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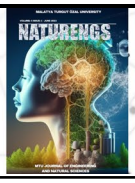

Research Article

Synthesis of Polyurethane from Apricot Kernel Oil and Characterization

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ABSTRACT

In the study, natural origin polyol was obtained from apricot kernel oil. The obtained polyol was used in the synthesis of polyurethane, which is an industrially important polymer. Obtaining polyol from apricot kernel oil was first epoxidized with a two-step process and then converted to the desired polyol structure by oxirane ring opening. The obtained biocompatible polyol structure was subjected to a polymerization process with the hexamethylene diisocyanate structure. The obtained polyurethane structures were characterized chemically, thermally, and morphologically. The chemical structure was investigated by FTIR spectra. The thermal stability, Tg values, and decomposition temperatures of the obtained polyurethane structure were investigated by TGA, DTA, and DSC techniques. The basic morphological features of the polyurethane structure were evaluated by SEM analysis.

***Keywords*:** *Polyurethane, Apricot kernel oil, Polyol, Characterization.*

Introduction

Polyurethane (PU) is obtained by the reaction of an oligomeric polyol and a diisocyanate [1]. The synthesis of polyurethane is given in Figure 1. The raw materials used in the synthesis of polyurethane are petroleum-based. However, due to the fluctuations in oil prices and the depletion of fossil fuel resources, the environmental awareness of society necessitated the replacement of petroleum-based polyols with natural oil-based polyols.

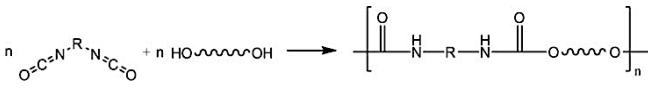

Figure 1. Synthesis of polyurethane from diol and diisocyanate [1]

In the production of biobased polyols, natural oils (vegetable or animal) are preferred, which are the most abundant and cheapest of renewable organic resources [2]. Vegetable oils, in particular, are potential alternatives due to their abundance, relatively low cost, and renewable nature [3]. It has also been used in oils obtained from the seeds of plants such as soybean oil, canola oil, and sunflower oil as renewable resources [4]. Polymers from these biobased polyols are prepared by chemical modification of the carbon-carbon double bonds, allylic carbon groups and ester groups of vegetable oils [5-8]. The chemical industry has shown great interest in the production of biobased polyols, especially those synthesized from vegetable oils [9-11].

In this study, apricot kernel oil was used as a polyol source for the first time and studied as a monomer in polyurethane synthesis. Conversion of apricot kernel oil to polyol was carried out by epoxidation/oxirane ring opening methods. The obtained polyurethane structure was characterized structurally, thermally, and morphologically. Structural characterizations were evaluated with FTIR spectra. The thermal stability, Tg values, and decomposition temperatures of the obtained PU structures were investigated by TGA and DSC techniques. The basic morphological features of the polyurethane structure were evaluated by SEM analysis.

Materials and Methods

The chemicals used in all experimental stages were obtained from Sigma. The apricot kernel oil used was obtained from local herbalists. The change in the chemical bond structures of PU samples was investigated with Thermo Matson 1100 brand Fourier transform infrared spectroscopy (FTIR) analysis technique in the wavelength range of 4000-400 cm-1. Thermogravimetric analysis (TGA) was determined by the Schimadzu TGA-50 device using 10 mg sample in a stable air atmosphere. Thermal stability and structural stability properties were determined by differential thermal analysis (DTA). The device is Shimadzu DTA-50 model. Differential scanning calorimetry (DSC) was performed using the Schimadzu DSC-60 device. Surface morphological properties of polyurethane samples were determined by Leo EVO 40 model scanning electron microscope (SEM) at different magnifications.

Epoxidation and Ring Opening of Apricot Kernel Oil

Here, apricot kernel oil was preferred as the polyol source. In the epoxidation of apricot kernel oil, firstly, the mixture containing glacial acetic acid and sulfuric acid was mixed at a specified temperature, and the mixture was oxidized with hydrogen peroxide in the epoxy. The mixture was separated with a separatory

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funnel [12,13]. The realization of epoxidation was followed by the FTIR spectrum taken at certain times. Epoxy ring opening is a common method for obtaining polyols from vegetable oils [14]. In the study, the ring opening was carried out in a vacuum-inert system for three days. Ring opening was followed by the FTIR spectrum taken at certain times. The produced apricot kernel oil-based polyol was obtained and it is in a ready state for polyurethane synthesis.

Polyurethane Synthesis

Polyol obtained from apricot kernel oil and PEG-200 were mixed in different ratios (95%, 5%) and hexamethylene diisocyanate (HMDI) monomer was added in equimolar form and dissolved in THF/Toluene mixture. The resulting mixture was stirred at room temperature under nitrogen gas. Then, a catalytic amount of triethylamine was added and refluxed at 90°C for four hours. [15]. The determination of the reflux time, that is, the completion of the polymerization was followed by the FTIR spectrum. The reaction was stopped when the free isocyanate peak at 2260 cm-1 in the FTIR spectrum which was caused by isocyanate disappeared.

Results and Discussion

Structural Characterization of Apricot Kernel Oil Based Polyurethane Structure by FTIR Spectrophotometer

In the study, for the first time in the literature, polyol structures obtained from apricot kernel oil were used in the synthesis of polyurethane. The polyurethane structure was prepared by reacting the synthesized apricot kernel oil based polyol/PEG with HMDI. In Figure 2, FTIR spectra of apricot kernel oil, apricot kernel oil in epoxy, apricot kernel oil based polyol (with oxirane ring opening) and polyurethane structures are given. In these spectra, especially in pure apricot kernel oil, the C-H stretch vibration peak is at 3007 cm-1 and the C-H stretch vibration peak of the saturated hydrocarbon group is 2850-2950 cm-1, the C=O stress vibration peak in the triglyceride ester bond is 1747 cm-1, the C-O-C stretching vibration peak of the ester group is at approximately 1100 cm-1, and the stretching vibration of the carbonyl group is observed at 723 cm-1 [17]. In polyol functional structures, this peak disappears and the hydrogen bond stretching vibration of the OH groups becomes evident at 3000-3600 cm-1 [18]. The formation of the urethane bond in the resulting polyurethane was confirmed by FTIR spectroscopy. After the polymerization synthesis, the peaks at 2260 cm-1 belonging to the free isocyanate groups disappeared and new bands were observed due to the urethane bond formed.

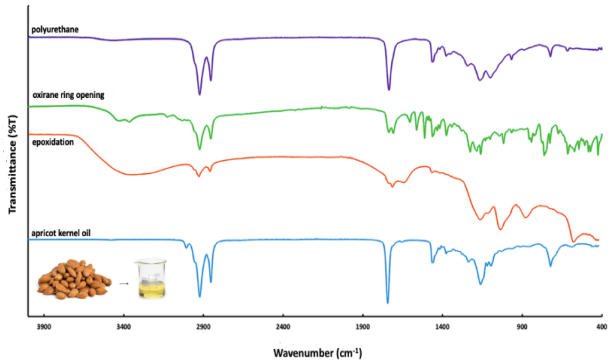

Figure 2. FTIR spectra of pure apricot kernel oil, epoxy apricot kernel oil, apricot kernel oil based polyol and polyurethane structures

When we look at the FTIR spectra of the polyurethane (PU) structure; We see the band corresponding to the NH stretch at a wavelength of 3300-3400 cm−1. Sharp peaks between 2859-2945 cm-1 are seen at –CH stretching and the -C=O absorption band in the urethane structure at 1734 cm-1 and the C–N stretching peak at 1450 cm-1. Characteristic PU absorption bands are observed at 1090 cm−1 C–O and 778 cm−1 C–H. All these peaks confirm the desired polyurethane structure. The peaks are compatible with the literature [19].

Thermal Characterization of Apricot Kernel Oil Based Polyurethane Structure by Tga/Dta/Dsc Thermal Analysis Techniques

The effect of apricot kernel oil used during the preparation of polyurethane on the thermal stability of polyurethane was investigated by TGA and DTA analysis. In Figure 3, TGA and DTA thermograms of apricot kernel structure-based polyurethane structure are given. According to the TGA thermogram, the polyurethane shows a three-stage degradation structure. First of all, between 260°-410°C, cross-linking points and degradation in soft segments are observed. Decomposition in hard segments is observed between 410-450°C. Thermal degradation and carbonization are observed between 450-590°C and consistent with the DTA thermogram. When the DSC thermogram was examined, the Tg transition value of the polyurethane structure was determined to be approximately -45oC below zero. The structure is flexible and durable. Melting endotherm at -25oC, endothermic endo I at 190oC, and endothermic endo II at 275 oC are seen on the DSC thermogram [20].

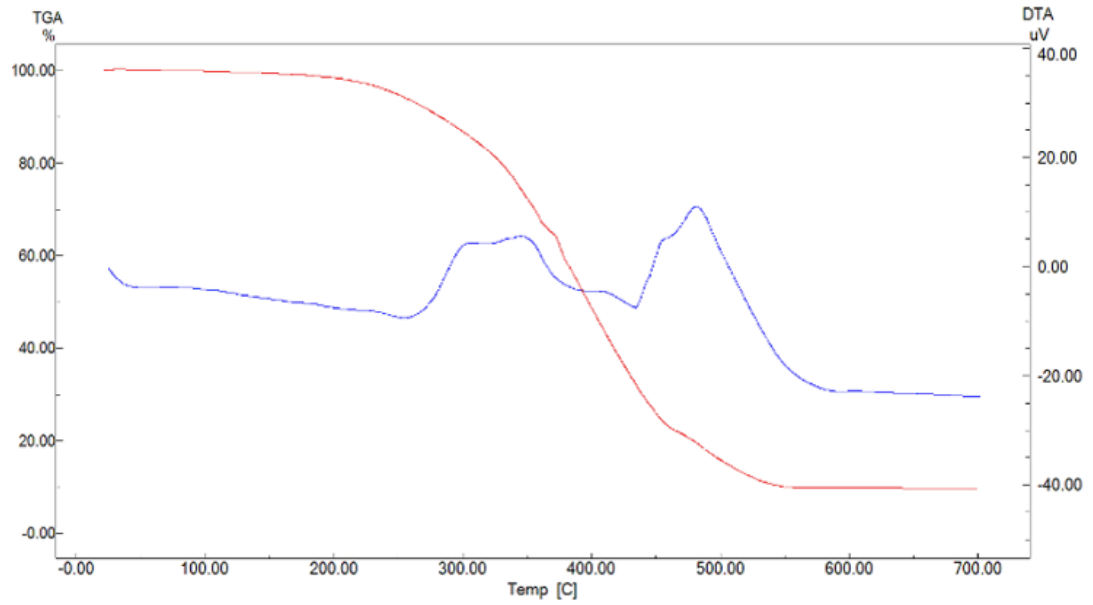

Figure 3. TGA and DTA thermograms of apricot kernel oil based polyurethane structure

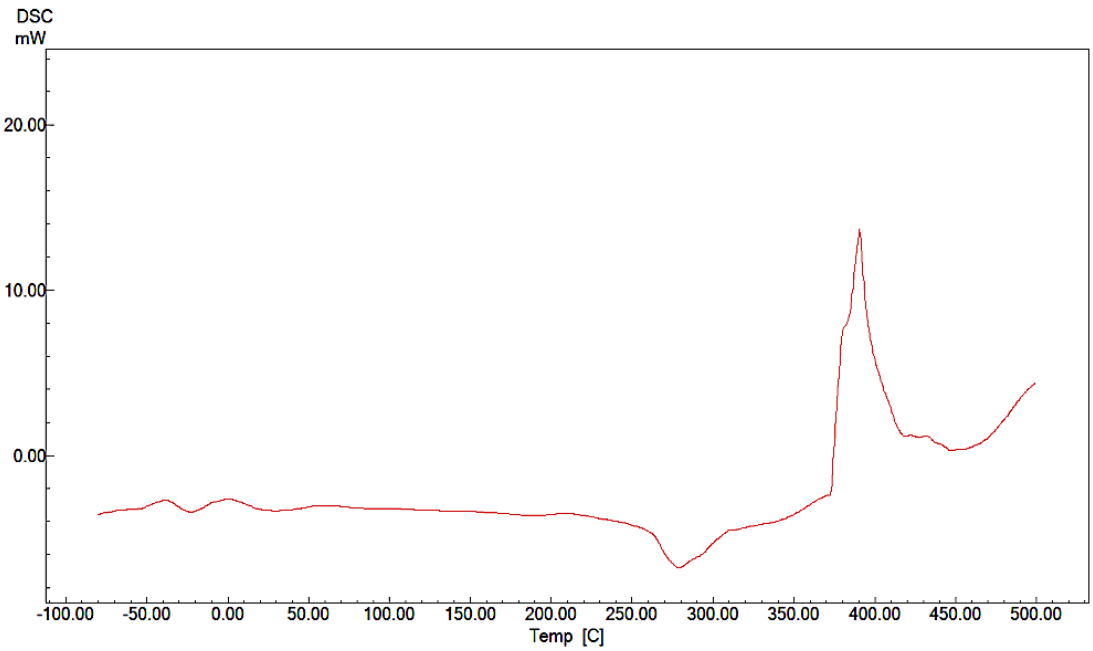

Figure 4. DSC thermogram of apricot kernel oil based polyurethane structure

SEM Images of Apricot Kernel Oil Based Polyurethane Structure

SEM images of the polyurethane structure taken at different magnifications are given in Figure 5. Accordingly, the surface is rough, uneven and the interface between the soft and hard segments observed on the surface is not sharp, indicating partial compatibility or poor interface interaction between the soft and hard segments.

Polyols are obtained from many vegetable oils. Castor oil, palm oil, cardanol oil, and vernonia oil have been used to synthesize polyols to replace petrochemical-based polyols [21,22]. There are polyurethane products based on vegetable oils such as corn oil, olive oil, soybean oil, hazelnut oil, canola oil, castor oil and safflower oil [23]. When we look at the literature, no publications were found on the use of apricot kernel oil in the synthesis of polyurethane. In previous studies, apricot kernel oil has been used in fields such as biodiesel [24], food packaging [25], biomaterials for textile purposes [26].

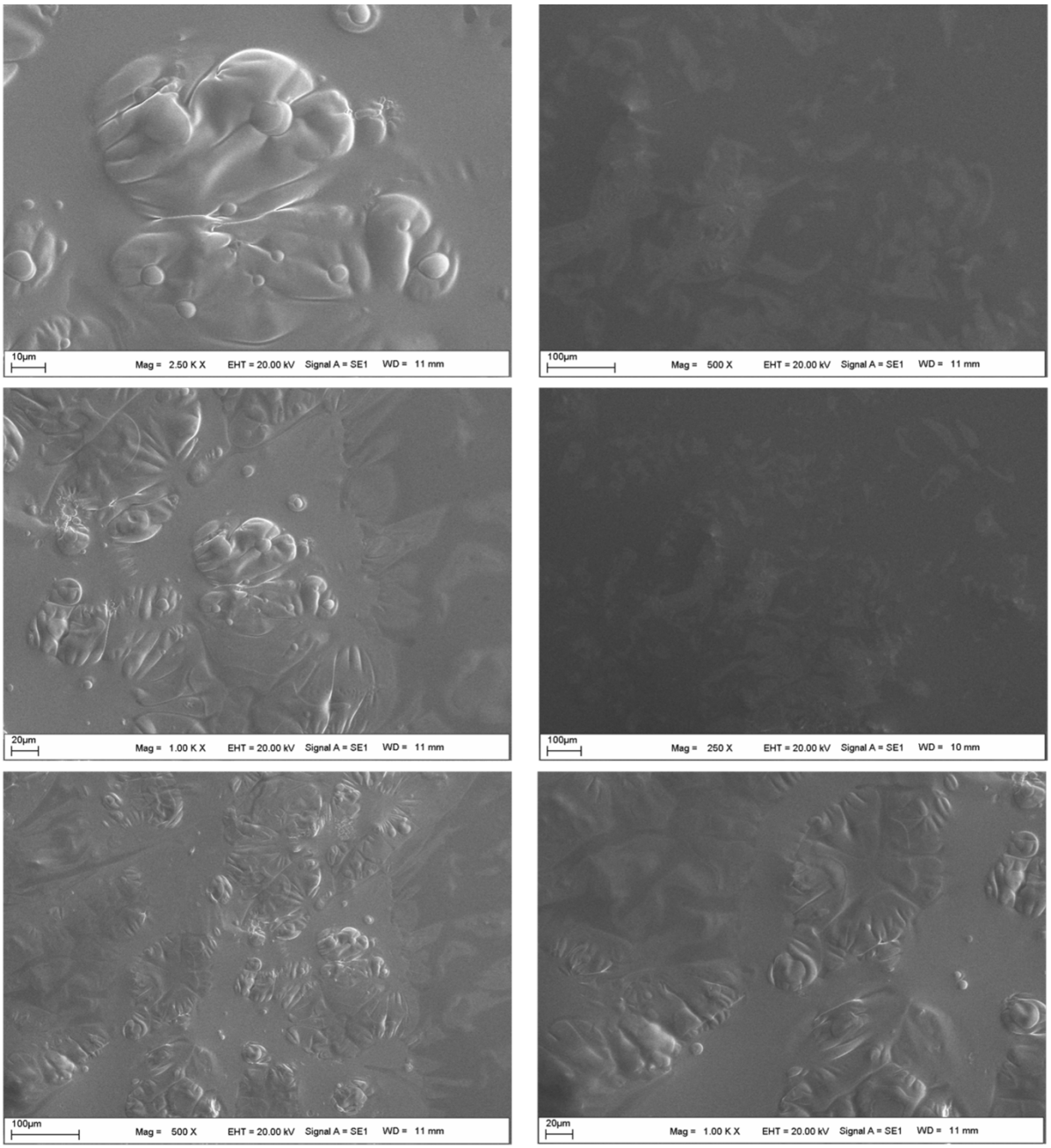

Figure 5. SEM images of apricot kernel oil based polyurethane structure

In this study, apricot kernel oil was used for the first time as a source of polyol. The polyol obtained from apricot kernel oil was used in the synthesis of polyurethane.

Conclusions

Today, great developments have occurred in the polymer world. These developments brought about the production of polymeric materials with different properties. Polyurethanes constitute an important part of the polymer material class. Polyurethanes are widely used in fields such as biomaterials [27], biomedical [28], and coating [29]. In this study, polyol was obtained for the first time from apricot kernel oil with known biocompatibility. The obtained polyol was used in the synthesis of polyurethane. Apricot kernel oil based polyurethane structure will contribute to the literature as a unique biomaterial. It also has the potential to be an important resource for researchers.

References

[1] Desroches, M., Escouvois M., Auvergne R., Caillol S., Boutevin B. (2012). From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products, *Polym Rev.,* 52(1): 38-79.

[2] Lligadas, G., Ronda, J.C., Gali`a, M., C`adiz, V. (2010). Plant oils as platform chemicals for

polyurethane synthesis: Current state-of-the-art, *Biomacromolecules*, 11(11): 2825–2835.

[3] Saad, N.M., Zubir, S.A. (2019). Palm kernel oil polyol-based polyurethane as shape memory material: effect of polyol molar ratio, *J. Phys. Sci.,* 30(2): 77-89.

[4] Babb, A.D. (2012). Polyurethanes from Renewable Resources, *Adv Polym Sci.,* 245: 315-360.

[5] Pfister, D.P., Xia ,Y., Larock, R.C. (2011). Recent advances in vegetable oil-based polyurethanes, *ChemSusChem.,* 4(6): 703-717.

[6] Xia, Y., Larock, R.C. (2010). Vegetable oil-based polymeric materials: synthesis, properties, and applications, *Green Chem.,* 12(11): 1893-1909.

[7] Ibrahım, S., Ahmad, A., Mohamed, N.S. (2015). Synthesis and characterization of castor oil-based polyurethane for potential application as host in polymer electrolytes, *Bull. Mater. Sci.,* 38, 1155-1161.

[8] Sahoo, S., Kalıta, H., Mohanty, S., Nayak, S. (2016). Synthesis of Vegetable Oil-Based Polyurethane: A Study on Curing Kinetics Behavior, *Int. J. Chem. Kinet.,* 48(10): 622-634.

[9] Campanella, A., Bonnaillie, L.M., Wool, R.P. (2009). Polyurethane foams from soyoil-based polyols, *J. Appl. Polym. Sci.*, 112(4): 2567–2578.

[10] Zlatanic, A., Lava, C., Zhang, W., Petrovic, Z.S. (2004). Effect of structure on properties of polyols and polyurethanes based on different vegetable oils, *J. Polym. Sci., Part B : Polym. Phys.*, 42(5): 809–819.

[11] Miao, S., Zhang, S., Su, Z., Wang, P. (2010). A novel vegetable oil-lactate hybrid monomer for synthesis of high-Tg polyurethanes, *J. Polym. Sci., Part A: Polym. Chem.,* 48(1): 243–250.

[12] Abril-Milán, D., Valdés, O., Mirabal-Gallardo, Y., de la Torre, F.A, Bustamante, C., Contreras, J. (2018). Preparation of renewable bio-polyols from two species of colliguaja for rigid polyurethane foams, *Materials*, 11(11): 2244.

[13] Monteavaro, L., da Silva, E,. Costa, A., Samios, D,. Gervase, A., Petzhold, C. (2005). Polyurethane networks from formiated soy polyols: Synthesis and mechanical characterization, *J. Am. Oil Chem. Soc.,* 82(5): 365–371.

[14] Zhang, J., Tang J.J. and Zhang J.X. (2015). Polyols prepared from ring opening epoxized soybean oil by a castor oil-based fatty diol, *Int. J. Polym. Sci.,*2015: 1-8.

[15] Açarı Karaca, İ. (2021). Investigation of the effectiveness of polyurethane composites containing gelatin at different rates on the release of ciprofloxacin, *J.Chem.Soc.Pak.,* 43(6): 645-655.

[16] Hao, Y., Wang, J., Qi, L., Qiu, Y., Liu, H., Zhang, Y., Wang, X. (2022). A comparative study of apricot kernel oil yield using different extraction methods, *Bioresources,* 17(3): 5146-5163.

[17] Janzen, D.A., Dınız, M.F., Azevedo, J.B., Pınto, J.R.A., Sanches, N.B., Dutra, Rıta de Cássıa L. (2021). Qualitative and quantitative evaluation of epoxy systems by Fourier transform infrared spectroscopy and the flexibilizing effect of mercaptans, *An Acad Bras Cienc.,* 93(2): e20200799.

[18] Simon, D., Borreguero, A.M., Lucas, A. de., Rodríguez, J.F. (2015). Valorization of crude glycerol as a novel transesterification agent in the glycolysis of polyurethane foam waste, *Polym. Degrad. Stab.*, 121: 126-136.

[19] Açarı Karaca, İ., Boran, F., Kolak, S., Tatlıcı, E., Yeşilada, Ö., Köytepe, S., Ateş, B. (2022). Preparation of 10-undecenoic acid based polyurethane/PCL fibers by electrospinning method and investigation of their antifungal properties, *Polym. Bull.,*79(2): 9179–9197.

[20] Bajsic, E.G., Rek,V. (2000). DSC study of morphological changes in segmented polyurethane elastomers, *J. Elastomers Plast.,* 32: 162-180.

[21] Pourjavadi, A., Rezai, N., Zohuriaan-M, M.J. (1998). A Renewable polyurethane: synthesis and characterization of the ınterpenetrating networks (ıpns) from cardanol oil. *J. Appl. Polym. Sci*., 68: 173-183.

[22] Bhunia, H.P., Jana, R.N., Basak A., Lenka, S., Nando, G.B. (1998). Synthesis of polyurethane from cashew nut shell liquid (cnsl), a renewable resource. *J. Appl. Polym. Sci.* 36 (3): 391-400.

[23] Badri, K.H. (2012). Biobased Polyurethane from Palm Kernel Oil-Based Polyol. In: Zafar, F., Sharmin, E., (Eds). Polyurethane, Croatia: InTech, (2012) 447-470.

[24] Gurau, V.S., Sandhu, S.S. (2018). Optimization and characterization of biodiesel production from India originated bitter apricot kernel oil, *J. Sci. Ind. Res.,* 77: 345-348.

[25] Priyadarshi, R., Sauraj, Kumar, B., Deeba, F., Kulshreshtha, A., Negi, Y.S. (2018). Chitosan films incorporated with Apricot (Prunus armeniaca) kernel essential oil as active food packaging material, *Food Hydrocoll.,* 85: 158-166.

[26] Chung, H., Kim, J-Y. (2014). Antimicrobial activity of β-cd finished and apricot kernel oil applied fabrics, *Fibers Polym.,* 15(5): 924-931.

[27] Grenier, S., Sandig, M., Mequanint, K. (2007). Polyurethane biomaterials for fabricating 3D porous scaffolds and supporting vascular cells, *J. Biomed. Mater. Res.,*82A(4): 802-809.

[28] Wendels, S., Avèrous, L. (2021). Biobased polyurethanes for biomedical applications, *Bioact. Mater.,* 6: 1083-1106.

[29] Çalıkoğlu, Y. (2017). New polyurethane synthesis and characterization from epoxidized soybean oil by ring-opening polyols with thioglycolic acid and thioglycolic acid methyl ester, MSc. Thesis, Sakarya University, Sakarya.