

# Solid Freeform Fabrication of Epoxidized Soybean Oil/Epoxy Composites with Di-, Tri-, and Polyethylene Amine Curing Agents

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**ABSTRACT:** Soybean oil/epoxy-based composites are prepared by solid freeform fabrication (SFF) methods. SFF methods built materials by the repetitive addition of thin layers. The mixture of epoxidized soybean oil and epoxy resin is modified with di-, tri-, or polyethylene amine gelling agent to solidify the materials until curing occurs. The high strength and stiffness composites are formed through fiber reinforcement. E-glass, carbon, and mineral fibers are used in the formulations. The type of fiber affects the properties of the composites. It was found that a combination of two types

of fibers could be used to achieve higher strength and stiffness parts than can be obtained from a single fiber type. In addition, the effects of curing temperature, curing time, and fiber concentration on mechanical properties of composites are studied and reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 356–363, 2004

**Key words:** epoxidized soybean oil; solid free form fabrication; di-, tri-, polyethylene amine; fiber reinforcement

## INTRODUCTION

Polymeric materials prepared from renewable natural resources have been enjoying a continuous growing interest in the past decade from the academic and applied point of view. The advantages of these polymers are their low cost, easy availability, and possible biodegradability.<sup>1</sup> The United States is both the biggest consumer of petroleum and the overseer of the largest farm product surplus in the world. For example, U.S. agriculture produces > 16 billion pounds of soybean oil annually; only 500 million pounds are used in industrial application, and frequent carry-over exceeds 1 billion pounds. Development of economically feasible new industrial products from vegetable oils for commercial application is highly desirable. This importance also becomes very clear with increasing social emphasis on the issue of environment, waste disposal, and depleting nonrenewable resources.

Solid freeform fabrication (SFF) is a method of making shapes without molds. It is best known in its stereo-

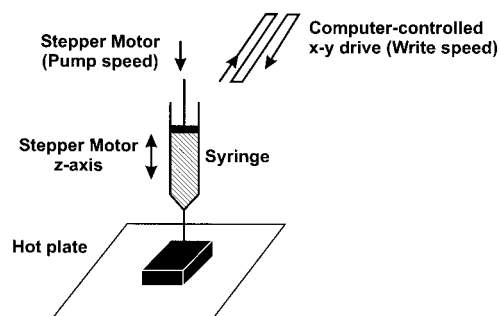
lithography form as a method of rapid prototyping. In stereolithography, a laser photopolymerizes successive thin layers of monomer to build up a solid object. Extrusion SFF was developed by the University of Arizona in collaboration with Advanced Ceramic Research (Tucson, AZ).<sup>2</sup> It functions essentially as a three-dimensional (3D) pen plotter. In this case, a slurry is extruded by a stepper motor pushing on a syringe and forcing the material through a needle. By moving the syringe over a computer-controlled path, nearly any geometry can be created (Fig. 1). This method has the potential to produce new materials and complex composites that could not be made in any other way. SFF methods were surveyed in detail by Calvert's review article.<sup>3</sup>

In the previous articles,<sup>4–5</sup> we reported preparation of soybean oil based composites by extrusion SFF method. These polymeric composites demonstrated a variety of properties, ranging from elastomers to rigid plastics. In the composites consisting of epoxidized soybean oil (ESO), cured with bis- or polyalkyleneamine (i.e., Jeffamine EDR-148, Jeffamine D-230, and Jeffamine T-403) agents, products exhibit rubberlike elastic properties. However, with triethylenetetramine (TETA) or diethylenetriamine (DETA) curing agent, using Epon 828 resin as comatrix, the mechanical properties of the composites are greatly improved. These high-performance composites have the potential to be used in agriculture equipment, the automotive industry, civil engineering, marine infrastructure,

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the products to the exclusion of others that may also be suitable.



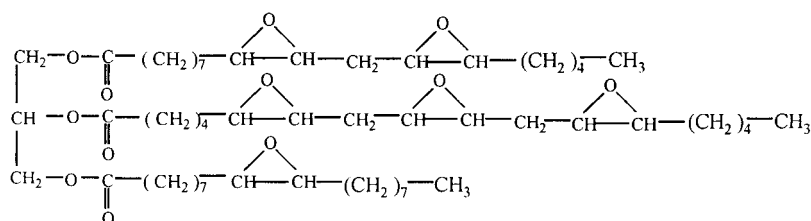
**Figure 1** Sketch of the extrusion freeform fabrication apparatus.

rail infrastructure, and the construction industry. In this work, we further explore the application of extrusion freeform fabrication to ESO/Epon 828 composites with di-, tri-, and polyethylene amine curing agents. The influence of curing temperature and curing time on the properties of the composites with TETA curing agent and effects of fiber types and fiber concentration are investigated. Effect of fiber combination is also studied. Glass, carbon, and mineral fibers are used in the formulations.

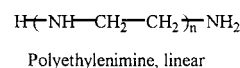
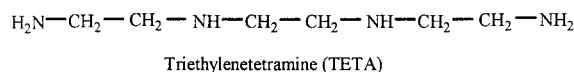
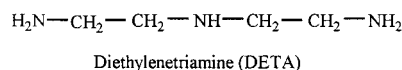
## EXPERIMENTAL

### Materials

The resin used as a comatrix is Epon® 828, provided by the Shell Chemical Co. (Houston, TX). Epon® resin 828 is a bisphenol-A/epichlorohydrin-based epoxy resin. ESO was obtained from Alf Atochem Inc. (Philadelphia, PA) and used as received. Scheme 1 shows the chemical structure of ESO. Calcium sulfate microfiber, Franklin Fiber® H-45, used in the experiments was provided by the U.S. Gypsum Co. (Chicago, IL) and used as received. Wollastonite mineral fiber, Fillex® fiber, is surface-modified wollastonite, an inorganic mineral reinforcement. The Fillex® fiber was provided by Intercorp Inc. (Milwaukee, WI) and used as received. Thixotropic agents, Aerosil R805, was obtained from Degussa Corp. (Ridgefield Park, NJ) and Montmorillonite K 10 was obtained from Aldrich Chemical Inc. (Milwaukee, WI). Both of them were used as received. Glass fiber is milled E-glass (electric glass) fiber with a nominal length of 1/32 in.



**Scheme 1** Chemical structure of ESO.



**Scheme 2** Chemical structure of curing agents.

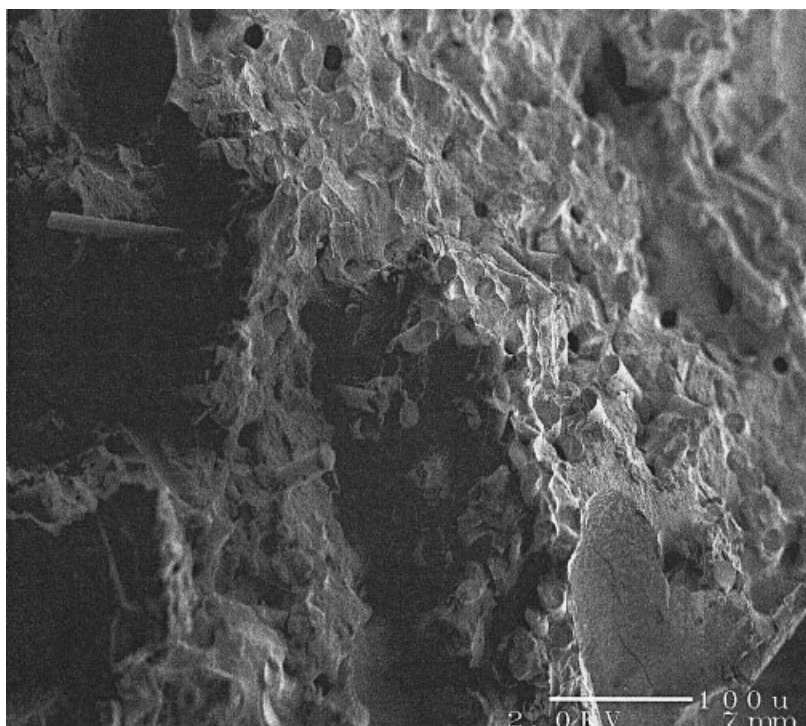
Fiber diameter of 10  $\mu\text{m}$  was used in all experiments. Short carbon fiber was obtained from DuPont Co. (Wilmington, DE) and was chopped in a coffee grinder for 20 s to reduce the length. Optical microscopy gave average length from 0.12 to 0.25 mm. A previous study<sup>6</sup> characterized length distributions, diameter distributions, and aspect ratios obtained for fibers chopped in this way. Curing agents, DETA, TETA, and polyethylenimine (linear) were provided by Aldrich (Milwaukee, WI) and used as received. Scheme 2 shows their chemical structures.

### Forming of composites

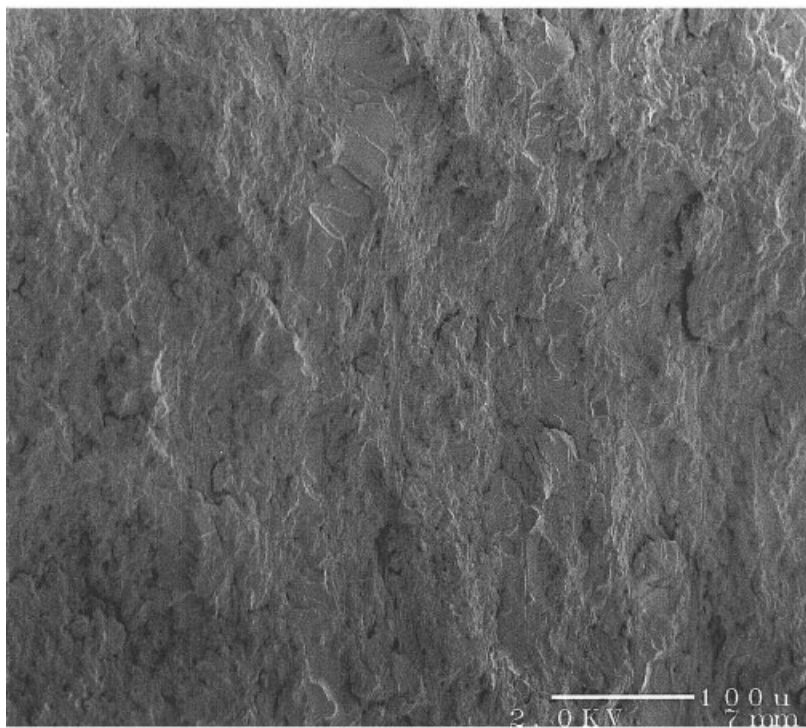
ESO and Epon 828 resin were mixed thoroughly in a weight ratio of 1 : 0.3. Vacuum was applied to remove air bubbles at 55°C for 30 min. Then, the mixture was mixed with Aerosil R805, 10 g/100 g (ESO+Epon 828), and fibrous fillers. The mixture was degassed in a vacuum system at 55°C for 30 min. The fiber-filled slurries show a yield point, such that the formed parts hold their shape until cured. The mixture was removed from the oven and cooled to room temperature. Curing agent, 23.3 g/100 g (ESO+Epon 828), was then added and mixed properly, and the paste was placed into a 20-mL plastic syringe. Bars 75 × 8 × 4 mm were formed by deposition of five layers and subsequently cured at 100°C for 24 h, then at 150°C for 48 h.

### Solid freeform fabrication

SFF was conducted by using an Asymtek model 402 fluid dispensing system, equipped with small step-

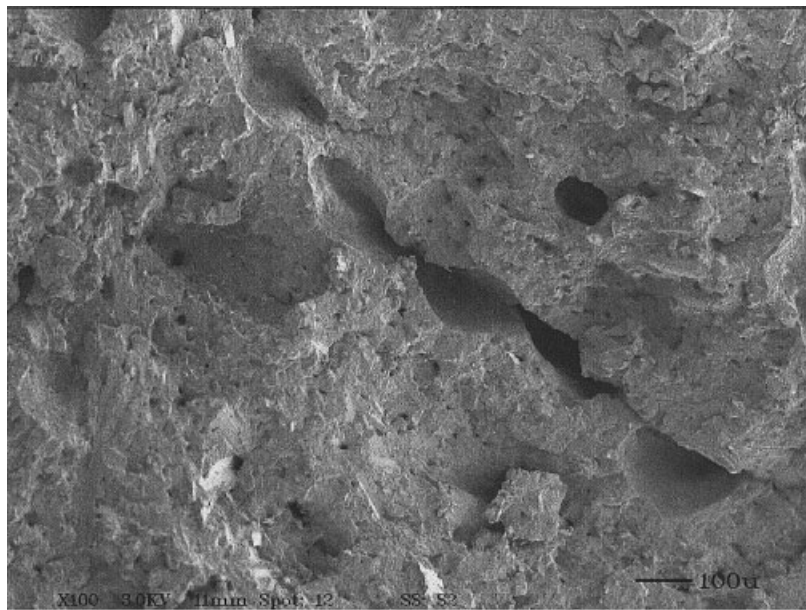


(a)



(b)

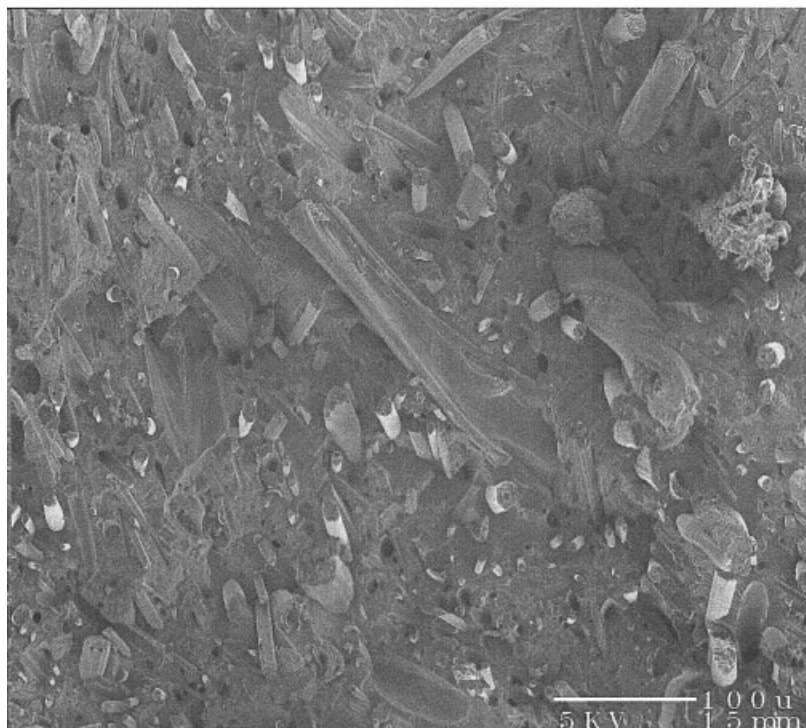
**Figure 2** Scanning electron microscope (SEM) photomicrograph of the freshly fractured surface of soybean oil based composites filled with four types of fibers: (a) E-glass fiber, (b) Franklin fiber, (c) carbon fiber, (d) Wollastonite fiber.



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(c)



(d)

Figure 2 (Continued from the previous page)

per motors (Oriental stepper motor) to drive the delivery syringe. The Asymtek and syringe were controlled by a program written in Microsoft Quick Basic. Solid bar samples were written as a series of lines.

#### Scanning electron microscopy

Scanning electron microscopy (SEM) was performed to investigate the interface between the filler and the polymeric matrix with a JEOL JSM 6400V instrument.

The specimens were mounted on aluminum stubs with graphite-filled tape and vacuum-coated with gold-palladium on a JEOL ion sputter coater and observed. SEM micrographs were obtained by using 5 kV secondary electrons.

### Mechanical testing

The mechanical properties testing was done by using a three-point bend test method with an Instron model 1100. The standard formulae for the modulus,  $E$  and strength,  $\sigma$  in three-point bending of a beam were used:

$$E = PL^3/4bd^3\delta, \quad \sigma = 3PL/2bd^2$$

where  $P$  is equal to the break load,  $L$  is the support span,  $\delta$  is the deformation at the center under load  $P$ ,  $d$  is the sample height, and  $b$  is the sample width.

## RESULTS AND DISCUSSION

### Composite morphology

SEM was performed to characterize the morphology of soybean oil based filled composite materials. In our previous article,<sup>4</sup> we reported SEM micrographs of four types of fibers, as follows: (1) The commercial milled glass fiber has a nominal length of 1/32 in. and fiber diameter of 10  $\mu\text{m}$ . The aspect ratio distribution of the fiber according to Peng<sup>7</sup> shows two main peaks at values of 3 and 7. (2) Calcium sulfate microfiber, Franklin Fiber® H-45, with an average length of 60 to 75  $\mu\text{m}$ , average diameter of 1.5–2  $\mu\text{m}$ , and average aspect ratio of 40 was used. (3) Wollastonite mineral fiber, Fillex® 17-AF1, has an average aspect ratio of 20 and diameter of 2.5  $\mu\text{m}$ . (4) The carbon fiber was grounded for 20 s in a coffee grinder. Optical microscopy gave average lengths from 0.25 to 0.12 mm. Those fibers were used in all the experiments. Figure 2 shows SEMs of freshly fractured surface for soybean oil based composites filled with four types of fibers. Figure 2(a–d) correspond to milled E-glass fiber, Franklin Fiber® H-45, Fillex® 17-AF1 fiber, and carbon fiber, respectively. They clearly indicate that the interfacial adhesion between the fiber and the matrix was fairly good. This can be readily seen from the physical contact between both components. The fibers are broken up from the matrix. However, holes and spacing occur along the fiber, resulting in poor contact and inferior stress transfer between the phases.

### Effect of curing agent

The chemistry of most of the curing agents currently used with epoxide resin is based on polyaddition reaction that results in coupling as well as crosslinking. The most widely used of these, based on active-hydrogen compounds (polyamines, polyacids, polymer-

captans, etc.), undergo polyadditions via the compounds containing the active hydrogen and the terminal carbon of the epoxide group, with a stabilization of the epoxide into a hydroxyl group. The polyamines (primary, mixed primary, and secondary) are typical of a useful type of this class of curing agents. Here DETA, TETA, and polyethylenimine (linear) are used as curing agents for the ESO/epoxy system. Table I presents flexural strength and flexural modulus data for a composite consisting of ESO 52.0 vol %, Epon 828 13.5 vol %, Franklin Fiber® H-45, 18.7 vol %, fumed silica, 10 g/100 g (ESO+Epon), and various curing agents, 23.3 g/100 g (ESO+Epon). As it can be seen, polyethylenimine does not provide the composite's mechanical properties as strong as TETA and DETA do. This is due to the fact that polyethylenimine has a longer molecular chain and is difficult to access the reactive site of a large ESO molecule because of chain entanglement. In other words, a low reactivity of polyethylenimine is probably due to steric factors. By comparison of molecular structures of DETA and TETA to polyethylenimine, both primary amine and secondary amine groups in small molecules of DETA and TETA are reactive because of easy accessibility. However, the reactivity of secondary amine groups in polyethylenimine is inhibited because of the groups trapped inside of the long molecular chains. Because of this, higher strength and stiffness composites can be obtained with TETA and DETA curing agents.

### Effect of curing temperature

Effect of temperature on the mechanical properties is presented in Table II. The flexural modulus increases as the curing temperature increases. This trend was also observed in the ESO/Epon 828/Jeffamine systems, reported in our previous article.<sup>5</sup> This is because at lower temperature, the epoxy groups are mainly consumed by primary amine hydrogen atoms; however, secondary amine reaction is small. Padma and coworkers<sup>8</sup> reported an intensity increase in the secondary amine peaks by FTIR, compared to primary amine peaks. At higher temperature, both primary and secondary amine hydrogen atoms react with epoxy groups. As the reaction proceeds further, higher epoxy-hydroxyl etherification reaction dominated the reaction. The crosslinking degree increases, and the composites show better mechanical properties.

### Effect of curing time

Table III presents flexural modulus data for composite consisting of 18.7 vol %, Franklin Fiber® H-45, ESO/Epon ratio of 1 : 0.3 at a changing of curing time. As can be seen, flexural modulus increases as curing time increases. At the above study of temperature effect, the results show the flexural modulus increases as the

**TABLE I**  
Effect of Curing Agents

Curing agent	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
TETA	110.0	4.0	1.54
DETA	65.0	3.9	2.11
Polyethylenimine (linear)	25.0	1.5	2.30

Conditions: ESO, 52.0 vol %; Epon 828, 13.5 vol %; Franklin Fiber® H-45, 18.7 vol %; 23.3 g/100 g curing agent; and fumed silica, 10.0 g/100 g (ESO + Epon) at 150°C for 48 h.

**TABLE II**  
Effect of Curing Temperature for TETA

Curing Temperature (°C)	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
110	85.0	2.50	4.0
120	100.0	3.90	4.4
130	109.0	3.95	5.1
150	110.0	4.00	2.1

Conditions: ESO, 57.0 vol %; Epon 828, 14.8 vol %; Franklin Fiber® H-45, 11.1 vol %; TETA, 23.3 g/100 g (ESO + Epon); and fumed silica, 10.0 g/100 g (ESO + Epon) at 150°C for 48 h.

curing temperature increases. An explanation is that primary amine reacts with the epoxy groups much faster than secondary amine. It is confirmed by FTIR that there is an intensity increase in the secondary amine peaks, compared to primary amine peaks at early reaction stage. When the curing temperature was kept constant, increasing curing time would favor the secondary amine taking part reaction with epoxy groups. Network structures of the composite are informed. The composites with higher crosslinking density demonstrate better mechanical properties. In the case of longer curing time, it also favors the epoxy-hydroxyl etherification reaction, which increases crosslinking density of the polymers.

**TABLE III**  
Effect of Curing Time at 150°C

Curing time (h)	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
9	80	3.5	3.5
17	81	4.6	3.2
27	95	4.7	2.3
39	110	5.5	2.5
48	120	6.8	1.5

Conditions: ESO, 52.0 vol %; Epon 828, 13.5 vol %; Franklin Fiber® H-45, 18.7 vol %; TETA, 23.3 g/100 g (ESO + Epon); and fumed silica, 10.0 g/100 g (ESO + Epon).

**TABLE IV**  
Effect of Fiber Type

Fiber	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
E-glass	120.0	6.7	1.91
Carbon	63.0	3.6	2.42
Franklin	54.5	3.4	2.11
Wollastonite	44.5	2.8	2.43

Conditions: ESO, 52.7 vol %; Epon 828, 13.7 vol %; and fiber, 17.1 vol %; in the composite formulations with TETA, 23.3 g/100 g (ESO + Epon) and fumed silica, 10.0 g/100 g (ESO + Epon) at 150°C for 48 h.

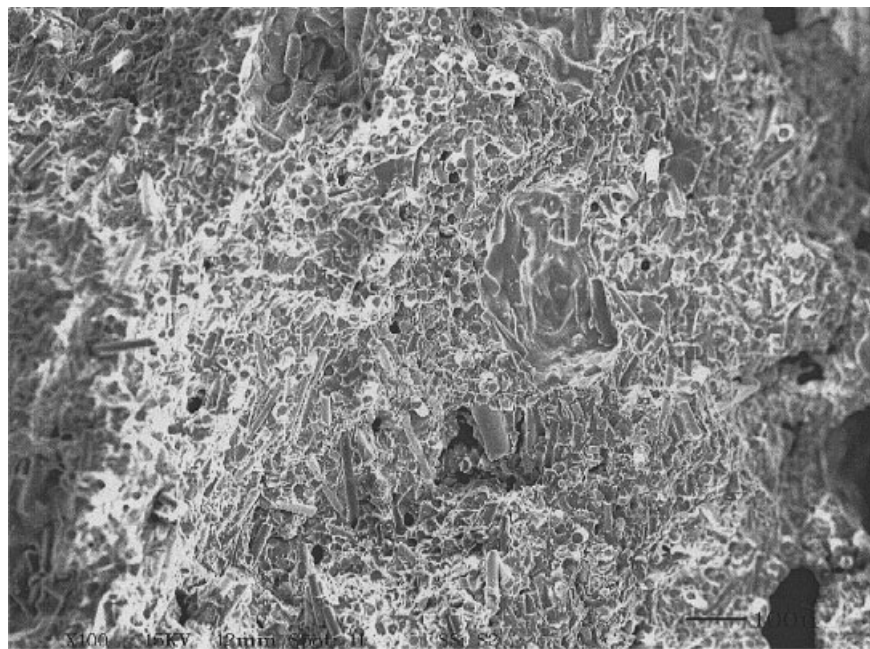
### Effect of fiber type

The experiments were carried out for systems containing four types of fibers. When fiber at 17.1 vol % in the composite formulates with TETA, 23.3 g/100 g (ESO+Epon), and fumed silica, 10.0 g/100 g (ESO+Epon), the mechanical properties of composites were determined as shown in Table IV. It can be seen that among different types of fibers, E-glass fiber and carbon fiber show better reinforcing effects than the mineral fibers. These results are probably due to glass and carbon fibers themselves having high strength; for example, E-glass fiber has a tensile strength of about 3 GPa and a modulus that approaches 100 GPa. They exhibit a large contribution to the strength and rigidity

**TABLE V**  
Mechanical Properties of Freeformed ESO/Epon/TETA or ESO/Epon/DETA with 32 vol % of E-glass fiber, 4.8 vol% Franklin fiber H -45

Curing agent	Fiber 1	Fiber 2	Flexural strength (MPa)	Flexural modulus (GPa)	Strain at break (%)
TETA	Glass	Franklin	110.0	6.3	1.9
TETA	Carbon	Franklin	96.3	5.48	2.1
TETA	Glass	****	69.0	4.1	1.8
TETA	Carbon	****	63.0	3.6	2.4
DETA	Glass	Franklin	104.3	5.5	2.3
DETA	Carbon	Franklin	86.0	4.7	2.6

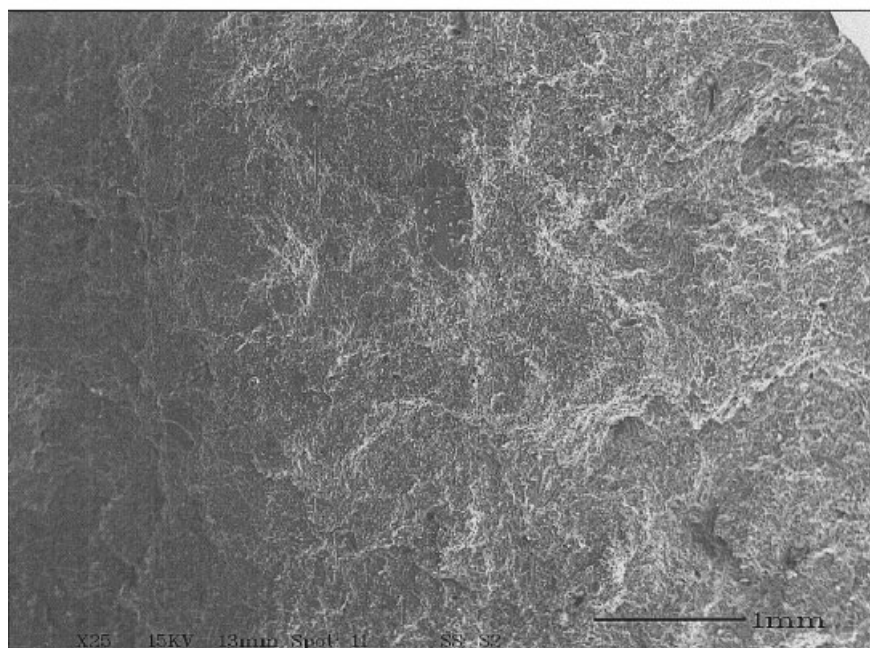
Three-point bend test, means of five samples, standard deviation 3%.



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(a)



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(b)

**Figure 3** SEM photomicrograph of the freshly fractured surface of soybean oil based composites filled with fiber combination: (a) E-glass fiber and Franklin fiber, (b) carbon fiber and Franklin fiber.

of the reinforced composites. The principal advantages of glass fibers commonly used as reinforcing fibers for polymer matrix are their high strength and their low cost. This phenomenon was also observed in the ESO/Jeffamine and ESO/Epon 828/Jeffamine systems, reported in our previous articles.<sup>4-5</sup>

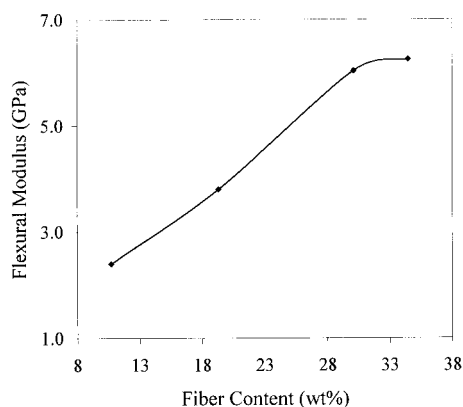
#### Effect of fiber combination

The research development in the use of mineral fibers has been limited to a single type and their usage in thermoplastic matrix or elastomers. The use of combination of glass or carbon fiber with mineral fiber in

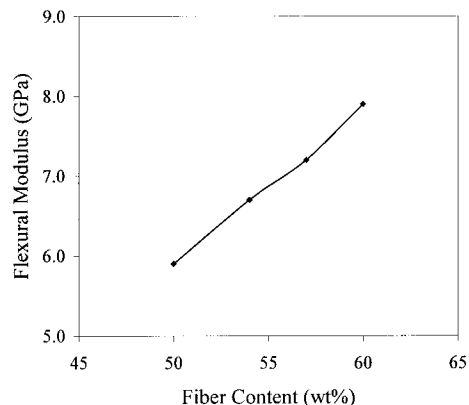
thermoset matrix has recently been investigated by Peng.<sup>7</sup> Their experimental results show with evidence that use of different fiber types combined in testing bars tends to get higher flexural modulus than single-type fiber-epoxy composites at the same conditions. Here, we studied the fiber combination such as short milled glass fibers (1/32 in.) with Franklin Fiber® H-45, as well as short carbon fibers with Franklin Fiber® H-45. The results are presented in Table V. It is clear that the moduli of the composites increase compared to single-type fiber-epoxy composites at the same conditions. SEMs of the fractured surfaces of the composites after the flexural test are given in Figure 3 (a, b). It can be observed that the near absence of holes around the fibers resulted in good contact between the phases. A combination of two fibers can be used to achieve composites with higher strength and stiffness properties than obtained with a single fiber type.

#### Effect of fiber loading

Figures 4 and 5 show the flexural modulus as a function of carbon fiber and glass fiber content. It is observed in Figure 4 that the flexural modulus showed an increase with an increase of carbon fiber content and then leveled off at more than 30 wt % of carbon fiber in the composite. However, Figure 5 shows the flexural modulus increases with increasing glass fiber content without leveling off. The high stiffness of these materials makes them suitable for structural applications. It is known that maximum fiber contents are limited by the relationships given in Milewski's models, which relate to maximum volume fraction to aspect ratio.<sup>9</sup> Increasing the volume fraction beyond this limit results in a slurry, which will not flow through the needle. Therefore, data for higher glass fiber contents are not available. It is presumably that there is a level-off phenomenon in the relationship between flexural modulus and glass fiber content.



**Figure 4** Flexural modulus of composites as a function of carbon fiber content.



**Figure 5** Flexural modulus of composites as a function of E-glass fiber content.

#### CONCLUSION

Fiber-reinforced epoxidized soybean oil/Epon 828 composites materials were formed with high-strength and stiffness properties by freeform fabrication method. TETA and DETA are more efficient curing agents than polyethylenimine curing agent. It was found that E-glass and carbon fibers demonstrated better reinforcing effects on mechanical properties than mineral fibers. By a combination of two fibers, higher strength and stiffness of composites can be achieved than can be obtained from a single fiber type. Higher curing temperature and longer curing time provided composites with better mechanical properties. These materials may be of great environmental interest because these composites consist of high amounts of agricultural resources.

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