



Vegetable oil thermosets reinforced by tannin–lipid formulations

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ABSTRACT

Totally bio-based thermosetting polymers which are comparable to synthetic polyester thermosets have been prepared from copolymerization of condensed tannin–fatty acid esters with vegetable oils. Oxidative copolymerization of tannin linoleate/acetate mixed esters with linseed oil and tung oil produced polymer films ranging from soft rubbers to rigid thermosets. Tannin incorporation into the formulations was essential for the final product to achieve necessary mechanical strength. Films had ambient modulus values between 0.12 and 1.6 GPa, with glass transition temperatures ranging from 32 to 72 °C and calculated crosslink densities of 1020–57,700 mol m⁻³. Film stiffness, T_g and crosslink density increase with greater tannin linoleate/acetate content due mainly to this tannin component providing rigidity through polyphenolic aromatic rings and unsaturated chains as crosslinking sites.

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1. Introduction

Polymers are materials that are used in a diverse range of applications. With polymers currently prepared predominantly from petrochemical sources, there is increasing effort to substitute petrochemical feedstocks for readily available renewable materials. A major challenge with feedstock replacement is to find renewables suitable for substitution into performance materials where strength and durability are required, such as the thermoset composites used in automotive and construction applications. Natural oils derived from both plant and animal sources are important renewable raw materials used in the chemical industry. Recently, natural oils have been investigated as raw materials to prepare thermoset resins and polymers because of their ready availability, potential biodegradability and multifunctionality [1–3]. Differing fatty acid compositions and levels of unsaturation present in the fatty acid side chains make these oils ideal feedstocks for the preparation of thermoset polymers. In this respect, polymer materials can be prepared either directly, by using the unsaturation available present in the oils, or by introducing polymerizable functional groups into the chemical structure of triglyceride units and using the functionalized oils in radical, condensation polymerizations [3,4] and oxidative polymerization applications [5,6]. In addition,

oils with high degrees of unsaturation may be polymerized directly via thermal or cationic polymerization [7–9] as thermosets. However, in order to provide sufficient mechanical strength and reinforcement to thermoset resins, the preparation of polymers from natural oils generally necessitates the incorporation of petroleum-based aromatic comonomers such as styrene or divinyl benzene into the chemical structure [8,10–13]. Condensed tannins are another class of renewables that have been used in the production of tannin-based adhesives [14]. Tannins are oligomeric polyphenolics possessing rigid aromatic structures which potentially could substitute petroleum-based comonomer components in natural oil-based polymer formulations. Consequently, the final products have the potential to be completely composed of renewable resources and capable of substituting current petrochemical-based formulations.

This work reports the first synthesis of totally bio-based, thermosettable polymers obtained from combination of tannin and lipids. Quebracho and pine bark tannins, which are two types of commercially available condensed tannins, are used to substitute petroleum-based aromatic vinyl monomers in the preparation of vegetable oil-based polymer systems. Both tannin types were sequentially esterified with linoleate and acetate groups to provide tannin–fatty acid esters. The functionized tannins were polymerized with linseed and tung oils to produce thermoset polymer films and the resulting materials characterized to determine any relationships between chemistry with polymer structure and properties, and the influence of tannin content on polymer performance.

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2. Experimental

2.1. Materials

Quebracho tannin (QT) was sourced as the commercially available product Colatan GT100 from Unitan (Argentina). Pine bark tannin (PT) was obtained by hot water extraction of *Pinus radiata* bark followed by spray drying of the extract liquor. Both tannin materials were vacuum dried at 80 °C for 24 h before use. Linoleic acid (95%) was purchased from Sigma Aldrich and used as received. 1-Methylimidazole ($\geq 99\%$, from Sigma Aldrich) was dried with 4 Å molecular sieves. Phosphorous trichloride ($\geq 99\%$) was purchased from Merck and used as received. Acetic anhydride (from Ajax Finechem) was used without further purification. Acetone was dried over K_2CO_3 then distilled. Linseed oil (LIN) was supplied by Oil Seed Extraction Ltd., New Zealand. Refined tung oil (TUN) was purchased from Watty Ltd., New Zealand. Cobalt octoate (6% solution in white spirit) and zirconium octoate (12% solution) were supplied by Nuplex Ltd., New Zealand.

2.2. Synthesis of linoleic acid chloride

A 250 ml three-neck flask equipped with a condenser, dropping funnel, nitrogen inlet and magnetic stirrer was flushed with nitrogen and phosphorous trichloride (20 ml, 0.23 mol) was added. Linoleic acid (120 ml, 0.38 mol) was then added dropwise with stirring. The reaction mixture was further stirred under nitrogen for 2 h at 55 °C. Excess phosphorous trichloride was removed by rotary evaporator and the phosphorous acid formed was removed from the product by centrifuge. The acid chloride product was flushed with nitrogen and stored in a fridge and used without further purification. 1H -nuclear magnetic resonance (NMR) δ (ppm): 5.36 (m, 4H), 2.88 (t, 2H), 2.78 (t, 2H), 2.06 (m, 4H), 1.72 (m, 2H), 1.33 (br, 14H), 0.89 (t, 3H).

2.3. Synthesis of fully substituted tannin linoleate/acetate

Linoleic acid chloride (25 ml) was added dropwise into a 500 ml flask containing tannin (10 g), 1-methylimidazole (12 ml) and acetone (250 ml). After the addition of acid chloride, the solution was stirred at reflux temperature under nitrogen for at least 3 h to ensure complete reaction. The solvent was removed by rotary evaporator and the oily mixture dried under vacuum for 24 h. At this time, chloroform (150 ml), acetic anhydride (100 ml) and 1-methylimidazole (3 ml) were added to the oily mixture and the reaction solution stirred at 60 °C for 12 h. After completion of the reaction, the reaction solution was extracted with distilled water four times to remove the excess acetic anhydride. The organic phase was recovered and concentrated, then the concentrated solution was poured into ethanol with stirring to give a precipitate. The precipitate was recovered by decantation and washing with ethanol three times to give the purified product which was dried under vacuum (60–70% yield). Note: this product should be stored under nitrogen in a freezer (–20 °C).

2.4. Copolymerization of tannin linoleate with vegetable oils

Crosslinked polymers were prepared as followed: tannin linoleate/acetate was dissolved in dichloromethane or tetrahydrofuran/ethyl acetate (1:1 v/v) followed by the addition of appropriate amount of vegetable oil (w/w) and Co/Zr catalyst (0.56 wt.%, consisting of 0.46% zirconium and 0.1% cobalt as a 3:1 M ratio of Zr to Co octanoates). The solution was degassed ultrasonically and applied onto a Teflon substrate to form a film which was then conditioned at 60 °C in an oven open to air for 15 days. The weight ratios

of vegetable oil to tannin ester were 0:100, 25:75, 50:50, 75:25 and 100:0. The nomenclature adopted for the polymer samples is as follows: QTLA100 and PTLA100 represent samples prepared from quebracho tannin linoleate/acetate and pine tannin linoleate/acetate, respectively; a copolymer prepared from 50 wt.% pine tannin linoleate/acetate and 50 wt.% linseed oil is designated as PTLA50-LIN50; and a copolymer prepared from 50 wt.% pine tannin linoleate/acetate and 50 wt.% tung oil is represent as PTLA50-TUN50.

2.5. Soxhlet extraction of polymer films

A polymer film sample (2 g) was placed in a Soxhlet extraction thimble and extracted in refluxing dichloromethane (100 ml) for 24 h. After extraction, the solution was separated and rotary evaporated to dryness then both the extract and insoluble fraction vacuum dried at 50 °C for 24 h.

2.6. Characterization techniques

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 8700 research FTIR spectrometer (Thermo Electron Corp.) with samples incorporated into KBr discs.

1H -NMR spectra were obtained on a Bruker Avance DRX-400 instrument using deuterated chloroform solution and tetramethylsilane as an internal standard and employed standard pulse sequences, unless otherwise stated. The degree of substitution (DS) of esters was obtained from 1H -NMR spectra by the reported method [15].

$$DS = \frac{I_1/3}{I_2/n} \quad (1)$$

where DS is the average degree of substitution of tannin esters; I_1 is the integrated intensity of terminal methyl protons of the linoleate and/or acetate groups; I_2 is the integrated intensity of aromatic protons of tannin unit; and n is the number average aromatic protons based on the hydroxylation pattern of the base tannin unit, being 5.0 for quebracho tannin and 3.9 for pine tannin respectively [18, 19].

Solid-state ^{13}C -NMR analysis was performed on a Bruker Avance 200 spectrometer with a 7 mm HX probe with samples packed in a zirconia rotor fitted with a Kel-F endcap. Samples were spun at 5 kHz and 2048 scans were acquired per spectrum, which were collected in the region between 250 and –50 ppm.

Cryogenically fractured surface morphologies of polymer films were studied with a Philips XL30S field emission scanning electron microscope (SEM), operating at an acceleration voltage of 20 kV. SEM samples were first cooled in liquid nitrogen and broken before being mounting the fractured cross-sections upright on aluminium studs using adhesive graphite tape and sputter-coated under vacuum with platinum before analysis.

Mechanical analysis was performed in tension using a Rheometrics dynamic mechanical thermal analyzer (DMTA IV). Viscoelastic properties of film samples (ca. 10 × 8 mm in length and width, and 0.2–0.4 mm in thickness) were measured at a frequency of 1 Hz, a strain rate of 0.05% and a heating rate of 3 °C min^{–1} over a temperature range from –50 to 200 °C.

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instruments Q1000 Differential Scanning Calorimeter. Samples (5–10 mg) were loaded into standard aluminium pans and run using a heat/cool/heat cycle with a heating rate of 10 °C min^{–1} and a cooling rate of 5 °C min^{–1}.

Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments Q500 Thermogravimetric Analyzer. Samples (8–14 mg) were weighed out on platinum pans and heated to 600 °C at 10 °C min^{–1} under a nitrogen atmosphere. All thermal analysis employed duplicate runs for each sample.

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