

TEKSTİL VE MÜHENDİS

(Journal of Textiles and Engineer)



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HEMP FIBER REINFORCED SUSTAINABLE "GREEN" COMPOSITE PRODUCTION WITH EPOXIDIZED SOYBEAN OIL

EPOKSİ SOYA YAĞIYLA KENEVİR LİFİ İLE GÜÇLENDİRİLMİŞ SÜRDÜRÜLEBİLİR "YEŞİL" KOMPOZİT ÜRETİMİ

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Online Erişime Açıldığı Tarih (Available online):30 Haziran 2024 (30 June 2024)

Bu makaleye atıf yapmak için (To cite this article):

Görkem GEDİK, İnan AĞIR, Cansu VAR, Ozan AVİNC (2024): HEMP FIBER REINFORCED SUSTAINABLE "GREEN" COMPOSITE PRODUCTION WITH EPOXIDIZED SOYBEAN OIL, Tekstil ve Mühendis, 31: 134, 78-87.

For online version of the article: https://doi.org/10.7216/teksmuh.1340701



TMMOB Tekstil Mühendisleri Odası UCTEA Chamber of Textile Engineers Tekstil ve Mühendis Journal of Textiles and Engineer

Araştırma Makalesi / Research Article

HEMP FIBER REINFORCED SUSTAINABLE "GREEN" COMPOSITE PRODUCTION WITH EPOXIDIZED SOYBEAN OIL

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Gönderilme Tarihi / Received: 10.08.2023 Kabul Tarihi / Accepted: 24.06.2024

ABSTRACT: Due to the rising environmental concerns, industry branches are pushed to research and invest sustainable materials and technologies. In this context, this study aimed to combine a sustainable fiber and matrix material to produce green composite. For this purpose, epoxidized soybean oil and hemp fiber were utilized for composite production. Sebacic acid and maleic anhydride were used as hardeners. Histidine and glycerol were applied as accelerator and starter, respectively. Mechanical performance of the composites was evaluated by tensile and impact tests. Hemp fiber reinforcement resulted in improvement on mechanical properties, up to 2.6 MPa tensile strength and 11.5 kJ/m² impact strength. Thermal properties were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses. The changes in molecular level after curing was traced with Fourier transform infrared spectroscopy (FTIR) measurements.

Key words: Hemp fiber, Epoxidized soybean oil, composite, sustainable

EPOKSİ SOYA YAĞIYLA KENEVİR LİFİ İLE GÜÇLENDİRİLMİŞ SÜRDÜRÜLEBİLİR "YEŞİL" KOMPOZİT ÜRETİMİ

ÖZ: Artan çevresel endişeler nedeniyle, endüstri dalları sürdürülebilir malzeme ve teknolojiler araştırmaya ve yatırım yapmaya itilmektedir. Bu bağlamda, bu çalışma, yeşil kompozit üretmek için sürdürülebilir bir lif ve matris malzemesini birleştirmeyi amaçlamıştır. Bu hedef doğrultusunda, epoksitlenmiş soya yağı ve kenevir lifi, kompozit üretiminde kullanılmıştır. Sertleştirici olarak sebasik asit ve maleik anhidrit kullanılmıştır. Hızlandırıcı ve başlatıcı olarak sırasıyla histidin ve gliserol uygulanmıştır. Kompozitlerin mekanik performansı çekme ve darbe testleri ile değerlendirilmiştir. Kenevir lifi takviyesi ile mekanik özelliklerde iyileşme sağlanmış, kenevir lifi takviyeli kompozitlerle 2,6 MPa'ya kadar çekme dayanımı ve 11,5 kJ/m2'ye çıkan darbe dayanımı elde edilmiştir. Termal özellikler termogravimetrik analiz (TGA) ve diferansiyel taramalı kalorimetri (DSC) analizleri ile belirlenmiştir. Kürlenme sonrası moleküler seviyedeki değişimler Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ölçümleri ile izlenmiştir.

Anahtar kelimeler: Kenevir lifi, epoksi soya yağı, kompozit, sürdürülebilir

1. INTRODUCTION

The environmental issues arising from both production and consumption of petroleum-based thermosets has encouraged to be developed bio-based thermoset resins as alternative materials to petroleum-based thermoset ones. Due to their cost efficiency, advantageous properties, and sustainable characteristics, biobased thermoset polymers derived from natural resources such as sugars, polysaccharides, and plant oils (POs), have attracted in both scientific research and industrial applications. Among them, POs has come into prominence with its abundancy and biodegradability properties. Soybean, canola, linseed, castor, and hemp are the most utilized plants for fabricating bio-based polymer resins [1]. POs typically consist of triglycerides, and these contain both saturated and unsaturated fatty acids. The reactivity of these oils depends on proportion of double bonds or the type of fatty acid. Among POs, soybean oil (SBO) possesses high double bond proportion, but these bonds don't exhibit high reactivity in free radical polymerization. Accordingly, it is required to convert the double bonds to highly reactive functional groups like hydroxyl groups, epoxide groups, and acrylate groups, that can be participated in free radical polymerization processes [2]. Epoxidized soybean oil (ESO) is fabricated via epoxidation process, in which SBO triglycerides are reacted with hydrogen peroxide in the existence of either acetic acid or formic acid [3]. By this way, ESO could be utilized as a polymer matrix in composite production. For this purpose, hardener and catalyst chemicals are required. Catalyst, which relies on reducing activation energy, accelerate the curing, whereas hardener facilitates crosslinking [4]. Hardeners, which is also referred as crosslinking or curing agents, have an important role in converting of epoxy resin into a thermoset network structure through opening the C–O–C ring at the ends of an epoxy molecule and bonding with the molecules [5]. The functionality of oxirane in ESO enables it to participate in cross-linking reactions with a hardener, allowing ESO to participate in constructing a cross-linked matrix structure [6]. For example, in case of amine hardeners, when ESO reacts with the hardener, epoxide rings undergo opening and construct new chemical chains with amine molecules, resulting in formation cross-linked polymer network [7]. It should be noted that the performance of cured ESO depends on the curing conditions, the curing and also hardener nature. Amines, anhydrides, and acids are the most common types of hardeners [8], it is reported that due to ESO included materials display poor strength and lower rigidity, utilization of anhydride agents has advantages of offering improved mechanical strength [4]. Espana et al. evaluated maleic anhydride as hardener for ESO and mixture of 1,3-butanediol anhydrous and benzyldimethylamine as initiator and catalyst. It was concluded that the ratio of 1:1.0 between the ESO and anhydride exhibited best mechanical properties [9]. Zeng et al. evaluated hardeners of adipic acid, sebacic acid, 1,12dodecanedicarboxylic catalyst of Nand 4-N. dimethylaminopyridine (DMAP) acid for ESO. Tensile strengths of adipic acid, sebacic acid and 1,12-dodecanedicarboxylic cured ESO were found as 526 \pm 36, 462 \pm 23 and 453 \pm 41 KPa, respectively, where Young's modulus was found as 2.79 ± 0.14 , 2.62 ± 0.05 and 2.30 ± 0.16 MPa, respectively, and elongations at break were found as 16.6 ± 1.9 , 16.4 ± 1.2 and $20.6 \pm 2.3\%$, respectively [10]. Espinoza et al. evaluated five amine hardeners in matrix of petroleum-based resin/plant oils of ESO and epoxidized canola oil. They concluded that among amine hardeners, bis (p-aminocyclohexyl) methane (PACM) displayed promising performance as hardener for epoxidized plant oil/petroleum-based resin system. Also, it was found that PACM composites exhibited a comparable performance to composites with an anhydride hardener [11]. Samper et al. evaluated hardeners of mixture of maleic anhydride and phthalic anhydride for ESO, epoxidized linseed oil (ELO), and blending of these oils. They used benzyl dimethyl amine as catalyst and ethylene glycol as initiator. They concluded that composites of 100% ELO (24.47 g MA/PA) and 80% ELO 20% ESO (25.54 g MA/PA) can be ideal matrix for green composites [12]. Ding et al. evaluated quercetin (QC) as hardener and N-methylimidazole (N-MI), 4methylimidazole (4-MI), and biobased histidine as imidazole type accelerators for ESO. They found that ESO-QC/4-MI thermosets showed maximum tensile and flexural strengths of 44.7 and 81.8 MPa, respectively, while the tensile modulus of 1058 MPa was exhibited by ESO-QC/N-MI thermosets [13].

Natural fibre-based reinforcements (e.g., hemp, flax, jute, sisal, pineapple leaf fibre, and bamboo) are other environmentally friendly materials for composites. Among natural fibres, hemp fibre offers several promising properties in terms of both sustainability and mechanical characteristic [14-16]. Green composites consist of bio based and biodegradable polymer matrix and reinforcement material [17,18]. A green composite that is a combination of hemp fibre and ESO has the potential of elimination of issues arising from both utilization and consumption of petroleum-based reinforcements and resin. In recent years, mechanical performance of natural fibre reinforced PO based green composites have been intensively explored. Boquillon [19] investigated flexural properties of hemp fibre reinforced ESO composites. The composite reinforced with 6 mm fibre exhibited the best performance which possessed 560 GPa modulus and 91 MPa flexural strength. Manthey et al. developed jute fibre reinforced epoxidized hemp oil (EHO)/epoxy blend composites and compared with ESO/epoxy blend composites. It was observed that EHO composites displayed superior mechanical characteristic when compared to ESO composites. However, both composite types were limited to bioresin concentrations under 30%. In both flexural and tensile properties for ESO composites, most promising results with 58.3 ± 8.9 MPa of flexural strength and 43.5 ± 1.8 MPa of tensile strength were obtained at 10/90 ESO/epoxy rates [20]. Niedermann et al. evaluated mechanical properties of woven jute fabric reinforced epoxy resins, blends of ESO with glycerol-based and pentaerythritol-based aliphatic epoxy resin and with bisphenol-A based aromatic epoxy. The substantial weakening influence of ESO in all composite samples was detected [21]. Sahoo et al. developed sisal fibre reinforced ESO modified epoxy blend composites. They stated enhanced tensile modulus and tensile strength for composite of epoxy/20% ESO/15 wt% sisal fibre [22]. Sahoo et al. unidirectional sisal

fabric reinforced ESO/epoxy composites having different orientations of reinforcement including [0/0] and [0/90]. It was observed that most promising mechanical properties were exhibited by composite of epoxy/20%ESO/SF [0/0] with 96.69 ± 3 MPa of tensile strength, 2984.0 ± 47 of tensile modulus, and % 4.4 ± 0.3 of elongation at break [23]. Fei et al. developed hybrid recycled polyethylene terephthalate, bamboo, polyester, and ES (ethylene-propylene side by side) fibre reinforced acrylated epoxidized soybean oil (AESO) matrix composite. They found that the developed composites have $\sim 50 \text{ kJ/m2}$ of impact strength and tensile strength [24]. Kumar et al. [25] evaluated the effect of ESO on petroleum-based epoxy at varying compositions cured with methylhexahydrophthalic anhydride as curing agent and 2-methyl imidazole as catalyst. It was concluded that the tensile strength of virgin epoxy with 42.94 MPa enhanced to 48.62 MPa with the inclusion of 20% of ESO. O'Donnell et al. [26] developed flax, cellulose pulp, and hemp reinforced AESO resin composites. They found that flexural modulus of the composite was in the range of 1.5 and 6 GPa depending on the nature of the fibre and fibre volume fractions. Lei et al. [27] produced biocomposites from ESO resin, citric acid hardener and sisal fiber. They reported 30.4 MPa tensile strength with 40% resin content. Another "green" approach to composite production was applied by Oztemur et al. [28]. In that study, AESO and epoxy resin blend was reinforced with denim wastes to produce composite panel. They stated that increased bio-resin amount resulted in higher impact strength. Liu et al. [29] produced flax fiber reinforced ESO-epoxy blend composites. They stated that longer fibers resulted in better mechanical properties. Nepomuceno et al. developed ESO composite materials with salicylic acid hardener loaded with chitosan which increased hydrophilicity and decreased crosslinking density [30].

Sustainable fiber and bio-based matrix material were combined to produce green composite, in this study. Though, epoxidized soybean oil composites are studied in the literature, this study combines environmentally friendly hemp fabric, safe starters and accelerators and aims eco-friendlier and safer for health composites. Necessary chemicals; hardeners, accelerator (histidine) and starter (glycerol) were chosen carefully to obtain sustainable composite material. Sebacic acid is a bio-based curing agent and anhydrides are less toxic from amines which are commonly used as hardeners in epoxy systems [8]. Moreover, histidine is a natural imidazole, which is suitable for fully biobased production [13]. Solid polymer matrix was obtained after curing and the results exhibited that crosslinking of epoxidized soybean oil was successfully achieved. Also, hemp fiber reinforcement improved mechanical characteristics. The combination of these chemicals and hemp fiber reinforcement is a novel issue.

2. MATERIALS and METHODS

2.1. Hemp Fabric

Plain weaved 100% hemp fabric was used in the applications. The yarn linear density was Nm 20 for warp and weft yarns. Warp and weft counts were 16 and 12 picks per cm, respectively. Alkaline

treatment was carried out with 5 g/L NaOH at 95°C for 30 minutes, for surface modification. After alkaline treatment, the fabrics were warm rinsed, neutralized with 1 g/L acetic acid and finally cold rinsed, in turn. The fabrics were left for air drying in room temperature, after washing step.

2.2. Composite production with epoxidized soybean oil

The epoxidized soybean oil (ESO) was kindly supplied from CHS. The epoxy equivalent weight (EEW) of the ESO was 254 and oxirane number was 6.3 cg/g.

Sebacic acid (SA) (Sigma Aldrich) and maleic anhydride (MA) (Acros Organics) were used as hardeners for green composite preparation. During composite production, carboxyl equivalent weight (CEW) of SA and anhydride equivalent weight (AEW) of MA were taken into account for compounding calculations. For the composite productions with SA, 1:0.8, 1:1 and 1:1.2 EEW:CEW ratios were investigated. For the experiments with MA, 1:0.8, 1:1 and 1:1.2 EEW:AEW ratios were applied.

In order to the epoxy soybean oil to be cured and transformed into a polymer matrix, the oxirene groups in the ESO must be opened and react with the hardener. This reaction takes place relatively slow, therefore, glycerol (Alfa Aesar) and histidine (Fluka) were carried out as initiator and accelerator chemicals, respectively. Initiator and accelerator concentrations were 1%.

2.2.1. Polymer matrix production with sebacic acid and maleic anhydride hardeners

ESO and SA hardener were mixed in the stated EEW:CEW ratios and glycerol initiator was added into the mixture, which was continuously stirred. The temperature was increased to 120°C. After 1 hour, histidine, which was dissolved in 50% water-ethanol, was added. The system was kept working under these conditions for another 1 hour and a viscous resin was obtained. This compound was transferred into silicon molds (40 shore) and treated at 140°C for 2 hours in vacuum oven. After this step, elastic polymeric structure was obtained. This material was subsequently cured at 160, 180 and 200°C for 2 hours at each temperature.

ESO and MA hardener (MAESO) were mixed in the stated EEW:AEW ratios and glycerol initiator was added into the mixture, which was continuously stirred. The temperature was increased to 60°C. After 30 minutes, histidine, which was dissolved in 50% water-ethanol, was added and the temperature was enhanced to 80°C. After 30 minutes working on these conditions, the temperature was increased to 100°C and kept constant for another 30 minutes. After that, mixture was kept stirred at 120°C for 2 hours and in the end, obtained resin was transferred into silicon molds. This material was subsequently cured at 160, 180 and 200°C for 2 hours at each temperature. Polymeric matrix formation with ESO is presented in Figure 1.

For the hemp fabric reinforced samples, 2, 4 and 6 plies of hemp fabric were used. Hand laying technique was carried out. Hemp fabrics were laid into the molds and composite production started with the resin at 120°C.



Figure 1. Schematic presentation of polymer matrix preparation with ESO

The reactivity of oxirane rings in ESO is low related with steric hindrance which results in an obstacle to the curing reaction, the curing requires very high temperatures. Therefore, curing accelerators are needed to decrease the reaction temperature and improve reactivity between the hardener and ESO [13]. The imidazole curing agent reacts with epoxy ring nucleophilically and forms zwitterions followed by the anion homopolimerization reaction [13]. Two reactions, esterification and etherification, drive the curing of epoxy-anhydride systems. Alkoxide anion from epoxy reacts with an epoxy group to form diester. Ether linkage occurs due to the competing reaction between epoxy and alkoxide anion [31].

2.3. Tensile tests

Tinius Olsen H10KT model universal tester equipped with 100 N load cell was utilized for tensile tests. ASTM D 3039 test procedure was applied. Tests were performed with 50 mm clamp distance and 1 mm/minute test speed. 5 repeats were applied for each sample.

2.4. Izod impact strength tests

Impact strength tests were carried out with the pendulum type impact method according to ASTM D 256 standard. CEAST Resil Izod Impact Tester with 7.5 J hammer, was used in the tests. 5 repeats were applied for each sample.

2.5. Thermal properties

The thermal characteristics of the produced composite materials were determined by TG, DTG and DSC analyses. Analyses were carried out with Setaram SENSYS evo DSC device. Measurements were applied in N_2 atmosphere (gas flow rate 50 ml/minute) at a temperature rise rate of 10°C/min in the range of 25-600°C.

2.6. FTIR analysis

The samples were examined with Thermo Nicolet iS50 FT-IR spectrometer, equipped with an ATR sampling module, in the band range of 400-4000 cm⁻¹, with a resolution of 1 cm⁻¹.

3. RESULTS and DISCUSSION

3.1. Tensile properties

Before hemp fiber reinforcement, neat polymer matrix materials were produced with determined hardener equivalent weight ratios with the two hardener materials, maleic anhydride and sebacic acid. The tensile strength values of neat polymer matrices were presented in Figure 2.



Figure 2. Tensile strength values of neat polymer matrices produced with MA or SA hardeners

The tensile strength values of the polymer material hardened with sebacic were determined to be quite low, compared to the material hardened with maleic anhydride. If the materials hardened with sebacic acid are compared; approximately 100 kPa tensile strength was obtained at a ratio of 0.8 EEW:CEW, a significant decrease was observed in strengths with an increase in the EEA:KEA ratio. The tensile strength values were measured as 76.1 and 46.8 kPa respectively for EEW:CEW 1:1, and 1:1.2, respectively. These outcomes are in parallel line with the findings of Zeng et al. [10] who stated that the optimum molar ratio of -COOH/epoxy molar ratio is 0.7 due to the maximum crosslinking. For this study,

above 0.8 EEW:CEW ratio, it is thought that, related to steric effect of long chains belong to ESO, free dicarboxylic acids may be remained unreacted, which consequently resulted in a decrease on the tensile strength [10].

The samples cured with maleic anhydride exhibited an opposite trend to that of hardened with sebacic acid, increased hardener ratio resulted in better tensile strength properties. Tensile strength values of 296.7, 534.5 and 938.9 kPa were determined for EEW:AEW ratios 0.8, 1 and 1.2, respectively. According to Espana et al [9] the higher the AEW proportion in the compound, the higher the crosslinking ratio (up to 1:1.1), regarding the

coefficient of thermal expansion. Comparing carboxylic acid and anhydride hardener systems in this study, better tensile strength results were obtained with anhydride hardener. This outcome is in parallel line with the statements of Albuquerque et al [4]. Considering the results of tensile tests that were applied to neat polymer matrices, it was decided to produce hemp fabric reinforced composites with 1:1.2 MAESO compound. Tensile strength & elongation at break values of hemp fiber reinforced composites are seen in Figure 3 and Young's modulus values are presented in Figure 4



Figure 3. Tensile strength and elongation at break values of hemp fiber reinforced composites



Figure 4. Young's modulus values of hemp fiber reinforced composites

0.9 MPa tensile strength value was measured for neat 1:1.2 EEW:AEW MAESO sample. Compared to the standard synthetic DGEBA epoxy sample, it could be considered low, however, the produced MAESO material has a serious advantage as being completely sustainable. -Hemp fabric reinforcement resulted in a notable increase on tensile strength values. The tensile strength values of the 2-plies and 6-plies hemp fabric reinforced MAESO samples were measured as 2.1 Mpa, both. 4-plies hemp fabric reinforced sample displayed the highest tensile strength value among all samples. It was thought that fabric reinforcement above 4-plies had interrupted the physical anchoring or chemical crosslinking which were responsible of force distribution and tensile strength properties, resulting in a slight decrease on tensile strength. The neat MAESO sample exhibited a high elongation at break of 18.3%. The Young's modulus of this sample is also very low, in other words, this sample can easily deform and has an elastic structure. The fabric reinforcement limited the elongation at break and also increased the Young's modulus, dramatically. The elongation at break of the 2, 4 and 6-plies hemp fabric reinforced samples were measured as 7.7%, 6.9% and 7.4%, respectively, while the Young's modulus values of the same samples were calculated as 31.9, 34.0 and 30.1 Mpa, in the same order. Tensile test results revealed that hemp fiber reinforcement of sustainable ESO based polymer material significantly modified the mechanical characteristics of the composite material. Photograph of hemp fiber reinforced composites are seen in Figure 5.



Figure 5. Hemp fiber reinforced composite samples

3.2. Impact strength

Impact strength is a parameter that indicates how well the material distributes or absorbs the applied shock force. Izod impact strength values of MAESO composite materials are presented in Figure 6.

The impact strength of the sample without hemp fabric additive was determined as 7.6 kJ/m². The sample containing 2 plies of fabric is the sample with the lowest impact strength among hemp fabric reinforced samples. The impact strength of this sample was measured as 8.2 kJ/m². With the increase in the number of hemp fabric layers to 4, 16.9% increase was detected, compared to the neat MAESO sample. The impact strength of 4 plies hemp fabric reinforced sample was 9.2 kJ/m². The highest value with 11.5 kJ/m² (approximately 51% increase compared to neat MAESO sample) was observed in the sample containing 6 layers of fabric. In the light of the impact test results of investigated samples, it was monitored that the impact resistance enhanced as the number of fabric layers increased. These results are in parallel line with the findings of Ribeiro et al., who stated an increase on Izod impact strength of hemp fabric reinforced epoxy composites with increased hemp fabric ratio. This phenomenon was related with the higher energy requirement to break the samples [32]. It was thought that the same mechanical characteristic played an important role on the Izod impact test results of this study, increased hemp fabric ply count improved the impact durability of the hemp-MAESO composite samples.

3.3. Thermal properties

Thermal behavior of hemp fabric reinforced MAESO composite was explored by TGA-DTG and DSC. Figures 7 and 8 present TGA- DTG and DSC-DDSC curves 4 plies hemp fiber reinforced MAESO composite material.

The thermal stability of MAESO and hemp reinforced MAESO composite were evaluated by TGA analysis. Two-step thermal degradation was detected for hemp reinforced sample. This could be related with the earlier degradation of cellulosic hemp fiber at 342°C. The second peak was observed at 380°C which could be attributed to the degradation of the MAESO matrix. The residual mass of hemp reinforced MAESO sample was around 13% which was probably due to the undegraded components of hemp fiber. These results were in parallel line with the findings of Miao et al. [33] who studied on ESO based paper composites. They detected two stage degradation and stated 13% residual mass for paper-ESO composites. The DSC thermogram of hemp fiber reinforced MAESO composite sample exhibited double main exothermic peaks. The first peak occurred between 321-344 °C, which was related with the initial degradation of the hemp fiber content. The second exothermic peak was detected between 403-516 °C and possibly based on the total thermal degradation of the composite components, MAESO matrix and hemp fiber.



Figure 6. Izod impact test results of the hemp-MAESO composites



Figure 7. TGA-DTG curves of 4 plies hemp fabric reinforced MAESO composite material



Figure 8. DSC curve of 4 plies hemp fabric reinforced MAESO composite material

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3.4. FTIR analysis

FTIR is a useful tool to investigate epoxy groups and opened oxirane rings in epoxidized soybean oil. FTIR spectra of raw ESO and cured (at 200°C) MAESO compound were presented in Figure 9. The broad band at 3526 cm⁻¹ on the spectrum of cured sample was related with -OH groups which indicates opened epoxide groups [34, 35]. The bands at 2925 and 2854 cm⁻¹ on raw ESO spectrum, 2928 and 2855 cm⁻¹ on cured composite spectrum were associated with terminal methyl, -CH and -CH₂ groups [34]. The bands detected at 1742 and 1722 cm^{-1} , 1155 and 1154 cm^{-1} on the spectrum of raw ESO and cured sample, respectively, were assigned to ester groups [34]. A new band appeared after curing at 1643 cm⁻¹, attributed to C=C stretching vibration, that could be related with crosslinking [36]. The band that was observed at 825 cm⁻¹ on the spectrum of ESO sample was related to epoxy groups [34, 36]. The intensity of this band decreased on cured composite sample which was an indicator that the epoxy groups were opened for crosslinking reactions.





4. CONCLUSION

Epoxidized soybean oil was transformed to cross-linked thermoset matrix by the aid of sebacic acid and maleic anhydride hardeners, histidine accelerator and glycerol starter. The crosslinking was confirmed by FTIR results. Higher tensile strength was obtained with maleic anhydride hardener. The neat sample that was prepared with maleic anhydride hardener exhibited up to 938.9 kPa tensile strength. For this reason, it is recommended to work with maleic anhydride for higher tensile strength. Best tensile properties were determined for 4 plies of hemp fabric reinforced sample with 2.6 MPa. The highest impact strength (11.5 kJ/m2) was observed for 6 plies hemp fabric reinforced sample which was attributed to more uniform shock distribution with increased ply count. The initial thermal degradation of hemp reinforced composite material was detected at 342°C. 4 ply hemp fabric reinforced MAESO composite material is recommended, in light of the outputs of this study, in terms of tensile properties.

Compared to petroleum based conventional and commercial epoxy resins, the tensile strength values of green composites produced in this study remained low. On the other hand, completely sustainable and bio-based products were obtained. Therefore, these kinds of composite materials could serve for special applications. In further studies, tensile strength increase, and reaction temperature decrease could be investigated. Moreover, other sustainable reinforcement fiber alternatives could be applied.

ACKNOWLEDGEMENT

This study was supported by Pamukkale University Scientific Research Projects Department (PAUBAP) with project number 2020BSP006. FTIR, TGA and DSC analyses were performed in PAU Iltam laboratories.

REFERENCES

- Mustapha, R., Rahmat, A. R., Abdul Majid, R. and Mustapha, S. N. H., (2019), Vegetable oil-based epoxy resins and their composites with bio-based hardener: a short review, Polymer-Plastics Technology and Materials, 58(12), 1311-1326.
- Saithai, P., Lecomte, J., Dubreucq, E. and Tanrattanakul, V., (2013), Effects of different epoxidation methods of soybean oil on the characteristics of acrylated epoxidized soybean oil-copoly(methyl methacrylate) copolymer, Express Polymer Letters, 7(11), 910-924.
- Takahashi, T., Hirayama, K., Teramoto, N. and Shibata, M., (2008), *Biocomposites composed of epoxidized soybean oil cured with terpene-based acid anhydride and cellulose fibers*, Journal of Applied Polymer Science, 108(3), 1596-1602.
- Albuquerque, A. K. C., Almeida D.E.O., Barreto J. V. M., Silva, I. D. S., Jaques, N.G., Nepomuceno, N. C., Medeiros, E. S. and Wellen, R. M. R., (2023), *Effect of hardener and*

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catalyst contents on curing and degradation of epoxidized soybean oil, Journal of Applied Polymer Science, 140(3).

- Ozeren Ozgul, E. and Ozkul, M. H., (2018), *Effects of epoxy*, hardener, and diluent types on the hardened state properties of epoxy mortars, Construction and Building Materials, 187, 360-370.
- Zhu, J., Chandrashekhara, K., Flanigan, V. and Kapila, S., (2004), *Manufacturing and mechanical properties of soybased composites using pultrusion*, Composites Part A: Applied Science and Manufacturing, 35(1), 95-101.
- Zhu, J., Chandrashekhara, K., Flanigan, V. and Kapila, S., (2004), *Curing and mechanical characterization of a soybased epoxy resin system*, Journal of Applied Polymer Science, 91(6), 3513-3518.
- Tang, Q., Chen, Y., Gao, H, et al., (2019) Bio-Based Epoxy Resin from Epoxidized Soybean Oil. In, Kasai, M. (Ed.) Soybean - Biomass, Yield and Productivity IntechOpen.
- España, J. M., Sánchez-Nacher, L., Boronat, T., Fombuena, V. and Balart, R., (2012), Properties of Biobased Epoxy Resins from Epoxidized Soybean Oil (ESBO) Cured with Maleic Anhydride (MA), Journal of the American Oil Chemists' Society, 89(11), 2067-2075.
- 10. Zeng, R. T., Wu, Y., Li, Y. D., Wang, M. and Zeng J. B., (2017), *Curing behavior of epoxidized soybean oil with biobased dicarboxylic acids*, Polymer Testing, 57, 281-287.
- Espinoza-Perez, J. D., Nerenz, B. A., Haagenson, D. M., Chen, Z., Ulven, C. A. and Wiesenborn, D. P., (2011), *Comparison* of curing agents for epoxidized vegetable oils applied to composites, Polymer Composites, 32(11), 1806-1816.
- Samper, M. D., Fombuena, V., Boronat, T., García-Sanoguera, D. and Balart, R., (2012), *Thermal and Mechanical Characterization of Epoxy Resins (ELO and ESO) Cured with Anhydrides*, Journal of the American Oil Chemists' Society, 89(8), 1521-1528.
- Ding, X-M., Chen, L., Guo, D-M., Liu, B-W., Luo, X., Lei, Y-F., Zhong, H-Y. and Wang, Y-Z., (2021), Controlling Cross-Linking Networks with Different Imidazole Accelerators toward High-Performance Epoxidized Soybean Oil-Based Thermosets, ACS Sustainable Chemistry & Engineering, 9(8), 3267-3277.
- 14. Panaitescu, D. M., Vuluga, Z., Sanporean, C. G., Nicolae, C. A., Gabor, A. R. and Trusca, R., (2019), *High flow polypropylene/SEBS composites reinforced with differently treated hemp fibers for injection molded parts*, Composites Part B: Engineering, 174, 107062.
- 15. Manaia, J. P., Manaia, A. T. and Rodriges, L., (2019) *Industrial Hemp Fibers: An Overview*, Fibers, 7(12), 106.
- 16. Gedik, G., Aydın Kızılkaya, Y. M. and Uyak, V., Koluman, A., (2023), Simultaneous Eco-friendly Bleaching and Retting Wastewater Treatment of Hemp Fiber with Ozone Application, Fibers and Polymers, 24(1), 57-72.

- Vázquez-Núñez, E., Avecilla-Ramírez, A. M., Vergara-Porras, B. and López-Cuellar, M del R., (2021), *Green* composites and their contribution toward sustainability: A review, Polymers and Polymer Composites, 29(9_suppl), 1588-1608.
- Gedik, G., Avinç, O. (2020). Hemp Fiber as a Sustainable Raw Material Source for Textile Industry: Can We Use Its Potential for More Eco-Friendly Production? In, Muthu, S.S., & Gardetti, M.A. (Eds.), Sustainability in the textile and apparel industries (pp. 87-109), Switzerland: Springer Nature.
- 19. Boquillon, N., (2006), *Use of an epoxidized oil-based resin as matrix in vegetable fibers-reinforced composites*, Journal of Applied Polymer Science, 101(6), 4037-4043.
- Manthey, N. W., Cardona, F., Francucci, G. and Aravinthan T., (2013), *Thermo-mechanical properties of epoxidized hemp oil-based bioresins and biocomposites*, Journal of Reinforced Plastics and Composites, 32(19), 1444-1456.
- 21. Niedermann, P., Szebényi, G. and Toldy, A., (2017), *Effect* of epoxidized soybean oil on mechanical properties of woven jute fabric reinforced aromatic and aliphatic epoxy resin composites, Polymer Composites, 38(5), 884-892.
- 22. Sahoo, S. K., Mohanty, S. and Nayak, S. K., (2017), Mechanical, thermal, and interfacial characterization of randomly oriented short sisal fibers reinforced epoxy composite modified with epoxidized soybean oil, Journal of Natural Fibers, 14(3), 357-367.
- 23. Sahoo, S. K., Mohanty, S. and Nayak, S. K., (2018), Mechanical, dynamic mechanical, and interfacial properties of sisal fiber-reinforced composite with epoxidized soybean oil-based epoxy matrix, Polymer Composites, 39(6), 2065-2072.
- Fei, M., Liu, T., Fu, T., Zhang, J., Wu, Y., Qiu, R. and Liu, W., (2019), Styrene-Free Soybean Oil Thermoset Composites Reinforced by Hybrid Fibers from Recycled and Natural Resources, ACS Sustainable Chemistry & Engineering, 7(21), 17808-17816.
- Kumar, S., Samal, S. K., Mohanty, S. and Nayak, S. K., (2017), Epoxidized Soybean Oil-Based Epoxy Blend Cured with Anhydride-Based Cross-Linker: Thermal and Mechanical Characterization, Industrial & Engineering Chemistry Research, 56(3), 687-698.
- 26. O'Donnell, A., Dweib, M. A. and Wool, R. P., (2004) *Natural fiber composites with plant oil-based resin*, Composites science and technology, 64(9), 1135–1145.
- Lei, B., Liang, Y., Feng, Y., He., H. and Yang, Z. (2018), Preparation and Characteristics of Biocomposites Based on Steam Exploded Sisal Fiber Modified with Amphipathic Epoxidized Soybean Oil Resin, Materials (Basel), 11(9), 1731-1743.
- 28. Öztemur, J., Sezgin, H. and Enis, İ.Y., (2021), *Design of an Impact Absorbing Composite Panel from Denim Wastes and*

Acrylated Epoxidized Soybean Oil based Epoxy Resins, Textile and Apparel, 31(3), 229-234.

- 29. Liu, Z., Erhan, S.Z., Akin, D.E. and Barton, F.E., (2006), "Green" Composites from Renewable Resources: Preparation of Epoxidized Soybean Oil and Flax Fiber Composites, J. Agric. Food Chem. 54, 2134-2137.
- 30. Nepomuceno, N.C., Fook, M.V.L., Ries, A., Mija, A and Wellen, R.M.R. (2023), *Bio-Based Epoxy Resins of Epoxidized Soybean oil Cured with Salicylic acid Loaded with Chitosan: Evaluation of Physical–Chemical Properties.* Journal of Polymers and the Environment, 31, 2566-2575.
- Park, W.H., Lee, J.K. and Kwon, K.J., (1996), *Cure Behavior* of an Epoxy-Anhydride-Imidazole System, Polymer Journal, 28(5), 407–411.
- 32. Ribeiro, M.P, Neuba, L., Silveria, P.H.P.M. and Luz, F., (2021), *Mechanical, Thermal and Ballistic Performance of Epoxy Composites Reinforced with Cannabis sativa Hemp Fabric,* Journal of Materials Research and Technology, 12, 221-233.
- 33. Miao, S., Liu, K., Wang, P., Su, Z. and Zhang, S. (2015) Preparation and Characterization of Epoxidized Soybean Oil-Based Paper Composite as Potential Water-Resistant Materials, Journal of Applied Polymer Science, 132, 41575-41581
- 34. Mustata, F., Tudorachi, N. and Rosu, D., (2011), Curing and thermal behavior of resin matrix for composites based on epoxidized soybean oil/diglycidyl ether of bisphenol A. Composites Part B: Engineering, 42(7), 1803-1812.
- 35. Liu, W., Xie, T. and Qiu, R., (2016), Improvement of properties for biobased composites from modified soybean oil and hemp fibers: Dual role of diisocyanate, Composites Part A: Applied Science and Manufacturing, 90, 278-285.
- 36. Tang, J., Zhang, J., Lu, J., Huang, J., Zhang, F., Hu, Y., Liu, C., An, R., Miao, H., Chen, Y., Huang, T. and Zhou, Y., (2020), *Preparation and Properties of Plant-Oil-Based Epoxy Acrylate-Like Resins for UV-Curable Coatings*, Polymers, 12, 2165-2180.