SYNTHESIS AND PREPARATION OF BIOBASED COMPOSITES WITH A NOVEL THERMOSET RESIN FROM LACTIC ACID

Fatimat O. Bakare[1*], Dan Åkesson[1], Mikael Skrifvars[1], Yanfei Wang[2], Nima Esmaeili[1], Shahrzad Javanshir Afshar[1]

[1]*School of Engineering, University of Boras, Boras, Sweden*
[2]*University of South China, China*
**fatimat.bakare@hb.se*

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Abstract

A lactic acid-based thermoset resin was produced from lactic acid and glycerol. The lactic acid resin was synthesized in two stages, by direct condensation of lactic acid and glycerol to an oligomer which was end-functionalized with methacrylic anhydride. The viscosities of the resins were measured and the properties were also characterized with FTIR and DMTA. The resin was then impregnated into regenerated cellulose fiber and compression moulded to produce thermoset composites, with different fiber alignments and fiber loads. Flexural, tensile and Charpy impact tests were performed to investigate the fiber alignments and fiber loads effect on mechanical properties. The results showed that the composite has comparable mechanical properties with many commercial petroleum based glass fiber reinforced (GFR) polyester composites.

1. Introduction

Resin production from bio-based materials has been of paramount interest in order to eliminate the use of fossil resources [1,2]. These resins are mostly made from vegetables oils like, soybean oil, linseed oil, mint oil, sunflower oil etc [1,3-7]. But recently, researches have been carried out on the preparation of the thermosetting resins from lactic acid/lactides [8-11]. This has led to a growth in demand for lactic acid because of its application in the synthesis of polylactic acid.

There have been several reports on the production of biobased composites by impregnating resins as a matrix on natural/regenerated fibers. More researches are still ongoing on the production of composite with the use of biobased resins as matrix to make it 100% biobased. These have been of interest because of the potential for biobased composites in the automotive, sport equipment, medical and aerospace industry applications. This is due to their strength, durability, biodegradability, and corrosion resistant properties. Biobased resins can be inexpensive and as they are renewable resources, these resins can be a good replacement to synthetic petroleum based fibers [1,12-14].

Previously, a biobased resin was prepared by direct condensation of pentaerythritol, itaconic acid and lactic acid [8]. The obtained star-shaped molecules with pentaerythritol as the core

molecule were end-capped by methacrylate groups. This resin had relatively good mechanical properties, but tests also showed that the resin had a relatively high viscosity, making the mechanical properties of the desired composite low due to improper impregnation.

In this study, an investigation on the synthesis of a polyester resin based on lactic acid and glycerol was made. The obtained resin was then impregnated into a viscose fiber in woven and nonwoven shapes and the mechanical properties of the composite formed were evaluated.

2. Approach

2.1. Synthesis

The synthesis was performed in two stages as shown in Figure 1. The chemical structure was confirmed by FTIR specytroscopy.

- The condensation reaction stage: branched oligomers of glycerol and lactic acid were prepared with chain length n = 3 lactic acid units
- End-functionalization stage: in this stage the resin was then reacted with methacrylic anhydride

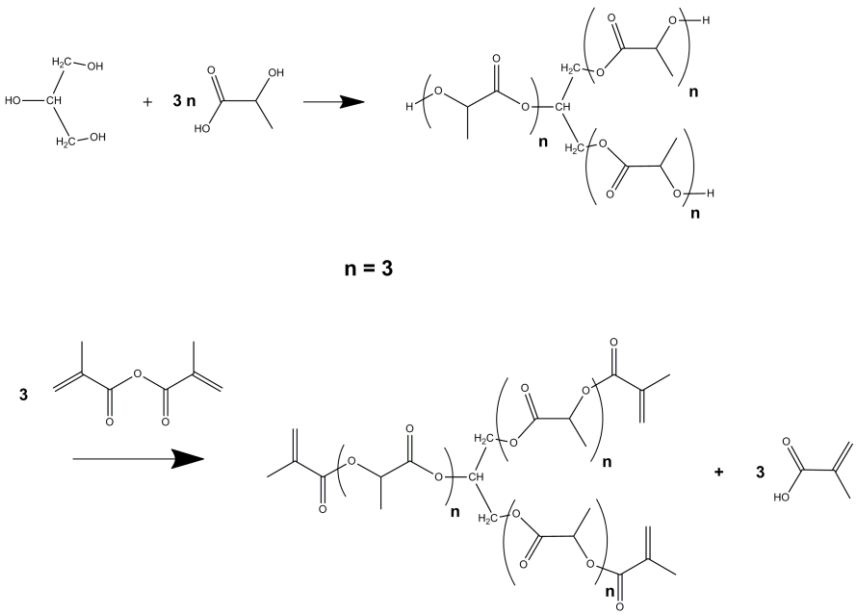

Figure 1. Reaction scheme of lactic acid and glycerol

2.2. Composite preparation

The viscose fibers were cut in desired sizes and dried in a vacuum oven at 107˚C for two hours. Then a manual layup of fiber was then prepared in three ways: bidirectional and unidirectional direction of the woven fiber and the non woven fiber. The lactic acid resin prepared as above was blended with a thermal initiator and impregnated manually by handspray on the fibers. Different fiber load of 65%, 70% and 75% were considered for the composite production. This was done by placing the impregnated fiber in a Rondol hydraulic press where the composite was cured at 150˚C for 5 minutes. The composite was then characterized using the tensile testing, flexural testing and Charpy impact testing.

3. Results and Discussion

3.1. FT-IR Spectroscopy characterisation of the resins

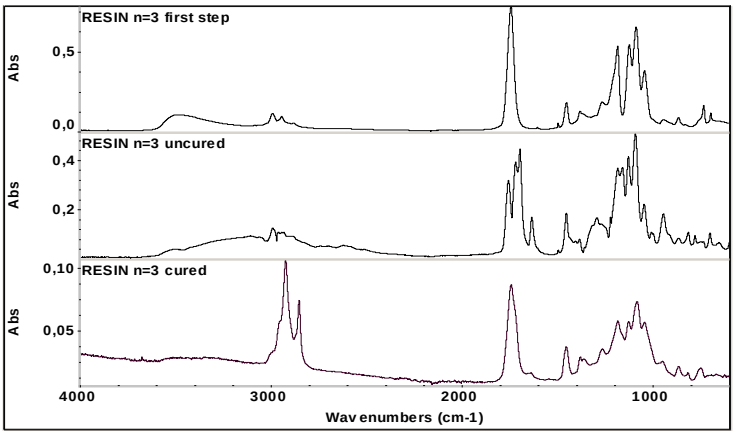

Figure 2. FT-IR Spectra of uncured and cured with the chain length n=3 resin

The spectra shows a carbon-carbon double bond signal at about 1640 cm^{-1} (stretching, C=C) and at 816 cm^{-1} (bending, $-C=CH_2$)[23] which was not present in the resin from the first step. This indicates that end-functionalization by methacrylic anhydride did occur. The disappearance of the carbon-carbon double bond peak and an increase in the band intensity for the –CH stretch at about 2900 cm^{-1} in the cured resin[4,15] indicates that the crosslinking reaction of the resin had occurred. The complete crosslinking reaction was verified as shown in Figure 2; which shows no band at 1640 cm^{-1} and this clearly indicates that all double bonds had reacted when crosslinked. The almost complete disappearance of an absorbance at 3500 cm^{-1} after reaction with methacrylic anhydride indicates that almost all the hydroxyl groups were reacted.

3.2. Dynamic mechanical analysis for the resin

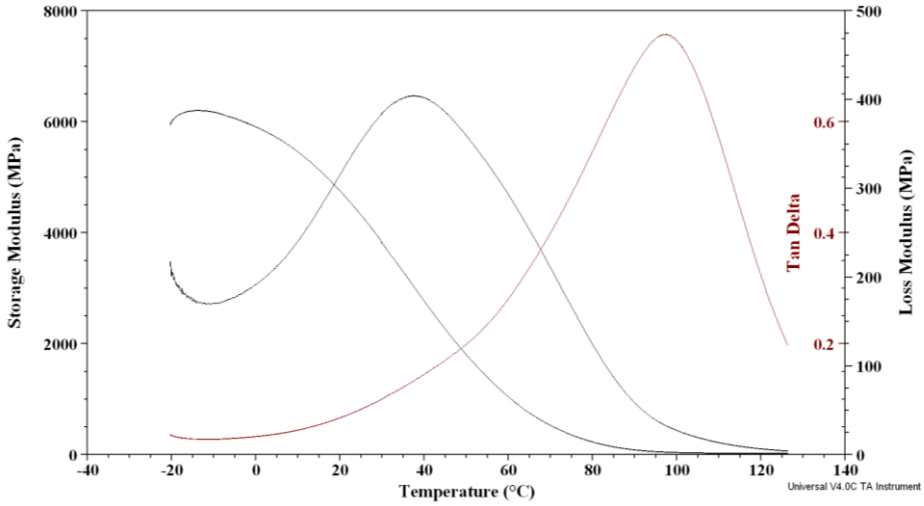

Figure 3. DMA curve for the crosslinked resin with chain length n=3 resin

The storage modulus (G´), loss modulus (G´´) and peak of tan delta (δ) for the resin with thye chain length n=3 is about 4314 MPa, 353.8MPa and 97°C respectively. The glass transition temperature of this resin which is measured at 97°C, which is the peak of tan delta, is higher than for thermoplastic PLA and it is comparable to commercial unsaturated polyester resins.

3.3. Viscosity measurement of uncured resins

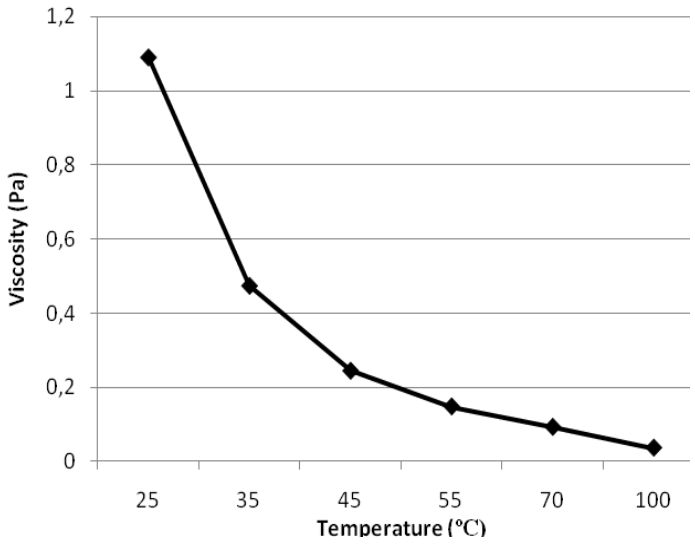

Figure 4. Viscosity for the resin with chain length n=3 in the temperature range 25 to 100 °C.

The viscosity of a thermoset resin is of importance regarding how the resin can be processed. It was monitored using stress viscometry at temperatures 25 °C, 35 °C, 45 °C, 55 °C, 70 °C and 100 °C. In Figure 4, the graph shows that at room temperature, the resin with the chain length n=3 has a viscosity at 1.09 Pas and upon heating to a temperature of about 100 °C, the viscosity drops to 0.0361 Pas. This novel resin clearly has a better processability and can be suited for processing at room temperature.

3.4. Flexural and impact properties

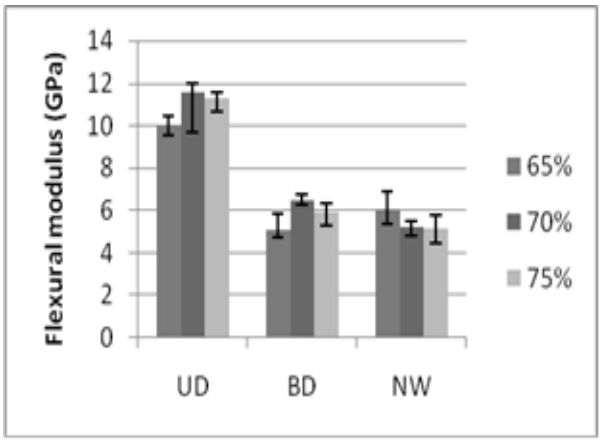

Figure 5. The flexural modulus of different composite treatments

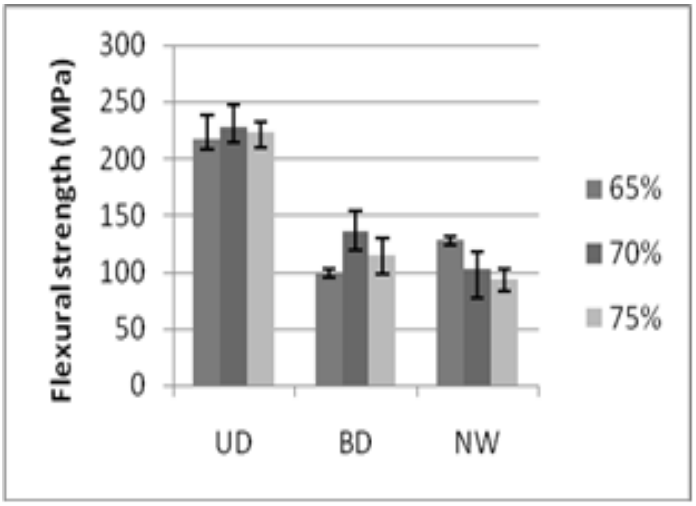

Figure 6. The flexural strength of different composite treatments

The flexural modulus and flexural strength for different fiber alignments increased with increasing fiber load from 65 to 70% for UD and BD composites, but a decrease for fiber load of 75%. Unlike non-woven that decreases by increasing fiber load from 65 to 75% which is a sign of improper impregnation for fiber loads higher than 65%.

3.5. Tensile properties

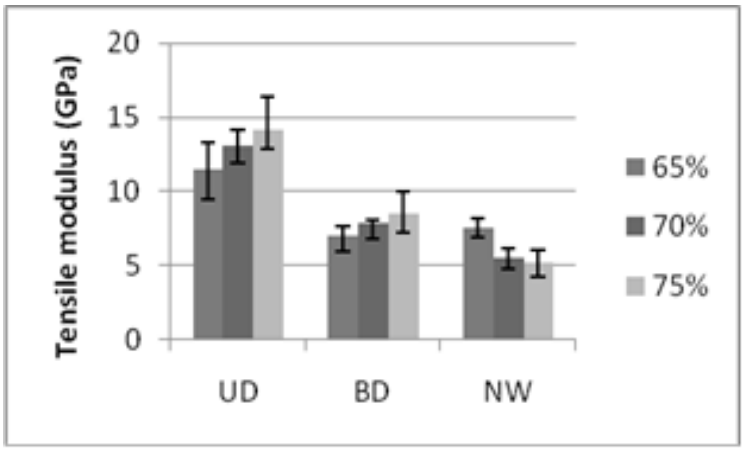

FIGURE 7. The tensile modulus of different composite treatments

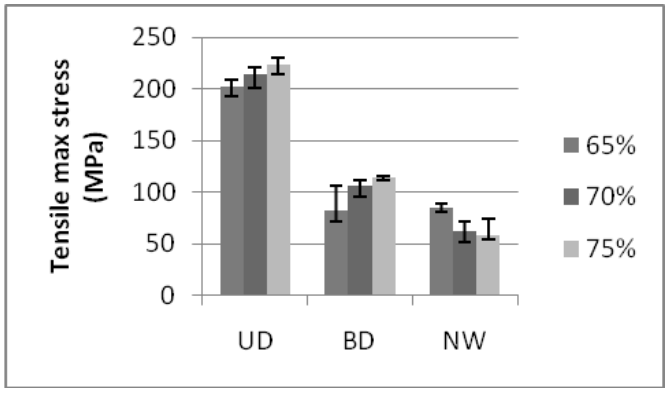

Figure 8. The tensile maximum stress of different composite treatments

The tensile modulus and tensile max stress for different fiber alignments increased with increasing fiber load from 65 to 75% for UD and BD composites. Unlike non-woven that decreases by increasing fiber load from 65 to 75% which is a sign of improper impregnation for fiber loads higher than 65%.

3.6. Charpy impact testing

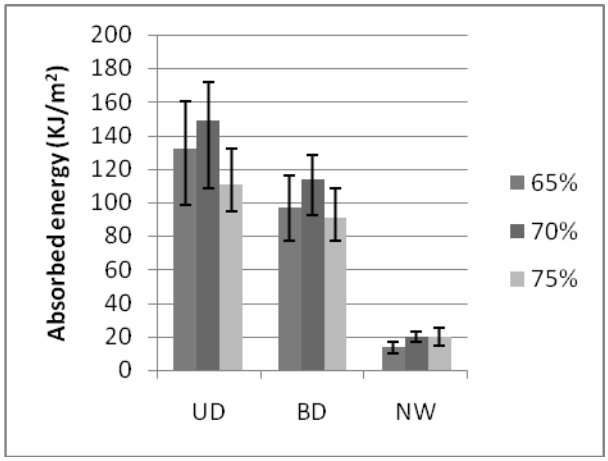

Figure 9. The Chary impact testing for different composite treatments

The absorbed energy for non-woven composites are much lower compared to aligned fiber composites. Sample investigation showed roughly soft fracture surface and no visible fiber pull out. It could be interpreted that fiber pull put occurred in very short length which leaded in lower absorbed dissipation.

4. Conclusion

The polyester resin based on lactic acid and glycerol resin with the chain length n=3 shows a promising rheological and thermal properties. The FT-IR and DMA showed that the required resin was obtained, that its characteristics are comparable with commercial polyester resins and could be used as matrix for cellulosic fibers with fiber load up to 70% and would yield good mechanical properties. Considering the high renewable ratio and relatively low price for cellulosic fibers this resin shows promising properties for making strong affordable, bio-degradable and renewable resourced composite for many applications.

References

[1] K. Adekunle, D. Åkesson, and M. Skrifvars. Synthesis of reactive soybean oils for use as a biobased thermoset resins in structural natural fiber composites. *Journal of Applied Polymer Science*, 115 (6): 3137-3145, 2010.

[2] G. Lopez Tellez, E. Vigueras-Santiago and S. Hernandez-Lopez. Characterization of linseed oil epoxidized at different percentages. *Sociedad Mexicana de Ciencia y Tecnologia de Superficies y Materiales*, 22 (1): 5-10, 2009.

[3] M. Galia, L. Montero de Espinosa, J. C. Ronda, G. Lligadas and V. Cadiz. Vegetable oil-based thermosetting polymers. *European Journal of Lipid Science Technology*, 111: 1-10, 2010.

[4] X. Liu and J. Zhang. High-performance biobased epoxy derived from rosin. *Polymer International*, 59 (5): 607-609, 2010.

[5] M. Shibata and M. Asano. Biobased thermosetting resins composed of terpene and bismaleimide. *Journal Applied Polymer Science*, 129 (1): 301-309 (2013).

[6] K. Das, D. Ray, C. Banerjee, N. R. Bandyopadhyay, A. K. Mohanty, and M. Misra. Novel materials from unsaturated polyester resin/styrene/tung oil blends with high impact strengths and enhanced mechanical properties. *Journal Applied Polymer Science*, 119 (4): 2174-2182, 2011.

[7] S. J. Park, F. L. Jin, and J. R. Lee. Effect of biodegradable epoxidized castor oil on physicochemical and mechanical properties of epoxy resins. *Macromolecular Chemistry and Physics.* 205 (15): 2048-2054, 2004.

[8] D. Åkesson, M. Skrifvars, J. Seppälä, M. Turunen, A. Martinelli, and A. Matic. Synthesis and characterization of a lactic acid-based thermoset resin suitable for structural composites and coatings. *Journal Applied Polymer Science*, 115: 480-486, 2010.

[9] S. Chang, C. Z. Jianbo Li and J. Ren. Synthesis of polylactide-based thermoset resin and it's curing kinetics. *Polymer International*, 61: 1492-1502, 2012.

[10] A. O. Helminen, H. Korhonen and J. V. Seppälä. Structure modification and crosslinking of methacrylated polylactide oligomers. *Journal Applied Polymer Science*, 86: 3616-3624, 2002.

[11] R. Sakai, B. John, M. Okamoto, J. V. Seppälä, J. Vaithilingam, H. Hussein and R. Goodridge. Fabrication of polylactide-based biodegradable thermoset scaffolds for tissue engineering applications. *Macromolecular Materials and Engineering*, 298**:** 45-52, 2013.

[12] E. Senoz, J. F. Stanzione III, K. H. Reno, R. P. Wool and M. E. N. Miller. Pyrolyzed chicken feather fibers for biobased composite reinforcement. *Journal Applied Polymer Science*, 128: 983-989, 2013.

[13] Y. Shen, S. Zhang, H. Li, Y. Ren, and H. Liu. Efficient synthesis of lactic acid by aerobic oxidation of glycerol on Au-Pt/TiO_2 catalysts. *Chemistry – A European Journal.* 16 (25): 7368-7371, 2010.

[14] K. Adekunle, D. Åkesson, and M. Skrifvars. Biobased composites prepared by compression molding with a novel thermoset resin from soybean oil and a natural-fiber reinforcement. *Journal Applied Polymer Science*, 116 (3): 1759-1765 (2010).