BIOBASED COMPOSITES PREPARED BY COMPRESSION MOULDING USING A NOVEL THERMOSET RESIN FROM SOYBEAN OIL AND A NATURAL FIBRE REINFORCEMENT

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SUMMARY

Biobased composites were manufactured by using a compression moulding technique. Novel thermoset resins from soybean oil were used as matrix while flax fibres were used as reinforcement. The airlaid fibres were stacked randomly while woven fabrics were stacked crosswisely (90°) and impregnation was done manually. The fibre/ resin ratio was 60% to 40%.

Keywords: Thermosetting, flax fibre, woven fabric, compression moulding

INTRODUCTION

There has been overwhelming interest in using biobased thermosetting polymers as matrix in natural fibre composites, not only because they are from renewable sources but also have comparable mechanical properties like other conventional thermosetting polymers.

The quests for these researches are based on substituting the conventional polymers with polymers from agricultural origin for the purpose of achieving sustainability. There has been an overwhelming campaign by the United Nations to reduce the CO_2 emission to between 50- 80% by 2050 in other to save the planet from global warming. The summit of the most industrialised nations (G8) held in Heiligendamn, Germany also focused on the accelerated process that can eventually lead to ´´substantial`` cuts in emissions (CO_2 and five other greenhouse gases) that contribute to global warming. The declaration recognized that climate change must be addressed as part of a broader agenda, which also should include energy security, economic growth and sustainable development.

There are many on going research to manufacture composites by using natural fibres as reinforcements and polymers from renewable resources as matrices [1]. There is an emerging market for biodegradable polymers which is expected to increase substantially in the coming years [1].

Polymer composites are made by embedding strong fibres, such as carbon, aramid, glass, or natural fibres in a polymer matrix [2,3]. Depending on their origin, vegetable fibres can be grouped into seed, bast, leaf or fruit qualities [3]. Bast and leaf qualities are so called hard fibres (e.g., flax, jute, and ramie) [4] and are the most used ones [3].

There are also many reports on the use of naturally occurring fibres, including jute, sisal, etc., as reinforcing fibres for polymers [5].

The high strength and modulus of the embedded fibres impart strength and rigidity to the material that surpass that of the neat polymer [6,7]. Whereas most composite materials utilize synthetic fibres, such as carbon or glass, but in recent years natural fibres have attracted the attention of the composites community as a potential replacement because of the high cost of synthetic fibres [2,8]. These natural fibres are based on cellulose and offer advantages of biodegradability, low density, nonabrasive nature, and low cost [9,10].

Significant improvements in mechanical properties have also been achieved due to the reinforcing efficiency of fibres coupled with enhancement through chemical modification in other to promote bonding at the fibre- matrix interface [5,9,11].

Interestingly, just as many studies have been done as regards the use of natural fibres as reinforcements in composites quite a few investigations has been made on the possibilities of using polymers from renewable resources as matrix [12,13], which informed our interest in this study. The objective of this study was to manufacture composites based on different types of functionalised soybean oil resins that are from renewable origin as matrix materials and using flax fibres as reinforcements. Styrene is being used as a reactive diluent to reduce the viscosity of the resin and ease the impregnation of the fibres and also improve the mechanical properties of the resulted composites. However this will lower the renewable content of the material. In this study both neat resins and resins blended with styrene were used in the preparation of the composites. The natural fibre composites prepared were characterised with mechanical testing.

EXPERIMENTAL

Materials

Thermoset resins from soybean oil MSO (methacrylated soybean oil), MMSO (methacrylic anhydride modified soybean oil) and AMSO (acetic anhydride modified soybean oil) were used as matrix in the natural fibre composites. These resins were obtained from the synthetic modification of soybean oil reported previously by us [14]. Two flax mat fibres were evaluated, one randomly oriented airlaid flax mat (Linapellava Oy., Finland) and one woven flax fibre (Engtex, Sweden) were supplied by the manufacturers. Free radical initiator tert-butylperoxybenzoate, accelerator dimethylaniline (diluted in styrene) and styrene were supplied by Aldrich Chemical Company USA.

Composite preparation

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

Composites were prepared by hand lay-up. Each composite consisted of 8 sheets of the fibre mat. The airlaid fibre mats were laid randomly while the woven fabrics were laid crosswisely at angle 90°. Composites were produced both from the neat resins as well as from the resins blended with 30 wt-% styrene. The composites prepared from the neat resins were cured at elevated temperature while the composites with styrene blended resin were cured at a moderate temperature and post cured at elevated temperature. Each neat resin was blended with 2 wt-% tert-butylperoxybenzoate as a free radical initiator. The compression moulding was done at a temperature of 170°C for 5 min at 40bar. The hot press was from Randol Technology. Composites containing styrene blended resin (30-wt% styrene) were accelerated by adding 0.3 wt-% of the accelerator and the composites were compression moulded at 40°C for 1h using a pressure of 40 bar and finally post cure at 170°C for 5 min at 40bar. The fibre / resin ratio was about 60% / 40%. In total, 12 different combinations were evaluated (three different resins, with and without styrene and with two different flax fibre mats).

CHARACTERISATION

Impact testing

The Charpy impact strength of unnotched specimens was evaluated in accordance with ISO 179 using a Zwick test instrument. A total of 10 specimens were tested to determine the mean impact resistance. The samples were tested edgewise.

Flexural testing

The flexural testing was performed according to ISO 14125, using a Tinius Olsen UTM (Universal Testing Machine) called H10KT (maximum capacity 10 kN). At least 5 specimens were tested for every material.

RESULTS AND DISCUSSION

The availability of these biobased thermoset resins from renewable resources provides unique opportunity of exploring the possibility of their utilisation in the manufacturing of biodegradable composites. The aim was to study the feasibility of using the three different types of soybean oil based resins in natural fibre composites. The compatibility of these novel biobased resins with two natural fibres was also ascertained.

Impact testing

Tables 1 to 4 represent the Charpy impact strength (energy absorbed/cross-sectional area) results of the biobased composites. The composites tested show relatively high impact strength of about 50 - 60 kJ / m^2 and this is even comparable with glass mat composites 54 kJ / m^2 reported by Jang and Lee in 2000 [15]. The exception are the composites with MMSO resin, these show relatively low impact strength compared with the other composites. This can be related to the very good fibre matrix adhesion for this resin, which is also seen in relatively high flexural strength and modulus. A higher fibre matrix adhesion results in shorter average pull-out lengths and therefore causes lower impact strength.

Table 1. Impact strength of the neat resins reinforced with airlaid flax fibre.

Resin	Reinforcement	Charpy Impact Strength (kJ/m^2)	STD
MSO	Airlaid flax fibre	52.34	17.561
MMSO	Airlaid flax fibre	25.25	10.574
AMSO	Airlaid flax fibre	51.08	8.841

Table 2. Impact strength of the styrene blended resins reinforced with airlaid flax fibre.

Resin	Reinforcement	Charpy Impact Strength (kJ/m^2)	STD
MSO/ Styrene	Airlaid flax fibre	49.39	12.297
MMSO/ Styrene	Airlaid flax fibre	23.96	11.093
AMSO/ styrene	Airlaid flax fibre	57.12	9.847

Table 3. Impact strength of the neat resins reinforced with woven flax fabric.

Resin	Reinforcement	Charpy Impact Strength (kJ/m^2)	STD
MSO	Woven fabric	48.87	12.297
MMSO	Woven fabric	24.54	2.365
AMSO	Woven fabric	34.15	12.478

Table 4. Impact strength of the styrene blended resins reinforced with woven flax fabric.

Resin	Reinforcement	Charpy Impact Strength (kJ/m^2)	STD
MSO/ Styrene	Woven fabric	63.04	8.900
MMSO/ Styrene	Woven fabric	29.15	7.114
AMSO/ styrene	Woven fabric	62.75	13.995

Although the flexural strength of the neat AMSO resin reinforced with airlaid fibre is quite low (Figure 1), it has a high impact strength of about 51 kJ / m^2 (Table 1). The impact strength of the composites manufactured with MSO, MMSO and AMSO blended with styrene also show the same trend (Tables 2 and 4), because from Figure 2 and 4, it could be seen that the flexural strength of MMSO, MSO and AMSO resins blended with styrene and reinforced with airlaid flax fibre is 118 MPa, 57 MPa and 43 MPa respectively, while this order is reversed in the impact strength showing 22 kJ / m^2, 49 kJ / m^2 and 58 kJ / m^2 respectively (Table 2). Contrary to the flexural properties, the impact strength decreases with increasing fibre matrix adhesion [16].

It is well known that the impact response of the fibre composites is highly influenced by the interfacial bond strength, the matrix and fibre properties. Impact energy is dissipated by debonding, fibre and/ or matrix fracture and fibre pull-out [17]. Generally the impact strength increases with decreasing fibre-matrix adhesion and with decreasing lateral fibre length. The variation in data within different composite could be due to different fibre lengths, different average diameters and different aspect ratios. However the decrease in impact strength of all the composites based on MMSO thermoset resin as matrix is generally explained by its chemical structure as this resin has a higher cross-linking density to a higher number of reactive double bonds in the molecular structure. The resin is also more brittle, while the other two resins have a lower cross-linking density, which is seen as higher flexibility.

Flexural testing

Figures 1 to 4 and Tables 5 to 8 show the flexural strengths and flexural modulus respectively, of the methacrylated soybean oil (MSO), methacrylic anhydride modified (MMSO) and acetic anhydride modified (AMSO) resins reinforced with both airlaid and woven flax fibres. It could be seen that the flexural strength of the MMSO resin (with or without styrene) reinforced with airlaid or woven fabric fibre show higher flexural strength between 84 and 118 MPa and flexural modulus between 4 and 6 GPa. The flexural strength of the MSO resin reinforced with the flax fibres is between 49 and 81 MPa and the modulus between 2 and 4 GPa compared with AMSO composites having low flexural strength and modulus between 30 to 43 MPa and 1.7 to 2.57 GPa respectively.

The better flexural properties achieved in the MMSO matrix reinforced with flax fibre could be attributed to the higher number of methacrylate groups per triglyceride unit which is about 3, while this value is lower for the other resins.

The blending of the thermosetting resins with styrene (acting as a reactive diluent) was to impact some stiffness and improve the mechanical properties of the resulted composites. With the addition of 30 wt% styrene, the flexural strength and modulus of the MMSO resin reinforced with both airlaid and woven fabric increase considerably, indicating that blending with styrene gives a mechanically more elastic composite, due to longer crosslinks. AMSO resin (with styrene) shows a minimal increase in both strength and modulus. In contrast the MSO resin (with styrene) reinforced with woven fabric shows a negative effect, instead the flexural strength dropped from 81.8 to 53.7 MPa and the modulus from 4.69 to 2.74 GPa.

The higher mechanical strength of MMSO can be understood from their chemical structure [14]. The MMSO resin contains more reactive double bonds in one molecule, due to a doubled functionalisation. Comparing the composites prepared from neat resins to composites containing styrene, it is clear that adding styrene had a positive effect on the mechanical properties. This is expected. By adding styrene, crosslinking styrene bridges are formed between the triglyceride molecules, which increase the molecular flexibility.

The MMSO resin is promising, owing to the fact that the composites prepared with the neat resin have flexural strength of about 90.62 MPa and flexural modulus of 4.87 GPa. The MSO resin also shows good possibility of being used in composite applications. Composites made using MSO neat resin show fairly good mechanical properties, having flexural strength of 81.8 MPa and a flexural modulus of 4.69 GPA.

The biodegradable composites made from soybean oil and flax fibres can however be used in some technical applications due to their good mechanical properties.

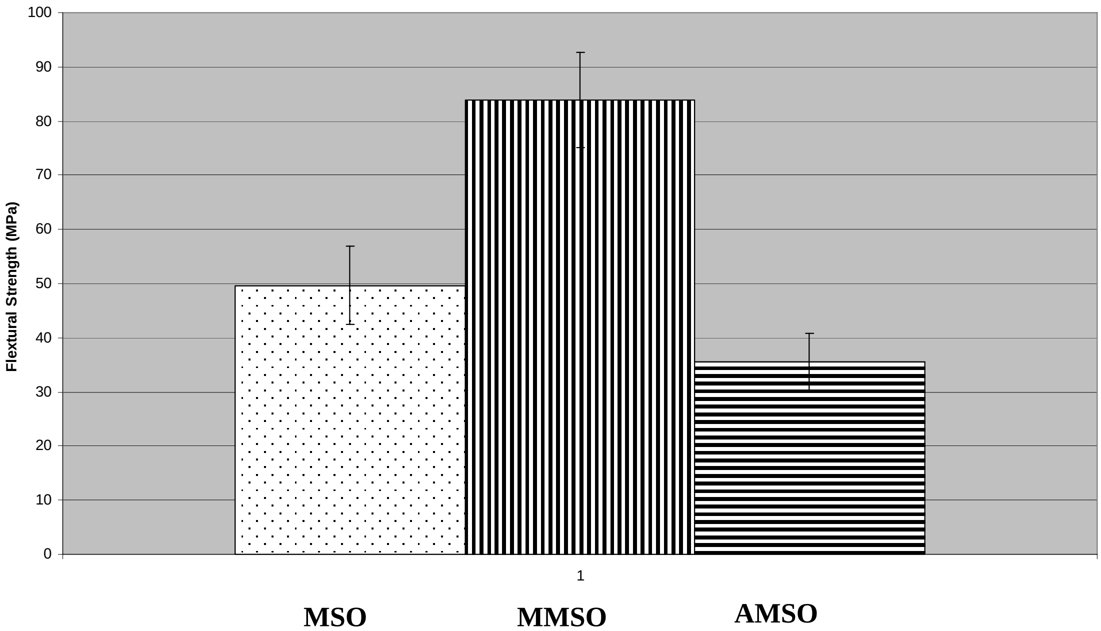

Figure 1. Flexural strength of the neat resins reinforced with airlaid flax fibre.

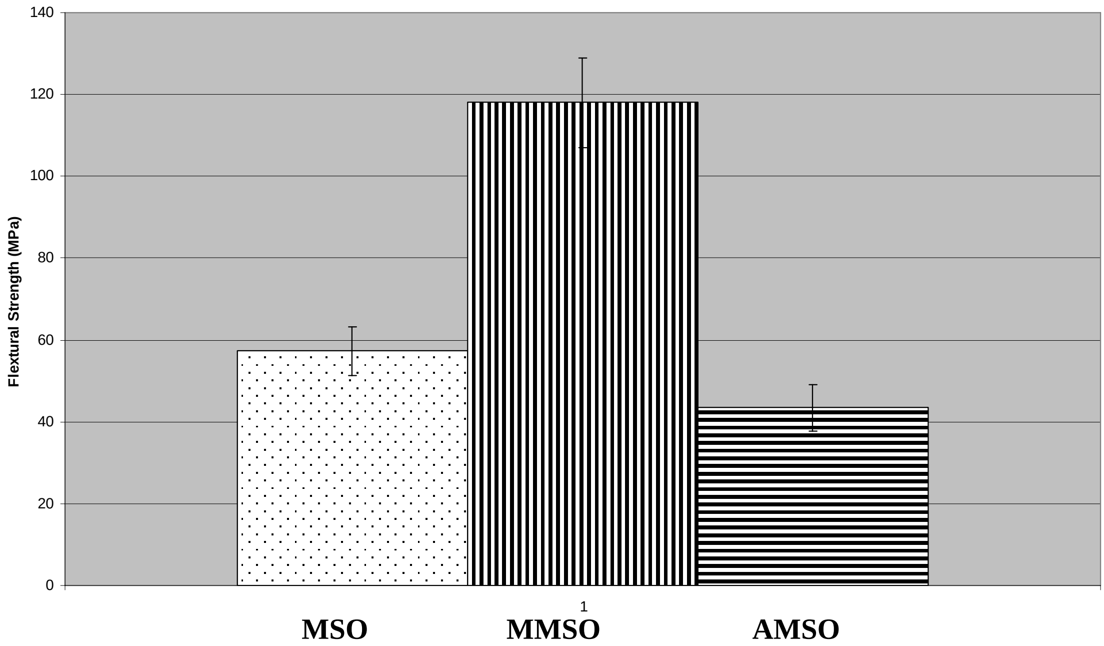

Figure 2. Flexural strength of the styrene blended resins reinforced with airlaid flax fibre.

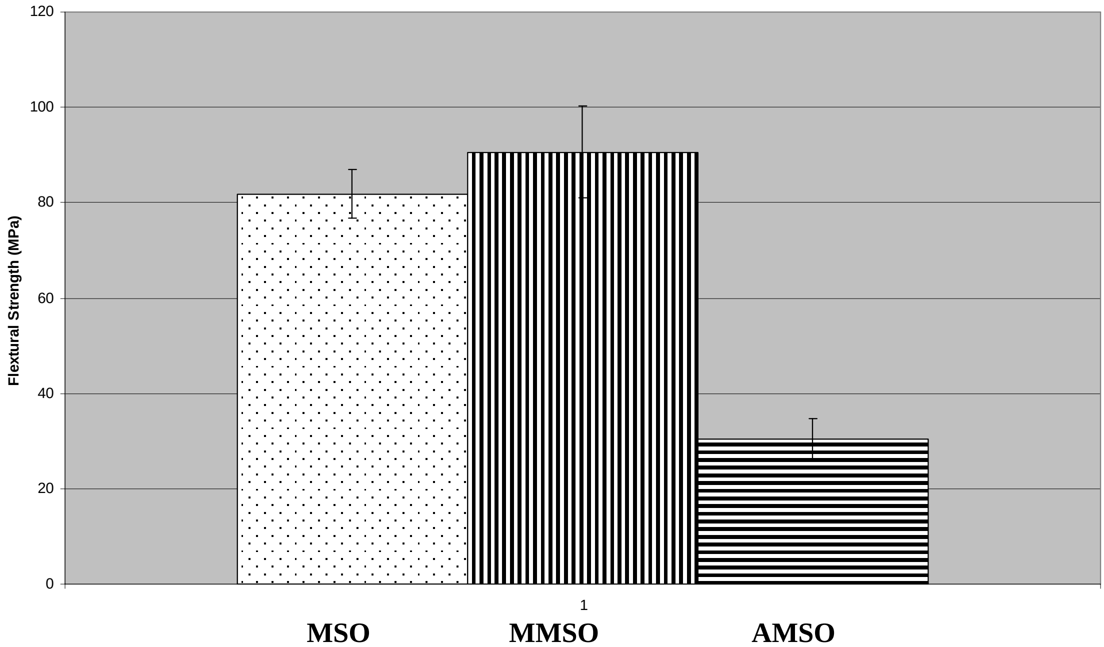

Figure 3. Flexural strength of the neat resins reinforced with woven flax fabric

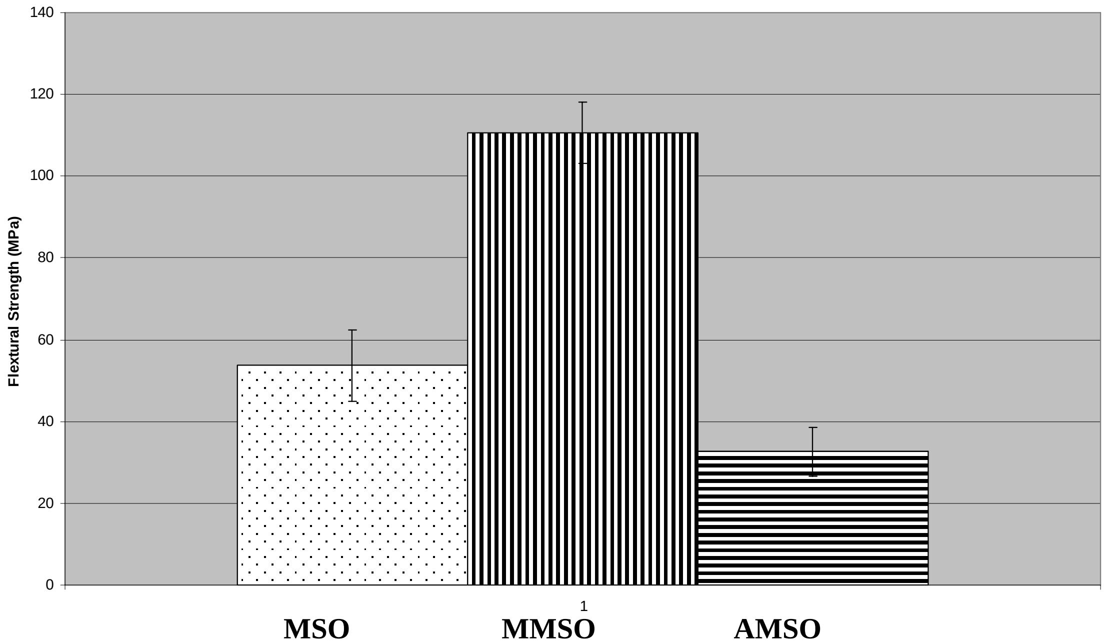

Figure 4. Flexural strength of the styrene blended resins reinforced with woven fabric.

Table 5. Flexural modulus of the neat resins reinforced with airlaid flax fibre

Resin	Reinforcement	Flexural Modulus (GPa)	STD
MSO	Airlaid flax fibre	2.774	0.948
MMSO	Airlaid flax fibre	4.349	0.782
AMSO	Airlaid flax fibre	1.834	0.881

Table 6. Flexural modulus of the styrene blended resins reinforced with airlaid flax fibre

Resin	Reinforcement	Flexural Modulus (GPa)	STD
MSO/ Styrene	Airlaid flax fibre	2.355	0.294
MMSO/ Styrene	Airlaid flax fibre	6.139	0.970
AMSO/ styrene	Airlaid flax fibre	2.576	0.761

Table 7. Flexural modulus of the neat resins reinforced with woven flax fabric

Resin	Reinforcement	Flexural Modulus (GPa)	STD
MSO	Woven fabric	4.694	0.78
MMSO	Woven fabric	4.876	0.86
AMSO	Woven fabric	1.745	0.96

Table 8. Flexural modulus of the styrene blended resins reinforced with woven flax fabric

Resin	Reinforcement	Flexural Modulus (GPa)	STD
MSO/ Styrene	Woven fabric	2.745	0.51
MMSO/ Styrene	Woven fabric	6.144	0.61
AMSO/ styrene	Woven fabric	1.832	0.89

CONCLUSIONS

This study investigated the processability and compatibility of methacrylated soybean oil thermosetting resins in natural fibre composites. Biobased composites can actually replace conventional composites from petrochemicals. The mechanical properties of the natural fibre composites produced using novel biobased thermosetting resins make them good candidates for technical applications.

The composites show relatively good flexural and impact strengths. MMSO neat resin reinforced with flax fibres show flexural strength between 83 MPa and 90 MPa and flexural modulus of 4.8 GPa, while the blending with styrene even show higher flexural strength between 110 MPa and 118 MPa and flexural modulus of 6.1 GPa. Composites manufactured with MSO and AMSO neat resins have a better impact strength up to 52 kJ / m^2 and 51 kJ / m^2 respectively. MSO and AMSO resins blended with styrene even gave higher impact strength up to 63 kJ / m^2 and 62 kJ / m^2 respectively. The SEM analysis of the sharp knife cut of composite specimens revealed the microstructure of the cross sectional area.

Addition of styrene gives an appreciable stiffness to the MMSO and AMSO resins reinforced with airlaid fibre, but has a negative effect on the MSO resin reinforced with airlaid fibre.

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