofil and nanozycosil, on the water absorption and contact angle of poplar wood. They found that samples coated with combined acid catalyzed lacquers and nitrocellulose lacquers

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and those coated with nanozycosil had the highest resistance to water absorption. The greatest contact angle was observed for the samples coated by nanozycosil[8]. Zahedsheijani R. *et al*(2012) found that adding Na^+MMT to MDF improved the thermal-oxidative stability and thermal conductivity of the boards. As the research suggests, X-ray diffraction and SEM observations showed adequate exfoliation and dispersion of NaMMT throughout the MDF structure[9].

Hashim *et al* (2005) studied the effect on fire retardancy and mechanical properties of making MDF from recycled corrugated cardboard containing aluminum trihydoxide (ATH) nanoparticles. The limiting oxygen index (LOI), used as an indicator of fire retardancy, and internal bonding increased as ATH loading increased. On the other hand, thickness swelling of panels also increased[10]. Faruk and Matuana (2008) compared two methods of incorporating nanoclay into wood-plastic composites to enhance their mechanical properties. The first method involved the reinforcement of HDPE matrix with nanoclay, which was then used as a matrix in the manufacture of the WPCs (melt blending process). The second method consisted of direct addition of nanoclay into HDPE/wood-flour composites during conventional dry compounding (direct dry blending process). The melt blending process turned out to impose better improvements in mechanical properties[11].According to Miller (2008) when nanoclays are surface modified in the form of a covalently or ionically bonded organic molecule, they can further improve yield stress and toughness of composites[12].

Lignin-based wood adhesives were obtained by Hong *et al*. (2008) in which ormaldehyde was substituted with glyoxal, a nonvolatile nontoxic aldehyde. The adhesives yielded good internal bond strength results of the panels, enough to pass relevant international standard specifications for interior-grade panels[3].Cai *et al*. performed ball-milling of the nanoclays for better dispersion of the nanoclays into the MUF resin. The effect of nanofillers both milled and unmilled, on the curing and viscoelastic properties of the MUF was investigated, using differential scanning calorimetry and dynamical mechanical thermal analysis methods[13]. Wang *et* al. (2008) suggested a method of forming a composite panel or board by adding phyllosilicate clay to a thermosetting resin and natural fibres[14].

Saraeian *et al* (2012) studied the effect of nanoclay particles on tensile strength and fire retardancy of polystyrene-nanoclay composites. The findings of the research showed that by increasing nanoclay up to 5%, the tensile strength and modulus of elasticity were increased, while the strengths were decreased when 6%, nanoclay was used [15]. In a study on the effect of nanoclay on water absorption of hybrid wood plastic composites, Eshraghi *et al* (2012) indicated that that water absorption of the composites increased after weathering but addition of nanoclay can reduce intensity of weathering through decreasing of water absorption [16]. Nemati *et al* investigated the mechanical properties of nanocomposites based on wood flour/recycled polystyrene and nanoclay. The obtained results indicated that the tensile strength and flexural strength were increased by raising nanoclay content in the composites [17]. In a separate study, Nemai*et al* (2013) investigated the effect of nanoclay on thermal properties of the same wood plastic composite. It was demonstrated that increasing the wood flour deteriorates thermal stability such that the sample experienced a weight loss at a lower temperature. Meanwhile, increasing the nanoclay concentration has improved the thermal stability since it reinforced resistance of the sample against heating [18].

In our research, we used nano-particles of sodium montmorillonite (Na^+MMT) to investigate its effects on physicomechanical properties of particleboards manufactured with urea formaldehyde and isocyanate resins. In particular, the aim of this research is to assess the potential of Na^+MMTnanoclay particles to improve the physical and mechanical properties of particleboards and the efficiency of UF resin through increasing the specific area and enhancing internal bonds. Similar tests have been carried out on MDF boards by Mousavi Hosseini *et al* (2012)[19].

2 MATERIALS AND METHODS

2-1 Materials

Three concentration levels of sodium montmorillonite:0, 3 and 6 percent based on resin dry weight were used in the manufacture and testing of particleboards. Two methods were used to mix nanoclay with resin: using (1) a 5500 rpm blenderand (2) ultrasonic mixing. The resins used were urea formaldehyde (UF) from Estehkam Glue Chemical Industries, Qom, Iran, and isocyanate (MDI) from Donyayepolimer Co., Tehran, Iran, the specifications of which are listed in Table 1.

Table 1 - Specifications of resins

Resin Type	Density (g/cm^3)	Gel Time (s)	Viscosity (cp)	Percentage of Solid Substance
UF	1.26	60	350	60
MDI	1.27	-	300	100

UF was used at 10% of total board dry weight and MDI at 4%. All boards were compressed at 42 kg/cm^2 pressure at 170°C for 5 min (UF boards) or 4 min (MDI boards). Three boards were used per treatment, i.e. 24 boards in total. Board target density was 0.7 g/cm^3 and target thickness of 16 mm.

Wood particles were supplied by Arian Sina Manufacturing Mill located in north of Iran. The nanoclayswere Cloisite ® Na^+, which were supplied by Southern Clay Products, Gonzales, TX, USA. The specifications of the nanoclayare listed in Table 2.

Table 2 - Specifications of nanoclay used

Modifier	Density (g/cm^3)	Gap between layers (nm)	Analysis of dimensions (µm)		
			10% less than	50% less than	90% less than
-	2.86	1.17	2	6	13

2-2 Preparation of Resin/Nanoclay Mixes

2-2-1 Mixing nanoclay with urea formaldehyde:

In order to prepare the resin, we used two mixing methods. In the first method, nanoclay was added to 50 ml of distilled water, and the suspension was added to the resin and stirred for five minutes at a rate of 5500 rpm. The second method involved adding the clay-water suspension to the resin and exposing it to ultrasonic waves for ten minutes. The EYELA Cleaner MUS-201 apparatus was used for ultrasonic mixing.

2-2-2 Mixing nanoclay with isocyanate:

Because of the excessive rise in concentration and viscosity of this resin as a result of adding nanoclay, we could not add it directly to the resin. Instead thenanoclay was first mixed into 12 grams of distilled water and stirred for five minutes, then subjected to ultrasonic mixing for 10 min. The clay-water suspension was sprayed onto the particles first, followed by the isocyanate resin.

For the six percent nanoclay concentration, only the stirring method was used, because at this level of concentration, the ultrasonic treatment increases the and viscosity of the resin so excessively that renders it impractical.

2-2-3 Particleboard fabrication and testing

Particleboards were manufactured in 40×40 cm^2 dimensions by use of laboratory press and were held in a acclimatized (temperature = 12 °C, relative humidity = 20%) room for a period of two weeks before they were cut according to EN310 (MOE and MOR), EN319 (IB) and EN317 (TS and WA) standards (Figure 1). AnInstron 4486 load frame was used for all the tests at a loading rate of 10 mm/min.

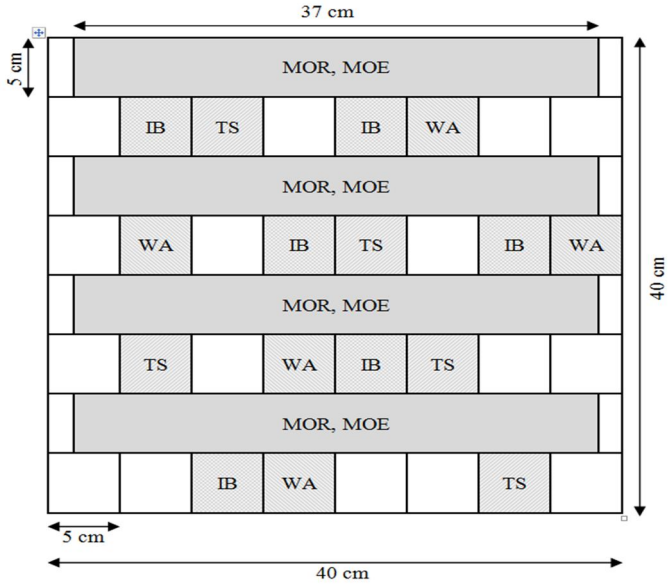

Figure 1 - Cutting pattern of specimens

3 RESULTS AND DISCUSSION

3-1 Modulus of Rupture

Modulus of rupture is one of the major properties of wood products including wood composites that represents the strength of products against bending forces and is often used to compare materials.

Analysis of variance at 99% confidence interval showed significant changes in MOR between different treatments. For boards manufactured with UF, addition of 6% of nanoclay resulted in a 39% increase in MOR (Figure 2). The improvement was less for MDI manufactured boards; nevertheless, adding 3% of nanoclay and mixing by ultrasonic method yielded a 33% rise in MOR.

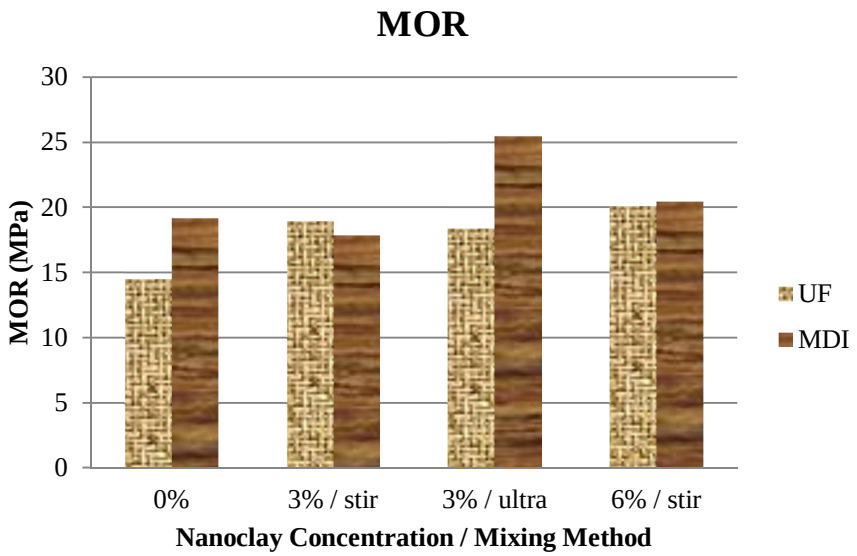

Figure 2 - The effect of nanoclay concentration and resin type on MOR

One alteration induced on composites by nanoclay particles is the higher effective surface to volume ratio as size of nano-particles get smaller, which results in stronger surface effects and catalyst properties. On the other hand, when nano-particles of clay are used as fillers in wood composites, they distribute stresses throughout the material which in turn improves its strength very effectively. Putting these two facts together, this enhancement in bending strength can be explained which is in agreement with the results of previous research [20, 5, 3].

In a similar study on MDF boards, MOR of UF-based boards containing 3% Na^{+}MMT increased by x%. Likewise, there was an enhancement for MDI-boards by adding 3% of Na^{+}MMT; however, MOR decreased when6% concentration of nanoclay was used (Mousavi Hosseini *et al*, 2012)[19].

3-2 Modulus of Elasticity

Modulus of elasticity is an indicator of the resistance of a solid material to elastic deformation.

FromFigure 3 it can be noted that MOE of UF-bonded boards containing 3 or 6% nanoclay were up to 73% higher than controls. MOE of MDI bonded boards also increased with up to 3% nanoclay but decreased again at 6% addition. One possible explanation for this decrease could be that the 6% concentration level is too high for MDI resin. The same trend was also found in our previous research on MDF (Hosseini *et al*, 2012)[19].

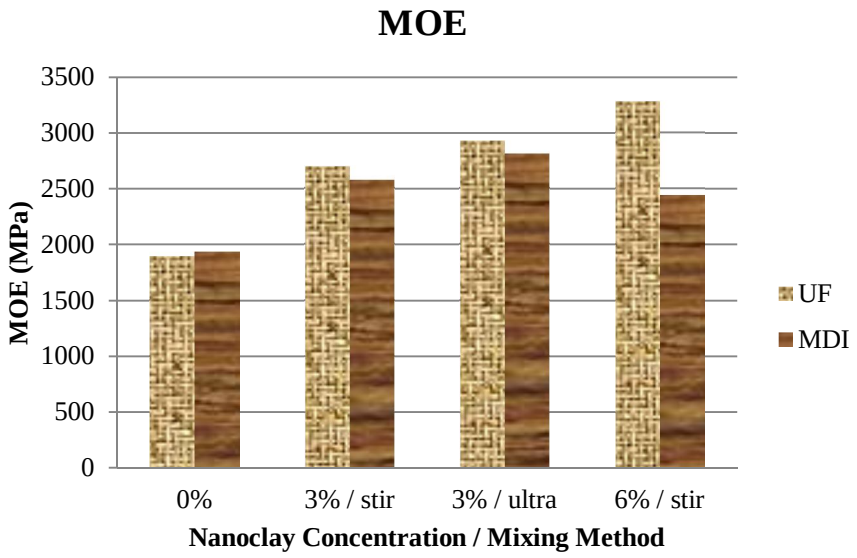

Figure 3 - The effect of nanoclay concentration and resin type on MOE

3-3 Internal Bonding

Internal bonding or perpendicular tension tests are used to compare boards under tensions perpendicular to their cross sections and to measure the internal adhesion of resins.

Statistically significant increases in IB occurred only in the case of the UF bonded boards. From Figure 4, a 6% addition of nanoclay particles increased IB by 25%.Na^+MMTnanoclay accelerates the adhesion and also strengthens transverse cohesion strength of UF. Adding nanoclay to UF resin has been shown to decrease the level of free formaldehyde [5], which suggests that most of the formaldehyde content of the resin has been consumed in the development of the resin polymer network, resulting in enhanced internal bonding. Moreover, applying the percolation theory to the networking capability of the clay nanoplatelets provides a complementary explanation of such an improvement to the performance of UF resins in particleboards [3].In contrast to the UF boards, there was no increase in IB strength in boards containing MDI plus nanoclay. This was also found in the case of the MDF bonded with MDI and nanoclay (Mousavi Hosseini *et al.* 2012)[19].

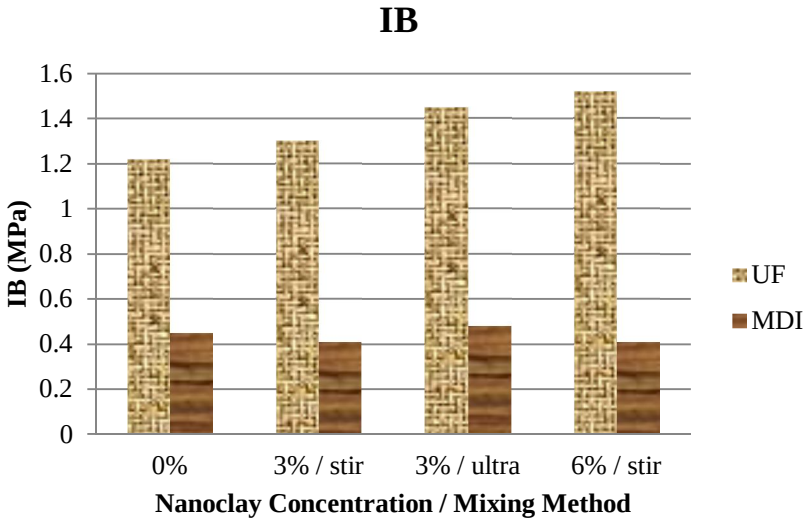

Figure 4 - The effect of nanoclay concentration and resin type on IB

3-4 Water absorption after 24 hours of soak in water

Water absorption in ligno-cellulose composites is one of the basic properties that determine their ultimate usability.

The 24-hour soak test determines the mass of water absorbed by the composite (WA%) and its effect on board dimensions (TS%). While there was no statistically significant effect of nanoclayadition on the WA of MDI bonded boards, adding 3% NaMMT by stirring resulted in a 35% decrease in WA. Further addition of 6% nanoclay produced no further decrease in WA (Figure 5). In our previous study on MDF boards (Hosseini*et al.* 2012), adding 6% NaMMT resulted in a small further reduction in WA[19].

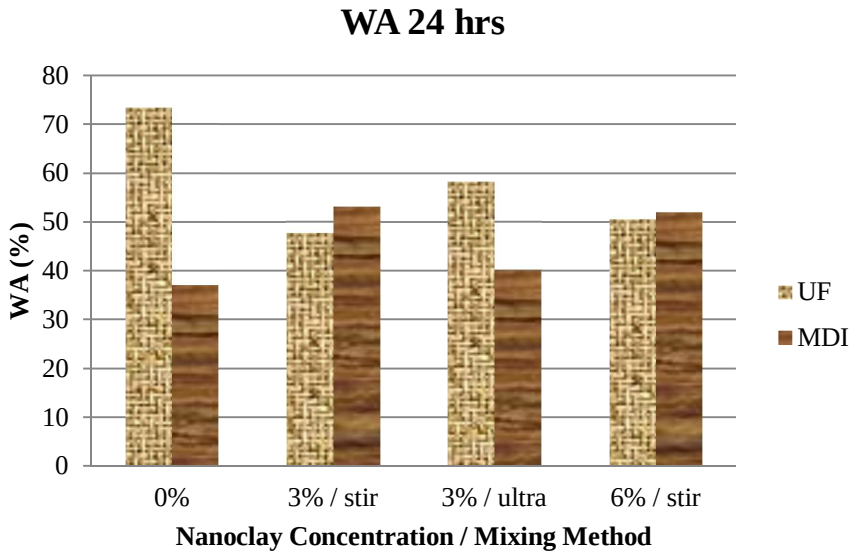

Figure 5 - Effect of nanoclay concentration and resin type on WA

3-5 Thickness swelling after 24 hours

Thickness swelling is one important property of wooden composites which determines their dimensional stability against absorption of water.

As might be expected, the trends for TS were similar to WA, and as can be seen in Figure 6, adding 3% or 6%nanoclay (stirring) to UF boards reduced the TS dramatically. For example, only 3% of nanoclay led to a 36% decrease in TS. In contrast, TS increased for the MDI-bonded boards containing nanoclay, which could be due to the fact that MDI is a water-resistant resin by itself, thus been negatively affected by nanoclay.

Nanoclay addition has also been found to have a highly beneficial effect on the moisture resistance of UF bonded MDF by [21], and[19]. One possible explanation for the observed improvement in dimensional stability of wood composites is the improved wood bonding strength of nanoclay-UF resin mixes compared with pure UF resin, as evidenced by the improved IB in our particleboards. Also, another similar study confirms the amelioration of water stability properties of MDF boards with an increase in nanoclay concentration level and press temperature [21].

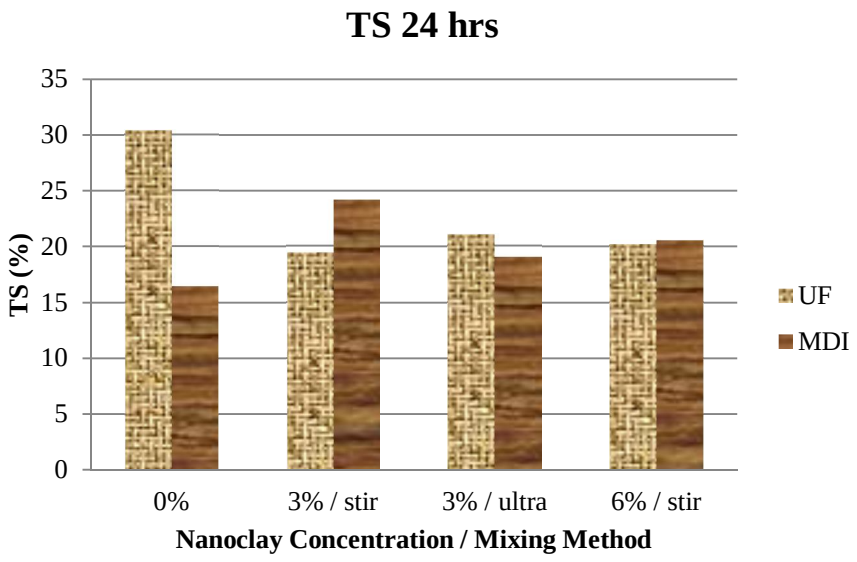

Figure 6 - Effect of nanoclay concentration and resin type on TS

CONCLUSIONS

Adding NaMMT at 3% or 6% had a positive effect on the strength properties (MOR, MOE, IB) of particleboards bonded with UF resin. All three properties were highest if 6% nanoclay was used. At 3% nanoclay, the clay was mixed with the resin either by stirring or ultrasonic mixing. While there were some noticeable differences between mixing methods, no one method produced consistently better board properties than the other. However for TS and WA, using 3% nanoclay proved to be the best treatment.

In the case of boards bonded with MDI, adding nanoclay had little effect on IB,

but did increase MOR and MOE. In contrast the dimensional stability (TS and WA) of MDI boards were little changed or made worse by adding nanoclay. For some reason MDI boards absorbed more water and swelled more if they were bonded with MDI-nanoclay mix.

In total, based on the above-mentioned observations, use of nanoclay is recommended for UF-resin boards, but not for MDI-resin ones.

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