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Using Sugar Mill Waste for Biobased Epoxy Composites

Ulku Soydal, Mustafa Esen Marti, Gulnare Ahmetli

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***Abstract*—**In this study, precipitated calcium carbonate lime waste (LW) from sugar beet process was recycled as the raw material for the preparation of composite materials. Epoxidized soybean oil (ESO) was used as a co-matrix in 50 wt% with DGEBA type epoxy resin (ER). XRD was used for characterization of composites. Effects of ESO and LW filler amounts on mechanical properties of neat ER were investigated. Modification of ER with ESO remarkably enhanced plasticity of ER.

***Keywords*—**Epoxy resin, biocomposite, lime waste, mechanical properties.

I. Introduction

IN traditional sugar beet processing, the sugar is extracted from plants and purified from impurities with the help of precipitation technique. The sequential addition of limewater (milk of lime and calcium hydroxide suspension) and carbon dioxide into raw beet juice results in flocculation of the non-sugar components with the calcium carbonate (CC) precipitate. This purification step is called carbonation and results in a waste sludge containing about 75% CC, 10% organics and nitrogen compounds and 1% phosphoric acid equivalent. The huge amounts of lime waste (LW) produced in sugar beet processing cause serious environmental and storage problems.

Environmental problems in traditional beet sugar processing are mainly related to the production of large amounts of pulp, the consumption of large quantities of lime (which are transformed into sludge), the production of vinasse, and the huge consumption of energy and water. Therefore, several researchers aimed 1) to utilize the pulp and carbonation sludge for the production of paper, 2) to utilize vinasse for the production of compost, and 3) to utilize new technologies for eliminating the utilization of lime (Fig. 1). Therefore, there is a critical need for the management and advantageous utilization of this waste material [1]-[4].

In the literature, there are only a limited number of studies on the composites containing CC. Cai et al. reinforced natural rubber latex film by using CC and obtained enhanced tear strength, tensile strength and modulus. They noted that surface tension and viscosity were slightly affected when the CC content was less than 20% [5]. Zhang et al. modified polypropylene with elastomer or CC particles. The authors observed improved toughness and modulus with elastomer and CC, respectively [6]. At another study, Supaphol et al. mentioned that nucleating efficiency of CC for syndiotactic polypropylene was found to be dependent on the purity, surface treatment method and particle size of the additive. They observed significant changes in the properties of the polymers with the CC addition [7]. In our previous studies, we reported how different coagulant types in marble waste and epoxy toluene oligomer modifier affect the mechanical and thermal properties of commercially available and modified ERs [8], [9]. In this study, we used sugar beet processing lime waste as a replacement of calcium carbonate in the preparation of composites using neat and ESO-modified epoxies.

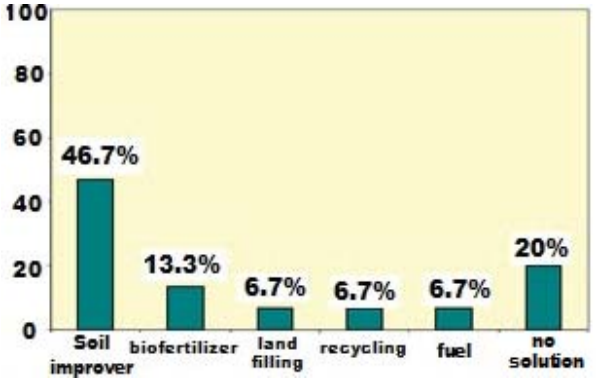


Fig. 1 Handling of lime waste in the world [1]

II. Experimental

A. Materials

Sugar beet processing lime waste (LW, d=1.6 g/cm^3) used in this experimental research was obtained from Konya Sugar Mill in the Anatolia Region of Turkey (Figs. 2 and 3).

The large amounts of lime utilized (Fig. 3) in the industry is very important and its exhaustion is critical and a considerable ecological problem. Using lime waste from sugar beet processing to replace natural lime will also save the natural reserves of this material [2].

A commercially available bisphenol A-type diluted epoxy resin NPEK 114, called as ER, (EEW 190 g/eq, d=1.16 g/cm^3, Konuray Chemical Co.) was used during the experimental studies. Epoxidized soybean oil (ESO, d=0.917 g/cm^3) was purchased from Sigma-Aldrich. Epamine PC17 (A cycloaliphatic polyamine, Konuray Chemical Co.) and 2,4,6-tris(dimethylaminomethyl)phenol (Sigma-Aldrich) were used

Ulku Soydal is with the Karapinar Aydoganlar Vocational School, Selcuk University, Konya, Turkey (e-mail: usoydal@selcuk.edu.tr).

Mustafa Esen Marti is with Chemical Engineering Department, Faculty of Engineering, Selcuk University, 42045, Campus, Konya, Turkey (e-mail: mustafaesenmarti@gmail.com).

Gülnare Ahmetli is with the Chemical Engineering Department, Faculty of Engineering, Selcuk University, 42045, Campus, Konya, Turkey (corresponding author; e-mail: ahmetli@selcuk.edu.tr).

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as the curing agent and epoxy embedding medium accelerator, respectively (Fig. 4).



Fig. 2 Sugar beet processing lime waste

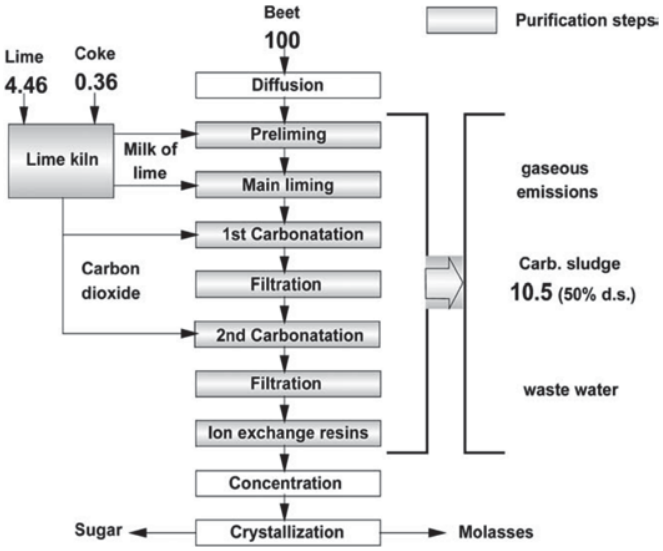


Fig. 3 Simplified flow diagram of a beet sugar factory [1]

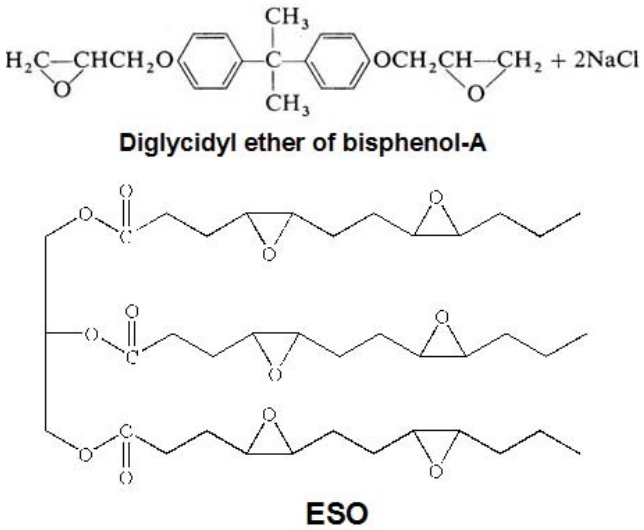


Fig. 4 Chemical formula of epoxy resin and ESO

B. Composite Preparation

The LW (particle size<63 μm) and neat ER or ESO-modified ER mixed at varying per cent values (10-50 wt% for LW) were mechanically stirred at 2000 rpm and room temperature for 3 hours. Then the mixture was ultrasounded for an hour at 60°C to obtain a good dispersion. Following that, 30 wt% epoxy hardener and 1 wt% epoxy accelerator were added into the blend. The mixture was degassed for 60 min. at 40ºC and transferred into the mould. Composite specimens were prepared according to the ASTM D 638 standard. The curing procedure was carried out in an oven at 100ºC for 24 hours and then the samples were post-cured at 120ºC for another 24 hours. The dimension of composite samples is shown in Fig. 5.

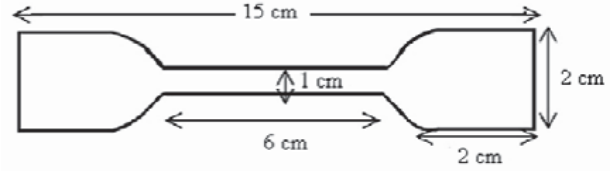


Fig. 5 The dimension of composite samples

C. Analysis and Testing

Powder X-ray diffraction (XRD) analyses were performed using a Bruker D8 Advance Powder Diffractometer with Cu-K α radiation (λ = 1.5406 A, power = 40 kV). All XRD analyses were performed at room temperature and the scanning was ranged from 10º to 70º. 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. Stress or elongation test is important for a theoretical understanding of viscoelastic materials. In stress-strain tests, the buildup of force (stress) measured as the specimen is being deformed at a constant rate. Stress-strain tests have traditionally been the most popular and universally used of all mechanical tests and are described by ASTM standard tests, such as D638, D882, and D412 [10].

III. Results and Discussion

A. Characterization of Composites

Figs. 6 and 7 show the X-ray diffraction (XRD) patterns of the ER-ESO, LW and composites in the range of 2θ=10–70°. As seen in the figures, the broad and weak XRD peak of the neat ER-ESO centered at 2θ=20º, which corresponds to the intensity of 1836. The XRD pattern of LW exhibited characteristic diffraction peaks at 2θ values of 29.5º, 36º, 39.5º, 43.2º, 47.5º and 48.5º. The composites included peaks centered at approximately 20° and 29.5°-48.5º were belongs to the ER-ESO (or ER) and LW, respectively. Due to the presence of LW in composites, the characteristic peaks of the filling material were observed in ER/LW and ER-ESO/LW samples.

B. Mechanical Properties of Composites

Most plastic materials were used in applications due to their desirable mechanical properties and economic cost. For this reason, mechanical properties are considered to be the most important properties among all types of properties. The

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mechanical properties of composites are critically based on the microstructure and performance of the interface between the reinforcing filler and matrix. The strength of the bond between the resin and fiber is not solely dependent on the adhesive properties of the resin system, but is also affected by the surface coating on the reinforcement fibers. Among the other resins, such as polyesters or vinyl ester resins, epoxy systems offer the best performance due to their chemical composition and the presence of polar hydroxyl and ether groups [11].

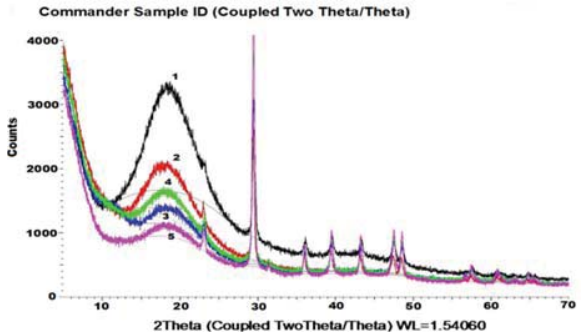


Fig. 6 XRD patterns of ER/LW composites with: 1)10 wt% LW; 2) 20 wt% LW; 3) 30 wt% LW; 4) 40 wt% LW; 5) 50 wt% LW

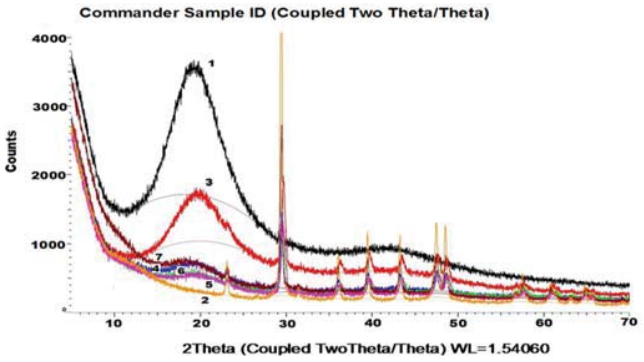


Fig. 7 XRD patterns of: 1) neat ER-ESO; 2) pure LW and ER-ESO/LW composites with: 3)10 wt% LW; 4) 20 wt% LW; 5) 30 wt% LW; 6) 40 wt% LW; 7) 50 wt% LW

TABLE I
EFFECT OF AMOUNT OF LW ON THE MECHANICAL PROPERTIES OF COMPOSITES

LW filler (wt%)	Elongation at break (%)	Tensile Strength (MPa)	e-modulus (GPa)	Hardness (Shore D)
		For neat ER		
-	0.487	41.75	5.59	70.0
		For ER/LW composites		
10	0.482	84.00	7.63	86.0.
20	0.397	86.63	10.78	85.5
30	0.351	70.15	9.62	85.0
40	0.267	64.00	8.81	86.0
50	0.234	56.27	7.26	86.4
		For modified ER with ESO		
-	0.883	39.45	3.88	63.0
		For ER-ESO/LW composites		
10	0.875	68.81	4.05	64.0
20	0.863	70.36	3.00	65.0
30	0.861	64.81	2.84	69.0
40	0.861	60.45	3.09	70.0
50	0.861	53.27	2.20	72.0

Mechanical tests were carried out to investigate the effects of modifier and filling material on tensile strength, elongation at break, and hardness of the composites. The results are summarized in Table I and Figs. 8-11. According to the tensile and hardness tests results, the mechanical properties of the composites changed with the amounts of filling material and modifier in the composite (Table I).

The elongation and e-modulus (Young's-modulus) of neat ER were determined as 0.487% and 5.59 GPa, respectively. According to Fig. 8, 50 wt% modification of ER with ESO increased the percent elongation by 79.67% while decreased the e-modulus and hardness.

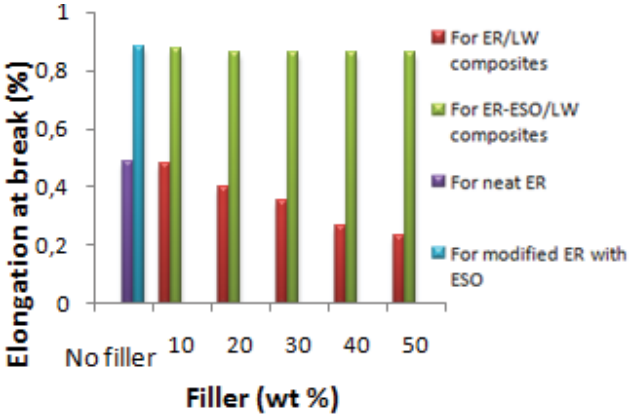


Fig. 8 Elongation % of composites

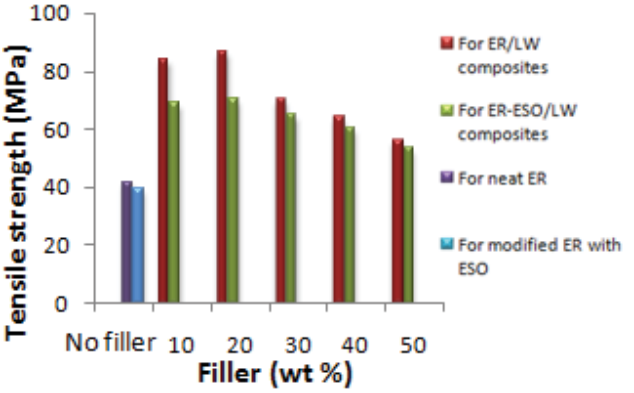


Fig. 9 Tensile strength of composites

The tensile strengths of neat ER and ER-ESO were found as 41.75 MPa and 39.45 MPa, respectively (Fig. 9). The LW addition significantly increased the tensile strength for both types of epoxy matrices. For both epoxy-type composites, the maximum tensile strengths were obtained with the 20% LW addition as 86.86 MPa and 70.36 MPa for ER/LW and ER-ESO/LW, respectively.

Surface hardness of the composite is considered to be one of the most important factors that govern the erosion resistance. Polymers have low hardness, which can be seen in Fig. 11. For both neat epoxy matrix types, the lowest values were obtained before the reinforcement. ESO further decreased the hardness of the neat ER. On the other hand, LW addition notably increased that of neat- and modified epoxy.

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Hardness of the composite increased with the increase in LW loading (Fig. 11).

For many materials, the relation between applied stress is directly proportional to the resulting strain (up to a certain limit), and a graph showing the relationship of these two quantities is generally a straight line. The linear-elastic region is either below the yield point; or if a yield point is not easily identified on the stress-strain plot, it is defined to be between 0 and 0.2% strain and as in the region of strain in which no yielding (permanent deformation) occurs. Brittle materials, like ceramics, do not experience any plastic deformation and will fracture under relatively low stress [12]. Therefore, since the polymer is hard and brittle, the e-modulus is high and elongation at break is low. On the other hand, for a soft and flexible polymer, the e-modulus is low and elongation at break is high [13].

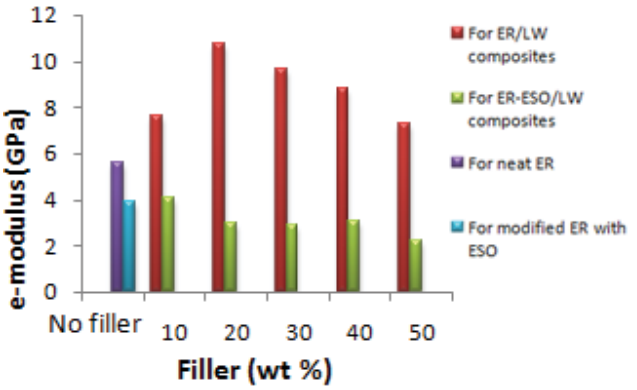


Fig. 10 Young's modulus of composites

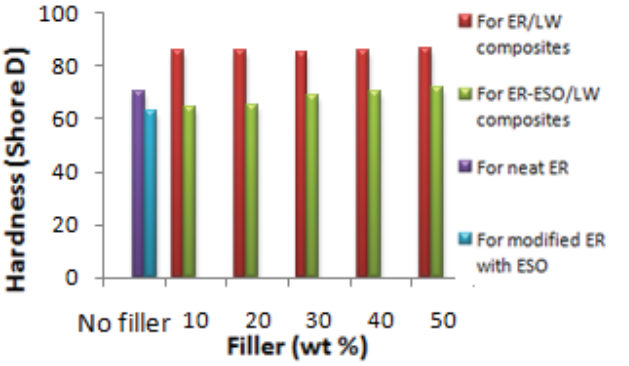


Fig. 11 Hardness of composites

In comparison to the curves of neat ER and ER-ESO in Fig. 12, it was clearly seen that the stress-strain curves of LW composites can be divided into two parts: elastic and plastic regions and the strain continued to rise with the increase in stress until the fracture of composites. The composites exhibited a short strain-hardening region, which means that they were more brittle than neat epoxy matrices and the addition of LW resulted in considerably lower plasticity.

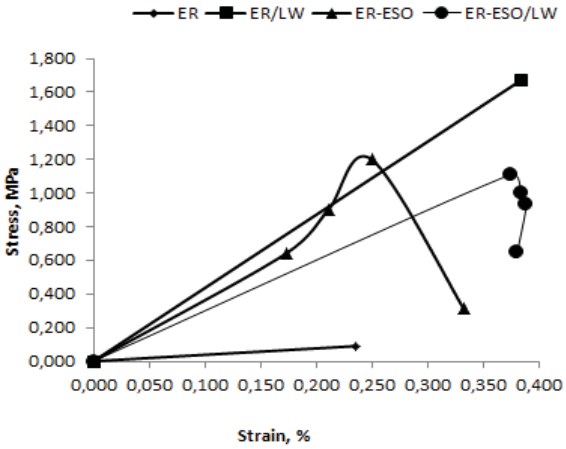


Fig. 12 Stress-strain curves

IV. Conclusion

Modification of ER with ESO remarkably enhanced the plasticity of ER. The inclusion of LW influenced most of the mechanical properties of the neat epoxy. The LW-containing epoxy systems exhibited higher tensile strength than neat epoxy systems, while e-modulus and hardness of composites increased with the increase in LW content.

Acknowledgment

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