Chemical Modification of Poplar Wood with Benzophenone Tetracarboxylic Di Methacrylates

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Received Date: 05.05.2020  Accepted Date: 08.12.2020

Abstract

Aim of study: The aim of this study was to analyze the use of benzophenone tetracarboxylic di methacrylates material in wood modification process and the changes in poplar wood.

Material and methods: Poplar wood (Populus euramericana) was impregnated with the hydroxyethyl (or glycidyl) methacrylate esters of 3,3,4,4-benzophenone tetracarboxylic dianhydride. The liquid esters were obtained by reaction of BTDA with hydroxyl ethyl (BTD-H) (or glycidyl, BTD-G) methacrylate. The wood-BTD-H (and BTD-G) interaction was confirmed by the characteristic signals in Fourier-transform infrared (FT-IR) spectroscopy. The decay resistance and physical behaviour of the modified wood was investigated.

Main results: The BDTA-H samples displayed less colour change than the BDTA-G samples. Before decay testing, mini-block samples were leached according to the European Committee for Standardization (EN 84 1997) standard, then control and modified samples were subjected to white-rot fungus (Trametes versicolor). Modification with BTD-G yielded a high improvement in decay resistance (68-72%).

Highlights: In the esterification of the chemical, it is benefited only from the sun's rays without the need for high temperature and pressure.

Keywords: Polymer Degradation, Hydroxy Ethyl Methacrylate Ester, Wood Modification, FT-IR Spectra

Kavak Odununun Benzofenon Tetrakarboksilik Di Metakrilatlarla Kimyasal Modifikasyonu

Öz
Çalışmanın amacı: Bu çalışmanın amacı, odun modifikasyon işleminde benzophenone tetracarboxylic di methacrylates maddeinin kullanılması ve kavak odununda meydana getirildiği değişimlerin incelenmesidir.

Materiyal ve yöntem: Kavak ağacı (Populus euramericana), 3,3,4,4-benzofenone tetrakarboksilik dianhidrit hidroksi etil (veya glisidil) metakrilat esterleri ile emprenye edildi. Sıvı esterler, BTDA’nın hidroksi etil (veya glisidil) metakrilat ile reaksiyona sonucu elde edilmiştir. Wood-BTD-H (ve BTD-G) etkileşimi, Fourier dönüşümü kizilötesi (FT-IR) spektroskopisindeki karakteristik sinyallerle incelendi. Modifiye edilmiş ahsabin mantar testi ve fiziksel özellikleri incelenmiştir.

Sonuçlar: BDTA-H örnekleri, BDTA-G örneklerinden daha az renk değişikliği göstermiştir. Çürüme testinden önce, mini blok numuneleri Avrupa Standardizasyon Komitesi (EN 84, 1997) standartına göre yıkanma işlemine tabi tutulmuştur. Daha sonra kontrol ve modifiye edilmiş numuneler beyaz çürüklik mantarına (Trametes versicolor) maruz bırakılmıştır. BTD-G ile modifikasyon işlemi uygulanmış örneklerde yüksek oranda çürüklik direnci (% 68-72) sağlanmıştır.

Önemli vurgular: Kimyasal maddenin polimerizasyonunda yüksek sıcaklık ve basınca ihtiyaç duymadan sadece güneş ışınlarından yararlanılmıştır.

Anahtar Kelimeler: Polimer Parçalanması, Hidroksietil Metakrilat Ester, Odun Modifikasyonu, FTIR Spektrumları

Introduction

Due to the negative impact of petroleum-based materials on the environment and the current pressure on these materials, the use of bio-based materials has become important. Bio-based materials play an important role in a sustainable environment (Miyagawa et al., 2007; Petersen et al., 2001; Rai et al., 2011;
Weiss et al., 2012). Wood - a renewable resource and one of the most abundant sources of biopolymer composites has been widely used as an engineering material for centuries, due to the high mechanical properties, low density, and low cost (Suttie et al., 2017; Klemm et al., 2011; Jiang et al., 2018; Devi et al., 2004). In Europe the use of wood material in the building industry is increasing (URL 1). Therefore, high strength (high mechanical resistance) is expected of the material to be used in building sector.

Wood has a heterogeneous structure and is a polymeric composite material consisting of two main components, carbohydrate and lignin. In addition, organic extractives and inorganic minerals are involved in the structure of wood. Notwithstanding the many positive features, wood has some negative properties including the variation of properties, the characteristic liability of distortion from absorption of moisture, and vulnerability to damage from fungal and insect attack. The main purpose of the modification methods used to reduce these negative properties of wood to provide dimensional stability or bio-resistance to the wood (Hon, 1996; Rowell, 2006; Hill, 2006; Kumar et al., 2009; Taherzadeh & Karimi 2008; Rowell, 2012). The 1–214 (Populus x euroamericana) and I-77/51 (Populus deltoides) are fast-growing hybrid poplar clones which make up nearly half of Turkey’s poplar production (Zoralioglu & Koçar 1996). Although they have a great commercial potential, their usage in outdoor applications and building construction is restricted by the low durability features of poplar wood. Modification techniques which can partially eliminate these disadvantages include wood impregnation methods, or treatments with acetylation, furfurylation, reactive oil, or dimethylol dihydroxyethylenurea (DMDHEU) (Hill, 2006; Qi et al., 2016; Homan & Jorissen 2004; Xie et al., 2005; Kwon et al., 2007).

In addition, wood modification is carried out using different monomers to improve physical, biological properties. By forming different combinations of these monomers in situ, polymerisation was achieved in solid pine, maple, and oak wood (Chan & Lau 1994; Espy, 1995; Devi & Maji 2002; Devi et al., 2003; Rowell, 2012). Studies in the literature have reported that when hydroxyethyl methacrylate (HEMA) was used, water absorption decreased in the modified wood, whereas hardness and dimensional stability increased. Wood treated with HEMA was harder and more water- and moisture-resistant, which was most likely caused by the greater polymer-wood interfacial adhesion resulting from the HEMA monomer polarity (Ibach & Rowell 2012). In addition, carboxylic acid-containing monomers have been used as cross-linkers to improve paper wettability and resistance properties (Chan & Lau 1994; Espy, 1995; Devi & Maji 2002; Devi et al., 2003; Ibach & Rowell 2012; Rowell, 2012).

In several literature studies, 3,3,4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) was attached to cotton cellulose by using different solvents (Hong & Sun 2011; Hou & Sun 2013). According to previous reports, BTDA material was shown to cross-link with cellulose. Esterification reactions between cellulose and BTDA occur in the anhydride and hydroxyl groups. However, these reactions have been reported to occur at high temperatures (Yang, 1993; Yang & Wang 1996b; Yang et al., 1997; Hou & Sun 2013).

In this study, the esterification reaction was carried out under sunlight only, without the need for high temperatures. No detailed information is available on the characterisation of the polymerisation of BTDA with both HEMA and glycidyl methacrylate (GMA) monomers, using sunlight and its interaction with the wood cell wall. In this work 3,3,4,4'-benzophenone tetracarboxylic dihydroxyethyl methacrylate (BTD-H) and 3,3,4,4'-benzophenone tetracarboxylic glycidyl methacrylate (BTD-G), which have carboxylic acid groups in their structure, were synthesised via the reaction of BTDA with GMA and HEMA. These products were then characterised by Fourier-transform infra-red (FT-IR). Poplar (Populus euramericana) wood samples were modified with these chemicals and after the modification process, the chemical structure of the modified samples was examined by FT-IR analysis. Furthermore, the decay resistance
and physical behaviour of the modified wood was investigated.

Material and Methods

Materials

Poplar (Populus euramerica) specimens (density 0.40 g cm\(^{-3}\)) were selected from boards cut entirely from sapwood into sizes of 5 (Radial, R) \(\times\) 15 (Tangential, T) \(\times\) 30 (Longitudinal, L) mm\(^3\) for the decay tests and 20 (R) \(\times\) 20 (T) \(\times\) 10 (L) mm\(^3\) for the water absorption test. The 3,3,4,4-Benzophenone tetracarboxylic dianhydride (BTDA, 96%) was obtained from Aldrich and the 2-Hydroxyethyl methacrylate (HEMA, 95%) and glycidyl methacrylate (GMA, 96%) were purchased from Fluka (Figure 1).

![Figure 1. Chemical structure of the monomers BTD-H and BTD-G.](image)

Synthesis and Characterisation of BTD-H and BTD-G

The BTD-H was synthesised by the reaction of BTDA and HEMA based on the modification method, reported in the literature (Atai et al. 2002). Briefly, a mixture of 8.28 g of HEMA (1077 mol) and 8.12 g of BTDA (2616 mol) was held at 120 °C for 50 min. The clear, viscous liquid (2.9 g) was dissolved in ethyl alcohol (15.6 g) for use in the wood impregnation. For the preparation of the BTD-G, the same procedure was repeated using 3.31 g of BTDA and 9.22 g of glycidyl methacrylate.

Wood Treatment Process

The poplar (Populus euramerica) sapwood specimens were treated with BTD-H and BTD-G obtained as described above. Eliminate the effect of potential chemical degradation in the wood caused by the selected solvents during the impregnation process, an ethanol pre-treatment was applied to the wood specimens. Hence, the specimens to be treated with BTD-H and BTD-G were placed in ethanol and stirred for 2 h. The ethanol was changed with new and the stirring continued for another 2 h, after which the specimens were held in the laboratory for 2 h and then dried at 40 °C for 4 h in a vacuum oven, followed by oven drying at 103 °C. Specimens serving as the controls were held in ethanol for 2 h for comparison with the impregnated specimens. The impregnation of the specimens with 7.74% BTD-G and 9.28% BTD-H diluted with ethanol. Impregnation method includes 20 min vacuum (650 mm/Hg) and 60 min pressure (1 atm). The weight percentage gain (WPG, %) for each compound was calculated based on the initial weight (\(M_i\)) and final weight (\(M_f\)) of each wood sample using Equation (1). The bulking coefficient (BC, %) was calculated using Equation (2).

\[
\text{WPG (\%) = 100(\frac{M_f-M_i}{M_i})}
\]

(1)

where \(M_i\) and \(M_f\) are the oven-dry weights of the untreated and treated wood blocks, respectively.

\[
\text{BC (\%) = 100(\frac{V_m-V_u}{V_u})}
\]

(2)

where \(V_u\) is the volume of the unmodified wood samples and \(V_m\) is the volume of the modified wood sample (Hill, 2006).

After impregnation, the samples were exposed to sunlight and esterification was performed. Samples were placed at a 0° angle for 10 min under sunlight (Fig. 2).

![Figure 2. Schematic showing polymerisation of wood using BTD-H and BTD-G.](image)
**Characterisation of Treated Wood**

The FT-IR spectroscopy was performed with a Shimadzu IRAffinity-1 spectrometer equipped with an ATR pike MIRacle accessory (resolution, 4 cm⁻¹).

**Colour Measurement**

Konica Minolta spectrophotometer (Osaka, Japan) was used to measure the color change in modified samples according to the procedure in the cited literature (Can & Sivrikaya 2019; Can et al., 2019). Total colour change (ΔE*) was calculated according to Equation (3).

\[
\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}
\]  

(3)

**Leaching, Water Absorption, and Tangential Swelling Tests**

The leaching procedure was similar to the EN 84 (1997) with wood size modifications.

For water absorption (WA) and tangential swelling (TS) tests, wood specimens measuring 20×20×10 mm were prepared from poplar sapwood. Before carrying out the experiments, the specimens were brought to a moisture content of 12% and the tests were then conducted at room temperature. Both control and modified samples were submerged in deionised water. The water in the glass beakers was changed after 10, 20, 30, 40, 50, and 60 min and 2, 3, 4, 24, 48 and 72 h and the mass and dimensions of the specimens were recorded. After each change of water, Equations (4) and (5) were used to calculate the WA and TS.

\[
WA (\%) = \frac{[W_2 - W_1]}{W_1} \times 100
\]  

(4)

\[
TS (\%) = \frac{[T_2 - T_1]}{T_1} \times 100
\]  

(5)

where \(W_1\) and \(W_2\) are the mass of the wood specimens before and after the swelling test; \(T_1\) is the tangential length at any given time under the water-soaked condition; and \(T_1\) is the initial tangential length of the specimen.

**Decay Test**

Decay test was handled with the white rot fungus *Trametes versicolor*. One treated and one untreated sample were incubated at a constant condition of 20 ± 2 °C and 70 ± 5% R.H for 8 weeks. Six replicates were used for each treatment. In addition, decay test was applied to the samples that were leaching. When the experiment is over, the oven dry weights of the samples were recorded. Mass loss was determined based upon the difference in oven-dry weight before and after decay test.

**Statistical Analysis**

The obtained results were evaluated by SPSS programme at 5% (\(P < 0.05\)) level of statistical error using One-Way Anova to compare the control and modified samples. The difference in the samples was assessed by Duncan test in which test parameters were ranked in the homogeneity groups.

**Results and Discussion**

Table 1 shows the average dry density, weight percentage gain (WPG, %), bulking coefficient (BC, %), and solution uptake (%) of the control and modified samples. After modification, the wood density increased slightly depending on the increase of solid content in the solution. It was concluded that the control and test samples were in different homogeneity groups according to Duncan test.

| Sample size 20×20×10 mm | Sample size 5×10×30 mm |
|-------------------------|------------------------|
| Dry density (g/cm³)      | Solution uptake (%)    | WPG (%) | BC (%) | Solution uptake (%) | WPG before leaching (%) | WPG after leaching (%) |
| Control                 | 0.40p (0.03)           | -       | -      | -         | -                    | -                    |

---

Table 1. Dry density, weight gain, bulking coefficient, and solution uptake of wood
In addition, Duncan’s homogeneity groups for the WPG results are indicated by letters ($p > 0.05$). In the homogeneity groups, each column is evaluated within itself. After the impregnation process, solution uptake was obtained between 168% and 175%. After impregnation, the samples were exposed to sunlight that resulted in the esterification. The WPG values of 15.27–20.99% were then obtained in the samples whose oven dry weights were taken at 103 °C. As can be shown in Table 1, WPG% values of the wood samples increased with the increasing in solid content in the solution (BTD-H). Contrary to the treatment with BTD-G, higher WPG values 20.35% and 20.99% were obtained by the treatment with BTD-H with the samples in different sizes 20×20×10 mm and 5×10×30 mm respectively.

Samples with 5×10×30 mm in size were subjected to leaching before the decay test. The leaching was performed to determine the amount of chemical leached from the modified samples. According to the results, WPG values of the BTDA-G and BTDA-H samples decreased by 47.25% and 21.53% after leaching (Table 1). It may be inferred that some components from wood and some from the modifying agents may probably be leach out.

Table 2 compares the colour changes ($L^*$, $a^*$, $b^*$, $\Delta E^*$) resulted from the wood samples before and after modification. According to CIELAB system, $\Delta a^*$ introduces the red and green hue, $\Delta b^*$ yellow and blue colour according to their values positive or negative (Can et al., 2019).

| Treatment | $L^*$ | $a^*$ | $b^*$ | $\Delta E^*$ |
|-----------|-------|-------|-------|--------------|
| Control   | 82.64a | 3.16b | 17.84b | -            |
| (2.07)    | (0.82) | (1.38) |        |              |
| BTD-G     | 79.58a | 5.46a | 32.85a | 14.67a       |
| (1.62)    | (0.77) | (3.17) | (3.56) |              |
| BTD-H     | 80.24a | 4.95a | 27.98a | 11.55ab      |
| (1.37)    | (0.74) | (2.55) | (1.91) |              |

In parentheses: standard deviation. $^{a,b}$ indicate Duncan’s homogeneity groups in the column. The fact that the letters are different shows that the variations take place in different groups.

No significant change was found with respect to $L^*$ value of the samples after modification according to Table 2. Both the control and test samples statistically were belong in the same homogeneity group (Table 2). However, the $a^*$ and $b^*$ values of the samples were increased by modification with BTD-G and BTD-H. The $a^*$ (redness) value, which was 3.16 before the modification process, was increased by 72–56% after the curing process. The same applied to $b^*$ (yellowness). The yellowness values of the samples were increased by 84–56% with the modification process.

As a result, no significant change was observed regarding lightness between the control and the modified samples, whereas $\Delta b^*$ was significantly changed towards the yellow hue by modification with BTDA-G and BTDA-H.

Characterisation of Modified Wood

The results of the FT-IR analysis of the unmodified and modified samples are illustrated in Figure 3.
Table 3. Average degradation parameters of wood and degree of conversion of BTD-H and BTD-G after sunlight curing

| Variation | \(I_{1506}/I_{1365}\) | \(I_{1317}/I_{1336}\) | \(I_{1615}\) |
|-----------|---------------------|---------------------|-----------------|
| Control   | 0.60                | 1.05                | 0.02            |
| BTD-G treated | 0.69                | 1.22                | 0.03            |
| BTD-H treated | 0.62                | 1.26                | 0.03            |

Table 3 shows the \(I_{1506}/I_{1365}, I_{1317}/I_{1336}\) and \(I_{1615}\) ratios. The \(I_{1506}/I_{1365}\) parameter increased from 0.60 to 0.69 for BTD-G and again decreased to 0.62 for BTD-H. The peak at 1336 cm\(^{-1}\) was attributed to the O-H functional group of amorphous cellulose, whereas the peak at 1317 cm\(^{-1}\) was attributed to the cellulose crystallinity of the CH\(_2\) functional group (Nelson & O’Connor 1964; Colom & Carrillo 2002). An increase of the \(I_{1317}/I_{1336}\) ratio implies an increase of crystallinity. The crystallinity index increases of 1.26 corresponds to an increase of 20%. Table 3 indicates that there was an increase of carbonyl groups conjugated with the double conjugated carbon. This new carbonyl structure was associated with the new colour (Table 2).

**Water Absorption and Tangential Swelling of Wood**

In a series of water absorption tests for varying periods, the BTDA-H- and BTDA-G-treated wood absorbed less water than the control samples. During the initial soaking period, the BTDA-H samples showed a bit more resistance to water absorption than the BTDA-G samples; however, both had reached the same level by the final stage. Table 5 indicated that statistically, the BTDA-G and BTDA-H samples were included in the same homogeneity group (Table 4). Water uptake was lowered from 134.64% (untreated) to 117.52% (BTDA-G-treated) and 117.12% (BTDA-H-treated) in the wood samples after 72 h in distilled water at room temperature. In addition, the reduction of the hydroxyl groups in the modified wood samples (Fig. 3) gave rise to the absorption of less water, hence improved the dimensional stability of the wood.

The characteristic anhydride peaks disappeared. The peaks at 1720 cm\(^{-1}\) and in the range of 2700–3000 cm\(^{-1}\) indicate the formation of carboxylic acid groups. In addition, the 2900 cm\(^{-1}\) for C-H stretching could be attributed to the methyl groups of BTD-H grafted on the wood cell walls and to copolymerisation of the GMA compound with the vinyl acetate in the wood cell lumens (Devi & Maji 2007; Qi et al., 2016; Yang & Wang 1996a; Yang & Wang 1996b; Yang & Wang 1997).

No characteristic anhydride peaks (1855 cm\(^{-1}\) and 1778 cm\(^{-1}\)) were seen in the FT-IR spectrum (Fig. 3), thus confirming that the chemical applied onto the wood was not an anhydride, but predominantly consisted of an acid or polycarboxylic acid. Nor was there a clear anhydride peak signal shown in the FT-IR spectrum of the wood after 10 min curing under sunlight. Studies in the literature support this finding. In the literature studies, it is emphasised that anhydride peaks occur at high temperatures (Yang, 1993; Hou & Sun 2013).

The sharp absorbance peak attributed to the ester band at 1727 cm\(^{-1}\) could only be observed in the spectra of the samples treated with BTD-G and BTD-H, indicating that the incorporation of BTD-G and BTD-H in the wood fibres had been successful.
Table 4. Water absorption (%) and tangential swelling (%) of wood

| Time      | Control            | BTD-G             | BTD-H             |
|-----------|--------------------|-------------------|-------------------|
| 10 min    | 27.61a             | 22.50b            | 19.83b            |
| 20 min    | 36.23a             | (2.06)            | (1.86)            |
| 30 min    | 41.98a             | (1.99)            | (1.68)            |
| 40 min    | 45.55a             | (1.91)            | (2.70)            |
| 50 min    | 48.21a             | (1.63)            | (2.86)            |
| 60 min    | 51.59a             | (1.78)            | (1.64)            |
| 120 min   | 61.74a             | (1.36)            | (1.40)            |
| 240 min   | 71.16a             | (1.81)            | (3.04)            |
| 24 hours  | 97.15a             | (2.33)            | (1.83)            |
| 48 hours  | 120.0a             | (3.45)            | (4.40)            |
| 72 hours  | 134.64a            | (3.44)            | (4.61)            |

In parentheses: standard deviation. *a* indicate Duncan’s homogeneity groups in the column. The fact that the letters are different shows that the variations take place in different groups.

Decay Resistance

Mass loss results of the control and test samples with or without leaching were presented in figure 4. Leach and unleached samples were evaluated independently of each other under Duncan test. All unleached test specimens were in the same homogeneity group, while all other variations of the leached specimens were in a different homogeneity group (Fig. 4). After the 8-week decay test, unleached control samples had a mass loss at a rate of 54.46% (Fig. 4), compared with the decay test standard (EN 113 2006) suggests mass loss as 20% in the untreated samples. Since the weight loss had exceeded 20% decay test has been terminated as 8 weeks total. Decay resistance to the white-rot fungus *T. versicolor* was achieved by the BTDA-H and BTDA-G treatments, ranging from 68% to 72% as shown in Figure 5. The lowest weight loss was obtained by BTDA-G (15.07), which corresponds to the WPG as 15.83 %. Obvious strength of the modified samples to the decay fungus might be explained by the improved water resistance property. This observation of the current study is consistent with those of Solpan & Güven (1998) who studied with wood polymer composites.

![Figure 4. Mass loss of unleached and leached BTD-G and BTD-H treated poplar after exposure to T. versicolor (n = 6)](image)

After the poplar wood samples had undergone leaching for two weeks, their weights were reduced. These reductions may have been from the cellulose, hemicellulose, lignin or extractive substances forming the wood structure, as well as from the leaching
of amounts of BTD-H and BTD-G material (Table 1). Studies have shown that the average cold-water solubility of hardwood samples is 4-6% (Pirayesh & Khazaen 2012; Kilic & Niemz 2012). Resistance to decay decreased due to the material losses after leaching. Mass loss of 38.54% and 25.06% were found in the BTD-H and BTD-G samples, respectively. In conclusion, both leached and unleached samples showed considerably high mass loss, as was to be expected. As a result of the small difference in mass loss, it was concluded that the treatment with BTDA-G enabled slightly higher resistance to T. versicolor than with BTDA-H. However, after the leaching process, samples treated with BTDA-G exhibited a greater mass loss, which was associated with the higher leaching, as confirmed in Table 1.

When wood is impregnated with polymers, it does not acquire good decay resistance because the polymer fills up the lumens only and there is no reaction with the cell walls that makes wood susceptible to moisture and decay fungi. Low resistance to brown-rot fungi was demonstrated after 5–20% concentration additions of methyl methacrylate and various types of crosslinking monomers (1,3-butylene dimethacrylate, ethylene dimethacrylate, and trimethylolpropane trimethacrylate) and polar monomers (2-hydroxyethyl methacrylate and glycidyl methacrylate) (Ibach & Rowell 2012). The polymer is able to penetrate the cell walls when methanol with styrene or methyl methacrylate is used, and the amount of polymer in the cell wall is an important factor in boosting decay resistance. A polymer content of 10% or more in the cell wall can provide some degree of protection against biological degradation (Rowell, 2006).

**Conclusion**

In this study, BTDA-based dihydroxyethyl methacrylate (BTD-H) and glycidyl methacrylate (BTD-G) were synthesised to use in wood modification. As a conclusion, Incorporation of the dihydroxyethyl methacrylate and glycidyl methacrylate into wood improved a number of properties including water absorption, tangential swelling, and decay resistance to T. versicolor compared to untreated wood samples. Furthermore, modification of wood with BTD-G improved the decay resistance against white-rot fungus T. versicolor. The FT-IR spectroscopy confirmed the interaction between wood, BTD-G, and BTD-H. Further investigation on the effect of BTDA modification on wood resistance against some other bio-performance tests could be performed in the future.

**Acknowledgements**

This work was partially supported by the Kapadokya University Research Funds (#KÜN.2018-BAGP-001).

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