SYNTHESIS AND CHARACTERIZATION OF A BIOBASED THERMOSET RESIN FROM LACTIC ACID AND ALLYL ALCOHOL

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Abstract

New bio-based thermoset resins have been synthesized using lactic acid oligomers to produce two different resin structures. The first resin comprises of an allyl alcohol terminated lactic acid oligomer, which was end-functionalized with methacrylic anhydride (MLA resin). The second resin composed of a mixture allyl alcohol -lactic acid oligomer and pentaerythritol. The mixture was then end-functionalized with methacrylic anhydride (PMLA resin). The resins were characterized using FTIR, 13C-NMR spectroscopy, differential scanning calorimetry as well as dynamic mechanical analysis to confirm the resin structure and reactivity. The flow viscosities were also measured in order to evaluate the suitability of the resins to be used as a matrix in composite applications. The results showed that the PMLA resin has better mechanical, thermal and rheological properties than MLA resin, and both had properties which were comparable with a commercial unsaturated polyester resin. The bio-based content of 90% and glass transition temperature at 113°C for the PMLA resin makes it a good candidate for composite applications where petroleum-based unsaturated polyester resins are normally used.

Introduction

Industries and manufactures are increasingly encouraging the use of materials from renewable resources in order to replace the use of petrochemical-based materials with agricultural based materials. Resins are used extensively in the production of composite materials for use in automotive/transportation parts, appliances, furniture, and construction. One of the commonly used resins in composite production is the various unsaturated polyester resins, which are synthesized using raw materials derived from petroleum [1-4].

Research on replacing some of these petroleum-based raw materials with renewable resource-based raw materials such as plant oils (e.g. soybeans oil, linseed oil, mint oil and sunflower oil) [5-10], glycerol, lactic acid and lactides [11-14] are very attractive economically, socially and for the safety of the ecosystem. Due to government demands on reducing emission and fuel efficiency, the industries are led to produce lighter components from fiber reinforced plastic composite. In the automotive industry, the main improvement in fuel efficiency is achieved by reducing the mass, which makes manufacturers focus on composite materials because of their low density. [15-16]. Several reports have been made on automobile interior parts from natural fiber and polymer matrix in order to have parts with low density and at a reduced production cost. Examples are the use of jute fiber with epoxy resin as the polymer matrix in the production of the door panel of Mercedes-benz E-class vehicles. The use of PLA matrix from sugar cane and sweet potatoes reinforced with kenaf fibers for the production of spare tires for Raum 2003 model of Toyota vehicle [15]. The use of polybutylene succinate (PBS) from plant-based resin reinforced with bamboo fiber for the production of the interior trim material of Mitsubishi Motor and also the use of PLA resin and nylon fibers for the production of car floor mat [17].
Thermosetting resins are preferred for many composite applications because their flow viscosity is lower, thus giving better homogeneous impregnation with the fiber reinforcement. Recently, our research group has carried out synthesis of thermosetting resins from lactic acid with different process route. The first resin was prepared by direct condensation of pentaerythritol, itaconic acid and lactic acid, to obtain a starshaped PLA molecule with pentaerythritol as the core unit which was then end-capped by methacrylate groups. The resin obtained had relatively high viscosity, which is a drawback when applying the resin together with reinforcement [18]. Another resin was later synthesized based on lactic acid, glycerol and methacrylic anhydride. This resin had improved mechanical properties and lower viscosity than the previous resin [19]. The resin had a viscosity of about 1 Pa at room temperature, which is too high for impregnation into fiber reinforcements. This resin can either be processed at elevated temperature to reduce the viscosity or by adding a solvent e.g styrene which will alter its biobased content. According to Li et. al [20], a resin can be used in an vacuum assisted infusion process, if the viscosity is below 5 Poise (0.5 Pa s) at room temperature. Therefore, there is a need to prepare resin with lower viscosity in order to have homogeneous impregnation into fiber reinforcement.

In this study, two alternative synthesis route for bio-based thermosets resin were evaluated using lactic acid and allyl alcohol. Linear lactic acid oligomers were first synthesised by the condensation reaction of lactic acid with allyl alcohol, named ALA (allyl alcohol lactic acid resin). The ALA resin was then end-functionalized with methacrylic anhydride to give the first resin structure called the methacrylated lactic acid resin (MLA resin). The second resin structure was obtained by first mixing the linear ALA oligomer with pentaerythritol and then end-functionalized with methacrylic anhydride to give methacrylated pentaerythritol-lactic acid resin (PMLA resin).

**Methods**

**Synthesis**

Two different resin structures were synthesized, the first resin was done in two stages:

1. The condensation reaction stage; allyl-lactic acid oligomers were formed by reacting 1 mole of allyl alcohol to 5 moles of lactic acid using methanesulfonic acid as catalyst and about 250g of toluene as the solvent. A three-necked round bottom flask equipped with a magnetic stirrer with an azeotropic distillation apparatus under nitrogen atmosphere was used for the synthesis. The reaction took place for about 5 hours with changes in temperature from 145°C for the first two hours, to 165°C for the next two hours and further one hour of synthesis at 195°C. This resin formed was called allyl-lactic acid oligomer (ALA resin).

![Figure 1: Structure of allyl-lactic acid oligomer (ALA resin).](image-url)
2. The end-functionalization stage; the allyl-lactic acid oligomer (ALA resin) obtained in the first stage was cooled to a temperature of about 90°C, while 0.2 wt% of hydroquinone was added as a stabilizer. Methacrylic anhydride of about 1.1 moles was added to the mixture dropwise for the first two hours and the reaction proceeded for an additional two hours while constantly stirred under nitrogen atmosphere. The product formed was purified by using a roto-vapour distillatory at temperature of 60°C and pressure of 13 mbar. This resin formed was called methacrylated lactic acid resin (MLA resin).

![Figure 2: Structure of methacrylated lactic acid resin (MLA resin).](image)

The second resin was synthesized by mixing 4 moles of the obtained ALA resin above at 90°C with one mole of pentaerythritol in a three-necked round bottom flask, a magnetic stirrer with an azeotropic distillation apparatus under nitrogen atmosphere. A stabilizer of 0.2 wt% of hydroquinone was added to the reaction mixture and methacrylic anhydride of about 10 moles was added drop-wise for the first two hours and the reaction proceeded for an additional two hours while constantly stirred under nitrogen atmosphere. The product formed was purified by using a roto-vapour distillatory at temperature of 60°C and pressure of 13 mbar. This resin formed was called methacrylated pentaerythritol-lactic acid resin (PMLA resin).

![Figure 3: Structure of methacrylated pentaerythritol-lactic acid resin (PMLA resin).](image)

**Biobased Content**

The biobased content of the two synthesized resins MLA and PMLA resin were calculated using the ASTM D6866 standard. The formula is as stated;
For Figure 2 and 3, the biobased content is as follows:

\[
\text{Biobased Content} = \frac{\text{biobased carbon content}}{\text{total carbon content}} \times 100
\]

For MLA and PMLA resins, the biobased content is 86% and 90% respectively.

Resin curing

The thermal curing of the resins was done by adding 2 wt% of t-butyl peroxybenzoate as the initiator and 2 wt% of N,N-dimethylaniline as the accelerator into 10g of the resin. The mixture was casted in a mould and left for one hour to cure in room temperature. After one hour, post curing was done in an oven at an elevated temperature of 160 °C for another one hour. The cured sample was then analyzed by DMTA, DSC, TGA and FT-IR.

Results and Discussion

\[^{13}\text{C-NMR spectroscopy analysis}\]

This was used to verify the condensation reaction of the allyl-lactic acid oligomer formed and the end-capping reaction of the lactic acid branches with methacrylic acid from the methacrylic anhydride used. Figure 4a, shows the ALA resin spectra, the lactic acid carbonyls give two major peaks, which are the carbonyl groups in the lactic acid branches and lactic acid oligomers not reacted with allyl alcohol, seen at 169-169.5 ppm. The other lactic acid carbonyls can be located at 174.3-174.7 ppm of the lactic acid end-group and at 171.3-171.7 ppm with two small peaks. No peak was detected at 176.5 ppm indicating that no unreacted lactic acid was detected. Figure 4b, shows the MLA resin spectra where three new peaks was identified at 162.5 ppm as the unreacted methacrylic anhydride, at 166.0 ppm as the reacted methacrylate ester indicating that the modification occurred and at 171.5 ppm as the free methacrylic acid. A small peak was identified at 174.3-174.7 ppm which shows that some unreacted MLA resin still remains, while the broad peak at 169-169.5 ppm is from the same lactic acid carbonyls as in the ALA spectra. Figure 4c, shows the PMLA spectra with similar peaks as in ALA and MLA resin, but with a new peak at 166.1 ppm identified as the carbonyl in pentaerythritol reacted with methacrylic anhydride, which shows that the wanted reaction has occurred.
Figure 4: (a) $^{13}$C NMR spectra for ALA resin; (b) $^{13}$C NMR spectra for MLA resin; (c) $^{13}$C NMR spectra for PMLA resin

FT-IR spectroscopy analysis

This was used to verify the reaction of lactic acid with allyl alcohol to form the lactic acid oligomer (ALA resin), the functionalization of the ALA resin with methacrylic anhydride to form the MLA and PMLA resin. The cured MLA and PMLA resin (CMLA and CPMLA) was also analyze to verify their double bond crosslinking reaction. In Figure 5, the spectra for the ALA resin show a small peak at about 1640 cm$^{-1}$, indicating the presence of the double bond peak of the allyl alcohol in the resin. At 3428 cm$^{-1}$ and 1759 cm$^{-1}$ shows the intensity reduction in the –OH stretch peak and the sharper absorption peak of C=O stretching indicating that the esterification reaction of lactic acid did occur. The uncured MLA resin spectra shows the carbon-carbon double bond peak at about 1640 cm$^{-1}$ and 816 cm$^{-1}$, and the splitting of the carbonyl bond at 1757 cm$^{-1}$ which was not present in the ALA resin. The disappearance of an absorbance at 3500cm$^{-1}$ after the reaction shows that all the hydroxyl groups were reacted and that the end-functionalization did occur. The cured MLA resin (CMLA) spectra show the disappearance of the carbon-carbon double bond peak at about 1640 cm$^{-1}$indicating that the crosslinking reaction of all the double bond in the resin had occurred. Both the uncured and cured PMLA resin shows the same trend as the MLA resin but with a higher absorbance intensity in all peaks due to the presence of pentaerythritol.
This was used to investigate the curing reaction efficiency of both the uncured and cured MLA and PMLA resins. Samples were placed in sealed aluminum pans and heated from -20 °C to 200 °C at 10 °C /min in a nitrogen atmosphere. This was done by determining the exothermal heat evolves when the resin is mixed with 2 wt% t-butyl peroxybenzoate in the DSC. The results of the exothermal heat from the first DSC scan for MLA resin shows an exothermic peak between 90°C and 150°C of about 194 J/g, while for PMLA resin was of about 26 J/g appears in the same interval. The exothermic peak was not detected during the second heating scan for both resin samples, which indicated that the resins were completely cured under the used conditions. For the resin samples cured at room temperature followed by postcuring at 160°C, much smaller exothermic peaks were detected of about 1.40 J/g for MLA and 0.03 J/g for PMLA. This results are listed in Table 1 and it can be confirmed that both the MLA and the PMLA resins can be cured.

Dynamic Mechanical Analysis

The DMTA was done on a Q800 instrument (TA Instruments, DE, USA) and in the dual cantilever bending mode. The specimen dimensions were: length 35 mm, width 8 mm and thickness 2–3 mm. The temperature ramp was from -40 to 150°C, a heating rate of 3°C/min, amplitude of 15 µm and frequency of 1 Hz was used. The storage modulus G’ with standard deviation at 25 °C for the cured MLA and PMLA resins is given in Table 1. The storage modulus G’ is related to the packing density of the glassy state, which increases as the degree of crosslinking is increased. This is seen for the PMLA resin, in which the methacrylate functionalized branched pentaerythritol component increases the crosslinking density, and thereby decreases the free volume of the chain segments, according to the free volume theory [11]. From the result, the PMLA resin shows higher storage modulus than the MLA resin which is due to better packing of all the molecular chain fragments. The result of the loss modulus gave low values above glass transition temperature which is due to the rubbery plateau state of the resin, which agrees with the theory of rubber elasticity. Therefore, the lower the peak value of the loss modulus, the higher the crosslinking density. The glass transition temperature measured as the peak of tan δ for the resins were recorded as 109 °C and 113 °C for resins MLA and PMLA respectively. This trend is expected since for the MLA resin, the rubbery plateau region in the storage modulus occurred earlier than the PMLA resin. Therefore, higher tan δ peak values for PMLA indicates a higher degree of crosslinking.
Thermogravimetric analysis

This was done to investigate the thermal durability of the cured resins measured as the percentage weight loss of the samples while heating. Sample of about 20mg were heated from 30°C to 650°C at a heating rate of 10°C/min in a nitrogen purge stream. The temperature for 10 wt% and 50 wt% loss of the resins were detected. The results in Table 1 show that the cured MLA resin was stable up to 270°C and a 10 wt% gravimetric loss occurred at about 290°C, while heating up to 400°C the resin has lost 50wt% of it’s weight. Maximum rate of degradation occurs at 346°C, while at 450°C the curve of the derivative weight has a second peak. On the otherhand, the cured PMLA resin was stable up to 275°C and a 10 wt% loss occurred at about 302°C, while at about 444°C the resin has lost 50wt%. The maximum degradation occurs at 344°C and at 461°C the curve of the derivative weight has a second peak. From the result, the temperature at which 50 % weight loss was detected for PMLA resin was approximately 44 °C higher than for MLA resin, showing a better thermal stability than the MLA resin.
### Table 1: Resin Characterization

<table>
<thead>
<tr>
<th>Resin</th>
<th>DSC</th>
<th>DMA</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heat of exotherm for uncured resin (J/g)</td>
<td>Temperature interval for the exotherm peak (ºC)</td>
<td>Heat of exotherm for cured resin (J/g)</td>
</tr>
<tr>
<td>MLA</td>
<td>194</td>
<td>83 - 170</td>
<td>1.40</td>
</tr>
<tr>
<td>PMLA</td>
<td>26</td>
<td>80 - 170</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Viscosity measurement

The viscosity of thermoset resins is of importance regarding how the resin can be processed together with reinforcement. It was monitored using stress viscometry at temperatures 25 °C, 35 °C, 45 °C, 55 °C and 70 °C. Table 2, shows that at room temperature, the resin PMLA has a lower viscosity (0.02 Pa s) than for resin MLA (0.04 Pa s). Upon increasing the temperature to about 70 °C, the viscosity drops to 0.01 Pas for the resin PMLA and 0.02 Pas for the resin MLA. The results shows that both resins are better suited for processing at room temperature and even penetration of the resin into fiber can be achieved.

Table 2: Viscosity Measurement

<table>
<thead>
<tr>
<th>Resin</th>
<th>Viscosity (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>MLA</td>
<td>0.04</td>
</tr>
<tr>
<td>PMLA</td>
<td>0.02</td>
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</tbody>
</table>

Summary

Biobased thermoset resins were synthesized from lactic acid, allyl alcohol, methacrylic anhydride and pentaerithrytol to develop two different resins (MLA and PMLA resin). The MLA resin was synthesized in two steps; first synthesis step involves a direct condensation of lactic acid with ally alcohol to form an allyl alcohol terminated lactic acid oligomer named ALA resin. The second synthesis step, the obtained ALA resin was modified to give methacrylic end-groups to the oligomer using methacrylic anhydride in order to provide a suitable site for crosslinks. The PMLA resin was synthesized by mixing the ALA resin with pentaerythritol and then end-functionalized with methacrylic anhydride in a similar way as for the MLA resin.

The result showed that PMLA resin has better mechanical properties than MLA resin with glass transition temperature based on the tan δ peak of 113°C compared to MLA resin of 109°C. Better thermal and rheological properties was also observed for the PMLA resin compared to MLA resin, with PMLA resin having much lower viscosities at all temperatures range used. A homogeneous impregnation with the fiber reinforcement could be achieved to produce composite with good mechanical properties. The high biobased content of the resins also makes them good candidates for commercial production of biobased thermoset resins.
Bibliography


