

**KARADENIZ TECHNICAL UNIVERSITY  
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**FOREST INDUSTRIAL ENGINEERING**



**EFFECT OF NANO-SIZED COMPOUNDS ON WOOD PRESERVATION**

**MASTER THESIS**

**Sulafa HOLY**

**JUNE 2018**

**TRABZON**



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**Sulafa HOLY**

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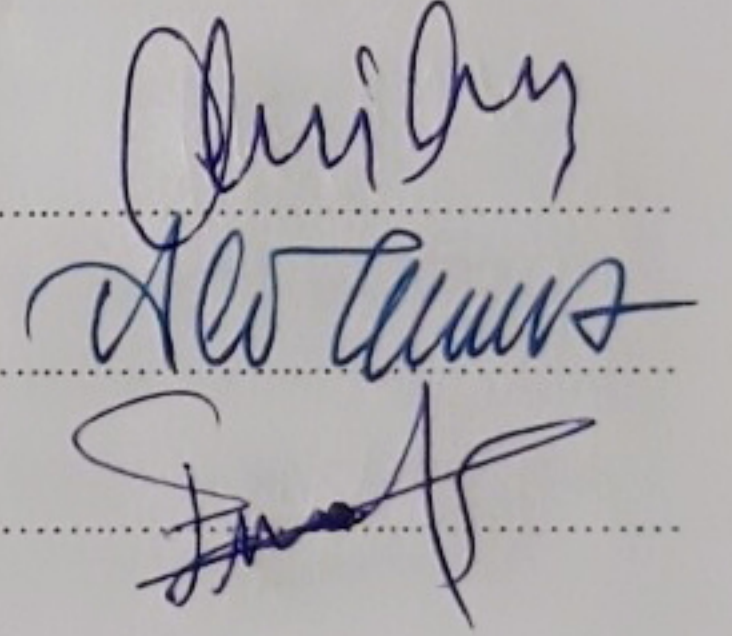
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Sulafa HOLY  
Trabzon, 2018

## **DECLARATION**

I am Sulafa HOLY hereby declare that this work, entitled “EFFECT OF NANO-SIZED COMPOUNDS ON WOOD PRESERVATION” is the results of my own research, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due reference acknowledgement have been given in the text.  
20/06/2018



Sulafa HOLY

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## CURRICULUM VITAE



Master Thesis  
SUMMARY

EFFECT OF NANO-SIZED COMPOUNDS ON WOOD PRESERVATION

Sulafa HOLY

Karadeniz Technical University  
The Graduate School of Natural and Applied Sciences  
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Supervisor: Prof. Dr. Ali TEMİZ  
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In today's wood protection technology, copper-based chemical substances are widely used. These substances have a limited effect on human health but have a negative effect on aquatic living organisms. For this reason, research on the new generation and less harmful chemicals is concentrated today. In this concept, the use of nano-sized chemical substances in wood preservation is being investigated.

In this thesis, the effects of nano-sized oxide-based Magnesium oxide, Zinc oxide, Aluminum oxide, Titanium oxide and nano-clay on the wood material were investigated. Wood samples were prepared from sapwood of Scotch pine (*Pinus sylvestris* L.). The impregnation process was carried out at different concentrations of nano-oxides and nano-clay. Then, as a secondary impregnation process, PMMA was used. The effect of nanoparticles on the physical properties of wood such as water absorption, tangential swelling, water repellent efficiency and anti-swelling efficiency was studied. Compared to control, nano-oxides and nano-clay which containing PMMA were had successful results, where water absorption rate decreasing by 25% approximately than in control samples.

By using thermo-gravimetric analysis and differential thermal analysis, the thermal properties of wood (TGA, DSC) were investigated. The results showed that addition of nanoparticles reduce flammability, as the temperature of deterioration increases of treated samples while the weight loss was lower when compared to control. In this study, also brown-rot (*Coniophora puteana*) fungi for leached samples were done. Decay results were revealed that treated wood samples generally had lower mass loss compared to control.

**Key Words:** Nano-oxides, Nano-clay, Wood Preservation



## Yüksek Lisans Tezi

### ÖZET

#### ODUN KORUMADA NANO BİLEŞİKLERİN ETKİSİ

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Günümüz odun koruma sektöründe bakır esaslı emprenye maddeleri yaygın bir şekilde kullanılmakla birlikte suda yaşayan canlılar ve insan sağlığına olası etkileri nedeniyle yeni nesil ve çevre dostu kimyasal maddeler üzerine araştırmalar devam etmektedir. Bu çalışma kapsamında nano-bileşenlerin odun korumada ki etkileri araştırılmıştır.

Tez kapsamında oksit esaslı nano bileşenlerden magnezyum oksit, çinko oksit, alüminyum oksit, titanyum oksit ve nano-kil araştırılmıştır. Sarıçam diri odunları farklı konsantrasyonlarda nano-oksitler ve nano-kil ile emprenye edilmiştir. Bu maddelerle emprenye sonrası ikincil kere PMMA (Poly Metil Metakrilat) ile muamele edilmişlerdir. Nano-oksit ve nano-kilin odunun su alması, teğetsel genişlemesi, su itici etkinliğe ve genişlemeye karşı etkinlik değerleri bulunmuştur. Kontrol örneğine kıyasla, PMMA ve nano-oksit ve nano-kil ile emprenye edilen örneklerde %25 su alımını azalttığı tespit edilmiştir.

Nano boyutlu kimyasalların odunun termal özellikleri üzerine etkisi ise TGA, DSC ile araştırılmıştır. Elde edilen sonuçlara göre, nano boyutlu kimyasal maddelerin yanmayı azalttığı ve kontrole göre daha düşük ağırlık kaybı bulunduğu tespit edilmiştir. Ayrıca, yıkanmış örnekler esmer çürüklük mantarına (*Coniophora puteana*) tabi tutulmuş olup kontrole göre daha düşük ağırlık kayıpları bulunmuştur.

**Anahtar Kelimeler:** Nano-oksitler, Nano-kil, particles, Odun Koruma

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## ABBREVIATIONS

ACA	Ammonitic Copper Arsenate
ACQ	Alkaline Copper Quaternary
ASE	Anti-Swelling Efficiency
CA	Copper Azole
CCA	Chromated Copper Arsenate
CX	Copper HDO
DSC	Differential Scanning Calorimetric
LOSP	Light Organic solvent preservative
MCQ/MCA	Micronized Copper systems
NC	Nano-Clay
NC, aa	Nano-clay solved by acetic acid
NC, ac	Nano-clay solved by acetone
NC, aa	Nano-clay solved by acetic acid
NC, ac	Nano-clay solved by acetone
PCP	Pentachlorophenol
PMMA	Polymethyl Methacrylate
TGA	Thermo Gravimetric Analysis
WA	Water Absorption
WRE	Water Repellent efficiency

## **1. INTRODUCTION**

### **1.1. Wood**

Since the inception of human being, wood material has played a crucial role in the humankind. A matter of fact is that, it still serves as a raw material for a great number of products and is also contributing to meet insatiable human demands. Constant growth in uses and an invariable part of traditional values, wood, has become an integral part of everyday human life.

Being a hygroscopic natural material, wood absorbs moisture from circumferential environment. This process depends upon a number of other factors like relative humidity, temperature, and presence of humidity in wood. In addition, these factors have a far reaching impact on properties and performance of wood. Hence, wood being used as an engineering material is greatly determined by the amount of moisture within the wood. (Samuel and Zelinka, 2010).

Anatomical classification of wood is as follows:

- Softwoods – Gymnosperms
- Hardwoods – Angiosperms

In the cross section of logs, there are two parts which are known as heartwood and sapwood. In some tree species, sapwood and heartwood can be easily distinguished by colors. However, the heartwood is sometimes the same color as sapwood. Sapwood composes of living cells but heartwood cells are dead (Shmulsky and Jones, 2011).

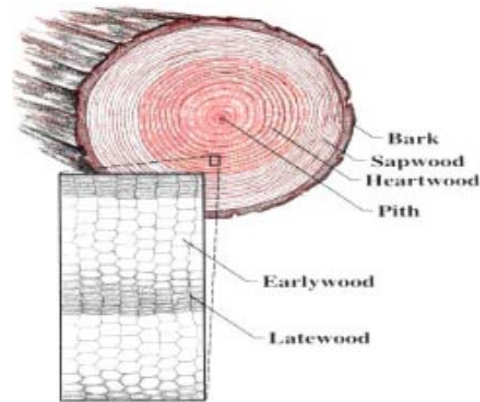


Figure 1. Cross section of log showing various wood components

## 1.2. Chemical Composition of Wood

Over time, wood has evolved as a series of complex chemical compositions. It is an amalgamation of irregular distribution of chemical compounds resulting from anatomical structure and complex physical mixtures.

The prime constituents of wood are materials with high molecular weight, which further results in high polymers penetrating deep into the interiors. This limits the capabilities to separate and isolate these polymers without significant structural changes. An exhausting research is required to clarify their structure and properties.

Elemental composition of wood is follows:

- 49% Carbon
- 44% Oxygen
- 7% Hydrogen, little traces of nitrogen, and metallic ions (ash) are also found in wood.

Organic constituents like hemicellulose, cellulose, extractives and lignin are also present in wood, as shown Table 1. The formulation of cellulose occurs by glucose anhydride units with repeating 10,000 units long. Much shorter branched chains like hemicelluloses are also polymerized by other sugars. Wood cells walls are formulated by laying down of such elements. Various sizes and shapes of these wood cells, structural elements of woody tissue, are also observed. Moreover, it is to be noted that they are firmly cemented together for the formation of wood. Some of the other structural properties of cells, usually termed as fibers, are that they are elongated, have pointed ends, and are oriented in the direction of the trunk. They come with a variable fiber length,

which depends upon the species of tree. The major cellular component, termed as cellulose, makes up about 50% of wood substance by weight. Long chains of glucose monomer are found in this high-molecular-weight linear polymer, cellulose. Considering individually, there are not large structures with largest being about 10 microns ( $\mu\text{m}$ ) in length and about 0.8nm in diameter, too small to be even observed by an electron microscope.

Table 1. Chemical Structure of Some Wood Species (Sjostrom, 1993)

<b>Compounds (%)</b>	<b>Scotch Pine</b> ( <i>P. sylvestris</i> )	<b>Spruce</b> ( <i>P. glauca</i> )	<b>Eucalyptus</b> ( <i>E. camaldulensis</i> )	<b>Silver Birch</b> ( <i>B. verrucosa</i> )
Cellulose	40	39.5	45.0	41.0
Glucomannan	16.0	17.2	3.1	2.3
Glucuronoxytan	8.9	10.4	14.1	27.5
Other polysaccharides	3.6	3.0	2.0	2.6
Lignin	27.7	27.5	31.3	22.0
Total extractives	3.5	2.1	2.8	3.0

Cellulose ( $\text{C}_6\text{H}_{10}\text{O}_5$ ), consisting of linear chains of D-glucose linked by -1,4-glycosidic bonds, contributes almost 40-45% of the dry weight of wood. Characteristics properties of molecular structure are as follows:

- Hydrophilicity
- Chirality
- Degradability
- Broad chemical variability

All of them are being characterized by reactivity of hydroxyl groups.

The character of fiber is determined by cellulose, which is essentially the most important character in the wood. Cellulose is classified as homopolysacchride, fabricated of repeating  $\beta$ -D-glucopyranosyl units, linked together by  $\beta$  (1-4) glycosidic bonds. Cellulose source and the treatment received determine the variation of DP (Hietala, 2013). Thus, the properties of cellulose are dependent upon the DP of cellulose molecules.

Hemicelluloses are considered as heteropolymers with elements like arabinoxylans, glucomannans, xyloglucons, glucuronoxytan, and xylans (Rowell et al., 2013). Hemicelluloses, which are essentially amorphous in nature, have lower DP (only 50-300)



with branched structure. The main hemicelluloses of softwood are galactoglucomannans and arabinoglucoronoxylan while hardwood consists of hemicelluloses like glucuronoxylan.

Lignin is a 3-dimensional highly branched network polymer. It is relatively an inert material, which serves the purpose of bonding and stiffening agent within the wood cell wall and the middle lamella. Lignin, which essentially consists of aromatic alcohol known as monolignols, is quite complex, amorphous and cross-linked in nature (Pettersen, 1984; Li, 2011; Stokke et al., 2014).

Wood extractives are non-structural wood constituents and simple sugars, fats, waxes, resins, proteins, terpenes, and gums are basic elements of wood extractives. For prevention system of the tree, these extractive compounds are considered quite crucial, contributing odor, color and durability as well as serve as energy reserves and support tree metabolism. (Clemons, 2008). Some traces of inorganic ash (about 1%) are also found in the wood (Rowell et al., 2013).

Wood is known as heterogeneous materials, lack of dimensional stability and easily deterioration by fungi, insects etc. The main drawback is its dimensional instability (swelling). With depend on the relative humidity of the air surrounding the wood (Mantanis, 1994; Berry and Roderic, 2005).

### **1.3. Wood Preservation**

Wood material has proved its versatility to be used in building materials. Conversely, it cannot withstand the growth of microorganisms like fungi, which by the process of enzymatic degradation breaks down the essentials of wood like cellulose, hemicellulose, and lignin. Prevention of this activity and treating wood to augment the strength and durability is termed as 'Preservation' (Corkhil, 1989).

The growth of microorganisms in the wood can be hindered by treating wood with chemicals, which either damage microorganisms' cell structure or make wood material non-suitable energy source for them. On the other hand, some preservative chemicals show the tendency to migrate from timber to neighboring area when exposed to outdoor conditions. Evaporation of chemicals from treated woods, leaching effect by water-soluble chemicals, and disintegration of solid chemicals are eventually termed as 'Migration of chemicals' from treated wood (Corkhil, 1989).

The effectiveness of biological preservation systems are depend on:

(a) The biological risk that wood has to endure during its lifetime as a commodity.

(b) Potency of the preservative chemical to destroy particularly dangerous organism for wood. Also, the lifetime of wood preservatives

(c) Penetration and retention of wood preservatives

There are three general classes of wood preservatives:

- Water-Borne
- Oil-Borne
- Organic Solvent Borne

Since 1830s, wood preservation industries have been using oil-borne and water-borne preservatives extensively to protect wood against insects, decay fungi and wood weathering. The service life of wood material can be extended by 25 to 50 years with the help of preservatives (Cooper, 2003; McBain et al., 1995).

### **1.3.1. Oil-Borne Preservatives**

Two of the most commonly used oil preservatives are creosote and pentachlorophenol (PCP). These preservatives serve the purpose to reduce surface checking and to repel suitable amount of water. In addition, these preservatives show little to no tendency to react with wood and are relatively hydrophobic with low volatility (Hunt and Garratt, 1967; Kollmann and Côté, 1968).

Construction essentials such as utility poles, bridge and railroad ties are currently preserved with the help of Creosote and Pentachlorophenol (PCP). Creosote, which is a coal tar by-product, is still every effective against fungal, insecticidal and molluscicidal properties (Schultz et al., 2008).

Wood with high moisture content is not a common effect of treatment with preservatives; however, it may shrink if there is a loss of moisture during the treating process. Wood can be protected from weathering with creosote treatment but their use also comes with disadvantages of adversely influencing the surface properties, odor, color, paintability and fire performance of wood. Removal of volatile oils or solvents with oil-borne preservatives may leave the wood cleaner than heavy oils but may not provide suitable immunity to wood. Adhesive can be applied to the wood after treating it with some preservatives, but one may also need to specially process or clean to remove surplus oils before spreading adhesive.

Application of oil-borne preservatives can be applied in hot and cold open bath or vacuum pressure impregnation. It is often quite difficult to change the concentration of oil-borne preservatives than the water-borne ones; consequently, required retentions for certain applications must be met by application in processing technique. Some of the properties of heavy-duty preservative creosote are:

- toxicity to most decay fungi and insects,
- water repellency, and
- Not altering the dimensions of wood during impregnation process

Wood treated with creosote is impervious to leaching and can be used for ground contact use classes. Excellent weathering characteristics are observed due to water repellency of creosote. There might be a strong characteristic odor when wood is treated with creosote and is usually black in color. This results in black deposits on the wood surface when 'bleeding' (Stirling and Temiz 2014).

Heavy-duty utilities such as transmission and telephone poles, railway sleepers, foundation and marine poles, bridge timbers etc. can be preserved in an excellent way with the help of creosote.

Residues of volatile inflammable solvent are observed in freshly treated timber. In order to prevent any mishap, proper evaporation of this residue in an open well ventilated is necessary for at least 48 hours before installation of the timber. Creosote is still popular in North America, for application in railroad ties. However, Europe has put reasonable regulations for its use in industrial and commercial applications and preservative industries need specific derogations to produce and sell creosote-treated products (OJEU, 2001). Since the commercialization of PCP in 1941 in North America (Lorber et al., 2002), it has been extremely popular in wood preservation due to its bacterial, fungal and algacidal abilities (Kao et al., 2005).

### **1.3.2. Organic Solvent-borne Wood Preservatives**

The term of Light Organic Solvent Preservative (LOSP) is the actual description of the carrier of the preservative and their properties vary according to their formulation with different preservative chemicals. Organic fungicides such as tributyltin-oxide and insecticides like synthetic pyrethroids are the key components of LOSPs. They are appropriate for interior and above ground hazards like housing and other buildings.

Impregnation in a vacuum pressure plant is the only way out for effective treatment of wood with LOSPs.

In comparison with Lindane (Banned), medium duty light organic solvent preservatives like TBTN-P and Azole-permethrin have relatively more acceptable ingredients regarding to health, safety, and environmental properties. They are an amalgamation of effective insecticides and fungicides into a solvent carrier, such as white spirits. This amalgamation allows them to penetrate the wood without any visible dimensional variation of the wood. Treated wood can be used internally (Undercover) or externally with the application of the appropriate protective coating and without any contact with the ground.

Some of the properties are:

- No visible discoloration.
- No odor after the solvent has fully evaporated.
- Easy to glue or paint.

These preservatives are applied in low-pressure vacuum plant and they may contain pigment or waxy oils, and plasticizers to substantially improve the appearance and capabilities of this preservative.

Residues of volatile inflammable solvent are found in freshly treated timber. Evaporation of such substances in open well-ventilated area for at least 48 hours is necessary before installation or use of treated timber (URL-1, 2018).

### **1.3.3. Water-borne Wood Preservatives**

Traditionally inorganic substance soluble in water are termed as water-borne preservatives. Recently, development has been made with additions of alternatives that contain either organic or a mixture of organic and inorganic chemicals. They come with a privilege of leaving the treated wood odorless and clean to touch and sometimes giving a color. Thus, these water-borne preservatives find their use whenever cleanliness and paint ability of wood are required. Formulations with combinations of copper, chromium, and arsenic have proved to be highly resistant to leaching and perform in an excellent way when in service (Ibach, 1999).

Two basic types of water-borne preservatives are:

- Leach Resistant: Insoluble compounds are formulated when leach resistant preservatives react chemically leading to the creation of bonds to the wood. There is no known loss of preservative on subsequent leaching.
- Leachable: There is no bonding of leachable compounds with wood; hence, they should not be used in areas with high decay hazard.

Chromated Copper Arsenate (CCA) and Ammoniacal Copper Arsenate (ACA) are two of the most commonly used salts, known for their leach resistant and suitable ground contact properties.

During treatment, often there is a dimensional variation due to wetting of the timber, but after drying out of carrier water, there is no serious repercussion on the moisture content of the wood. There is an obvious reintroduction of substantial amounts of water content in the timber when treated with water borne preservatives. Re-drying critically depends upon the dimensional stability and painting requirements of the commodity. Thus, it is absolutely necessary for timber used for building construction, playground equipment, or decorative landscaping than it is in fence posts or transmission poles. Before being transported from the treatment site, it is always recommended to dry freshly treated timber to touch. Lumber, timber posts, building foundations, poles, and piling specification include water-borne preservatives.

#### **1.3.3.1. Water-Borne Copper Containing System**

For most living cells copper is a basic micro-nutrient. In larger treat though, the copper ion proves activity as an algacide, bactericide, fungicide, insecticide, and moldicide (Richardson, 1997).

Exponentially the quantity of wood products were treated with copper-based preservatives grew through the 1970s and the 1980s and remain high till today. The features of copper compounds are: (i) comparatively easy to form water-based formulations (ii) easily to analyze and determine penetration inside wood, as well copper lags photo degradation by UV radiation and water, (Archer and Preston, 2006).

According to concerns of environmental effects of chromium and arsenic and resulting limitation of chromated copper arsenate (CCA) usage the focus on copper-based preservatives were increased. Numerous early work on copper-based formulations forms

the foundation for the ammoniacal and amine copper-based systems currently in the marketplace as CCA replacements (Preston et al., 1985, Gezer 2003).

Quate and azole as co-biocides are included in these formulations. Eventually, micronized copper formulations have been utilized with the same co-biocides. Disadvantages of using copper compounds contain; Copper tolerance appeared in a number of fungus species, a possibility of erosion to metal fasteners and aquatic toxicity (Archer and Preston, 2006).

To date, the major fungicide used for treating wood in contact with the soil is Cu (Cu carbonate, Cu citrate), and actually, there is no promising alternative yet. Soft rot fungi and other soil borne fungi are destroyed only biocides that biocides that containing copper. This is a source of the greatest damage to wood products in contact with the soil (Hughes, 2004).

More likely ion exchange followed by permeation throughout the cell is the primary uptake of copper in cells. Copper is passively accumulating in fungal spores via unappointed reactions with cell constituents. The action of fungicides in fungus requires high levels of copper absorption and it is proposed that there are different sites of action for the fungistatic and fungicidal processes (Somers, 1963, Stirling and Temiz 2014). An accumulated copper distribution in spores varies with fungal species and fungal cell walls have a varying attraction for copper. The fungal feature of copper is dependent on the affinity of different groups on the fungus proteins, especially thiol groups. Increased copper uptake by spores has noticed under anaerobic conditions and with increasing temperature, the absorption rate at 35 ° C, approximately three times at 4 ° C. The enzymatic processes are interrupted by the damage caused by excess copper, which damages proteins and lipids (Eaton and Hale, 1993; Rui and Morrell, 1994).

A specific mechanism proposed to explain is the interaction of  $\text{Cu}^{2+}$  with hydrogen peroxide, the resultant of which is reduction to  $\text{Cu}^+$  and release of free radicals from hydrogen peroxide and oxygen. An uncontrolled oxidation process is initiated via the Haber- Weiss cycle with free radicals. (Simpson et al., 1988; Gunther et al., 1995)

Copper toxicity can easily be suppressed. It can also be suppressed in some copper tolerant fungal species with augmented ammonia in alkaline copper quarternary (ACQ) i.e. presence of nitrogen source. It is attributed to stimulation of oxalic acid production. (Ruddick and Xie, 1994; Humar et al., 2005). The most commonly used biocides for wood

preservation is copper-based wood preservatives (Nicholas and Schultz, 1997, Stirling and Temiz 2014).

Microbes possess an extent of tolerance mechanisms, most featuring some kind of detoxification. Copper tolerance has been attributed to distinct mechanisms encompassing trapping of the metal by cell-wall components, changed uptake of copper when the plasma membrane of mycelium is less permeable to copper, extracellular chelation or precipitation by excreted metabolites and intracellular complexing by metallothioneins and phytochelatins (Cervantes and Gutierrez-Corona, 1994).

Copper tolerance of fungi can be tied to oxalic acid producing species like *Wolfiporia cocos* and *Poria placenta* (Sutter et al., 1983; Clausen et al., 2000; Woodward and De Groot, 1999). Calcium oxalate and copper oxalate crystals are frequently determined in decayed wood that previously treated with copper-based wood preservatives. (Choi et al., 2002) explained that copper blocks germination of the spores of copper-tolerant fungi as long as spores are not actively producing oxalic acid.

The proportional tolerance of fungal strains to copper-containing preservatives differs with the formulation of the preservative. Oxine copper displays excellent protection against decay fungi inclusive copper-tolerant fungi. In the antithesis to encourage production of oxalic acid by ACQ, CC, and CCA, oxine copper has been proved to inhibit oxalic acid production and weight loss by *P. placenta*, *W. cocos*, *Meruliporia incrassata*, and *Antrodia vaillantii*. (Clausen and Green, 2003).

#### **1.3.4. Micronized Copper System**

There are recent developments in the field of particulate-based wood preservatives, in terms of composition and size range of the particles, so as to maximize the biocidal effect and effectively shields wood in contact with the soil from biodeterioration. A mean particle size that is nano scale is evident in the currently available Cu based NPs formulations.

The durability of wood against fungal decomposition is enhanced by the use of Cu-based NPs instead of bulk Cu (Kartal et al., 2009; Cookson et al., 2010; McIntyre and Freeman, 2009; Akhtari et al., 2013b). Following are the properties, which contribute to durability:



- Ability to penetrate bordered pits because they are smaller than the mean opening (300 nm),
- Increase in the effective surface area of Cu, and enhanced dispersion stability;
- Less viscous formulations than bulk ones, and
- Presence of a reservoir effect that allows a continuous protection over time (Xue et al., 2014; Freeman and McIntyre, 2013).

These properties, which enable easier impregnation and deeper and more homogeneous uptake of the biocide into the wood, can be further enhanced by selecting specific supporting systems (e.g. surfactants) (Green and Arango, 2007). Moreover, the presence of chromium and arsenic is redundant, treatment procedure and product formulation determine the leaching of the nano-metal (Kartal et al., 2009; Preston et al., 2008; Ding et al., 2013).

#### **1.3.4.1. Water-Borne Micronized Copper Formulations**

These formulations consist of small “micronized” particles of copper compounds dispersed in the carrier rather than using dissolved copper. A number of patents and patent applications are there, which specifically cover the micronized copper technology as it relates to wood preservatives. The following provides a general review of the literature. Production of micronized particles is achieved by mechanical grinding of water or oil-insoluble copper compounds with aid of dispersing/wetting agents in a carrier using a commercial grinding mill or by chemical means resulting in 90 percent or more of the particles being less than 1000nm size.

Most frequently used carrier and dispersing agent is water and polymeric dispersant respectively, which keep the particles away from each other by attaching themselves to the surface of particles. Their presence also improves particle size reduction during milling. In addition to this, they also stabilize the particles during storage and treating. The size of these particles can range from 1 to 25000nm, penetration of wood cell walls and reaction with wood’s molecular constituents is affected by their particulate character.

There is an inverse relationship between the degree of penetration and uniformity of distribution of particles into the wood cellular structure to the prevalence of particles with relatively large particle size. Larger particles can be prepared easily but particles with long axes greater than 25000 nm may clog tracheids and inhibit the uptake of additional

preservative. If the particle size of the micronized preservative is less than the diameter of the window pit (typically 10,000nm) or membrane openings in a bordered pit (typically 400 to 600nm) openings, one can expect complete penetration and a uniform distribution of micronized preservative in wood.

Copper with slightly higher concentration in the middle lamella than in the secondary wall layer was also found out in the cell walls. In this regard, the micro distribution of copper in wood treated with dispersed copper resembles that observed in wood treated with conventional soluble copper-based wood preservatives but the amounts of copper in the cell wall components differed between the formulations. Further, experimental techniques by (Matsunaga et al., 2008) were refined and they revealed that a comparison is being made between the concentrations of metals in cell walls of wood samples treated with conventional and micronized formulations.

Distributions similar to those of Matsunaga were reported by (Stirling et al., 2008), based on Environmental Scanning Electron Microscopy (ESEM) and Energy Dispersive X-Ray Spectrometry (EDS) results. In analysis of X-ray, it was indicated that a small amount of Cu in the cell walls in both micronized copper and soluble systems was present. In their opinion, authors suggested that mobile copper was slowly released by copper containing particles in treated wood, which has the potency to further penetrate through the cell wall.

The numerous particulate deposits of copper in voids within the wood have also been discussed.

A concern was raised by (Archer, 2007) that soft rot attack might cause an issue for micronized formulations. In parallel, cell wall treatment inhibits more white rot organisms than cellumen treatment. Studies have demonstrated that copper levels in S2 layer of wood cell wall determine the capability to control soft rot in hardwoods (Hale and Eaton, 1986; Ryan and Drysdale, 1988). The effectiveness of a preservative system in withstanding depletion is also improved by cell wall treatment and hence, the good performance of many water borne wood preservatives has been attributed, in part, to the fact that there is an absorption into the cell wall and uniform distribution in the microstructure of wood (Arsenault, 1973).

To obtain micronized particles any suitable copper source can be used but copper carbonate is the most preferred one. Micronized formulations are not only limited to water-borne compositions but also organic carriers, such as oils; effectively penetrate into wood as well. Non-biocidal components are also added to enhance performance. These may

include water repellants, colorants, emulsifying agents, dispersants, stabilizers, solubilizing agents, UV inhibitors and wood dimensional stabilizers. Insecticides are consorted with micronized metal formulations, with preferred co-fungicides like quats and triazoles. Micronized copper carbonate generally has a pH in the range of 7 to 9, but more neutral or acidic pH can be procured by the inclusion of acids in the compositions.

Micronized copper treated wood shows slightly more corrosiveness in comparison with untreated lumber, but lower corrosiveness than other water-borne copper formulations to metal fasteners. A hue of lighter color is also observed in the treated wood; hence, light colored paints and stains can be implemented on the treated wood. There is no listing of micronized formulations in the AWWA standards, which contain only the various soluble formulations. The factors responsible for this are formulation confidentiality, extent of testing, and sponsor preferences (Freeman and McIntyre, 2008).

#### **1.3.4.2. Micronized Copper Fixation Mechanisms**

The micronized copper preservative particles with polymeric dispersant molecules attached to the particle surface are carried into wood through vacuum/pressure impregnation and physically deposited into the wood structure. This is in contrast to soluble copper-based wood preservative systems such as CCA, CA-B, and ACQ, wherein the  $\text{Cu}^{+2}$  ions are believed to chemically 'fix' in wood after treatment. After treatment, strong adhesion of polymeric dispersants and wood fiber by similar mechanisms occurs and micronized particles are believed to 'fix'.

The adhesion serves the purpose to anchor the micronized copper particles within the wood and arrests the particles from being dislodged by the normal weathering conditions that the treated wood may be subjected to in service. Additionally, as confirmed by the AWWA E11 leaching study (Stirling et al., 2008) and SEM Studies (Matsunaga et al 2007; Stirling et al., 2008), there is a small quantity of free  $\text{Cu}^{+2}$  is present in wood after treatment. It is quite a possibility that binding occurs between minor amounts of free  $\text{Cu}^{+2}$  ions associated with the micronized particle formulations and various components of the wood by similar mechanisms as other soluble copper preservatives such as ion exchange (Cooper, 1991). It is believed that majority of fixation in micronized systems is simple deposition as opposed to reaction.

Earlier, the micronized copper system were significantly less than the losses from the matched soluble system. Interestingly, an inverse relationship between retention and copper loss was discovered. In that, lowest retention samples showed that about 30 percent as much copper as ACQ-D lost, was lost in micronized formulation. Conversely, highest retention samples showed that the about 10 percent as much copper as ACQ-D lost, was lost in micronized formulation. In addition, the middle retention of the micronized system lost about 20 percent of the copper that ACQ-D lost (Freeman and McIntyre, 2008).

### **1.3.5. Nano-Sized System**

Nanotechnology is described as the development and application of materials, devices and systems using particles in the size range of iota 100 nanometers. Developments made by using nanotechnology are attributed to have fundamentally new properties and functions because of their structure (Siegel et al., 1999).

Unique characteristics are observed in nano-preparations of metals, such as zinc, that are completely different from the characteristics of the elemental metal. Several characteristics of metals are altered when prepared from Nano-preparation. Notable changes are in size, charge, and dispersion properties that have an exhaustive effect on performance in wood protection applications (Clausen, C.A., 2007).

Precisely controlled particle size in the 1 to 100 nanometers ranges is observed in nano-metals created by pyrolysis. It may improve penetrability of the chemical into wood relative to nano-metals prepared by grinding. Complete penetration and uniform distribution can be expected if the particle size is smaller than the diameter of the wood window pit (<10,000 rims) or the opening of the bordered pit (400 to 600 nm)(Freeman and McIntyre, 2008).

Nanotechnology can drastically affect the wood protection industry by crafting nano-materials with novel properties. An integration of small amounts of these nano-materials in coating or impregnation formulation can assist preserve the existing wood properties and can also introduce new ones. However, considering the environmental and health aspects of the technology, it is fundamental to make an emerging market sustainable (Fufa and Hovde, 2010).

In 2004, an exclusive workshop on Nanotechnology for the Forest Products Industry was conducted with the sole purpose to discern the key issue that nanotechnology can

address for the Forest Products Industry. American Forestry & Paper Association (AF&PA) and USDA Forest Products Laboratory were the sponsors of the workshop. The outcome of the workshop was a published Vision and Technology Roadmap (2005) which was developed by sponsors and participants. This Roadmap is available on the Forest Products Laboratory website (URL-2, 2017) for further reference. The discussion is about the content of roadmap for the wood protection industry. The vision includes utilizing nanotechnology to revolutionize product offerings. The key strategies to be implemented are adapting and deploying novel new nanotechnologies that can enable new generations of cost effective and value for money products. One of the key priorities is to utilize nano-materials to improve the raw material. This vision can be addressed by utilizing nanotechnology to augment durability and resistance to moisture and decay. Their key strategies always balance out our vision and key strategies. It is our charge to develop and evaluate applications for nano-materials in the frame of reference of wood protection.

Four stages of nano-development are predicted by The U.S National Nanotechnology Initiative (NNI) which will certainly take place during the nanotechnology revolution.

Stage I or the first generation of nanotechnology consists of development of passive nanostructures, which involves the development of new materials with distinctive properties and functions that would be used as part of a product. Development of coatings, films, nanobiocides or reinforcing nanofibers in new composite products will be targeted in this stage. This first stage unfolded in 2000 and is supposed to continue indefinitely as the field of nanotechnology evolves.

The second stage or the second generation undertook in 2005. It involves the revolutionary nanostructures that have the ability to change shape, size, conductivity or other properties during their use. Applications involve targeted delivery systems for drugs or nanodelivery systems for preservatives. Stage third aka the third generation nanotechnology saw its inception in 2010, when nano components materialized specific end products. Self-assembly of three-dimensional devices such as networks and guided assemblies or novel robotic devices are involved in this particular stage.

The period from 2010 to 2015 saw the expansion of nanotechnology including molecular Nano systems, heterogeneous networks in which molecules and supramolecular structures became distinct devices with self-assembly capabilities (Roco, 2006). Small robotic devices or molecular nanosystems that can operate at a high rate of speed over a wide range of environmental conditions are some of the examples of this stage.

There is an accrued interest for research and development for the use of nano-particles as filler and additives in polymers to achieve desired effects. To modify polymer capabilities, various kinds of nano-particles, including nano-carbon, carbon nano-tubes, nano-clays and metal oxides are being utilized.

#### **1.3.5.1. Zinc Oxide, Aluminium Oxide, Titanium Oxide, Magnesium Oxide**

Nano-metals may provide the basis for the next generation of wood protection products by either using them alone or in amalgamation with existing biocides. To date, there are a few reports that acknowledge the efficacy of nano-metal preparation as biocides. A wide range of antimicrobial activities against gram-positive and negative bacteria, yeast and molds are exhibited by silver (Kourai, 1996).

According to a study by Green and Arango, that evaluated silver formulations in combination with copper or zinc nanometals against termites, there were reports that testified the inhibition of termite feeding by zinc nano-particles with and without silver (Green and Arango, 2007). Conversely, a little effect on inhibition of decay and mold fungi in laboratory tests was exhibited by a report (Dorau et al., 2004).

Recently, wide attention has been received by functionalization of wood surface using inorganic nano-materials such as SiO<sub>2</sub>, titanium dioxide (TiO<sub>2</sub>), and ZnO. The key factors behind this attention are excellent mechanical, thermal, and optical properties as well as their low toxicity (Mahltig et al., 2008).

TiO<sub>2</sub> can be classified as one of the most promising functional materials. It has wide applications such as photocatalysis, solar cells, paints, and coatings because of the chemical stability and low toxicity displayed by this compound (Chen and Mao, 2007). In addition to this, protection against fungal decay and termite attack can be achieved by deposition of inorganic particles on the surfaces of woody materials (Yu et al., 2011; Shupe et al., 2012).

### 1.3.5.2. Nano-clay

With the increased commercial interest, the viable interest for the use of nano clays for the modification of polymeric material for numerous applications is quite evident (Sherman, 2007). In addition, in 2005, the consumption of clay nano-composites was almost one-quarter (24pct) of the total nano-composite consumed (Williams, 2007.) Moreover, the utilization of nano-clay composites is estimated to raise its market share to 44 pct by 2011.

Siddiqui and Ahmed (2005) reported that clay belongs to the family of minerals, however, in chemistry all clay minerals may simply be described as hydrous silicates. With essential raw material as montmorillonite, clay minerals can be classified into two broad arrays namely:

- Residual Clay
- Transported Clay (Sedimentary Clay)

Fine-grained sheet-like geometry natural structure is one of the common characteristics of clay minerals. The sheet-structured hydrous silicates are generally referred to as phyllosilicates (Uddin, 2008) With dimensions and diameter ranging from 0.002 to 0.001 mm in quartz, mica, feldspar, iron, and aluminium oxides, individual natural clay particles are smaller than 0.4mm (Anon, 2008). Colloidal clay particles, which can be spotted in layered silicate, are finer (<0.001 mm in diameter).

An important source on Montmorillonite is Bentonite. This rock formulates from highly colloidal and plastics clays composed of montmorillonite (URL-3, 2017).

Thermal barrier properties of clay minerals are known for their in heat-resistant and flame retardant applications. Similarly recently introduced nano-clays polymer composites are also being investigated for the same.

Clay minerals have various applications, ranging from industrial materials to consumption in health-related products. Moreover, an enormous interest for research and development studies of the introduction of nano-clays as fillers or additives in polymers for various desired effects is present. The increased consumption indicated by clay nano-composites had almost approached one-quarter (24pct) in 2005 of the total nano-composites utilized (Uddin, 2008).



As explained above, in today's wood preservation industry widely rely on the copper based wood preservatives such as ACQ, Tanalith E but copper has limited effect on human health but it may negative effect on aquatic living organisms. Therefore, researchers have focused on different wood modification processes such as heat and environmental chemicals. Several wood modification process were commercialized in Europa and US. One of the great potential for wood preservation is nanotechnology and nano-sized chemicals including silver, titanium, zinc, aluminum.

In this thesis, it was aimed to determine the effect of Magnesium oxide, Zinc oxide, Aluminum oxide, Titanium oxide and nano-clay (Montmorillonit) on wood properties. Physical (water absorption, tangential swelling, water repellent efficiency and anti-swelling efficiency), biological (decay resistance) and thermal properties were determined.

## **2. MATERIAL AND METHODS**

### **2.1. Material**

#### **2.1.1. Wood Material**

In this study, sapwood of Scotch pine, Class: Gymnospermae Coniferae, Subclass: Pinodidae, Family: Pinaceae, Species: Pinus) (*Pinus sylvestris* L.) specimen were utilized. The specimens have been obtained from Kepenekler Forest Products, a commercial Company in Trabzon, Turkey. The kiln dried wood samples were free from defects, splits, cracks, knots. Annual ring orientation of samples was parallel to the tangential longitudinal surface, as possible as. The Scotch pine is mainly distributed along the Black Sea area. Total distribution natural of *P.sylvestris* is 1.2 million ha (Kizilarслан and Sevgi 2013).

#### **2.1.2. Nano-sized Chemicals**

##### **2.1.2.1. Zinc Oxide**

Zinc Oxide Nanoparticles (ZnO) was obtained from GRAFEN Company in Turkey. The properties of Zinc Oxide are as follow: surface area is 30 - 50 m<sup>2</sup>/g, Average particle size is 10 - 30 nm and it has high purity 99.98 %. In wood treatment, ZnO was used at the concentration of 0.5%.

##### **2.1.2.2. Aluminum Oxide**

Aluminium Oxide Nanoparticles (Al<sub>2</sub>O<sub>3</sub>, gamma) was obtained from GRAFEN Company in Turkey. The properties of this material are as follow: surface area is 230 - 400 m<sup>2</sup>/g, Average particle size is 20 nm and it is characterized by high purity 99.99 %. In wood treatment, Al<sub>2</sub>O<sub>3</sub> was used at the concentration of 0.5%.

### **2.1.2.3. Titanium Oxide**

Titanium Oxide Nanoparticles ( $\text{TiO}_2$ , anatase) was obtained from GRAFEN Company in Turkey. The features of this compound are as follow surface area  $> 50 \text{ m}^2/\text{g}$ , average particle size 10 - 25 nm and purity 99.5 %. In wood treatment,  $\text{TiO}_2$  was used at the concentration of 0.5%.

### **2.1.2.4. Magnesium Oxide**

Magnesium Oxide Nanoparticles was obtained from GRAFEN Company in Turkey. The properties of this material are as follow surface area  $> 60 \text{ m}^2/\text{g}$ , Average particle size 10 - 30 nm and purity 99.99 %. In wood treatment,  $\text{MgO}$  was used at the concentration of 0.5%.

### **2.1.2.5. Nano Clay**

Montmorillonite nano-clay with dimethyl dialkyl amine was obtained from GRAFEN Company in Turkey. Characteristics of Nano-clay are as follow: content bulk density 200- 500  $\text{kg}/\text{m}^3$ , lateral width 0.5-2 micron, thickness (1-10 nm). Three different concentrations (5%, 10% and 15%) were prepared from Nano-clay for wood treatment.

Acetone was used as a solvent for two concentration of nano-clay (15%, 10%).

Acetic acid was used as a solvent for 15%, 10%, and 5% concentrations of nano-clay and also to dissolve nano-clay for all variations containing nano-clay as a primary treatment and then PMMA as a secondary treatment.

### **2.1.3. PMMA**

Polymethyl methacrylate (PMMA) is a transparent thermoplastic, which used to keep nano-sized and nano-clay chemicals in wood structure. PMMA was obtained from IŞIK PLASTİK Company, Gebze, Kocaeli, Turkey. Characteristics of this material are 3 mm thickness, 92% light transmittance value, confident value of up to less than 1% and very high transparency. 10% of PMMA was prepared from this material for wood treatment.

## 2.2. Methods

### 2.2.1. Preparing Nano-sized Chemicals

Nano-sized substances were prepared at 0.5% concentration and dissolved in Acetone by using Ultrasonic mixture (Sonic-VCX-750) with 25mm of mixture diameter and 50 Hz frequency. The chemicals were placed in the ultrasonic mixer at 50° C for 15 min.



Figure 2. Ultrasonic mixture

### 2.2.2. Wood Treatment process

The impregnation process was applied on all samples which have dimensional 5 x 15 x 30 mm (Radial x Tangential x Longitudinal) under vacuum (600 mmHg) for 20 min. Then samples were submerged into solutions for 20 min at atmospheric pressure. After impregnation process, the samples were taken out from solution and the extra treatment solution was mopped up from outside. Uptake was determined and used to calculate the retention for each sample. The shown below Equation 1 was used to calculate the retention of treatment solutions.

$$R = \frac{[G \times C]}{V} \times 10 \text{ kg / m}^3, \dots\dots\dots(1)$$

Where

G is the grams of treated solution uptake by the block,

C is the grams of preservative or preservative solution in 100 g of the treating solution,

V is volume of block in cubic centimeters.

After the treatment, samples treated with PMMA were polymerized at 60 °C, for 24 hour.



Figure 3. Wood treatment process

### 2.2.3. Water Absorption, Tangential Swelling, Water Repellent Efficiency, Anti Swelling Efficiency

Water absorption (WA) and thickness swelling (TS) of wood was calculated according to the AWP A E4-03. In this test, 12 replicates with 5 x 15 x 30 mm (Radial x Tangential x Longitudinal) were prepared for each formulation. Before test, the samples have dried in oven for 24 h at 70 °C, thereafter cooled in desiccators and weighed (W1) immediately. The dried samples were placed in distilled water at room temperature for 1, 2, 6, 24, 48 and thereafter 48 h intervals for 2 weeks. The specimens have been removed from distilled water after each sampling time and there were placed in filter paper to take out the surplus water from the surface and instantly their weights were taken (wet weight). Specimen thickness was determined by using wireless dimensional measurement

instrument. The values of water absorption (WA) and thickness swelling (TS) were calculated through the following formula:

$$WA(\%) = \left[ \frac{W_2 - W_1}{W_1} \right] * 100 \dots\dots\dots (2)$$

Where;

$W_1$  : The dry weight of samples (in grams)

$W_2$  : The wet of specimen in (grams)

$$TS(\%) = \left[ \frac{T_2 - T_1}{T_1} \right] * 100 \dots\dots\dots (3)$$

Where

$T_1$  : Thickness of dry samples (in millimeter)

$T_2$  : The thickness of wet specimen (in millimeter)



Figure 4. Water absorption test

Anti-swelling efficiency (ASE) was evaluated from the control and treated specimens. The maximum anti-swelling was based on volume, initially; volume swelling was estimated by calculating the volume of each sampling time for each sample and the initial volume of the same samples and calculated using the following Equation 4;

$$VS(\%) = [(V_n - V_o)/V_o] \times 100 \dots\dots\dots (4)$$

Where  $V_S$ : is the volume swelling,  $V_n$ : is the volume of sample at that sampling time,  $V_o$ : is the initial volume of same sample.

Then the ASE value was calculated by the given below formula

$$\text{ASE (\%)} = [(V_{Sc} - V_{So})/V_{Sc}] \times 100 \dots\dots\dots(5)$$

Where;

ASE: is the Anti-swelling efficiency,

$V_{Sc}$ : is the volumetric swelling for control (untreated),

$V_{So}$ : is the volumetric swelling of the treated sample.

The WRE value was estimated by calculating the water absorption average of the control for each sampling time and water absorption average per treatment for each sampling time. According to the following equation;

$$\text{WRE (\%)} = [(W_r - W_t)/W_r] \times 100 \dots\dots\dots(6)$$

Where;

$W_r$  is the water absorption average of untreated wood samples,

$W_t$  is the water absorption average of treated wood sample for every sampling time.

#### **2.2.4. Thermal Properties**

The thermal deterioration behaviors of wood samples treated with Nano-sized chemicals were measured by using a SDT Q600 Thermogravimetric Analyzer (TA Instrument Inc., USA). The tests were carried out under nitrogen at a heating rate of 10 °C/min over a temperature range of 30–600 °C. The used samples' weight for each run ranged from 5 to 10 milligrams. The weight change was recorded to be used as a function of the heating temperature. Differentiated peak temperature (DCP) was recognized as it is the temperature of the upper derivative of the weight changes over time. Heating and cooling were measured for each sample at a heating average 10 °C / min under nitrogen atmosphere. Each test sample of 5–10 mg was put in an aluminium pan and heated from 30 to 200°C and keeping at this degree for 3min, thereafter cooled down to 30 °C. The glass

transmission temperature ( $T_g$ ), melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ), and crystallinity ( $X_c$ ) have determined from the first heating scan, whereas the crystallization temperature ( $T_c$ ) and crystallization enthalpy ( $\Delta H_c$ ) were gained from the first cooling scan.  $T_m$  is known as the maximum of the endothermic melting peak and  $T_g$  as the deviation of the baseline temperature from the initial heating scan. The  $X_c$  was calculated as:

$$X_c (\%) = \left[ \frac{\Delta H_m}{\Delta H_{m(crys)}} \right] \times 100 \dots\dots\dots(7)$$

### 2.2.5. Decay Test

Sapwood specimens with the dimensions of 5 x 15 x 30 mm, (Radial x Tangential x Longitudinal) were exposed to brown rot fungi (*Coniophora puteana*) in the petri dishes, including 3% of malt agar extract. The wood samples were sterilized using autoclave at 120 °C for 30 min. Half of the each groups were leached according to AWWA E11 to determine leaching characteristic of Nano-sized chemicals. The used replicates were 6 for each treatment in the study. The incubation time was 5 months at 22 °C and 65% RH. After the decay test, samples were taken out from petri dishes and dried at 103 °C and determined mass losses according to Equation 8,

$$\text{Mass loss (\%)} = ((M_o - M_d) / M_o) \times 100 \dots\dots\dots(8)$$

Where,  $M_o$  is the oven dry mass prior to test

$M_d$  is the oven dry mass after the test.





Figure 5. Decay Test

### 2.2.6. Statistical Analyses

The tests were evaluated by using Statistical Package for the Social Sciences statistical program (IBM SPSS 22.0).

### **3. RESULTS AND DISCUSSION**

#### **3.1. Water Absorption, Tangential Swelling, Water Repellent Efficiency (WRE), Anti-Swelling Efficiency (ASE)**

According to the statistical analysis results, there were significant differences between the variables because the significance level of samples in immersion time was  $<0.05$ , thus differences between groups were found. In order to detect these differences, Duncan homogeneity for group's variations was determined.

Results were discussed statistically after immersion at 336h.

The average value ( $\bar{X}$ ) and standard deviation (St.D) of water absorption tests carried out in two weeks immersion for treated and untreated wood. Water absorption test results (%) of treated and untreated wood for nano-oxide are demonstrated in Table 2.

Table 2. Water absorption (%) of wood treated with nano-oxides and untreated wood

		WA (%) Nano-Oxides												
Variations		1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h		
ZnO	X	57.44 <sup>d,e</sup>	60.07 <sup>c,d</sup>	62.88 <sup>c</sup>	76.29 <sup>d</sup>	98.02 <sup>c</sup>	138.83 <sup>c</sup>	151.75 <sup>c</sup>	157.76 <sup>c</sup>	175.01 <sup>c</sup>	188.01 <sup>d</sup>	191.72 <sup>d</sup>		
	St.D	4.19	4.94	5.22	4.89	6.15	8.41	8.84	10.58	10.96	10.60	10.684		
ZnO + PMMA	X	32.66 <sup>b</sup>	38.61 <sup>a</sup>	40.99 <sup>a</sup>	50.01 <sup>a,b</sup>	59.61 <sup>a</sup>	86.11 <sup>a</sup>	100.23 <sup>a</sup>	110.88 <sup>a</sup>	121.91 <sup>a</sup>	128.99 <sup>a</sup>	137.81 <sup>a</sup>		
	St.D	5.27	5.03	3.92	3.16	3.98	5.77	6.10	9.06	8.17	8.19	10.19		
Al <sub>2</sub> O <sub>3</sub>	X	58.10 <sup>d,e</sup>	61.30 <sup>d</sup>	64.12 <sup>c</sup>	75.37 <sup>d</sup>	89.74 <sup>b</sup>	127.24 <sup>b</sup>	142.31 <sup>b</sup>	151.05 <sup>b,c</sup>	166.77 <sup>b</sup>	174.74 <sup>c</sup>	180.35 <sup>c</sup>		
	St.D	5.07	3.84	3.62	3.57	4.05	6.26	6.99	8.22	7.72	7.21	8.04		
Al <sub>2</sub> O <sub>3</sub> +PMMA	X	30.30 <sup>a,b</sup>	37.42 <sup>a</sup>	40.39 <sup>a</sup>	47.42 <sup>a</sup>	59.87 <sup>a</sup>	86.82 <sup>a</sup>	100.98 <sup>a</sup>	114.00 <sup>a</sup>	122.27 <sup>a</sup>	129.75 <sup>a</sup>	133.82 <sup>a</sup>		
	St.D	4.93	3.89	4.21	1.79	3.59	10.40	5.34	7.49	6.66	6.87	7.74		
TiO <sub>2</sub>	X	58.47 <sup>e,f</sup>	62.39 <sup>d,e</sup>	61.74 <sup>c</sup>	74.52 <sup>d</sup>	89.75 <sup>b</sup>	127.67 <sup>b</sup>	142.06 <sup>b</sup>	152.06 <sup>b,c</sup>	167.68 <sup>b</sup>	172.97 <sup>b,c</sup>	180.03 <sup>b,c</sup>		
	St.D	5.08	3.45	2.76	2.60	2.90	4.39	4.98	6.85	5.71	6.09	6.73		
TiO <sub>2</sub> + PMMA	X	27.47 <sup>a</sup>	36.25 <sup>a</sup>	38.89 <sup>a</sup>	48.37 <sup>a</sup>	62.02 <sup>a</sup>	85.85 <sup>a</sup>	99.06 <sup>a</sup>	112.02 <sup>a</sup>	121.95 <sup>a</sup>	128.20 <sup>a</sup>	135.27 <sup>a</sup>		
	St.D	6.94	5.8	5.00	3.94	4.99	5.73	5.68	6.17	8.42	7.46	7.53		
MgO	X	53.58 <sup>d</sup>	56.80 <sup>c</sup>	60.80 <sup>c</sup>	66.65 <sup>c</sup>	89.26 <sup>b</sup>	126.71 <sup>b</sup>	141.60 <sup>b</sup>	147.86 <sup>b</sup>	166.25 <sup>b</sup>	174.17 <sup>c</sup>	179.21 <sup>b,c</sup>		
	St.D	3.79	4.18	4.38	4.58	5.12	6.46	7.82	10.21	9.87	10.08	9.91		
MgO + PMMA	X	37.12 <sup>c</sup>	42.80 <sup>b</sup>	45.67 <sup>b</sup>	52.29 <sup>b</sup>	58.15 <sup>a</sup>	88.91 <sup>a</sup>	100.29 <sup>a</sup>	107.25 <sup>a</sup>	117.84 <sup>a</sup>	124.54 <sup>a</sup>	132.31 <sup>a</sup>		
	St.D	4.93	3.79	3.53	2.68	2.61	3.51	4.32	3.13	5.48	5.88	6.34		
Control	X	62.71 <sup>f</sup>	65.40 <sup>e</sup>	69.40 <sup>d</sup>	74.23 <sup>d</sup>	86.25 <sup>b</sup>	123.47 <sup>b</sup>	139.05 <sup>b</sup>	146.84 <sup>b</sup>	161.97 <sup>b</sup>	166.38 <sup>b</sup>	172.59 <sup>b</sup>		
	St.D	7.43	7.11	6.88	7.86	6.96	7.95	7.88	11.026	9.48	9.75	10.16		

According to Table 2, the water absorption values for ZnO treatment were between 57.44 and 191.72 and (when PMMA was added to this oxide values were ranged from 32.66% to 137.81%). Water absorption values for Al<sub>2</sub>O<sub>3</sub> samples were ranged between 58.10% to 180.35%, after the addition of PMMA was 30.30 –133.82%. It was noted that the water absorption values for TiO<sub>2</sub> were ranged between 58.47- 180.03% while with PMMA was determined 27.47-135.27%. When looking at the MgO, it was found that the water absorption values were between 53.58% and 179.21% and the values of MgO with PMMA were 37.12-132.31%. The values of control for all these groups were ranged between 62.71-172.59%.

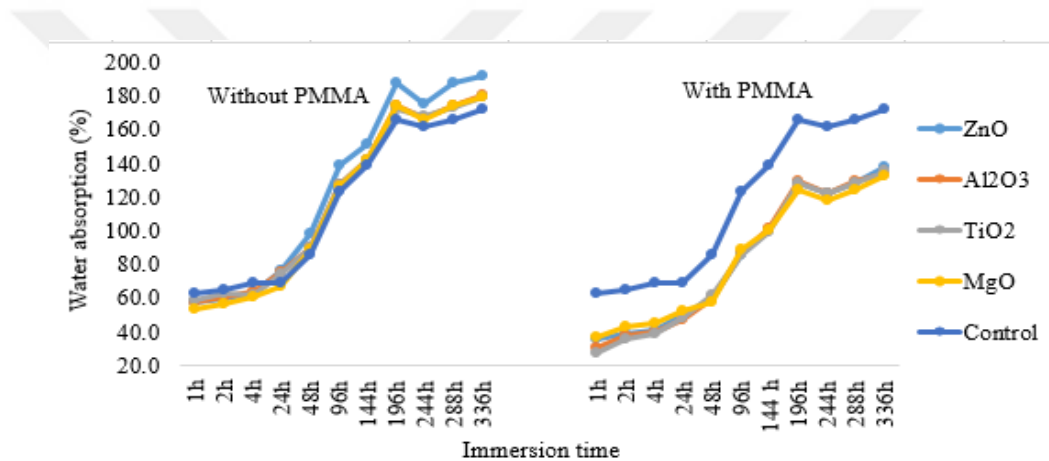


Figure 6. Water absorption (%) for wood treated with nano-oxide and untreated wood

According to Fig. 6, the control values were ranged from 62.71-172.59%. The lowest water absorption value after 336 h was in ZnO+PMMA, Al<sub>2</sub>O<sub>3</sub>+PMMA, TiO<sub>2</sub>+PMMA, MgO+PMMA 137.81%, 133.82%, 135.27%, 132.31% respectively, where statistically there were no differences among them. The addition of PMMA to the samples as a secondary impregnation for oxides treatment samples showed a significant impact of this material, as wood absorption of water decreased about 20%. This was maybe due to the nanoparticles effects and chemical structure of PMMA.

Water as liquid or vapor leads to deterioration of the wood. Nano composite coatings create a rough hydrophobic surface without affecting softness and corrosion resistance of the wood. Likewise, impregnation of nano nanoparticle reduces the pore size and space available within the cell wall which is used for absorption of water molecules.

The full and empty cell method were used in impregnation. Wood samples were first impregnated with oxides, then impregnated with PMMA. In this case, the second layer of PMMA resultant from a second impregnation process formed a layer on the wood surface which caused a slight blockage of water penetration.

The water absorption values for  $\text{TiO}_2$  180.03% and  $\text{MgO}$  179.21% were equal to the control value and slightly that  $\text{ZnO}$  191.72% and  $\text{Al}_2\text{O}_3$  180.35 % were higher than control samples.

Water absorption values (%) of treated and untreated wood for nano-clay are showed in Table 3.



Table 3. Water absorption (%) of treated with nano-clay and untreated wood

		WA (%) Nano-clay												
Variations		1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h		
15% NC, ac	X	57.64 <sup>c,d</sup>	57.34 <sup>c</sup>	62.73 <sup>c</sup>	64.84 <sup>d,e</sup>	79.08 <sup>c,d</sup>	115.64 <sup>c,d</sup>	115.64 <sup>d</sup>	139.20 <sup>d</sup>	153.63 <sup>d,e</sup>	162.00 <sup>d,e</sup>	167.97 <sup>d</sup>		
	St.D	7.17	8.49	5.19	4.39	5.30	6.02	5.92	6.34	6.09	6.68	6.76		
10%NC, ac	X	59.20 <sup>c,d</sup>	60.66 <sup>c,d</sup>	62.28 <sup>c</sup>	64.13 <sup>d</sup>	87.89 <sup>f</sup>	118.91 <sup>c,d</sup>	134.99 <sup>d,e</sup>	145.20 <sup>d,e</sup>	160.19 <sup>c,f</sup>	164.73 <sup>d,e</sup>	170.88 <sup>d</sup>		
	St.D	5.44	5.52	4.89	5.29	7.02	6.75	6.73	6.52	7.89	8.20	8.68		
15% NC, aa	X	55.33 <sup>c</sup>	60.15 <sup>c,d</sup>	60.78 <sup>c</sup>	67.90 <sup>d,e</sup>	83.81 <sup>e,f</sup>	117.06 <sup>c,d</sup>	130.45 <sup>d</sup>	138.32 <sup>d</sup>	152.70 <sup>d</sup>	159.01 <sup>d</sup>	164.76 <sup>d</sup>		
	St.D	6.53	5.45	5.22	5.14	5.13	6.27	7.47	9.39	9.29	9.75	10.33		
10% NC, aa	X	61.33 <sup>d</sup>	64.00 <sup>d</sup>	67.09 <sup>d,e</sup>	68.28 <sup>d,e</sup>	81.48 <sup>e,e</sup>	117.98 <sup>c,d</sup>	132.84 <sup>d</sup>	139.53 <sup>d</sup>	155.85 <sup>d,e,f</sup>	160.09 <sup>d,e</sup>	165.77 <sup>d</sup>		
	St.D	9.61	11.96	6.64	7.34	6.69	8.21	8.94	8.37	9.96	10.39	10.80		
5%NC,aa	X	62.08 <sup>d</sup>	62.74 <sup>c,d</sup>	64.53 <sup>c,d</sup>	68.54 <sup>e</sup>	78.84 <sup>c,d</sup>	111.23 <sup>c</sup>	131.00 <sup>d</sup>	139.86 <sup>d</sup>	156.65 <sup>d,e,f</sup>	161.93 <sup>d,e</sup>	166.82 <sup>d</sup>		
	St.D	5.14	5.05	4.71	4.78	3.84	4.72	5.35	7.06	5.49	5.98	8.08		
15% NC + PMMA	X	29.84 <sup>a,b</sup>	37.05 <sup>a,b</sup>	40.52 <sup>a,b</sup>	46.42 <sup>b</sup>	59.11 <sup>b</sup>	84.53 <sup>a</sup>	99.57 <sup>b</sup>	111.07 <sup>b</sup>	120.67 <sup>a,b</sup>	125.47 <sup>a,b</sup>	130.79 <sup>a,b</sup>		
	St.D	5.35	3.92	2.99	2.51	2.17	2.33	2.88	7.24	4.35	4.75	5.38		
10% NC + PMMA	X	28.00 <sup>a</sup>	35.95 <sup>a,b</sup>	38.61 <sup>a</sup>	42.71 <sup>b</sup>	51.47 <sup>a</sup>	80.14 <sup>a</sup>	93.98 <sup>a</sup>	101.99 <sup>a</sup>	116.11 <sup>a</sup>	121.38 <sup>a</sup>	128.24 <sup>a</sup>		
	St.D	8.39	3.97	2.83	2.90	3.00	4.20	5.13	6.10	7.47	7.92	8.46		
5% NC + PMMA	X	26.47 <sup>a</sup>	34.47 <sup>a</sup>	39.03 <sup>a</sup>	38.16 <sup>a</sup>	76.85 <sup>c</sup>	98.62 <sup>b</sup>	116.40 <sup>c</sup>	121.69 <sup>c</sup>	135.50 <sup>c</sup>	140.20 <sup>c</sup>	143.86 <sup>c</sup>		
	St.D	3.72	4.26	3.74	1.42	1.68	28.58	3.78	3.68	4.46	4.54	4.74		
PMMA	X	33.93 <sup>b</sup>	40.22 <sup>b</sup>	43.32 <sup>b</sup>	50.52 <sup>c</sup>	60.60 <sup>b</sup>	87.75 <sup>a</sup>	102.56 <sup>b</sup>	112.84 <sup>b</sup>	125.96 <sup>b</sup>	131.49 <sup>b</sup>	136.78 <sup>b</sup>		
	St.D	3.84	2.92	2.39	2.35	3.07	5.40	6.44	10.83	8.67	9.00	10.68		
Control	X	62.71 <sup>d</sup>	65.40 <sup>d</sup>	69.40 <sup>e</sup>	74.23 <sup>f</sup>	86.25 <sup>f</sup>	123.47 <sup>d</sup>	139.05 <sup>e</sup>	146.84 <sup>e</sup>	161.97 <sup>f</sup>	166.38 <sup>e</sup>	172.59 <sup>d</sup>		
	St.D	7.43	7.11	6.88	7.86	6.96	7.95	7.88	11.026	9.48	9.75	10.16		

Regarding to the results of nano-clay that the water absorption values of %15 nano-clay treatment by using acetone as solvent were ranged from 57.64 to 167.97 and with the same solvent at 10% of Nano-clay water absorption values were ranged from 59.20 to 170.88. The results of water absorption for 15% nano-clay, 10% Nano-clay, 5% nano-clay dissolved in acetic acid indicated that the values were recorded (55.33-164.76%) (61.33-165.77%) (62.08-166.82%) respectively. Values for nano-clay+ PMMA which were used a different concentration of nano-clay 15% , 10%, 5% were ranged as such (29.84-130.79%) (28.00-128.24%) (26.47-143.86%) respectively. PMMA value was (33.93-136.78%). The control value for all these groups ranged from 62.71 to 172.59%.

Water absorption of treated and untreated wood at room temperature are shown in Figure 7.

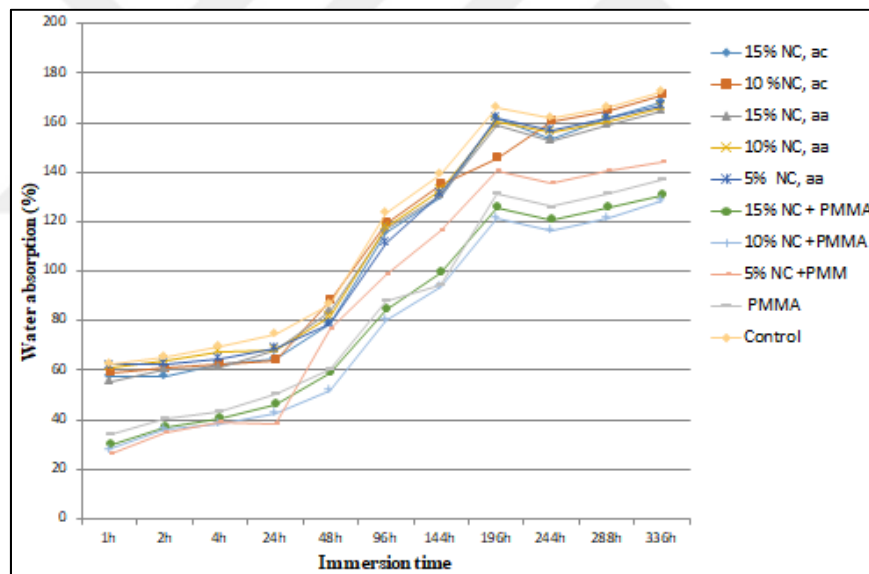


Figure 7. Water absorption (%) for wood treated with nano-oxide and untreated wood

Figure 7 shows that water absorption from the first hour to 336 h for control samples ranged (62.71-172.59%).

At 336h 15% NC, ac, and 10% NC, aa absorbed 167.97%, 170.88% water which were lower than that of control samples, however statistically, there were no significant differences between treated and untreated specimens, although the concentration varied, they gave the same result.

It was also found that water absorption of (15% NC, ac) 167.97%, (10%NC, ac) 170.88%, and (15% NC, aa) 164.76%, (10%NC, aa) 165.77% which have used a different solvent have the same result in statistical analysis. However still lower than that of control values.

(15% NC, aa) 164.76%, (15% NC + PMMA) 130.79%. It is noted that when adding PMMA water absorption decreased 20.62%, as well as in 10% NC, aa, and 10% NC +PMMA.

When considering at 15% NC + PMMA, 10% NC +PMMA, and 5% NC +PMMA the water decreases with an augmentation of the nanoclay concentration, whereas the concentration of PMMA was constant.

The uptake of both PMMA and 10% NC +PMMA were lower than control as shown in Figure 7, however statistically, 10% NC +PMMA is better because nano-clay was used as a first impregnation thus PMMA as a second impregnation. Hence, it was concluded that nanoparticles reduced wood absorption of water, thus preserving the wood properties.

Due to the small size of nanotechnology like nano-sized profoundly able to penetrate, as well as surface chemistry is change efficiently. Also give appropriate immunity against wetness (Mantanis and Papadopoulos 2010a, b).

The average value (X) and standard deviation (ST.D) Tangential swelling tests done by two weeks immersion for both treated and untreated wood are shown in Table 4.



Table 4. Tangential Swelling (%) of wood treated with nano-oxide and untreated wood

Variations	Tangential Swelling (%) - Oxides												
	1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h		
ZnO	X	6.44 <sup>a</sup>	6.21 <sup>d</sup>	6.19 <sup>d</sup>	6.59 <sup>d</sup>	6.48 <sup>c</sup>	6.53 <sup>f</sup>	6.50 <sup>d</sup>	6.38 <sup>f</sup>	6.51	6.72 <sup>d</sup>	6.47 <sup>d</sup>	
	St.D	0.54	0.46	0.41	0.50	0.58	0.42	0.40	0.73	0.46	0.65	0.53	
ZnO+PMMA	X	5.07 <sup>a</sup>	5.23 <sup>ab</sup>	5.01 <sup>ab</sup>	5.41 <sup>b</sup>	5.40 <sup>b</sup>	5.33 <sup>b,c</sup>	5.19 <sup>a</sup>	5.22 <sup>b,c</sup>	5.04 <sup>a</sup>	5.04 <sup>a</sup>	4.86 <sup>a</sup>	
	St.D	0.94	0.77	0.56	0.61	0.59	0.59	0.53	0.54	0.59	0.60	0.51	
Al <sub>2</sub> O <sub>3</sub>	X	5.77 <sup>b,c</sup>	5.93 <sup>c,d</sup>	5.78 <sup>c,d</sup>	6.05 <sup>c</sup>	5.94 <sup>c,d</sup>	5.99 <sup>d,e</sup>	5.97 <sup>b,c</sup>	5.87 <sup>d,e</sup>	5.99 <sup>b,c</sup>	6.04 <sup>b,c</sup>	5.86 <sup>b,c</sup>	
	St.D	0.35	0.42	0.37	0.50	0.53	0.47	0.60	0.40	0.46	0.43	0.43	
Al <sub>2</sub> O <sub>3</sub> +PMMA	X	4.90 <sup>a</sup>	5.00 <sup>a</sup>	5.39 <sup>b,c</sup>	5.17 <sup>ab</sup>	5.18 <sup>ab</sup>	5.37 <sup>b,c</sup>	5.05 <sup>a</sup>	5.15 <sup>b,c</sup>	5.12 <sup>a</sup>	5.22 <sup>a</sup>	4.96 <sup>a</sup>	
	St.D	0.91	0.61	0.65	0.60	0.63	0.61	0.49	0.53	0.54	0.58	0.53	
TiO <sub>2</sub>	X	5.92 <sup>c,d</sup>	6.11 <sup>c,d</sup>	6.14 <sup>d</sup>	6.38 <sup>c,d</sup>	6.31 <sup>d,e</sup>	6.35 <sup>e,f</sup>	6.45 <sup>d</sup>	6.56 <sup>f</sup>	6.35 <sup>c,d</sup>	6.33 <sup>c,d</sup>	6.27 <sup>c,d</sup>	
	St.D	0.49	0.55	0.51	0.52	0.48	0.52	0.61	0.53	0.48	0.56	0.41	
TiO <sub>2</sub> + PMMA	X	4.78 <sup>a</sup>	4.78 <sup>a</sup>	4.66 <sup>a</sup>	4.86 <sup>a</sup>	4.81 <sup>a</sup>	4.79 <sup>a</sup>	4.74 <sup>a</sup>	4.59 <sup>a</sup>	4.90 <sup>a</sup>	4.92 <sup>a</sup>	4.71 <sup>a</sup>	
	St.D	0.82	0.68	0.48	0.41	0.42	0.48	0.60	0.39	0.54	0.36	0.46	
MgO	X	6.10 <sup>c,d</sup>	6.15 <sup>d</sup>	6.15 <sup>d</sup>	6.25 <sup>c,d</sup>	6.30 <sup>d,e</sup>	6.31 <sup>e,f</sup>	6.27 <sup>c,d</sup>	6.26 <sup>e,f</sup>	6.18 <sup>c,d</sup>	6.28 <sup>c,d</sup>	6.11 <sup>c</sup>	
	St.D	0.60	0.62	0.62	0.65	0.72	0.71	0.70	0.75	0.59	0.74	0.71	
MgO+ PMMA	X	5.24 <sup>ab</sup>	5.05 <sup>a</sup>	4.99 <sup>ab</sup>	5.29 <sup>ab</sup>	5.21 <sup>ab</sup>	5.14 <sup>ab</sup>	5.20 <sup>a</sup>	5.04 <sup>b</sup>	5.23 <sup>a</sup>	5.06 <sup>a</sup>	4.96 <sup>a</sup>	
	St.D	0.68	0.51	0.33	0.48	0.50	0.51	0.46	0.50	0.49	0.45	0.49	
Control	X	5.63 <sup>b,c</sup>	5.65 <sup>b,c</sup>	5.78 <sup>c,d</sup>	5.58 <sup>b</sup>	5.65 <sup>b,c</sup>	5.76 <sup>c,d</sup>	5.75 <sup>b</sup>	5.61 <sup>c,d</sup>	5.73 <sup>b</sup>	5.69 <sup>b</sup>	5.64 <sup>b</sup>	
	St.D	0.30	0.33	0.31	0.32	0.51	0.41	0.34	0.31	0.36	0.38	0.29	

The tangential swelling values of samples submerged in water from the first hour until the time 336h were as follows: Control(5.63-5.64%), ZnO(6.44-6.47%), ZnO+PMMA (5.07-4.86%), Al<sub>2</sub>O<sub>3</sub> (5.77-5.86%), Al<sub>2</sub>O<sub>3</sub>+PMMA (4.90-4.96%), TiO<sub>2</sub> (5.92-6.27%) TiO<sub>2</sub>+PMMA (4.78-4.71%), MgO (6.10-6.11%), MgO+PMMA (5.24-4.96%).

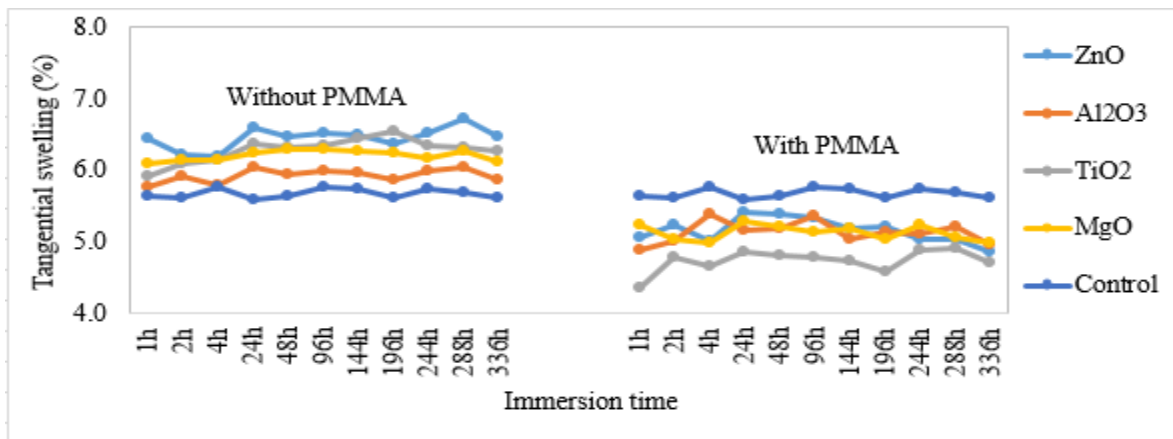


Figure 8. Tangential swelling (%) for wood treated with nano-oxide and untreated wood

The tangential swelling of wood samples at room temperature was illustrated in Figure 8.

As can be seen from Figure 8, that tangential swelling rates of wood samples can be explained at 336h. The results obviously showed that untreated wood had higher thickness swelling 5.64% than those containing PMMA. ZnO+PMMA, Al<sub>2</sub>O<sub>3</sub>+PMMA, TiO<sub>2</sub>+PMMA, MgO+PMMA 4.86%, 4.96%, 4.71%, 4.96% respectively, statistically these values were equal and they were the lowest thickness swelling.

It was evident in the figure that thickness swelling of Al<sub>2</sub>O<sub>3</sub> was equal to the values of control samples. Wood impregnated with oxides had higher tangential swelling compared to those untreated and treated with oxides+PMMA.

Table 5. Tangential Swelling (%) of wood treated with nano-clay and untreated wood

Variations	Tangential Swelling (%) - Nano-clay													
	1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h			
15% NC, ac	X	6.11 <sup>e</sup>	6.08 <sup>f</sup>	6.08 <sup>d</sup>	6.21 <sup>e</sup>	6.27 <sup>e</sup>	6.05 <sup>d</sup>	5.89 <sup>e</sup>	6.29 <sup>f</sup>	6.15 <sup>e</sup>	5.89 <sup>e</sup>			
	St.D	0.41	0.61	0.49	0.47	0.59	0.65	0.44	0.58	0.56	0.62			
10% NC, ac	X	5.90 <sup>d,e</sup>	5.73 <sup>d,e,f</sup>	5.98 <sup>d</sup>	5.99 <sup>d,e</sup>	5.90 <sup>d,e</sup>	5.76 <sup>c,d</sup>	5.62 <sup>d,e</sup>	5.83 <sup>e</sup>	5.74 <sup>d</sup>	5.54 <sup>c,d,e</sup>			
	St.D	0.51	0.47	0.63	0.54	0.41	0.40	0.38	0.59	0.40	0.47			
15% NC, aa	X	4.73 <sup>a,b</sup>	5.16 <sup>a,b</sup>	4.93 <sup>a,b</sup>	5.21 <sup>a,b,c</sup>	5.12 <sup>a,b</sup>	5.01 <sup>a</sup>	4.95 <sup>a,b</sup>	4.90 <sup>a,b</sup>	4.97 <sup>b,b</sup>	4.61 <sup>a</sup>			
	St.D	0.38	0.40	0.37	0.36	0.28	0.50	0.43	0.52	0.39	0.47			
10% NC, aa	X	5.13 <sup>b,c</sup>	5.18 <sup>a,b</sup>	5.15 <sup>a,b,c</sup>	5.30 <sup>b,c</sup>	5.07 <sup>a,b</sup>	5.14 <sup>a,b</sup>	5.04 <sup>a,b</sup>	5.11 <sup>a,b,c</sup>	5.18 <sup>a,b</sup>	5.01 <sup>a,b</sup>			
	St.D	0.64	0.74	0.78	0.62	0.56	0.58	0.68	0.62	0.59	0.64			
5% NC, aa	X	5.44 <sup>c,d</sup>	5.26 <sup>a,b,c</sup>	5.14 <sup>a,b,c</sup>	5.23 <sup>a,b,c</sup>	5.27 <sup>b,c</sup>	5.16 <sup>a,b</sup>	5.09 <sup>b,c</sup>	5.29 <sup>b,c,d</sup>	5.17 <sup>a,b</sup>	5.03 <sup>a,b</sup>			
	St.D	0.36	0.34	0.35	0.41	0.36	0.39	0.30	0.28	0.30	0.46			
15% NC + PMMA	X	4.80 <sup>a,b</sup>	5.31 <sup>a,b,c</sup>	5.29 <sup>b,c,d</sup>	5.36 <sup>b,c</sup>	5.36 <sup>b,c</sup>	5.27 <sup>b,c</sup>	5.19 <sup>a,b</sup>	5.23 <sup>a,b,c</sup>	5.30 <sup>a,b</sup>	5.23 <sup>b,c,d</sup>			
	St.D	0.92	0.44	0.49	0.51	0.49	0.54	0.48	0.50	0.50	0.43			
10% NC + PMMA	X	4.86 <sup>a,b</sup>	5.52 <sup>b,c,d</sup>	5.46 <sup>c,d,e</sup>	5.46 <sup>b,c</sup>	5.46 <sup>b,c</sup>	5.44 <sup>d</sup>	5.48 <sup>c,d</sup>	5.50 <sup>c,d,e</sup>	5.38 <sup>b,c</sup>	5.18 <sup>b,c</sup>			
	St.D	0.66	0.52	0.41	0.36	0.47	0.40	0.37	0.55	0.40	0.45			
5% NC + PMMA	X	4.50 <sup>a</sup>	4.92 <sup>a</sup>	5.19 <sup>a,b,c</sup>	5.09 <sup>a,b</sup>	5.16 <sup>a,b</sup>	5.11 <sup>a,b</sup>	5.05 <sup>a,b</sup>	5.18 <sup>a,b,c</sup>	5.21 <sup>b,c,d</sup>	4.88 <sup>a,b</sup>			
	St.D	0.86	0.52	0.64	0.52	0.48	0.49	0.49	0.61	0.57	0.42			
PMMA	X	4.97 <sup>a,b,c</sup>	4.91 <sup>a</sup>	4.77 <sup>a</sup>	4.82 <sup>a</sup>	4.84 <sup>a</sup>	4.89 <sup>a</sup>	4.77 <sup>a</sup>	4.80 <sup>a</sup>	4.79 <sup>a,b</sup>	4.72 <sup>a</sup>			
	St.D	0.59	0.50	0.53	0.49	0.47	0.36	0.34	0.62	0.51	0.41			
Control	X	5.63 <sup>d,e</sup>	5.63 <sup>c,d</sup>	5.78 <sup>e,f</sup>	5.58 <sup>c</sup>	5.65 <sup>c,d</sup>	5.75 <sup>d,e</sup>	5.61 <sup>d,e</sup>	5.73 <sup>d,e</sup>	5.69 <sup>c,d</sup>	5.62 <sup>d,e</sup>			
	St.D	0.30	0.33	0.31	0.32	0.51	0.34	0.31	0.36	0.38	0.29			

As shown in Table 5, the tangential swelling of nano-clay values were as follows: 15% NC, ac/ 10%NC, ac/ 15% NC, aa/ 10%NC, aa/ 5%NC, aa (6.08-5.89) %, ( 5.73-5.54) %, ( 4.73-4.61) %, (5.13-5.01) %, (5.44-5.03) % respectively, and nano-clay with PMMA were 15% NC + PMMA (4.80-5.23), 10% NC + PMMA (4.86-5.18) %, 5% NC + PMMA (4.50-4.88) %, PMMA (4.97-4.72)%.

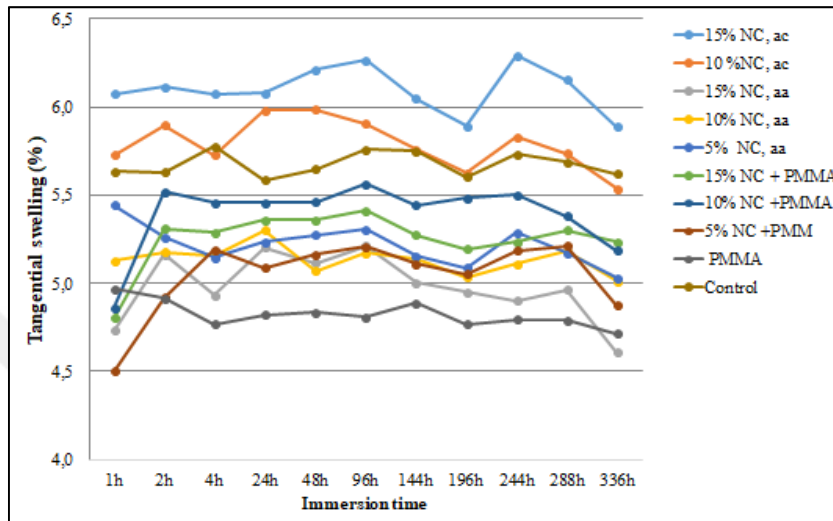


Figure 9. Tangential swelling (%) for wood treated with nano-clay and untreated wood

The results showed that the tangential swelling of control samples at 336h was 5.62%.

15% NC, aa (4.61) %, 10%NC, aa (5.01) % were lower in tangential swelling compared to control samples. This is due to the fact that the treatment of wood with nanoparticles had a significant effect in maintaining the dimensions of wood. In spite of the increased swelling values of than it was with PMMA, the swelling ratio remains lower than control samples. At the same time, impregnated wood without PMMA has given a result less than the control sample. The results showed that 10%NC, ac (5.54) %, was similar to control that meaning the concentration 10% of nanoclay using acetone as a solvent has no big effect, while the same concentration 10%NC, aa (5.01) using acetic acid as a solvent gave a good result compared to the control samples, perhaps due to the homogenization with acetic acid was better than with acetone. Control and 15%,10% NC,ac had similar result.

For reducing the swelling of wood there are numerous of approaches have used. The instability of dimensions and conformational in wood results from variable moisture

content, surface coating and adhesive can impede completion of another substances within wood, such as adhesives and surface coatings, latterly, by using wood impregnation with an appropriate hydrobes and other materials the disadvantages has been addressed (Kumar 1994, Rowell 2005, Hill 2006).



Table 6. WRE (%) of wood treated with nano-oxide and untreated wood

Variations	WRE (%) Nano-Oxide													
	1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h			
ZnO	X	8.15 <sup>ab</sup>	9.39 <sup>a</sup>	15.29 <sup>c</sup>	-13.64 <sup>a</sup>	-12.44 <sup>a</sup>	-9.13 <sup>a</sup>	5.18 <sup>a</sup>	-8.05 <sup>a</sup>	-13.00 <sup>a</sup>	-11.09 <sup>a</sup>			
	St.D	7.56	7.52	7.03	7.13	6.52	6.36	6.36	6.77	6.37	6.19			
ZnO+PMMA	X	47.91 <sup>d</sup>	40.96 <sup>d</sup>	40.94 <sup>c</sup>	32.63 <sup>d,e</sup>	30.26 <sup>c</sup>	27.92 <sup>c</sup>	33.3 <sup>c</sup>	24.74 <sup>c</sup>	22.48 <sup>c</sup>	20.15 <sup>c</sup>			
	St.D	8.02	7.70	5.65	4.26	4.47	4.39	5.45	5.05	4.92	5.90			
Al <sub>2</sub> O <sub>3</sub>	X	9.62 <sup>ab</sup>	6.27 <sup>a</sup>	7.60 <sup>a</sup>	-1.53 <sup>a</sup>	-4.05 <sup>b</sup>	-2.34 <sup>b</sup>	9.21 <sup>ab</sup>	-2.96 <sup>b</sup>	-5.03 <sup>b</sup>	-4.49 <sup>b</sup>			
	St.D	6.36	5.87	5.21	4.81	4.69	5.03	4.94	4.76	4.33	4.66			
Al <sub>2</sub> O <sub>3</sub> +PMMA	X	51.68 <sup>d,e</sup>	42.78 <sup>d</sup>	41.81 <sup>c</sup>	36.12 <sup>c</sup>	30.58 <sup>c,d</sup>	27.38 <sup>c</sup>	31.48 <sup>c</sup>	24.51 <sup>c</sup>	22.01 <sup>c</sup>	22.47 <sup>c</sup>			
	St.D	7.52	5.96	6.06	2.41	4.16	3.84	4.50	4.11	4.13	4.49			
TiO <sub>2</sub>	X	6.76 <sup>a</sup>	4.60 <sup>a</sup>	11.04 <sup>a</sup>	-0.38 <sup>a</sup>	-4.06 <sup>b</sup>	-2.17 <sup>b</sup>	8.61 <sup>ab</sup>	-3.53 <sup>b</sup>	-3.96 <sup>b</sup>	-4.31 <sup>b</sup>			
	St.D	7.76	5.28	3.98	3.50	3.37	3.58	4.11	3.53	3.66	3.90			
TiO <sub>2</sub> +PMMA	X	56.20 <sup>c</sup>	44.57 <sup>c</sup>	43.97 <sup>c</sup>	34.84 <sup>e</sup>	28.09 <sup>c</sup>	28.76 <sup>c</sup>	32.67	24.71 <sup>c</sup>	22.95 <sup>c</sup>	21.62 <sup>c</sup>			
	St.D	10.60	8.86	7.21	5.31	5.78	4.09	3.71	5.20	4.48	4.36			
MgO	X	14.56 <sup>b</sup>	13.15 <sup>b</sup>	12.39 <sup>a</sup>	10.21 <sup>b</sup>	-3.49 <sup>b</sup>	-1.83 <sup>b</sup>	11.13 <sup>b</sup>	-2.64 <sup>b</sup>	-4.68 <sup>b</sup>	-3.83 <sup>b</sup>			
	St.D	5.79	6.40	6.31	6.17	5.94	5.62	6.14	6.10	6.06	5.74			
MgO+PMMA	X	40.81 <sup>c</sup>	34.55 <sup>c</sup>	34.19 <sup>b</sup>	29.55 <sup>d</sup>	32.58 <sup>d</sup>	27.87 <sup>c</sup>	35.54 <sup>c</sup>	27.24 <sup>c</sup>	25.15 <sup>c</sup>	23.34 <sup>c</sup>			
	St.D	7.52	5.80	5.08	3.61	3.02	3.11	1.88	3.38	3.53	3.68			

Water repellent values of samples submerged in water from the first hour until the time 336h were ranged as follows: ZnO (10.63-(-11.09))%, ZnO+PMMA (47.91-20.15)%, Al<sub>2</sub>O<sub>3</sub> (9.62-(-4.49))%, Al<sub>2</sub>O<sub>3</sub>+PMMA (51.68-22.47)%, TiO<sub>2</sub> (6.76-(-4.31))% TiO<sub>2</sub>+PMMA (56.20-21.62)%, MgO (14.56-(-3.83))%, MgO+PMMA (40.81-23.34)%.

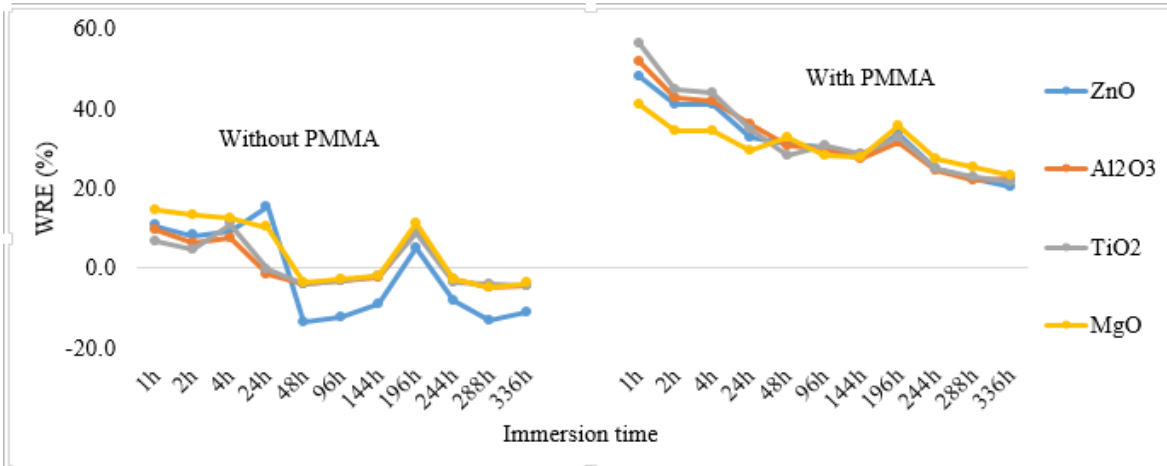


Figure 10. WRE (%) for wood treated with nano-oxide and untreated wood

Results evidenced that the water repellent values for oxides +PMMA were higher compared to oxides without PMMA. The highest WRE was occurred in MgO+PMMA 23.34 %.

Table 7. WRE (%) of wood treated with nano-clay and untreated wood

Variations	WRE (%) Nano-clay (%)													
	1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h			
15% NC, ac	X	12.32 <sup>b</sup>	9.61 <sup>b</sup>	12.65 <sup>ab</sup>	8.31 <sup>c,d</sup>	6.34 <sup>a</sup>	6.59 <sup>a</sup>	16.34 <sup>ab</sup>	5.15 <sup>b</sup>	2.63 <sup>a</sup>	2.68 <sup>a</sup>			
	St.D	12.99	7.48	5.92	6.15	4.66	4.26	3.81	3.76	4.02	3.92			
10 %NC, ac	X	7.25 <sup>ab</sup>	10.26 <sup>b</sup>	13.61 <sup>b</sup>	8.46 <sup>a</sup>	3.69 <sup>a</sup>	2.92 <sup>a</sup>	12.73 <sup>a</sup>	1.10 <sup>a</sup>	0.99 <sup>a</sup>	0.99 <sup>a</sup>			
	St.D	8.43	7.05	7.13	2.48	5.23	4.84	3.92	4.87	4.93	5.03			
15% NC, aa	X	8.03 <sup>ab</sup>	12.42 <sup>b</sup>	8.52 <sup>a</sup>	2.83 <sup>b</sup>	5.19 <sup>a</sup>	6.18 <sup>a</sup>	16.87 <sup>b</sup>	5.73 <sup>b</sup>	4.43 <sup>a</sup>	4.54 <sup>a</sup>			
	St.D	8.34	7.52	6.92	5.95	4.86	5.37	5.64	5.73	5.86	5.98			
10% NC, aa	X	2.14 <sup>a</sup>	3.32 <sup>a</sup>	8.01 <sup>a</sup>	5.53 <sup>b,c</sup>	4.45 <sup>a</sup>	4.46 <sup>a</sup>	16.14 <sup>ab</sup>	3.79 <sup>ab</sup>	3.78 <sup>a</sup>	3.95 <sup>a</sup>			
	St.D	18.28	9.57	9.88	7.76	6.37	6.43	5.03	6.15	6.24	6.26			
5%NC,aa	X	4.07 <sup>ab</sup>	7.01 <sup>ab</sup>	7.67 <sup>a</sup>	8.59 <sup>c,d</sup>	9.91 <sup>a</sup>	5.79 <sup>a</sup>	15.94 <sup>ab</sup>	3.30 <sup>ab</sup>	2.67 <sup>a</sup>	3.34 <sup>a</sup>			
	St.D	7.73	6.79	6.44	4.45	3.66	3.85	4.24	3.39	3.59	4.68			
15% NC + PMMA	X	43.35 <sup>c,d</sup>	41.61 <sup>c,d</sup>	37.46 <sup>d</sup>	31.47 <sup>e</sup>	31.54 <sup>c</sup>	28.39 <sup>c</sup>	33.24 <sup>d</sup>	25.50 <sup>d,e</sup>	24.59 <sup>c,d</sup>	24.22 <sup>c,d</sup>			
	St.D	6.00	4.30	3.39	2.52	1.81	2.07	4.35	2.69	2.85	3.11			
10% NC +PMMA	X	45.03 <sup>c,d</sup>	44.36 <sup>d</sup>	42.46 <sup>c</sup>	40.33 <sup>f</sup>	35.10 <sup>c</sup>	32.41 <sup>c</sup>	38.70 <sup>e</sup>	28.31 <sup>e</sup>	27.05 <sup>d</sup>	25.70 <sup>d</sup>			
	St.D	6.07	4.07	3.90	3.48	3.26	3.69	3.67	4.61	4.76	4.90			
5% NC +PMMA	X	47.30 <sup>d</sup>	43.76 <sup>d</sup>	48.59 <sup>f</sup>	10.90 <sup>d</sup>	20.12 <sup>b</sup>	16.29 <sup>b</sup>	26.86 <sup>c</sup>	16.34 <sup>c</sup>	15.73 <sup>b</sup>	16.64 <sup>b</sup>			
	St.D	6.51	5.40	1.92	1.95	22.16	2.72	2.21	2.76	2.73	2.75			
PMMA	X	38.50 <sup>c</sup>	37.58 <sup>c</sup>	31.94 <sup>c</sup>	29.74 <sup>e</sup>	28.93 <sup>c</sup>	32.16 <sup>c</sup>	19.05 <sup>d</sup>	22.23 <sup>d</sup>	20.97 <sup>c</sup>	20.75 <sup>c</sup>			
	St.D	4.47	3.45	3.16	3.56	4.19	20.95	16.69	5.35	5.41	6.19			



According to Table 7, WRE for wood treated by nano-clays were ranged as follows: 15% NC, ac/ 10%NC, ac/ 15% NC, aa/ 10%NC, aa/ 5%NC, aa (8.09-2.68) %, (5.61-0.99) %, (11.76-4.54) %, (2.21-3.95) %, (1.01-3.34) % respectively. Nano-clay with PMMA are 15% NC + PMMA (52.41-24.22), 10% NC + PMMA (55.35-25.70) %, 5% NC + PMMA (57.79-16.64) % and PMMA was (45.90-20.75) %.

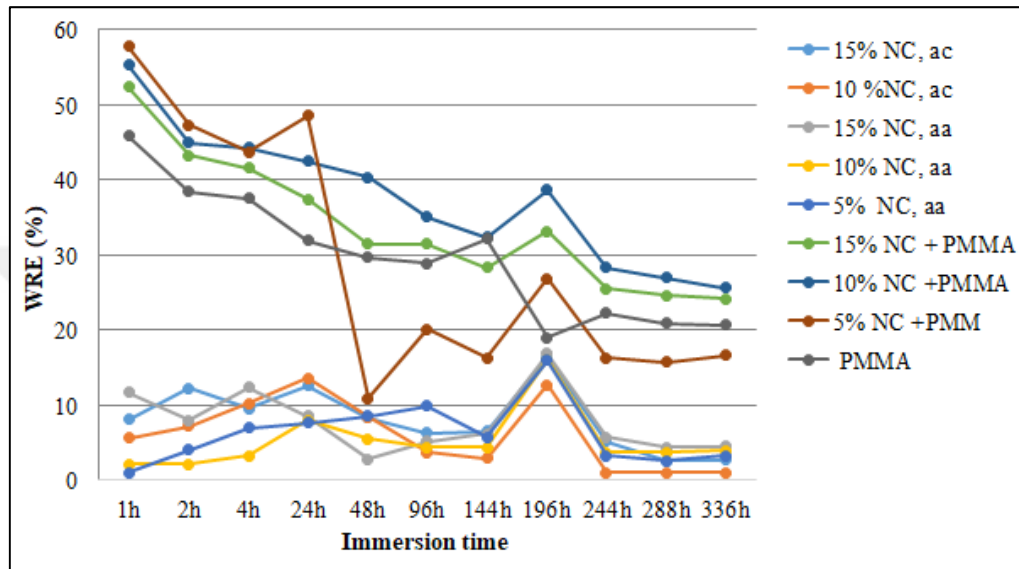


Figure 11. WRE (%) for wood treated with nano-clay and untreated wood

The highest values for WRE were 10% NC + PMMA 25.70%, 15% NC + PMMA 24.22% and 5% NC + PMMA 16.64%.

Obviously, as shown in Fig.11, the rate of WRE decreased with the decreased of nano-clay concentration. 10%NC, ac 0.99%, where was the lowest value of WRE .

It is noticed using a different solvent did not do an effect on WRE(15% NC, ac/15% NC, aa).

Nanotechnology can drastically affect the wood protection industry by crafting nano-materials with novel properties. An integration of small amounts of these nano-materials in coating or impregnation formulation can assist preserve the existing wood properties and can also introduce new ones (Fufa and Hovde, 2010).

Table 8. ASE (%) of wood treated with nano-oxide and untreated wood

		ASE (%) -Nano-Oxides													
Variations		1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h			
ZnO	X	13.95 <sup>a</sup>	15.57 <sup>a</sup>	15.26 <sup>b</sup>	14.48 <sup>b</sup>	12.87 <sup>ab</sup>	15.15 <sup>b</sup>	15.10 <sup>b</sup>	21.64 <sup>c</sup>	12.98 <sup>b,c</sup>	13.66 <sup>a</sup>	11.37 <sup>a</sup>			
	St.D	5.61	5.95	7.47	7.40	4.98	8.72	2.30	2.57	4.13	9.25	4.41			
ZnO+PMMA	X	36.10 <sup>d</sup>	34.79 <sup>c</sup>	37.72 <sup>d,e</sup>	37.35 <sup>d</sup>	36.02 <sup>c,d</sup>	33.63 <sup>d</sup>	36.08 <sup>d</sup>	36.45 <sup>d</sup>	40.32 <sup>c,d</sup>	44.43 <sup>c</sup>	47.37 <sup>e</sup>			
	St.D	3.70	6.63	7.55	8.45	7.60	8.51	8.37	6.63	7.07	8.61	9.72			
Al <sub>2</sub> O <sub>3</sub>	X	17.67 <sup>a</sup>	15.89 <sup>a</sup>	18.44 <sup>b,c</sup>	14.58 <sup>b</sup>	16.09 <sup>b</sup>	17.21 <sup>b,c</sup>	22.87 <sup>c</sup>	17.05 <sup>b</sup>	17.22 <sup>b</sup>	14.76 <sup>a</sup>	9.03 <sup>a</sup>			
	St.D	7.72	6.76	7.53	7.92	10.72	3.86	7.00	6.43	7.31	5.72	5.37			
Al <sub>2</sub> O <sub>3</sub> +PMMA	X	40.33 <sup>c</sup>	43.05 <sup>d</sup>	34.46 <sup>d</sup>	39.00 <sup>d</sup>	37.97 <sup>d</sup>	40.76 <sup>e</sup>	39.22 <sup>d</sup>	34.39 <sup>d</sup>	38.90 <sup>c</sup>	38.77 <sup>b,c</sup>	38.94 <sup>c,d</sup>			
	St.D	8.90	7.29	6.96	6.36	6.60	7.14	7.70	7.63	5.60	7.42	5.89			
TiO <sub>2</sub>	X	14.33 <sup>a</sup>	15.47 <sup>a</sup>	6.61 <sup>a</sup>	6.06 <sup>a</sup>	6.52 <sup>a</sup>	9.53 <sup>a</sup>	8.23 <sup>a</sup>	6.16 <sup>a</sup>	11.90 <sup>a</sup>	13.10 <sup>a</sup>	13.29 <sup>ab</sup>			
	St.D	4.71	6.04	3.19	3.36	3.73	3.46	2.53	3.43	5.27	7.88	7.60			
TiO <sub>2</sub> +PMMA	X	44.93 <sup>c</sup>	40.03 <sup>d</sup>	40.74 <sup>e</sup>	38.77 <sup>d</sup>	37.59 <sup>c,d</sup>	39.60 <sup>e</sup>	46.82 <sup>e</sup>	44.98 <sup>e</sup>	44.72 <sup>d</sup>	42.81 <sup>c</sup>	42.78 <sup>d</sup>			
	St.D	9.53	8.80	7.84	8.59	7.78	5.68	5.89	5.90	5.79	9.07	6.64			
MgO	X	15.12 <sup>a</sup>	21.13 <sup>b</sup>	22.13 <sup>c</sup>	17.92 <sup>b</sup>	12.84 <sup>ab</sup>	20.91 <sup>c</sup>	16.46 <sup>b</sup>	17.96 <sup>b,c</sup>	16.76 <sup>b</sup>	13.34 <sup>a</sup>	16.48 <sup>b</sup>			
	St.D	7.78	4.43	2.57	8.06	7.55	6.74	9.73	8.47	7.57	9.78	5.32			
MgO+PMMA	X	30.85 <sup>b</sup>	32.57 <sup>c</sup>	38.92 <sup>d,e</sup>	31.18 <sup>c</sup>	30.22 <sup>c</sup>	35.92 <sup>d,e</sup>	36.11 <sup>d</sup>	38.58 <sup>d</sup>	36.26 <sup>c</sup>	35.89 <sup>b</sup>	35.35 <sup>c</sup>			
	St.D	9.02	9.61	6.12	6.90	7.54	8.02	5.10	6.17	8.49	7.44	8.38			

Returning to the Table 8 above, it was found that anti-swelling efficiency values were as follows: ZnO (13.95-11.37)%, ZnO+PMMA (36.10-47.37)%, Al<sub>2</sub>O<sub>3</sub> (17.67-9.03)%, Al<sub>2</sub>O<sub>3</sub>+PMMA (40.33-38.94)%, TiO<sub>2</sub> (14.33-13.29)% TiO<sub>2</sub>+PMMA (44.93-42.78)%, MgO (15.12-16.48)%, MgO+PMMA (30.85-35.35)%.

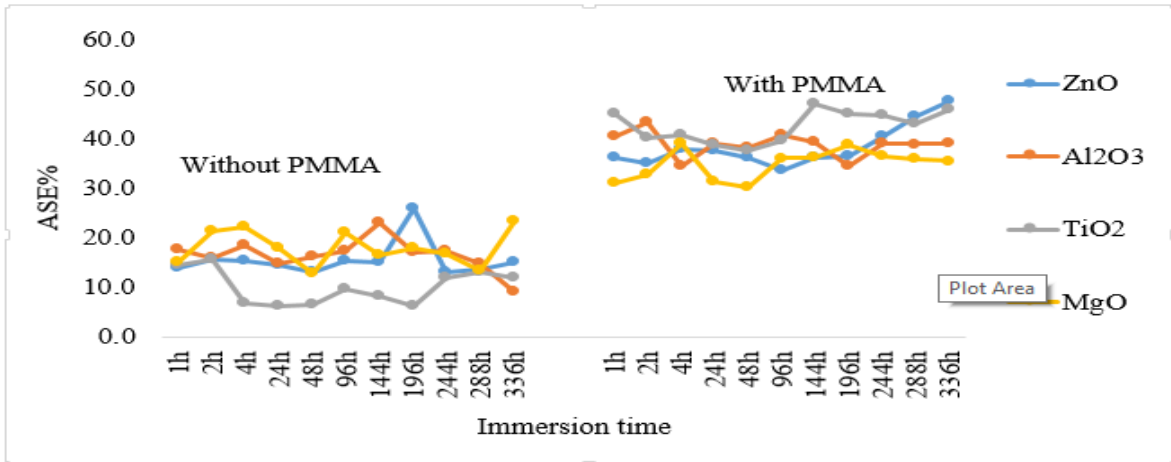


Figure 12. ASE (%) of wood treated with nano-oxide and untreated wood

According to Figure 12, the highest value of ASE was found in ZnO+PMMA 47.37%.

Results showed that the oxides with PMMA had a higher ASE values compared to those without PMMA, hence, the effect of the PMMA was evident when added to the oxides. For instance, TiO<sub>2</sub> 13.29% and when PMMA was added ASE was increased 68.9%.

Table 9. ASE (%) of wood treated with nano-clay and untreated wood

		ASE (%) - Nano-clay											
		1h	2h	4h	24h	48h	96h	144h	196h	244h	288h	336h	
15% NC, ac	X	20.88 <sup>b</sup>	15.42 <sup>a</sup>	17.72 <sup>a</sup>	19.65 <sup>a</sup>	10.81 <sup>a</sup>	11.18 <sup>a</sup>	11.71 <sup>a</sup>	14.14 <sup>a</sup>	9.00 <sup>a</sup>	12.07 <sup>a</sup>	14.63 <sup>a</sup>	
	St.D	9.58	4.65	8.04	6.07	5.38	3.01	4.41	4.17	3.61	7.10	6.57	
10 %NC, ac	X	13.33 <sup>a</sup>	22.18 <sup>b</sup>	19.06 <sup>a</sup>	20.72 <sup>a</sup>	19.02 <sup>b</sup>	16.72 <sup>b</sup>	10.55 <sup>a</sup>	15.73 <sup>a</sup>	15.67 <sup>b</sup>	21.12 <sup>b</sup>	19.92 <sup>b</sup>	
	St.D	7.18	4.62	6.81	6.98	6.57	3.85	4.58	5.99	4.82	7.87	8.0	
15% NC, aa	X	42.07 <sup>d</sup>	42.65 <sup>e</sup>	34.25 <sup>b</sup>	37.54 <sup>c</sup>	35.80 <sup>d</sup>	34.12 <sup>c,d</sup>	41.12 <sup>d</sup>	40.48 <sup>c,d</sup>	36.41 <sup>c</sup>	36.10 <sup>c</sup>	42.93 <sup>e,f</sup>	
	St.D	8.33	7.79	7.60	7.76	8.95	8.46	5.46	7.50	7.24	6.20	4.29	
10% NC, aa	X	29.56 <sup>c</sup>	31.92 <sup>c,d</sup>	34.40 <sup>b</sup>	34.60 <sup>c</sup>	36.80 <sup>d,e</sup>	36.79 <sup>c,d,e</sup>	37.35 <sup>c</sup>	37.24 <sup>b,c</sup>	37.57 <sup>c</sup>	39.26 <sup>c,d</sup>	34.56 <sup>c</sup>	
	St.D	5.78	7.68	7.44	9.70	7.26	7.76	6.52	6.82	9.46	7.38	5.06	
5%NC,aa	X	23.29 <sup>b</sup>	28.24 <sup>c</sup>	32.46 <sup>b</sup>	28.74 <sup>b</sup>	28.08 <sup>c</sup>	32.08 <sup>c</sup>	35.23 <sup>b,c</sup>	35.12 <sup>b</sup>	35.26 <sup>c</sup>	38.42 <sup>c,d</sup>	36.59 <sup>c,d</sup>	
	St.D	4.06	7.71	8.05	7.71	7.95	4.77	5.06	7.27	5.80	4.90	9.88	
15% NC + PMMA	X	39.76 <sup>d</sup>	40.16 <sup>e</sup>	35.83 <sup>b</sup>	35.11 <sup>c</sup>	35.07 <sup>d</sup>	36.06 <sup>c,d,e</sup>	34.47 <sup>b,c</sup>	39.03 <sup>b,c,d</sup>	35.83 <sup>c</sup>	36.01 <sup>c</sup>	36.68 <sup>c,d</sup>	
	St.D	8.87	4.48	6.28	7.64	7.12	6.79	5.68	6.01	6.65	7.34	8.08	
10% NC +PMMA	X	39.75 <sup>d</sup>	35.61 <sup>d</sup>	33.89 <sup>b</sup>	37.97 <sup>c</sup>	37.23 <sup>d,e</sup>	37.73 <sup>d,e</sup>	34.12 <sup>b,c</sup>	41.81 <sup>d</sup>	35.37 <sup>c</sup>	42.65 <sup>d</sup>	40.95 <sup>d,e,f</sup>	
	St.D	7.37	5.55	6.80	7.83	8.20	5.36	4.91	3.47	8.74	5.72	4.51	
5% NC +PMMA	X	36.95 <sup>d</sup>	40.10 <sup>e</sup>	34.54 <sup>b</sup>	36.89 <sup>c</sup>	34.95 <sup>d</sup>	36.00	31.49 <sup>b</sup>	38.94 <sup>b,c,d</sup>	36.93 <sup>c</sup>	39.59 <sup>c,d</sup>	38.21 <sup>c,d,e</sup>	
	St.D	9.68	5.23	5.94	8.86	7.94	4.19	5.80	4.53	8.93	6.87	7.27	
PMMA	X	42.55 <sup>d</sup>	42.47 <sup>e</sup>	42.00 <sup>c</sup>	45.66 <sup>d</sup>	42.45 <sup>e</sup>	39.94 <sup>f</sup>	42.47 <sup>b</sup>	42.36 <sup>d</sup>	45.30 <sup>d</sup>	43.75 <sup>d</sup>	46.06 <sup>f</sup>	
	St.D	7.90	8.58	8.37	6.43	9.06	8.47	6.38	9.31	6.73	8.74	8.70	

As mentioned in Table 9 ,the ASE values of nano-clay were: 15% NC, ac/ 10%NC, ac/ 15% NC, aa/ 10%NC, aa/ 5%NC, aa (20.88-14.63) %, (13.33-19.92) %, (42.07-42.93) %, (29.56-34.56) %, (23.29-36.59) % respectively. Nano-clay with PMMA are 15% NC + PMMA (39.76-36.68), 10% NC + PMMA (39.75-40.95) %, 5% NC + PMMA (36.95-38.21%) and PMMA was (42.55-46.06%).

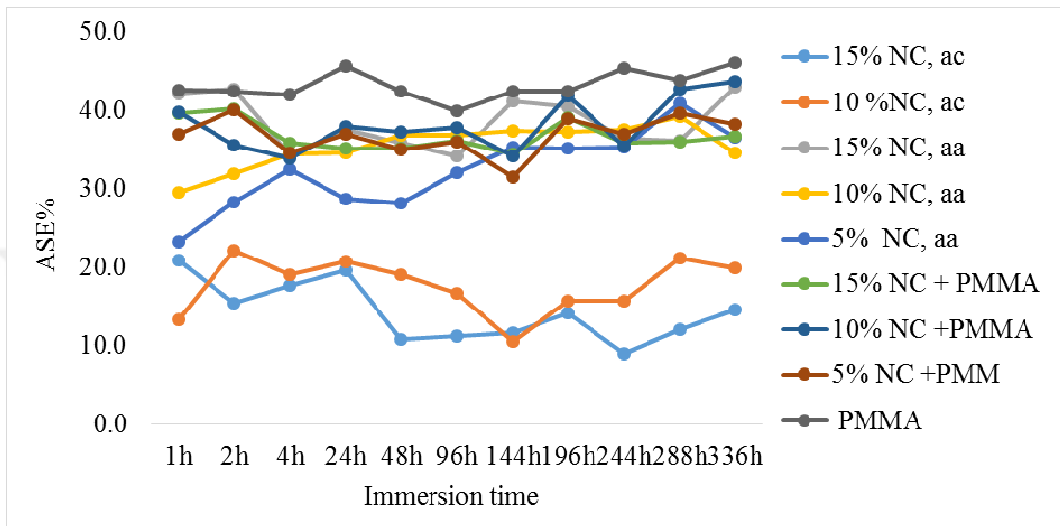


Figure 13. ASE (%) of wood treated with nano-clay and untreated wood

According to Fig.13 at 336h 15% NC, aa 42.93%, 10% NC + PMMA 40.95% and PMMA 46.06% were the highest values recorded for the anti-swelling test.

The lowest value for anti-swelling was in 15% NC, ac 14.63%. In the anti-swelling efficiency, it was obvious that the difference in solvent may affect on the effectiveness of swelling as shown in Fig.13.

When acetone was used as a solvent values dropped significantly, for example 15% NC, ac 14.63%, and 15% NC, aa 42.93%, this may be attributed to the rapid evaporation of acetone leaving a vacuum inside the wood.

Nanotechnology can drastically affect the wood protection industry by grafting nano-materials with novel properties. An integration of small amounts of these nano-materials in coating or impregnation formulation can assist preserve the existing wood properties and can also introduce new ones (Fufa and Hovde 2010).

## **3.2. Thermal Properties of Wood**

### **3.2.1. Thermo Gravimetric Analysis (TGA)**

The measurement of weight loss used as a function of time and temperature has included in the thermogravimetric analysis. In the thermal Mass Analysis, each variation was heated to 800 ° C.

Weight loss in the initial temperature value (°C), deteriorated temperature value (°C) and deterioration steps and amount of substance remaining at 790 °C (%) of the samples are given in Table 10.

One of the most common methods which is used to determine the efficiency of the fire is TGA, in existence of nitrogen in a heated chamber a fine ground samples is weighted and exposed to this chamber, the specimen is hanging on a sensitive balance that gauges the mass loss when the system is heated. Nitrogen or another gas influx around the sample to eliminate the pyrolysis or combustion output. Weight loss is be restricted as a function of time and temperature (Hill, 2006).

In thermogravimetric analysis, first the thermal degradation of hemicelluloses and then the degradation of the cellulose occurs. Due to dehydration, polymerization, oxidation, CO<sub>2</sub> formation, formation of carbonyl and carboxyl groups, thermal degradation occurs at low temperatures. At higher temperatures, evaporation quickly occurs. Unlike hemicellulose and cellulose, lignin degradation takes a long time (Guo et al., 2000; Nassar et al., 1999).

Weight loss percentage at different temperature and residual ratio at 790°C for both treated nano- (oxide and,clay) and untreated wood were shown in Tables 10,11 and Figures 14,15.

Table 10. TGA (%) of wood treated with nano-oxide and untreated wood

Nano-Oxides												
Variations	Starting temp. (°C)	Distortion point (°C)	TGA %								Residual at 790°C %	
			10%	20%	30%	40%	50%	60%	70%	80%		
ZnO	28.75	403.31	247.23	307.62	330.60	348.17	361.24	370.76	382.25	516.13	16.82	
ZnO+PMMA	31.00	433.91	267.75	315.61	338.45	355.03	366.28	374.95	391.85	450.93	15.19	
Al <sub>2</sub> O <sub>3</sub>	26.98	403.31	246.92	307.32	330.25	347.82	360.83	370.34	379.99	467.62	15.46	
Al <sub>2</sub> O <sub>3</sub> +PMMA	30.94	430.46	260.43	312.70	334.66	352.13	364.21	373.71	387.99	436.90	14.03	
TiO <sub>2</sub>	31.40	402.44	254.30	308.37	330.37	347.03	360.07	370.45	380.10	478.65	15.94	
TiO <sub>2</sub> +PMMA	26.58	433.91	259.95	314.07	336.98	354.49	365.73	375.25	393.13	465.75	15.73	
MgO	32.23	405.06	242.55	306.41	330.17	346.82	360.72	370.23	381.74	533.80	17.32	
MgO+PMMA	24.86	433.91	266.96	314.81	336.77	354.23	365.39	374.05	390.10	436.48	14.35	
Control	24.33	402.86	241.50	297.36	322.14	340.55	354.50	365.80	376.35	465.45	15.62	

Table 10 shows that ZnO+PMMA, TiO<sub>2</sub>+PMMA, MgO+PMMA 433.91 °C were the highest distortion temperature. The lowest distortion temperature was TiO<sub>2</sub> 402.44 °C. It also showed that at 790 °C Al<sub>2</sub>O<sub>3</sub>+PMMA samples was the lowest residual percentage, and MgO was the highest residual percentage.

The results evidence that the highest residual percentages were, MgO, ZnO, TiO<sub>2</sub> (17.32 °C) (16.82 °C) (15.94 °C) respectively, while residual %of control samples were (15.62 °C).

Oxides+PMMA have the highest distortion temperature degree. The distortion temperature of TiO<sub>2</sub> was less than control samples but at 790 °C the residual percentage of it was higher than control samples. In view of the oxides without PMMA, they found that they had a greater residual ratio when compared to control samples.

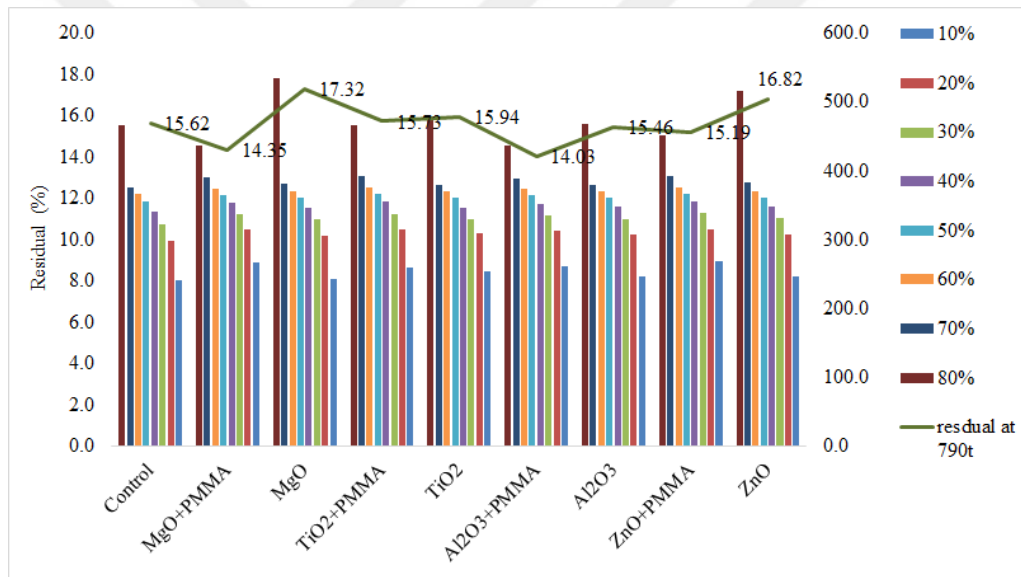


Figure 14. Weight loss (%) of wood treated with nano-oxides and untreated wood at different temperatures

As shown in Fig.14 although distortion temperature for MgO was lower than some formulations in distortion temperature it was the largest residual percentage. This may be refer that MgO was a high fire-resistant.

It was noticed that distortion temperature of oxides such as ZnO, TiO<sub>2</sub>, and MgO was lower than of those containing PMMA, but their residual percentages were higher.



Table 11. TGA (%) of wood treated with nano-oxide and untreated wood

Group	Starting temp. (°C)	Distortion point (°C)	Nano-clay										Residual at 790°C %	
			TGA %											
			10%	20%	30%	40%	50%	60%	70%	80%				
%15 NC, ac	37.56	404.47	260.96	309.55	348.18	348.18	348.18	348.18	348.18	361.14	370.63	381.30	519.15	17.18
%10 NC, ac	25.80	405.14	251.77	307.61	329.60	347.16	347.16	347.16	347.16	360.18	369.67	379.36	466.97	15.41
15% NC, aa	24.93	403.14	248.86	304.75	326.76	344.33	344.33	344.33	344.33	357.33	366.82	378.28	483.52	16.05
10% NC, aa	27.36	403.81	253.11	306.27	328.23	345.73	345.73	345.73	345.73	357.89	368.25	379.83	511.88	16.99
5% NC, aa	35.96	408.26	257.89	307.38	329.33	346.79	346.79	346.79	346.79	358.90	368.38	379.90	511.96	16.91
15% NC +PMMA	24.97	433.74	259.78	311.16	333.10	350.60	350.60	350.60	350.60	362.72	372.25	389.21	464.41	15.67
10% NC +PMMA	29.02	435.51	254.89	309.67	332.48	349.91	349.91	349.91	349.91	361.97	371.45	387.58	453.41	15.24
5% NC +PMMA	32.22	433.84	258.48	311.49	334.34	351.79	351.79	351.79	351.79	363.85	373.37	392.09	439.83	11.66
PMMA	25.73	436.89	264.06	312.88	334.81	352.26	352.26	352.26	352.26	364.33	372.97	388.12	429.97	13.67
Control	24.33	402.86	241.5	297.36	322.14	340.55	340.55	340.55	340.55	354.50	365.80	376.35	465.45	15.62

In Table 11, it was found that the highest distortion temperature was for PMMA 436.89°C and the lowest distortion temperature was for control samples 402.86°C. The distortion temperature for 15% NC, aa was 403.14 °C and Arrived to 433.74°C when PMMA was added. The same case happened with 10% NC, aa and 10% NC +PMMA.

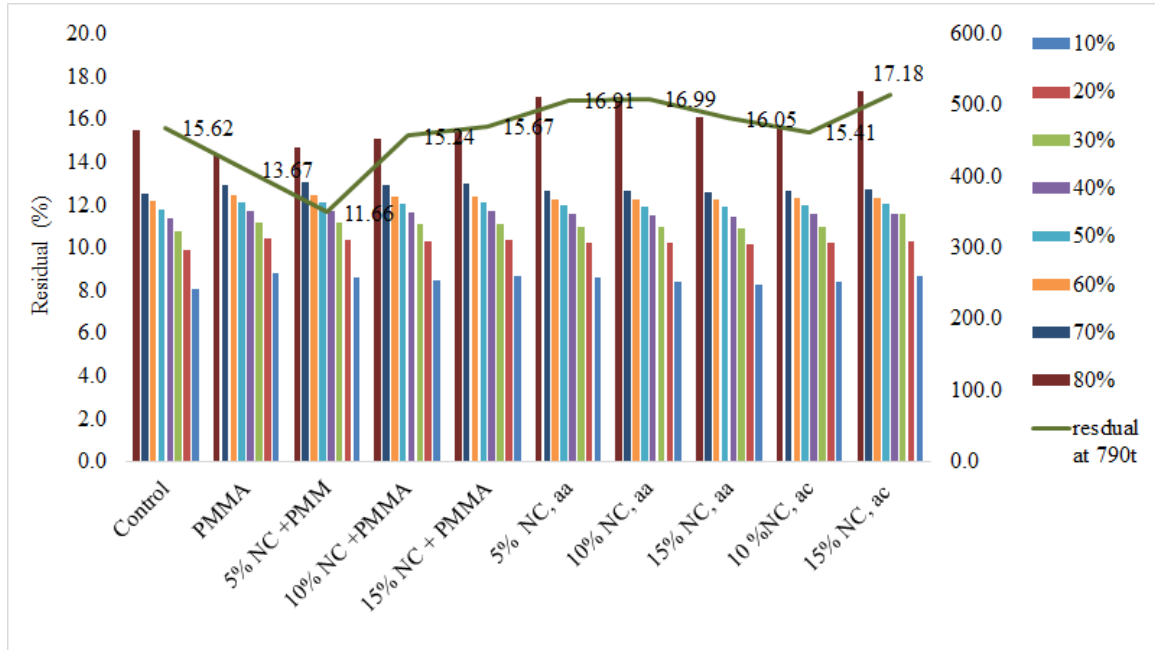


Figure 15. Weight loss (%) of wood treated with nano-clay and untreated wood at different temperatures

In Fig.15, it was noticed that, although %15 NC, ac, had a distortion temperature lower than some variations, it had the largest residual percentage.

The residual percentage of 15% NC, aa was higher than the residual percentage for 15% NC +PMMA as well as for control samples. This clearly demonstrated that the effect of nano-clay was greater than nano-clay + PMMA on thermal properties.

Kiaei et al., 2017 has mentioned that the ability of nanoparticles to crystallize and increase the temperature required for flammability has been the reason for improvement of thermal sustainability. Moreover, thermally or chemically, the wood could be altered, so the elected features can be improved in a more or less constant fashion such as dimensional stabilization (Hill 2006).

### 3.2.2. Differential Scanning Calorimetry (DSC)

The Table 12 shows approximate melting temperatures ( $M_t$ ) for DSC analysis of test and control samples.

The sample and reference in DSC test are heated by separate heaters, so if the variance a temperature increases between the sample and reference due to the exothermic or endothermic reactions in the sample, the power contribution is taken out this difference. Consequently, the sample holder temperature is constantly recorded congruous to the reference.

Table 12. DSC for wood treated with nano-oxides and control samples

Nano-Oxides	
Variations	Melting temperature (°C)
ZnO	371.31
ZnO+PMMA	372.52
Al <sub>2</sub> O <sub>3</sub>	373.52
Al <sub>2</sub> O <sub>3</sub> +PMMA	371.91
TiO <sub>2</sub>	373.32
TiO <sub>2</sub> +PMMA	374.32
MgO	372.32
MgO+PMMA	374.33
Control	368.79

According to Table 12, MgO+PMMA samples were the highest melting temperature (374.33 °C), this sequence followed TiO<sub>2</sub>+PMMA samples(374.32 °C) followed by Al<sub>2</sub>O<sub>3</sub>(373.52 °C) samples and TiO<sub>2</sub> (373.32 °C), and the lower one was for Control (368.79 °C).

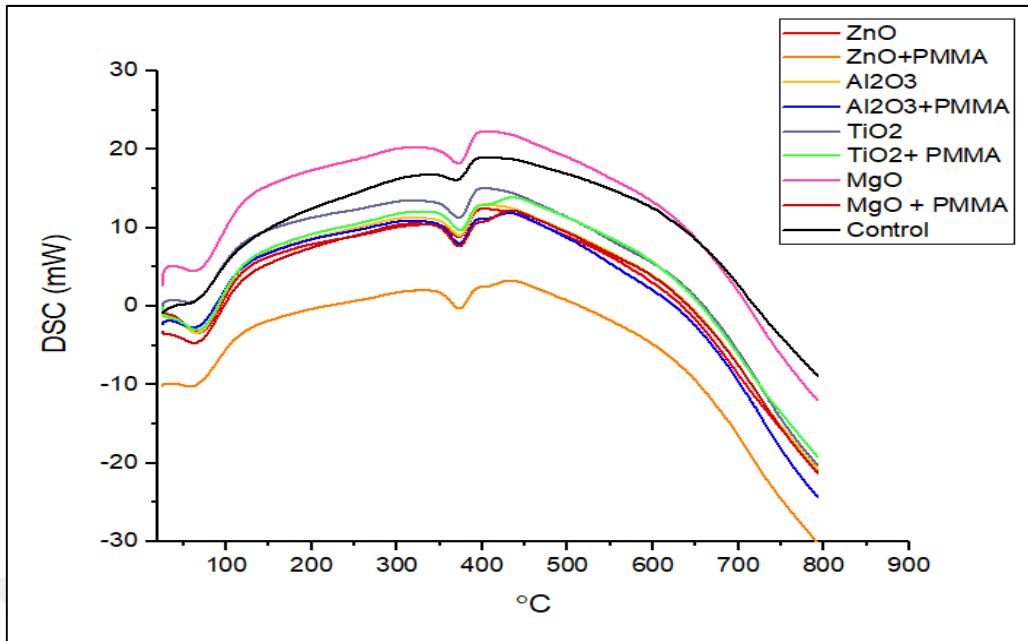


Figure 16. DSC for nano oxides and control samples

As can be seen in Fig.16 which explained DSC for oxides groups, the highest melting temperature for control samples subjected to DSC test was (368.79 °C), and when it compared to all others variations groups it was the lowest melting temperature in this test.

Table 13. DSC for wood treated with nano-clay and control samples

Nano-clay	
Variations	Melting temperature (°C)
15% NC, ac	375.54
10 %NC, ac	368.79
15% NC, aa	367.01
10% NC, aa	368.99
5% NC, aa	368.79
15% NC + PMMA	370.38
10% NC +PMMA	373.73
5% NC +PMMA	372.16
PMMA	375.54
Control	368.79

The Table 13 shows approximate melting temperatures ( $M_t$ ) for DSC analysis of test and control samples

Table 13 exhibited that 15% NC, ac, and PMMA had the highest melting temperature (375.54 °C) Followed by 10% NC +PMMA(373.73 °C), in the reverse, the lowest melting temperature was for 10 %NC, ac samples and control (368.79 °C).

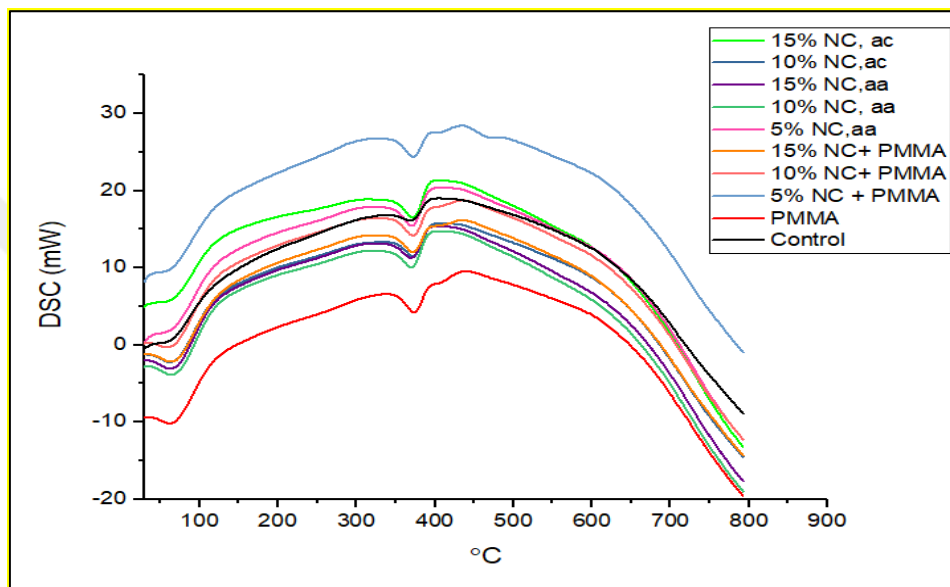


Figure 17. DSC for Nano-clay and control samples

DSC for Nano-clay and control According to Fig.17 which exhibited DSC of nano-clay groups, the melting temperature for control samples undergo to DSC test was (368.79 °C), it was lower than the all values of variations except 15% NC, aa (367.01°C) samples.

It was noticed that the melting temperature for nano-clay compounds without PMMA (15% NC, aa / 10% NC, aa / 5% NC, aa) was lower than that contained it.

### 3.3. Decay Test

Table 14. Mass loss of leached wood samples treated with nano-(oxides and clay) and untreated samples

Brown Rot					
Oxides			Nano-Clay		
Variations	Mass Loss (%)		Variations	Mass Loss (%)	
ZnO	X	2.76	%15 NC, ac	X	2.86
	St.D	0.91		St.D	1.35
ZnO+PMMA	X	2.22	%10 NC, ac	X	2.66
	St.D	0.79		St.D	0.58
Al <sub>2</sub> O <sub>3</sub>	X	3.88	15% NC, aa	X	3.36
	St.D	1.90		St.D	0.54
Al <sub>2</sub> O <sub>3</sub> + PMMA	X	1.73	10% NC, aa	X	2.15
	St.D	0.96		St.D	0.48
TiO <sub>2</sub>	X	2.13	5% NC, aa	X	23.54
	St.D	1.09		St.D	6.48
TiO <sub>2</sub> + PMMA	X	2.57	15% NC +PMMA	X	1.91
	St.D	1.11		St.D	0.84
MgO	X	2.46	10% NC +PMMA	X	2.06
	St.D	1.21		St.D	0.59
MgO + PMMA	X	1.36	5% NC +PMMA	X	2.69
	St.D	0.51		St.D	0.57
			PMMA	X	2.39
				St.D	1.07
Control	X				20.26
	St.D				8.64

The test was considered successful according to EN 113 standards which required that control samples must be losing more than 20% of their weight.

According to Table 13, which demonstrates leached samples that were exposed to brown fungus *Coniophora puteana*, TiO<sub>2</sub> and ZnO+PMMA were resistant to brown fungi but MgO + PMMA and Al<sub>2</sub>O<sub>3</sub>+ PMMA proved to be more resistant. The lower mass-loss percentage was 15% NC +PMMA (1.91%) in nano-clay group.

All variations demonstrated their resistance to fungi compared to control samples except 5% NC,aa (23.54) %, where its weight loss rate was higher than control samples (20.26) %.

The nano-oxide groups containing PMMA like ZnO+PMMA, Al<sub>2</sub>O<sub>3</sub>+ PMMA, MgO + PMMA when compared to the control were found that their mass loss lower than those variations without PMMA.

As shown in Table 14, the difference in weight loss in all nano-oxide was significantly lower than the control samples, where the lower value of mass loss between

nano-oxide groups was MgO (1.36). As a result, nano-oxide was contributed to reducing the growth of fungi on the treated samples.

In nano-clay, the lower mass loss was 15% NC +PMMA (1.91) % and this was indicated by the fact that the higher concentration of nano-clay with PMMA gave the greatest resistance.

There were no significant differences between the variations in other nan-o clay groups despite differences in concentration and solvent used except in 5% NC,aa (where the nano-clay concentration was reduced, the mass loss rate was higher than the control samples).

These findings were similar to (Clausen et al., 2009) was mentioned that nanoparticles have a highly effective in wood protection by developing the new and improved biocides with an unique features. 2.5% and 5.0% nano-ZnO were estimated for leaching, rot and decay preventing, termite resistance, and an evident indication of weathering. The elevated concentration of nano ZnO estimated in inhibition average of rot growth (20-32% coverage).

#### 4. CONCLUSION

In the proposed work, different variations were conducted for two groups of nanoparticles and PMMA.

The concentration of nano-oxide was determined based on the degree of solubility in the acetone, and the optimum concentration was 0.5%.

As well as different percentages of nano-clay 15%, 10% and 5% using acetone and acetic acid as solvents. The ratio of PMMA was 10%. After the impregnation process, several tests were carried out on the samples. The water absorption, tangential swelling, water repellent efficiency and anti-swelling efficiency were measured after immersion of the samples for two weeks in water, clearly the treatment was given an important effects.

The lowest water absorption ratio was ZnO+PMMA, Al<sub>2</sub>O<sub>3</sub>+PMMA, TiO<sub>2</sub>+PMMA, MgO+PMMA as well as 15% NC, ac, 10%NC, ac. The tangential swelling of wood was also improved and was highest ratio found in nano-oxides + PMMA ,15% NC, aa,10% NC, aa, 5% NC, aa,15% NC + PMMA and PMMA.

On the other hand, the thermal characteristics of the samples were checked to detect their resistance to heat and flammability thus protect them from degradation. The results showed that samples treated by nanoparticles then exposed to high temperature increased the deterioration temperature of these samples compared to control samples while maintaining a constant residual percentage, Where the MgO 17.32%, %15 NC, ac 17.18% were the highest residual %, and (TiO<sub>2</sub>,ZnO,MgO)+PMMA 433.91%, 10% NC +PMMA 435.51%, were the highest distortion temperature.

The brown rot test and its effect on leached samples for a period of 5 months resulted that variations were successful and gave satisfactory results compared to control. The usage of acetone or acetic acid as solvents for nano-clay did not have that important effect.

It was concluded that the addition of PMMA as a secondary impregnation for nano-oxides and nano-clay gave excellent effects in wood preservation from degradation, especially in preventing uptake of water, where this material was made a secondary layer that encapsulated wood.



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