Biobased Composites Prepared by Compression Molding with a Novel Thermoset Resin from Soybean Oil and a Natural-Fiber Reinforcement

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ABSTRACT: Biobased composites were manufactured with a compression-molding technique. Novel thermoset resins from soybean oil were used as a matrix, and flax fibers were used as reinforcements. The air-laid fibers were stacked randomly, the woven fabrics were stacked crosswise (0/90°), and impregnation was performed manually. The fiber/resin ratio was 60 : 40. The prepared biobased composites were characterized by impact and flexural testing. Scanning electron microscopy of knife-cut cross sections of the specimens was also done to investigate the fiber–matrix interface. Thermogravimetric analysis of the composites was carried out to provide indications of thermal stability. Three resins from soybean oil [methacrylated soybean oil, methacrylic anhydride modified soybean oil (MMSO), and acetic anhydride modified soybean oil] were used as matrices. The impact strength of the composites with MMSO resin reinforced with air-laid flax fibers was 24 kJ/m^2, whereas that of the MMSO resin reinforced with woven flax fabric was between 24 and 29 kJ/m^2. The flexural strength of the MMSO resin reinforced with air-laid flax fibers was between 83 and 118 MPa, and the flexural modulus was between 4 and 6 GPa, whereas the flexural strength of the MMSO resin reinforced with woven fabric was between 90 and 110 MPa, and the flexural modulus was between 4.87 and 6.1 GPa. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1759–1765, 2010

Key words: biodegradable; blending; fibers; renewable resources; thermosets

INTRODUCTION

Concerted efforts are being made by scientists and researchers in both research and educational institutions to manufacture polymer composites based on renewable resources, such as plant seed oils and natural fibers, to improve their physical, structural, and mechanical properties.

There are many ongoing research projects aiming to manufacture composites with natural fibers as reinforcements and polymers from renewable resources as matrices. There is an emerging market for biobased polymers, which is expected to increase substantially in the coming years.[1] Natural fibers, such as flax, jute, sisal, hemp, and ramie, are currently being used as reinforcements in composite manufacturing.[2–4]

The high strength and modulus of the fibers impart strength and rigidity to the material that surpass that of the neat polymer.[5,6] These natural fibers are based on cellulose and are attractive because of their biodegradability, light weight, low combustibility, nontoxicity, nonabrasive nature, and low cost.[2,7–11]

Significant improvements in mechanical properties have also been achieved by the reinforcing efficiency of fibers coupled with enhancement through chemical modification to promote bonding at the fiber–matrix interface.[4,8,12] Natural fibers have an advantage over glass fibers in that they are less expensive and abundantly available from renewable resources and have a high specific strength.[7] For certain applications, the mechanical properties of natural-fiber composites, such as those made from flax or hemp fiber, are not sufficient because of the low strength of these fibers.[4,13] However, combining natural fibers with stronger synthetic fibers, such as glass, could offer an optimum balance between performance and cost.

The interfacial adhesion of the fiber and matrix are of utmost importance to the mechanical properties of composite materials, and one way to mechanically improve the interface is to achieve efficient chemical bonding between the polymer matrix and the fiber.[6,14] Chemical bonding can generally be improved by fiber surface treatment, the coating of the fiber, or the addition of a coupling agent.[4,14] Physical and chemical methods for the modification of natural fibers were extensively discussed by Bledzki et al.[3] Some disadvantages of natural fibers are their moisture uptake, quality variation, low thermal stability, and poor wettability.[1,15,16]

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Interestingly, just as many studies have been done on the use of natural fibers as reinforcements in composites quite a few investigations have been done on the possibilities of using polymers from renewable resources as matrices.[17,18] The need to replace fossil-based materials has led to an increased interest in biobased materials.[19] The objective of this study was to manufacture composites based on different types of functionalized soybean oil resins from renewable origins as matrix materials and with flax fibers as reinforcements.

Styrene was used as a reactive diluent to reduce the viscosity of the resin, ease the impregnation of the fibers, and also improve the mechanical properties of the resulting composites. Consequently, this lowered the renewable content of the material. Both neat resins and resins blended with styrene were used in the preparation of the composites. The natural-fiber composites prepared were characterized with mechanical testing, thermogravimetric analysis, and scanning electron microscopy.

EXPERIMENTAL

Materials

Thermoset resins from soybean oil [methacrylated soybean oil (MSO), methacrylic anhydride modified soybean oil (MMSO), and acetic anhydride modified soybean oil (AMSO)] were used as matrices in the natural-fiber composites. Two flax-mat fibers were evaluated: one randomly oriented air-laid flax mat (Linapellava Oy, Särkisalmi, Finland) and one woven flax fabric (Engtex, Mullsjö, Sweden). These were supplied by the manufacturers. The free-radical initiator *tert*-butylperoxybenzoate, accelerator dimethylaniline (diluted in styrene), and styrene were supplied by Aldrich Chemical Co. (Wyoming, IL).

Resin synthesis

These resins were synthesized as reported previously.[20] MSO was synthesized through the reaction of epoxidized soybean oil with methacrylic acid. Epoxidized soybean oil was heated for 12 h with the addition of excess methacrylic acid at 120°C, and the obtained resin was MSO. MSO was divided into two portions. Methacrylic anhydride was added to a portion and heated to about 69°C for 4 h, and the resin obtained was MMSO, whereas acetic anhydride was added to the other portion, and the conditions for the polymerization reaction were the same. AMSO was obtained (see Fig. 1 for the chemical structures).

Composite preparation

The fiber mats were first treated with 4% sodium hydroxide solution for 1 h and then washed with plenty of water until the water was neutral. The fibers were dried at room temperature for 24 h and then dried in a vacuum oven for 1 h at a temperature of 105°C.

The composites were prepared by hand lay-up. Each composite laminate consisted of eight sheets of the fiber mat. The air-laid fiber mats were laid randomly, whereas the woven fabrics were laid crosswise at an angle of 90°. See Figure 2 for the picture of fibers. Composites were produced both from the neat resins and from the resins blended with 30 wt % styrene. The composites prepared from the neat resins were cured at 170°C, whereas the composites with blended resin were cured at 40°C and postcured at 170°C. *tert*-Butylperoxybenzoate (2 wt %) was used as a free-radical initiator. The compression molding was done at a temperature of 170°C for 5 min at 40 bar on a hot press from Rondol Technology (Staffordshire, UK). Composites made with blended resin as a matrix were accelerated by the addition of 0.3 wt % of the accelerator. The fiber/resin ratio was about 60 : 40, and the reason we chose this fiber/resin ratio was that it provided optimum mechanical properties. In total, 12 different combinations were evaluated (three different resins, with and without styrene and with two different flax fiber mats).

Characterization

Impact testing was done on the composites to determine the Charpy impact strength of the unnotched specimens; they were evaluated in accordance with ISO 179 with a Zwick test instrument (Zwick GmbH, Ulm, Germany). A total of 10 specimens were tested to determine the mean impact resistance. The samples were tested edgewise.

The flexural testing was performed according to ISO 14125 with a Tinius Olsen (Salfords, UK) H10KT universal testing machine equipped with a 5 kN load cell. At least five specimens were tested for every material.

A knife-fractured cross section of the composites were studied with scanning electron microscopy to investigate the fiber–resin interface.

Thermogravimetric analysis was done with a TA Instruments TGA Q 500 supplied by Waters LLC (New Castle, DE). Samples of approximately 15 mg were heated at 20°C/min in a nitrogen purge stream between 30 and 600°C. The flow rate of the nitrogen stream was 50 mL/min.

RESULTS AND DISCUSSION

The availability of these biobased thermoset resins provides a unique opportunity for their utilization in the manufacturing of composites with a high degree of biobased materials. The aim was to study the feasibility of using the three different types of soybean
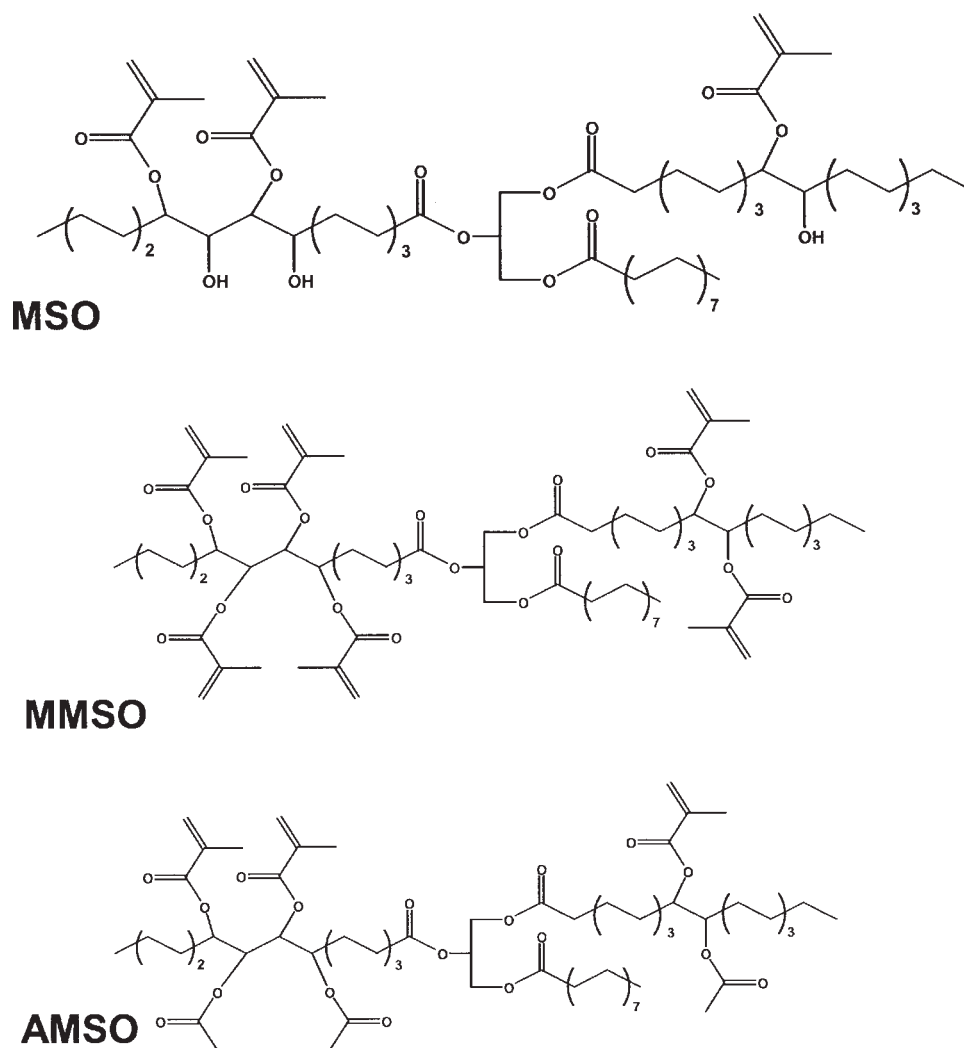
Figure 1 Chemical structures of the biobased thermosetting resins used in the composite preparation.

oil based resins in natural-fiber composites. The compatibility of these novel biobased resins with natural fibers was also ascertained.

Impact testing

Figure 3 presents the Charpy impact strength (energy absorbed/cross-sectional area) results of the
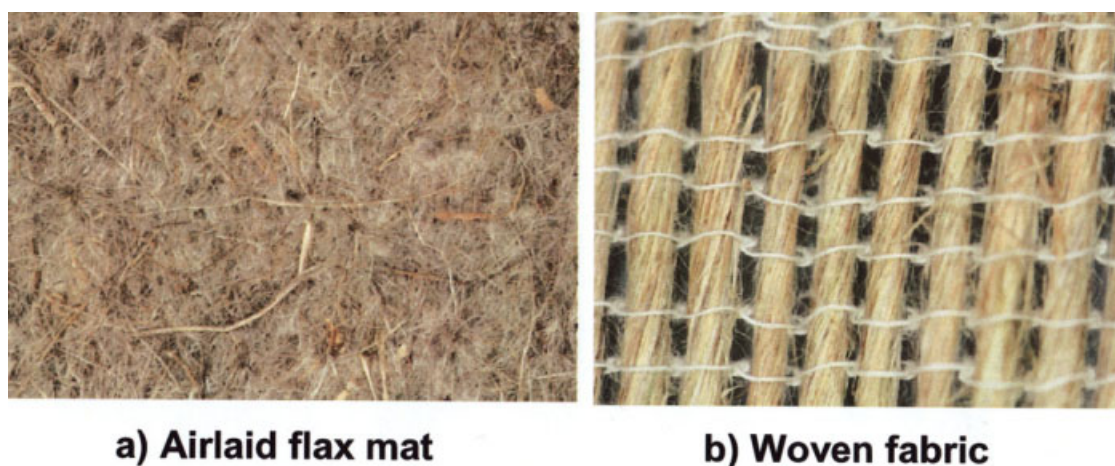

Figure 2 Air-laid and woven flax fibers used as reinforcements in the composite preparation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
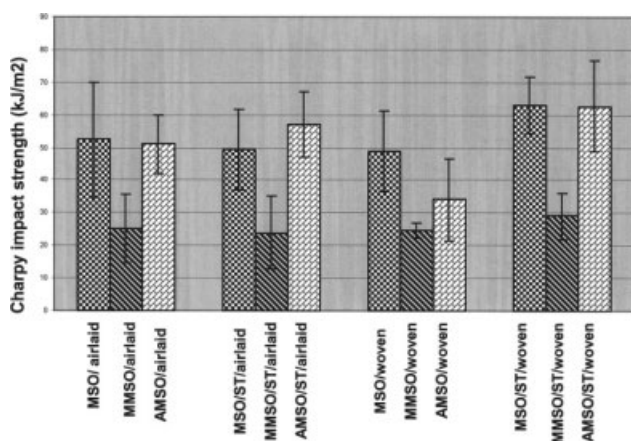
Figure 3 Impact strength comparison of the composites (ST = styrene).

biobased composites. The composites tested showed relatively high impact strengths of about 50–60 kJ/m^2, and these were even comparable with the glass mat composites (54 kJ/m^2) reported by Jang and Lee[21] in 2000. The exception was that the composites with MMSO resin showed relatively low impact strengths compared with the other composites. This was attributed to the good fiber matrix adhesion of the MMSO resin, which was also obvious in the flexural testing. The composites with MMSO as a matrix had higher flexural strengths and moduli. A higher fiber matrix adhesion resulted in shorter average pullout lengths and, therefore, caused lower impact strengths.

Although the flexural strength of the neat AMSO resin reinforced with air-laid fibers was quite low (Fig. 4), it had a high impact strength of about 51 kJ/m^2 (Fig. 3). The impact strength of the composites manufactured with blended MSO, MMSO, and AMSO resins also show the same trend (Fig. 3) because, as shown in Figure 4, the flexural strengths of the blended MMSO, MSO, and AMSO resins rein-
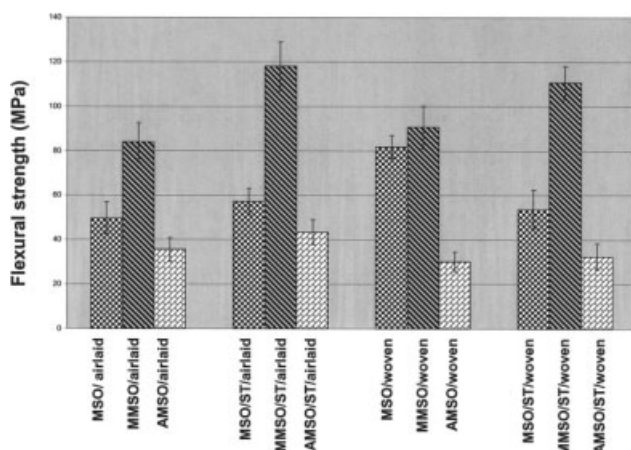
forced with air-laid flax fibers were 118, 57, and 43 MPa, respectively, whereas this order was reversed in the impact strengths, which were 22, 49, and 58 kJ/m^2, respectively (Fig. 3). Contrary to the flexural properties, the impact strength decreased with increasing fiber matrix adhesion.[22]

It is well known that the impact response of the fiber composites is highly influenced by the interfacial bond strength and the matrix and fiber properties. The impact energy is dissipated by debonding, fiber and/or matrix fracture, and fiber pullout.[23] Generally, the impact strength increases with decreasing fiber–matrix adhesion and with decreasing lateral fiber length. The variation in data within different composites could have been due to different fiber lengths, different average diameters, and different aspect ratios. However, the decrease in the impact strength of all of the composites based on the MMSO thermoset resin as the matrix was generally explained by its chemical structure because it had a higher crosslinking density, due to a higher number of reactive double bonds in the molecular structure. The MMSO resin was also more brittle, whereas the other two resins had lower crosslinking densities, which meant that they had higher flexibilities.

Flexural testing

Figures 4 and 5 show the flexural strengths and flexural moduli, respectively. The MMSO resin (with or without styrene) reinforced with air-laid flax fibers or woven fabric showed higher flexural strengths, between 84 and 118 MPa, and flexural moduli, between 4 and 6 GPa. The flexural strengths of the MSO resin reinforced with flax fibers were between 49 and 81 MPa, and the moduli were between 2 and 4 GPa, compared with the AMSO composites with
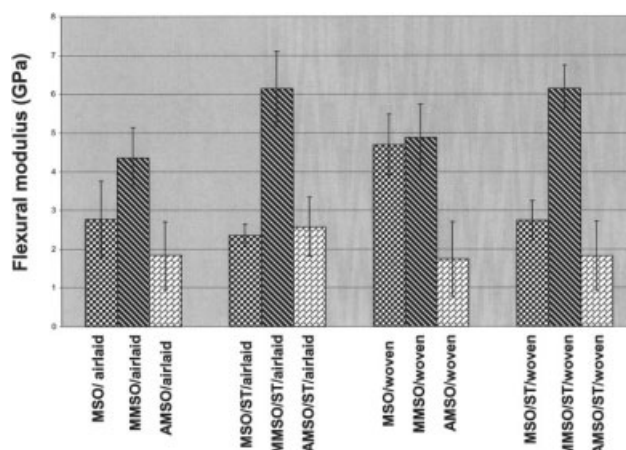

Figure 4 Flexural strength comparison of the composites (ST = styrene).

Figure 5 Flexural modulus comparison of the composites (ST = styrene).
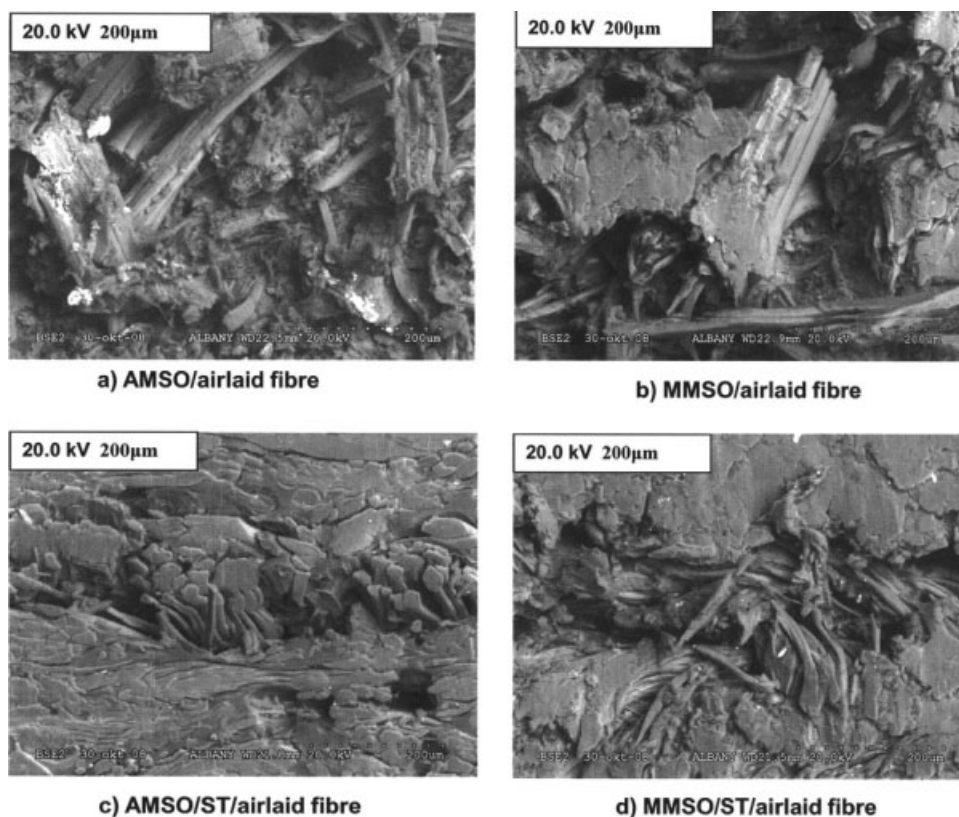
Figure 6 Scanning electron micrographs of fractured surfaces due to knife cuts (ST = styrene).

low flexural strengths and moduli between 30 and 43 MPa and 1.7 and 2.57 GPa, respectively.

The better flexural properties achieved in the MMSO matrix reinforced with flax fiber were attributed to the higher number of methacrylate groups per triglyceride unit, which was about 3; this value was lower for the other resins. The blending of the thermosetting resins with styrene (acting as a reactive diluent) was done to impact some stiffness and improve the mechanical properties of the resulting composites. With the addition of 30 wt % styrene,

the flexural strengths and moduli of the MMSO resins reinforced with both air-laid and woven fabrics increased considerably; this indicated that blending with styrene gave a mechanically more elastic composite because of longer crosslinks. The AMSO resin (with styrene) showed minimal increases in both strength and modulus. In contrast, the MSO resin (with styrene) reinforced with woven fabric showed a negative effect; the flexural strength dropped from 81.8 to 53.7 MPa, and the modulus dropped from 4.69 to 2.74 GPa.
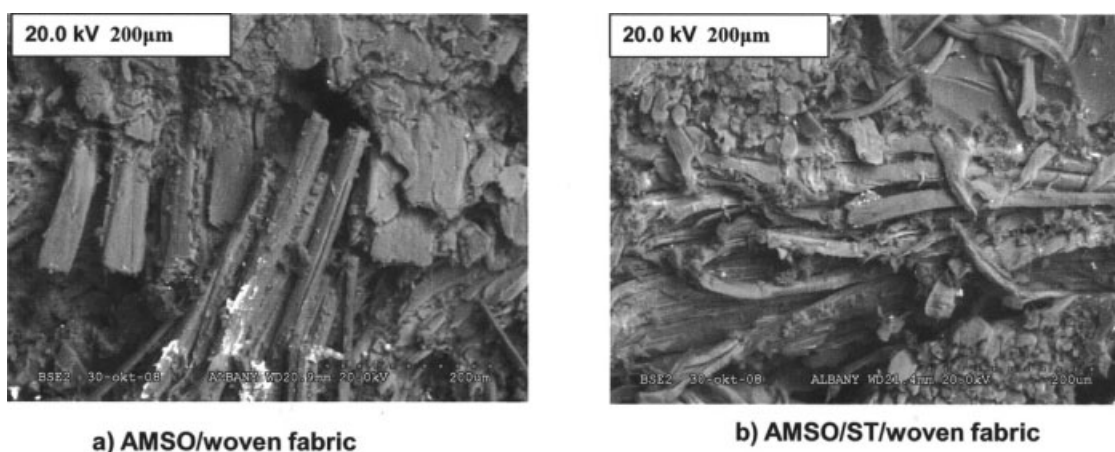

Figure 7 Scanning electron micrographs of fractured surfaces of the AMSO resin reinforced with woven fabric (ST = styrene).

Figure 8 Thermogravimetric curve of the MSO resin reinforced with air-laid flax fibers.
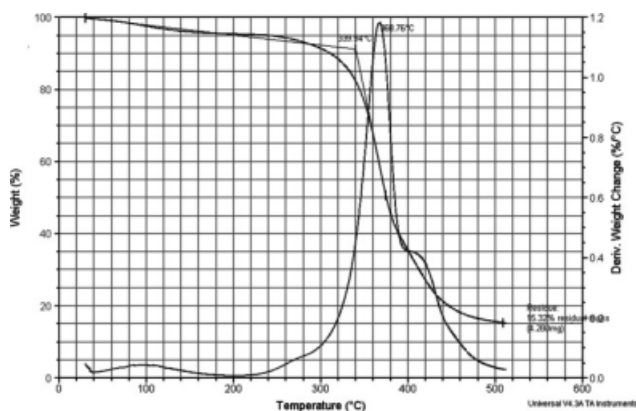

Figure 9 Thermogravimetric curve of the MMSO resin reinforced with air-laid flax fibers.

The higher mechanical strength of MMSO could be understood from its chemical structure.[20] The MMSO resin contained more reactive double bonds in one molecule because of a doubled functionalization. When the composites prepared from neat resins were compared to composites containing styrene, it was clear that the addition of styrene had a positive effect on the overall mechanical properties. This was expected. When styrene was added, crosslinking styrene bridges were formed between the triglyceride molecules, which increased the molecular flexibility.

The MMSO resin was promising because the composites prepared with the neat resin had a flexural strength of about 90.62 MPa and a flexural modulus of 4.87 GPa. The MSO resin also showed a good possibility of being used in composite applications. Composites made with the MSO neat resin showed fairly good mechanical properties, with a flexural strength of 81.8 MPa and a flexural modulus of 4.69 GPa.

Scanning electron microscopy

Figures 6 and 7 show the scanning electron micrographs of surfaces fractured by a knife cut. The fiber pullout lengths from the composites were examined to actually determine which composites had low fiber–matrix adhesion. The AMSO and the MMSO resins blended with styrene and reinforced with air-laid fiber mats showed better fiber–matrix adhesion compared to the neat AMSO and MMSO resins reinforced with air-laid fiber mats [Fig. 6(a–d)]. There was a long fiber pull in the composite without styrene. The flexural strength and modulus were also higher in the composite containing styrene. The composites with styrene showed shorter fiber pullout, which could have been a result of good fiber–matrix adhesion within the composite system.
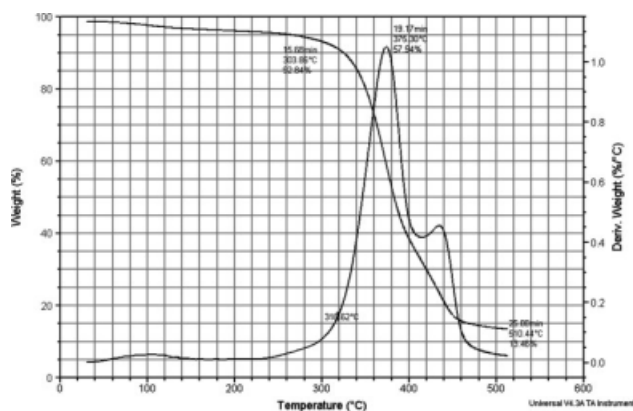
Thermogravimetric analysis

Figures 8–10 show the thermogravimetric curves of the neat biobased resins (MSO, MMSO, and AMSO) reinforced with air-laid flax fibers. The percentage weight loss of the composite was recorded when the sample was heated at a uniform rate in an appropriate environment. The loss in weight over a specific temperature range (30–600°C) provided an indication of the composition of the samples, including volatiles and inert fillers, and indications of the thermal stability.

The thermogravimetric curve in Figure 8 represents the MSO resin reinforced with air-laid flax fibers. The degradation occurred in the temperature region 220–480°C. The temperature of the maximum rate of oxidation was about 370°C, and the residual mass was around 4.3 mg. Figure 9 shows thermogravimetric curve of the MMSO resin reinforced with air-laid flax fibers, but there were double peaks at 375 and 440°C, which could have been due to some volatile components in the composite, although degradation occurred between 220 and 480°C. Figure 10 shows the thermogravimetric curve of the AMSO
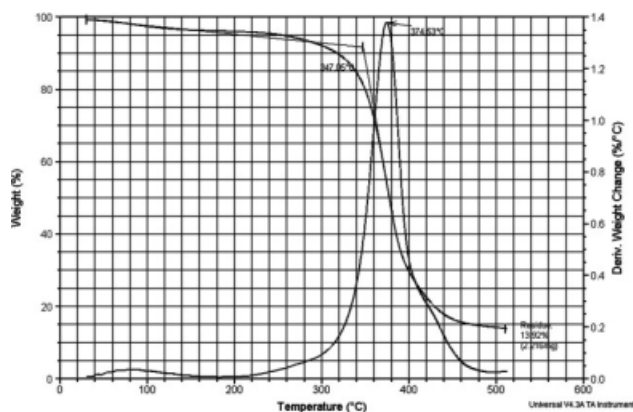

Figure 10 Thermogravimetric curve of the AMSO resin reinforced with air-laid flax fibers.

resin reinforced with air-laid flax fibers, and this resin had an oxidation temperature at 374°C and a residual mass of 2.2 mg.

The composites had relatively low thermal stability, which could have been inherited from the natural-fiber reinforcement because one of the disadvantages of natural fibers is a low thermal stability.

CONCLUSIONS

In this study, we investigated the possibilities of using biobased thermosetting polymers from soybean oil as matrices in natural-fiber composites. Biobased composites can actually replace conventional composites made from petrochemicals. The mechanical properties of the natural-fiber composites produced with novel biobased thermosetting resins made them good candidates for technical applications.

The composites showed relatively good flexural and impact strengths. MMSO neat resin reinforced with flax fibers showed flexural strengths between 83 and 90 MPa and a flexural modulus of 4.8 GPa, whereas the addition of styrene resulted in an even higher flexural strength, between 110 and 118 MPa, and a flexural modulus of 6.1 GPa. Composites manufactured with MSO and AMSO neat resins had better impact strengths, up to 52 and 51 kJ/m^2, respectively. MSO and AMSO resins blended with styrene gave even higher impact strengths, up to 63 and 62 kJ/m^2, respectively. The scanning electron microscopy analysis of the fractured knife cuts of the composite specimens revealed that the composites showed relatively good mechanical properties when the matrix was blended with styrene, particularly the AMSO and MMSO resins reinforced with fibers.

The addition of styrene resulted in an appreciable stiffness in the MMSO and AMSO resins reinforced with air-laid fibers but had a negative effect on the MSO resin reinforced with air-laid fibers. The thermogravimetric analyses of the biobased composites showed that they had relatively low thermal stabil-

ities because the oxidation temperature was between 368 and 375°C.

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