Araştırma Makalesi - Research Article

Synthesis and Characterization of Bio-Derived Monoliths

Biyolojik Kaynaklı Monolitlerin Sentezi ve Karakterizasyonu

Burcu Kekevi[1*]

ABSTRACT

Colloidal templating is a versatile and practical method to prepare macroporous polymer monoliths with a well-defined two-stage porosity and tuneable morphology. Due to their advantageous morphology colloidal templated monoliths can find application in many areas. In this study, a renewable monomer was used for the development of sustainable macroporous polymer monoliths. Copolymerization of a renewable monomer mixture in a colloidal system was achieved by using a flexible diacrylate crosslinker. For this purpose, *d*-limonene was copolymerized with ethylene glycol dimetacrylate (EGDMA) in equivalent ratios to investigate the effect of monomer structure on the final material properties. In the end, thermal and morphological properties of the resulting sustainable macroporous polymer monoliths were investigated by Differential Scanning Calorimetry (DSC), Thermal Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM), respectively. Additionally, the specific surface area of the obtained monolithic materials was measured through N_2 adsorption/desorption analyses by applying Brunauer–Emmet–Teller (BET) equation to the N_2 isotherms of the samples. It was determined that the presence of *d*-limonene led to an extraordinary one-hollowed ring morphology due to the porogen effect of this renewable monomer.

Keywords- Colloidal Templating, Terpene, D-Limonene, One-Hollowed Ring Morphology

ÖZ

Kolloidal şablonlama, iyi tanımlanmış iki aşamalı gözenekliliğe ve değişen morfolojiye sahip makro gözenekli polimer monolitleri hazırlamak için kullanılan çok yönlü ve pratik bir yöntemdir. Bu yöntemle sentezlenen monolitler, avantajlı morfolojileri nedeniyle birçok alanda uygulama bulabilirler. Bu çalışmada, sürdürülebilir makro gözenekli polimer monolitlerin geliştirilmesi için yenilenebilir bir monomer kullanılmıştır. Bu amaçla, yenilenebilir monomer karışımının kopolimerizasyonu kolloidal sistemde esnek bir diakrilat çapraz bağlayıcı kullanılarak sağlandı. Monomer yapısının nihai malzeme özellikleri üzerindeki etkisini araştırmak için *d*-limonen eşdeğer oranlarda etilen glikol dimetakrilat (EGDMA) ile kopolimerize edildi. Son olarak, elde edilen sürdürülebilir makro gözenekli polimer monolitlerin termal ve morfolojik özellikleri sırasıyla Diferansiyel Taramalı Kalorimetri (DSC), Termal Gravimetrik Analiz (TGA) ve Taramalı Elektron Mikroskobu (SEM) ile araştırıldı. Ek olarak, elde edilen monolitik malzemelerin spesifik yüzey alanı, numunelerin N_2 izotermlerine Brunauer–Emmet–Teller (BET) denklemi uygulanarak N_2 adsorpsiyon/desorpsiyon analizleri ile ölçülmüştür. Bu yenilenebilir monomerin porojen etkisinden dolayı *d*-limonen varlığının olağanüstü tek delikli halka morfolojisine yol açtığı belirlendi.

Anahtar Kelimeler- Kolloidal Şablonlama, Terpen, D-Limonen, Tek Delikli Halka Morfoloji

[1]*Sorumlu yazar iletişim: bkekevi@yalova.edu.tr (https://orcid.org/0000-0002-2364-1957)
Material and Material Processing Technologies Department, Yalova Vocational School, 77200, Yalova, Türkiye

I. INTRODUCTION

Depletion of fossil sources, uncontrollable population growth, greenhouse effect and destructions in the ecosystem leads to growing attention on the environmental awareness and led scientific studies to direct towards renewable resources [1]. As renewable organic compounds, carbohydrates, and proteins are frequently preferred in so many different applications. However, terpenes and terpenoids, which are composed of a vast range of molecules, generally find application in fragrances, cosmetics, food, and pharmacy, due to the pleasant smell of these compounds [2].

Terpenes are inexpensive, abundant, and easily synthesized renewable structures that they do not compete with natural sources and isoprene like chain structure of these molecules has made them ideal for different applications. Depending on the number of isoprene units, terpenes are classified as monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), sesterterpenes (C25), triterpenes (C30), and rubber (C5)n. Among all terpenes, monoterpenes, especially, myrcene, ocimene, and alloocimene are unsaturated compounds showing similar structure to classical petrochemicals [3]. A monocyclic terpene, limonene is an optically active renewable compound which is a by-product of citrus industry [4] Limonene, which is an effective and non-toxic terpene, is generally preferred as a solvent instead of the solvents, such as toluene, acetone, and chlorinated solvents [5,6]. However, the main advantage of this molecule is the presence of two double bonds; an internal and an external vinyl groups which made this compound suitable as a monomer to synthesize bio-derived polymers. The polymerization reaction of *d*-limonene succeeded in the presence of a Lewis acid as a catalyst and yielded with thermoplastics resins with relatively low molecular weight [7].

The kinetics and mechanisms on the homo-polymerization of *d*-limonene was performed by Singh and Kamal [8] in the presence of benzoyl peroxide as a catalyst. Poly (*d*-limonene) was synthesized by photo-induced free radical polymerization at low temperature and soft, gum-like polymer, which could be used as an additive in coatings and adhesives, obtained [9]. Mathers et al. [10] investigated the effect of *d*-limonene as a solvent and a chain transfer agent in ring opening metathesis polymerizations of alkene monomers. The resulting polymer had alkene at one terminal of polymer chain whereas a monoterpene at the other end. Thiol-ene polymerization of *d*-limonene is attracting much more attention in order to synthesize multi-functional polymers for post-functionalization [11]. Among the studies performed on the polymerization of *d*-limonene, emulsion polymerization of *d*-limonene is so limited. Nanoemulsion of *d*-limonene in water was performed by ultrasonic emulsification for investigating the efficiency of resulting structure in drug-delivery [12]. In another study, process optimization and the stability of *d*-limonene-in-water nanoemulsions which were synthesized by ultrasonic emulsification method, were determined by response surface methodology [13].

Emulsion templating can be defined as a method in which the internal phase ratio of the emulsion is over 74 vol%. By varying the experimental parameters such as surfactant ratio, stirring rate, monomer and cross-linker ratio, etc., internal phase volumes of the high internal phase emulsions (HIPE) can be reached up to 99%. By polymerization of the external monomer phase and removal of the internal phase by extraction process, highly cross-linked, open porous, and low density monoliths which termed as polyHIPE, can be synthesized for specific applications such as catalysis, energy storage and tissue engineering [14-16]. The first time in the literature, Mert and Kekevi [17] achieved to synthesize porous terpene based monoliths by free radical polymerization of β-myrcene with ethylene glycol dimetacrylate (EGDMA) by using emulsion templating process and showed that in the presence of β-myrcene, monoliths has gained elasticity.

In this study, a monocyclic terpene, *d*-limonene copolymerized with EGDMA via free radical copolymerization by emulsion templating method, for the first time in literature. The aim of the study is determining the effect of the cyclic structure of terpene on the polymerization of this monomer. The resulting poly (*d*-Lim-co-EGDMA) monoliths can find application in chromatography columns due to the high Mercury adsorption capacity of *d*-limonene [18].

II. MATERIAL AND METHODS

D-Limonene (98%, Alfasol, Spain), ethylene glycol dimethacrylate (EGDMA; 98%, Sigma-Aldrich), Pluronic® L121 (poly(ethyleneglycol)-block-poly(propyleneglycol)-block-Poly(ethyleneglycol), M_n ~ 4400, non-ionic surfactant, Aldrich), sorbitane monooleate (Span®80, non-ionic surfactant, Sigma-Aldrich), potassium persulfate (KPS; ≥ 99%, ACS reagent), and calcium chloride hexahydrate ($CaCl_2.6H_2O$; 98%, Sigma-Aldrich) were used as received. In all experiments, ultrapure double distilled deionized water was used.

Chemical structure of PLE was confirmed by Fourier Transform Infrared (FTIR) spectroscopy. For this purpose, spectrums of the *d*-limonene, EGDMA and PLE were all recorded on a Perkin Elmer Spectrum 100 Fourier transform infrared spectrometer in 400–4000 cm^{-1}.

Thermal properties of PLE was investigated by DSC and TGA analysis. To determine glass transition temperatures of the samples, DSC analysis was conducted by using a Mettler Toledo TGA/DSC 3+ STAR system under N_2 flow. For each sample, heating-cooling-heating cycles were performed between −30 and 200°C at a heating rate of 10°C/min. TGA analysis of PLE and PME was carried out by a Mettler Toledo TGA/DSC 3+ STAR system thermogravimeter between 30 and 650°C at a heating rate of 10°C/min. All analysis were carried out under the nitrogen purge to inhibit sample oxidation [19].

Morphology of the PLE polyHIPEs was determined by SEM analysis with a Zeiss Supra 40 VP model scanning electron microscope. To take the SEM images of the samples, the samples were cutted into small pieces which were firstly coated with gold [16]. BET surface area (δ_{BET}) of the resulting monoliths was determined by using Micromeritics Gemini VII Surface Area and Porosity Analyzer (Micromeritics Instrument Corporation,USA). Prior to analysis, degassing of each sample, which was performed with a Micromeritics FlowPrep060 Sample Degas Unit (Micromeritics Instrument Corporation, USA), continued at 25°C for 48 h. In order to calculate the BET surface areas, three measurements were taken for each monolith sample by using three different specimens and the resulting BET surface area value was calculated by taking the arithmetic average of three measurements [20].

A. Synthesis of d-Limonene Based Monoliths

The synthesis of PLE polyHIPEs was performed by using a classical HIPE preparation method with a nominal porosity of 80% and monomer: comonomer ratio of 50:50. Monomer phase comprised of *d*-limonene, EGDMA and surfactants were weighed in a three-necked round bottom reactor equipped with a mechanical stirrer. For increasing the stability of the emulsions, mixture of the surfactants, hydrophobic emulsifier Span 80 and hydrophilic emulsifier Pluronic L121 was used depending on the amounts of hydrophilic and hydrophobic moieties in the monomer phase. The internal phase, comprising of degassed water, $CaCl_2.6H_2O$ and the initiator, KPS added to the monomer phase dropwise at a certain rate of 50 rpm and the mixing process was continued for 15 min. after the addition of the internal phase. Synthesized HIPEs were transferred into glass jars and the HIPEs were kept in an air-circulated oven at 60°C for 24 h. Subsequent to polymerization, the resulting monoliths were extracted with ethanol in a Soxhlet apparatus for 24 h to achieve typical polyHIPE morphology. The samples were air-dried at 40°C until the weight kept constant [17].

III. RESULTS AND DISCUSSION

Terpenes are widely occurring organic compounds in nature. Due to the presence of unsaturations in the chemical structure of terpenes and terpenoids, they show high reactivity towards the chemical reactions but also towards polymerization reactions. Additionally, by integrating terpenes in a polymer network, elasticity of the resulting material increases due to the isoprene like structure of these compounds. The studies performed on different types of terpenes has shown that due to high reactivity and regioselectivity of terpenes, polymerization of this compounds generally results with polymers with different chemical structures due to the tendency of terpene molecules to react with its monomers, inself [21]. Among previous studies, emulsion polymerization is widely preferred as a polymerization method in free radical polymerization of linear terpenes [22-25]. On the other hand, the polymerization of cyclic terpenes widely succeeded by cationic polymerization [9,10,26,27]. In this study, different than other studies, emulsion templating was preferred in the copolymerization of an acrylate with *d*-limonene, a monocyclic terpene to synthesize porous polymers.

A. Structural Characterization of d-Limonene Based PolyHIPE

In the copolymerization of *d*-limonene with EGDMA by emulsion templating method, the main aim is performing cross-linking structure between the –ene structures of *d*-limonene and –ene structures of EGDMA. The indicative peak, which is verifying the reaction between *d*-limonene and EGDMA, is appeared at 1645 cm^{-1} due to the stretching of the double bonds (C=C) found in the endocyclic and exocyclic positions of the limonene structure. As it can be seen from Figure 1, the peak at 1641 cm^{-1} disappeared in the FTIR spectrum of PLE as a result of the reaction of *d*-limonene with EGDMA, successfully. The disappearance of this peak indicates that -ene structures of *d*-limonene wholly consumed during copolymerization reaction [8]. Additionally, the peaks at 1715 cm^{-1} and 1146 cm^{-1} corresponds to C=O and C-O stretching vibrations of acrylate unit of EGDMA,

respectively. In the FTIR spectrum of PLE, these peaks appeared at same region with low intensity due to the formation of poly (*d*-lim-co-EGDMA) chains at the end of copolymerization.
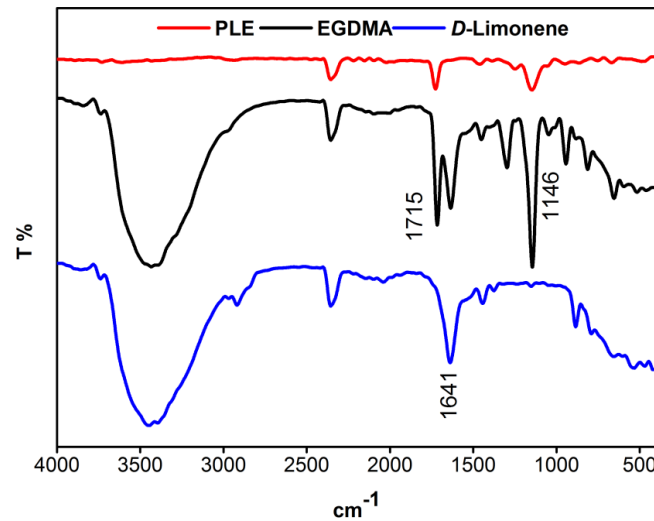

Figure 1. FTIR spectrum of PLE in comparison with the monomers, *D*-Limonene and EGDMA

B. Surface properties of d-Limonene Based PolyHIPE

Surface properties of PLE monoliths were investigated in terms of SEM and BET analysis. SEM images of PLE monoliths which were given in Figure 2, has shown an arbitrary morphology with one-holed ring pore network [28]. Furthermore, the morphology of PLE has shown similarity with morphology of macro porous resin [29]. This morphology is generally formed in the presence of a porogen. In the presence of a highly compatible porogen with the network, polymers with high conversion rate can be obtained. However, in the presence of *d*-limonene, a separate porogen phase is formed, usually with monomer and cross-linker. This leads to the formation of two polymer networks with different cross-linking rate, contrarily. By using *d*-limonene as a monomer in the synthesis of polyHIPE, some of the *d*-limonene was polymerized and a highly cross-linked polymer was obtained [30]. However, some of *d*-limonene acted as a porogen and has been formed another porogen phase, which was resulted in homopolymerization of *d*-limonene.

The effect of *d*-limonene on the change of BET specific surface area (δ_{BET}) value of PLE was also determined. The BET specific surface area of the PLE monolith was determined as 20.47 m^2 g^{-1} as given in Table 1. This result indicated that by incorporating *d*-limonene into polyHIPE network, the specific BET area value of the obtained monoliths slightly increased due to the increment in cross-linking ratio of monoliths when compared with monoliths synthesized by using 100% EGDMA [17].
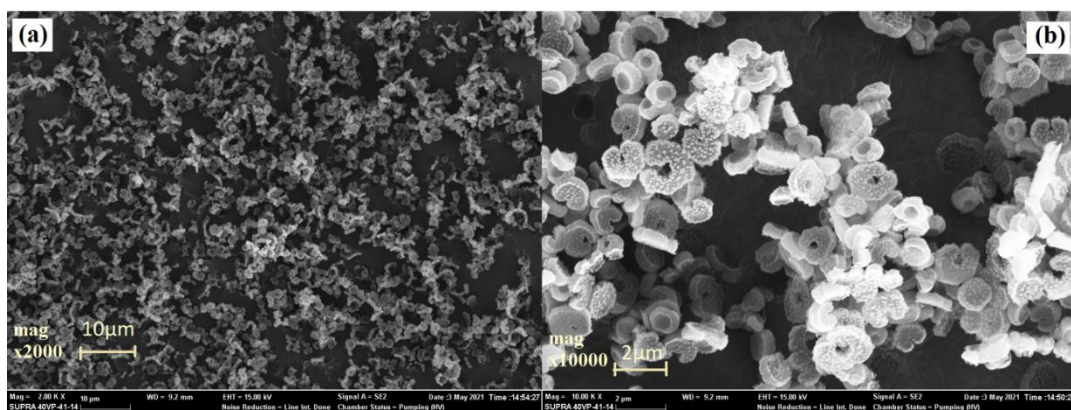

Figure 2. SEM micrograph of PLE monolith a) at x2000 magnification rate b) at x10000 magnification rate

Table 1. Thermal and Surface Properties of PLE monolith

	Glass Transition Temperature (Tg,ºC)	Thermal Degradation Temperature (ºC)	Specific BET Surface Area (δ_{BET} ; $m^2.g^{-1}$)
PLE	105.7; 153.6	310.75; 429.18	20.47

C. Thermal Properties of d-Limonene Based PolyHIPE

Thermal properties of PLE monoliths were investigated in terms of DSC and TGA analysis. Glass transition temperature, thermal degradation temperature and specific BET surface area values of the monolith were given in Table 1, where DSC and TGA thermogram was given in Figure 3. As seen from the DSC curve, three thermal transitions were detected for PLE monolith. The first transition referred to the removal of water entrapped in the monolithic polymer network. The melting peak observed at 105.7ºC corresponded to the polymer chains which were formed by the reaction of *d*-limonene monomers inself [8]. The third transition detected at 156.13ºC was an indication of the cross-linking of *d*-limonene with EGDMA.

TGA thermogram of PLE in Figure 3 was shown similarity with the DSC results of PLE. In the thermogram, two-step degradation was observed. The first degradation step at 310.75ºC corresponded to the thermal degradation of poly (*d*-limonene) whereas the second degradation, which was observed at 429.18ºC, referred to the thermal degradation of poly (*d*-lim-*co*-EGDMA) [9,31].
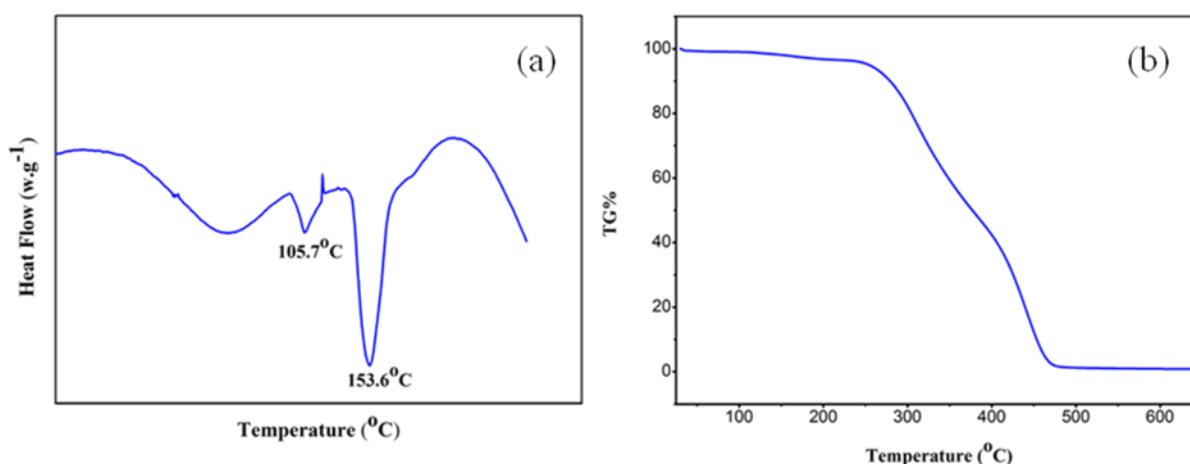

Figure 3. (a) DSC thermogram of PLE monolith **(b)** TGA thermogram of PLE monolith

IV. CONCLUSION

As a conclusion, *d*-limonene was copolymerized with ethylene glycol dimethacrylate, an acrylate monomer with a spacer group of ethylene glycol by free radical polymerization via emulsion templating method, successfully. In the presence of *d*-limonene, the morphology of polyHIPE was extraordinary but thermal properties of PLE monoliths were not changed dramatically. As a future perspective, effect of experimental parameters on the morphology of PLE monoliths will be investigated and the application of this bio-derived polymer network as an adsorbent will be evaluated.

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