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EFFECTS OF IMPREGNATION WITH STYRENE AND NANO-ZINC OXIDE ON FIRE-RETARDING, PHYSICAL, AND MECHANICAL PROPERTIES OF POPLAR WOOD

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ABSTRACT: Nanoparticles have been vastly applied in wood polymer composites (WPCs) in the recent years to improve some of the drawbacks of solid wood species. In the present study, the effects of ZnO nanoparticles on fire retarding, physical, and mechanical properties of polymerized poplar wood were investigated. Poplar specimens were impregnated with styrene monomer, containing four different contents of nano-zinc oxide (ZnO) (0, 0.5, 1 and 1.5%, based on the dry weight of monomer). Results of the scanning electron microscopy (SEM) showed homogeneous dispersion of ZnO nanoparticles in the WPC matrix. Nano-zinc oxide improved physical properties such as dimensional stability and water absorption. Moreover, mechanical properties increased in comparison to the control specimens. The impregnation process also significantly improved some of the fire-retarding properties, including the ignition time; however, the flammability nature of styrene aggravated some others, such as carbonized area. It was concluded that, although most of the properties were improved, the final application of WPC should be taken in to consideration before making decision on whether or not to impregnate populus wood with styrene.

EFEITOS DA IMPREGNAÇÃO COM ÓXIDO DE ESTIRENO E NANO-ZINCO SOBRE PROPRIEDADES RETARDADORAS DE FOGO, FÍSICAS E MECÂNICAS DA MADEIRA DE *POPULUS*

RESUMO: Nanopartículas são amplamente aplicadas em compósitos de polímero-madeira (WPCs) nos últimos anos para melhorar algumas das desvantagens das espécies de madeira sólidas. No presente estudo, os efeitos de nanopartículas de ZnO nas propriedades de retardamento do fogo, propriedades físicas e mecânicas da madeira polimerizada de *Populus* foram investigadas. Espécimes de Poplar foram impregnados com monômero de estireno, contendo quatro diferentes conteúdos de óxido de nano-zinco (ZnO) (0, 0,5, 1 e 1,5%, com base no peso seco do monômero). A microscopia eletrônica de varredura (SEM) revelou homogênea dispersão das nanopartículas de ZnO na matriz WPC. O ZnO melhorou propriedades físicas da madeira tais como a absorção de água e estabilidade dimensional. Além disso, as propriedades mecânicas aumentaram em comparação com as amostras de controle. O processo de impregnação também significativamente melhorou algumas das propriedades retardadoras de fogo, incluindo o tempo de ignição; no entanto, a natureza de inflamabilidade do estireno agravada alguns outros, como a área carbonizada. Concluiu-se que embora a maioria das propriedades foram melhoradas, a aplicação final do WPC deve ser tomada em consideração antes de tomar a decisão sobre a impregnar a madeira de *Populus* com estireno ou não.

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INTRODUCTION

With the development of human society, tree plantations and the consumption of wood are rapidly increasing year by year; moreover, a multi-purpose attitude towards plantation of trees is growing worldwide (AMUSANT et al. 2015). However, wood and wood composites are susceptible to some organisms such as fungi and termites, as well as to fire (HILL, 2008; OZDEMIR & TUTUS, 2013&2016). These vulnerabilities limit the applications of wood and wood composites. Researchers have therefore worked on engineered wood to improve the drawbacks, using new production techniques and modern materials at micro or nano scales (ANDRADE et al. 2016; BAL 2016; WANG et al. 2016).

Nano materials have been the subject of intense scientific and technological activities due to their interesting size dependent physicochemical and bio and green properties and consequently have exciting application potential (LI 2012; GHARIEB et al. 2016). The first practical application of nanotechnology in wood science and technology was the use of metal nanoparticles with high thermal conductivity (SABER et al., 2013) that increased the rate of heat transfer in solid wood (TAGHIYARI, 2012&2014), increased resistance to decay (HABIBZADE et al., 2014; FARAHANI and BANIKARIM, 2013), and decreased the hot press time in particleboard manufacture. There was an improvement in physical and mechanical properties and fungal and fire retardancy by infusing wood with some mineral nanomaterials (KARIMI et al., 2013; TAGHIYARI et al., 2013; RANGAVAR et al., 2016).

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has achieved and increasing attention in recent years due to its many significant physical and chemical properties, such as chemical stability, high light transmittance, effective antibacterial properties, and intensive ultraviolet and infrared adsorption (TURTON et al., 2004; HAMMINGA et al., 2004; WU et al., 2002; WU and XIE, 2004; KITANO and SHIOJIRI, 1997; KAMAT et al., 2002). Moreover, the advance of nano-ZnO particles could improve the mechanical and optical properties of the polymer matrix (RASHMI et al., 2012).

There are studies reporting the use of nano-zinc oxide to improve physical and mechanical properties (RASHMI et al., 2012), to act as a fire retardant (RASHMI et al., 2013), and also as a wood preservative (HABIBZADE et al., 2014, FARAHANI & BANIKARIM, 2013).

It should be added that the ZnO nanoparticles, like other nanoparticles, possess a high surface energy, which may result in the agglomeration of particles when ZnO nanoparticles are dispersed in an organic solvent

and matrices. Therefore, it is necessary to prepare ZnO/polymer nanocomposites to prevent the formation of agglomerated nanoparticles. Surface modification is a common strategy to prevent the agglomeration of nanoparticles in polymers. On the other hand, grafting polymers on the surface of the nanoparticles effectively improves their dispersibility in the polymer matrix, resulting in enhanced properties of the composites. The surface modification of ZnO nanoparticles is achieved by grafting with silane coupling agent or with some polymers (SHU-RUI et al., 2008; TANG et al., 2006).

Poplar wood (*Populus deltoids*), a fast growing species with low-quality, is not useful for constructional purposes due to its poor dimensional stability, vulnerability to wood-deteriorating fungi, and low mechanical properties. The present study focused on the preparation of wood polymer nanocomposite by impregnating poplar specimens with styrene monomer, vinyl trichlorosilane (VTCS) and modified ZnO nanoparticles. The aim of the study was to find the effects of nano-ZnO on fire retarding, physical and mechanical properties of wood.

EXPERIMENTAL

Materials

Poplar wood (*Populus deltoids* L.) was collected from the Gorgan province, located in the Northern part of Iran. The chemicals for the production of WPCs were styrene (St) and glycidyl methacrylate (GMA), purchased from Merck & Co., Inc. (Germany). ZnO nanopowder (<50 nm, 90 m².g⁻¹) was purchased from Nano Pars Lima Co. (Tehran, Iran). Tetrahydrofuran (THF, anhydrous) and vinyl trichloro silane (VTCS) were purchased from Sigma-Aldrich chemical company (Darmstadt, Germany). All other chemicals and solvents used in this study were of analytical grade.

Sample preparation

Wood samples used for testing were prepared from clear and defect-free poplar wood, cut into blocks for different experiments. The dimensions of blocks were 2×2×2 cm³ for dimensional stability test (ASTM D4442), 1×1×10 cm³ (radial × tangential × longitudinal) for flexural strength (ASTM D790), 10×0.5×2 cm³ for tensile strength (ASTM D638), and 2×2×6 cm³ for compression strength (ISO 3787). Seven replicate specimens were prepared for each treatment.

Surface modification of nano-zinc oxide

ZnO nanoparticles were treated with silane coupling agent. The surface modification of nanoparticles

was carried out as follows: firstly, a 1.0 g portion of ZnO nanoparticle, 1.0 mL of VTCS, and 40 mL of toluene were added into a three-necked round-bottom flask (250 mL) and refluxed at 80°C for 6 h under mechanical stirring. Then, the precipitate was centrifuged and extracted with ethanol for 12 h to remove the residual silane. At the last stage, the precipitate was dried in vacuum for 48 h, and the double bonds were introduced onto the surface of the ZnO nanoparticle (Hong et al., 2009).

Preparation of St/ZnO nanocomposite

Glycidyl methacrylate (GMA) was mixed with styrene (St), as a cross-linker. Then, the different amounts of modified ZnO nanoparticles (0/5, 1 and 1/5 wt% of St) were dispersed in St monomer in the presence of minimum amount of solvent (THF) and the dispersion was treated by ultrasonic instrument for 30 min at room temperature.

Impregnation and polymerization procedure

All the samples were oven dried at 100°C to constant weight before treatment and weights were measured. The samples were then impregnated by St monomer and ZnO nanoparticles for half an hour, using Bethel method. Once impregnated, the samples were kept in a chamber at room temperature for 30 min so that the excess chemicals would be drawn out of the samples. Each sample was then wrapped in aluminum foil to be cured in an oven for 24 h at 90°C. The cured samples were then Soxhlet extracted using chloroform to remove homopolymers, if any, formed during polymerization. Finally the samples were dried and weights were measured.

MEASUREMENTS

Weight percent gain

The weight percent gain (WPG) after polymer loading was calculated according to Equation 1, where W_1 ($\text{g}\cdot\text{cm}^{-3}$) is oven-dry weight of wood blocks before polymer treatment, and W_2 ($\text{g}\cdot\text{cm}^{-3}$) is oven-dry weight of block after polymer treatment.

$$\text{WPG}(\%) = (W_2 - W_1) \cdot (W_1 \times 100)^{-1} \quad [1]$$

Volume increase (%) after impregnation

Percentage of volume increase after curing of wood samples was calculated using Equation 2, where V_0 is the oven-dry volume of the control wood and V_t is the oven-dry volume of the impregnated wood.

$$\text{Volume increase}(\%) = (V_t - V_0) \cdot (V_0 \times 100)^{-1} \quad [2]$$

Water uptake test

Both control and impregnated wood samples were immersed in distilled water at 20°C and weight was taken after different time intervals. It is expressed as, where W_t is the weight after immersion in distilled water for specific time period (0-160 hours) and W_d is the weight of the oven-dry sample.

$$\text{Water uptake}(\%) = (W_t - W_d) \cdot (W_d \times 100)^{-1} \quad [3]$$

Mechanical properties

A Universal Instron testing machine with a load capacity of 2000 kgf was used to carry out the mechanical tests. Samples were stored at $20 \pm 1^\circ\text{C}$ and relative humidity of $65 \pm 5\%$ inside a climatic chamber for two weeks before the tests.

Fire-retardant testing apparatus

Due to the unavailability of the standard tests by cone calorimeter and heat release measurement apparatus, Slide Fire Test Apparatus (SFTA) was designed and built (TAGHIYARI, 2012), using piloted ignition (WHITE & DIETENBERGER, 1999) (Figure 1). The fuel in the present study was natural gas comprised mainly of methane CH_4 (90-98%); however, other hydrocarbons were also reported by the supplier to be accompanied (C_2H_6 : 1.8%; C_3H_8 : 2%; $\text{H}_4\text{H}_{10} + \text{C}_5\text{H}_{12}$: less than 1%; and also $\text{N}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$: less than 1.5%). The flow rate was $0.096 \text{ L}\cdot\text{s}^{-1}$. The specimen was vertically mounted on a holder up-straight and exposed to a Bunsen type burner held at 45 degrees to the surface of the specimen for 120 seconds in accordance with the standard ISO 11925-3. The burner nozzle internal diameter was 11 mm. The burner was fixed on a slide, moving back and forth, equipped with an adjustable stop to keep flame at a certain distance from the specimen. While the slide was back, the burner was turned on; the slide was then pulled forward abruptly to expose the flame to the specimen. The time for each specimen to catch fire with an evident visible flame on the spot nearest to the Bunsen-type burner, as well as the time the spot started to glow, were registered as ignition and glowing times. After 120 seconds, the slide was pulled back to prevent over exposure of the specimen to the flame. The time the specimen showed a visible fire, after the removal of the burner, was also registered as fire endurance time (the duration time of a visible flame).

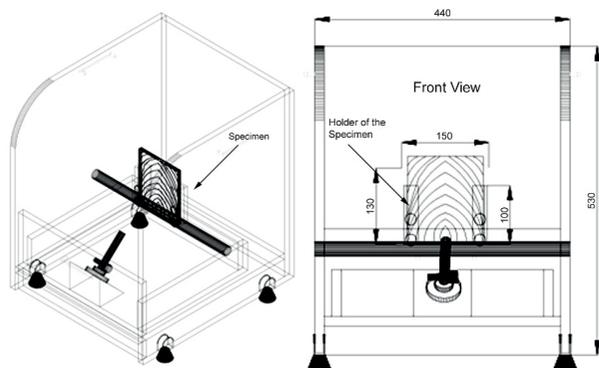


FIGURE 1 Schematic picture of the slide fire testing apparatus (SFTA) (invented by the second author under Iranian Patent No. 67232; approved by Iranian Research Organization for Science and Technology under license No. 3407 issued to H.R. Taghiyari) (TAGHIYARI, 2012).

Once the flame was extinguished and the specimen was no longer burning, the length and width of burning were measured. The weight was also measured just before, as well as 2 h after the test, to measure the weight loss. The whole structure of the apparatus was placed in a three-wall-compartment in order to protect the burning flame from wind and air movements.

Statistical analysis

SPSS (16) was used for statistical analysis and significance was determined at 1 and 5% level of confidence using analysis of variance (ANOVA). Treatments were then classified as per Duncan’s multiple range test.

Weight percent gain (WPG %)

The values of WPG for both raw wood and WPCs for samples test were measured (Table 1).

TABLE 1 Average weight gain of specimen after polymerization for fire-retarding, physical, and mechanical properties.

Sample particulars	Weight gain (%)	Volume increase (%)
Impregnated with ST/THF/BP/GMA/ZnO		
100/20/2/1/0	50(± 5.6)*	3.28(±3.8)
100/20/2/1/0.5	50(± 4.1)	3.64(±0.9)
100/20/2/1/1	50(± 6.8)	3.17(±2.6)
100/20/2/1/1.5	50(± 2)	3.84(±2.8)

* Numbers in the parenthesis are the standard division.

RESULTS AND DISCUSSION

Analysis of the scanning electronic microscope

SEM results

Figure 2 shows the SEM micrographs of the control (Figure 2a) and impregnated poplar wood

(Figure 2b-d). The empty cell wall and pits were clearly observed in the control wood (Figure 2a). In the impregnated specimens (Figure 2b), the empty spaces and part of the cell cavities were filled with St-polymer. The impregnated nanoparticles as white spots were uniformly scattered in the composite (Figure 2c-d). No agglomeration of nanoparticles was observed.

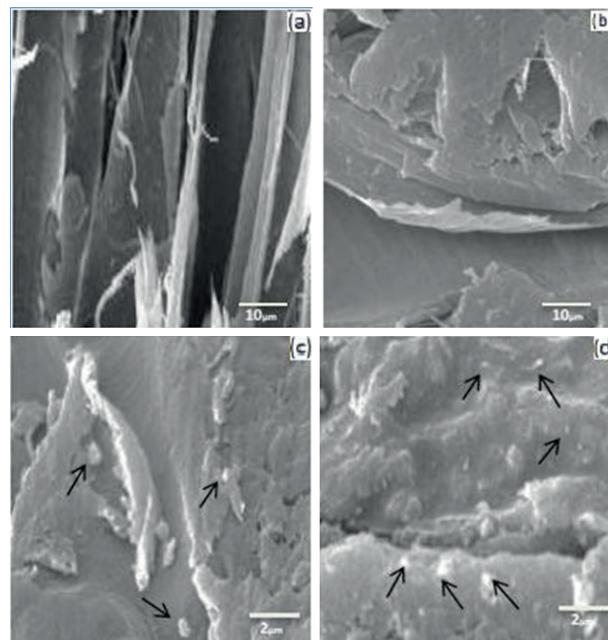


FIGURE 2 SEM images of wood (a) control and impregnated with (b) St, (c) St/ZnO (0.5%), and (d) St/ZnO (1.5%).

Water uptake

Results of the water uptake tests showed that impregnation with styrene significantly decreased water uptake in comparison to the control samples (Figure 3). In both impregnated and control samples, water uptake increased with increasing time of immersion. The hydrophilic nature of wood (high contents of hydroxyl groups in cellulose and hemicelluloses) was responsible for the increasing trend. Additionally, large number of porous tubular structures in the control wood accelerated the penetration of wood due to the capillary action. The decreased water uptake was due to the hydrophobic characteristic of monomers, acting as a physical shield for the wood surface, keeping cell wall and lumen from getting wet by water penetration. The average water absorption percentage decreased with increasing nano-zinc oxide. In addition, the lowest water uptake of WPCs showed in high concentration samples of nano-zinc oxide. The tortuous path provided by the nano-zinc oxide layers increased the barrier property for water transport (CLAUSEN et al., 2010; RASHMI et al., 2012).

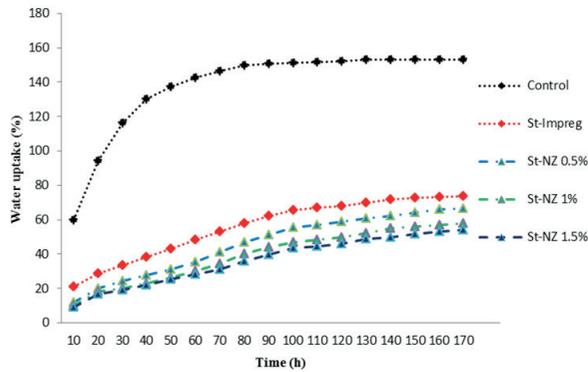


FIGURE 3 Effect of nano-ZnO content on water absorption (%) in the control, impregnated with styrene (St-Impreg), impregnated with styrene containing 0.5% (St-NZ 0.5%), 1% (St-NZ 1%), and 1.5% nano-ZnO (St-NZ 1.5%) poplar specimens.

Dimensional stability test

The results of volumetric swelling in water for control and impregnated wood samples at room temperature for different time periods are shown in Figure 4. The reduction in volumetric swelling with increasing nano-zinc oxide suggested that higher concentrations of ZnO provided substantial water resistance (SOLTANI et al., 2013). The improvement in dimensional stability samples containing ZnO can be attributed to the void being occupied by ZnO nanoparticles (RASHMI et al., 2012).

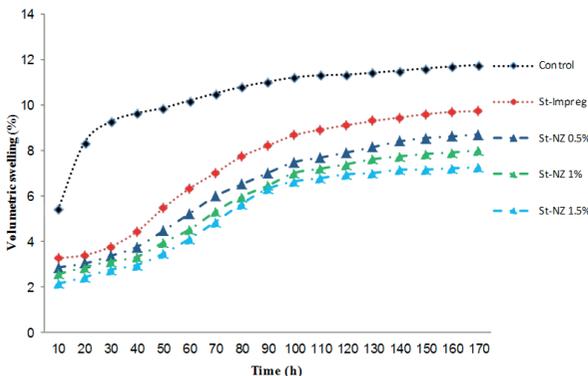


FIGURE 4 Effect of nano-ZnO content on dimensional stability (%) of the control (W), impregnated with St (WPCN 0), poplar impregnated with styrene containing 0.5% nano-ZnO (WPCN 0/5), ST/ 1% nano-ZnO (WPCN1), ST/1.5% nano-ZnO (WPCN 1/5).

Mechanical properties

Tensile strength and modulus

Figure s 5 (a) and (b) illustrate the tensile strength and modulus of WPCs made with different nano-zinc oxide contents. It can be seen that with the increase in the nano-zinc oxide loading from 0 to 1.5 wt%, there was improvement in the tensile strength and modulus of

nanocomposite. The maximum improvement in tensile strength (26%) and modulus (26.1%) was achieved when 1.5 wt% of ZnO was added into the styrene matrix. The increased tensile strength up to 1.5 wt% ZnO may be attributed to the higher extent of interaction of ZnO with wood and styrene through its surface hydroxyl and vinyl groups of polymer chains (RASHMI et al. 2012, 2013; GUO et al. 2006, 2008). Nevertheless, with further increase in nano-zinc oxide loading from 1 to 1.5 wt%, a low increase in the tensile strength and tensile modulus was observed. This indicated the nano-zinc oxide was distributed more uniformly through the polymer matrix at its lower concentrations (1wt%); this uniform distribution, in turn, improved a better surface contact between nano-zinc oxide and polymer matrix. However, it should be noticed that more concentrations of ZnO (1.5wt%) caused decreased tensile properties of nanocomposite.

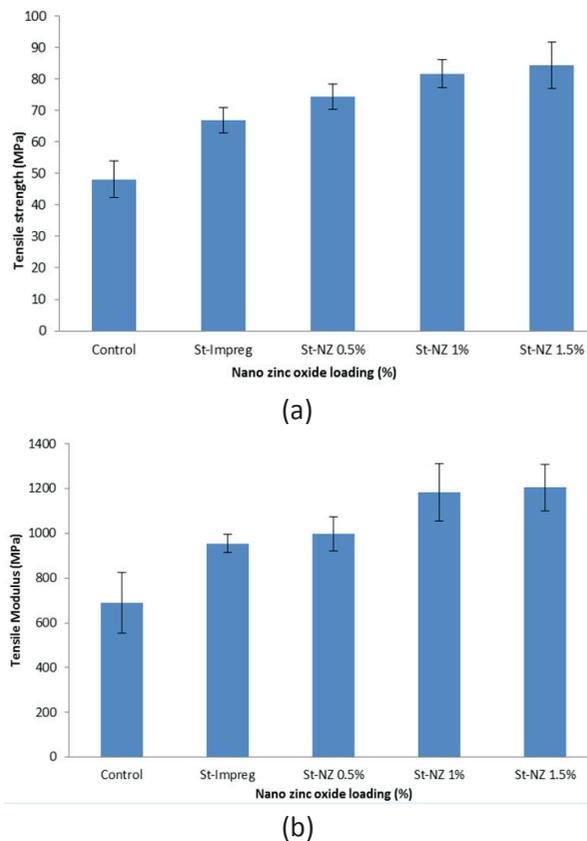


FIGURE 5 Effects of nano-ZnO content on: a) tensile strength; b) tensile modulus

Flexural strength and modulus

Results of flexural strength and flexural modulus are shown in Figure 6 (a and b), respectively. MOR and MOE values increased with the increasing ZnO content. The maximum improvement in MOR (24.8%) and MOE (20.4%) was achieved when 1.5 wt% of ZnO was added in the styrene matrix. The increase in properties was

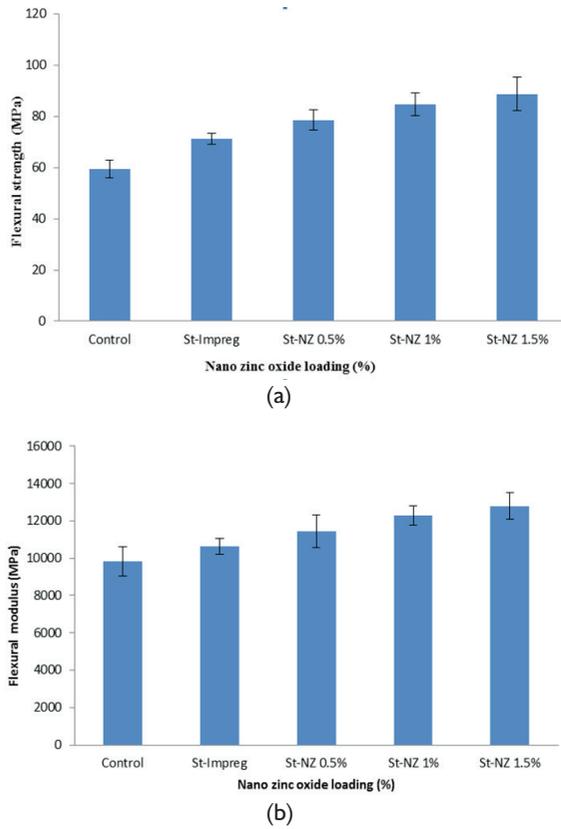


FIGURE 6 Effects of nano-ZnO content on: a) flexural strength; b) flexural modulus

attributed to the increasing positive interaction between wood, styrene and ZnO (RASHMI et al., 2012), as well as good interfacial adhesion between the nano particles and the polymer chain.

Compression strength

A noticeable increase in compression strength was observed in the WPCs with nano-zinc oxide content (Figure 7). The highest strength was obtained in samples containing the highest ZnO content. The maximum improvement in compression strength (47.1%) was achieved when 1.5

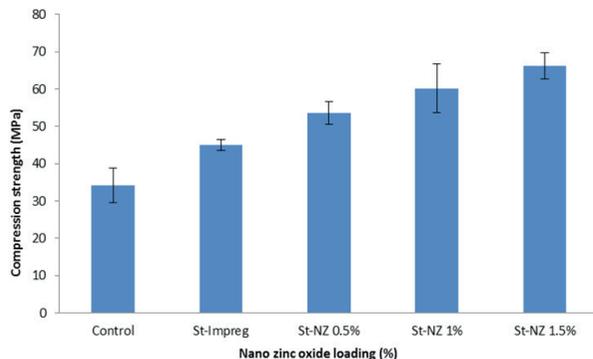


FIGURE 7 Effects of nano-ZnO content on compression strength

wt% of ZnO was added in the styrene matrix. This was attributed to the increasing positive interaction between wood, styrene and nano-zinc oxide. In addition, this interaction might have stiffened the composite due to reduction in mobility of the intercalated polymer chains, resulting in the enhancement of the compression strength.

Fire retarding properties

Ignition Time

ZnO-containing WPCs demonstrated an improvement in the ignition time (Figure 8). The highest and lowest flammability times were observed in specimens containing 1.5% nano-zinc oxide (20 s) and the control ones (15.4 s), respectively.

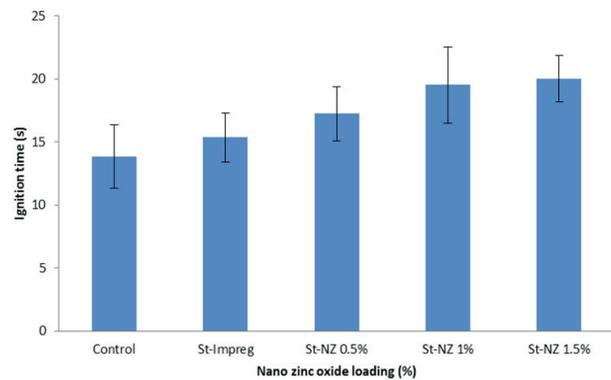


FIGURE 8 Effect of nano-zinc oxide loading content on ignition time.

Glowing time

Figure 9 shows the results of glowing time for all of treatments. Although nano-zinc oxide impregnated specimens indicated a slight increase in glowing time in the WPCs, the amount of increase was not significant in WPCs.

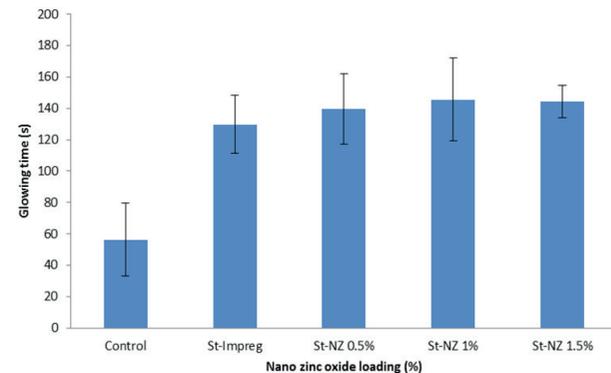


FIGURE 9 Effect of nano-znO content on glowing time.

Carbonized area

Nano-zinc oxide impregnation in all three concentrations resulted in a significant increase in the carbonized area (Figure 10). However, different

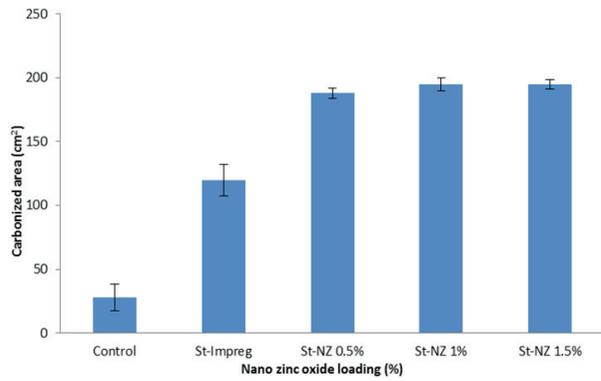


FIGURE 10 Effect of nano-zinc oxide content on carbonized area.

concentration levels showed no significant difference in the carbonized area.

The increase in the ignition time was attributed to the heat-transferring property of metal nanoparticles (WANG et al., 2010; LI, 2012; TAGHIYARI, 2012 & 2014). In fact, the heat was more quickly transferred from the spot nearest to the burning flame of the Bunsen-type burner, preventing the accumulation of heat to initiate the ignition on the spot (TAGHIYARI, 2012). However, the flammability nature of styrene caused significant easier burning effect on the surrounding area of the spot, resulting in a significant increase in the carbonized area (Figure 10).

Cluster analysis based on all physical, mechanical, and fire-retarding properties showed clear remote clustering of the control specimens (Figure 11 A). The other four treatments containing styrene and zinc oxide were clustered rather based on their nano-zinc oxide content; that is, those treatments having no or little NZ (0 or 0.5%) were clustered similarly, and those with higher NZ content (1 and 1.5%) were closely clustered together. This indicated the significant effects of both impregnation with styrene and NZ content on the overall properties of WPC.

However, cluster analysis based only on physical properties showed that although the control specimens were clustered significantly different, the other four treatments were similarly clustered, showing no significant difference between them (Figure 11 B). This demonstrated that impregnation with styrene had very significant effect on physical properties but ZnO content had no significant effect on water uptake and dimensional stability. Cluster analysis based only on mechanical properties demonstrated that the control specimens were clustered differently from the other four treatments (Figure 11 C); however, the control was more closely clustered to the treatments with no or lower ZnO contents (St and St-NZ0.5% treatments). This indicated that both St and ZnO nanoparticles had significant effect on mechanical properties. Cluster analysis based only on

the fire properties showed that the control specimens were clustered significantly different (Figure 11 D). This showed that the flammability effect of styrene on ignition time and carbonized area (Figure s 8 and 10) resulted in the final clear different clustering of St-impregnated specimens. However, the cluster analysis also showed that those specimens impregnated with only styrene (with ZnO content of zero) showed a difference, although not very significant, with those St-impregnated specimens with ZnO content (Figure 11 D). This indicated that ZnO nanoparticles could prevent some of the negative effects on fire properties caused by the flammability of styrene.

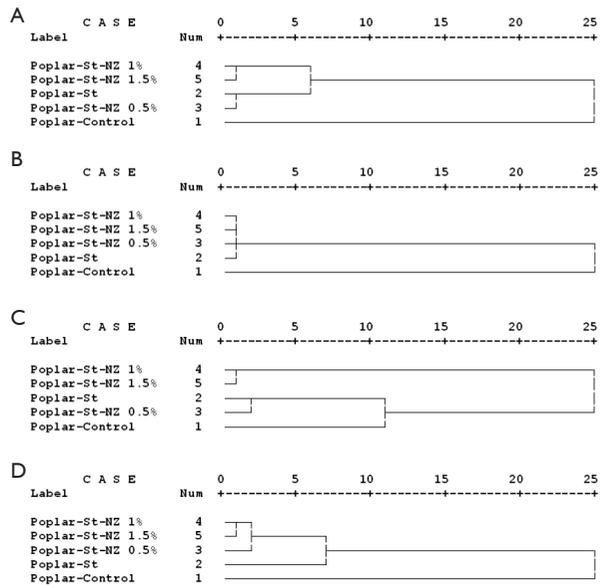


FIGURE 11 Cluster analysis of the five treatments based on all physical, mechanical, and fire-retarding properties (A); based only on physical properties (B); based on mechanical properties (C); and based only on fire-retarding properties (D) (St=styrene; NZ=nanozinc-oxide content).

It was therefore concluded that impregnation with styrene and ZnO depends entirely on the final application of the impregnated poplar wood; if the physical properties are of preliminary importance, St-impregnation can be recommended. If the mechanical properties are to be significantly improved, then both impregnation with St and NZ would be a better option. As to the fire properties, ignition time can be improved by impregnation with ZnO+ST; however, careful attention should be made because other fire properties could be aggravated.

CONCLUSIONS

Following conclusions were made based on the results of the present research project:

1- Presence of zinc oxide nanoparticles significantly improves the physical and mechanical properties in poplar wood impregnated with styrene.

2- Nano-zinc oxide effectively improves some fire-retarding properties in the modified poplar wood. However, it should be noticed that the flammability nature of styrene does not allow all fire-retarding properties to be improved. The final application of WPC should therefore be carefully supervised.

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