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An investigation of the use of recovered vegetable oil for the preparation of starch thermoplastics

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Abstract

The main components (~90%) in recovered vegetable oil (RVO) are esters of higher carboxylic acids and glycerol (triglycerides) which consist of three fatty acids: oleic (C18:1, *Z*), palmitic (C16:0) and linoleic (C18:2, *Z*) in the ratio 2.8:1.4:1. RVO may provide a low cost new supply of unsaturated fatty acid chlorides. Modification of potato starch using the mixture of fatty acid chlorides derived from RVO and using acid chlorides of the two major pure component acids has been performed. Films were prepared from the starch esters and mechanical properties tested. Commercially available potato starch, modified to DS-value 1.5 with RVO-derived acyl chlorides, was thermoplastic with a maximum tensile strength of 1.4 MPa and an elongation at break of 54%.

Keywords: Potato starch; Recovered vegetable oil; Esterification

1. Introduction

Interest in the preparation and potential applications of chemically modified starches remains high (see, e.g. Aburto et al., 1999b; Aggarwal & Dollimore, 1998; Bloembergen & Narayan, 1995; Ellis et al., 1998; Shogren, 1996) despite the fact that the vast majority of commercially available modified starches today derive from work carried out in the 1940s and 1950s (Beyer, 1941; Caldwell, 1949; Caldwell & Wurzburg, 1957; Kesler & Hjermstad, 1950; Konigsberg, 1950).

A substantial body of current starch research is underpinned by UK and EU funding mechanisms that support sustainable development. As the over-production of food crops in Europe coupled with the finite nature of petrochemical resources are expected to create environmental, economic and social upheaval (Okkerse & van Bekkum, 1996), research to discover sources of new materials based on non-food crops as alternatives to oil-based products becomes more pressing.

In its native state, starch is a hydrophilic and brittle polymer. Processing by extrusion (Bae & Lim, 1998; Miladinov & Hanna, 2000), graft co-polymerisation (Athawale & Lele, 2000; Athawale & Rathi, 1999; Rahman et al., 2000), incorporation of plasticisers (Poutanen & Forssell, 1996; Stein, Gordon, & Greene, 1999), preparation of blends with thermoplastic polymers (Bastioli, 1998; Bloembergen & Narayan, 1995; Narayan & Krishnan, 1995; Reis, Mendes, Cunha, & Bevis, 1997) and chemical modification by esterification (Aburto, Alric, & Borredon, 1999a; Fang, Fowler, Tomkinson, & Hill, 2002; Hylnianski, 1997; Jeon, Viswanathan, & Gross, 1999; Lower, 1996; Mullen & Pascu, 1942; Peltonen & Harju, 1996) have all been studied as means to extend its properties. We take the view that starch is an ideal prototype polymer skeleton on which to build extensive functionality and recognise chemical modification as the most versatile route to achieve this. However, chemical modification is costly and opportunities to limit this cost are sought.

Work at this centre (Fang et al., 2002), among others (Aburto et al., 1999a,b; Peltonen & Harju, 1996), has revealed that potato and wheat starches become thermoplastic when modified with saturated fatty acid chlorides, but are brittle. However, our preliminary studies in the derivatisation of starch with an unsaturated fatty acid chloride, oleoyl chloride (C18:1, *Z*), have shown that the incorporation of unsaturated side chains onto the polymer has a significant impact on the plasticity of the material. A major drawback is that even technical grades of oleoyl chloride are much more expensive than the saturated counterpart. However, the availability of recovered

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Table 1
Reagents and quantities to derivatise potato starch (6 g) to theoretical DS-value 1.5, and yields of product

Derivative	Reagents and amounts added		Yield (%)
	Pyridine (ml)	Acyl chloride (g)	
Palmitoyl starch	4.5	15.3	93
Oleoyl starch	4.5	16.7	96
RVO-modified starch	4.5	16.3	93

vegetable oil (RVO), containing predominantly C18:1, *Z*-configurated fatty (oleic) acid esters, and also linoleoyl (C18:2, *Z*) (and palmitoyl) groups in significant amounts, as the triglyceride, allows access to a new relatively inexpensive supply of unsaturated fatty acid chlorides that we have exploited in the preparation of starch esters. Mechanical testing of physical properties of the starch esters was performed to assess how the presence of two unsaturated side chains in the mixture mediated film properties compared with the pure saturated and monounsaturated derivatives.

2. Experimental

2.1. Materials

RVO was provided by C and C Oils. Potato starch was purchased from Fluka AG. Thionyl chloride ($SOCl_2$), *N*,*N*-dimethylacetamide (DMAC), *N*,*N*-dimethyl formamide (DMF), and pyridine were purchased from Aldrich Chemical Company; all other chemicals were of commercial grade and were used without further purification.

2.2. Chemical characterisation

Chromatographic analysis of RVO was performed by gas chromatography of its methyl esters on a DB225, 30 m × 0.25 mm i.d. column with split injection and FID. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} aluminium sheet plates (05554). Development of the plate was made by dipping into a solution of 10% sulphuric acid containing 1.5% w/v of phosphomolybdic acid and 1.5% w/v of ceric sulphate. Excess reagent was removed by carefully wiping the rear of the plate. Visualisation of the components was completed by heating the TLC plate on a hot plate at approximately 140 °C.

For Fourier transform infrared (FT-IR) spectroscopic analysis, solid samples were ground using a Mikro-Dismembrator (2000 rpm for 3 min). The fine powder sample was then mixed with potassium bromide (KBr). The KBr was dried in an oven at 100 °C overnight before use. The sample to KBr ratio was 1:100, and mixing was performed in a vibratory ball mill capsule. The mixture was ground for 5 min. The ground mixture was then transferred to a Specadie, which produced an 8.5 mm diameter film between two highly polished bolt ends. The thin film holder was directly mounted on a Specac holder, and mounted in the beam of the FT-IR spectrometer (Nicolet 750, series II). Liquid samples were applied directly as a thin film between two pre-formed NaCl discs and the spectrum was acquired.

^{1}H-NMR spectra of the samples were recorded on a Bruker 250 MHz Fourier transform (FT) spectrometer. Samples (30 mg) were dissolved in $CDCl_3$ (1 ml).

2.3. Preparation of fatty acids

A magnetically stirred suspension of RVO (100 ml) in 2 M aqueous NaOH solution (400 ml) was heated at 80 °C for 6 h, after which time analysis by TLC (ethyl acetate/-hexanes, 1:9) indicated complete consumption of the starting material. The mixture was left to cool to room temperature, and the acidity thereof was adjusted to pH 2 by dropwise addition of concentrated HCl with constant stirring. The aqueous suspension was extracted with ethyl acetate (3 × 150 ml). The solvent was removed and the combined extracts were dried over anhydrous Na_2SO_4. The product was obtained as a waxy solid (100 g); mp 33–37 °C.

2.4. Preparation of fatty acid chlorides

The fatty acids were converted to the corresponding fatty acid chlorides as follows. A catalytic amount of DMF (0.5 ml) was added to the crude acids (160 g, 0.57 mol) and the mixture was stirred mechanically at 23 °C in a flask fitted with a gas scrubber. $SOCl_2$ (65 ml, 0.89 mol) was added dropwise over 20 min under reflux conditions. Evolution of SO_2 and HCl was noted. After the addition was complete, reflux was maintained for 30 min. Excess of $SOCl_2$ was removed under reduced pressure on a rotary evaporator at 40 °C. The product (173.04 g) was used in the next step without further purification.

2.5. Starch esterification

Potato starch (6 g) was placed in a 150 ml round bottom flask, equipped with a magnetic stirrer and a condenser, and H_2O (50 ml) was added. The solution was heated to 80 °C for 1 h and DMAC (50 ml) was added. A mixture of H_2O and DMAC was removed from the flask at 80 °C under reduced pressure with periodic addition of DMAC (2 × 50 ml) to maintain a solvent volume of ⩾50 ml. When ca. 150 ml of solvent had been removed the solution was presumed anhydrous. LiCl (0.3 g) was added, the reaction mixture was stirred for 5 min and the requisite amounts of pyridine and desired fatty acid chlorides were added (Table 1) to provide, after heating at 80 °C for 30 min, starch esters with theoretical DS-values of 1.5. In the case of the mixture of acid chlorides derived from RVO, the

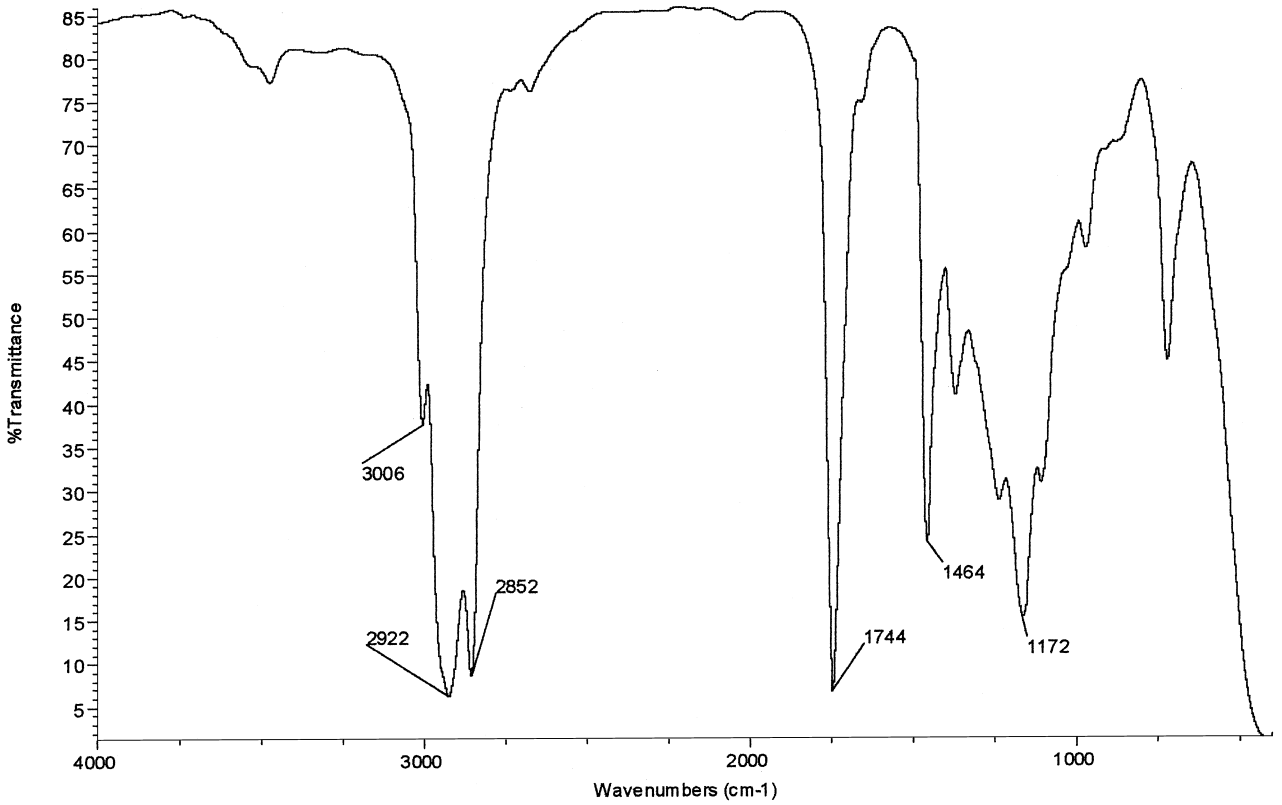

Fig. 1. FT-IR spectrum of RVO.

composite molecular formula $C_{17.5}H_{32.1}OCl$, derived from the proportions of component acid chlorides, was used as the basis for molecular weight and DS-value calculations.

Upon the completion of the reaction, the esters were isolated by precipitation in industrial ethanol (IMS) (150 ml) and washed with 70% aqueous IMS (2 × 150 ml) to remove coloured impurities and by-products. After filtration, residual IMS was allowed to evaporate in air and the esters were stored overnight at 50 °C, weighed and the yield calculated (Table 1). The dried samples were kept in a vacuum desiccator over P_2O_5 for further analysis.

2.6. Mechanical testing

Films were deposited from a 12% w/v solution of modified starch in toluene or chloroform by evaporation under ambient conditions. Test samples were excised from sheets of film using a template, the section of film under investigation typically having dimensions of 11 mm × 2 mm × 0.5 mm. Accurate film thicknesses were determined using vernier callipers. Stress–strain curves were constructed from data acquired on a Polymer Laboratories MiniMat miniature materials tester, coupled to a stepper motor. Data was captured and processed using the Minimat data catching routine.

3. Results and discussion

3.1. Characterisation of the RVO, fatty acids and fatty acid chlorides

Chromatographic analysis of RVO indicated that ~90% of the material consisted of three fatty acids: oleic (18:1, *Z*, 49%), palmitic (16:0, 24%) and linoleic (18:2, *Z*, 17%). Its FT-IR spectrum (Fig. 1) was consistent with the structures of a mixture of triglycerides. A typical ester carbonyl stretch was observed at 1744 cm^{-1}, a peak at 3006 cm^{-1} (C=C) confirmed the presence of unsaturation, while two peaks at 2925 and 2850 cm^{-1} of significant intensity were characteristic ($-CH_2$ and $-CH_3$ stretching bands) of the presence of long chain alkyl groups. Weak absorbances at ca. 3400 and 2700 cm^{-1} were attributed to the presence of a small proportion of free fatty acids in the sample and this assignment was supported by the presence of a low frequency shoulder on the carbonyl signal at 1744 cm^{-1}. In the ^{1}H-NMR spectrum, a characteristic ABX splitting pattern was observed, with signals centred on δ 4.29 and δ 4.13. These signals were assigned to the methylenic signals of the glyceryl moiety shifted downfield by the presence of the adjacent acyl groups. The glyceryl methine signal appeared as a shoulder of the alkenyl signals (δ 5.4–5.1), attributed to the presence of the oleoyl and linoleoyl groups.

The RVO was first converted to its constituent fatty acids and then to the acid chlorides in two steps. RVO was

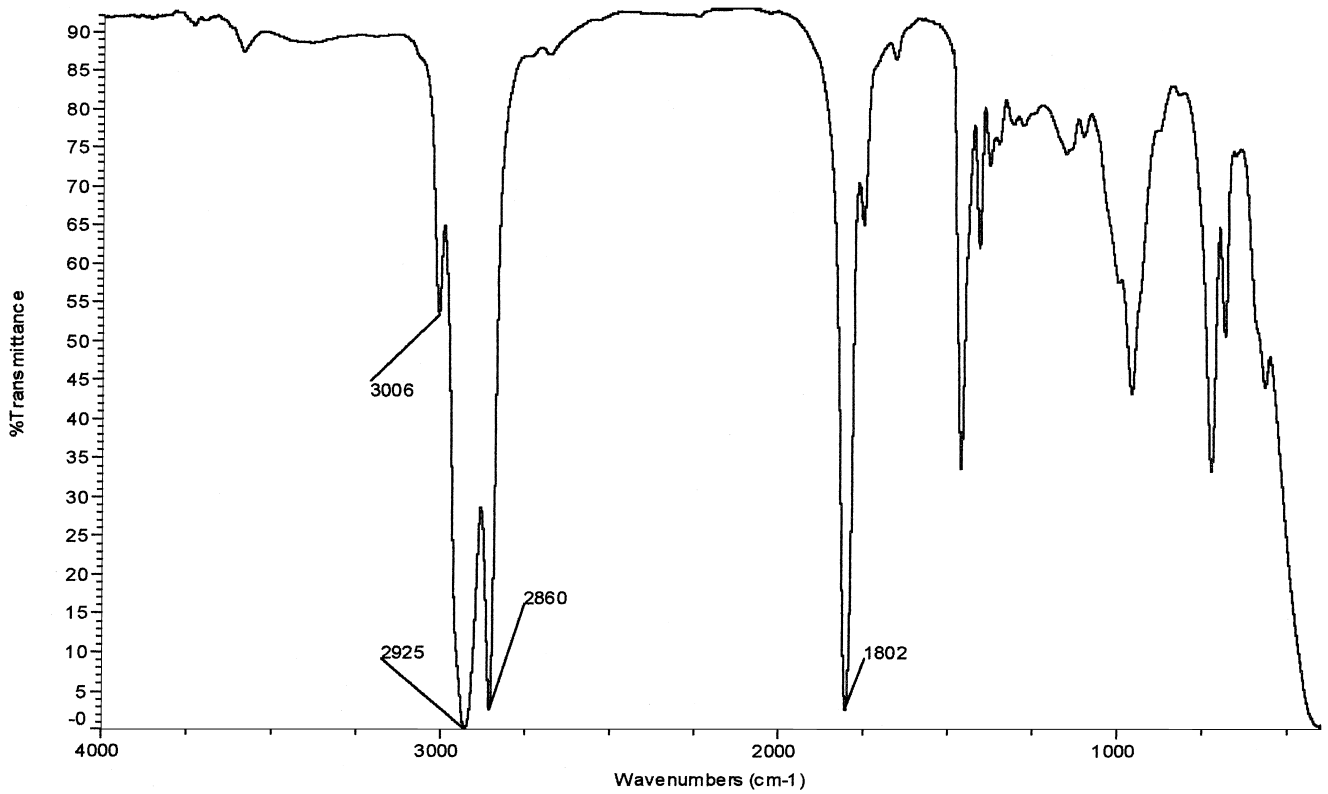

Fig. 2. FT-IR spectrum of acid chlorides derived from RVO.

hydrolysed in sodium hydroxide solution at 80 °C. The reaction temperature was maintained below 100 °C to avoid the significant problem of foaming as the reaction progressed that had been noted in trial experiments. Upon complete hydrolysis (monitored by TLC analysis), the solution was acidified to pH 2 to prepare the free fatty acids from the sodium carboxylates. Extraction of the fatty acids from the aqueous solution with ethyl acetate and evaporation of the solvent afforded the mixture of free fatty acids as a pale yellow, low melting point (33–37 °C) solid. The formation of the free fatty acids was confirmed by FT-IR spectroscopy. The FT-IR spectrum showed an intense carbonyl stretch at 1711 cm^{-1} that corresponded to the free carboxylic acid, which replaced the original ester carbonyl stretch of the starting material at 1744 cm^{-1}. The intense signals centred on 1172 cm^{-1} (C–O stretch) (Fig. 1) associated with the glyceryl moiety had disappeared. Furthermore, a very broad O–H stretch associated with the carboxyl group was noted between 3500 and 2500 cm^{-1}. ^{1}H-NMR spectroscopic analysis of the mixture was consistent with the presence of three major fatty acids being present in a 2.8:1.4:1 ratio. Additionally, the doublet of doublets at δ 4.29 (J 11.9, 4.3 Hz) and δ 4.13 (J 11.9, 5.8 Hz) which were present in the starting material and assigned to the methylenic protons of the glyceryl moiety had disappeared.

The free fatty acids were transformed to the acid chlorides by standard treatment using thionyl chloride in the presence of a catalytic quantity of DMF. Considerable darkening of the reaction mixture was noted as the reaction progressed. Upon evaporation of excess thionyl chloride, the product was obtained as a dark brown, fuming liquid that was characterised by FT-IR spectroscopy (Fig. 2). Formation of the acid chlorides was confirmed by the presence of an intense carbonyl absorption in the FT-IR spectrum at 1802 cm^{-1} and the absence of the broad O–H band of the acid in the region of 3500–2500 cm^{-1}.

3.2. Preparation of fatty acid esters of potato starch

Potato starch was modified to a theoretical DS-value of 1.5 with the acid chlorides derived from palmitic and oleic acids and RVO according to our standard conditions (Hylnianski, 1997), data collected in Table 1. The resulting materials, isolated as free-flowing powders, were characterised on the basis of their FT-IR spectra. In the spectrum of the palmitoyl derivative, intense signals at 2926 and 2853 cm^{-1} were assigned to the 16-carbon alkyl chain and the signal at 1739 cm^{-1} to the ester carbonyl stretch. The spectrum of the oleoyl derivative was almost superimposable on that of the palmitoyl derivative except for the presence of an additional signal of weak intensity at 3006 cm^{-1}, confirming the presence of the alkenyl functionality. As expected, the FT-IR spectrum of the RVO-derived starch ester was virtually identical to that of the oleoyl-containing material with those key signals of the

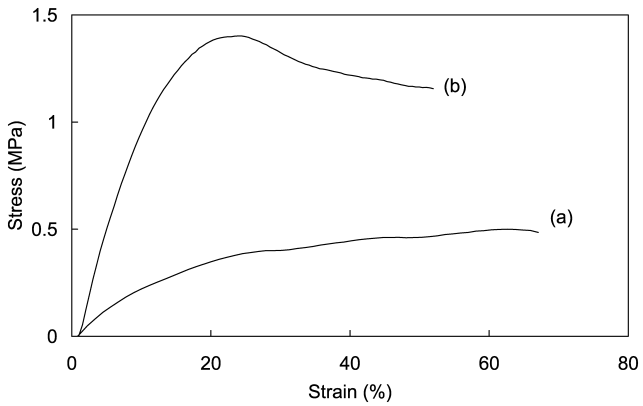

Fig. 3. Stress–strain curves for potato starch modified with (a) oleoyl chloride and (b) acid chlorides derived from RVO. Note that the palmitoylated starch film was too fragile for use in comparison studies.

long chain alkenyl and carbonyl moieties present at exactly the same frequencies.

3.3. Film formation and mechanical testing

Films of the modified starches were prepared by casting solutions from solvent onto a glass plate. All three modified starches afforded transparent lustrous films. The RVO and oleoyl derivatives were readily recovered from the glass plate. However, the palmitoyl-derived film was too fragile to be recovered without cracking. The extreme brittleness of the palmitoyl starch film made it impossible to obtain samples for further testing.

Samples of the RVO and oleoyl-derived starch films were characterised on the basis of their stress–strain curves (Fig. 3) with tensile strengths and elongations at break being determined. The oleoyl starch had a rather poor tensile strength (0.49 MPa) but a relatively long extension at break (69%). However, the RVO-derived film, revealed a significantly greater tensile strength, which increased rapidly to a yield point (1.4 MPa) and then decreased as plastic flow began and the film stretched. Elongation continued with applied stress until the film broke at about 54% elongation.

In the case of the unsaturated, *Z*-configurated acid chlorides used in this study, transparent and flexible films were formed at the moderate level (DS-value 1.5) of substitution. In the case of the RVO derivative, the proportion of linoleoyl moiety containing the skip *Z*-diene functionality imparted improved film characteristics.

4. Conclusion

Modification of commercially available potato starch with acyl chlorides derived from palmitic and oleic acids and RVO afforded thermoplastic materials. The extreme brittleness of the palmitoyl starch and the rather poor mechanical properties of the oleoyl starch preclude their use as thermoplastic materials without considering their uses in blends. However, the significantly improved mechanical properties of the modified starch obtained by derivatisation with RVO-derived acid chlorides suggests that further investigation of its use for the preparation of thermoplastics is worthwhile.

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