Synthesis and Characterization of a Lactic Acid-Based Thermoset Resin Suitable for Structural Composites and Coatings

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ABSTRACT: A new biobased polyester resin was developed for thermoset composite applications. The resin is potentially inexpensive and can be produced industrially by relatively simple means. The resin consists of star-shaped methacrylated oligomers of lactic acid (LA). LA oligomers were synthesized in a two-step process: in the first step, oligomers of LA were polymerized by direct condensation of LA. In the second step, the oligomers were end-functionalized by methacrylic anhydride. The resin was characterized by differential scanning calorimetry, Raman spectroscopy, NMR, rubber process analyzer, and TOF-SIMS. Tests show that the resin can be cross-linked into a rigid network within a couple of minutes upon thermal initiation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 480–486, 2010

Key words: thermosets; crosslinking; synthesis; biopolymers; renewable resources

INTRODUCTION

Polylactic acid (PLA) is an attractive polymer because it is biodegradable and as the monomer, lactic acid (LA), can be made from renewable sources by fermentation. Today, PLA is therefore used in many products, such as medical applications,[1–3] packaging,[4] and also in structural fiber-reinforced composites.[5–7] Thermoplastic PLA can be produced by ring-opening polymerization or by direct condensation.[8,9] The latter method offers a cheap and simple production but it gives low-molecular-weight polymers lacking good mechanical properties as a result. Ring-opening polymerization, on the other hand, offers a more controlled chemistry resulting in high-molecular-weight PLA. The drawback of this method is that it is a more complicated process.

An alternative route to high-molecular-weight PLA is to synthesize a low-molecular-weight telechelic prepolymer by direct condensation of LA. By end-functionalizing the prepolymers with reactive groups and then coupling the prepolymers by a chain-extender, a high-molecular-weight PLA can be achieved. The synthesis of telechelic PLA has been studied by several authors but mainly for medical applications.[10–12]

In this study, we have synthesized a crosslinkable resin based on LA. The resin consists of star-shaped oligomers of LA. In the first step of the synthesis, LA is reacted with pentaerythritol (PENTA) and itaconic acid (IT) by a direct condensation reaction. In the second step, the obtained oligomers are end-functionalized by reaction with methacrylic anhydride (MAAH). This reaction gives a thermoset resin consisting of the methacrylated oligomers of lactic acid together with the methacrylic acid (MAA), which forms in the anhydride hydrolysis. Hence, reactive double bonds are introduced in the LA oligomer by the IT, by methacrylate end-groups, and by the free MAA. The resin is thus a free radical crosslinkable resin, based on the renewable LA, and can be considered as a thermoset PLA.

Thermoset resins are frequently used in many composite and coating applications. Unsaturated polyesters and epoxy resins are frequently used thermosets. Such resins are however produced from petroleum-based resources. The resin presented in this article offers a LA-based type of unsaturated polyester with a high content of renewable material, and which can be processed similarly as conventional unsaturated polyesters. Comparing the synthesized resin to the common thermoplastic PLA, it

has several advantages: first, it has a low viscosity, which is a major advantage when producing fiber-reinforced composites. Low viscosity is required for several composite processing methods, such as vacuum infusion, spray and hand lay up, filament winding, and pultrusion. This is a clear advantage for industrial manufacture of composites from the synthesized resin. Second, the resin can by copolymerized with small amounts of reactive diluents capable of participating in the crosslinking reaction. This will make it possible to adjust the crosslinking density, and thus the thermal and mechanical properties of the cured resin. Finally, the nature of the rather straightforward synthesis methodology enables an easy scale-up with low investments, and industrial production of the biobased thermoset should therefore be of interest.

The objective of this study was to investigate the technical feasibility of the resin and its curing behavior, in order to be able to prepare composites. The curing of the resin was characterized by thermal, rheological, and spectroscopic methods.

EXPERIMENTAL

Material

The oligomers were synthesized from L-lactic acid (88% in water, Purac, Gorinchem, Netherlands), pentaerythritol (98%, Lancaster, Ward Hill, MA), and itaconic acid (99%, Acros Chemicals, Geel, Belgium). Sn(II)octoate (95%, Sigma, St. Louis, MO) was used as a catalyst in the condensation reaction. Hydroquinone (J.T. Baker, Deventer, Holland) was used as an inhibitor during the end-funtionalization reaction. The reagent for end-functionalization was methacrylic anhydride (92%, Fluka, Buchs, Switzerland). The reactions were performed under nitrogen atmosphere (N_2, 99.5%). All the reagents were used as received.

Andonox PB (*tert*-butyl peroxybenzoate) from Norac Andos (Azusa, CA) was used as initiator, 2 wt %, for the free radical-initiated crosslinking of the synthesized resin.

Synthesis

Bulk polymerization of the star-shaped oligomer of LA

A total of 89 mol % of LA, 5 mol % of IT, and 6 mol % of PENTA were added into a 250 mL of glass reactor. The glass reactor was immersed in an oil bath with a set temperature of 120°C and a set stirring rate of 140 rpm. Then 0.05 wt % of tin octoate calculated from the amount of LA was added dropwise into the reaction mixture. The oil bath temperature was then increased to 140°C. The nitrogen flow was directed into the reactor via a stainless steel capillary tube. After the formed water had distilled off from
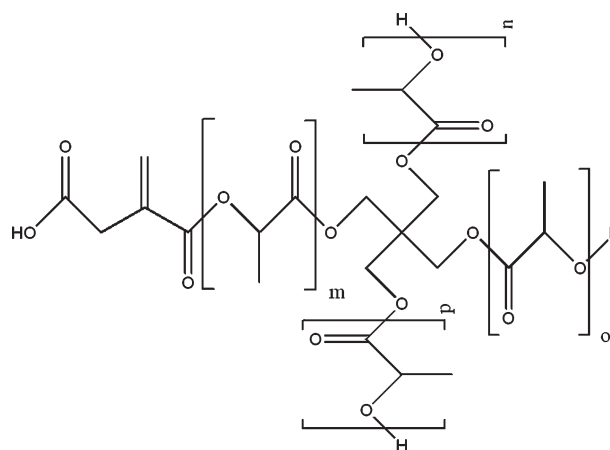

Figure 1 Idealized structure from the first step of the synthesis. The IA branch will be ─COOH-terminated.

the reactor, the set temperature was increased at a rate of 15°C/h during 4 h to 180°C, where the temperature was kept until finalizing the polymerization. The total polymerization time was 15 h. The product resin was transparent, rigid, brittle, and slightly yellowish in color. An idealized structure of the obtained star-shaped oligomer is presented in Figure 1. As the molar amount of the IT is much lower than the molar amount of the other components, it can be assumed that IT segment will be only present in one of the PENTA branches.

End-functionalization of the LA-based oligomer

The obtained star-shaped hydroxyl-terminated oligomers were reacted further with MAAH. After the condensation reaction, the oligomer was cooled down to 100–110°C, and 0.1 wt % of hydroquinone was added into the stirred reaction mixture as a stabilizer. Subsequently, MAAH (15 wt %, calculated from the amount of oligomer) was added dropwise into the reaction mixture. After the addition, the temperature was increased to 120°C and kept for 3 h under nitrogen atmosphere. An idealized structure of the obtained end-functionalized oligomer is presented in Figure 2. The PENTA branches containing IT will be carboxyl-terminated and cannot thus react in the end-functionalization. Instead, these might undergo coupling with an other PENTA-oligomer.

Characterization

The synthesized resins were analyzed by ^{13}C-NMR. Samples were dissolved in $CDCl_3$ and analyzed on a Chemagnetics CMX Infinity spectrometer operating at 400 MHz. Two samples were analyzed: the resin without end-functionalization with MAAH and the final resin with the end-functionalization.

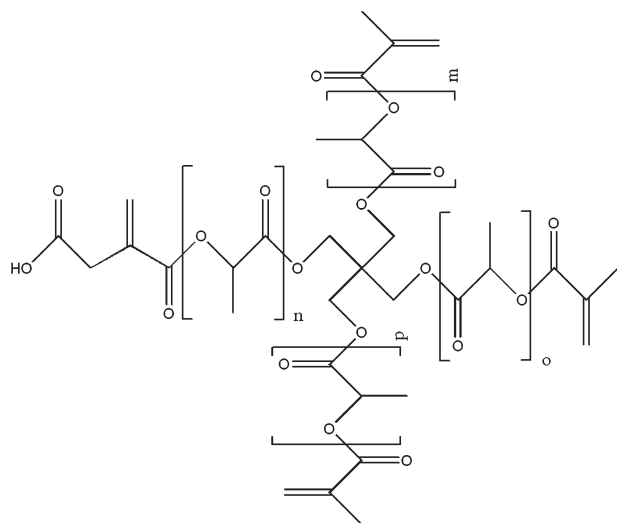The resins were further analyzed by means of time-of-flight-secondary ion mass spectrometry

Figure 2 Idealized structure from the second step of the synthesis. Only the ─OH-terminated chains will be terminated with MAA.

(TOF-SIMS) using a TOFS-SIMS IV, IONTOF, GmbH, Germany. Spectra were recorded for both positive and negative secondary ions. About 1 mg of the resin was dissolved in 2 mL of chloroform. Positive secondary ion mass spectra were measured from an area of 500 μm × 500 μm, using 25 keV Bi_3^+ primary ion beam. The acquisition time for each measurement was 100 s.

Raman spectroscopy was used to verify the end-functionalization of the oligomers and to follow the crosslinking of the molecule. Raman scattering experiments were performed on using a DILOR-XY800 triplegrating spectrometer, in the double subtractive mode in a 180° back scattering geometry. The spectrometer was equipped with a liquid nitrogen cooled charge coupled device detector, and the 514.5 nm line from an Ar^+Kr^+ laser was chosen as the excitation source. Measurements were performed on samples before and after free radical-initiated curing.

The crosslinking reaction of the resin was also monitored by means of a rubber process analyzer (RPA) from Alpha Technologies. A total of 2 wt % of the initiator (*tert*-butyl peroxybenzoate) was blended into the resin, and the rheological measurements were performed at 1 Hz at temperatures ranging from 130 to 170°C.

The cured samples from the RPA measurements were further analyzed by differential scanning calorimetry (DSC). The measurements were performed on a Q1000 from TA Instruments. Samples were sealed in aluminum pans and the measurements were run typical from −20 to 200°C at a heating rate of 10°C/min and at a cooling rate of 20°C/min. Data from the first heating run were used to investigate the efficiency of the crosslinking reaction.

Dynamical mechanical thermal analysis (DMTA, Perkin Elmer) was performed on the cured resins. DMTA was run in the single cantilever bending mode, and the typical sample dimensions were as follows: thickness 1–2 mm, length 25 mm, and width 7 mm. The temperature interval was from 0 to 180°C with a heating rate of 3°C/min and using a frequency of 0.1 Hz.

The viscosity of the uncured resin was determined using a Bohlin rheometer CS30 from Malvern Instruments. All measurements were done with a truncated cone plate configuration (Ø15 mm, 5.4°).

Thermogravimetric analysis (TGA) was performed on cured samples (about 20 mg) using a Q500 from TA instruments. The analysis was performed under N_2 atmosphere using a heating rate of 10°C/min.

RESULTS

Nuclear magnetic resonance spectroscopy

The NMR analysis was done to identify the chemical structure of the synthesized resins, and especially to verify the MAAH modification done in the second synthesis step. The ^{13}C-NMR spectra of the unmodified and end-capped resin are shown in Figure 3,
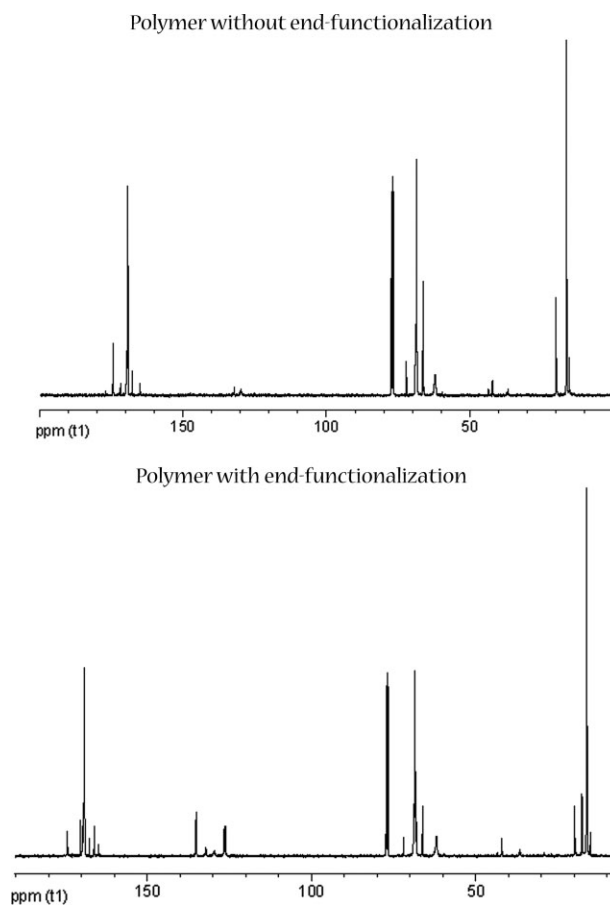

Figure 3 Full-scale spectra of the two polymers in CDCl$_3$.

TABLE I
Assignments of Peaks From ^{13}C-NMR

Peak number	Chemical shift (ppm)	Assignment
1	169–170	C=O, main chain
2	174.4	C=O, endgroup of LA
3	165	C=O, of itaconic acid
4	171.8–172.1	C=O, of itaconic acid
5	167.8	C=O, from residual LA
6	129.8	C=CH$_2$, of itaconic acid
7	132.2	C=CH$_2$, of itaconic acid
8	68–69	―CH, of lactic acid
9	66.4	―CH―OH, of lactic acid
10	72.2	―CH, from lactide
11	62	CH$_2$ of pentaerithytol
12	59.7	CH$_2$ of unreacted pentaerithytol
13	42	Quaternary C of pentaerithytol, fully reacted
14	43.5	Quaternary C of pentaerithytol, partly unreacted
15	36.5	CH$_2$ of itaconic acid
16	16.2–16.4	CH$_3$ of lactic acid
17	19.5–20	CH$_3$ of lactic acid, hydroxyl-terminated
18	15.2	CH$_3$ of lactide
19	166.3	C=O, of methacrylate end-group
20	170	C=O of lactic acid when end-functionalized
21	171	C=O of free methacrylic acid
22	126–127	―C=CH$_2$ of methacrylate
23	135	―C=CH$_2$ of methacrylate
24	17.6–17.8	CH$_3$ of methacrylate

whereas the assignments of the chemical shifts are shown in Table I. The peaks were assigned based on data from the literature[10] and also by comparing to previously synthesized model compounds.

The most interesting area is the carbonyl area, where all resin components will give a signal. The LA component will give two signals, of which the main-chain carbonyl C=O can be found at 169–170 ppm (1). The signal is broad, as LA carbonyls next to the PENTA core molecule, as well as the IT, will give different signals compared with a LA carbonyl next to another LA component. The carbonyl in the LA end-group gives a signal at 174.4 ppm (2), and from the chemical shift it can be seen that it is a hydroxylic end-group. The IT component gives two small signals, at 165 ppm (3) and at 171.8–172.1 ppm (4). These signals were identified by comparing with spectra for previously synthesized model compounds. In the spectra residual cyclic lactide from the synthesis can also be detected at 167.8 ppm (5). The methylene group in the IT component gives two weak signals at 129.8 (6) and 132.2 ppm (7), respectively.

The carbons adjacent to an oxygen atom can be seen in the range of 60–75 ppm. The CH next to the reacted LA carbonyl gives a broad signal at 68–69 ppm (8), whereas the CH adjacent to the hydroxyl

end-group gives a signal at 66.4 ppm (9). The lactide CH gives a signal at 72.2 ppm (10). The CH$_2$ group in the PENTA core group can be seen as a weak signal at 62 ppm (11), and it is even possible to detect a very weak signal at 59.7 ppm (12), because of an unreacted PENTA branch. The quaternary carbon atom in PENTA gives two signals, the fully reacted core molecule at 42 ppm (13), and a partly unreacted core at 43.5 ppm (14). The CH$_2$ group from the IT component can be seen in the same area at 36.5 ppm (15). The LA methyl group can be detected in the 15–20 ppm range. The main-chain methyl group is found at 16.2–16.4 ppm (16), and the methyl group in the hydroxyl-functionalized end-group at 19.5–20 ppm (17). The lactide CH$_3$ is seen at 15.2 ppm (18). The same signals can be identified in the resin end-capped with the methacrylate end-group, in addition signals from methacrylate end-group as well as free MAA can be identified. The carbonyl group in the methacrylate end-group gives one distinct signal at 166.3 ppm (19), and the reaction can further be verified by the partial shifting of the LA carbonyl to 170 ppm (20). Free MAA, which is formed in the end-capping reaction by anhydride hydrolysis, is detected by the signal at 171 ppm (21). The olefinic carbons of both metacrylate components give signals at 126–127 ppm (22) and around 135 ppm (23), and the methyl groups give two signals at 17.6–17.8 ppm (24).

From the peak areas of the LA end-group at 174.4 ppm and the main-chain LA components at 169−170 ppm, it is possible to estimate that the average chain length of the branches is around five LA units.

The NMR analysis can be summarized as follows: oligomers from the first synthesis step have mainly alcohol end-groups as expected. In the second step, the MAAH reacts with the alcohol groups of the LA and with a small amount of residual alcohol groups from PENTA. In the oligomers analyzed, the monomer ratio among LA, PENTA, and IT has been adjusted to give hydroxyl-ended oligomer. IT has reacted in the polymerization, because there is no proof of carboxylic acid groups in the NMR spectrum. This means that coupled PENTA-oligomers have been formed, by reacting the COOH group of the IA containing PENTA-branch with an OH-terminated PENTA-branch in an other molecule. However, the interpretation of IT position in the polymer structure is problematic. The position of IT is therefore unknown in the structure.

Time-of-flight secondary ion mass spectrometry

Size exclusive chromatography (SEC) is known to be inaccurate for molecular weights below 20,000 g/mol; additionally, SEC is usually used for linear molecules. TOF-SIMS mass spectroscopy can be
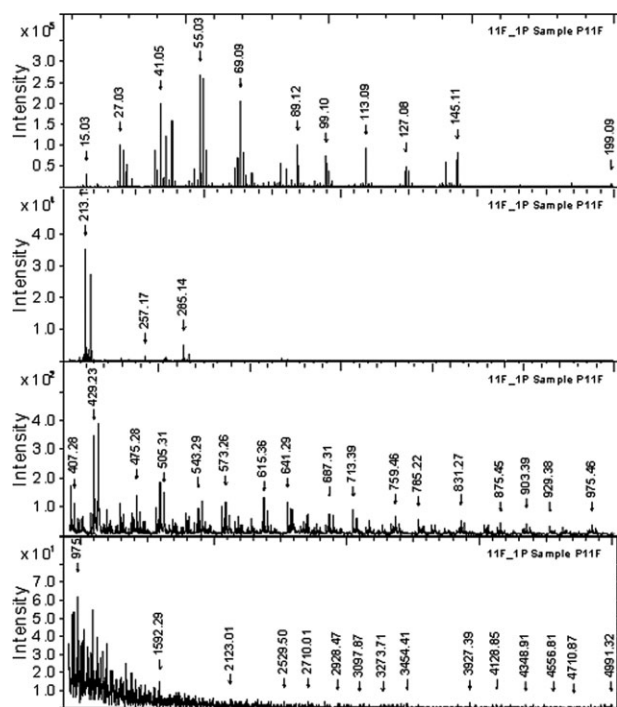
Figure 4 Mass spectra from (a) 0–200 mass units, (b) 200–400 mass units, (c) 400–1000 mass units, and (d) 1000–5000 mass units.

used as an alternative to characterize low-molecular-weight oligomers, which are branched. The mass spectrum is shown in Figure 4. The molecular weights of the oligomers detected in the TOF-SIMS analysis are rather small. Molecular weights up to about 2000 g/mol were detected. Considering the stochiometric balance between PENTA and LA, this is expected. The spectrum is however very complicated and a complete interpretation is not very straightforward. The spectrum between 500 and 720 mass units (u) is summarized in Table II. In this part of the spectrum, six different oligomer distributions were observed (series A–F). Each series has a difference in molecular weight of 72 mass units between the peaks. This is the repeating unit of LA. Each series is shifted in relation to each other, indicating that they have the same repeating unit, LA, but with

TABLE II
Oligomer Distributions Between 500 and 720 Mass Units

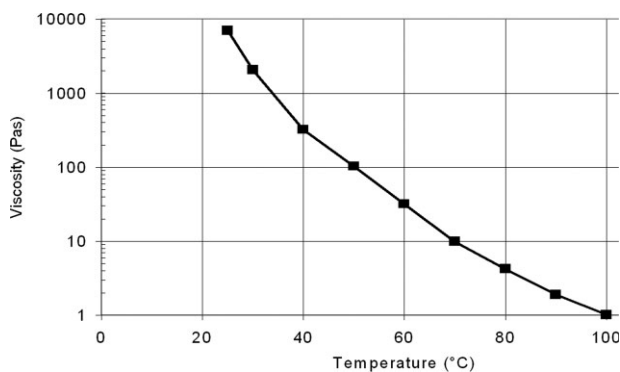| Mass	Series	Mass	Series	Mass	Series
517.227	A	521.2297	B	561.1958	C
589.3367	A	593.2589	B	633.2172	C
661.299	A	665.2712	B	705.2341	C
733.3607	A	737.3021	B		
531.2171	D	563.2746	E	501.2328	F
603.2537	D	635.303	E	573.3015	F
675.288	D	707.3204	E	645.3037	F
				717.3008	F

Figure 5 Viscosity measurement of the resin.

different groups connected to the chain—either in the chain or as end-groups.

Viscosity

The viscosity of a thermoset resin is very important as it will determine how the resin can be processed. The viscosity of the resin was monitored by means of stress viscometry in the temperature range 25–100°C and is shown in Figure 5. The resin is very viscous at room temperature with a viscosity of about 7000 Pa s at 25°C.

Upon heating to 80°C, the viscosity of the resin drops to about 4 Pa s. The resin is therefore best suitable for processing at higher temperatures, for example, by using heated molds. Dilution by a reactive diluent can also be a possibility to reduce viscosity.

Crosslinking characterization

The crosslinking reaction was followed by monitoring the increase in viscosity during the reaction by the RPA.[13] The result is shown in Figure 6. The maximum viscosity and the time to the maximum
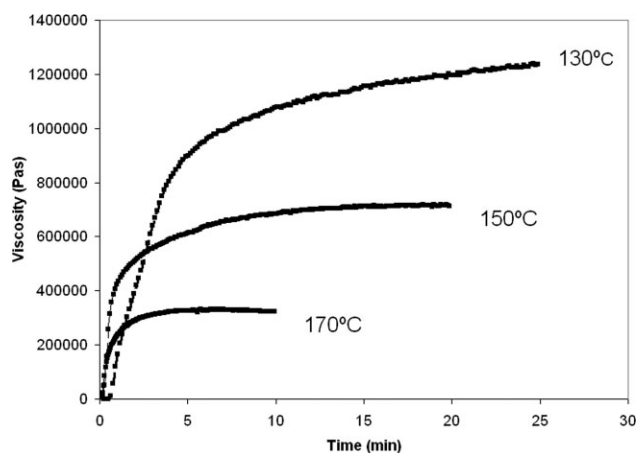

Figure 6 Curing curves measured by RPA at various temperatures.

TABLE III
Rheological and Thermal Analysis of the Cured Neat Resin

	RPA		DSC
Curing temperature (°C)	Maximum viscosity (Pa s)	Time to maximum viscosity (min)	Residual heat energy (J/g)
130	1,240,000	25	32.05
150	718,000	20	14.06
170	332,000	6.5	0

viscosity were recorded. The test pieces of the RPA analysis were subsequently analyzed by dynamical DSC scans. The results are summarized in Table III. The reaction goes very slowly at 130°C, and the DSC analysis of the residual heat exotherm also reveals that the material was not completely cured. At 170°C the resin cures to completion within a few minutes. At 170°C, there is no residual heat exotherm giving further proof that the material is completely crosslinked. The used *tert*-butyl peroxybenzoate requires therefore a high temperature to decompose and produce radicals. Crosslinking at a lower temperature requires the use of another peroxide.

Raman spectroscopy

Several researchers have used Raman spectroscopy to characterize thermoplastic PLA.[14–16] The crosslinking reaction of unsaturated polyester resins has also been studied by Raman spectroscopy.[17] Raman spectroscopy is a fast and sensitive technique, the signals can be captured by using fiber optics, and carbon–carbon double bonds are particularly easy to detect. In this study, Raman spectroscopy was used to give a qualitative verification of the second step of the synthesis, where the oligomers are end-functionalized, and to verify that the crosslinking goes to completion, see Figure 7. In the crosslinking reaction, the carbon–carbon double bonds react, and the most interesting part of the spectra is therefore the region for the carbon–carbon double bonds at about 1640 cm^{-1}. The rest of the spectra is more or less the same for all samples and will not be interpreted further. As for the oligomer without end-functionalization, only a low-intensity band can be observed. This peak can be assigned to the double bond of IT. Functionalizing the oligomers with MAAH, the band at 1640 cm^{-1} becomes stronger. The Raman spectroscopy analysis supports the NMR interpretation that end-functionalization occurs as expected. The complete crosslinking reaction can also be verified by the Raman analysis. From the lower diagram of Figure 7, no band can be detected at 1640 cm^{-1}. This clearly demonstrates that all double bonds had
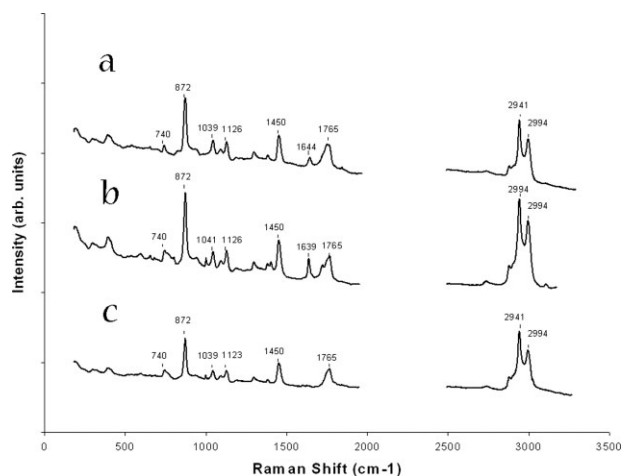

Figure 7 Raman spectra for (a) unfunctionalized polymer, (b) functionalized, uncured polymer, and (c) functionalized, cured polymer.

reacted when crosslinking the oligomers. This is in accordance with the thermal analysis which did not reveal any residual heat exotherm.

DMTA and TGA

Dynamical mechanical tests were run to characterize the neat crosslinked resin, see Figure 8. The resin has a storage modulus of about 1.6 GPa at 20°C; increasing the temperature to 150°C the storage modulus decreased to 9.8 MPa. The glass transition temperature, measured as the peak of tan δ, was recorded to 83°C. This is slightly higher than for thermoplastic PLA. Comparing this value with a commercial polyester resin, the glass transition is lower for this biobased resin. This indicates the lower degree of crosslinking, and that a less dense network is obtained. Secondly, commercial
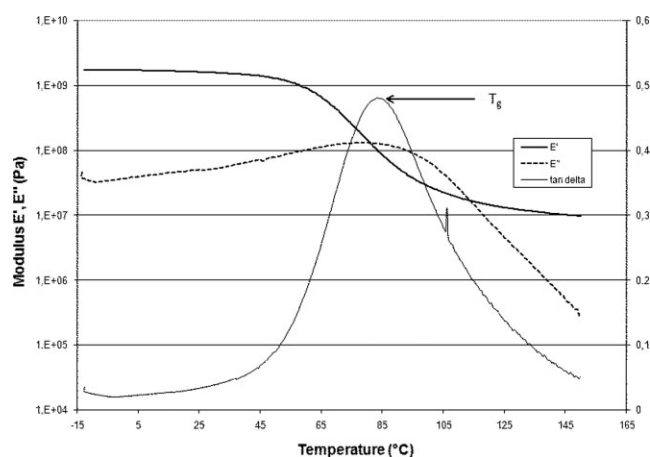

Figure 8 DMTA curve for the neat crosslinked resin. Temperature dependence of the storage modulus (E') and loss modulus (E'').
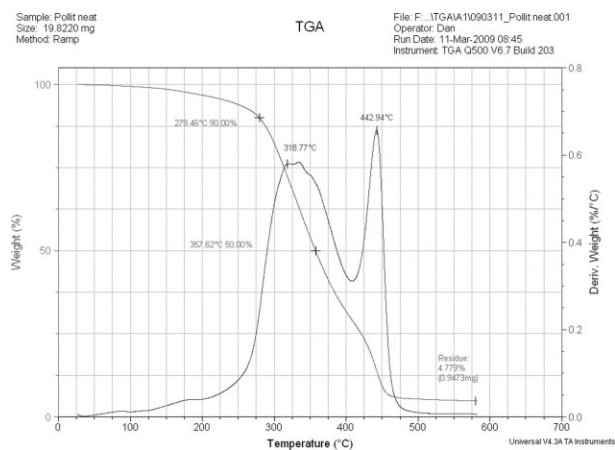
Figure 9 Thermogravimetric analysis of the crosslinked resin.

unsaturated polyester resins are preblended with styrene, which act as a reactive diluent. Adding stiff aromatic rings to the crosslinked chemical structure usually increases the glass transition temperature. The T_g values for the resins are therefore not directly comparable. The loss modulus increased slightly when temperature was raised up to a temperature of 63°C where it has its maximum.

The crosslinked resin was finally characterized by TGA, see Figure 9. The polymer is relatively stable up to 200°C. At about 279°C, the resin has lost 10 wt %, and at about 358°C the resin has lost 50 wt %. The maximum degradation occurs at 319°C. At 443°C the curve of the derivative weight has a second peak.

CONCLUSIONS

A biobased crosslinkable resin was prepared in two steps from LA. In the first step, star-shaped oligomers of LA were prepared by a direct condensation with penthaerithrytol and IT. In the second step, the obtained oligomers were methacrylated by using MAAH. An unsaturated LA-based polyester capable of undergoing free radical-initiated crosslinking is thus produced. The synthesis is relatively simple and has the potential of being upscaled for industrial production by relatively simple means.

This study shows that the resin can be completely crosslinked within a few minutes upon thermal decomposition of a peroxide initiator. Thermal, rheological, and spectroscopic analyses show that the reaction goes to completion, forming a strong rigid material, which is crosslinked.

The crosslinked resin has a glass transition temperature of 83°C, which is higher than for thermoplastic PLA; this can obviously be advantageous for some applications. The resin is rather viscous at room temperature. Heating the resin to 80°C the viscosity drops to 4 Pa s, and the resin can be processed at elevated temperatures by several processing techniques. Another option is to dilute the resin in a reactive solvent, which decreases the viscosity, and which is capable of participating in the crosslinking reaction. By using a solvent of biobased origin, the degree of renewable content is not decreased.

This novel resin could obviously find applications as a thermoset resin for composite or coating applications. The feasibility to use the resin for the preparation of thermoset composites needs to be evaluated in coming studies.

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