Thermoset Lactic Acid-Based Resin as a Matrix for Flax Fibers

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ABSTRACT: Thermoset composites were produced from flax fibers and a novel lactic acid (LA)-based thermoset resin. This resin is based on methacrylated, star-shaped oligomers of LA. The main purpose of this work was to evaluate whether this resin can be used to produce structural composites from flax fibers. Composites were prepared by spray impregnation followed by compression molding at elevated temperature. The tests showed that composites can be produced with as much as 70 wt% fiber. The composites were evaluated by tensile testing, flexural testing, charpy impact test, dynamic mechanical thermal analysis (DMTA), and low-vacuum scanning electron microscopy. The ageing properties in high humid conditions were evaluated, the Young's modulus ranged from 3 GPa to 9 GPa in the best case. This work shows that structural composites can be produced from renewable material. It is clear from the results that these composites have properties that make them suitable for furniture, panels, or automotive parts. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3004–3009, 2011

Key words: thermosets; biopolymers; composites; fibers; renewable resources

INTRODUCTION AND BACKGROUND

Today, glass fiber-reinforced (GFR) composites are very versatile in terms of price and mechanical properties. Industrial applications range from the manufacture of boats and automobiles to construction of windmills. From an environmental viewpoint, however, GFR composites are not only made from nonrenewable resources but also glass fibers are known to consume a relatively high amount of energy when produced. Apart from that, the recycling of GFR is not straightforward.[1,2] As environmental considerations are becoming more and more important, there is a need for more environmentally benign composite materials. Natural fibers are generally considered to be superior to glass fibers from an environmental standpoint.[3] Natural fibers have many advantages over their synthetic counterparts, such as biodegradability, low density, and low cost. Reduced weight can be a substantial advantage, especially in the automotive industry, because it will give reduced fuel consumption. Natural fiber-reinforced composites are already being used extensively in the automotive industry,[4] but mainly for nonstructural applications. Many publications have described the combined use of natural fiber reinforcement and a commercial thermoset resin. For example, several researchers have investigated the combination of natural fibers and epoxy resins.[5–7] However, these composites can only be partially made from renewable resources because synthetic resins are invariably derived from crude oil. Thus, to produce composites with a low effect on the environment, it is desirable to use a bio-based matrix as well.

There are several reports describing composites prepared from thermoplastic biopolymers such as polylactic acid (PLA)[8–10] and polyhydroxybutyrate[11–13] together with natural fibers. This will yield composites with a very high content of renewable material. Because both the melt viscosity and the melting point of these biopolymers are relatively high, the processing methods for these composites will involve high temperatures or high compression pressures. For structural applications, thermoset resins such as epoxy or polyester resins are therefore preferred. Generally, these resins have relatively low molecular weights and lower viscosity, which will facilitate processing at room temperature or at lower compression pressures.

Bio-based thermosets are, however, a relatively new concept, and there are few commercial products available. Research in this area is progressing. To date, most researchers have focused on the use of vegetable oils as starting material for the synthesis of thermoset resins. Some attempts have been made to produce composites from natural fibers and chemically modified natural oils such as epoxidised

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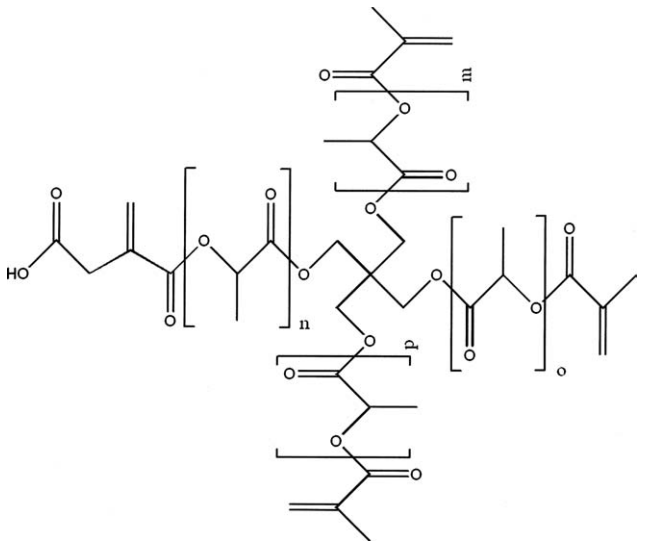

Figure 1 Idealised structure of the LA-based resin.

soybean oil. For example, Boquillon used epoxidised linseed oil together with hemp fibers.[14] Composites prepared from acrylated epoxidised soybean oil[15,16] and from maleinated acrylated epoxidised soybean oil[17] have also been reported.

Bio-based thermoset resin can also be produced from other starting materials. In a recent article, we described a new bio-based crosslinkable polyester resin.[18] This resin is produced in two steps. In the first step, pentaerythritol is reacted with lactic acid (LA) and itaconic acid. In the second step of the synthesis, the obtained star-shaped oligomers are end capped with methacrylic acid. The structure of the resulting resin is shown in Figure 1. Because the resin contains unsaturated carbon-carbon bonds in both the itaconic acid segment and the methacrylic acid segment, it can be cured by a free radical polymerization.

The objective of this study was to develop thermoset composites from flax fibers and the LA-based resin. To our knowledge, such composites have not been reported previously.

MATERIALS AND METHODS

Materials

Pollit, a crosslinkable resin based on LA, was obtained from JVS-Polymers. (Helsinki, Finland). The resin is a semisolid amorphous material with a viscosity of 7000 Pas at room temperature. Pollit was blended with 2.5 wt% tertiary-butyl peroxybenzoate (Norac Andos, Sweden), which is a high-temperature active initiator for thermosets. Nonwoven flax mats were obtained from Linapellava Oy (Särkisalmi, Finland). This flax mat consists of randomly oriented flax fibers and has a surface weight of 450 g/m^2.

Preparation of composite

The flax fiber mats were impregnated by spray impregnation. The fiber mats were cut either to a size of 15 $\times$ 15 cm for the flexural tests and impact tests or to 20 $\times$ 30 cm for the tensile tests. All fiber mats were dried in a vacuum oven at $\sim$ 40 m bar for 1 h at 105°C before use, to remove any humidity. Spray impregnations were done by means of conventional, air-driven, hand-held equipment for spraying ink. To reduce viscosity and to facilitate spray impregnation, the LA-based resin was dissolved in acetone (1 : 1). The fiber mats were placed on a balance to determine the fiber content. Each fiber mat was sprayed on one side. Two mats were assembled and were subsequently compression molded. The composites were molded at 170°C for 5 min, using a pressure between 1 and 4 MPa.

Characterization

Dynamic mechanical thermal analysis (DMTA Mark IV, Rheometric Scientific) was performed on the composites. DMTA was run in the dual cantilever bending mode and the typical sample dimensions were: thickness 1–2 mm, length 50 mm, and width 8 mm. The temperature interval was -10 to 150°C with a heating rate of 5°C/min and using a frequency of 1 Hz.

Dog bone-shaped test bodies, 150 mm long, for tensile tests were milled with a cutter and tested on an MTS 20/M (MTS System, Eden Prairie, MN) fitted with a 10-kN load cell. A cross-head speed of 50 mm/min was used and a minimum of five test pieces were tested. The composites were characterized by three-point bending tests with the same MTS 20/M testing machine. The cross-head speed was 10 mm/min, and the length between the holders was 40 mm. At least five test pieces were tested. For the mechanical test results, mean values and standard deviations were calculated.

The Charpy impact strengths of unnotched specimens were evaluated in accordance with ISO 179 using a Zwick test instrument (Zwick GmbH and Co. KG, Germany). Composites were produced with fiber ratios ranging from 40 wt% to 70 wt%. In total, 10 test pieces were tested to determine the mean impact resistance and standard deviation. The samples were tested edgewise.

The durability of the composites was evaluated by an ageing test. Test bodies for tensile testing were placed in a climate chamber (Vötsch VC 4057, Germany), at 38°C and 95% relative humidity for 1000 h. Composites with 70 wt% fiber were chosen for this test, as it was assumed that the degradation is higher for a composite with high fiber content due to the hydrofilic nature of the flax fiber. The tensile

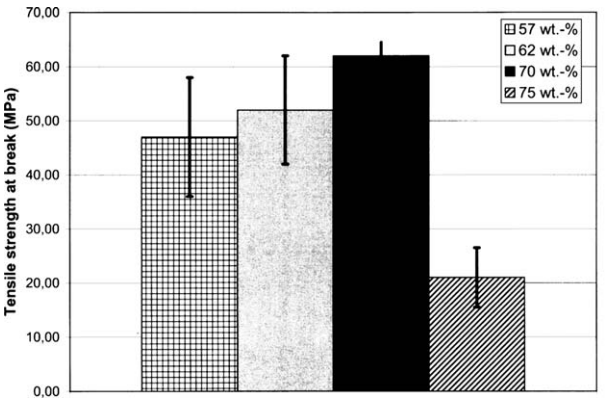

Figure 2 Comparison of the tensile strength of the composites prepared with different fiber ratios.

properties were evaluated before the test, directly after the test, and after 24 h of reconditioning at room temperature. The test procedure was the same as described earlier.

RESULTS AND DISCUSSION

Mechanical testing

The influence of the fiber content was evaluated by tensile testing. The results are summarized in Figures 2 and 3. The fiber content was varied from 57 wt% to 75 wt%. Both the tensile stress and the modulus increased with increasing fiber ratio up to 70 wt% fiber, where the highest values were recorded. The increase in mechanical properties as a result of increased reinforcement weight fraction is a sign of good adhesion between the fiber and the resin. At a fiber content of 75 wt%, the mechanical properties became drastically reduced. On inspection of the fracture surface, individual fiber bundles could be seen. At this fiber ratio, it is clear that the matrix does not impregnate the fibers completely, thus creating a weak composite. Composites with a fiber

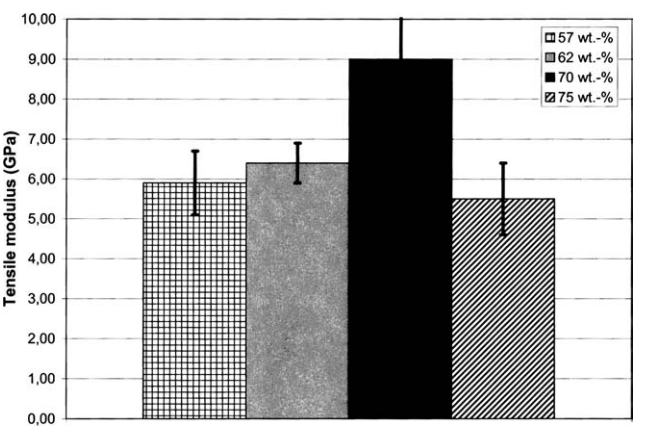

Figure 3 Comparison of the tensile modulus of the composites prepared with different fiber ratios.

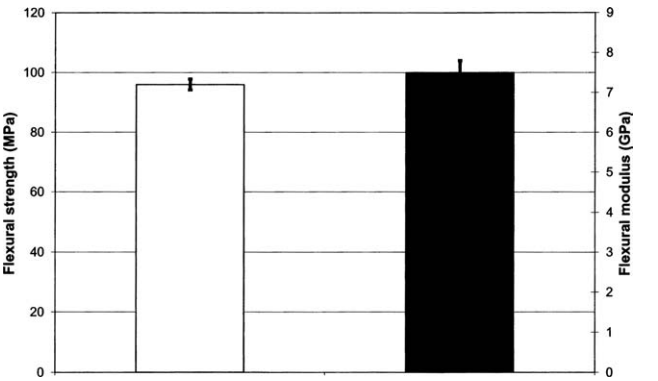

Figure 4 Flexural strength (left) and flexural modulus (right) of the composites reinforced with 70 wt% fibers.

content of 70 wt% have the highest possible fiber content with the impregnation methodology used. With this fiber content, the composite has a tensile strength of 62 MPa and a tensile modulus of 9 GPa. The flexural properties were also evaluated for the composite with 70 wt% fiber; see Figure 4. The composite has a flexural strength of 96 MPa and a modulus of 7,5 MPa.

The results of the unnotched impact tests for composites with a flax content of 40 to 70 wt% are shown in Figure 5. It can be seen that the impact resistance increases with increased fiber content. Usually, good adhesion between the fiber and the matrix is necessary to obtain good resistance to crack propagation during impact tests. Second, increasing the fiber content will increase the contact area between the fiber and the matrix, if there is good impregnation of fibers in the resin. The impact transfer should be more efficient at higher fiber loadings. This would explain the data obtained.

Dynamic mechanical thermal testing

Dynamic mechanical measurements give valuable information about the viscoelastic properties over a

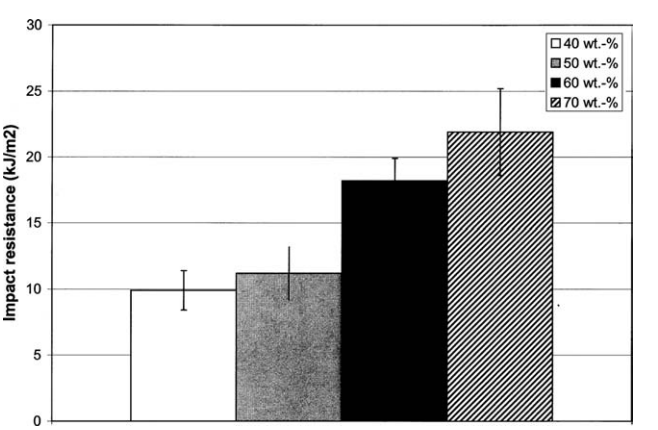

Figure 5 Comparison of the impact resistance of the composites prepared with different fiber ratios.

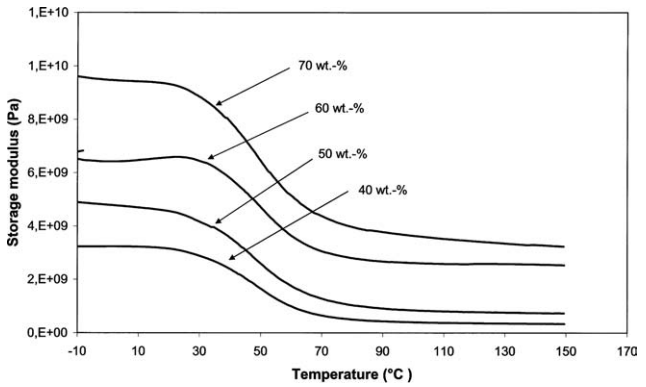

Figure 6 Comparison of the storage modulus of the composites prepared with different fiber ratios.

wide range of temperature. Composites were made from the flax mat with fiber ratios ranging from 40 to 70 wt%, and the results are shown in Figures 6 and 7. The results are summarized in Table I. For the 70 wt% fiber composite, the storage modulus drops from 9.32 GPa at 20°C to 3.29 GPa at 140°C. When the storage modulus of the composite with 70 wt% fiber was compared with the result of the flexural testing, a fairly good correlation was obtained (9.3 GPa and 7.5 Gpa, respectively). Increasing the fiber content had a positive effect on the storage modulus over the whole temperature range. The composite with the lowest fiber content (40 wt%) had a storage modulus of 3.15 GPa at 20°C, while increasing the fiber content to 70 wt% increased the storage modulus to 9.32 GPa. This is a threefold increase in the storage modulus, showing the reinforcing effect of the fiber. This trend corresponds well with the results of the tensile test, where the 70 wt% composite also gave the highest modulus.

The tan δ curves are shown in Figure 7. The glass transition temperature was recorded at the maximum value of the tan δ. The authors reported the glass transition temperature of the neat resin to be 83°C.[18] Surprisingly, reinforcing the resin with flax

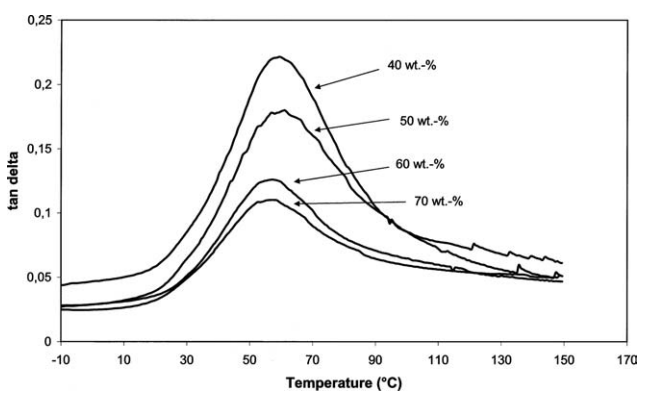

Figure 7 Tan δ of the composites prepared with different fiber ratios.

TABLE I
Summary of DMTA Results

Fiber ratio (%)	E′ at 20°C (GPa)	E″ at 20°C (GPa)	T_g (°C)
40	3.15	0.18	59.4
50	4.56	0.18	61.2
60	6.58	0.24	57.3
70	9.32	0.30	57.3

fiber lowered the glass transition temperature by more than 20°C. However, the sample preparations in the two studies are different. In the first study, the neat resin was polymerized in a closed silicon mold. In this study, the resin was dissolved in acetone and sprayed onto the surface of the fiber mat. The results are therefore not directly comparable. The impregnated fibers were cured in an open mold, and it is likely that there were traces of acetone still present in the sample. When the acetone evaporates, other low-molecular weight compounds can evaporate as well. This will affect the crosslinking density and shift the glass transition temperature to lower temperatures. This might be a possible explanation. In this study, the glass transition temperatures recorded varied somewhat between the different fiber ratios, from 57 to 61°C. This difference between the composites of different fiber ratios might perhaps be caused by a slightly different curing between the individual samples, rather than by an actual difference between the samples.

Scanning electron microscopy

A critical factor when producing composites is the ability of the resin to wet out the fiber and the resulting adhesion between the reinforcement and the matrix. Natural fibers are hydrophilic, whereas most commercial resins are hydrophobic. This can create a lack of adhesion between the fibers and the matrix[19] and several authors have tried to modify the natural fibers to obtain better adhesion. The LA-based resin is most probably more hydrophilic than conventional thermosets such as epoxy resins and unsaturated polyester resin, which are usually aromatic compounds. The slightly polar oxygen in the

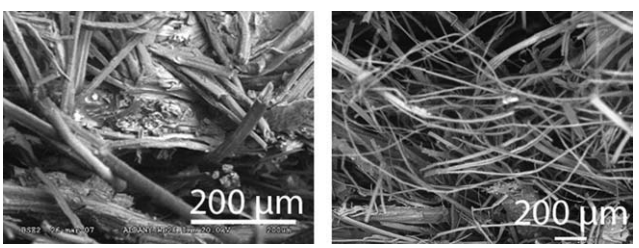

Figure 8 SEM image of the fracture surface of the composite with 70 wt% flax fiber (left) and 75 wt% flax fiber (right).

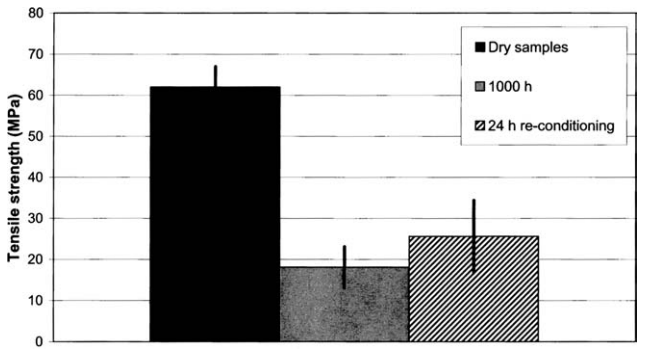

Figure 9 Tensile strength of dry samples after 1000 h of ageing, and after 24 h of reconditioning.

resin could possibly form hydrogen bonds with the hydroxy groups of the cellulose. However, conventional thermoplastic PLA reinforced with flax fibers has been evaluated previously,[8,20] and the adhesion between the fiber and the matrix is not optimal. Figure 8 shows the fracture surface of the composite with 70 wt% flax and 75 wt% flax. When measuring the tensile properties, there was a significant difference between these two composites, as the latter clearly had a lower tensile strength and modulus. By inspecting the two samples, it was even possible to see individual fibers that were not dispersed in the matrix of the 75 wt% composite. With the impregnation methodology chosen, the highest possible fiber ratio is 70 wt%.

Humidity ageing test

The composites were placed in a climate chamber for 1000 h at 38°C and 95% relative humidity to study their ageing properties. The tensile properties are shown in Figures 9 and 10. The test showed that the prepared composites were relatively sensitive to the test conditions. After 1000 h, the composites had lost as much as 70% of their tensile strength. Reconditioning of the samples did not have any significant effect. The modulus followed the same pattern; see Figure 10. It dropped from 9 GPa to 2.5 GPa. The elongation increased from 1.4% (dry) to 3.1% (wet) and dropped back to 1.5% when reconditioned.

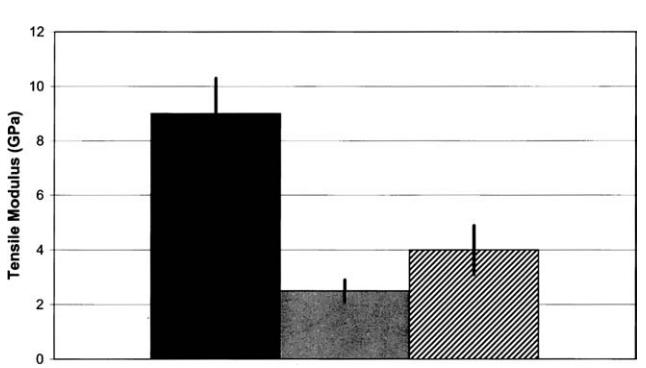

Figure 10 Tensile modulus of dry samples after 1000 h of ageing and after 24 h of reconditioning.

Vegetable fibers are known to be hygroscopic, due to the presence of hydroxy groups in the structure of cellulose, and their moisture content typically reaches 8-13 wt%.[21] Also, thermoplastic PLA is sensitive to humidity[22] and it is not surprising that the composites in this study lost most of their mechanical strength during the humid conditions of the tests. Considering the high fiber content of these composites (70 wt%) and the high relative humidity in the climate chamber, the moisture absorbed may have hydrolyzed the ester bonds of the resin. The stability of the composites would probably be improved by copolymerising the resin with styrene. This would probably alter the crosslink network by adding aromatic rings to the structure. This should be evaluated in future investigations.

CONCLUSIONS

The objective of the study was to determine whether a LA-based thermoset resin can be used for the preparation of natural fiber-reinforced composites. The results showed that the resin can be used as a matrix for flax fibers with a fiber ratio of as much as 70 wt% and that the composites produced had relatively good mechanical properties. As natural fibers are relatively cheap, such a high fiber ratio allows affordable composites to be produced. The results of the mechanical tests and of the microscopy study indicate that there was fairly good adhesion between the fiber and the matrix. It would probably have been possible to improve the mechanical properties in this study further by surface treatment of the fibers.

The result of the weathering test indicates that the mechanical properties of the flax-reinforced composites deteriorate when exposed to humidity, which was expected. This suggests that the main applications of the composites should be indoor products, such as furniture and construction panels. Their mechanical properties should be sufficient for these products.

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