Mechanical Properties of Natural Fiber Hybrid Composites Based on Renewable Thermoset Resins Derived from Soybean Oil, for Use in Technical Applications

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Received 13 September 2010; accepted 13 August 2011
DOI 10.1002/app.35478
Published online 2 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Natural fiber composites are known to have lower mechanical properties than glass or carbon fiber reinforced composites. The hybrid natural fiber composites prepared in this study have relatively good mechanical properties. Different combinations of woven and non-woven flax fibers were used. The stacking sequence of the fibers was in different orientations, such as 0°, +45°, and 90°. The composites manufactured had good mechanical properties. A tensile strength of about 119 MPa and Young's modulus of about 14 GPa was achieved, with flexural strength and modulus of about 201 MPa and 24 GPa, respectively. For the purposes of comparison, composites were made with a combination of woven fabrics and glass fibers. One ply of a glass fiber mat was sandwiched in the mid-plane and this increased the tensile strength considerably to 168 MPa. Dynamic mechanical analysis was performed in order to determine the storage and loss modulus and the glass transition temperature of the composites. Microstructural analysis was done with scanning electron microscopy. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4530–4541, 2012

Key words: fibers; reinforcement; mechanical properties; thermosets; renewable resources

INTRODUCTION

Health-related issues, stringent environmental protection policies, the search for cost-effective and alternative materials, and quest for renewability, sustainability, and high-performance materials for technical applications has led to intense research in the manufacture of bio-based composites, which are based on renewable thermosetting resins and natural fibers. Thermosetting polymers have been particularly attractive from the point of view of their relatively high service temperature, stiffness, fatigue resistance, low cost, and relative ease of processing due to lower viscosity and/or lower processing temperatures, as well as excellent prepregging. A major disadvantage of thermoset composites is their poor reuse/recycling.

Fiber-reinforced composites offer great potential for use in aircraft and automotive[1] primary structures, in civil infrastructure, by the military, in sports etc.[2] During the past few years, there has been growing interest in the use of polymers obtained from renewable resources because the advantages of these polymers include their biodegradable properties and, in many cases, lower cost.[3] While high-performance carbon fibers remain superior to natural fibers in high-end applications, natural fibers have comparable properties to glass fibers in high-volume applications.[4–6]

Flax fiber has good specific strength and modulus.[7] Flax fiber is also less dense and thus produces a lighter composite with good mechanical properties.[8–10] The use of thermosets is gaining interest in the field of natural fiber composites,[11,12–14] and manufacturers are looking toward "greener" and more environmentally friendly alternatives relative to conventional polymers and composites.[15] Triglyceride-based resins such as methacrylated soybean oil and methacrylic anhydride modified soybean oil have been characterized by Adekunle et al.[16] as having low viscosities and can be used as matrices in composite manufacturing.

In the current work, we developed flax fiber reinforced composites which had the same tensile modulus as glass fiber reinforced composites but had a lower tensile strength than glass fiber reinforced composites. These natural fiber reinforced composites have technical and structural applications, and most importantly in the automotive industry. In

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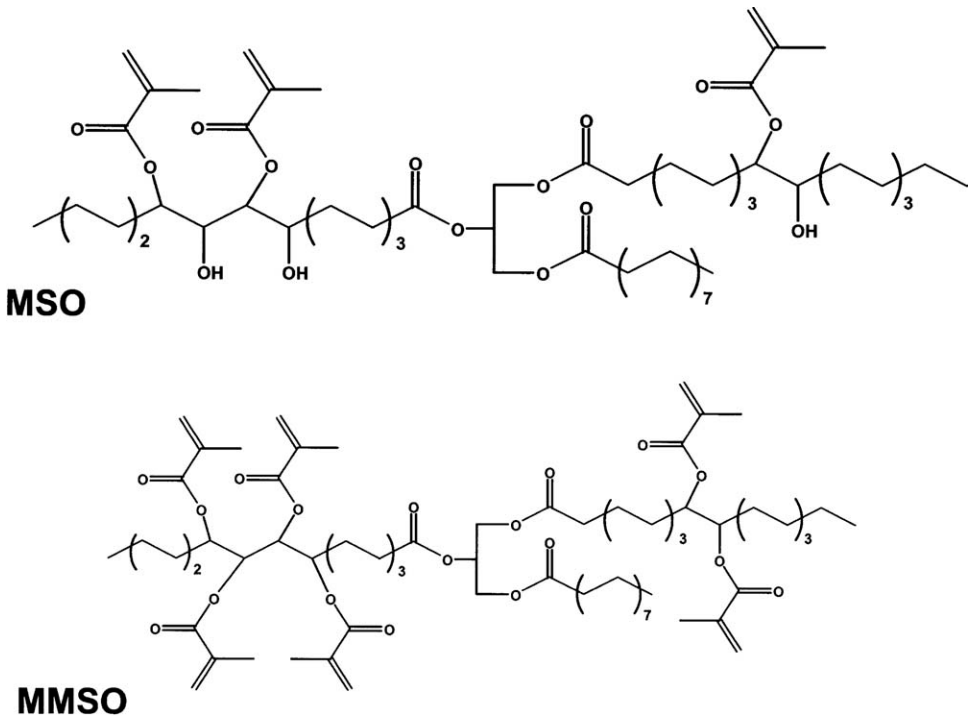

Figure 1 Chemical structures of the thermosetting resins used in the preparation of composite.

particular, such natural fiber composites are already being used in interior panels, door interior panels, and car seat backs of automobiles.

EXPERIMENTAL

Materials

Bio-based thermoset resins from soybean oil, MSO (methacrylated soybean oil), and MMSO (methacrylic anhydride modified soybean oil) were used as matrices. The chemical structures of the resins which were initially characterised by Adekunle et al.[17] are shown in Figure 1. Two different types of flax fibers and a glass fiber mat were used as reinforcements: a randomly oriented non-woven flax mat (surface weight: 300 g/m^2) supplied by Linapellava Oy, Särkisalmi, Finland [Fig. 2(a)], a woven flax fabric (surface weight: 230 g/m^2) supplied by Engtex AB, Mullsjö, Sweden [Fig. 2(b)] and a woven glass fiber fabric (surface weight: 500 g/m^2) supplied by Ahlstrom, Mikkeli, Finland [Fig. 2(c)]. Free radical initiator (tert-butyl peroxybenzoate), accelerator (dimethylaniline), and styrene were supplied by Aldrich Chemical Company, Wyoming, IL.

Preparation of composite

The fibers (both the woven and non-woven flax fibers) were treated with 4% NaOH, whereas the glass fiber was used as supplied by the manufacturer. The fibers were dried at room temperature for 24 h and then thermally treated by drying in a vacuum oven for 2 h at a temperature of 105°C. The woven fabric was straightened with an electric iron in order to keep the fabric in the longitudinal direction. The temperature of the electric iron was 100°C. This was necessary because the fiber got disorientated during washing with NaOH solution.

Laminates consisting of seven laminae (plies) each were made by stacking sheets of woven fabric mats at 0°, +45°, and 90° orientations (see Fig. 3). Three sheets of non-woven flax mats were sandwiched in-between the woven fabrics. In the case of the hybrid composites reinforced with woven fabric and glass fibers (bi-axially woven), the glass fiber was sandwiched in the mid-plane. Hybrid composites were produced both from the neat resins and from the resins blended with 30 wt % styrene. The composites prepared with the neat resins were cured at 170°C for 5 min, using 2 wt % tert-butyl peroxybenzoate as free radical initiator. For the styrene-blended resin, compression molding was done at 40°C for 1 h at 40 bar, and post-cured at 170°C for 5 min. The hot press was from Rondol Technology Ltd., Staffordshire, UK. The fiber-resin ratio was about 60 : 40 wt %. In total, 16 different combinations were evaluated (four different resins and four different stacking sequences and orientations; see Tables I and II). Individual laminates containing each fiber were made and tested to determine their contribution to the hybrid composite. Each composite or hybrid composite laminate has eight replicates, out of which test specimens were cut.

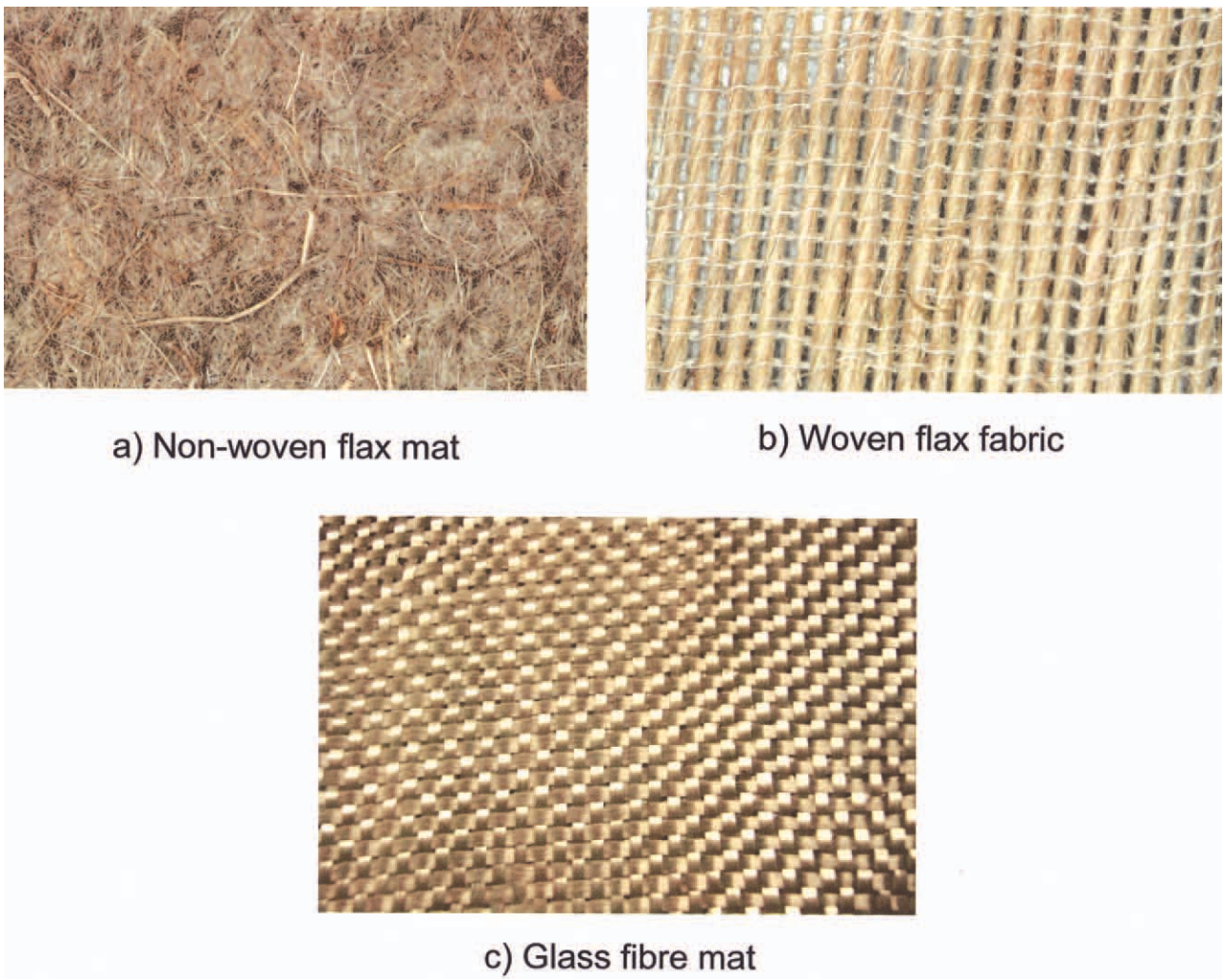

Figure 2 Fiber reinforcements used in the hybrid composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

The tensile testing was performed according to the ISO 527 standard test method for fiber-reinforced plastic composites, with a universal H10KT testing machine (maximum capacity 10 kN) supplied by Tinius Olsen Ltd., Salford, UK. The loading rate was 10 mm/min and the load range was 10 kN. Ten specimens were analyzed for each composite laminate. Cutting of the specimens was done with a laser machine. The specimens were cut in a dumbbell shape with an overall length of 150 mm (length of narrow, parallel-sided portion: 60 mm; width at ends: 20 mm; width of narrow portion: 10 mm; guage length: 50 mm; and initial distance between grips: 115 mm). Composites with the stacking sequence/ orientations such as $[+45_4/N_3]$ and $[90_2/N_3/+45_2]$ were cut in perpendicular direction (see Table I), whereas composites with orientations such as $[0_4/N_3]$ and $[0_6/G_1]$ were cut in the fiber direction (0°) (i.e., warp direction) (see Table II).

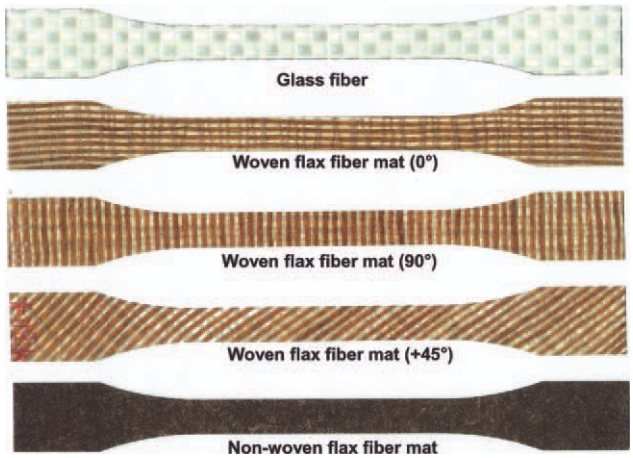

Figure 3 Individual sample ply and fiber orientations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Stacking Sequence and Orientation of the MSO Reinforced Composites

Hybrid[a] composite notations	Resin	1st ply	2nd ply	3rd ply	4th ply	5th ply	6th ply	7th ply
$[+45_4/N_3]_M$	MSO	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°
$[90_2/N_3/+45_2]_M$	MSO	Woven 90°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven 90°
$[0_4/N_3]_M$	MSO	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°
$[0_6/G_1]_M$	MSO	Woven 0°	Woven 0°	Woven 0°	Glass mat	Woven 0°	Woven 0°	Woven 0°
$[+45_4/N_3]_{MST}$	MSO/ST	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°
$[90_2/N_3/+45_2]_{MST}$	MSO/ST	Woven 90°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven 90°
$[0_4/N_3]_{MST}$	MSO/ST	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°
$[0_6/G_1]_{MST}$	MSO/ST	Woven 0°	Woven 0°	Woven 0°	Glass mat	Woven 0°	Woven 0°	Woven 0°

[a] Hybrid composites are designated as follows: Flax fiber mats in the warp direction of 0°, 45°and 90°, respectively, correspond to '0,' '45,' '90' in the notations. 'N' and 'G' indicate the non-woven flax fiber and the glass fiber mats. The subscript digits show the number of ply and the subscript part outside square brackets abbreviates the resins used in the composites: *M* (MSO), *MST* (MSO/ST).

The flexural testing was performed according to ISO 14125, with the same testing machine. At least 5 specimens were tested for every material. The loading rate was 10 mm/min and the load range was 5 kN. The specimen dimension was 80 × 15 mm^2 (length × width), while the thickness varied depending on the sample. The outer span was taken to be 64 mm and the displacement range was 10 mm.

The time-temperature dependency of the mechanical properties was determined by dynamic mechanical thermal analysis (DMTA), with a Q series TA instrument (dual cantilever) supplied by Waters LLC, Newcastle, DE. The dimension of the test specimens was 62 × 10 × 2 mm^3, whereas the temperature range was from 30°C to 150°C at frequency of 1 Hz. Three specimens were analyzed per composite.

Scanning electron microscopic (SEM) analysis was performed on the tensile fractured specimens. The gold coating of the fractured specimens was prepared with a sputter coater (S150B) in argon gas and at 3 mbar. The specimens were later analyzed with DSM 940A equipment, supplied by Blue Lion Biotech LLC, Snoqualmie, WA. The equipment was run at a current of 85 μA and a voltage of 10 kV.

RESULTS AND DISCUSSION

Tensile testing

Figures 4 and 5 show the results of the tensile testing. Neat MSO resin was reinforced with woven fabrics and non-woven flax mats (see Table I). Composite $[+45_4/N_3]_M$ had a tensile strength of 50 MPa and a tensile modulus of about 6.0 GPa, whereas the same MSO resin reinforced with similar reinforcements (non-woven flax mats and woven fabrics) but different fiber direction of the woven fabric, such as composite $[90_2/N_3/+45_2]_M$, gave a tensile strength of 49 MPa and a tensile modulus of 7 Gpa.

TABLE II
Stacking Sequence and Orientation of the MMSO Reinforced Composites

Hybrid[a] composite notations	Resin	1st ply	2nd ply	3rd ply	4th ply	5th ply	6th ply	7th ply
$[+45_4/N_3]_{MM}$	MMSO	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°
$[90_2/N_3/+45_2]_{MM}$	MMSO	Woven 90°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven 90°
$[0_4/N_3]_{MM}$	MMSO	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°
$[0_6/G_1]_{MM}$	MMSO	Woven 0°	Woven 0°	Woven 0°	Glass mat	Woven 0°	Woven 0°	Woven 0°
$[+45_4/N_3]_{MMST}$	MMSO/ST	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven +45°
$[90_2/N_3/+45_2]_{MMST}$	MMSO/ST	Woven 90°	Non-woven	Woven +45°	Non-woven	Woven +45°	Non-woven	Woven 90°
$[0_4/N_3]_{MMST}$	MMSO/ST	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°	Non-woven	Woven 0°
$[0_6/G_1]_{MMST}$	MMSO/ST	Woven 0°	Woven 0°	Woven 0°	Glass mat	Woven 0°	Woven 0°	Woven 0°

[a] Hybrid composites are designated as follows: Flax fiber mats in the warp direction of 0°, 45°and 90°, respectively, correspond to '0,' '45,' '90' in the notations. 'N' and 'G' indicate the non-woven flax fiber and the glass fiber mats. The subscript digits show the number of ply and the subscript part outside square brackets abbreviates the resins used in the composites: *MM* (MMSO), *MMST* (MMSO/ST).

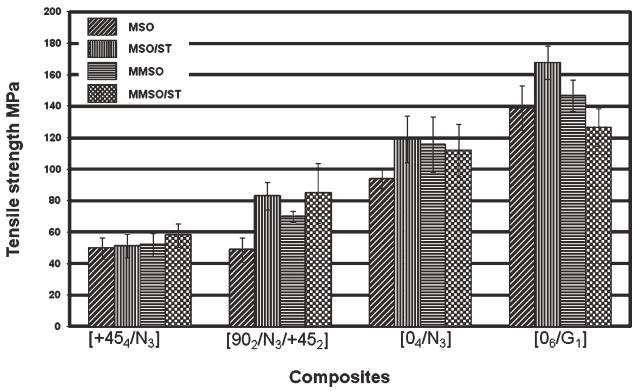

Figure 4 Tensile strength of the hybrid composites.

However, the reinforcement with woven fabric in the 0° direction (see composite $[0_4/N_3]_M$) gave better mechanical properties in terms of strength and stiffness. In this case, the tensile strength increased to 94 MPa and the Young modulus to about 10 GPa, which indicated that by testing the composite in the direction of the fiber, the strength of the composite doubled and the modulus increased by about 31%. This means that by changing the top and bottom plies in composite $[+45_4/N_3]_M$ from +45° to 90° (composite $[90_2/N_3/+45_2]_M$), there will be no appreciable difference in mechanical properties, but when the fiber orientation is changed from 90° to 0° (composite $[0_4/N_3]_M$), a great difference in mechanical properties can be seen (see Figs. 4 and 5).

In composite $[0_6/G_1]_M$ (Table I), reinforcement was done with both flax fabrics and glass fiber (bi-axial fiber direction), and tensile testing was performed in the warp direction, which resulted in improved mechanical properties. The tensile strength increased to 139 MPa (Fig. 4) and the Young modulus to 14 GPa (Fig. 5). The inclusion of a glass fiber mat increased the mechanical properties appreciably.

Composite $[+45_4/N_3]_{MST}$ had similar fiber sequence and orientation to composite $[+45_4/N_3]_M$, but the MSO resin used in composite $[+45_4/N_3]_{MST}$ was blended with styrene, which gave a slight improvement in mechanical properties when compared to composite $[+45_4/N_3]_M$ (see Figs. 4 and 5). The comparison of composites $[90_2/N_3/+45_2]_M$ to $[90_2/N_3/+45_2]_{MST}$, which had similar fiber orientations but a different matrix because of the addition of styrene, showed a great difference in mechanical properties. The tensile strength increased from 49 to 83 MPa (Fig. 4), and the modulus increased from 7 to 12 GPa in composite $[90_2/N_3/+45_2]_{MST}$ (Fig. 5). It can be concluded from the descriptions above that fiber orientation, inclusion of glass fiber, and the addition of styrene improved the mechanical properties of the composites.

Comparison of two sets of composites such as $[0_4/N_3]_M$ and $[0_4/N_3]_{MST}$, which were similar in fiber composition but had a different matrix, showed that the strength of composite $[0_4/N_3]_{MST}$ increased by about 21% (Fig. 4) and the modulus increased by 30% (Fig. 5). This indicates further that the addition of styrene gives better fiber-matrix adhesion and good cross-linking characteristics. It can be explained on the basis of good fiber impregnation of the low-viscosity resin as a result of addition of styrene.

The same result was also observed with composite $[0_6/G_1]_{MST}$ (Table I), where the addition of styrene constituted the difference between composites $[0_6/G_1]_M$ and $[0_6/G_1]_{MST}$. The addition of styrene to the matrix gave superior mechanical properties. The strength increased by 17.3% and the modulus increased by 26.3% (see Figs. 4 and 5).

Composites $[+45_4/N_3]_{MST}$, $[90_2/N_3/+45_2]_{MST}$, and $[0_4/N_3]_{MST}$ were manufactured using similar techniques and the same matrix, but they had different fiber orientations (see Table I). By changing the orientation of the top and bottom plies from +45° (composite $[+45_4/N_3]_{MST}$) to 90° (composite $[90_2/N_3/+45_2]_{MST}$), the tensile strength increased from 51 to 83 MPa (see Fig. 4) and the Young modulus increased from 8 to 12 GPa (see Fig. 5). In composite $[0_4/N_3]_{MST}$, the fiber orientations were changed to 0°, and the tensile strength and modulus increased further to 119 MPa and 14 Gpa, respectively (Figs. 4 and 5). Composite $[0_6/G_1]_{MST}$ was manufactured with glass fiber mat sandwiched in the mid-plane, and the tensile strength and modulus increased further to 168 MPa and 19 Gpa, respectively. From the considerations discussed above, it is clear that that even within the same resin system, the contribution of the direction of the fiber plays an important role in improving the mechanical properties and that inclusion of glass fiber improves the mechanical properties of the composites even further. This was to be expected.

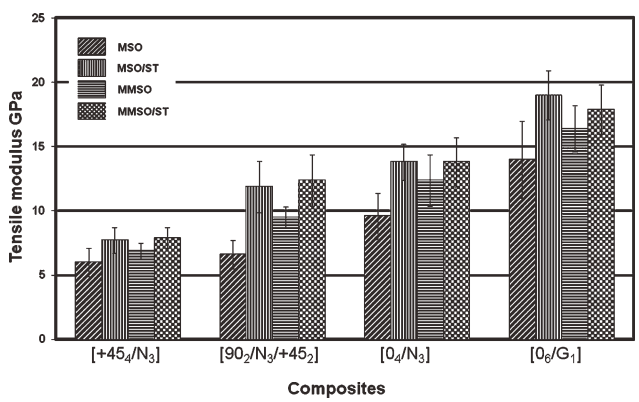

Figure 5 Tensile modulus of the hybrid composites.

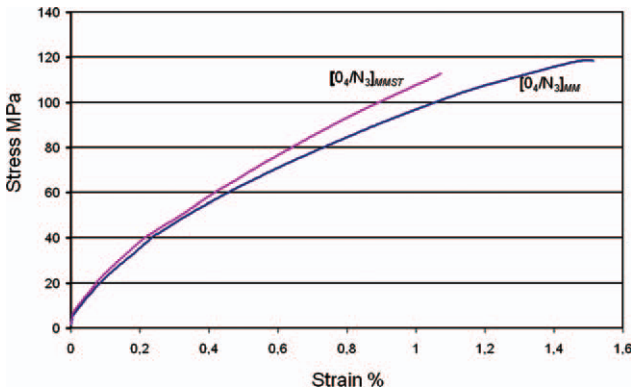

Figure 6 Stress-strain curves of selected MMSO composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II shows the other composites made with the MMSO resin as a matrix. All the composites were made as described above. The same result was observed as described above, and both the fiber direction and the inclusion of glass fiber considerably improved the mechanical properties of the composites.

The effect of styrene was more conspicuous in the composites made with MSO because both the tensile strength and the modulus increased appreciably. Neat MMSO resin reinforced with natural fibers was superior to neat MSO resin with similar reinforcements. The reason for this is that neat MMSO resin had additional methacrylate functionalities that led to higher cross-linking capabilities and, ultimately, excellent fiber-matrix adhesion.

Neat MMSO resin reinforced with both woven fabrics and non-woven fiber mats can compete favorably with styrene-blended resin reinforced with woven fabrics and glass fiber mat.

The percentage elongation of the hybrid composites with styrene-blended resin is lower compared to the neat resin (see Fig. 6). The stress-strain curves of MMSO-reinforced composites with similar fiber orientation but different matrix composition due to styrene blending (Fig. 6) show the ductility of the material. The average percentage elongation for composite $[0_4/N_3]_{MMST}$ was 1.14% and it was 1.46% for composite $[0_4/N_3]_{MM}$. These results show that materials with neat resin (without styrene) are more ductile than materials containing styrene. Composite manufactured with a matrix blended with styrene are stiffer; this makes them more brittle. The general observation from all the composites manufactured was that the properties of the MSO resin improved greatly with the addition of styrene, whereas the properties of the MMSO resin improved only slightly.

Table III shows the tensile properties of the individual laminates prepared with each of the fiber mats. The glass fiber composites had a modulus in the range of 13–18 GPa and the woven fabric-reinforced composites in the 0° direction had a modulus in the range of 14–18 GPa. Similar trend was also observed in the non-woven flax which had a modulus in the range of 4–9 GPa. The contribution of these plies to the hybrid composite cannot be overemphasized, and this was the reason for the superior mechanical properties achieved in all the composites containing glass fiber and woven fabric (0° direction). The tensile strength of the individual glass fiber composites was between 217 and 360 MPa and that of woven fabric (0° direction) was between 137 and 146 MPa. In all cases, the composites manufactured with glass fiber only or woven fabric only (0° direction) showed superior tensile properties compared to other individual laminates such as woven fabric in the +45° or 90° direction, and the non-woven fiber composite.

Using simple rule of mixtures to calculate the tensile modulus and tensile strength of the hybrid composites (see Table IV), we observed that the calculated values were lower than the measured values. This was to be expected, however, because the measured values were obtained from the composite laminate prepared with compression molding at about 40 bars. The plies are more compact due to the higher pressure exerted compared to a single-ply composite.

TABLE III
Tensile Properties of the Individual Laminate Prepared with Each of the Fiber Mats

Composites		E-modulus (GPa)		Tensile strength (MPa)	
Fiber mat	Resin				
Glass	MSO	14.7	(±1.7)	216.8	(±25.3)
	MMSO	12.8	(±1.9)	234.2	(±35.5)
	MSO/ST	17.5	(±2.0)	284.4	(±18.0)
	MMSO/ST	17.9	(±2.3)	360.5	(±36.4)
Woven flax (0°)	MSO	13.8	(±1.9)	137.5	(±19.5)
	MMSO	14.7	(±1.8)	136.9	(±22.2)
	MSO/ST	16.4	(±1.9)	146.3	(±25.0)
	MMSO/ST	17.7	(±3.3)	141.6	(±27.0)
Woven flax (90°)	MSO	1.3	(±0.6)	9.1	(±3.9)
	MMSO	3.2	(±0.4)	17.5	(±3.9)
	MSO/ST	1.4	(±0.3)	6.6	(±0.9)
	MMSO/ST	4.1	(±0.7)	13.9	(±3.8)
Woven flax (±45°)	MSO	0.5	(±0.2)	5.2	(±1.7)
	MMSO	1.0	(±0.9)	5.3	(±4.8)
	MSO/ST	1.4	(±0.5)	6.9	(±1.6)
	MMSO/ST	1.9	(±1.2)	10.8	(±10.8)
Non-woven flax	MSO	3.9	(±1.7)	33.1	(±9.0)
	MMSO	5.4	(±0.6)	43.6	(±8.2)
	MSO/ST	7.2	(±0.6)	68.0	(±6.4)
	MMSO/ST	8.9	(±0.8)	75.0	(±9.3)

The values in parenthesis represent the standard deviation.

TABLE IV
Tensile Properties of the Seven-Ply Hybrid Composites

Hybrid composites Notation	Tensile strength (MPa)		Modulus (GPa)	
	Calculated*	Measured	Calculated*	Measured
$[+45_4/N_3]_M$	19.6	49.5	2.26	6.0
$[90_2/N_3/+45_2]_M$	21.3	48.8	2.51	6.6
$[0_4/N_3]_M$	74.8	94.0	7.84	9.6
$[0_6/G_1]_M$	149.6	139.0	13.94	14.0
$[+45_4/N_3]_{MST}$	37.4	51.3	4.28	7.7
$[90_2/N_3/+45_2]_{MST}$	36.8	82.8	4.23	11.9
$[0_4/N_3]_{MST}$	108.9	119.0	11.97	13.8
$[0_6/G_1]_{MST}$	167.4	168.0	16.53	19.0
$[+45_4/N_3]_{MM}$	24.4	52.1	3.18	6.9
$[90_2/N_3/+45_2]_{MM}$	28.4	69.8	3.79	9.5
$[0_4/N_3]_{MM}$	83.5	115.8	9.39	12.4
$[0_6/G_1]_{MM}$	152.9	147.0	14.38	16.4
$[+45_4/N_3]_{MMST}$	43.1	57.9	5.41	7.9
$[90_2/N_3/+45_2]_{MMST}$	43.5	84.8	5.92	12.4
$[0_4/N_3]_{MMST}$	108.1	112.0	13.27	13.8
$[0_6/G_1]_{MMST}$	174.7	126.6	17.76	17.9

* The calculated modulus and the tensile strength were obtained on the basis of the tested value of each ply tabulated in Table III.

Simple predictions using longitudinal rule of mixtures may have caused the differences between the predicted values and the test values. In the laminate, every layer contributes to the Young's modulus and maximum stress. For the stiffness, it should be possible to use an "additive" relationship: $E_{tot} = \sum T_i \times E_i$(where E and T are the stiffness and the relative thickness of each individual ply, respectively, "tot" refers to the total laminate values, and the index i is the number of layers).

As a consequence of the calculated values based on the stiffness of each ply, it should also be possible to estimate the hybrid effect. Since the tested modulus is higher than the calculated modulus, it can be said that positive reinforcement was achieved in the hybrid composites and it can be concluded therefore that there was a hybrid effect due to combination of reinforcements. The weld strengths between the plies may have an effect on the test values, whereas poor welding can lead to deterioration of the hybrid effect.

The difference between the measured values and the calculated values using the simple rule mixtures could also be due to the physical factors such as fiber–fiber interaction, inhomogeneous fiber distribution in the matrix, and disorientation of fibers from the loading direction. Additional modifications to the rule of mixtures to incorporate both fiber disorientation and inhomogeneous spread may lead to good agreement between the measured and predicted values. However, the discussion about the variation in mechanical properties of the composites cannot be completed without taking into account the experimental errors and not just the mean values of the parameter.

Flexural testing

Comparing composites $[+45_4/N_3]_M$, $[90_2/N_3/+45_2]_M$, and $[0_4/N_3]_M$ (see Table I), the fiber orientation played a vital role in both the flexural strength and modulus. Changing the fiber direction of the first and the seventh ply from +45° in composite $[+45_4/N_3]_M$ to 90° in composite $[90_2/N_3/+45_2]_M$ increased the flexural strength from 93 to 100 MPa and the modulus from 7 to 8 GPa (Figs. 7 and 8). When the fiber orientation was changed to 0° in composite $[0_4/N_3]_M$, the flexural strength and modulus increased to 143 MPa and 17 Gpa, respectively. The inclusion of glass fiber in the mid-plane of composite $[0_6/G_1]_M$ did not improve the flexural properties and this is to be expected, because in the flexural test, bending of the composite results in tensile stress below the mid-plane of the specimen.[13]

Composites $[+45_4/N_3]_M$ and $[+45_4/N_3]_{MST}$ (Table I) had similar fiber orientation but a different matrix because of the addition of styrene in composite $[+45_4/N_3]_{MST}$, which resulted in a slight increase in flexural properties. Comparing other composites in Figures 7 and 8, the addition of styrene to the matrix increased the flexural properties of the composites. The same trend was also observed in the MMSO-reinforced composites.

The difference in the flexural properties of composites $[+45_4/N_3]_{MM}$ and $[+45_4/N_3]_{MMST}$ was due to the addition of styrene to the MMSO resin. Composite $[+45_4/N_3]_{MMST}$ showed flexural properties that were superior to those of composite $[+45_4/N_3]_{MM}$ (see Figs. 7 and 8). The same trend was also

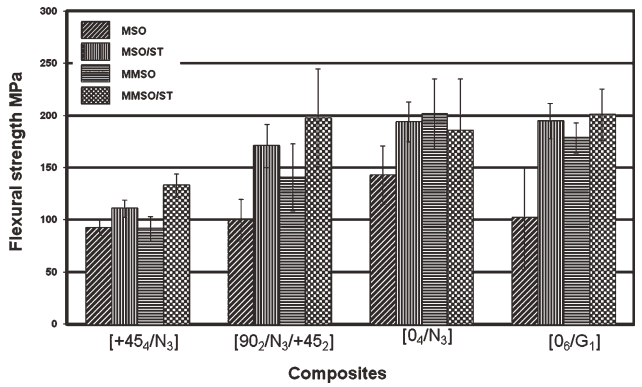

Figure 7 Comparison of flexural strength of the hybrid composites.

observed when we compared composites $[90_2/N_3/+45_2]_{MM}$ and $[90_2/N_3/+45_2]_{MMST}$.

Composites $[+45_4/N_3]_{MM}$, $[90_2/N_3/+45_2]_{MM}$, and $[0_4/N_3]_{MM}$ (see Table II, and Figs. 7 and 8) gave good flexural properties in that order, and this was because the fiber orientation was changed from +45° to 90° and then to 0°, respectively.

Scanning electron microscopy

Figure 9(a–d) shows the scanning electron micrographs of composites $[0_4/N_3]_M$, $[0_6/G_1]_M$, $[0_4/N_3]_{MM}$, and $[0_6/G_1]_{MM}$. The hybrid composites showed good fiber-matrix adhesion. The fibers were well-embedded in the matrix, and this was to be expected because all of the 16 composites that were manufactured showed good mechanical properties. During alkali treatment, waxes, hemicelluloses, and part of the lignin present on the fiber surface were removed.[18] The removal of these compounds enhances the surface roughness, which allows mechanical interlocking.[18] The tensile and flexural properties are relatively high. Flax fibers are known to have a high specific strength and modulus; in this case, woven flax fabrics were used in all the composites. Woven fabrics have aligned fiber knitted together at an angle of 90° to the fiber direction. Composites $[0_6/G_1]_M$ and $[0_6/G_1]_{MM}$ did not show any conspicuous fiber pull-out, which could also be explained by their high tensile strengths and moduli. The fiber pull-out length in composites $[0_4/N_3]_M$ and $[0_4/N_3]_{MM}$ were quite short and did not therefore undermine the fiber-matrix adhesion. These composites have high strengths and moduli.

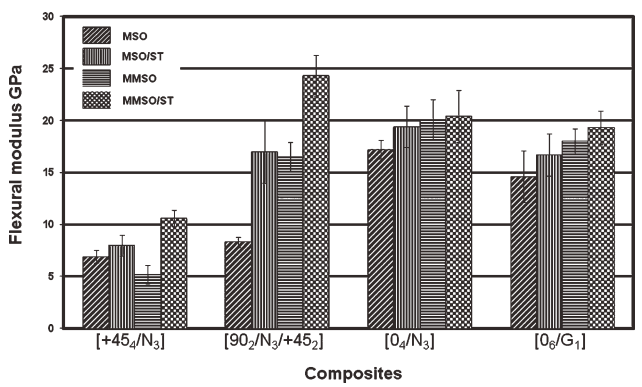

Figure 8 Comparison of flexural modulus of the hybrid composites.

Figure 10 shows the scanning electron micrograph of composites $[+45_4/N_3]_M$ and $[+45_4/N_3]_{MM}$. A short fiber pull-out could also be observed, although the tensile strengths and moduli of these composites were lower when compared to others. The fiber-matrix adhesion may not be that strong in these composites. The scanning electron microscopy revealed the microstructural image of the cross-sectional region, and one could see the fracture across the length of the specimen, which was due to the laser cutter (see Fig. 11).

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis is regarded as a sensitive technique; it is used in studying the effect of temperature on the mechanical properties of materials, including polymers and composites. Dynamic mechanical thermal analysis of natural fiber composite has been discussed extensively by various authors.[19,20–25] The important parameters measured by this technique are the storage modulus (E'), the loss modulus (E''), tan δ, and the glass transition temperature (T_g). The ratio of E'' to E' (loss modulus to storage modulus) gives the tangent of the phase angle δ; tan δ is known as the damping and is a measure of energy dissipation. Such parameters provide quantitative information about the behavior of a material.

The effects of fiber orientation, addition of styrene, type of matrix, and fiber surface treatment on the dynamic mechanical properties were examined. Both storage and loss moduli decreased with increase in temperature. The storage and loss moduli of the composites are higher because of the improved fiber-matrix interfacial adhesion.

O'Donnell *et al.*[19] reported the influence of different ratios of styrene on the storage modulus, E', and the glass transition temperature, T_g, of AESO (acrylated epoxidized soybean oil) resin samples cured at room temperature. It was found that both E' and T_g increased with increasing styrene content and that 33.3 wt % styrene gave optimal properties. We found a similar trend in this study, where we reinforced MSO and MMSO resins (with and without styrene) with flax fibers.

The variations in the storage modulus of the MSO composites in Table I are shown in Figure 12. Notations such as 1a, 1b, 2a, 2b, etc. were used for easy

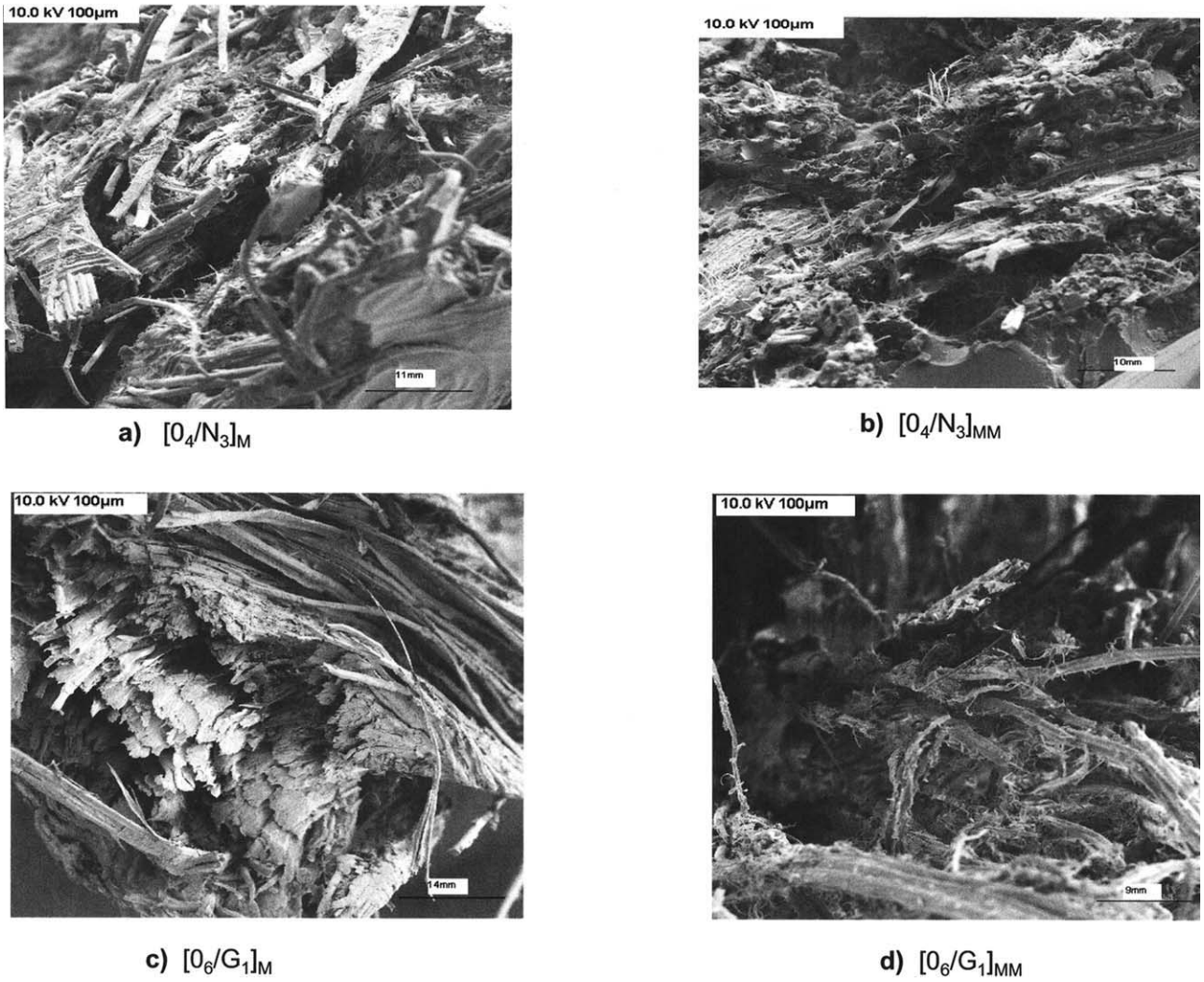

Figure 9 Comparison of the hybrid composites by scanning electron microscopy.

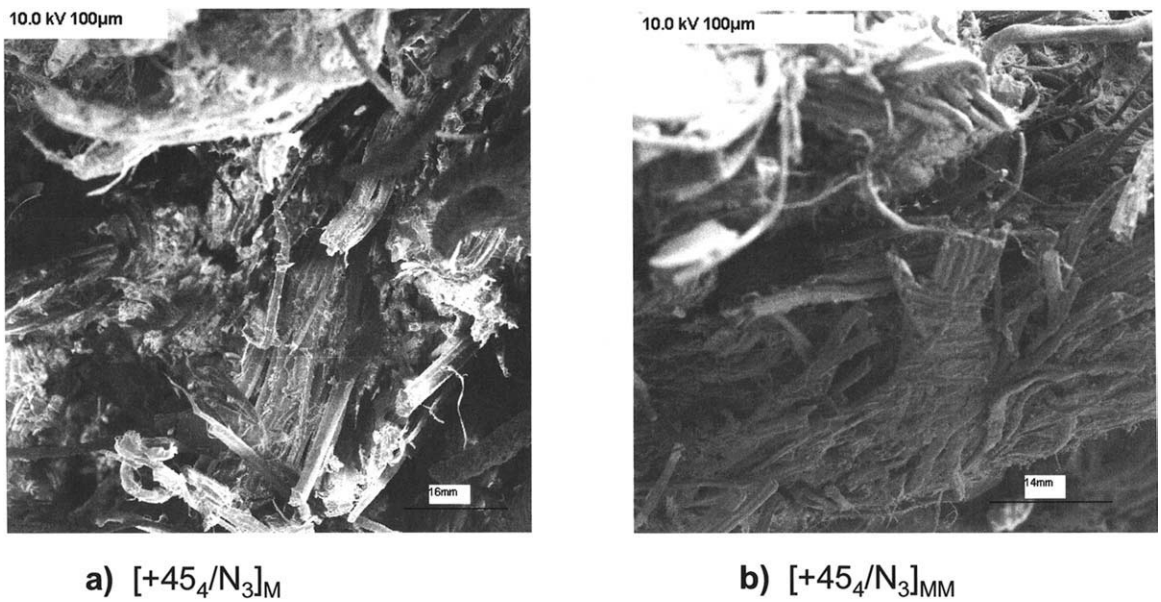

Figure 10 Scanning electron micrographs of composites reinforced in the +45° direction.

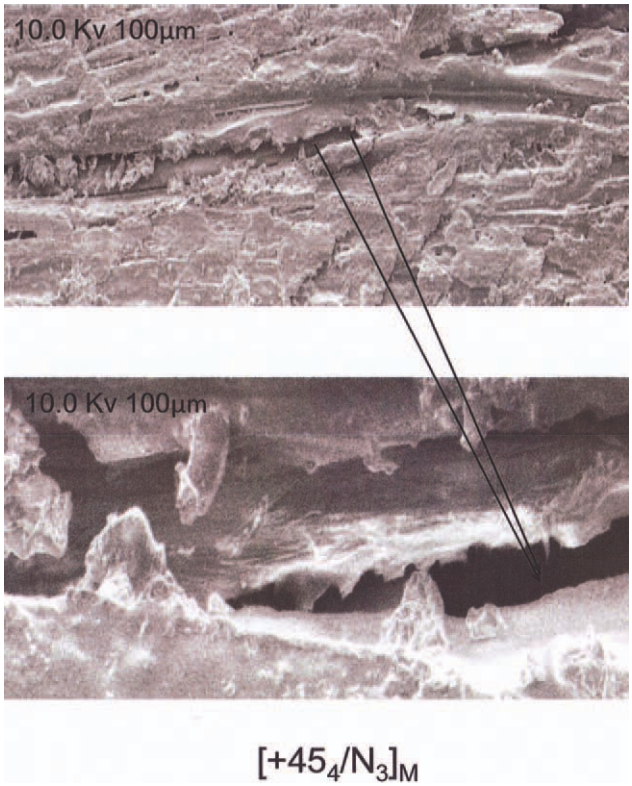

Figure 11 Micrographs of fracture across specimen length of composite $[+45_4/N_3]_M$. [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

labeling of the curves. Composites 3b, 4b, 4a, and 3a had higher storage modulus (E') of about 15, 11, 9, and 8 GPa compared to composites 1a, 2a, 1b, and 2b. This was to be expected, considering their high tensile and flexural properties. Composites 3b and 4b had superior mechanical properties when compared to other MSO composites. Composites 1a, 2a,

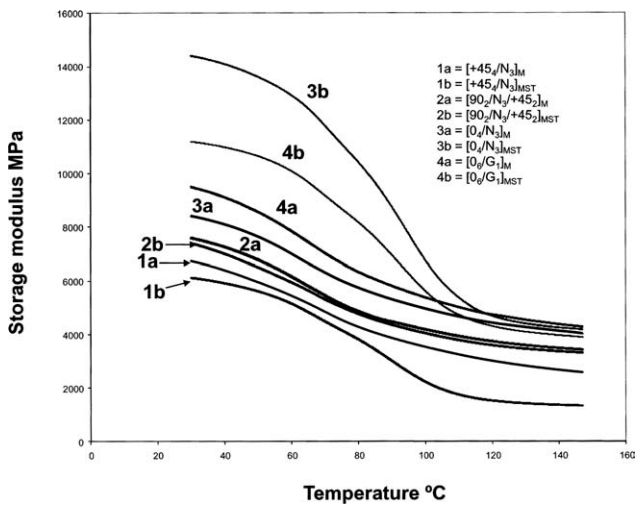

Figure 12 Variation in the storage modulus of the MSO composites.

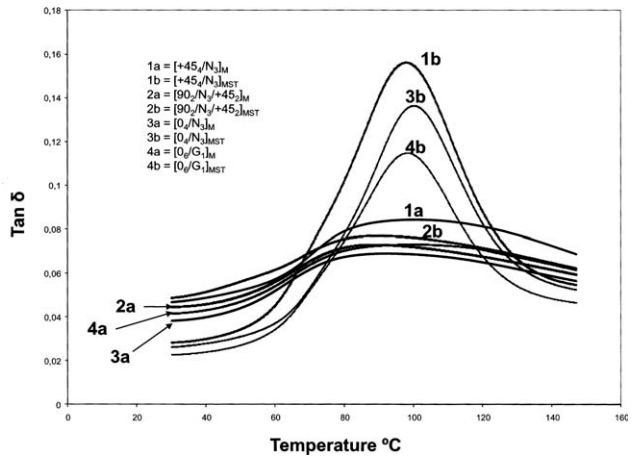

Figure 13 Tan δ curve of the MSO composites.

1b, and 2b showed a relatively lower storage modulus than composites 3b and 4b, and this could also be explained on the basis of their flexural and tensile properties. Composite 3b had the highest flexural modulus when compared to other MSO composites, and this was explainable by the fact that this composite had the highest storage modulus. Generally speaking, all the composites showed good fiber-matrix adhesion which could be inferred from the high values of their storage moduli, but the superior properties of composites 3b and 4b over a wide range of temperatures were associated with better interfacial adhesion between the fiber and the matrix.

Variation in tan δ with temperature of the MSO composites is shown in Figure 13. The glass transition temperature T_g was obtained from the maximum point of the tan δ curve. The T_g of composites 1a, 1b, 3b, and 4b was about 105°C, whereas that of the other composites was about 90°C. Increase in T_g may be attributable to better interfacial interaction between treated fiber composites. The highest peak temperature for tan δ was also observed for composites 1b, 3b, and 4b, which indicated better fiber-matrix adhesion, whereas the peak temperature for composites 2a, 2b, 3a, and 4a was lower.

Figure 14 shows the variation in the loss modulus of the MSO composites. Akay[26] reported that the T_g values obtained from peak in loss modulus (E'') are more reliable than those obtained from the tan δ curve. Saha et al.[27] also reported that the temperature of the maximum loss modulus is very close to T_g (at low frequency) and that the temperature of the tan δ peak heavily overestimates the value of T_g. It was also observed in the present study that the T_g value obtained in the tan δ peak for composites 1b, 3b, and 4b was 105°C, whereas the T_g value obtained in the loss modulus peak was 95°C. The same trend was also observed for composites 2a, 2b, 3a, and 4a, which had a T_g value of 90°C at the tan δ peak,

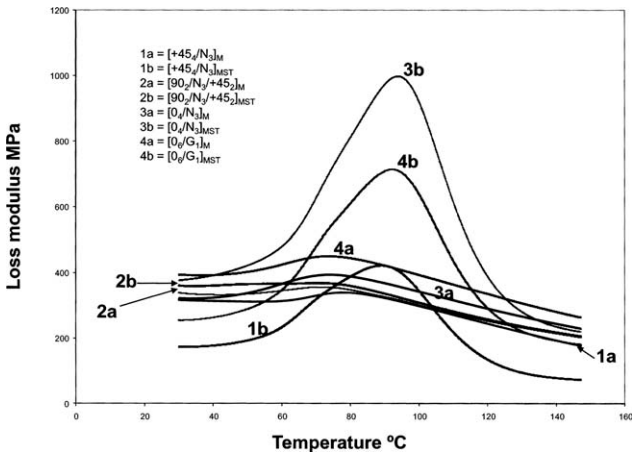

Figure 14 Variation in the loss modulus of the MSO composites.

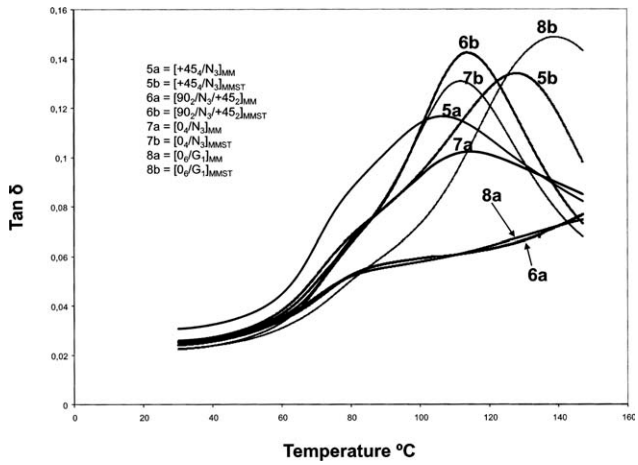

Figure 16 Variation in the tan δ of the MMSO composites.

whereas the T_g value obtained from the loss modulus peak was about 75°C.

From the loss modulus curves in Figure 14, composites 1b, 3b, and 4b showed the highest value of loss modulus at 95°C, whereas composites 2a, 2b, 3a, and 4a showed the lowest value at 75°C. Increase in loss modulus (and hence T_g) indicates better interfacial interaction in fiber composites, which reduces the polymer chain mobility.[21] The results of the dynamic mechanical thermal analysis are in accordance with the tensile and flexural results, which indicated that composites 3b and 4b had superior mechanical and thermal properties compared to other MSO composites.

Figure 15 shows the variation in the storage modulus of the MMSO composites (Table II). Composites 6b, 7a, 7b, 8a, and 8b had higher storage modulus than the other MMSO composites. This is indicative of the tensile and flexural properties of these composites. There is good fiber-matrix adhesion. Composite 6b had the highest flexural modulus of all the MMSO composites, which can be explained by the fact that this composite had the highest storage modulus. Composites 5a, 5b, and 6a had lower storage modulus and this is in accordance with their flexural properties.

Variation in the tan δ of the MMSO composites is shown in Figure 16. The glass transition temperature T_g was obtained from the maximum point of the tan δ curve. Composites 5a, 6b, 7a, 7b, 5b, and 8b had the maximum tan δ peaks corresponding to 110, 115, 115, 115, 130, and 140°C, respectively. High T_g values indicate better fiber-matrix interfacial adhesion. Figure 17 shows the variation in the loss modulus of the MMSO composites, where the T_g of composites 6b, 7a, and 7b was found to be 110°C, whereas the T_g of composites 5a, 5b, and 8b was 90, 115, and 125°C, respectively. The same trend was also observed in the MSO composites, where all the T_gs

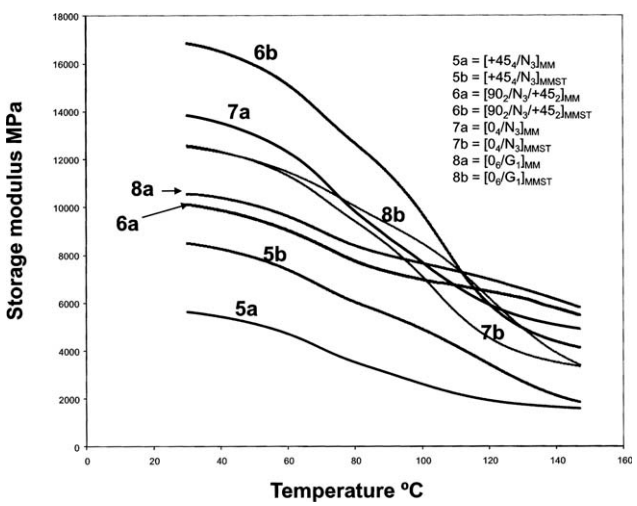

Figure 15 Comparison of storage modulus of the MMSO composites.

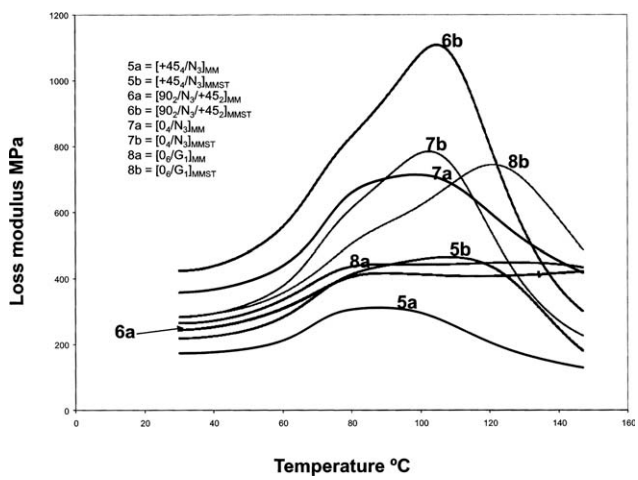

Figure 17 The loss modulus curves of the MMSO composites.

were overestimated by between 10°C and 20°C using the tan δ curve.

An increase in loss modulus which corresponds to high T_g indicates better fiber-matrix interfacial adhesion. Composites 6b, 7a, 7b, and 8b showed high loss modulus, which corresponded to high T_g values. The results from the flexural test were also in line with this finding. Composites 3b, 4b, 6b, 7b, and 8b showed superior mechanical and thermal properties when compared to other composites because all of these composites were manufactured with styrene and with reinforcement in the 0° direction (except for composite 6b).

CONCLUSION

The natural fiber hybrid composites based on continuous reinforcement showed good mechanical properties. These composites can even compete with glass fiber composites in terms of stiffness, especially when their specific properties are considered. The low weight of the natural fiber (without glass fiber) gave lighter composites. The properties of composite materials reinforced with unidirectional fibers are known to be highly anisotropic, with high values of stiffness and strength in the fiber direction and poor mechanical behavior in the transverse direction.[28] These composites have similar mechanical properties to the ones reported by Goutianos et al.,[6] although unsaturated polyester resin and epoxy resin were used as matrices. The bio-based thermoset resins can actually substitute for the conventional thermosetting polymers because they are similar in properties.

In the automotive industry, strength of 62 MPa and a modulus of 2 GPa are required for composite applications. The results from the mechanical analyses show that there are differences in both the tensile properties and the flexural properties of all 16 hybrid composites, and this was a result of the addition of styrene to the resin, the orientation of fibers, the stacking sequence, addition of glass fiber, and the type of resin. The good mechanical properties of the composites are evidence that there is good fiber-matrix adhesion, which could be due to the good fiber wetting. Although fiber volume plays an important role in the overall mechanical properties of a composite, we found that a fiber-matrix ratio of 60 : 40 wt % gave optimal properties.

Addition of styrene to the resin, alignment of the woven fabric in the 0° direction, and testing of the composite in the direction of the fiber gave superior mechanical properties to the composite. Styrene need not be blended with the MMSO resin because there was no great difference in the mechanical properties of the composites; however, this is good for the environment because the addition of styrene reduces the renewable content of the bio-based composites.

It can be concluded that the addition of styrene, the inclusion of glass fiber, or changing the fiber orientation can increase the tensile strength and modulus of composites, but the most sustainable way is to change the orientation of the fiber—which has a consistent effect on the mechanical properties of a composite. A fully bio-based hybrid composite without glass fiber as reinforcement and without styrene as reactive diluent has excellent mechanical properties and a high percentage of renewable content.

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