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EFFECT OF SIO_2 AND AL_2O_3 NANOPARTICLES TREATMENT ON THERMAL BEHAVIOR OF ORIENTAL BEECH WOOD

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ABSTRACT

In this study, investigation of the thermal properties of Oriental beech (*Fagus orientalis* L.) wood samples treated with 1.50 and 3.00% aqueous solutions of SiO_2 and Al_2O_3 nanoparticles were performed by using thermogravimetric analysis (TGA), differential-thermogravimetric (DTG), and differential-thermal analysis (DTA) under argon atmosphere.

Thermal degradation of SiO_2 and Al_2O_3 nanoparticles treated Oriental beech wood could be separated in three district regions. These regions could be called as drying, pyrolysis, and

charring. Our results showed that Al_2O_3 and SiO_2 nanoparticle treatment increased residual char yield of Oriental beech wood samples. The highest residual char yield was obtained for wood samples treated with 3.00% Al_2O_3 nanoparticles. Moreover, higher concentration levels resulted in lower T_{max} values, higher T_i values and higher char yield of Oriental beech wood.

KEYWORDS: Oriental beech wood, thermal behavior, SiO_2 nanoparticles, Al_2O_3 nanoparticles.

INTRODUCTION

Wood is a porous material consisting of various cell structures composed primarily of biopolymers (carbohydrate polymers of cellulose, hemicelluloses and phenolic polymers of lignin) and minor amounts (5-10%) of extractives. Wood is anisotropic longitudinally, radially, and tangentially (Devi and Maji 2012a). The fibrous nature of wood has made it one of the most appropriate and versatile raw materials for a variety of uses. However, three properties restrict its much wider use: dimensional changes when subjected to fluctuating humidity, susceptibility to biodegradation by microorganisms and to be easy-burning material (Mantanis and Papadopoulos 2010).

Fire safety is an important concern in all types of construction. Wood is exceptionally important in this regard; it burns when exposed to heat and air. Thermal degradation of wood occurs in stages. The degradation process and the exact products of thermal degradation depend upon the rate of heating as well as the temperatures (Taghiyari 2012). Thus, increased efforts to expand the use of wood products in institutional and commercial structures may require wood to be treated with fire retardants. Flame retardancy is generally imparted to woods by impregnating phosphate, silica, boron type compounds into wood (Li and He 2004, Devi and Maji 2013). Mahmoud et al. (2004) explained that the composites impregnated with bis (2-chloroethyl) vinyl phosphonate have shown maximum improvement in thermal stability. It has been reported that the improvement in fire retardancy of wood has been obtained on treatment with thio-urea–formaldehyde resin and orthophosphoric acid. Hamdani et al. (2009) reported that the addition of a relatively low amount of silicon-based compounds (silicones, silicas, organosilanes, silsequioxanes and silicates) to polymers has been reported to substantially improve their flame retardancy. Nano-based treatments present new opportunities to enhance wood attributes more effectively for different applications in the horizon of wood modification processes. Nano-modified wood could be a promising new approach to obtain effective products with better physical, thermal, and mechanical properties (Devi and Maji 2012b). This situation was explained by Mantanis and Papadopoulos (2010) that the small size nanoparticles of such SiO_2 and Al_2O_3 nanoparticles can deeply penetrate into the wood effectively alter its chemical structure of wood. Employing nanotechnology on wood can result in a next generation of products having hyper-performance and superior service ability when used in severe environments, since it is well known that the cell wall of wood exhibits porosity of molecular scale dimensions due to the partial filling of space between the cellulose microfibrils by lignin, hemicelluloses and extractives (Wegner et al. 2005, Wegner and Jones 2006). However, there are not enough systematic studies on fire retardancy of nanoparticles based preservatives treated wood in literature. Therefore, knowledge of the thermal degradation and fire performance of wood treated with these chemicals can be critical. Various methods have been developed for evaluating the effectiveness of fire retardant treated wood and the most common of them; thermal analysis is a simple, convenient, reproducible, and fast method for evaluating the pyrolysis and flame retardants under air or inert gas flow (Tomak et al. 2012,

Liodakis et al. 2003, Tsujiyama and Miyamori 2000). Wood is exposed to thermal degradation reactions under the effect of increased temperatures using differential thermalanalysis (DTA) and thermogravimetry (TG) techniques at heating rates 20 and 30°C min^{-1} in temperature range 30–650°C (Kiziltas et al. 2011, Gao et al. 2004, Wielage et al. 1999). The temperatures at which decomposition reactions of wood start and the changes in sample weight with the reactions can be followed (Yorulmaz and Atimtay 2009). The thermal conversion process is generally conducted in a chamber in one of the three ways; pyrolysis, gasification, and combustion or incineration (Chandrasekaran and Hopke 2012, Helsen and Van den Bulck 2005). With this in view, the aim of this study is to evaluate the thermal behavior of Oriental beech wood treated with 1.50 and 3.00% aqueous solutions of SiO_2 and Al_2O_3 nanoparticles by thermogravimetric analysis (TGA), differential thermogravimetry (DTG), and differential thermal analysis (DTA).

MATERIAL AND METHODS

Material

SiO_2 and Al_2O_3 were purchased from Ege Nanotek Chemical Industry Limited Company. SiO_2 is white color and consists of nanoparticles with a diameter of 30 nm. Al_2O_3 is white color and consists of nanoparticles with a diameter of 20 nm. In our study, Oriental beech (*Fagus orientalis* L.) wood which is commercially important raw material for woody product in Turkey was investigated. Sapwood of Oriental beech (*Fagus orientalis* L.) timber free of knots, excessive cross-grain was machined into narrow strips. The strips were carefully chosen for having the same annual ring and then cut into small pieces prior to milling. Wood flour was prepared by grinding the small wood pieces in a Wiley mill with a 50 meshes. Before treatment of nanoparticles, the samples were stored at 65% relative moisture content and 20°C for two weeks.

Impregnation method

Aqueous solutions of the wood preservatives having concentration of 1.50 and 3.00% were prepared using distilled water for the impregnation procedure. For this purpose, the required amount of nanoparticle was dispersed in 100 ml distillated water with the help of ultrasonic dispenser. The solution was heated and stirred continuously at 60°C. The wood flour approximately 100 g was immersed into this dispersion at 60°C for 2 h. The treated wood specimens were subsequently dried at 60°C until they had the unchangeable weight. Similar impregnation procedure of wood flour and wood specimens are described in TG and DTA studies on fire retardant treated wood by Jiang et al. (2010) and Yunchu et al. (2000). The treated wood specimens were then moisture conditioned for two weeks at 20°C and 65% relative moisture content.

Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed under inert atmosphere with heating rate of 10°C·min^{-1} and a purgerate of 20 mL·min^{-1} (Argon) using a LABSYSTG-DTA analyzer between room temperature to 600°C. For each individual experiment, 10 mg of sample was analyzed, and the weight loss of the sample was recorded continuously. Derivative TG (DTG) curves were obtained from TG curve in a function of time.

RESULTS AND DISCUSSION

TG curves, first derivative of TG curves (DTG) and DTA curves of Al_2O_3 and SiO_2 nanoparticle treated Oriental beech wood with different concentrations (1.50 and 3.00 %) were obtained by pyrolysis of sample under argon atmosphere with heating rate of 10°C·min^{-1}. Thermal analysis results of Al_2O_3 and SiO_2 nanoparticle treated samples were compared with the results obtained for non-treated Oriental beech wood called as control. The temperature of the initial weight loss of pyrolysis (T_i), the maximum degradation temperature (T_{max}) and residual char yield of the samples are listed in Tab. 1.

Tab. 1: T_i (the temperature of the initial weight loss of pyrolysis), T_{max} (maximum degradation temperature) and amount of residual char yield of Al_2O_3 and SiO_2 nanoparticle treated Oriental beech wood.

	Concentration (%)	T_i (°C)	Residual char yield (%)	T_{max} (°C)
Control	-	231	33	353
Al_2O_3 nanoparticle	1.50	242	61	352
	3.00	245	79	343
SiO_2 nanoparticle	1.50	254	67	346
	3.00	262	76	342

TG curves, first derivative of TG curves (DTG) and DTA curves of and SiO_2 nanoparticle treated Oriental beech wood with different concentrations (1.50 and 3.00%), are shown in Figs. 1 and 2, respectively.

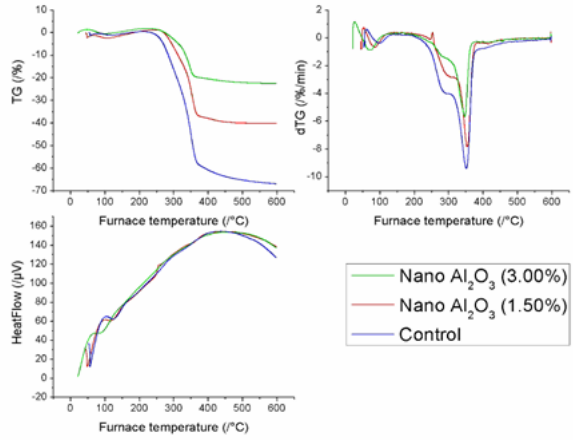

Fig. 1: TG, DTG and DTA curves of Al_2O_3 nanoparticle treated Oriental beech wood.

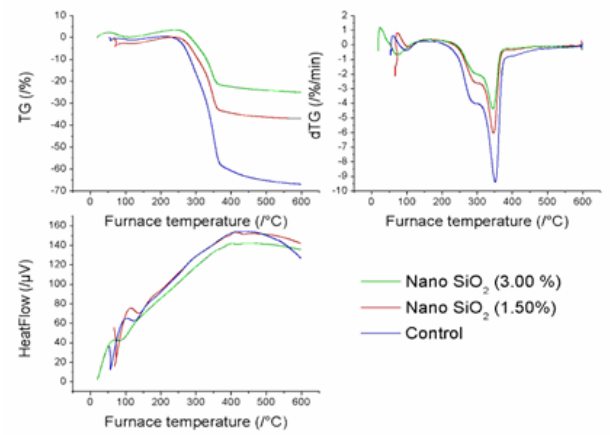

Fig. 2: TG, DTG and DTA curves of SiO_2 nanoparticle treated Oriental beech wood.

It is understood in Figs. 1 and 2 that there were three districts region that could be took under consideration in TG curves of un-treated (control) sample. For the first region below 231°C, it was observed that the mass of control sample nearly remained constant. In this region, as seen in DTA curves of control sample small endothermic peak might be related with removal of adsorbed water was observed at 110°C. It could be clearly seen that rapid and sharp decrease in mass (nearly 57%) of control sample was observed in second region between 231 to 367°C of initial weight of un-treated sample decreased in this stage. In third region, between 367 to 600°C the mass of control sample was decrease slightly. Nearly, 10 % of initial mass was converted into volatile compounds during this stage. Residual mass of the un-treated wood samples at 600°C was found as 33% of initial weight. As listed in Tab. 1, (T_i) and (T_{max}) values of the untreated wood specimen was found as 231°C and 353°C, respectively.

As seen in Figs. 1 and 2, TG curves of Al_2O_3 and SiO_2 nanoparticle treated samples showed same decomposition characteristics with the untreated sample. There were three different stages observed in all obtained curve. In DTA curves, endothermic peak related with the evaporation of physically bound water was observed for all samples between 90 and 150˚C. For SiO_2 and Al_2O_3 nanoparticle treated samples, first stage was the region between room temperature and T_i values of the sample. T_i values of 1.50% and 3.00% Al_2O_3 nanoparticle treated samples were found as 242˚C and 245˚C, respectively and T_i values of 1.50% and 3.00 % SiO_2 nanoparticle treated samples were 254˚C and 262˚C. In this stage there was no significant change in mass of sample observed in TG curves. It was observed that T_i values for both Al_2O_3 and SiO_2 nanoparticle treated samples were higher than that of control sample in all concentrations. In second stage for 1.50% and 3.00 % Al_2O_3 nanoparticle treated samples severe decrease in mass was observed. In this stage 36.5% (between 242 and 364˚C) and 18.9 % (between 245 and 355˚C) of initial mass of 1.50% and 3.00 % Al_2O_3 nanoparticle treated samples converted into volatile compound, respectively.

Fig. 2 shows second region for SiO_2 nanoparticle treated samples were determined in range between 254-362˚C for concentration of 1.50% and 262-362˚C for the concentration of 3.00%. Nearly 32% and 21% of initial mass decreased for 1.50% and 3.00 % SiO_2 nanoparticle treated samples, respectively. Rapid decrease in mass in this stage probably originated because of degradation of cellulose, hemicelluloses, and lignin which are main constituents of woods.

It is well known that hemicelluloses which is thermally unstable with respect to others; degrade between 200-280°C. It was reported that when hemicelluloses decomposed, CO, CO_2, condensable vapors, and organic acids formed (Sinha et al. 2000). Organic acids formation improves the degradation of polysaccharides and increases the decomposition rate of wood in inert atmosphere (Brosse et al. 2010, Esteves and Pereira 2008). Also it was mentioned that lignin and celluloses degrade in temperature ranges of 250- 350°C (Pétrissans et al. 2014).

As seen in Figs. 1 and 2, the decrease in mass of Al_2O_3 and SiO_2 nanoparticle treated samples was much lower than the untreated samples and it was observed that the mass loos were inversely proportional with the increasing of applied concentration of Al_2O_3 and SiO_2 nanoparticle. These phenomena could be originated from monolayer or multilayer coverages of wood sample with the Al_2O_3 and SiO_2 nanoparticles. Treatment with Al_2O_3 and SiO_2 nanoparticles might protect the wood samples from excessive heat and formed organic vapors during the pyrolysis. In third region slight decrease in mass was observed for both Al_2O_3 and SiO_2 nanoparticle treated samples. At the end of experimental run (nearly 600°C) residual char yield of 1.50% and 3.00 % Al_2O_3 nanoparticle treated samples were found as 61% and 79% respectively. For 1.50% and 3.00 % SiO_2 nanoparticle treated samples, nearly 67% and 76% of initial mass of samples remains as char at 600°C. T_{max} was another important parameter listed in Tab. 1 and seen in Figs. 1 and 2. T_{max} values of Al_2O_3 and SiO_2 nanoparticle treated samples were found lower than the untreated sample. Moreover, T_{max} values decrease inversely proportional with the concentration of applied solutions.

In literature, various kinds of chemicals were investigated for improving the properties of the wood samples against heat and fire. Thermal behavior of the wood not only depends on the chemicals used, but also depends on wood's chemical composition, moisture content, and other factors related with its own species. There are limited number of articles deal with the thermal behavior of the woods treated with Al_2O_3 and SiO_2 nanoparticle. In literature, Giudice and Pereyra (2010) studied the fire performance of wooden panels (*Pinus radiata*) impregnated with silica nanoparticles. They used the diameter of 12 nm silica nanoparticles for this purpose. In agreement with our study, they found that self-quenching character of nanosilicate tread wood showed significant increase. Recently, Aydemir et al. (2016) investigated thermal behavior of nano-sized boron nitride treated Scots pine, Ash, and Iroco woods. They found that the thermal stability of woods treated with nano-sized boron nitride was improved after the impregnation.

CONCLUSIONS

Nanoscale modification of materials gives us new opportunities for producing more effective and more stable goods in many areas. In this study, Al_2O_3 and SiO_2 nanoparticles were used for treatment of Oriental beech wood and thermal behavior of the treated samples was compared with the untreated sample by using thermal analysis methods. As a result of our study, it was found that the residual char yield of Al_2O_3 and SiO_2 nanoparticle treated samples much higher than untreated sample. Residual char content of 3% Al_2O_3 and 3% SiO_2 nanoparticle treated Oriental beech wood samples was found as 79% and 76%, respectively. T_{max} values of 3% Al_2O_3 and 3% SiO_2 nanoparticle treated samples and untreated samples were found as 243, 242, and 253°C, respectively. While T_{max} values of the treated samples were lower than that of untreated (control) sample, T_i values of the treated samples were higher than that of untreated (control) sample. Higher concentration levels resulted in lower Tmax values, higher T_i values and higher residual char yield. It was thought that the improvement in thermal properties could be related

mainly on barrier effects of nanoparticles against heat. Lower thermal conductivity of the surface and indirect exposure of chemicals produced during the pyrolysis resulted in increase of char content of the Oriental beech wood. Our preliminary study indicated that both Al_2O_3 and SiO_2 nanoparticles could be the good alternative as flame retardants for woody products. Further investigation should be done for better understanding.

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