

# Eco-Friendly Natural Filler Based Epoxy Composites

Suheyla Kocaman, Gulnare Ahmetli

**Abstract**—In this study, acrylated soybean oil (AESO) was used as modifying agent for DGEBF-type epoxy resin (ER). AESO was used as a co-matrix in 50 wt % with ER. Composites with eco-friendly natural fillers-banana bark and seashell were prepared. MNA was used as a hardener. Effect of banana peel (BP) and seashell (SSh) fillers on mechanical properties, such as tensile strength, elongation at break, and hardness of M-ERs were investigated. The structure epoxy resins (M-ERs) cured with MNA and sebacic acid (SAC) hardeners were characterized by Fourier transform infrared spectroscopy (FTIR). Tensile test results show that Young's (elastic) modulus, tensile strength and hardness of SSh particles reinforced with M-ERs were higher than the M-ERs reinforced with banana bark.

**Keywords**—Biobased composite, epoxy resin, mechanical properties, natural fillers

## I. INTRODUCTION

**B**IOCOMPOSITE is a material made from natural filler and petroleum-derived non-biodegradable polymers or biopolymers. Therefore, the development of “green products” based on natural resources for both matrices and reinforcements has been increasing in recent years [1]. Such agro wastes being organic in nature are also a source for carbon and especially useful materials for the production of “green” materials. The natural plant-derived filler materials include many plant wastes, such as banana bark, coconut shell etc. Due to their low cost they are potential biofillers. On the other hand, the advantages of natural plant fibres over traditional glass fibres: acceptable specific strengths and modulus, low density and good biodegradability [2]. Also shell wastes amounting to millions of tons were generated in the shellfish aquaculture annually, most of which were dealing in the landfills. Marine shell wastes consist of calcium carbonate (CC) and organic matrices, with the former accounting for 95-99% by weight. Being the richest source of biogenic  $\text{CaCO}_3$ , shell wastes are suitable to prepare high purity  $\text{CaCO}_3$  powders, which have been extensively applied in various industrial products, such as paper, rubber, paints and pharmaceuticals [3], [4]. But in the literature, there are only a limited number of studies on the composites containing CC. Cai et al. [5] reinforced natural rubber latex film by using CC and obtained enhanced tear strength, tensile strength and modulus. Zhang and co-workers modified polypropylene with elastomer or CC particles [6].

It is well known that synthetic materials are not degraded by microorganisms in the environment, which contribute to their long lives. Therefore, if the matrix is non-biodegradable,

blending with biodegradable compounds has become an economical and versatile route to obtain new types of matrices with a wide range of desirable properties.

Partially biodegradable polymers obtained by blending biodegradable and non-biodegradable commercial polymers can effectively reduce the volume of plastic waste. They are more useful than completely biodegradable polymers due to the economic advantages and superior properties imparted by the commercial polymer used as a blending component [7], [8]. Biodegradable polymers from renewable resources, such as vegetable oil-based polymers, can be used as toughening agents in fabricating improvement ERs. In this study, epoxy matrix was modified with AESO and used as polymer matrix for preparation of BP and SSh composites.

## II. EXPERIMENTAL

### A. Materials

Commercially available diluted epoxy resin NPEF 170 called as ER, (Konuray Chemical Co.) was a bisphenol F-type epoxy resin. Some typical properties of the resin are indicated in Table I.

TABLE I  
PROPERTIES OF NPEF-170

Physical state	Liquid
Epoxy equivalent weight (g/eq)	160~180
Color (Gardner)	3.0 max
Flash point (°C)	150↑
Viscosity (cps, at 25 °C)	2000~5000
Density (g/cm <sup>3</sup> 25°C)	1.16

Acrylated epoxidized soybean oil ( $d=1.04 \text{ g/cm}^3$ ) was purchased from Sigma-Aldrich. The epoxy embedding medium accelerator is 2,4,6-tris(dimethylaminomethyl)phenol (Sigma-Aldrich) (Fig. 1).

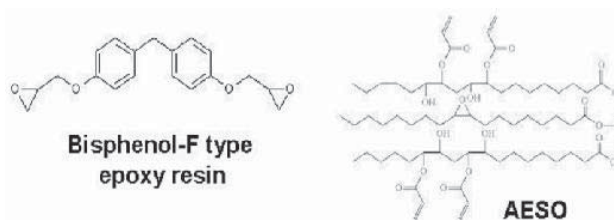


Fig. 1 Chemical formula ER and AESO

Methyl nadic anhydride (MNA) and sebacic acid (SAC) were used as curing agents. The chemical structures of them are schematically represented in Fig. 2.

Suheyla Kocaman and Gulnare Ahmetli are with the Chemical Engineering Department, Faculty of Engineering, Selcuk University, 42045, Campus, Konya, Turkey (e-mail: suheyla@selcuk.edu.tr, ahmetli@selcuk.edu.tr).



Fig. 2 Chemical formula of the curing agents

The SSH used in this research was obtained from Caspian Sea Region. Banana as imported product was obtained from nearby local market (Fig. 3).



Fig. 3 SSH and BP

#### B. Composite Preparation

The AESO was mixed with an epoxy matrix in 50 wt%, using an IKA T18 digital ultra turrax homogenizator (stirring rate of 7000 rpm) for 15 min. The biobased filler (particle size <63  $\mu\text{m}$ ) with various wt% (10-50 wt%) and epoxy matrix (50 wt% of ER and 50 wt% of AESO) were mixed with mechanical stirring (stirring rate of 2000 rpm) for 3 h and ultrasounded for 1 h at 60  $^{\circ}\text{C}$  in order to obtain a good dispersion. Afterwards, the curing agent at 30 wt% and epoxy accelerator (1 wt%) were added, and the mixture was degassed for 60 min at room temperature and then transferred into the mold. Samples were prepared in stainless-steel molds according to ASTM D 638 standard. The curing temperature for MNA is 120  $^{\circ}\text{C}$ . The dimension of composite samples is shown in Fig. 4.

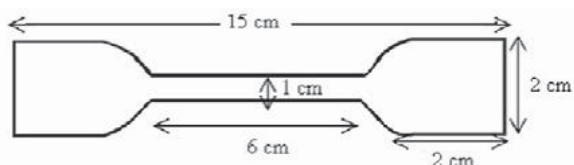


Fig. 4 The dimension of composite samples

#### C. Analysis and Testing

The FTIR spectra of the composites were recorded with Bruker-Platinum ATR-vertex 70 between 500 and 4000  $\text{cm}^{-1}$  wavenumbers at a resolution of 4  $\text{cm}^{-1}$  using an attenuated total reflectance (ATR) accessory.

According to the Beer-Lambert law, the absorption peak at 1600-1616  $\text{cm}^{-1}$  of a benzene ring can be regarded as an internal standard; thus, the degree of curing can be determined from the FTIR spectra of uncured and cured epoxy [9].

The density of the M-ER systems was measured using Archimedes' principle with doubly distilled water as the liquid medium by an analytical balance (Radwag AS220/C/2, capacity 220 g, readability 0.1 mg, Poland) and a kit of density (Radwag 220, Poland). A Shore Durometer TH 210 tester was used for measuring the hardness of the samples. The resistances to stretch properties were determined by Stretch and Pressing Equipment TST-Mares/TS-mxe.

### III. RESULTS AND DISCUSSION

#### A. Curing Degree of M-ERs

The chemical structures of uncured ER and cured M-ERs are confirmed by FTIR spectra (Figs. 5-7). Almost all epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermoset networks by curing with cross-linkers. In real reactions, the density of cross linking is typically less than 100%, and this affects the chemical resistance, electrical properties, mechanical properties, and heat resistance of the cured thermosets. The curing degree of the M-ERs was determined via the FTIR spectra and the results were given in Table II.

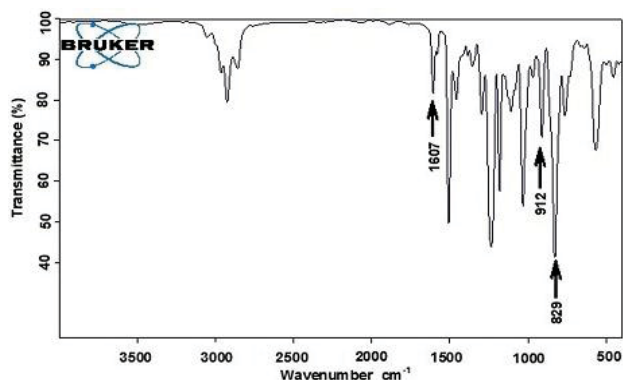


Fig. 5 FTIR spectrum of uncured ER

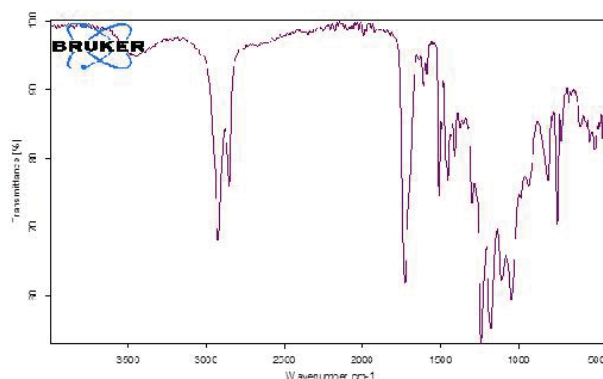


Fig. 6 FTIR spectrum of cured M-ER with SAc

The presence of epoxide groups is characterized by the appearance of typical bands at 1250, 913, and 830  $\text{cm}^{-1}$  corresponding to stretching C-O-C of ethers, stretching C-O of oxirane group, and stretching C-O-C of oxirane group (Fig. 5).

Figs. 6 and 7 show the spectra of the blends for the 3300–3600  $\text{cm}^{-1}$  wave number range, in which only one wide band can be observed due to stretching vibration of the hydroxyl groups. The wide distribution of hydrogen-bonded hydroxyl stretching vibrations in the blends can be attributed to the very broad bands, shifted to a lower wavenumber by the addition of AESO. This result suggests that in the ER-AESO blends, the hydroxyl groups in the epoxy matrix and the carbonyl groups in the ESO form an association via hydrogen bonding.

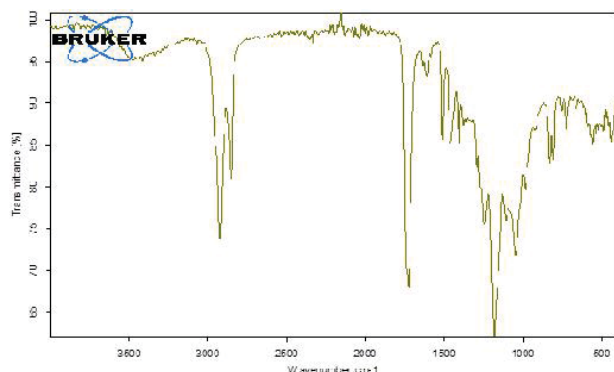


Fig. 7 FTIR spectrum of cured M-ER with MNA

In some studies, it has been reported that the reactivity of the used amine curing agents depended on the chemical structure and decreased as the number of phenyl groups increased in the chemical structure [10], [11]. For an epoxy/ESO (epoxidized soybean oil) system cured with sebacic acid hardener, it was observed that the glass transition temperatures of the studied samples were lower than that of the samples cured with anhydride or amine. This can be easily attributed to the lower cross-link density of the studied cured system and the difference in their chemical structures [12]. Apparent from Table II, curing degree of M-ER cured with MNA was higher than M-ER cured with SAc. The most important indicator of a composite's performance is density, which basically affects all properties of the composite.

TABLE II  
CURING DEGREE AND DENSITY VALUES OF THE M-ERS CURED WITH 30 WT% OF HARDENERS

Hardener	Curing degree (%)	Measured density ( $\text{g/cm}^3$ )
SAc	78.67	1.0032
MNA	97.56	1.1274

It was reported by Jeyranpour et al. [13] that the density of epoxy systems with different hardeners increased as the cross-linking density increased. As seen from Table II, the lowest measured density ( $1.0032 \text{ g/cm}^3$ ) was found for the M-ER system cured with SAc.

### B. Mechanical Properties of Composites

Mechanical tests were carried out to investigate the effects of modifier, filling material and curing agents on tensile strength, elongation at break, and hardness of the composites.

The results are summarized in Figs. 8-11 for SAc and in Figs. 12-15 MNA hardeners, respectively.

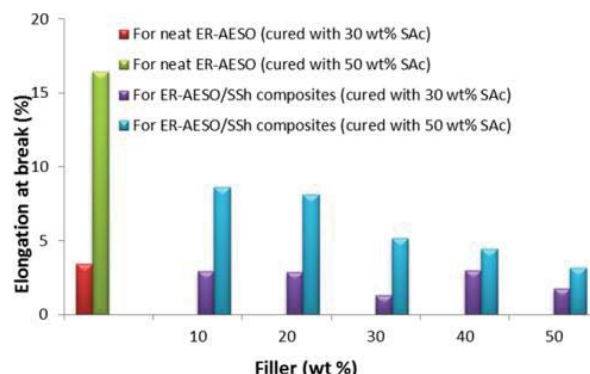


Fig. 8 Elongation % of composites cured with SAc hardener

As seen from Figs. 8 and 9, cured modified ER with 50 wt% SAc has a low tensile strength, but high elongation percent. Tensile strength slightly decreased with increasing SAc amount, despite that increased the elongation at break about 4.8 times. Also, SSh composites with 30 wt% SAc curing agent has a higher tensile strength and hardness values than composites with 50 wt% SAc.

For ER-AESO/SSh composites, MNA was obtained more effective curing agent than SAc (Figs. 12-15). Mechanical properties of SSh composites were found better than BP composites.

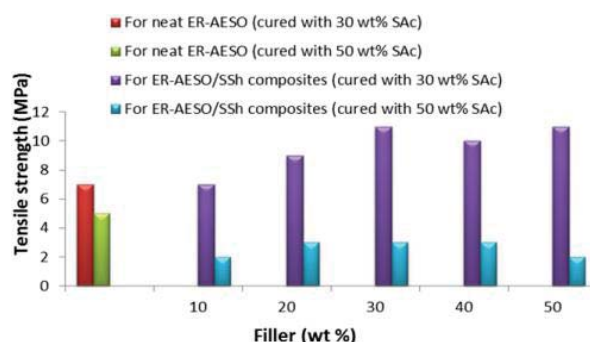


Fig. 9 Tensile strength of composites cured with SAc hardener

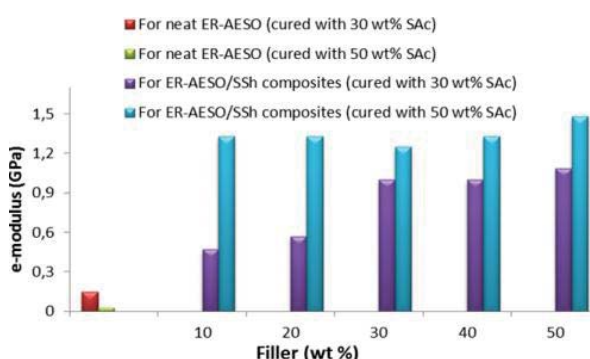


Fig. 10 Young's modulus of composites cured with SAc hardener

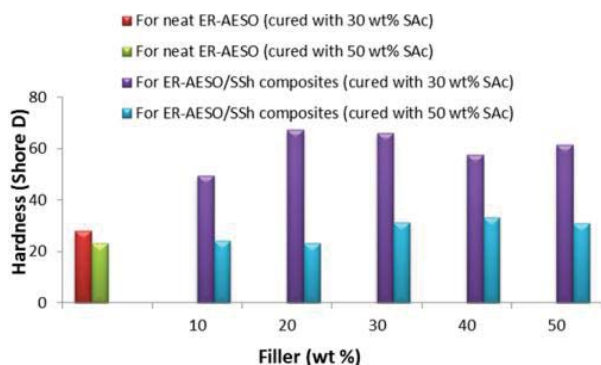


Fig. 11 Hardness of composites cured with SAc hardener

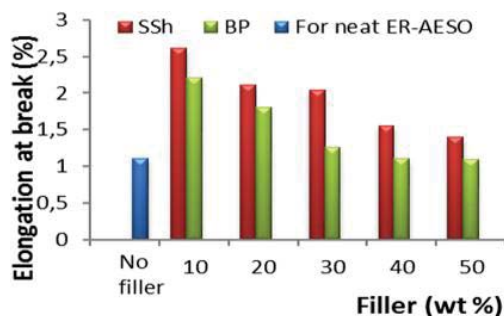


Fig. 12 Elongation % of composites cured with MNA hardener

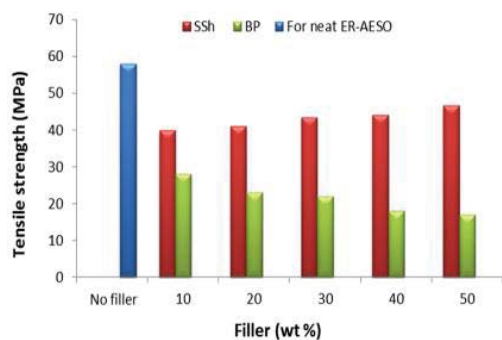


Fig. 13 Tensile strength of composites cured with MNA hardener

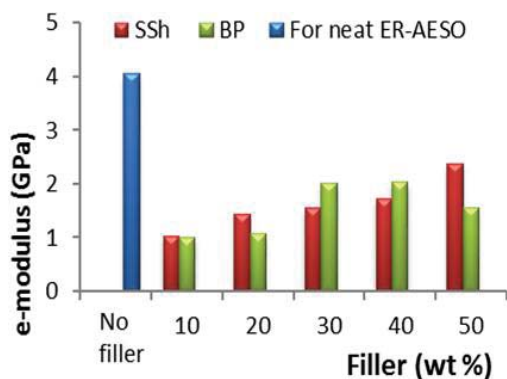


Fig. 14 Young's modulus of composites cured with MNA hardener

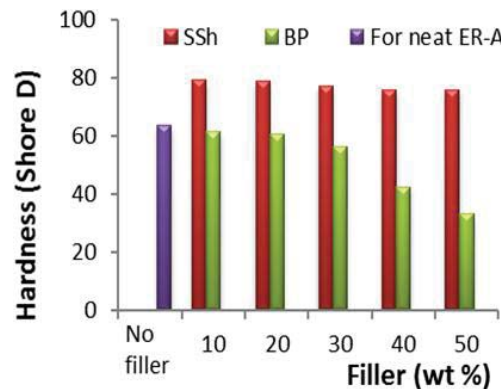


Fig. 15 Hardness of composites cured with MNA hardener

As seen from Figs. 11 and 15, SSH increased the hardness of composites. Also, Young's modulus values for SSH composites cured with MNA were determined higher than composites cured with SAc.

#### IV. CONCLUSION

Modification of ER with AESO remarkably enhances the plasticity of ER. The inclusion of SSH and BP influences most of the mechanical properties of the neat polymer matrix. The SSH-containing epoxy systems exhibit higher tensile strength, e-modulus and hardness than neat epoxy system and BP composites.

#### ACKNOWLEDGMENT

We express our thanks to the TUBITAK BİDEB 2211-A Domestic Doctoral Fellowship Program and Academic Staff Training Program, which has financed the Project 2013-ÖYP-068, a part of which is presented in this study.

#### REFERENCES

- [1] U. Riedel, Biocomposites: Long Natural Fiber-Reinforced Biopolymers, *Reference Module in Materials Science and Materials Engineering*, v. 10: Polymers for a Sustainable Environment and Green Energy, 2012, Pages 295–315.
- [2] J. Bolton, *Outlook Agric.*, 24, 85 (1995).
- [3] J. Lu, Zh. Lu, X. Li, H. Xu, X. Li, *J. Cleaner Product.*, 92, 223 (2015).
- [4] S. Yoo, J.S. Hsieh, P. Zou, J. Kokoszka, *Bioresour. Technol.*, 100, 6416 (2009).
- [5] H.H. Cai, S.D. Li, G.R. Tian, H.B. Wang, J.H. Wang, *J. Appl. Polym. Sci.*, 87, 982 (2003).
- [6] L. Zhang, C. Li, R. Huang, *J. Polym. Sci. Part B*, 42, 1656 (2004).
- [7] K. Leja, G. Lewandowicz, *Polish J. Environ. Stud.*, 19, 255 (2010).
- [8] S. Garg, A.K. Jana, *Eur. Polym. J.*, 43, 3976 (2007).
- [9] I. Ozaytekin, H. Turedi, G. Ahmetli, *Polym. Compos.* (2015), doi: 10.1002/pc.23542 (2015).
- [10] I. Jirasutsakul, B. Paosawatyanong, W. Bhanthumnavin, *Prog. Org. Coat.*, 76, 1738 (2013).
- [11] T. Okabe, T. Takehara, K. Inose, N. Hirano, M. Nishikawa, T. Uehara, *Polymer*, 54, 4660 (013).
- [12] G. M. Roudsari, A. K. Mohanty, M. Misra, *ACS Sustainable Chem. Eng.*, 2, 2111 (2014).
- [13] F. Jeyranpour, Gh. Alahyarizadeha, B. Arab, *J. Molecular Graph. Modelling*, 62, 157 (2015).