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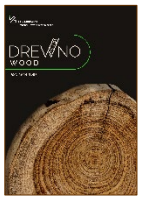

Thermal Analysis of Oriental Beech Treated With Some Dimensional Stability Chemicals and Fire-Retardant Salts

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In this study, Oriental beech (Fagus orientalis L.) wood was treated with 0.5%, 1.5% and 4.5% concentrations of two different dimensional stability chemicals (glyoxal and glycerol), two different fire-retardant salts (sodium acetate and sodium pentaborate), and their mixtures (1:1; weight/weight). The thermal degradation properties of wood samples treated with different types and concentrations of compounds were investigated using thermogravimetric analysis (TGA). When only glyoxal or glycerol was used, they had an adverse effect on the thermal properties of samples. The use of these chemicals together improved the thermal properties, due to the formation of longer polymer chains compared with the control group. Sodium acetate and sodium pentaborate salts, both singly and in a mixture, improved the char yield. The highest char yield (72.13%) was obtained using sodium pentaborate at 4.5% concentration.

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Introduction

Wood has been utilized for construction and engineering since ancient times because it is an easy-to-process, practical, and attractive material. In addition, wooden materials are preferred for their chemical and anatomical structures as well as their physical and mechanical properties [Ergün 2021]. One such material is Oriental beech (*Fagus orientalis* L.) wood, which offers desirable mechanical properties, high density, hardness, and durability. These properties ensure durability and structural stability in construction and engineering materials [Şimşek and Baysal 2015]. On the other hand, some disadvantageous properties of wood, such as poor dimensional stability and fire resistance, limit its use as a construction material [Fengel and Wegener 2011]. Numerous studies have been performed over many years with the aim of improving the dimensional stability of wood. For example, the selection of wood

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species suitable for the place of use, the use of certain types of construction, treatment with various chemical substances (paraffin, polyethylene glycol, styrene, methyl methacrylate, etc.), and the production of materials such as plywood, countertop, chipboard, and fiberboard are linked to efforts to conserve dimensional stability, among other goals [Bozkurt and Göker 1985]. Some dimensional stability studies have involved pretreatments with silane [İstek et al. 2016], ammonia [Čermák and Dejmal 2013], glycerol [Martha et al. 2021], and glyoxal [Toussaint-Dauvergne et al. 2000].

Glyoxal is produced naturally, for example, as a byproduct of biological processes or the oxidation of lipids [Ramires et al. 2010]. It is a highly active molecule, being a non-formaldehyde dialdehyde with two aldehyde groups. When combined with the hydroxyl group in the wood component, it may produce a hemiacetal structure [Yan et al. 2015]. Glycerol, a polar organic trihydroxy alcohol, is a significant byproduct of biodiesel production. As the production of biodiesel increases, the cost of glycerol diminishes. Glycerol facilitates the production of various derivatives that can be fixed in the wood structure, stabilizing wood cell wall polymers as a result of interactions between impregnated polymers and wood hydroxyl groups [Liu et al. 2018].

Wood can perform essential functions in many industries under the right conditions of use. Moreover, fire and unfavorable usage environments can damage the wood material. It is therefore a very important requirement to treat wood with fire retardant materials. The effective application of fire retardants both protects the wood material against burning and prolongs its service life [Dubey et al. 2011]. An oxygen flame source and combustible material are required for wood to ignite. Wood is a material that will burn when exposed to heat and air. The final state of wood after thermal degradation emerges as a result of several stages. Heat rate and temperature value are significant for the emergence of thermal decomposition products and the decomposition process. The events that occur during the ignition of wood are listed as follows: 1) Wood material exposed to heat decomposes into liquid, which can turn into volatile gas and undergo carbonization. Carbonization occurs below 300 °C, in contrast to the effluent produced above 300 °C. 2) The liquid substance that separates from the wood material between 400 and 500 °C can ignite when it comes into contact with air. Gaseous ignitions are observed as flames. 3) Carbonization and oxidation, which occurs with air circulation, is observed at 180 °C, with peak points at 360 and 518 °C [White and Dietenberger 1999].

Sözen et al. [2018] found that the thermal resistance of four different wood species – Oriental beech (*Fagus orientalis* L.), oak (*Quercus robur* L.), Scots pine (*Pinus sylvestris* L.), and fir (*Abies bornmulleriana* Mattf.) – was improved by impregnation with firetex (stone water). Kesik et al. [2015] determined that stone water led to a significant improvement in the residual mass of Scots pine wood. Ayhan [2019] investigated the combustion properties of Scots pine (*Pinus sylvestris* L.) and Oriental beech (*Fagus orientalis* L.) wood impregnated with 10% and 20% concentrations of the Alfa-x chemical. They found that in both wood species, Alfa-x led to a decrease in the weight loss following a combustion test. In another study [Ustaömer 2008] the properties of medium-density fiberboard (MDF) resulting from interaction with various flame retardant chemicals were investigated, considering the chemical substances and their concentrations in the adhesive, as well as the melamine additive ratio. TGA results indicated that increases in the chemical substance density in the adhesive and the melamine additive ratio resulted in a higher proportion of the remaining undecomposed portions of samples.

In our study, test samples were prepared from Oriental beech wood, which is the preferred wood species in the furniture industry. The main aim was to investigate the thermal characteristics of Oriental beech wood treated with various concentrations of dimensionally stable compounds (glyoxal and glycerol), as well as some fire-retardant substances (sodium acetate and sodium pentaborate). Our aim in using glycerol and glyoxal, which are chemicals that provide dimensional stability, was to determine what effects these chemicals have on the thermal properties of wood, in addition to providing dimensional stability. Chemicals were used individually and in mixtures. The purpose of using mixtures is to enable them to compensate for each other's weaknesses in terms of fire retardance. The initial maximum thermal degradation temperatures and char yields of treated samples were determined by thermogravimetric analysis (TGA).

Materials and methods

1. Preparation of test samples

The compounds used to provide dimensional stability were glycerol (99.5%) and glyoxal (40 wt% in H_2O), supplied by the chemical company Sigma Aldrich. Sodium pentaborate was obtained from Eti Mine Works General Management in Turkey. Sodium acetate (CAS-No: 127-09-3) was purchased from Merck Chemicals. Glycerol, another name for

glycerin, is a straightforward polyol substance with the chemical formula $C_3H_8O_3$. It is a colorless, odorless, sweet-tasting liquid that is used in a number of food, personal care, and medicinal products [Fluhr et al. 2008]. Glyoxal is a chemically defined organic substance having the formula OCHCHO. With two aldehyde groups, it is the smallest dialdehyde compound. It is a crystalline solid that turns yellow close to its melting point (15 °C) and white at lower temperatures. The vapor is green, while the liquid is yellow [Liggio et al. 2005].

Sodium acetate can be found as sodium ethanoate, as sodium acetate anhydrous (meaning that it does not contain water for hydration), or as a sodium salt of acetic acid. It has a hygroscopic character and is readily soluble in both water and alcohol. It is normally odorless, but when heated to the point of breakdown, it releases an acetic or vinegary scent. Its chemical formula is CH_3COONa [Zhang et al. 2014].

The elemental formula of sodium pentaborate, also known as disodium decaborate, is NaB5O8, $Na_2B_{10}O_{16}$, or $Na_2O{\cdot}5B_2O_3$. It is a salt composed of sodium, boron, and oxygen. It is a colorless, water-soluble, crystalline solid [Mary et al. 2008].

We acquired sapwood of Oriental beech (*Fagus orientalis* L.), free of knots, excessive cross-grain, and other obvious flaws, from Yücel Wood Products in Muğla, southwest Turkey. The test samples in our study were in the form of flour. This is because in the case of solid wood, some parts may not become impregnated during the impregnation process, which will impair the accuracy of the results obtained in thermal analysis tests. To make wood flour, small pieces of wood were processed in a Wiley mill until they could pass through a 50 mesh screen.

2. Impregnation method

In this study, concentrations of 0.5%, 1.5% and 4.5% were selected as low, medium and high levels. For the impregnation procedure, the wood preservatives were made into aqueous solutions with concentrations of 0.5%, 1.5%, and 4.5% using distilled water. Samples of Oriental beech wood flour weighing 100 g were dissolved in the solutions for two hours at 60 °C. The modified samples were then baked at 60 °C for a set amount of time until their weight remained constant. Similar impregnation methods for wood flour and wood samples are described by Jiang et al. [2010] and Yunchu et al. [2000] in reports on TG and DTA experiments on wood treated with fire retardants. After this step, the treated samples underwent two weeks of moisture conditioning at 20 °C and 65% relative humidity.

3. Thermal analysis

Using a thermogravimetry differential thermal (TGA/DTA) analyzer from LABSYS (France), differential thermogravimetry (DTG) and thermogravimetry analysis (TGA) were performed under argon at a heating rate of 10 °C/min and a purge rate of 50 mL/min. The temperature was increased from room temperature to 600 °C. The weight loss was continuously measured while the sample, originally weighing 12.78 ± 1.55 mg, was heated and pyrolyzed. Four repetitions were made for each treatment group.

4. Statistical analysis

Statistical analysis of the impact of the chemicals on the wood was performed using one-way analysis of variance (ANOVA) in the SPSS 16 program.

Results and discussion

The thermal behavior of Oriental beech wood treated with glyoxal and glycerol for dimensional stability and with the fire retardants sodium acetate and sodium pentaborate was analyzed using TGA and DTG under an argon atmosphere. The TGA results were influenced by the type and concentration ratio of chemicals, which was expected based on the test results. In Table 1, letters (A, B, C, D, etc.) are used to indicate the grouping of samples of equivalent relevance.

T_i% was found to lie within the temperature range 97–447 °C. T_{max}% was between 195 and 488 °C. The highest char yield following thermal degradation at 600 °C (72.13%) was obtained for wood impregnated with sodium pentaborate at 4.5% concentration, and the lowest char yield (10.24%) was obtained with glycerol at 4.5% concentration. It was shown that the use of glycerol and glyoxal had an adverse effect on the thermal stability of the samples. An increase of free volume within the glyoxal enabled it to thermally degrade more fully; this may be led by the growth of a side chain at the C-3 and C-5 positions with the introduction of $-CH_2OH$ and $-CH_2CHO$ groups [Wang et al. 2018]. Glycerol begins to evaporate at 200 °C and evaporates completely at 300 °C. Because wood has lower thermal stability, the use of glycerol may reduce the thermal degradation of wood [Erbaş Kızıltaş et al. 2016]. On the other hand, sodium acetate and sodium pentaborate salts have different physical characteristics and chemical compositions. These wood treatments may result in various fire retardance processes. Most typically, they either limit oxygen penetration by forming a carbonaceous protective layer

over the burning wood, or cool the flame due to the release of water from the salt. Fire retardants can also act as flammable gas diluents or reduce pyrolysis temperatures to increase the amount of char produced [Vargün et al. 2019].

TG and DTG curves for the control group and for glycerol- and glyoxal-treated Oriental beech wood are shown in Figure 1 and Figure 2, respectively. DTG curves depict the rate of weight loss during thermal degradation.

Table 1. Initial and maximum temperature (°C) of thermal degradation and char yield (%) after thermogravimetric analysis

Chemicals	$T_{i\,\%}$ (°C)	H.G.	$T_{max\,\%}$ (°C)	H.G.	Char yield (%)	H.G.
Control (untreated)	274±32	D	325±42	DEF	19.63±2.3	ABC
Glyoxal 0.5%	200±22	BC	256±33	BCD	19.05±3.4	ABC
Glyoxal 1.5%	187±20	B	223±31	BC	13.08±2.1	AB
Glyoxal 4.5%	182±16	B	221±27	BC	11.39±1.5	AB
Glycerol 0.5%	97±13	A	195±29	AB	20.31±2.6	ABC
Glycerol 1.5%	174±15	B	329±40	DEF	11.72±1.8	AB
Glycerol 4.5%	196±23	BC	263±25	BCDE	10.24±1.1	A
Glycerol + glyoxal 0.5%	290±35	D	354±38	F	23.36±3.0	BC
Glycerol + glyoxal 1.5%	288±29	D	356±45	F	27.84±4.6	C
Glycerol + glyoxal 4.5%	259±22	CD	356±36	F	27.87±3.9	C
Sodium acetate 0.5%	286±33	D	308±29	CDEF	54.08±6.1	DE
Sodium acetate 1.5%	283±25	D	298±34	CDEF	54.61±7.3	DE
Sodium acetate 4.5%	276±30	D	474±53	G	61.86±6.9	EF
Sodium pentaborate 0.5%	307±39	D	321±37	DEF	49.93±5.7	D
Sodium pentaborate 1.5%	321±42	D	348±48	EF	67.15±7.3	F
Sodium pentaborate 4.5%	148±18	AB	129±14	A	72.13±7.7	F
Sodium acetate + sodium pentaborate 0.5%	254±28	CD	283±22	CDEF	53.43±6.7	DE
Sodium acetate + sodium pentaborate 1.5%	296±45	D	297±25	CDEF	66.15±6.2	F
Sodium acetate + sodium pentaborate 4.5%	447±63	E	488±41	G	71.24±8.8	F

Homogeneity groups (H.G.): means followed by the same letters (A, B, C, D, E, F, G) in the same column are not significantly different ($p < 0.05$). ±: standard deviation

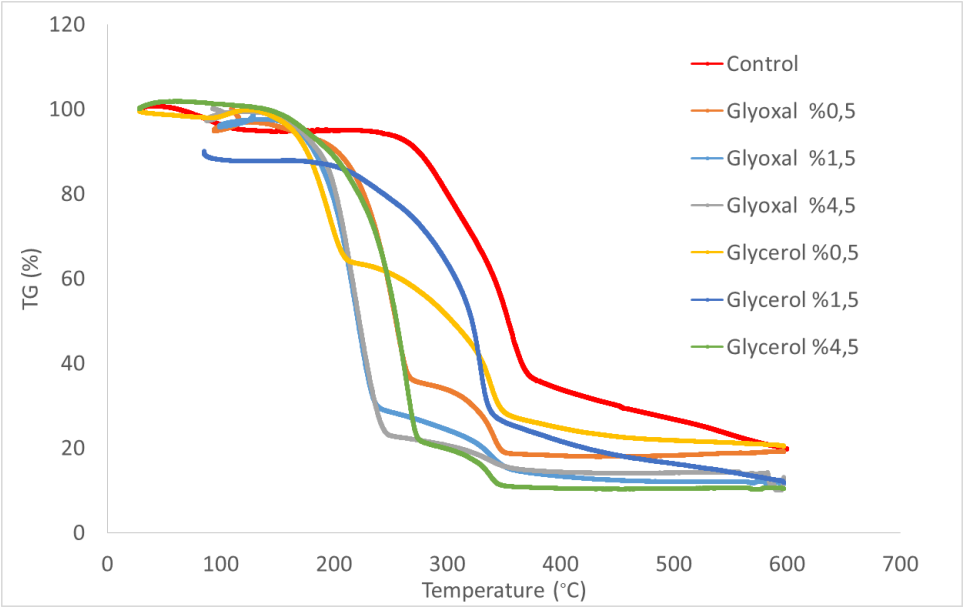

Fig. 1. TGA results for Oriental beech wood treated with different concentrations of glyoxal and glycerol

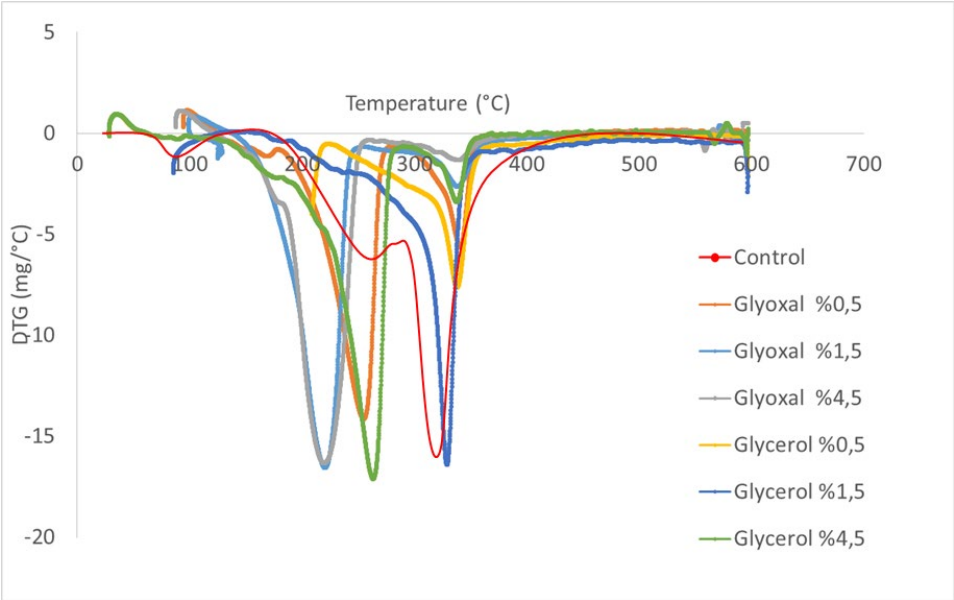

Fig. 2. DTG results for control and treated samples

It was determined that the char yield of glyoxal- and glycerol-impregnated Oriental beech wood ranged between 10.24% and 20.31%. The char yield of the control group was 19.63%. The TG and DTG curves for the control group indicate an initial weight loss at around 100 °C due to moisture evaporation in the wood. Hemicelluloses and cellulose decomposed between 200 and 350 °C. During thermal decomposition, hemicellulose is deacetylated into acetic acid [Bianchi et al. 2010]. Decarboxylation, oxidation, hydrolysis, oxidation, and free radical generation all contributed to the degradation of cellulose, which produced volatile, combustible components. The thermal degradation was caused by the generation of hydrogen peroxide, carboxyl, and carbonyl groups by free radicals [Junges et al. 2019]. Even though the weight loss occurred across a wide temperature range, the lignin degradation process began at about 200 °C. During the gradual breakdown of lignin, temperatures can reach 600 °C or higher, which is higher than the maximum degradation temperatures of cellulose and hemicellulose. The observed three-stage heat degradation processes were similar to those described in the literature [Renner et al. 2022; Li et al. 2021].

For samples of Oriental beech wood impregnated with glyoxal and glycerol, the weight loss up to 600 °C was higher than with the controls. Glyoxal, composed of aldehyde groups, was cross-linked with wood substances, and led to higher thermal degradation [Kan et al. 2021]. The degradation of Oriental beech wood treated with glyoxal occurred in three main peaks, the first between 80 and 180 °C, the second between 240 and 290 °C, and the third between 290 and 400 °C. The first peak on the DTG curves corresponds to the removal of moisture and glyoxal from the Oriental beech wood. Glyoxal evaporates at around 160 °C [Alkan et al. 2022]. The second and third peaks were similar to those of the control group and corresponded to the decomposition of cellulose, hemicellulose, and lignin. The height of the DTG peaks was increased compared with the control group, meaning that glyoxal caused acceleration in the rate of weight loss during thermal degradation. TGA results showed that the glyoxal interacted with the Oriental beech wood. The glyoxal-treated wood was less stable and exhibited earlier degradation than the control group. This phenomenon can be explained by the introduction of 3D cross-links upon glyoxalation, which are weaker and begin decomposing quickly. As a result, the glyoxalation of wood resulted in cross-linking rather than glyoxal inclusion [Van Nieuwenhove et al. 2020]. On the other hand, glycerol may accelerate thermal degradation in the TGA analysis [Mubarok et al. 2019]. Similarly, for Oriental beech wood treated with glycerol, degradation of the samples occurred in three main peaks, in the temperature ranges 40–140 °C, 195–270 °C, and 290–375 °C. The second peak on the DTG curves is due to the removal of glycerol from the wood. Glycerol evaporates between 200 and 300 °C [Cui et al. 2017]. The height of the DTG peaks increased compared with the control group when glycerol was added, meaning that glycerol caused acceleration in the rate of weight loss during thermal degradation. It is unclear how glycerol reacted with the Oriental beech wood. However, one possibility is that it accelerated the thermal decomposition of the carbohydrate components, as these polymers were had a smaller quantities at the initial stage of TGA analysis [Liu et al. 2018]. Like those treated with glyoxal, the samples of Oriental beech wood treated with glycerol were less stable and underwent earlier degradation than the control samples. The increase in weight loss on addition of glycerol may be attributed to the formation of a less stable structure in the wood [Choi et al. 2021]. Also, it is thought that the size of the organic substance-rich area changes as the glycerol content increases [Choi et al. 2011]. Liu et al. [2018] found that the char yield of poplar wood treated with glycerol ranged from 8.55% to 14.68%. This result was similar to our findings.

TG and DTG curves for Oriental beech wood treated with sodium acetate and sodium pentaborate, compared with those of the control group, are shown in Figure 3 and Figure 4, respectively.

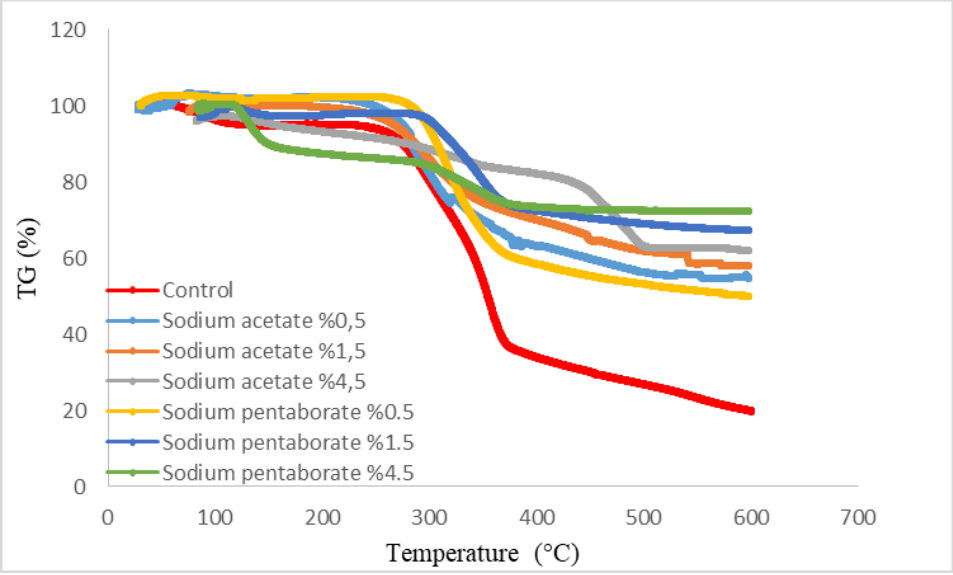

Fig. 3. TGA results for Oriental beech wood treated with different concentrations of sodium acetate and sodium pentaborate

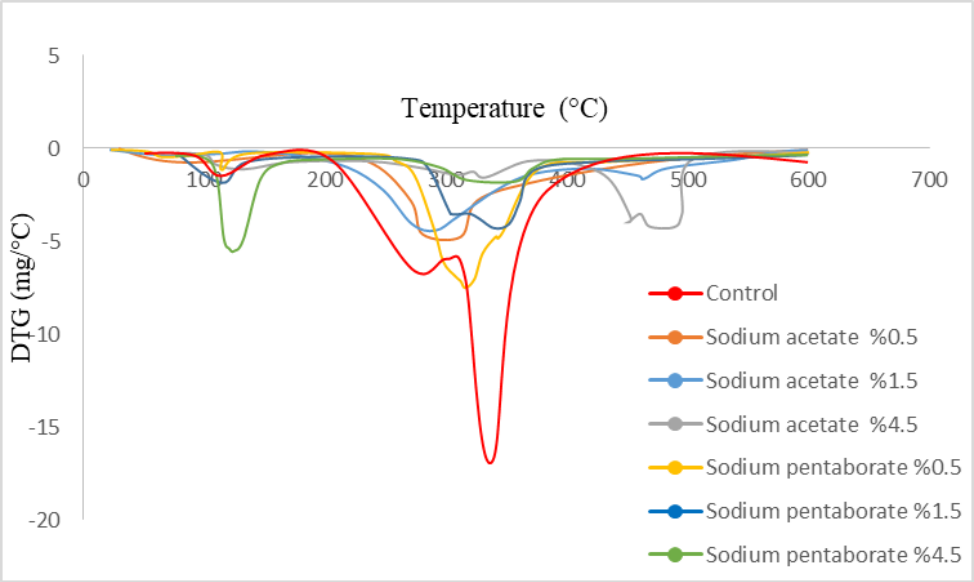

Fig. 4. DTG results for control and treated samples

It was found that the char yield of Oriental beech wood impregnated with sodium acetate and sodium pentaborate ranged from 53.43% to 72.13%. The weight loss of Oriental beech wood treated with sodium acetate began below 100 °C, proceeded rapidly at 200 °C, and was complete at around 500 °C. The thermal stability of sodium acetate-treated Oriental beech wood is much higher than that of the control group, indicating the efficient removal of oxygen-containing functional groups by sodium acetate [Zhang et al. 2014]. Agasti and Kaushik [2014] found that the thermal properties of nanoparticles were improved with the addition of sodium acetate. The weight loss of Oriental beech wood treated with sodium pentaborate was reduced. The increased thermal resistance of wood is attributed to boron compounds preventing the diffusion of heat and oxygen, thereby effectively delaying combustion during the pyrolysis process. [Rallini et al. 2018]. A boron compound can effectively insulate fire and oxygen, cover the surface of wood, and form a high-temperature molten B_2O_3 film [Wang et al. 2015]. Another reason is that boron compounds cause water and oxide formation in the environment during thermal decomposition. This endothermic reaction increases charring and cools the material surface [Zhang et al. 2018].

The thermal behavior of Oriental beech wood treated with sodium acetate during the TGA process was characterized by four peaks. The first peak represents degradation occurring between 50 and 150 °C, which is related to the release of crystalliferous water from sodium acetate. The second and third peaks correspond to wood components such as cellulose, hemicellulose, and lignin. The fourth peak was related to sodium acetate, which has a defective OH grouping. The sodium acetate exhibits thermal degradation in the further heating process, with a second decomposition peak at temperatures between 430 and 530 °C [Hou et al. 2019]. For samples of Oriental beech wood treated with sodium pentaborate, decomposition occurred in three main peaks, within the temperature ranges 60–180 °C, 260–380 °C, and 395–500 °C. It is clear that the borate significantly improved the thermal properties of the wood. The lignocellulosic decomposition temperature ranged from 200 to 350 °C, this being related to cellulose and hemicellulose [Kumar et al. 2019]. The height of the DTG peaks decreased compared with the control sample, because sodium pentaborate caused a decrease in the rate of weight loss during thermal degradation. On the other hand, the wood decomposed at lower temperatures, and the formation of a charred layer was promoted [Li and Xu 2006]. With an increase in the quantity of sodium pentaborate, which contains water of crystallization, T_{max} was recorded at 129 °C, because more water was removed from the material. TGA analysis showed that 31% of water was removed from sodium pentaborate between 100 and 200 °C. As Figure 4 shows, treatment with sodium acetate and sodium pentaborate improves the properties of Oriental beech wood. These salts form a physical protective barrier due to sodium acetate losing its crystalliferous water [Liu et al. 2021].

TG and DTG curves for Oriental beech wood treated with mixtures of glyoxal and glycerol and of sodium acetate and sodium pentaborate, compared with those of the control group, are shown in Figure 5 and Figure 6, respectively.

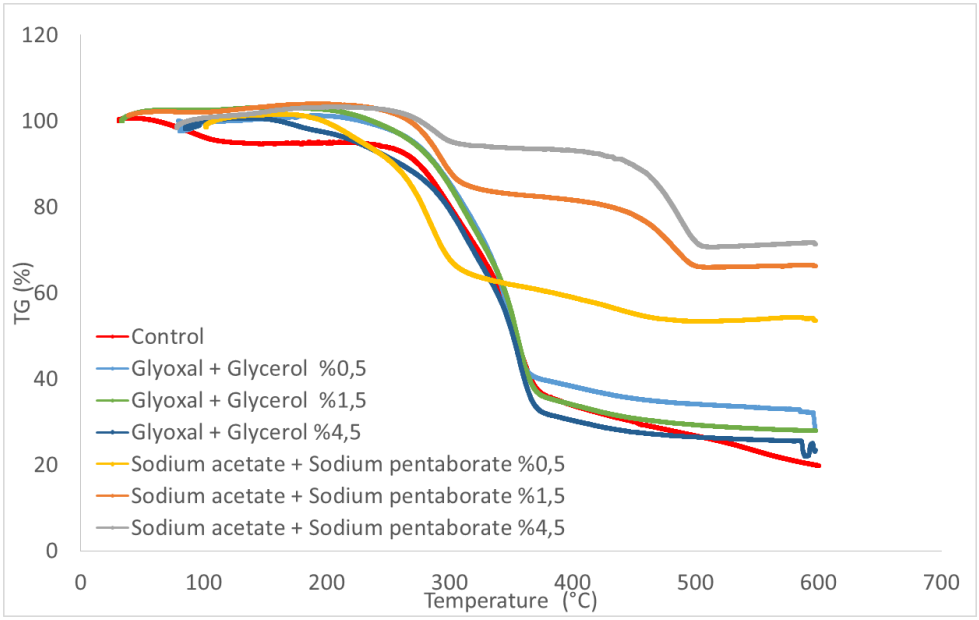

Fig. 5. TGA results for Oriental beech wood treated with different concentrations of mixtures of glyoxal and glycerol and of sodium acetate and sodium pentaborate

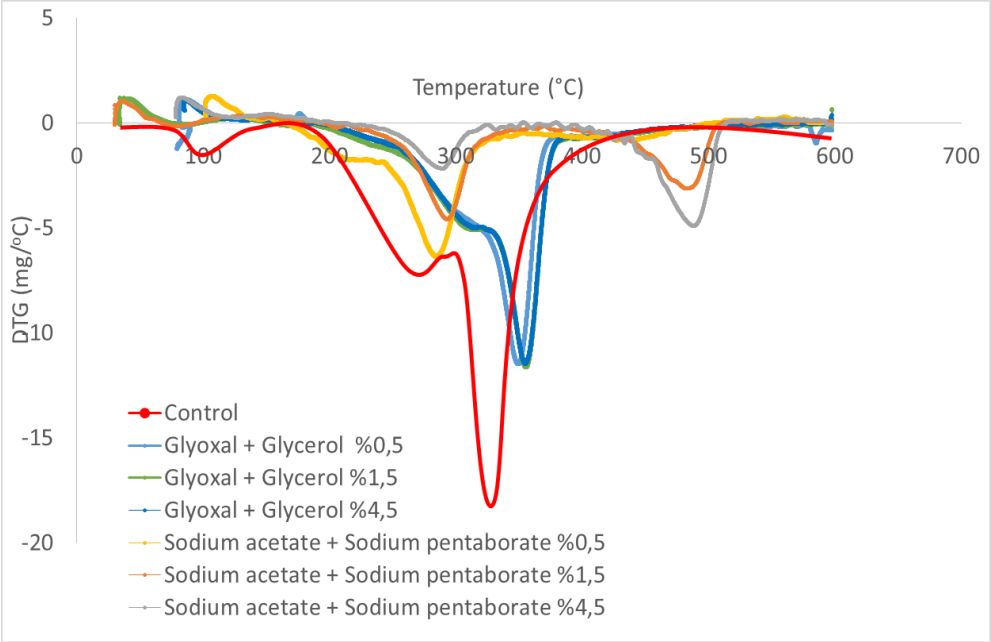

Fig. 6. DTG results for control and treated samples

The char yield of Oriental beech wood impregnated with a glyoxal and glycerol mixture (1:1; w/w) ranged between 23.36% and 27.87%. Compared with the control group, the char yield increased by 8.24%. Although the use of glyoxal or glycerol alone had a negative effect on the thermal stability of Oriental beech wood, their use as a mixture improved the thermal properties. This is thought to be because wood reacts with glyoxal and glycerol to form long polymer chains [Toussaint-Dauvergne et al. 2000]. Schorr et al. [2018] found that the polymer chain length increases, and thermal properties are enhanced. On the other hand, the char yield of Oriental beech wood impregnated with a mixture of sodium acetate and sodium pentaborate (1:1; w/w) ranged from 53.43% to 71.24%. Khelfa et al. [2013] reported that some salts have a significant catalytic effect, and their presence was sufficient to cause a significant change in the pyrolytic behavior of biomass and cellulose.

As the DTG curves show, the rate of burning of samples treated with glyoxal and glycerol was diminished. This is thought to be due to the growth of polymer chains with the addition of glyoxal and glycerol together. When Oriental beech wood was impregnated with sodium acetate and sodium pentaborate, the burning rates of the samples again decreased. It was observed that a new significant peak occurred between 400 and 520 °C, due to the addition of sodium acetate. This peak corresponds to the condensation of defective OH groupings in the material [Mary et al. 2008]. Vargün et al. [2019] showed via TGA analysis that inorganic salt mixtures improved thermal properties. Higher crosslinking and heat stability of the char yield were achieved through intra- and intermolecular rearrangements [Collard and Blin 2014]. Due to interactions between lignin, cellulose, and hemicellulose-derived compounds, sodium acetate and sodium pentaborate salts may work in synergy to improve the yield of char. In addition, the salts used in this study and their combinations provided fire retardancy in wood.

Conclusions

In this study, a TGA instrument was used to analyze the thermal degradation of Oriental beech wood treated with 0.5%, 1.5%, and 4.5% concentrations of glycerol, glyoxal, sodium acetate, sodium pentaborate, and their mixtures. When only glyoxal or glycerol was used, they increased the burning rate and decreased the char yield. On the other hand, using these chemicals together caused a slight improvement in the thermal properties compared with the control group, due to the formation of longer polymer chains. Sodium acetate and sodium pentaborate salts, both singly and in a mixture, led to a decrease in the burning rate and increased char yield. As a result of the use of these salts, the char yield increased by between 30.30% and 52.50% compared with the control group. The highest char yield was obtained from the sample impregnated with sodium pentaborate at 4.5% concentration. In addition, a new peak occurred between 400 and 520 °C in the samples containing sodium acetate, due to the removal of defective OH groupings from the wood.

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