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THERMAL CHARACTERIZATION OF CHEMICALLY MODIFIED WOOD MATERIALS BY ε-CAPROLACTONE

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Abstract- Wood materials as renewable biodegradable green biomaterials are used in many applications such as furniture, composite materials, construction, interior design, building etc. However, wood materials have some disadvantageous which are low dimensional stability and biological resistance. These undesired properties restrict end-use potential of wood materials. Various modification techniques have been developed to enhance its end-use performance properties. In this work, wood materials were chemically modified with poly(ε-caprolactone) (PCL) which is one of the most promising synthetic biodegradable polymers. Dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) were carried out to evaluate thermal characteristics of the wood materials. Storage modulus and loss modulus values were determined with DMTA, while thermal stability and weight loss were studied with TGA. The findings of this present work showed that the chemical modification of the wood materials by PCL affected the thermal characteristics.

Key Words- Thermal analysis, DMTA, TGA, poly(ε-caprolactone) (PCL), wood material, chemical modification.

ε-KAPROLAKTON İLE KİMYASAL MODİFİYE EDİLEN AHŞAP MALZEMELERİN TERMAL KARAKTERİZASYONU

Özet- Yenilenebilir biyobozunur yeşil biyomalzeme olarak ahşap malzemeler birçok uygulama alanında kullanılmaktadır. Bunlara örnek olarak; mobilya, kompozit malzemeler, konstrüksiyon, iç mimari uygulamalar, yapı vb. verilebilir. Pozitif özelliklerinin yanında ahşap malzeme bazı dezavantaj sayılabilecek özellikleri de bünyesinde barındırmaktadır. Bunlar düşük boyutsal stabilite ve biyolojik dayanımdır. Arzu edilmeyen bu özellikler ahşap malzemelerin potansiyel uygulama alanlarını kısıtlamaktadır. Ahşap malzemelerin son kullanım performans özelliklerini geliştirmek için çeşitli modifikasyon yöntemleri geliştirilmiştir. Bu bilimsel çalışmada, çeşitli ahşap malzemeler en çok gelecek vadeden sentetik biyobozunur polimerlerden birisi olan poli(ε-kaprolakton) (PCL) ile kimyasal olarak modifiye edilmiştir. Ahşap malzemelerin termal karakteristiklerini ortaya koymak için dinamik mekanik termal analizler

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(DMTA) ile termogravimetrik analizler (TGA) gerçekleştirilmiştir. DMTA ile ahşap malzemelerin storage modulus ve loss modulus değerleri belirlenirken, TGA ile termal stabilitesi ve ağırlık kayıpları tespit edilmiştir. Bu araştırma sonucu elde edilen veriler göstermiştir ki, PCL ile yapılan kimyasal modifikasyon ahşap malzemelerin termal özelliklerini etkilemiştir.

Anahtar Kelimeler- Termal analizler, DMTA, TGA, poli(ε-kaprolakton) (PCL), ahşap malzeme, kimyasal modifikasyon

1. INTRODUCTION

Wood materials as renewable biodegradable green biomaterials are used in many applications such as furniture, composite materials, construction, interior design, building etc. It is known that there is a growing interest to develop technologies in which renewable materials are used as direct replacements for nonrenewable materials in many industries. However, wood materials have some disadvantageous which are low dimensional stability and biological resistance. These undesired properties restrict end-use potential of wood materials. Various modification techniques have been developed to enhance its end-use performance properties. Because of environmental concerns regarding use of wood preservatives, there has recently been a renewed interest in wood modification techniques, which indicates a process that is used to enhance properties of wood materials [1]. There are various wood modification methods such as chemical modification, thermal modification, enzymatic modification, and impregnation modification [2]. Previous studies performed by Rowell [3], Kumar [4], Militz et al. [5], Roussel et al. [6], Rowell [7], Rowell [8], Militz and Lande [9], Mattos et al. [10], Gerardin [11], Mantanis [12] evaluated chemical modification of various wood materials.

Poly(ε-caprolactone) (PCL) is a type of aliphatic polyesters which are often biodegradable and biocompatible, and have enhanced mechanical performance [13]. PCL is a partially crystalline, synthetic aliphatic polyester with low melting point and glass transition temperature. PCL also has good biocompatibility and degradability [14, 15]. Poly(ε-caprolactone) (PCL) modification of wood materials examined by Ermeydan et al. [16], Ermeydan [17], Candan et al. [18].

There is limited data in the literature examining thermal characteristics of wood materials chemically modified by PCL. In this study, wood materials were modified with PCL, which is one of the most promising synthetic biodegradable polymers. Dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) were carried out to evaluate thermal characteristics of the wood materials. Storage modulus values were determined with DMTA, while thermal stability and weight loss were studied with TGA.

2. MATERIALS AND METHODS

2.1. Materials

ε-caprolactone (CL), pyridine, tin(II) octoate ($Sn(oct)_2$), acetone, dimethyl formamide (DMF) were bought from SiAl and used as received.

Paulownia (*Paulownia* spp.), poplar (*Populus tremula* L.), and eucalyptus (*Eucalyptus camaldulensis* Dehn. (Turkish river red gum)) were used as wood materials in this work.

Twenty paulownia, poplar, and eucalyptus sapwood sample (10 mm × 5 mm × 10 mm; radial × tangential × longitudinal) for each wood species were cut along the grain, and dried at 63°C over night. The samples were divided in two sets: 10 samples as control (untreated), 10 samples as modification (poly(ε-caprolactone) grafted).

2.2. Impregnation and Grafting Polymerization of ε-caprolactone

Samples from each wood species separately put into round bottom flask. Samples for modification were immersed into DMF for overnight for swelling. A solution of 20 g ε-caprolactone with 0.8 g initiator $Sn(Oct)_2$ were rinsed onto wood samples and samples were kept in the overnight to increase impregnation of monomer into cell walls before polymerization reaction. On the other day, dry DMF (20 ml) were poured into the reaction media and nitrogen was used to degas reaction solution by bubbling for 10 min.

Polymerization was carried out at 105°C (overnight). Reaction was completed by starting acetone washing with many portions of acetone for 4 hours, and then with distilled water (overnight). At the end, wood samples were dried at 63°C (overnight). DMF and acetone which were used for polymerization and washing process are good enough for dissolving both polycaprolactone and ε-caprolactone monomer.

2.3. Thermal Analysis

2.3.1. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis (DMTA) was carried out to obtain thermo-mechanical characteristics of the chemically modified or unmodified (control) samples by a DMTA analysis equipment (Nanotechnology Laboratory & Thermal Analysis Laboratory at Istanbul University). The temperature was raised from 30 to 250°C.

2.3.2. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed to determine thermal stability properties of the chemically modified or unmodified (control) samples by a TGA/DTA analysis equipment (Nanotechnology Laboratory & Thermal Analysis Laboratory at Istanbul University). The samples were exposed to a heating rate of 10°C/min over a temperature range of 30°C to 800°C.

3. RESULTS

3.1. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA results of the chemically modified or unmodified poplar wood materials are shown in Fig. 1.

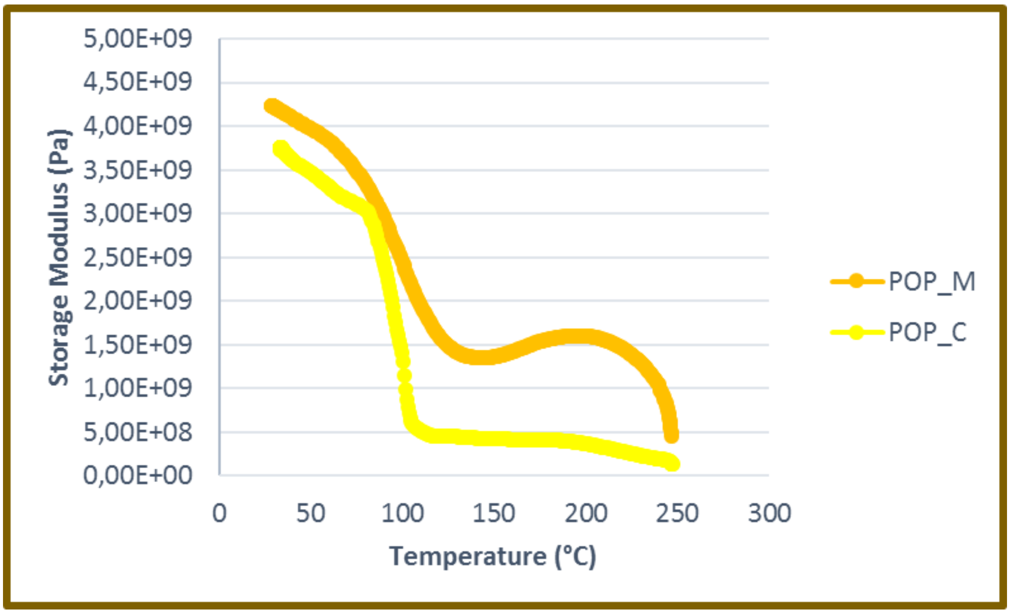

Figure 1. Storage modulus curves of the modified or unmodified poplar wood materials

It is indicated that the storage modulus values of the chemically modified poplar materials decrease with increasing temperature from 30 °C to about 150 °C. After 150 °C, heating continues and a slight increase is observed in the storage modulus. The average initial storage modulus value of the chemically modified poplar materials was 4.23E+09 Pa while the value was 3.73E+09 Pa in the control poplar materials. It clearly revealed that the initial storage modulus performance of the poplar wood materials was increased by 13.4% with the PCL modification.

DMTA results of the chemically modified or unmodified eucalyptus wood materials are given in Fig. 2.

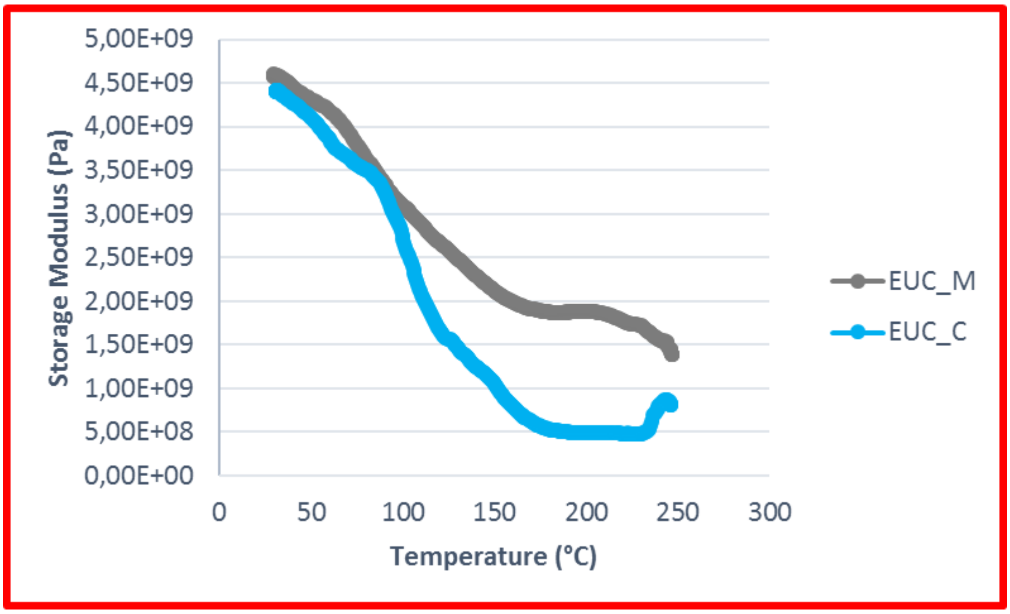

Figure 2. Storage modulus curves of the modified or unmodified eucalyptus wood materials

Fig. 2 shows that the storage modulus values of the chemically modified eucalyptus wood materials by PCL decrease with increasing temperature. The chemically modified materials had an average initial storage modulus value of 4.58E+09 Pa whereas the unmodified eucalyptus wood materials had an average initial storage modulus value of 4.39E+09 Pa. The findings obtained from the DMTA analysis indicate that the PCL modification slightly enhanced the initial storage modulus values of the eucalyptus wood materials.

It was also determined that the chemically modified eucalyptus wood materials had higher storage modulus values (1.89E+09 Pa) at 200 °C than those of the unmodified materials (0.49E+09 Pa). The increment was 285%.

DMTA results of the chemically modified or unmodified paulownia wood materials are provided in Fig. 3.

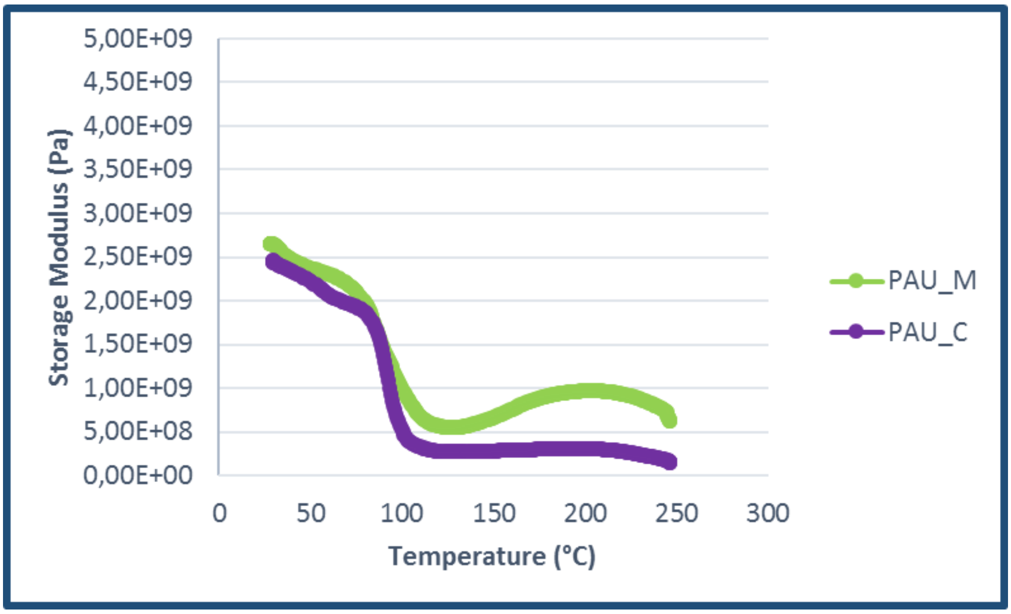

Figure 3. Storage modulus curves of the modified or unmodified paulownia wood materials

It is obvious that the storage modulus values of the chemically modified paulownia wood materials by PCL decreased until temperature reached 125°C. After that point, the storage modulus slightly increased as temperature increased up to 200 °C. The average initial storage modulus value of the chemically modified paulownia wood materials was 2.66E+09 Pa. It was acquired that the storage modulus of the unmodified materials was 2.44E+09 Pa. It indicates that the initial storage modulus values of the chemically modified materials was enhanced by around 9%.

3.2. Thermogravimetric Analysis (TGA)

TGA results of the chemically modified or unmodified wood materials are given in Fig. 4, Fig. 5, and Fig. 6.

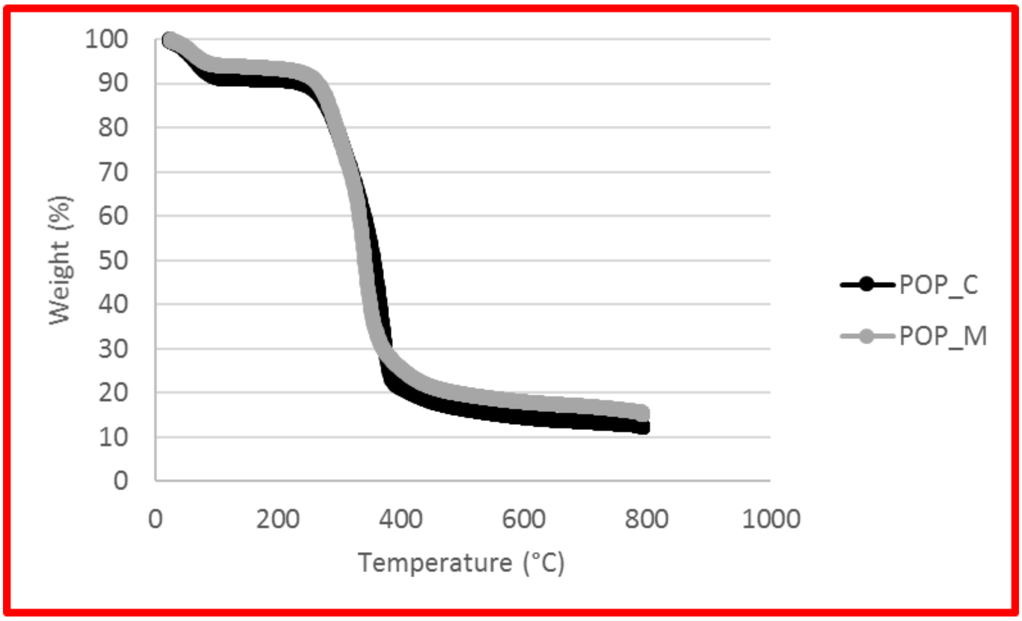

Figure 4. TG curves of the modified or unmodified poplar materials

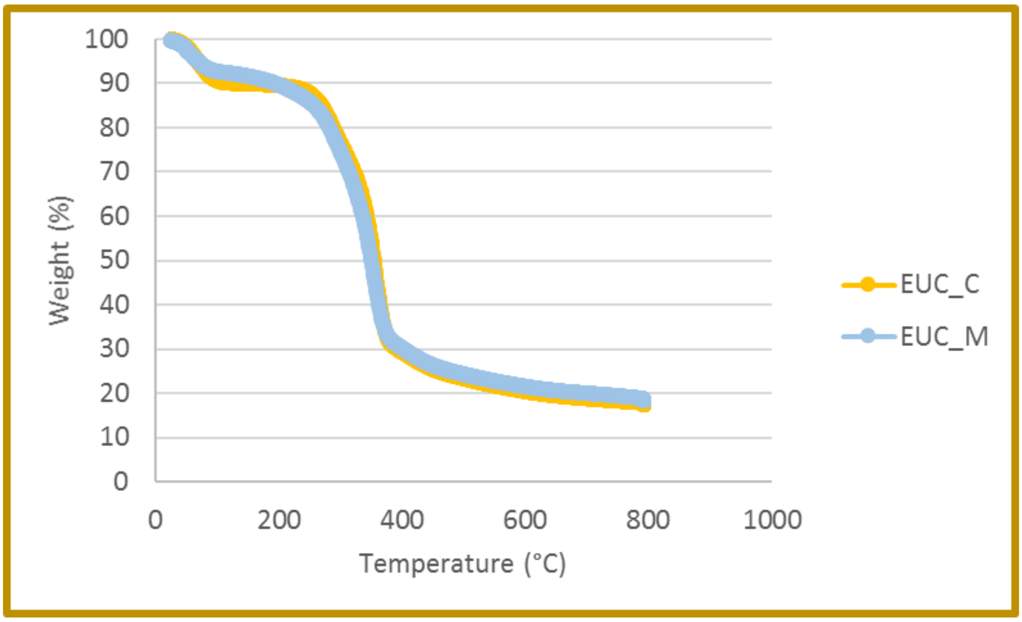

Figure 5. TG curves of the modified or unmodified eucalyptus materials

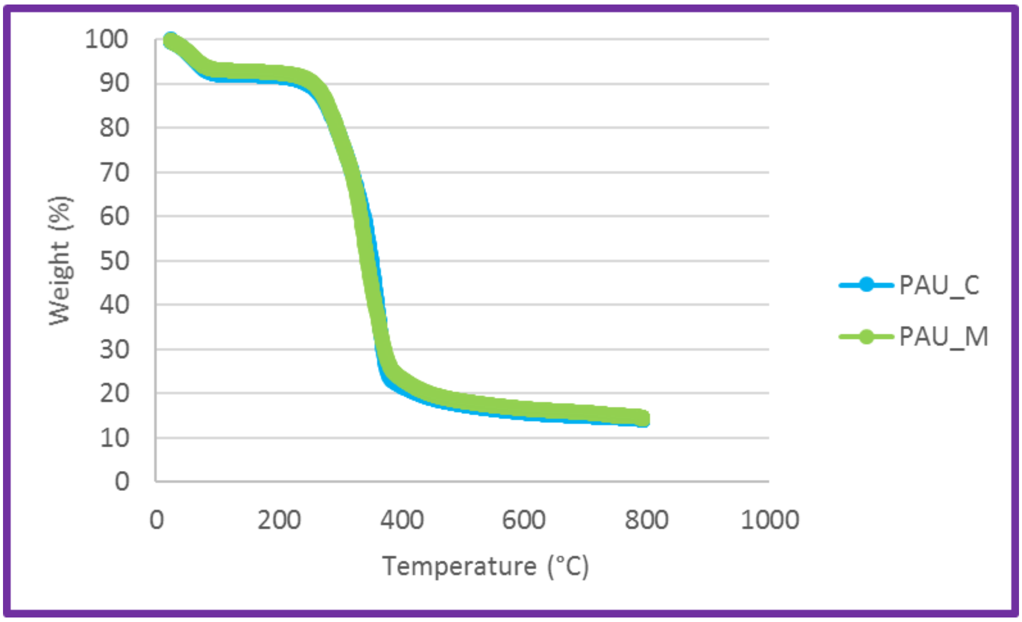

Figure 6. TG curves of the modified or unmodified paulownia materials

The findings determined from the TGA analysis show that the chemical modification by PCL significantly affected the thermal properties of the wood materials. The materials presented two separate decomposition procedures. TG% values of the chemically modified materials were higher than those of the unmodified materials at 800°C.

4. CONCULUSION

The wood materials were chemically modified by PCL. The DMTA and TGA analyses of the modified or unmodified materials were carried out. It was revealed that the PCL modification process significantly influenced dynamic mechanical thermal characteristics and thermal stability of the materials. PCL is biodegradable, thus there will be no disposal problem of material after its lifetime so wood materials can be modified it to obtain new materials having higher performance.

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