*Research Article*

# Evaluation of Fatty Acid Waste in the Synthesis of Oligo(Ether-Ester)s

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In this study, the waste of sunflower oil refinement was converted to a fatty acid glycidyl ester (FAGE). An unsaturated oligo(ether-ester) (OEE) was synthesized by ring-opening polymerization using propylene oxide (PO) and FAGE. Oligo(ether-ester) production was achieved with a high yield of 80% at 5 h and 0°C when the mole ratio of PO : FAGE was 1 : 1. Synthesized OEE was characterized by FTIR and several chemical analysis methods. According to the TGA results, $T_5$, $T_{10}$, and $T_{50}$ values of OEE-styrene copolymers increased up to a 7 : 3 mole ratio then decreased. The weight losses of these copolymers changed in the range of 3-5%. The data of longitudinal and transversal wave velocities showed that copolymers with styrene had better elastic properties and impact resistances compared to those with pure polystyrene.

## 1. Introduction

Recently there has been an increasing interest in the utilization of the polymers attained from renewable resources due to their advantages in the biodegradability and cost of the process. For example, natural oils contain useful raw materials to be used in polymer syntheses [1, 2]. In the alkali deacidification step, soapstock is produced as a by-product and it includes a significant amount of soap and water. Acidulation of the soapstock provides acid oil, which contains free fatty acids (FFAs), acylglycerols, and other lipophilic components. On the other hand, disposal of biodegradable wastes such as food wastes and activated sludge causes environmental pollution [3].

Biermann et al. stated that more than 90% oleochemical reactions occur due to a fatty acid carboxyl group [1]. Previously, numerous reports on the enzymatic and chemical conversion of acid oil to fatty acid methyl esters (FAMEs) were published and several researchers studied the esterification of FFAs in waste cooking oil in order to obtain low-cost biodiesel [4–7]. Kojima et al. reutilized the waste-activated bleaching earth to produce FAME with the use of a microbial catalyst and waste materials [8]. A thermochemical pretreatment was optimized to develop anaerobic biodegradation of slaughterhouse wastes, i.e., long-chain fatty acids by Battimelli et al. [9]. Vaca-Garcia and Borredon studied mixed acylation of cellulose with acetic anhydride and linear fatty acids that were derived from lignocellulosic wastes [10]. Fatty acid alkyl esters (FAAEs) have been widely utilized in the syntheses of several types of products such as biodegradable polyesters, fatty alcohols, biodiesel, plasticizers biosurfactants, antirust agents, and hydraulic and drilling fluids in oleochemistry [11–14]. Recently, fatty acid cellulose esters have been shown as biodegradable plastics that can be produced by a vacuum-acid chloride process [15]. Lara and Park investigated the synthesis of FAAEs by lipase-catalyzed alcoholysis of waste plant oil [16]. The traditional technique for the production of FAMEs is based on the transesterification of triglycerides into methyl esters [17]. Fatty acids have been evaluated in several polymeric applications [18]. Conjugated and nonconjugated tall oil fatty acid-based alkyd resins were produced and copolymerized by emulsion polymerization with acrylates. The ratio of alkyd resin and acrylate monomers was changed, and the

influence on copolymerization and copolymer-binder properties was investigated [19]. Murillo et al. studied the synthesis of hyperbranched alkyd resins from the fourth generation hydroxylated hyperbranched polyester and tall oil fatty acids using acid catalysis. The alkyd resins presented good adhesion, drying time, flexibility, and chemical resistance [20]. Bat et al. investigated the production of alkyd resins based in a hydroxylated hyperbranched polyester and modification with benzoic acids, castor oil fatty acids, and linseed oil fatty acids. The researchers observed that the hardness of the resins improved with the contents of castor oil and linseed oil fatty acids. On the other hand, it did not alter with benzoic acid content [21].

The wastes of sunflower oil refinement cause environmental pollution. The transformation of these waste materials into valuable polymeric materials via economic means is a promising method for the elimination of the problem. Moreover, they may reduce the production costs. In our previous studies, we transformed several types of waste materials into valuable products with the use of polymeric syntheses. Synthesized unsaturated oligomers (oligoethers containing unsaturated ester groups) were utilized for the production of polymeric materials with high adhesion and physicomechanical properties [22, 23]. We also investigated the electrochemical chlorination reaction of fatty acid wastes (FAWs) in the electrolysis of HCl. Physicomechanical properties, heat resistance, and the influence of chloride to the fire strength of the composite materials, which were obtained from this reaction, were determined [24]. The aim of this study was to prepare an unsaturated oligo(ether-ester) (OEE) by using soap stock which is the waste material of a vegetable oil refining process and study the thermal behavior of prepolymer OEE with styrene comonomer. For this purpose, soap stock was transformed into unsaturated ester (FAGE) using epichlorohydrin; then it was reacted with PO to obtain an unsaturated OEE. Finally, unsaturated glycidyl ester copolymers were obtained from its copolymerization with styrene. In this respect, the synthesis and ring-opening copolymerization of the glycidyl ester of fatty acid are important for the reprocessing of the waste materials for the production of valuable products. This will also help to decrease the environmental pollution.

## 2. Materials and Method

*2.1. Materials.* Soap stock was obtained from Zade Chemical Industry, Konya, Turkey. Propylene oxide (PO), epichlorohydrin (ECH), styrene, benzoyl peroxide (BPO), and boron trifluoride diethyl etherate ($BF_3O(C_2H_5)_2$) were supplied from Merck (Darmstadt, Germany).

*2.2. Analyses.* Gas chromatography analyses of FAW were performed using a GC-15A model Shimadzu Gas Chromatography. The FTIR spectra of the synthesized copolymers were obtained with a UNICAM SP 1025 spectrometer. Ultrasound speed measurement was conducted by an ultrasound speed device, PR5800 Pulser-Receiver Olympus NDT. Density was measured using a Radwag 202 density kit.

*2.2.1. Determination of the Epoxy Group.* The epoxy groups in the samples were cleaved with excess HCl to determine their percentage. The residual HCl was back titrated with KOH (0.1 N) [22].

*2.2.2. Determination of the Ester Group.* The number of the ester groups in the unsaturated OEE and FAGE was determined. The solution was prepared by mixing ethanol (25 mL) and benzene (50 mL). The sample (2-3 g) was dissolved in this mixture. Then, 25 mL of an ethanolic solution of KOH (2 N) was added into the mixture, and it was refluxed for an hour. Excess KOH was titrated with HCl (1 N), and phenolphthalein was used as the indicator after cooling the mixture to room temperature. The number of ester groups was calculated with the following equation:

$$\text{Ester group} \, (\text{mg KOH/g sample}) = \frac{56.1(V_1 . N_1 - V_2 . N_2)}{m}, \quad (1)$$

where $N_1$ is the normality of the KOH solution, $N_2$ is the normality of the HCl solution, $V_1$ is the volume of the KOH solution (mL), $V_2$ is the volume of the HCl solution (mL), $m$ is the amount of the sample (g), and 56.1 is the molecular weight of KOH.

*2.2.3. Determination of the Acid Number (A.N.).* The functional group analysis was used to determine the amount of carboxyl groups. The method was previously described in detail [25].

*2.2.4. Determination of the Double Bond.* A titration method was used to determine the number of double bonds. The sample (0.2-0.4 g) was dissolved in 15 mL ethanol at 50-60°C. 25 mL of an iodine solution (2.57 g iodine in 100 mL of ethanol) and 200 mL of water at 30-35°C were added into the mixture. The solution in the stoppered vial was mixed and allowed to settle in the dark for 5 minutes. Next, the excess iodine was back titrated with 0.1 N $Na_2S_2O_3$ using a starch indicator. A control titration was also carried out without a sample under the same conditions. Titration was continued until the disappearance of the blue color of the solution. The iodine value (I.V.) was calculated using the following equation:

$$\text{I.V.} = \frac{(V_1 - V_2) \times 0.012697}{m} \times 100, \quad (2)$$

where $V_1$ is the volume of 0.1 N $Na_2S_2O_3$ used for control titration (mL), $V_2$ is the volume of 0.1 N $Na_2S_2O_3$ used for titration with a sample (mL), 0.012697 is the amount of iodine (g) corresponding to 1 mL of 0.1 N $Na_2S_2O_3$, and $m$ is the amount of sample (g).

*2.2.5. Thermogravimetric Analysis.* Thermogravimetric analyses (TGA) of the samples were conducted with the use of a NETZSCH-Geratebau GmbH model thermogravimetric analyzer in a nitrogen atmosphere. The instrument was calibrated over all heating rates, using a gas purge, under the same conditions. 10 mg of polymer samples in platinum

crucibles was heated in the range of 25–500°C with a heating rate of 10°C min⁻¹.

### 2.3. Synthesis

*2.3.1. Synthesis of the Glycidyl Ester of Fatty Acid (FAGE).* FAGE was attained via the esterification reaction of potassium salt of fatty acid with epichlorohydrin in the alkaline medium. 10 g FAW, 10 mL of benzene, and 4 mL 40% KOH solution were mixed in the flask for the reaction. 3 g ECH was added to the solution drop by drop within 20–30 minutes at 40°C. Then, the temperature of the mixture was increased to 70-80°C, and it was boiled for 5 hours. The ester was obtained by distillation under the vacuum.

*2.3.2. Synthesis of the Unsaturated Oligo(Ether-Ester)s (OEE).* A volumetric flask (150 mL) equipped with a magnetic stirrer and thermometer was used. For the synthesis of the unsaturated oligo(ether-ester)s, PO and FAGE were used in different molar ratios, which were from 1 : 1 to 4 : 1. The mixture was cooled to 0°C with stirring, and later, $BF_3O(C_2H_5)_2$ (1 wt%) was added to the mixture. The time was investigated in the range of 3-8 h at 0°C. Methanol (1 mL) was supplemented to the mixture to deactivate the catalyst by creating boron trifluoride-alcohol complex after the completion of the synthesis. Excess of the methanol and the reactants was removed by vacuum distillation under reduced pressure (2 mmHg, 53°C). The yield was calculated using the following equation:

$$\text{Yield(\%)} = \frac{W_{\text{OEE}} \times 100}{W_{\text{initial}}}, \qquad (3)$$

where $W_{\text{OEE}}$ was the amount of OEE (g) while $W_{\text{initial}}$ was the total amount of PO and FAGE at (g), initially.

*2.3.3. Synthesis of the OEE-Styrene Copolymers.* Copolymers of unsaturated OEE (PO : FAGE mole ratio 1 : 1) with styrene in the weight ratios of styrene : oligomer from 9 : 1 to 5 : 5 were synthesized in the presence of BPO (1 wt%) increasing temperature up to 125°C.

## 3. Results and Discussion

The synthesis of FAGE and copolymerization reaction of PO with FAGE are shown in Figure 1. As seen from the figure, firstly, the FAGE was synthesized by using the sunflower oil refinement waste fatty acid soap stock and ECH. Then, the OEE was produced with the use of FAGE and PO via ring-opening polymerization reaction in the presence of $BF_3O(C_2H_5)_2$ cationic catalyst. The reaction proceeded with the opening of epoxy groups which was also shown by FTIR and other chemical analyses.

*3.1. Characterization.* The results of the gas chromatography analyses of FAW are presented in Table 1. As it is seen from Table 1, the isomers of the hydrocarbons of $C_{12}$-$C_{24}$ were determined and it was shown that the majority of the isomerism was due to the $C_{18:2}$—cis isomers. 54.59% and 24.41% of

fatty waste belong to cis-linoleic acid and oleic acid, respectively [24].

The chemical structure of FAGE and unsaturated oligomer was determined via FTIR analysis (Figure 2). The FTIR spectra showed that the characteristic bands for FAGE and OEE appeared at 1740 cm⁻¹ and 1746 cm⁻¹ for C=O of ester, 1661 cm⁻¹ for C=C, 1454 cm⁻¹ and 1455 cm⁻¹ for -$CH_2$-C=O in acids, and 722 cm⁻¹ and 724 cm⁻¹ for fatty acid –$(CH_2)_4$- units. The absorption band at 1246 cm⁻¹ for the epoxide group was observed in the spectrum of FAGE, which was not seen in the spectrum of OEE. The appearance of band at 1065 cm⁻¹ for ether showed that the ring-opening copolymerization reaction was achieved.

*3.2. Effect of Reaction Conditions.* The effects of input mole ratios and time on the copolymer yield and percentage of the epoxy group were studied (Figure 3). The reaction was completed in 5 h as it is seen in Figure 3(a). The change in the reaction time did not affect the percentage of the epoxy group.

The mole ratio of PO : FAGE was changed between 1 : 1-4 : 1 at 0°C, 1 wt% of catalyst, and 5 h of reaction time. The percentage of epoxy groups on the OEE chain increased, and the iodine value decreased with increasing the mole ratio of PO : FAGE (Table 2 and Figure 3(b)).

These results showed that the reaction progressed by cleaving the epoxide ring at the mole ratio of 4 : 1. It might also proceed due to the reaction of unsaturated bonds at the side chain. However, a significant difference between the yields was not observed. According to the data, the most appropriate values for the molar ratio (PO : FAGE) and time were found as 1 : 1 and 5 h, respectively. Under these conditions, the reaction yield was 80%.

As seen in Table 2, the ester numbers were calculated as 338.2-341 mg KOH/g for unsaturated OEE and as 349.4 mg KOH/g for FAGE. The obtained results demonstrate that there is no more change in the number of ester OEE. The decrease in the refractive index due to the mole ratio of PO : FAGE showed that the density of OEE decreased with the increase in the amount of PO (Table 2).

*3.3. OEE-Styrene Copolymers.* Styrene is frequently used as a comonomer for the syntheses of unsaturated polyester resins. The variations of the styrene content in polyester influence the resulting properties. The unsaturated polyester resins become stiffer with an increased styrene content [26]. Styrene-hydroxyethyl acrylate copolymer-based alkyd resins were obtained with a high solid content and may be alternatives for use in the coating industry [27]. The addition of styrene in amounts of up to 50% helps to make the resin easier to handle by reducing its viscosity. The styrene acts both as a cross-linking agent and a viscosity reducer in resin production [28]. Therefore, in this study, the percentage of styrene was changed in the range of 10-50%.

*3.3.1. Thermogravimetric Analysis.* Thermogravimetric analysis is an important analytical method in understanding the structure-property relationships and thermal stability
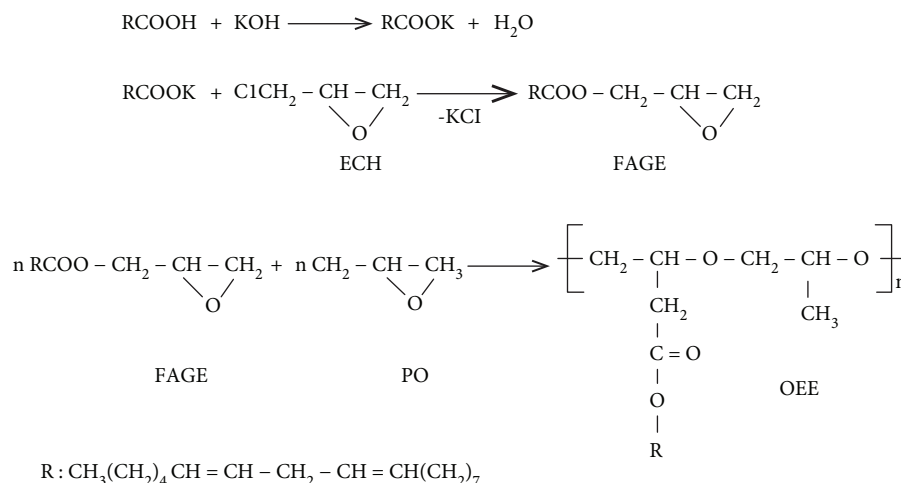
$$RCOOH + KOH \longrightarrow RCOOK + H_2O$$

$$RCOOK + ClCH_2 - \underset{\diagdown O \diagup}{CH - CH_2} \xrightarrow{-KCl} RCOO - CH_2 - \underset{\diagdown O \diagup}{CH - CH_2}$$

ECH                 FAGE

$$n\ RCOO - CH_2 - \underset{\diagdown O \diagup}{CH - CH_2} + n\ \underset{\diagdown O \diagup}{CH_2 - CH - CH_3} \longrightarrow \left[ CH_2 - \underset{\displaystyle \underset{\displaystyle \underset{\displaystyle \underset{\displaystyle R}{O}}{C=O}}{CH_2}}{CH} - O - CH_2 - \underset{CH_3}{CH} - O \right]_n$$

FAGE                 PO                 OEE

$$R: CH_3(CH_2)_4 CH = CH - CH_2 - CH = CH(CH_2)_7$$

Figure 1: Synthesis reactions of FAGE and OEE.

Table 1: The composition of FAW (%).

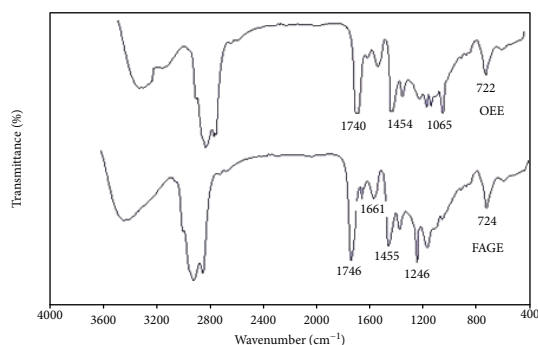| % | Fatty acid |
|---|---|
| $C_{12:0}$ | 0.26 |
| $C_{14:0}$ | 0.34 |
| $C_{16:0}$ | 7.95 |
| $C_{16:1}$ | 0.38 |
| $C_{18:0}$ | 3.97 |
| $C_{18:1}$ | 24.41 |
| $C_{18:1}$ cis | 0.93 |
| $C_{18:2}$ trans | 0.5 |
| $C_{18:2}$ cis | 54.59 |
| $C_{20:0}$ | 0.33 |
| $C_{18:3}$ trans | 0.57 |
| $C_{18:3}$ cis | 0.15 |
| $C_{20:1}$ | 1.56 |
| $C_{22:0}$ | 0.97 |
| $C_{22:1}$ | 2.29 |
| $C_{24:0}$ | 0.61 |



Figure 2: FTIR spectra of FAGE and OEE.

of the polymers. Fiori et al. showed the change of the glass transition temperature ($T_g$) with the styrene amount in unsaturated polyester resin networks based on maleic anhydride and 1,2-propane diol. A styrene monomer had a considerable effect on the $T_{\max}$ that varied from 130°C (for 20 wt% styrene) to 202°C (for 40 wt% styrene) [29]. Eisenberg et al. presented that the $T_g$ of the cured polyester resin increased with the increase in styrene concentration [30]. Sanchez et al. showed that the temperature corresponding to the maximum degradation (TMD) rate increased with the amount of styrene until 38 wt% and, above this level, it decreased [26]. In this study, TGA was used in order to investigate the thermal properties of the copolymers obtained in various weight ratios of OEE with styrene. Thermal degradation of OEE-styrene copolymers has been carried out in the temperature range of 50-450°C. The TGA curves presented in Figure 4 show only a single degradation process for all samples. Table 3 presents the decomposition temperatures at which different weight losses were noticed for all copolymers.

The maximum thermal stability of the resulting copolymer was obtained at the weight ratio of 7:3 (Figure 4(c)). The stability slightly increased from 9:1 to 7:3, and then it dramatically decreased. This behavior is due to the cross-linking density and the phase segregation in the varied styrene amount. Sanchez et al. reported that the cross-linked resins, regardless of the composition of polyester polymer, underwent spontaneous decomposition near 300°C [26]. Synthesized OEE-styrene copolymers showed 5 wt% decomposition temperature ($T_5$) at nearly the temperature of 300°C. In the range of the further thermal decomposition from 300°C to 450°C, copolymers were more stable than pure PS. The copolymer prepared in weight ratio 7:3 had better thermal stability. Thermal analysis results demonstrated that the weight loss of this copolymer began at 300°C, reaching to 50% at 416°C and 80% at 450°C, whereas PS has almost 100% weight loss at this temperature. We previously studied the effect of fatty acid or FAGE on thermal properties of copolymers with styrene [22, 24]. Compared to the results obtained for the copolymer of FAGE with styrene in a weight ratio of
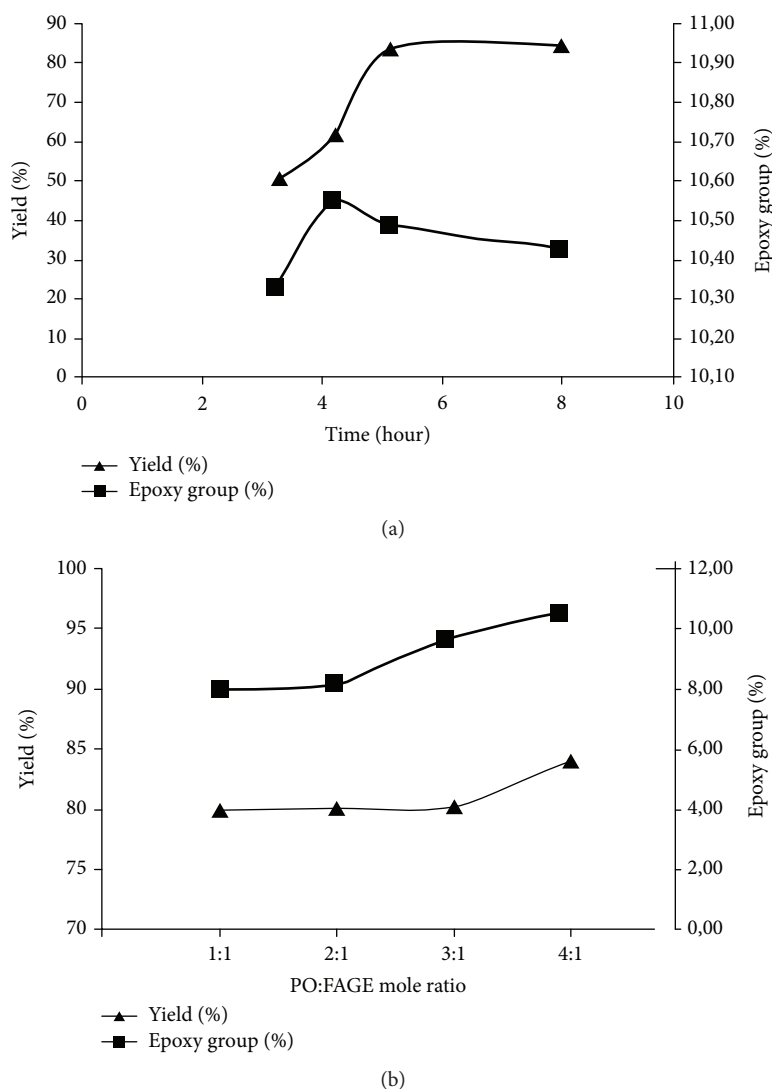
(a)



(b)

FIGURE 3: Effect of reaction conditions on the copolymer yield and percentage of the epoxy group.

TABLE 2: Chemical analysis results.

| Substance | Ester number (mg KOH/g) sample | Iodine value (g $I_2$/100 g) sample | A.N. (mg KOH/g) sample | Refractive index ($n_D^{20}$) |
|---|---|---|---|---|
| FA waste | — | 172.41 | 102.54 | |
| FAGE | 349.4 | 161.6 | 13.1 | |
| OEE (PO : FAGE = 1 : 1) | 340.6 | 156.80 | — | 1.4557 |
| OEE (PO : FAGE = 2 : 1) | 338.2 | 143.2 | — | 1.4553 |
| OEE (PO : FAGE = 3 : 1) | 341 | 121.5 | — | 1.4548 |
| OEE (PO : FAGE = 4 : 1) | 340.1 | 113 | — | 1.4543 |

8 : 2 at 350°C, OEE caused an increase of 31% in thermal stability. The thermal stabilities of all OEE/styrene copolymers were also higher than those of FA/styrene copolymers.

*3.3.2. Density and Sound Velocity.* The variations of densities of PS and copolymers with styrene are shown in Table 4. The densities for the copolymers were between 1.0629 and 1.0834 g/cm$^3$ and were higher than the density of pure PS. There is a strong relation between the density and embranchment of the polymer. Highly branched chains are lighter while shortly branched chains are denser because they interlock each other. Pure PS was a straight-chain polymer; therefore, the density of PS was lower than those of the copolymers. As the weight ratio of OEE in copolymers
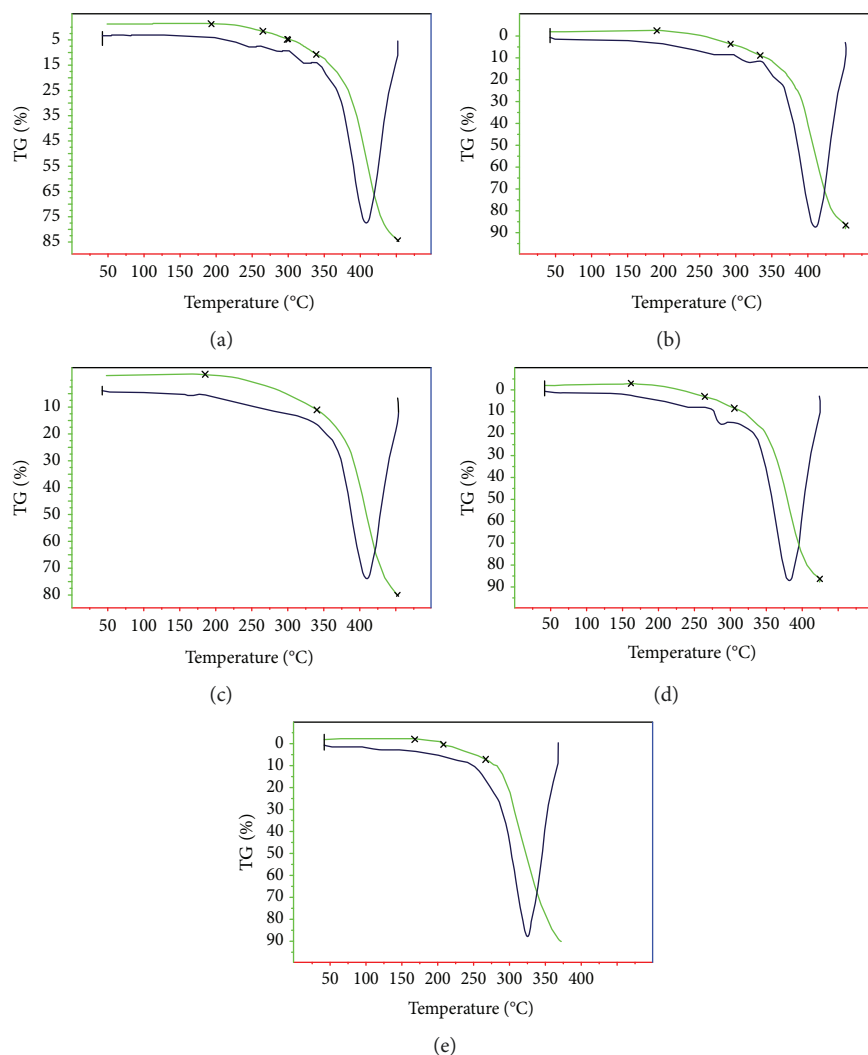
FIGURE 4: TGA curves OEE-styrene copolymers in a mole ratio: (a) 9 : 1, (b) 8 : 2, (c) 7 : 3, (d) 6 : 4, and (e) 5 : 5.

TABLE 3: Weight losses at different decomposition temperatures for OEE/styrene copolymers.

| Styrene : OEE weight ratio | Weight losses (%) | | | | | | Decomposition temperatures | | |
|---|---|---|---|---|---|---|---|---|---|
| | 150°C | 250°C | 300°C | 350°C | 400°C | 450°C | $T_5$ | $T_{10}$ | $T_{50}$ |
| 9 : 1 | 0 | 0 | 5 | 13 | 43 | 85 | 300 | 340 | 412 |
| 8 : 2 | 0 | 0 | 3 | 13 | 37 | 85 | 304 | 348 | 415 |
| 7 : 3 | 0 | 0 | 3 | 10 | 36 | 80 | 307 | 350 | 416 |
| 6 : 4 | 0 | 0 | 8 | 20 | 76 | 87 | 275 | 326 | 380 |
| 5 : 5 | 0 | 10 | 23 | 77 | 94 | 95 | 242 | 250 | 330 |
| Pure PS | 0 | 0 | 7 | 9 | 35 | 100 | 288 | 365 | 420 |

increased, the density decreased, which is a sign of more OEE copolymerized with styrene.

The velocity of ultrasonic waves in a material depends on the composition, elasticity properties, compressibility, and density. It is also influenced by the microstructural properties (porosity, imperfections, etc.) of the material. It has been noticed that the longitudinal and transversal wave velocities were higher in the weight ratios of 9 : 1 and 8 : 2 than those of pure PS (Table 4). Consequently, these copolymers have better elastic properties and impact resistances compared to PS. Transverse and longitudinal sound velocities in this sample have smaller values than those in both the pure PS and

TABLE 4: Variation of density ($\rho$), longitudinal wave velocity ($V_L$) and transversal wave velocity ($V_T$).

| Styrene : OEE weight ratio | Density (g/cm$^3$) | $V_L$ (m/s) | $V_T$ (m/s) |
|---|---|---|---|
| 9 : 1 | 1.0834 | 4560 | 2365 |
| 8 : 2 | 1.0715 | 2853 | 1578 |
| 7 : 3 | 1.0629 | 1650 | 1012 |
| Pure PS ($M_n$ $500 \times 10^3$) | 1.051 | 2355 | 1155 |
| Pure PS ($M_n$ $350 \times 10^3$) | 1.043 | 2352 | 1153 |

other copolymers. Hence, a better sound insulation is thought to be obtained with the copolymer in a weight ratio of 7 : 3.

## 4. Conclusion

The most suitable mole ratio and reaction time for the copolymerization of PO with FAGE were determined as 1 : 1 (PO : FAGE) and 5 h, respectively. Under these conditions, copolymer yield was 80%. The results obtained for the epoxy group and iodine value presented that the reaction mainly progressed by the cleavage of the epoxide ring. Besides that, it proceeded due to the reaction of the unsaturated bonds at the side chain. The copolymers with styrene showed high thermal stability. It has been noticed that the data of longitudinal and transversal wave velocities were higher in weight ratios 9 : 1 and 8 : 2 than those of pure PS. Consequently, these copolymers had better elastic properties and impact resistances compared to PS. This study also demonstrated that sunflower oil wastes can be used in the production of new and less-expensive polymeric materials.

## Data Availability

The experimental data used to support the findings of this study are available from the corresponding author upon request.

## Disclosure

An earlier version of the manuscript was presented as a poster at the European Polymer Congress (EPF 2013).

## Conflicts of Interest

The authors declare that they have no conflict of interest regarding the publication of this paper.

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