Synthesis and characterization of tall oil fatty acid based thermoset resin suitable for natural fiber reinforced composite

Rong Chen
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Rong Chen, s104509@student.hb.se
melody19861005@163.com

Master thesis

Subject Category: Technology

University of Borås
School of Engineering
SE-501 90 BORÅS
Telephone +46 033 435 4640

Examiner: Mikael Skrifvars
Supervisor,name: Dan Åkesson
Supervisor,address: School of engineering, University of Borås, Borås SE 501 90, Sweden

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Keywords: Tall oil fatty acid, modification, biobased thermoset resin, viscose fibre, biobased composite, compression moulding
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Abstract

Biobased thermoset resins were synthesized by functionalizing the tall oil fatty acid with hydrogen peroxide and then methacrylic anhydride. The obtained resins were characterized by FTIR to confirm the conversions. The cross-linking ability of the resins were checked by curing experiments and followed by DSC analysis regarding the extent of cross linking. TGA analysis was conducted to identify the thermal degradation patterns of cured resins. The obtained resins (blended with or without 33wt% styrene) were used as matrix and knitted viscose fibers were used as reinforcements to make biobased composites. Ten layers of knitted viscose fibers were stacked crosswise (0/90⁰C) and hand lay-up impregnation was performed. The fiber ratio of all composites was around 63-66%. The composites were characterized by flexural testing, dynamic mechanical thermal analysis and charpy testing. This work demonstrates that manufacture of composites with both matrix and reinforcement fiber coming from renewable resources is feasible, and the resulted composites have satisfied mechanical performance.

Keywords: Biobased thermoset, tall oil fatty acid, modification, viscose fibre, composite
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1. Introduction

Biobased thermosets have attracted more and more attention recently due to its sustainability and environment friendly characteristics [1]. Since biobased thermosets derive from renewable resources, which can be replaced at equal or greater rate than their rate of consumption, undoubtedly, biobased thermosets will substitute the position of traditional petroleum derived materials. New biobased thermoset is on its rapid developing, however, it is much more complicated than thermoplastic [2], since thermoset require its resin undergo cross-linking [3], which means the starting material for resin must contain reactive groups which can undergo cross-link by themselves, or reactive function groups which can be introduced into the resin’s molecules.

Plant oils are the good raw materials for thermosets [4], because they mainly consist of triglycerides, and they have different degree of unsaturations which due to the fatty acids inside. The most common plant oil, such as soybean oil and linseed oil, have been researched for a long time in the synthesis of biobased thermoset resins [1] since they are produced in large volumes and at relatively cheap price. Their high unsaturations make them very attractive as the starting material in the resin synthesis. Other vegetable or plant oils like castor oil [5, 6], sunflower oil and palm oil have been researched or undergoing research for more alternatives in the synthesis of biobased thermoset resin. Recently, tall oil has attracted special attention. Tall oil, the low cost, large quantity by-product of forest and pulp industry, has been used mainly in protective coatings, soaps and ore floatation [7, 8]. Tall oil fatty acids refined from crude tall oil consist predominantly of free-fatty acids (FFAs) i.e. oleic acid and linoleic acid, which make tall oil an attractive feedstock for the manufacture of fatty acid methyl esters (FAME), the biodiesel. Many researchers have reported their studies on the conversion of tall oil fatty acid to FAME products [9-11]. Since tall oil fatty acid also has unsaturation, it is can be considered as a possible option for the starting material of biobased thermoset.

Plant oils, although contain unsaturation and ester bonds; they are not reactive enough for cross linking, for this reason natural plant oils must be functionalized to improve their reactivity in order to synthesize the desired resin [12]. Unsaturated plant oil can be readily epoxidized, and the produced reactive epoxy groups make the resin more inclined to be able to react with other functional groups for further modification [13]. Therefore, epoxidation has been used widely as the first step of modification, which can be achieved by reactions with organic peracid or hydrogen peroxide [13]. Other paths have also been considered, for example hydroxylation [14-16]. Hydroxylation aims to transfer the unsaturation in plant oil into polyols. In this report, hydroxylation instead of epoxidation was adapted to convert the double bonds in tall oil fatty acid into hydroxyl groups, which provides another way to modify the tall oil fatty acid. In order to obtain good mechanical properties for composites, it is essential to produce the resin with high cross-linked densities when cured, therefore hydroxylated oils are limited in this aspect, which lead to further modification of the oil. The introduction of acrylate or methacrylate functional groups into polymer is generally used with the purpose of the double bonds inside can undergo free radical polymerization when cured, which can lead to the formation of a 3D net-work polymer [17]. In this report, some synthetic attempts to modify hydroxylated tall oil fatty acid by reaction with methacrylic anhydride were described. The resulted resin was therefore used as matrix in biobased composite preparation. Besides methacrylic anhydride, other chemicals like maleic anhydride and glycidyl methacrylate have been tested to increase the cross-linking ability of tall oil fatty acid; however the results are not ideal as that of methacrylic anhydride.
Polymer reinforced with fiber to generate high performance composite is quite sophisticated in today’s market. Fossil oil based polymers reinforced by synthetic fibers like glass fiber have their broad applications in different areas, however, from the sustainable development point of view, those composites cannot meet nowadays requirements. There are many ongoing research projects aim at producing composite with both polymer and fiber come from renewable resources. Natural fibers such as flax, jute, hemp and sisal are currently being used as reinforcement in industry for non-structural applications [18, 19]. Compared with synthetic fibers, natural fibers have several superior advantages like abundant resources, light weight, renewable and less expensive. The high modulus and rigidity which fiber impart to the material surpass that of the neat polymer [20]. However, natural fibers are not as strong as synthetic fibers and natural fibers’ properties may be fluctuated due to the seasonal reasons. For certain applications, the mechanical properties of natural fiber reinforced composite are not sufficient because of the low strength of the fiber, therefore, synthetic fibers blending with natural fiber offers an improved performance and possibly optimum cost.

The interfacial adhesion of the fiber and polymer is crucial to the mechanical properties of the composite. Natural fibers are hydrophilic, while most resins are hydrophobic, which create problems in the interfacial adhesion. The way of improve the interfacial adhesion will affect the resulting composite’ mechanical properties. Bledzki et al have discussed many physical and chemical methods for the modification of natural fibers to increase the chemical bonding between matrix and the fiber [21], such as fiber surface treatment, fiber coating and addition of coupling agent etc. In this report, all the fiber mats have been dried under vacuum at 105°C for 1h to reduce the water content in order to achieve better interfacial adhesion between the matrix and fiber.

Styrene, as a reactive diluent, is used frequently in available commercial synthetic resins. Blending styrene with resin can reduce its viscosity thus to ease the impregnation of the fibers. The double bond and aromatic ring in styrene make it a reactive co-monomer, resins combined with 30-50wt% styrene when undergo free radical polymerization can form rigid polymers with very high crosslink density, which improve the mechanical properties of the resulting composites, both storage modulus and flexural strength improvements have been observed [22-24]. However, blending styrene into the resin lowered the renewable content of the material in the composites, furthermore, styrene is a very volatile compound, when processing with the hot compress, styrene can easily evaporate which possess a substantial health risk [25, 26]. In this report, both neat resins and resins blended with 33wt% styrene were used in the preparation of the composites. The natural fiber reinforced composites were characterized by different mechanical testing.
2. Literature review

2.1 Plant oil

Plant oil which obtained from plant sources is quite abundant in nature. Soybean oil, castor oil, rape seed oil, palm oil are different examples of plant oils. Edible oils like soybean oil has its extensive application in food industry and inedible oil like tung oil and castor oil have been used widely in lubricants, pharmaceuticals and protective coatings. Plant oils are triglycerides which contain different fatty acids (see table 1) such as oleic acid, linoleic acid, stearic acid, myristic acid, licanic acid and palmitic acid. Those fatty acids are either saturated or unsaturated, have significant difference in chain length, distribution, location and composition, which lead to differences in the physical and chemical properties of those oils [27]. Most plant oils compared with other kinds of oils are relatively cheap.

Table 1. The composition of some fatty acid in plant oils [28]

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid</td>
<td>C_{14}H_{28}O_{2}</td>
<td>CH_{3}(CH_{2})_{13}COOH</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C_{15}H_{31}O_{2}</td>
<td>CH_{3}(CH_{2})_{15}COOH</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>C_{16}H_{33}O_{2}</td>
<td>CH_{3}(CH_{2})_{15}COOH</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C_{17}H_{35}O_{2}</td>
<td>CH_{3}(CH_{2})_{17}COOH</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>CH_{3}(CH_{2})_{16}COOH</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>CH_{3}(CH_{2})_{15}COOH</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>CH_{3}(CH_{2})_{14}COOH</td>
</tr>
<tr>
<td>α-Eleostearic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>CH_{3}(CH_{2})_{15}COOH</td>
</tr>
<tr>
<td>Ricinoleic acid</td>
<td>C_{18}H_{34}O_{2}</td>
<td>CH_{3}(CH_{2})_{16}COOH</td>
</tr>
</tbody>
</table>

The chain length of the fatty acids varies from 16 to 20 carbon atoms is most common in nature. Fatty acids can be saturated, unsaturated, conjugated or isolated. And the unsaturation can be either mono-saturated or polysaturated. Different fatty acids have different levels of unsaturation, and the unsaturated parts that can be chemically modified to give the desired matrix which can be used in the composite. The more unsaturated a fatty acid is, the more susceptible it is to be functionalized. The liquid resin obtained from chemical modification with various functional groups can undergo free radical polymerization during curing process. Usually, the degree of unsaturation is measured by the iodine value. For example, the iodine value for tall oil fatty acid is 155 and the iodine value for oleic acid is 89 [29].

2.2 Chemical modification of plant oil

The plant oil itself cannot be used as the matrix in composite, because the carbon-carbon double bonds inside are not sufficient enough to undergo polymerization to give resin with any degree of stiffness or structural strength, however those plant oil molecules offer reactive cites for modification such as the ester group, double bond and alkyl carbons. Active functional groups can be introduced into those cites.
Unsaturated plant oil can be readily epoxidized (see figure 1). Epoxidized plant oil is manufactured by expoxidation of the double bonds of the plant oil with hydrogen peroxide. And the double bonds can be hydroxylized (see figure 2) in a similar way.

Figure 1 An epoxidized triglyceride [15]

Figure 2 A hydroxylated triglyceride [15]
2.3 Acrylated and methacrylated plant oil for bio-based polymers

To produce the thermosetting resin with good cross linking ability, epoxidized plant oil or hydroxylated plant oil needs further modification. Various synthetic ways have been reported regarding this aspect. The modifications were done with different reagents, for example epoxidized soybean oil (ESO) or hydroxylated soybean oil react with methacrylic acid to give methacrylated soybean oil (MSO), react with maleic anhydride to give maleinized soybean oil (MASO).

Adekunle et al. [17] made a ring opening polymerization with methacrylic acid to produce methacrylated soybean oil, see figure 3.

Figure 3 Methacrylated soybean oil [17]

After reaction with methacrylic acid through hydrolysis, the methacrylate groups have been attached into the soybean oil molecule. The newly formed hydroxyl groups and unreacted epoxy group can be modified further with other functional groups like alkyl or aromatic diols, anhydrides, carboxylic acids, and diamines. See figure 4.
MSO undergo further modification with acetic anhydride to produce acetic anhydride modified methacrylated soybean oil (AMSO) [17]

The obtained resin can be cured by using an initiator through free radical polymerization. In the presence of initiators like benzoyl peroxide, tert-butyl peroxy benzoate, methyl ethyl ketone peroxide and dibenzoyl peroxide, the resin can be cured and give a stiff polymer.

Lu et al [23] synthesized thermosetting resins, maleic anhydride was used to modify the oil. The resulted resin was blended with 33wt% styrene to form rigid polymer. Those authors found out that increase the maleic anhydride’ molar ratio in the reaction can increase the corresponding storage modulus and glass transition temperature. Scala et al [30] also conclude that the cross linking density is directly proportional to the number of acrylates per triglyceride. In this report, a similar experiment was also performed, three different ratio of methacrylic anhydride to tall oil fatty acid were synthesized to compare their cross linking ability and the resulted resins were blended with 33wt% styrene to compare the resulting composites’ stiffness. It was found that more methacrylate groups in the resin more cross link density were observed and the addition of styrene increased both flexural strength and storage modulus. Styrene reduces the viscosity of the resin and its aromatic ring and double bond increase the cross linking density, however, styrene is volatile and toxic, healthy problems should be highly concerned for its emission.

Compared with maleic anhydride, methacrylic anhydride seems have better performance in the further modification because when using maleic anhydride, carboxylic acid is formed. This will cause hydrogen bonds formation in the resin, which leads to higher viscosity in the resin, while for composite making, complete wetting of the fiber is crucial. In this case, for methacrylic anhydride modified resin, the addition of reactive diluent such as styrene may not be necessary. And the produced methacrylic acid during the modification procedure does not need to be isolated, since the purpose of modification is to introduce more reactive functional groups like double bond and methacrylate groups into the resin.
2.4 Natural fiber as the reinforcement

Natural fiber as reinforcement has its superior advantages over the synthetic fiber such as low cost, light weight, lack of toxicity, abundant availability, renewability, biodegradability and carbon neutrality etc, therefore have attracted many researchers’ attention. Natural fiber such as flax, viscose, hemp, jute, sisal, bamboo has been researched extensively [31, 32]. A lot of factors can affect the properties of natural fiber, for example: climate changes, geographic conditions, how the fiber is being harvested etc. Those factors lead to the irregular properties of natural fiber, which is the major disadvantage when compared with synthetic fibers [32], because synthetic fibers have constant properties which due to the sophisticated production techniques. The inconsistency of the natural fiber affects their applications, especially in high performance applications. The disadvantage of natural fiber causes negative effect on the resulting composites, such as poor interfacial adhesion, low thermal stability, moisture uptake, poor wettability etc [33]. Natural fibers are hydrophilic, while many resins are hydrophobic, and this will make the prediction of the resulting composites’ properties difficult. Table 2 shows the chemical composition of some natural fibers and table 3 exhibits the comparison of some mechanical properties between natural fibers and synthetic fibers.

Table 2: chemical composition and structural parameters of some natural fibers [21]

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Cellulose (Wt %)</th>
<th>Cell Length (mm)</th>
<th>Spiral Angle (Deg)</th>
<th>Hemi-cellulose (Wt %)</th>
<th>Pectin (Wt %)</th>
<th>Lignin (Wt %)</th>
<th>Wax (Wt %)</th>
<th>Moisture Content (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute</td>
<td>61.0</td>
<td>2.3</td>
<td>8.0</td>
<td>20.4</td>
<td>0.2</td>
<td>13.0</td>
<td>0.5</td>
<td>12.6</td>
</tr>
<tr>
<td>Flax</td>
<td>71.0</td>
<td>20.0</td>
<td>10.0</td>
<td>18.6</td>
<td>2.3</td>
<td>2.2</td>
<td>1.7</td>
<td>10.0</td>
</tr>
<tr>
<td>Hemp</td>
<td>74.4</td>
<td>23.0</td>
<td>6.2</td>
<td>17.9</td>
<td>0.9</td>
<td>3.7</td>
<td>0.8</td>
<td>10.8</td>
</tr>
<tr>
<td>Ramie</td>
<td>68.6</td>
<td>14.0</td>
<td>7.5</td>
<td>13.1</td>
<td>1.9</td>
<td>0.6</td>
<td>0.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Sisal</td>
<td>78.0</td>
<td>2.2</td>
<td>20.0</td>
<td>10.0</td>
<td>—</td>
<td>8.0</td>
<td>2.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Coir</td>
<td>43.0</td>
<td>0.8</td>
<td>45.0</td>
<td>0.3</td>
<td>4.0</td>
<td>45.0</td>
<td>—</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 3: Comparative Values of natural fibers with Conventional Reinforcing Fibers [21]

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Density (g/cm³)</th>
<th>Elongation to Break (%)</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jute</td>
<td>1.45</td>
<td>1.5</td>
<td>550</td>
<td>13</td>
<td>0.3</td>
</tr>
<tr>
<td>Flax</td>
<td>1.50</td>
<td>2.4</td>
<td>1100</td>
<td>100</td>
<td>—</td>
</tr>
<tr>
<td>Hemp</td>
<td>—</td>
<td>1.6</td>
<td>690</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.50</td>
<td>1.2</td>
<td>870</td>
<td>128</td>
<td>—</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.45</td>
<td>2.9</td>
<td>640</td>
<td>15</td>
<td>0.36</td>
</tr>
<tr>
<td>Coir</td>
<td>1.15</td>
<td>15.0</td>
<td>149</td>
<td>5</td>
<td>0.25</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.50</td>
<td>2.5</td>
<td>2000-3500</td>
<td>70</td>
<td>3.25</td>
</tr>
<tr>
<td>S-glass</td>
<td>2.50</td>
<td>2.8</td>
<td>4570</td>
<td>88</td>
<td>—</td>
</tr>
<tr>
<td>Aramid (normal type)</td>
<td>1.40</td>
<td>3.3-3.7</td>
<td>3000-3150</td>
<td>63-67</td>
<td>—</td>
</tr>
<tr>
<td>Carbon (high tensile strength)</td>
<td>1.70</td>
<td>1.4-1.8</td>
<td>4000</td>
<td>230-240</td>
<td>&gt; 16</td>
</tr>
</tbody>
</table>
2.5 Pretreatment of natural fiber

In view of all those disadvantages and shortcomings of natural fiber, pretreatment of fiber is important to improve the overall properties of the fiber. To achieve strong adhesion between the fiber and matrix, fiber needs to be treated either by chemical or physical methods.

Alkali treatment, for instance a chemical treatment has been used widely for cotton materials, during the treatment, impurities, wax and lignin can be removed, therefore the surface roughness can be enhanced, and the hydrogen bonds exist in the cellulose molecules may break and form a bond with the coupling agent, as a result, the number of functional groups available to bond with resins will be increased in the fiber [34]. Pothan et al chemically modified the banana fiber to achieve better interfacial interaction; they concluded that significant influence on the surface polarity can be achieved after chemical treatment. Wang et al [35] investigated the effects of different chemical treatments on the mechanical and physical properties of the resulting natural fiber reinforced composites. Use of enzyme provides an environmentally friendly way of improving the quality of fiber, which was explored by Stuart et al [36].

Physical methods such as stretching and thermo treatment do not change the chemical composition of the fiber, but they can change the structural and surface properties of natural fiber, therefore the mechanical bonding to polymer can achieved. Åkesson et al [37] dried the fiber mat in vacuum oven for 1h at 105°C prior to use, aims to reduce the water content in the fiber mat to achieve better interfacial adhesion. And plasma treatment is a process which changes the surface energy of the fiber, depending on the type and nature of the gases, various surface modifications can be done by using plasma treatment, therefore the surface energy of fiber can be either increased or decreased, while surface cross linking, reactive free radicals can be produced [38].

Natural fibers are excellent alternative for reinforcement, but they have to be treated before use to achieve the desired technical properties. Physical and chemical methods can be chosen depending on what kind of modification need to be achieved. Since natural fibers are grown in different geographic locations and have different climates and sources, therefore, the need to use an appropriate method of modification is crucial. The effects of different fiber treatments actually improve the adhesion between the matrix and fiber, thereby providing good mechanical properties for the resulting natural fiber reinforced composite.

2.6 Regenerated cellulose fibers for composites

As mentioned before, natural fibers have the advantages of being natural, renewable and biodegradable; however, fibers’ properties are highly variable due to the inherent natural conditions. Regenerated cellulose fibers, which are produced by dissolution of pulp in a suitable solvent and subsequent spinning, show a possible advantage of being less variable. Adusumali et al. [39] compared the mechanical properties of regenerated cellulose fiber with that of flax fiber, which is the currently most important natural reinforcement fiber, they found out that the average modulus of tensile strength and elasticity of regenerated cellulose fiber is lower than that of flax fiber, but when variability was considered, both fibers performed similarly. Regenerated cellulose fiber such as viscose, modal and lyocell are among the most important fibers from the point of environment aspect [40], and in this report, knitted viscose fiber was chosen as the reinforcement for the composite.
2.7 Preparation of biocomposites

Biocomposites mean, in this report, both matrix and reinforcement all come from biobased resources. Biocomposites which are light and strong can, to some extent, even compete with traditional materials such as wood or metals. There are a lot of methods that can be used to produce composites, such as hand lay-up, spray impregnation, sheet moulding compound etc. While among all those methods, hand lay-up is the most basic technique for producing composites. Fiber mat as the reinforcement is laid at the bottom of the mould and the resin blended with initiator is poured onto the surface of the reinforcement and compressed by compression moulding at a high temperature. Hand lay-up is simple but laborious method for producing composite.

2.7.1 Composites prepared from acrylated and methacrylated thermoset resins with natural fiber as the reinforcement

There have been several reports about the composites made from acrylated or methacrylated soybean oil. Åkesson et al [37] produced composites from acrylated soybean oil with air laid flax mat as the reinforcement. A spray impregnation method was adopted. The composites were compression molded at 160°C for 6 min. The fiber content varied between 30 and 70wt% and the tensile modulus of the resulting composites ranged from 5 GPa to 9.7 GPa (see table 4).

<table>
<thead>
<tr>
<th>Fibre mat</th>
<th>Fibre content (wt %)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air laid flax</td>
<td>70</td>
<td>78 (±14)</td>
<td>9.7 (±0.9)</td>
</tr>
<tr>
<td>Air laid flax</td>
<td>60</td>
<td>71 (±26)</td>
<td>9.7 (±2.8)</td>
</tr>
<tr>
<td>Air laid flax</td>
<td>50</td>
<td>61 (±7.8)</td>
<td>6.3 (±1.2)</td>
</tr>
<tr>
<td>Air laid flax</td>
<td>40</td>
<td>50 (±6.4)</td>
<td>5.0 (±0.5)</td>
</tr>
</tbody>
</table>

The standard deviation is given in the brackets.

In another study, Adekunle et al [22] examined the properties of composites made from three different resins reinforced by two different fibers. Three resins from soybean oil: methacrylated soybean oil (MSO), methacrylic anhydride modified soybean oil (MMSO), and acetic anhydride modified soybean oil (AMSO) were used as matrix, two different fibers: air-laid flax fibers and woven flax fabric were used as the reinforcement. Three resins were blended with 30wt% styrene to compare the effects on the resulted composites. The composites prepared from neat resins were cured at 170°C, while the composites with blended resin were cured at 40°C and postcured at 170°C. The fiber/resin ratio was 60:40. The impact strength and flexural modulus varied depending on the nature of the fibers and resins. See figure 5 and 6 below:
In another report, Williams and Wool [41] prepared the composites from acrylated epoxidized soy oil. The thermoset resin was blended with styrene and divinylbenzene in the ratio 100: 45: 5 by weight. Two different fiber flax and hemp were used. The composites were prepared by resin transfer moulding. Fiber ratio varied from 20% to 40%. Both tensile and flexural strength varied according to the nature of fiber and different fiber ratios.

2.7.2 The use of styrene in the production of composites

A lot of studies showed that commercial resins are always blended with styrene. Styrene as a reactive diluent is quite suitable for blending with resins. Blending resin with styrene can reduce resin’s viscosity, which ease the impregnation process, especially when using the infusion techniques. Since styrene has aromatic ring and carbon carbon double bond in its molecule, styrene can impact more stiffness into the composites, which will improve the composites’ mechanical performance. However adding styrene inside lower the content of
renewable material in the resulting composites, and its volatile nature and toxic properties possess high health risk. So it is desirable to produce composite with as high renewable content as possible.

3. Synthesis schemes

In order to synthesize the thermosetting resin from tall oil fatty acid, reactive functional groups must be introduced into the molecule to increase its cross-linking ability, three different synthetic schemes have been considered and trial experiments have been carried out to testify their feasibility.

Scheme 1

Figure 7: synthesis scheme 1
Scheme 1 (see figure 7) used hydrogen peroxide and formic acid in the first step to convert the double bond in tall oil fatty acid into hydroxyl groups by oxidation, then introduce the methacrylate into the molecule chain by esterification between methacrylic anhydride and hydroxyl groups.

Both scheme 2 and scheme 3 share the same first modification step as scheme 1.

Scheme 2

Figure 8: synthesis scheme 2

Instead of using methacrylic anhydride, maleic anhydride was used to modify the hydroxylated tall oil fatty acid[23], since maleic anhydride can also undergo esterification with hydroxyl groups according to the theory (see figure 8).
Glycidyl methacrylate seems to be a good modifier since it contains both methacrylate and epoxy group in its molecule, scheme 3 (see figure 9) tried to conduct a epoxy ring opening route to attach the GMA into the TOFA molecule chain [42].

After trial experiments, only scheme 1 seemed promising as the obtained resin can be cured to form stiff solid, while for scheme 2 and scheme 3, only rubber-like solids were obtained, which indicating unsuccessful cross linking modification, therefore, this report focus on the first scheme to modify the tall oil fatty acid and make the corresponding composites.
4. Experimental

4.1 Resin synthesis

4.1.1 Materials
Tall oil fatty acid (Sylfat 2LT) was supplied by Arizona Chemical AB, Sweden. Formic acid (98-100%) and hydrogen peroxide (30%, w/w) purchased from Scharlau, Spain were used in the first step modification. Methacrylic anhydride (94%), maleic anhydride, glycidyl methacrylate were used for further modification of hydroxylated tall oil fatty acid in different synthesis schemes. 1-Methylimidazole (99%) was used as catalyst and hydroquinone (99%) was used as cross-linking inhibitor in scheme 1 and scheme 2. N,N,N′,N′-Tetraethylmethanediamine was used as catalyst and dimethyl sulfoxide was used as co-solvent in scheme 3. All chemicals used in further modification steps were supplied by Sigma-Aldrich chemical company, USA except for hydroquinone, which was supplied by Fisher Scientific, Sweden. Benzoyl peroxide (75%) and tert-Butyl peroxybenzoate (98%) were used as the free radical initiator for the curing process and composite making process, N, N-Dimethylaniline (99%) was used as accelerator in the curing process.

4.1.2 Synthesis of hydroxylated tall oil fatty acid (HOTOFA)
300g tall oil fatty acid in a three-necked round bottom flask placed in oil bath was stirred vigorously at 35°C (see figure 10); 60g formic acid was added in one portion, after stirring for a few minutes, 120g hydrogen peroxide was then slowly added (drop wise). During addition, the temperature was carefully kept below 40°C. At the end of addition, the temperature was raised to 70°C, after heating for 7h, the heat source was removed and stirring was continued to allow the reactants mixture to cool down to room temperature. The mixture was transferred into a separatory funnel, after standing still for a while, the mixture separated into two layers and the aqueous layer containing formic acid and hydrogen peroxide was removed, then 200g ethyl acetate was added as diluents into the cream-colored product and followed by washing sequentially with saturated NaCl solution and saturated NaHCO₃ to reach a pH of 7, then the organic layer was washed multiple times with deionized water. After removal of the aqueous layer, the washed solution was dried over anhydrous sodium sulfate. Ethyl acetate was removed from the mixture by rotatory evaporation under vacuum. The yield of hydroxylated tall oil fatty acid was 316g.
4.1.3 Further modification of hydroxylated tall oil fatty acid with methacrylic anhydride to produce methacrylated tall oil fatty acid (MHOTOFA)

The iodine value for tall oil fatty acid (TOFA) used in this report is 155, therefore TOFA has approximately 1.7 double bonds per one molecule, after hydroxylation, hydroxylated tall oil fatty acid (HOTOFA) has 3.4 hydroxyl (–OH) per one molecule. According to synthesis scheme, one methacrylic anhydride (MA) molecule reacts with one –OH group, in view of possible steric hindrance and incomplete reaction, three different molar ratios of methacrylic anhydride to HOTOFA (table 5) were used to synthesize the resins in order to compare the effect of the ratio on the resulting polymer properties.

120 g Hydroxylated tall oil fatty acid (HOTOFA) dissolved in 60g toluene was heated under reflux at 70°C in a three-necked round bottom flask with (1wt%, 1.8g) 1-Methylimidazole (99%) as the catalyst. After stirring for a few minutes to reach the homogeneous solution, 120g methacrylic anhydride (1:1 mass ratio) containing (0.25wt% 0.3g) hydroquinone was added slowly (drop wise) into the flask. At the end of addition, the temperature was raised to 82°C. Then the reaction proceeded for 3h with vigorous stirring. After 3h, the heat was removed and the reactants mixture was stirred continually to cool down to room temperature. Toluene was removed by rotatory evaporation under vacuum.
Mass ratio 1.5 to 1 and 1.76 to 1 was synthesized as above described.

Table 5: Different mass ratio of MA to HOTOFA

<table>
<thead>
<tr>
<th>MHOTOFA1 : 1</th>
<th>Molar ratio (MA: HOTOFA)</th>
<th>Mass ratio (MA:HOTOFA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.3 : 1</td>
<td>1 : 1</td>
</tr>
<tr>
<td>MHOTOFA1.5 : 1</td>
<td>3.4 : 1</td>
<td>1.5 : 1</td>
</tr>
<tr>
<td>MHOTOFA1.76 : 1</td>
<td>4 : 1</td>
<td>1.76 : 1</td>
</tr>
</tbody>
</table>

Figure 11: the obtained resins with three different mass ratio of MA to HOTOFA

As the amount of methacrylic anhydride is increasing in the reactions, the obtained resins show a decreasing viscosity (see figure 11).

4.1.4 Curing process
The curing process was carried out in two steps by first mixing the obtained resins (blended with or without 33wt% styrene) with 2wt% benzoyl peroxide as the catalyst and 0.5wt% N,N-Dimethylaniline as the accelerator and let them cure in room temperature for 1h, then placing them in an oven heated up to 150 °C for another 1h as post-cure. All the scheme 1 resins solidified at room temperature and became into stiff solids after one hour high temperature curing.
4.2 Trial experiments for scheme 2 and scheme 3

4.2.1 Further modification of hydroxylated tall oil fatty acid with maleic anhydride to produce maleated tall oil fatty acid
16 g HOTOF A dissolved in 8 g toluene was heated under reflux at 70°C in a three-necked round bottom flask with (1wt%, 0.24 g) 1-Methylimidazole (99%) as the catalyst. After stirring for a few minutes to reach the homogeneous solution, 8 g maleic anhydride (ground into powder) containing (0.25wt% 0.02 g) hydroquinone was added slowly into the flask. At the end of addition, the temperature was raised to 82°C. Then the reaction proceeded for 3 h with vigorous stirring. After 3 h, the heat was removed and the mixture was stirred continually to cool down to room temperature. Toluene was removed by rotatory evaporation under vacuum. The obtained resin after evaporation is quite thick. After curing, the resin could not form stiff solid, only rubber like solid was obtained, which indicating unsuccessful crosslink leading-in into the hydroxylated tall oil fatty acid.

4.2.2 Further modification of hydroxylated tall oil fatty acid with glycidyl methacrylate (GMA) to produce glycidyl methacrylated tall oil fatty acid
10 g HOTOF A dissolved in 20 g dimethyl sulfoxide (DMSO) was heated under reflux at 62°C in a three-necked round bottom flask. 0.18 g N,N,N’,N’-Tetraethylmethanediamine (1mol% relative to the HOTOF A hydroxyl groups) was added into the flask as the catalyst. After stirring for a few minutes to reach the homogeneous solution, 16.34 g glycidyl methacrylate was then added slowly into the flask. The molar ratio of GMA to the hydroxyl groups in HOTOF A is 1:1. The temperature was kept at 62°C and vigorous stirring was continued for 36 h. After 36 h, the heat was removed and the mixture was allowed to cool down to room temperature. The mixture was transferred into a separatory funnel and washed with deionized water sequentially to get rid of the DMSO. After removal of the aqueous layer, 30 g ethanol was added as the diluent for further extraction of possible DMSO remained in the resin. Ethanol was removed by rotatory evaporation under vacuum. Similar as scheme 2, after curing, only rubber like solid was obtained, which indicating unsuccessful modification.

4.3 Characterization of resins

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the synthesized resins in order to testify the chemical modification reactions. The FTIR analysis was carried out by NICOLET, iS10. Cured samples have been checked also to see the degree of curing.

The differential scanning calorimetry (DSC) analysis was done by a TA instrument DSC Q1000. For solid sample, around 5 mg sample size was used, while for liquid sample, 1 to 2 mg sample size was taken to avoid possible leakage when sealed into aluminum pan by compression. Samples were equilibrated at 0°C, and then heated at a ramping rate of 10°C/min to 250°C; cooling rate of 20°C/min was applied and then heated again at the same ramping rate 10°C/min to 250°C. The heat-cool-heat cycles were conducted with a nitrogen purge steam, with a flow rate at 50 ml/min.
The thermogravimetric analysis (TGA) was done by using TA instrument TGA Q500 to identify the thermal degradation patterns of cured resins. Samples of 10 to 15mg were heated from room temperature to 600°C with a ramping speed of 10°C/min under a nitrogen atmosphere.

4.4 Results and discussion of resins

4.4.1 FTIR analysis of the synthesized thermoset resins

Figure 12: FTIR spectra comparison of TOFA and HOTOFA resins

Figure 12 shows the first step of modification: hydroxylation of the double bond in tall oil fatty acid. Typical hydroxyl absorption is around 3200-3650 cm⁻¹, which is absent in TOFA, while strong and broad hydroxyl absorption can be seen in HOTOFA. The weak absorption at 3008 cm⁻¹ in TOFA is the CH stretching of double bond(CH=CH), this absorption became weaker in HOTOFA, which indicates a successful hydroxylation of the double bond in TOFA. The remaining weak absorption of CH=CH may due to the polyunsaturated acids and some free fatty acids in TOFA.
Figure 13: FTIR spectra comparison of HOTOFa, MHOTOFA 1:1, MHOTOFA 1.5:1 and MHOTOFA 1.76:1 resins.

Figure 13 shows the second step: further modification of HOTOFa with different mass ratios of methacrylic anhydride. Hydroxyl group at 3200-3650 cm\(^{-1}\) in HOTOFa disappeared in three different ratios MHOTOFA, while double bond (C=C) appears at 1636 cm\(^{-1}\) and carbonyl group (C=O) appears at 1784 cm\(^{-1}\) in the FTIR spectra of MOHOTA respectively, which shows the functional groups of methacrylic anhydride have been successfully attached to the HOTOFa molecules.

4.4.2 Differential scanning calorimetry, investigation of the curing result
When heated initially, thermosetting resins undergo curing to form a three dimensional cross linked network. Once the thermoset is cured, it cannot be reformed or reprocessed. DSC can be used to check the curing results of the thermosetting resin. Both neat resins and resins blended with 33wt% styrene were blended with 2wt% benzoyl peroxide (BPO) as the initiator and 0.5% N, N-Dimethylaniline as the accelerator, all the resins were firstly cured at room temperature for 1h and post cured in 150\(^{\circ}\)C for another 1h. Uncured resins were prepared without addition of accelerator for the comparison. Both cured and uncured resins were analyzed by DSC.
Figure 14: DSC curve of uncured MHOTOFA 1to1 (no styrene) resin

Figure 14 shows a DSC scan profile for the sample of uncured MHOTOFA 1to1 (no styrene) resin, the peak above the baseline representing an exothermic event. The peak of this curing exotherm is 113.57°C, indicating that the fastest cure for this resin will occur at this temperature. The onset of the cure peak for this resin is 89.84°C and the total heat of the reaction is 205.8J/g.
The DSC scan for the sample of cured MHOTOFA 1to1 resin (no styrene, cured in room T for 1h and post cured in 150°C for another 1h) shows no exotherm peak indicating most of the theoretical cross-linking reactions were completed during the cure process (see figure 15).

Figure 15: DSC curve for cured MHOTOFA 1to1 resin (no styrene, room T for 1h and post cure in 150°C for another 1h)

Figure 16: Comparison of the DSC scan for cured and uncured MHOTOFA 1to1 (no styrene) resin.
All cured resins were checked by DSC, the heat of exotherm is almost 0J/g, indicating all resins can be cured to completion by room temperature for 1h and 150°C for another 1h (see figure 16).

Table 6: DSC analysis table of all uncured resin samples

<table>
<thead>
<tr>
<th></th>
<th>Uncured resins</th>
<th>Onset temperature (°C)</th>
<th>Derivative temperature(°C)</th>
<th>Heat of exotherm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without blending with styrene</td>
<td>MHOTOFA1:1</td>
<td>89.8</td>
<td>113.6</td>
<td>205.8</td>
</tr>
<tr>
<td></td>
<td>MHOTOFA1.5:1</td>
<td>89.8</td>
<td>119.6</td>
<td>188.8</td>
</tr>
<tr>
<td></td>
<td>MHOTOFA1.76:1</td>
<td>89.1</td>
<td>114.9</td>
<td>138.2</td>
</tr>
<tr>
<td>Blending with styrene</td>
<td>MHOTOFA1:1</td>
<td>81.1</td>
<td>107.6</td>
<td>101.3</td>
</tr>
<tr>
<td></td>
<td>MHOTOFA1.5:1</td>
<td>90.3</td>
<td>115.2</td>
<td>138.5</td>
</tr>
<tr>
<td></td>
<td>MHOTOFA1.76:1</td>
<td>85.8</td>
<td>109.4</td>
<td>107.0</td>
</tr>
</tbody>
</table>

From the table 6, it can be seen that resins without blending styrene released out more heat during the curing process, which indicates more double bonds inside the resins. While for resins blended with styrene, smaller heat of exotherm was observed, this can be explained by the volatile nature of styrene, when the resin was heated, the styrene inside evaporated vigorously and at the same time took some resin away, thereby, less resin left to be cured.

4.4.3 Thermogravimetric analysis of the cured resins

TGA for cured resins was conducted to identify their degradation characteristics. The percentage weight loss of the cured sample is recorded when sample is heated, the loss in weight over specific temperature range (room temperature to 600°C) indicates the composition of the resins. The cured MHOTOFA 1:1 resin (without blending styrene) was stable up to 190°C with no significant weight loss, the initial 5% weight loss was observed at 196.77°C, indicating the loss of volatiles and moistures. Significant weight loss (10%) began at 227.87°C due to the degradation of the resin. When temperature reached 420.59°C, 90% weight loss was recorded. The maximum rate of decomposition occurred at 414.78°C with a degrading rate of 1.164%/°C, the residual mass is around 0.21mg (see figure 17).

The same experiment was conducted for other cured resins.
Figure 17: TGA analysis of cured MHOTOFA 1:1 resin (no styrene)

Table 7: TGA analysis for different cured resins

<table>
<thead>
<tr>
<th></th>
<th>Initial loss (5%) temperature/°C</th>
<th>Significant loss (10%) temperature/°C</th>
<th>90% weight loss temperature/°C</th>
<th>Derivative temperature/°C</th>
<th>Residue (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No styrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MHOTOFA 1:1</td>
<td>197</td>
<td>228</td>
<td>421</td>
<td>415</td>
<td>2.19</td>
</tr>
<tr>
<td>MHOTOFA 1.5:1</td>
<td>189</td>
<td>223</td>
<td>422</td>
<td>416</td>
<td>3.08</td>
</tr>
<tr>
<td>MHOTOFA 1.76:1</td>
<td>196</td>
<td>231</td>
<td>423</td>
<td>417</td>
<td>3.28</td>
</tr>
<tr>
<td>Blend with styrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MHOTOFA 1:1</td>
<td>210</td>
<td>260</td>
<td>410</td>
<td>401</td>
<td>0.17</td>
</tr>
<tr>
<td>MHOTOFA 1.5:1</td>
<td>206</td>
<td>250</td>
<td>398</td>
<td>388</td>
<td>0.27</td>
</tr>
<tr>
<td>MHOTOFA 1.76:1</td>
<td>198</td>
<td>238</td>
<td>405</td>
<td>395</td>
<td>0.29</td>
</tr>
</tbody>
</table>

From table 7, we can see that, for cured resins which blended with styrene are relatively more resistive to temperature increasing, the significant loss occurred above 238°C, while for resins without styrene, significant loss began below 231°C, this is due to styrene as the reactive co-
monomer increased the cross-linking network of the resins. As the temperature is increasing, the maximum degradation rate of cured resins blended with styrene appeared at lower temperature; this could be explained by the volatile nature of styrene, which speeds up the degradation, the residue percentage is in accordance with this.

4.5 Composite preparation

4.5.1 Materials
Methacrylated tall oil fatty acid (MHOTOFA), the cross-linkable resin obtained from previous synthesis. Knitted viscose fiber mat (see figure 18) with a surface weight 184g/m² was supplied by Engtex Company, Sweden. The following chemicals were used: styrene and tert-butyl peroxybenzoate, both come from Sigma-Aldrich. Styrene as a reactive diluent can reduce the viscosity of the resin and can also improve the mechanical properties of the resulting composite because it can undergo the copolymerization when cured. Both neat resins and resins blended with 33wt% styrene were used to prepare the composites. The natural fiber reinforced composites were characterized with DMTA, flexural test, charpy test and tensile test.

Figure 18: Viscose fiber and fiber mats lay-up orientation

4.5.2 Hand lay-up impregnation
The knitted viscose fiber was cut into two sizes, 9cm X 9cm and 18cm X 18cm, the smaller was used for preparing the samples for DMTA test, while the bigger was for samples of tensile, charpy and flexural test. All fiber mats were dried in a vacuum oven at 105°C, approximate 30mbar for 1 hour prior to use to reduce water content in order to achieve a better interfacial contact with the resins. 10 layers fiber mats were used to reach the desired thickness of the resulting composite and were laid cross wise at an angle of 90°. Blend different resins (with or without 33wt% styrene) with 2wt% tert-butyl peroxybenzoate as the free radical initiator, then the resin was distributed evenly on one side of the fiber mat. Fiber mats were placed on a balance in order to control the resin mass sprayed on each piece of
fiber mat. For every composite making, sprayed resin mass equals to the 10 sheets fiber mass. Two or more mats were assembled and were subsequently compression molded; the compression moulding was done at a temperature of 170 °C for 7 min on hot press, using pressure between 246kpa and 370kpa. 6 different combinations were evaluated (three different resins, with and without 33wt% styrene). The fiber ratio of composites varies between 63% and 66% (see figure 19).

Figure 19: Six different composites from 3 different resins (with or without styrene) reinforced by viscose fiber.

4.6 Characterization of composites

Flexural testing, since the composite is fiber reinforced plastic composite, therefore, international standard ISO14125 was adopted for the determination of flexural properties. The testing machine was equipped with a 250N load cell and 10mm/ min test speed was set up. At least five specimens were tested for every combination.

Dynamic mechanical thermal analysis (DMTA) was performed to determine the temperature dependency of the mechanical properties of the composites and resins. TA instrument DMA Q800 was used for this testing. DMTA was run in the dual cantilever mode. The dimensions for sample specimens were: thickness 3-3.5mm, length 62mm, width 10mm for composites and thickness 1.68-1.9mm, length 60mm, width 7.5-7.9mm for resins. The temperature interval was from -20°C to 140°C at frequency of 1Hz with a heating rate of 3°C/min. Two specimens were analyzed per composite, and three specimens were analyzed per amplitude.

The charpy impact properties were determined by a charpy test instrument according to ISO 179-1 international standard. The dimensions for sample specimens were: thickness 3-4mm, length 80mm, width 10mm. The unnotched Charpy impact tests were performed using a 2.7J hammer. All test pieces were tested edge wise. 10 specimens were tested for each sample to determine the impact strength (see figure 20).
4.7 Results and discussion of composites

4.7.1 Flexural testing
Figure 21, 22 and 23 show the flexural strength, flexural modulus and strain at break of different combinations respectively. Figure 21 shows that there is significant difference of flexural strength between the composites blended with and without styrene. For resins blended with styrene, the resulting composites showed higher flexural strength, between 50 MPa and 61 MPa, while the resins with no styrene, the resulting composites’ flexural strength only vary between 20 MPa and 36 MPa. Both combinations with and without styrene present an increase in flexural strength as methacrylic anhydride’s ratio in resin is increasing. Higher flexural strength was attributed to the higher number of methacrylate groups per tall oil fatty acid unit because of more crosslink among the molecules.

Figure 21: Flexural strength comparison of the composites
Flexural moduli of composites without styrene were between 3 GPa and 3.8 GPa, and the composites with styrene present relatively higher flexural modulus performance, between 3.5 GPa and 3.8 GPa. The blending of the thermosetting resins with styrene aims to impact more stiffness into the resulting composites and therefore to increase composites’ mechanical performance. With the addition of 33wt% styrene, both flexural strength and flexural modulus of the MHOTOFA resins reinforced with knitted viscose fiber increased considerably, which indicate that the styrene give the composite more mechanically elastic property because of more amount of longer crosslink between the molecules.

![Flexural modulus comparison of the composites](image1)

Figure 22: Flexural modulus comparison of the composites

![Strain at break% comparison of the composites](image2)

Figure 23: Strain at break% comparison of the composites
4.7.2 Dynamic mechanical thermal analysis

DMTA is viewed as a sensitive measurement, which provides valuable information for the materials. The important parameters measured by this test are storage modulus, loss modulus and tan δ. Storage modulus reflects the elastic response of a material, loss modulus measures the viscous response of a material, while tan δ represent the tangent of the phase angel and the ratio of loss modulus/ storage modulus. Those parameters provide quantitative analysis information about the behavior of a material over a wide temperature range. The effects of fiber reinforcement, addition of styrene on the dynamic mechanical properties were checked by DMTA.

Figure 24: variation in the storage modulus of the MHOTOFA composites

Figure 24 shows the variation in the storage modulus of the MHOTOFA composites. Composites, which resin blended with 33wt% styrene have higher storage modulus than that without styrene. The DMTA result is consistent with the flexural test, indicating that blending with 33wt% styrene had a positive effect on the composites’ mechanical properties. The composites without blending with styrene have a storage modulus around 2.1-2.3 GPa at 25°C, while for the composites blended with styrene, the storage modulus varies from 3 GPa to 5.4 GPa, which is almost double amount.
Tan delta curves of the MHOTOFA composites

Tan delta, or damping, is the tangent of the phase angle and the ratio of $E''/E'$, which gives information about the internal friction of the materials. Molecular motion in the interface contributes the damping in composite. The peak of damping takes place in the region of glass transition; therefore, the $T_g$ was taken from the maximum point of the tan delta curve. From figure 25, we can see that the composites without blending with styrene show higher glass transition temperature, above 100°C, while those blended with styrene show relatively low $T_g$, from 85°C to 93°C. A possible explanation is that the addition of styrene did not increase the cross-linking density. Rather, the addition of styrene binds the MHOTOFA molecules into long flexible chains which lower the glass transition temperature.
Figure 26: the loss modulus curves of MHOTOFA composites

The composites blended with styrene show higher loss modulus at 25°C which corresponds to higher storage modulus (see figure 26).

In order to find out how much mechanical performance can be improved by the reinforcement of viscose fiber, cured MHOTOFA resins (with styrene) were checked by DMTA to make the comparison with MHOTOFA composites (with styrene).

Figure 27: Comparison of the storage modulus between the reinforced resin (composite) and the unreinforced resin, both blended with styrene
Figure 27 shows clearly that the fiber reinforcement greatly improved the mechanical performance of the corresponding composite. The storage modulus of the MHOTOFA 1.76:1 composite is 5.4 GPa at 25°C, while the MHOTOFA 1.76: 1 resin only exhibits 2.4 GPa at the same temperature. In the summary table, the loss modulus comparison between the composites and resins demonstrate the same trend.

However, reinforcing the resins with viscose fiber lowered the glass transition temperature; significant difference of glass transition temperatures was observed (see table 8), this could be explained by adding fiber into the matrix may change the cure mechanism when the composites were made by compression moulding. Similar drop of the glass transition temperature was also observed by other authors [37, 43].

The drop of glass transition temperature is quite negative, because the composites’ technical applications can be limited due to the lower T_g.

Table 8: Summary of the DMTA result

<table>
<thead>
<tr>
<th></th>
<th>E’ at 25°C (MPa)</th>
<th>E” at 25°C (MPa)</th>
<th>T_g(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHOTOFA composite( no styrene)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 : 1</td>
<td>2134</td>
<td>183.3</td>
<td>unknown</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>2166</td>
<td>186.1</td>
<td>109.84</td>
</tr>
<tr>
<td>1.76 : 1</td>
<td>2382</td>
<td>209.4</td>
<td>110.02</td>
</tr>
<tr>
<td>MHOTOFA composite( with styrene)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 : 1</td>
<td>3848</td>
<td>269</td>
<td>85.42</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>3068</td>
<td>168.8</td>
<td>93.43</td>
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<td>1.76 : 1</td>
<td>5478</td>
<td>388.7</td>
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<td>1.76 : 1</td>
<td>2464</td>
<td>179.6</td>
<td>98.27</td>
</tr>
</tbody>
</table>
4.7.3 Charpy testing

![Charpy impact strength graph](image)

Figure 28: Impact strength of the composites

Impact strength test is used to investigate the behavior of composite specimens under the defined impact conditions and therefore estimate the brittleness or toughness of specimens. For composite applications, the toughness is a very important property. The composites tested show high impact strength around 44 to 55 kJ/m$^2$ (see table 9), which is even comparable with the glass fiber reinforced composites (around 54kJ/m$^2$). Except for the MHOTOFA 1to1 composite (without styrene), a general decreasing impact strength trend is observed, which is on the contrary to the flexural properties. This decrease in impact strength may be explained by assuming that a better fiber matrix adhesion will result in shorter average pull out length which therefore reduces impact strengths. From 1 : 1 to 1.76 : 1, with the increasing amount of methacrylate in the thermoset resins, more crosslinking bonds can be formed due to more numbers of reactive double bonds in the molecular structure, and the decreasing resin viscosity enable better wettability of the fiber mat, therefore lead to better fiber-matrix adhesion, which cause lower impact resistance or strength. However, the standard deviation makes it difficult to draw any definite conclusion (see figure 28).

Table 9: Summary of charpy properties

<table>
<thead>
<tr>
<th>Composites</th>
<th>Impact strength kJ/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHOTOFA 1 : 1 no styrene</td>
<td>46</td>
</tr>
<tr>
<td>MHOTOFA 1 : 1 with styrene</td>
<td>55</td>
</tr>
<tr>
<td>MHOTOFA 1.5 : 1 no styrene</td>
<td>49</td>
</tr>
<tr>
<td>MHOTOFA 1.5 : 1 with styrene</td>
<td>49</td>
</tr>
<tr>
<td>MHOTOFA 1.76 : 1 no styrene</td>
<td>46</td>
</tr>
<tr>
<td>MHOTOFA 1.76 : 1 with styrene</td>
<td>44</td>
</tr>
</tbody>
</table>
5. Conclusions

Bio-based thermoset resins were synthesized from tall oil fatty acid. Tall oil fatty acid was hydroxylated by hydrogen peroxide; the resulted resin was further modified by methacrylic anhydride using three different mass ratios. Higher conversion of hydroxyl groups was achieved by using more methacrylic anhydride, the conversion results were verified by FTIR. Three different mass ratio methacrylated tall oil fatty acids were mixed with 2wt% benzoyl peroxide and 0.5wt% N, N-dimethylaniline and then were cured at room temperature for 1h and 150°C for another 1h, completely cross-linked thermoset polymers were obtained, which was confirmed by FTIR and DSC analysis. The TGA analysis showed derivative temperature of the cured resins in the range of 388-417°C, which corresponded to the decomposition of the cross-linked structure. The obtained resins were then used in the preparation of the bio-based composites, knitted viscose fibers were used as the reinforcement. The composites were characterized by different mechanical analysis, and showed relatively good flexural and impact strengths. MHOTOFA composites (without styrene) exhibited flexural strength between 18 and 35MPa, storage modulus between 2.1GPa and 2.3GPa, while MHOTOFA composites (with styrene) gave higher flexural strength between 50 and 60MPa and higher storage modulus between 3GPa and 5.4GPa. The addition of styrene gave a significantly positive effect in the stiffness of the composites. All MOHOTOFA composites showed high impact strength around 44 to 55 kJ/m², which is comparable with the glass fiber reinforced composites.
6. References


