

Vegetable oil-based Composite Vitrimers containing Dynamic Bonds of Amide-Imide and Boronic Ester

Amid-İmit ve Boronik Esterin Dinamik Bağlarını İçeren Bitkisel Yağ Bazlı Kompozit Vitrimeler

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Abstract

Eco-friendly, sustainable, renewable cross-linked materials have become a highly focused area of research in recent years. In this study, vegetable oil-based fully sustainable materials were developed. For this purpose, the composite films were prepared from tung oil and vegetable-based amine, gallic acid, and boric acid. The materials exhibited excellent self-healing properties without any catalyst by dynamic bonds. Self-healing of the materials has been achieved through both amide-imide exchange reactions and boric acid ester bonds. The results show that these materials have the potential as a cost-effective solution for various industrial applications.

Keywords: sustainable materials, vitrimer, self-healing, vegetable oils

Öz

Son yıllarda çevre dostu, sürdürülebilir, yenilenebilir çapraz bağlı malzemeler oldukça odaklanılan bir araştırma alanı haline gelmiştir. Bu çalışmada bitkisel yağ esaslı tamamen sürdürülebilir malzemeler geliştirilmiştir. Bu amaçla tung yağı ve bitkisel bazlı amin, gallik asit ve borik asitten kompozit filmler hazırlanmıştır. Malzemeler, herhangi bir katalizör olmadan dinamik bağlarla mükemmel kendi kendini iyileştirme özellikleri sergilemiştir. Malzemelerin kendi kendine iyileşmesi hem amid-imid değişim reaksiyonları hem de borik asit ester bağları yoluyla sağlanmıştır. Sonuçlar, bu malzemelerin çeşitli endüstriyel uygulamalar için uygun maliyetli bir çözüm olma potansiyeline sahip olduğunu göstermektedir.

Anahtar kelimeler: sürdürülebilir malzemeler, vitrimer, kendi-kendini onarma, bitkisel yağlar

I. INTRODUCTION

Thermoset polymers, which are permanently cross-linked, exhibit excellent thermal and dimensional stability, superior mechanical strength, and chemical resistance. Due to these properties, they are preferred in many fields such as coatings, adhesives, and composites. However, thermoset polymers cannot be reshaped and reprocessed because of their covalent bonding [1].

Vitrimers are a new material class that allows three-dimensional polymer network structures to be recycled through dynamic covalent bonds. Ester bonds, disulfide linkages, acetal linkages, acyl hydrazone bonds, and imine bonds are preferred [2]. The interest in sustainable materials worldwide contributes to developing new bio-based vitrimer. Vitrimers are covalently addable networks (CANs). Bond exchange reactions allow CANs to alter their topology [1].

In particular, vegetable oils are an important resource due to their wide availability in nature and high biocompatibility [3]. For example, Altuna et al. prepared bio-based vitrimer materials from epoxidized soybean oil and citric acid [4]. Zhang et al. synthesized fully bio-based vitrimers based on castor oil and lignin [5]. Tung oil (TO), is a vegetable oil obtained from tung tree, and is mostly used in the coatings and paint industry. Approximately 80% of it is composed of α -eleostearic acid. These abundant conjugated unsaturated groups allow

for advanced modification reactions [6]. For example, TO can be used to prepare cross-linked tung oil derivatives through electrophilic substitution reactions with polyphenols [6]. Copolymerization reactions can be performed on the unsaturated groups of tung oil via free radical or cationic mechanisms [7]. Polyurethanes can be obtained through esterification reactions with bio-based polyols [8]. TO can also participate in highly selective Diels-Alder reactions due to its conjugated double bonds. Maleic anhydride is commonly used in Diels-Alder reactions [9].

It is known that neighboring groups accelerate the rate of exchange reactions in CANs. In particular, carboxylic acid end-groups form a cyclic structure, allowing exchange reactions to occur at a lower energy level. The recyclability of the material improves with faster exchange reactions [11]. Du Prez et al. studied transesterification reactions of phthalic acid derivatives. The results show that the formation of anhydride intermediate cause to higher stress relaxation rates [12]. It has been observed that acetoacetyl-based amide groups exhibit the same behavior during transamidation reactions [13].

In this study, fully bio-based vitrimers prepared from TO and vegetable-based amine (Priamine 1074). The recyclability of the vitrimer materials provided by both amide-imide and boronic ester exchange reactions. Thermal stability and self-healing properties of the materials were analyzed. The vitrimers exhibited a fast thermal reprocessability without a catalyst because of their dynamic nature.

II. MATERIALS AND METHODS

2.1. Reagents

Tung oil was purchased from the local market. Malic anhydride (99%), boric acid ($\geq 99.5\%$), and gallic acid (anhydrous) were provided by Sigma-Aldrich. Priamine 1074 (DDA) was kindly supplied by Croda.

2.2. Apparatus

The chemical structure of maleated-tung oil (TOMA) was verified by using FTIR (Perkin-Elmer Spectrum100 ATR-FTIR Spectrophotometer). The thermal performance of the cured samples was investigated by thermal gravimetric analysis (Perkin Elmer STA6000). The samples were performed at 30 to 750°C with heating at a rate of 20°C/min under a nitrogen atmosphere. Additionally, the glass transition temperature (T_g) of the samples was evaluated by a Differential Scanning Calorimeter (Perkin Elmer Diamond DSC).

The density of crosslinking was calculated by the gel content method. The dried samples were immersed in

chloroform for 24 h. The gel content was calculated as $\frac{w_r}{w_i} \times 100$. (w_r ; residual weight, w_i ; initial weight).

2.3. Synthesis of maleated-tung oil (TOMA)

The functionalization of tung oil with anhydride groups was carried out via the Diels-Alder reaction. Methods from the relevant articles in the literature were followed [14,15]. Tung oil (0.118 mol) and maleic anhydride (0.0472 mol) were placed in a round bottom equipped with a condenser. The reaction was continued for 6 h. finally, the mixture was cooled to room temperature and unreacted maleic anhydride was removed with previous study procedures [16]. The product was obtained with an acid number of 194,74 mg/g. The reaction scheme is shown in Figure 1.

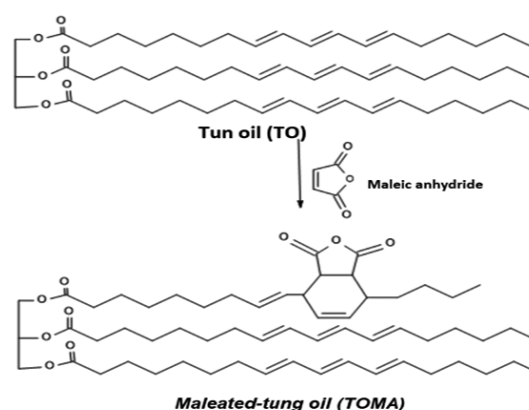


Figure 1. The synthesis pathway of maleated-tung oil

2.4. Preparation of GA-borate complex (GAB)

The synthesis of the GA-borate complex was adapted from the literature procedure [17]. Gallic acid (5 g) and distilled water (10 mL) were stirred until a homogenous solution. Boric acid (0.05 g) was added to the solution. The mixture was stirred for 2.5 h at 65 °C. Subsequently, the temperature of the mixture was increased to 95 °C and stirred for 2 h. The reaction scheme is shown in Figure 2.

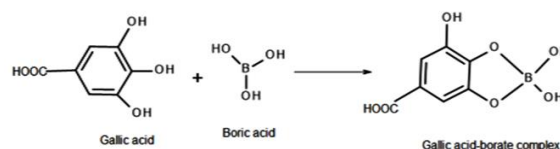


Figure 2. Synthesis pathway of gallic acid-borate (GAB) complex

2.5. Preparation of films

TOMA and DDA were used as anhydride and amine sources, respectively. All formulations were prepared with anhydride/epoxy ratios 1. The GA-borate complex was added to the two formulations as 0.001 g and 0.03 g. The names of the prepared formulations were TOMA-DDA, TOMA-DDA-0.001GAB, and TOMA-DDA-0.03GAB.

III. RESULTS AND DISCUSSION

3.1. FTIR Spectra

The structural analysis of the product obtained from the reaction of tung oil and maleic anhydride was performed using FTIR spectroscopy. The FTIR spectrum of TO and TOMA is given in Figure 3. Figure 3a shows the FTIR spectrum of TO. The characteristic aliphatic C-H peaks of tung oil were observed in the 2900-2800 cm^{-1} region. The peak observed at 1740 cm^{-1} is attributed to the carbonyl stretching linked to glycerol units in vegetable oil [18]. The C-O stretching is observed at 1115 cm^{-1} . Additionally, the sharp peak observed at 990 cm^{-1} is due to the unsaturated groups in the fatty acid units. After the modification of anhydride groups, new peaks were observed (Figure 3a). The characteristic carbonyl stretching of the anhydride ring appeared at 1847 cm^{-1} and 1740 cm^{-1} . The peaks at 1210 and 1094 cm^{-1} correspond to the C-O stretching of TO [16].

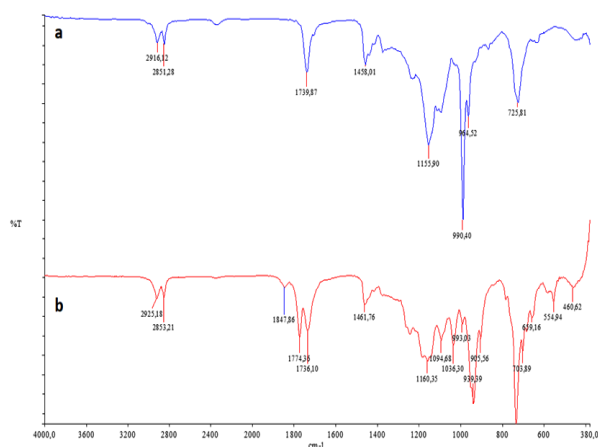


Figure 3. FTIR spectra of (a) TO and (b) TOMA

3.2. Thermal Analysis

The TGA spectrum of boric acid and CA-borate is shown in Figure 4. Up to approximately 120 $^{\circ}\text{C}$, no mass loss of boric acid was observed in the TGA spectrum. After this temperature, a two-step decomposition curve was observed. The first mass loss occurred in the temperature range up to 200 $^{\circ}\text{C}$. In this region, metaboric acid (HBO_2) is formed through the dehydration of boric acid. As metaboric acid is heated at higher temperatures, boron trioxide (B_2O_3) is formed. The first mass loss is due to dehydration, and the second is due to the conversion of HBO_2 to B_2O_3 [19]. After gallic acid bonded to boric acid, the decomposition temperatures shifted to higher temperatures. This indicates that the thermal stability of the resulting GA-borate complex is higher. Additionally, the ash percentage decreased due to the increase in organic content from GA.

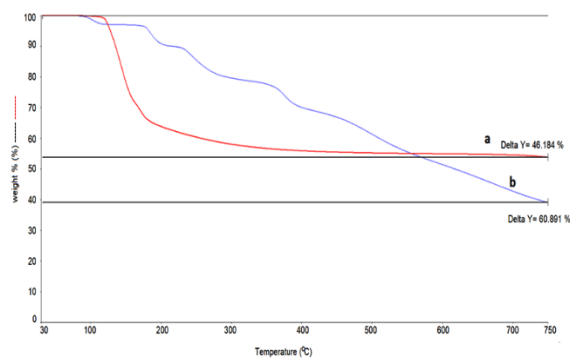


Figure 4. TGA curves of (a) Boric acid and (b) GA-borate

Figures 5a and b show the TGA and DTG curves of TO and TOMA. The mass loss of TO was observed between 400-510 $^{\circ}\text{C}$. However, the two-step degradation profile was observed with the grafting of anhydride groups onto TO. Two spectrums have similar degradation profiles.

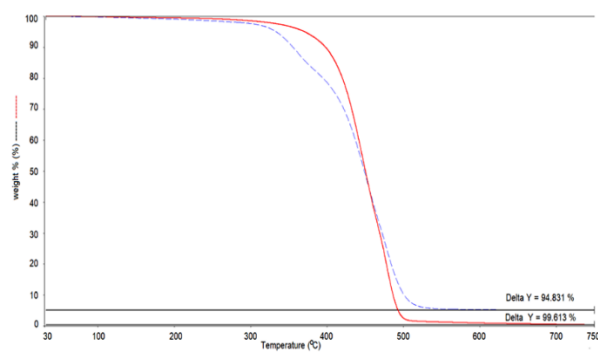


Figure 5a. TGA curves of TO and TOMA

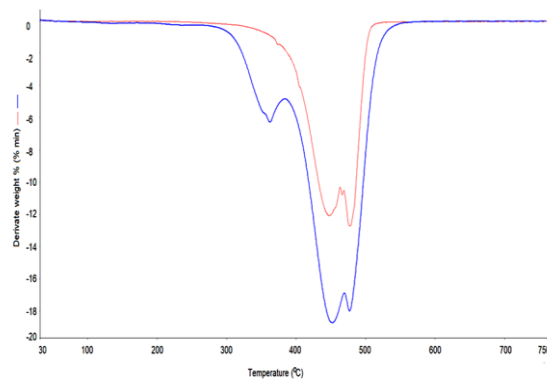


Figure 5b. DTG curves of TO and TOMA

The thermal stability and degradation mechanism of the prepared fully bio-based films were investigated by TGA analysis. TGA curves and data are given in Figure 6. All samples exhibited a one-step degradation profile. The initial decomposition temperature of the materials increased with the rise in the amount of GAB. Samples containing free GAB (TOMA-DDA) and 0.01% of

GAB (TOMA-DDA-0.001GAB) exhibited decomposition at similar temperatures. However, with the increase in GAB content (TOMA-DDA-0.03GAB), the temperature shifted to a higher value. In addition, the ash content also increased with the rise in boron content.

Table 1. Thermal degradation temperatures and ash values of the materials

| Samples | TOMA-DDA | TOMA-DDA-0.001GAB | TOMA-DDA-0.03GAB |
|-----------------------|----------|-------------------|------------------|
| T _{5%} (°C) | 206 | 205 | 338 |
| T _{50%} (°C) | 473 | 476 | 478 |
| Char (%) | 1.32 | 2.5 | 12.17 |
| Gel content (%) | 90 | 66 | 50 |
| T _g (°C) | -2 | -5 | -9 |

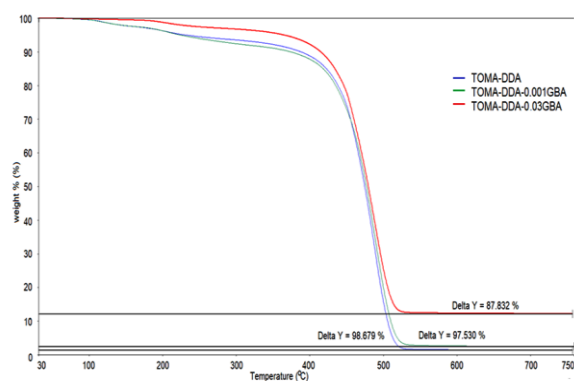


Figure 6. TGA curves of the films

The glass transition temperatures (T_g) values of the materials were measured using DSC. The results are given in Table 1. T_g is ranged from -9 to -2 °C. The T_g value of TOMA-DDA is -2 °C. However, the T_g values of TOMA-DDA-0.001GAB and TOMA-DDA-0.03GAB samples have shifted to lower temperatures. It can be stated that the cross-link density in samples containing GAB is lower compared to the TOMA-DDA sample. This is consistent with the gel content results. There is a decrease in gel content values from TOMA-DDA to TOMA-DDA-0.03GAB.

3.3. Self-healing performance of the films

The films were cut in half to examine the self-healing properties. First, the films were cut into two parts. Then two parts of the films were re-adhered by press at room temperature, 80 °C and 100 °C, respectively. The films

were kept for 15 minutes at each temperature value. The images showing the healing profile of the films are presented in Figure 7-9.

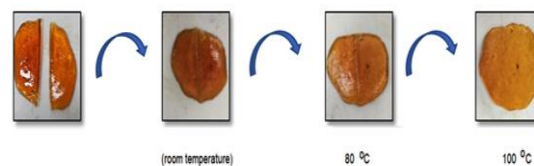


Figure 7. The healing process of TOMA-DDA

For TOMA-DDA, no recovery is observed at room temperature and 80 °C. However, full healing of the film is observed with the increase in temperature to 100 °C (Figure 7). The healing of the sample is facilitated by the reversible amide-imide bond between TOMA and DDA [10]. Since this bond exchange occurs above 80 °C, the healing is limited at temperatures below 80 °C. However, full recovery can be achieved when the temperature exceeds 80 °C.

The images of the healing process on TOMA-DDA-0.001GAB films are shown in Figure 8. This formulation contains reversible amid-imide bond and also boronic ester bonds that contribute to the healing. Boronic ester bonds are expected to be effective in the healing process at below 80 °C. However, these bonds were not sufficient for full recovery. This may be due to the limited amount of GAB (0.0001 g GAB) used in the formulation. Complete healing was not observed under room temperature and 80 °C conditions. As in the case of the TOMA-DDA sample, full recovery was achieved when the temperature exceeded 80 °C.

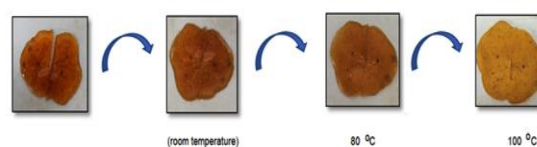


Figure 8. The healing process of TOMA-DDA-0.001GAB

The healing in films containing GBA is expected to occur through the metathesis of boronic acid esters [20]. Boronic ester metathesis reaction occurs without the addition of any catalyst at low temperatures [21]. It has been observed that boronic ester bonds contribute to the recovery in the case of TOMA-DDA-0.03GAB (Figure 9). For TOMA-DDA-0.03GAB, higher healing rate is observed at room temperature, while full recovery is achieved at 80 °C. In addition, amic acid groups are converted to imide groups through imidization [10], and full healing was achieved at 100 °C.

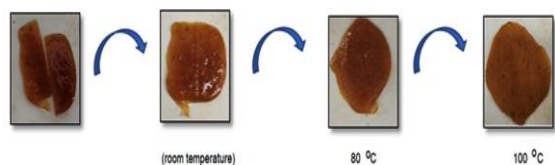


Figure 9. The healing process of TOMA-DDA-0.03GAB

IV. CONCLUSION

In recent years, there has been an increasing interest in reusable materials to prevent environmental damage and reduce raw material waste. In this study, vegetable oil based films containing tung oil and fatty acid diamine were prepared using a simple, fast, and environmentally friendly method. Additionally, a dynamic bond concept has been incorporated into the prepared materials, providing them with self-healing properties. Dynamic covalent network structures allow materials to be reprocessed repeatedly. Therefore, prevents raw material waste and also reduces environmental pollution. For this study, two dynamic covalent bond concepts created an amide-imide exchange reaction and boric acid ester bonds. Boric ester bonds enable the deformed material to return to its original state under room temperature and 80 °C. When the temperature rises above 80 °C, the amide-imide exchange reaction contributes to the renewal. Among all samples, TOMA-DDA-0.03GBA has exhibited the best healing process. It is expected that using this concept will lead to the development of functional materials and contribute to sustainability.

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