CHARACTERISATION OF RAPESEED OIL BASED RESINS USING INFRARED AND THERMOGRAVIMETRY TECHNIQUES

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ABSTRACT

Rapeseed oil which is a triglyceride had undergone chemical modification on its structure to obtain hydroxyl groups. The hydroxylated chemical structure was crosslinked using methylene-p-phenyl diisocyanate to produce a thermoset rapeseed oil resin. The cross linking process was monitored in situ using the Attenuated Total Internal Reflectance Fourier Transform-Infrared spectroscopy and the thermogravimetric analysis techniques. The infrared technique was also used to monitor chemical groups of the unmodified rapeseed oil. A reduction of the absorption band around 3300 cm^{-1} which is due to the presence of hydroxyl groups was observed indicating the occurrence of the reaction between the hydroxylated rapeseed oil and methylene-p-phenyl diisocyanate. The thermogravimetric analysis technique recorded the reduction of the hydroxyl groups as the loss in mass of the reactants as a function of temperature. The two analytical techniques provided about the same cure time. Both, the infrared and thermogravimetric techniques elucidated useful cure characteristics of the rapeseed oil resin. The applications of more than one analytical method offer a complement of the results.

Keywords: Triglycerides, hydroxylation, cure, polyurethane, characterisation

INTRODUCTION

The ever decreasing source of precursors for the production of polymeric materials and more importantly the environmental disadvantages of using fossil-origin precursors has resulted in the search for alternative feedstocks for the synthesis of polymers. For instance, it is reported that vegetable oil-based polyurethane has been synthesised using soy, sunflower, palm and rapeseed oil (Badri *et al*. 2001, Javni et al. 2003, Javni *et al*. 2000). The composition of fatty acid varies from oil to oil, and it determines the degree of unsaturation of the oils (Goodrum and Geller 2005). Polyols are formed by introducing hydroxyl groups at ydroxylation is shown in Scheme 1.

the position of double bonds. Hence, oils with higher unsaturation should give polyols with higher functionality (Hu *et al*. 2002). Generally, oils are converted into polyols through two steps, first by epoxidation of the double bonds followed by hydroxylation (see scheme 1). Rapeseed oils are triglycerides of fatty ($C_{12} - C_{22}$) acids, mainly consisting of mono-unsaturated fatty acids such as oleic acid and poly-unsaturated fatty acids such as linoleic and linolenic acids (Javni *et al*. 2000). A schematic representation of the structure of rapeseed triglyceride and its corresponding structures after epoxidation followed by h
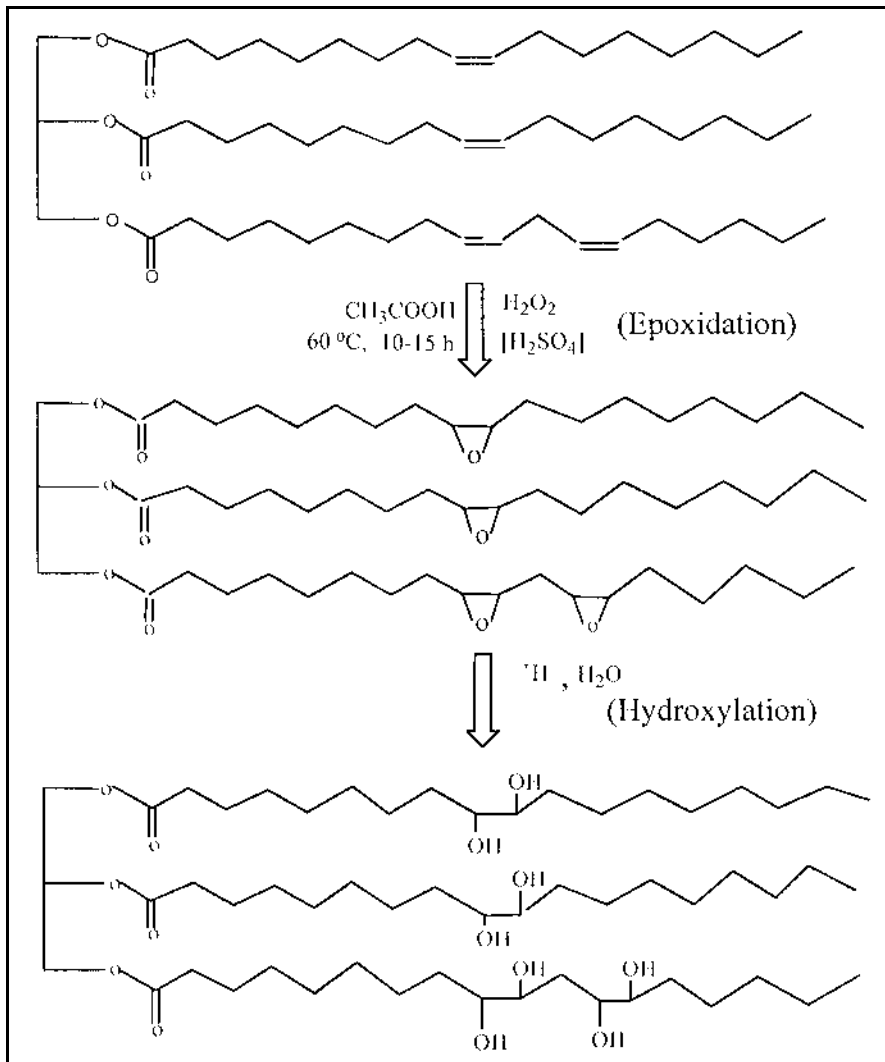
Scheme 1:   Schematic representation of the rapeseed triglyceride

Vegetable oils have a number of excellent properties, which could be utilised in producing valuable polymeric materials such as polyurethane. Polyurethane is a generic term used to classify polymers composed of synthetic linear macromolecules having in the chain recurring aliphatic groups joined by urethane groups which together comprise at least 85% (by mass) of the chain (Beech *et al*. 1986). The structure of these polyurethanes can be tailor made to suit specific requirements by selecting the type of polyols and based on the hydroxyl group density (Javni *et al*. 2003, Monteavaro et al. 2005). Polyurethanes are produced via the reaction of polyisocyanate with polyols and water in the presence of catalysts. The formation reaction of polyurethane polymers basically consists of two routes. The first route (1) involves the reaction of isocyanate with the polyol to form urethane and the second route (2) involves the reaction of

isocyanate and water to form urea and carbon dioxide. Scheme 2 shows two (Reactions (1) and (2)) general reactions routes involved in the production of polyurethane polymer.

$$R\text{—}NCO + R'\text{—}OH \longrightarrow R\text{—}\overset{\overset{\displaystyle H}{|}}{N}\overset{\overset{\displaystyle O}{\|}}{C}O\text{—}R' \qquad (1)$$

$$2R\text{—}NCO + H_2O \longrightarrow R\text{—}\overset{\overset{\displaystyle H}{|}}{N}\overset{\overset{\displaystyle O}{\|}}{C}\overset{\overset{\displaystyle H}{|}}{N}\text{—}R + CO_2 \qquad (2)$$

Scheme 2: The two general reactions routes involved in the production of polyurethane polymer

The balance of the two reactions in Scheme 2 is quite critical to obtain the required physical properties (Javni 2000). The cure characteristics of most fossil-based synthetic polyurethane indicates complete resin cure temperature of around 50 - 60 $^{\circ}$C within / for? 45 - 60 minutes (Javni *et al*. 2003, Javni et al. 2000, Ravey and Pearce 1997). Currently, research work has shown that it is possible to produce monomers from plant-based oils as indicated in Scheme 1, which can be used for the synthesis of polymers (Filip *et al*. 1992). However, whereas the cure characteristic of fossil-based resins has been well documented (Ravey *et al*. 1997, Chao *et al*. 1998, Shibata *et al*. 2002, Belousova 2002), those of plant-based polymers have not been thoroughly carried out. It has been found that the chemical structure of virgin rapeseed oil can be modified to obtain reactive groups such as hydroxyl groups (Hu *et al*. 2002, Ren *et al*. 2007) using inorganic catalysts and peroxides mixed with water. A general reaction is shown in Scheme 1. A detailed hydroxylation process of the oil will be reported in a future publication.

The introduction of hydroxyl groups on the rapeseed triglyceride is essential for polymer synthesis (Hu *et al*. 2002, Ren *et al*. 2007). In this study a polymer was synthesised by reacting hydroxylated (polyol) rapeseed oil with methylene-p-phenyl diisocyanate (MDI). The chemical composition of the virgin rapeseed oil, hydroxylated rapeseed oil (RASO-OH) and MDI polymerised hydroxylated rapeseed oil were analysed using the Attenuated Total Internal Reflectance Fourier Transform-Infrared (ATIR FT-IR) technique. The thermal analysis of the virgin rapeseed oil, hydroxylated rapeseed oil and MDI polymerised hydroxylated rapeseed oil were also investigated using the Thermogravimetric Analysis (TGA). The resulting polymer has characteristics similar to conventional polyurethane reported by Ravey *et al*. (1997) and Belousova (2002).

MATERIALS METHODS
Materials and Equipment
Hydroxylated rapeseed oil was synthesized in the laboratory of the Department of Chemistry University of Warwick. Other chemicals used include Mathylene-p-phenyl diisocyanate (MDI) and toluene bought from Aldrich Chemicals. The equipment used in this study was FT-IR and TG.

Infrared Analysis
The Attenuated Total Internal Reflectance Fourier Transform-Infrared (ATIR FT-IR) model Nicolet was used to collect the spectra of *in situ* curing of RASOR. Blobs of the mixture of hydroxylated rapeseed oil and methylene-p-phenyl diisocyanate were dissolved in toluene and the solution placed on the FT-IR bottom 'plate' and a head was lowered so that it just touched the solution.

The whole set-up was then closed and the sample was scanned at room temperature (20 °C). The control on the preparation speed was essential in order not to lose significantly the initial cure of the resin. The spectra of the cross linking resin were collected and analysed (Mwaikambo 2001).

Thermogravimetric Analysis
The reaction was studied by monitoring the loss in mass as a function of temperature of the resin. Pelkin Elmer TG7 equipped with thermal analysis controller TCA 7/DX was used. Samples of the mixture of hydroxylated rapeseed oil and methylene-p-phenyl diisocyanate solution weighing between 5 - 10 mg were placed in a crucible in the furnace chamber and heated in dynamic mode in nitrogen between 40 ^{o}C - 900 ^{o}C at the rate of 10 ^{o}C/min. The isothermal mode was operated at temperatures between 20 °C and 80 °C in steps of 5 °C. The collected thermograms were analysed (Mwaikambo 2001).

RESULTS AND DISCUSSION
FT-IR analysis
Figure 1 shows the transmittance spectra of virgin rapeseed oil, hydroxylated rapeseed oil (RASO-OH) and MDI polymerised rapeseed oil (RASOR). It is observed that the virgin rapeseed oil shows no absorption bands above 3300 cm^{-1} indicating the absence of hydroxyl groups and amine groups but shows intensive absorption bands at 2852 cm^{-1} and 2915 cm^{-1} indicating the presence of C-H bond (Ravey *et al.* 1997, Chao *et al.* 1998). The absorption observed at 2274 cm^{-1} is due to the presence of the isocyanate group present in MDI. Other absorptions of interest to this study are observed at 1740 cm^{-1} and near 1164 cm^{-1} representing the C=O and aliphatic ether chemical groups, respectively (Chao *et al.* 1998). The presence of the carboxyl groups at 1740 cm^{-1} is of great interest in reactivity particularly in the cross-linking with cellulosics (Shibata *et al.* 2002). Following hydroxylation a broad absorption is observed between 3300 - 3500 cm^{-1} indicating the presence of O-H bonds/groups and designated A (Fig. 1). The reduction in the absorption bands at 2852 cm^{-1} and 2915 cm^{-1} for polymerised rapeseed oil compared to unmodified rapeseed oil shows that some of the C–H groups have participated in the grafting of the O-H groups. However, the reduction in the absorption band is not significant implying that the reaction was at an early stage. Similar results are observed at 1740 cm^{-1} and 1164 cm^{-1} band. The MDI cross-linked RASO-OH show a decrease in band intensity between 3300 - 3500 cm^{-1} which implies that some of the O-H groups have been used in the polymerisation reaction (Ravey *et al.* 1997, Chao *et al.* 1998). Similarly the reduction in the band intensity of the RASO-OH at 1740 cm^{-1} (Fig. 1) entails that some of the carboxyl groups (C=O) participates in the polymerisation reaction. Similar observations were reported by Chao, *et al.*, 1998 when carrying out a study on the synthesis and physical properties of fire retardant polyurethane ionomers using the FTIR technique. The aromatic double bond is observed at 1600 cm^{-1} while the amine (NHCO) is observed at 1525 cm^{-1} band, which is also characteristic of the benzene ring (Chao *et al.* 1998).

It is worth noting that whereas the presence of C=O groups indicates that the RASO-OH would not require a catalyst, the presence of the NCO in the polymerised RASOR indicates possible further reactions (cure) of the polyol to form polyurethane polymer. Since, the determination using the hydroxyl value is tedious and time consuming particularly in industry. The FT-IR method adopted in this study was considered to be convenient, quick and comparably accurate.
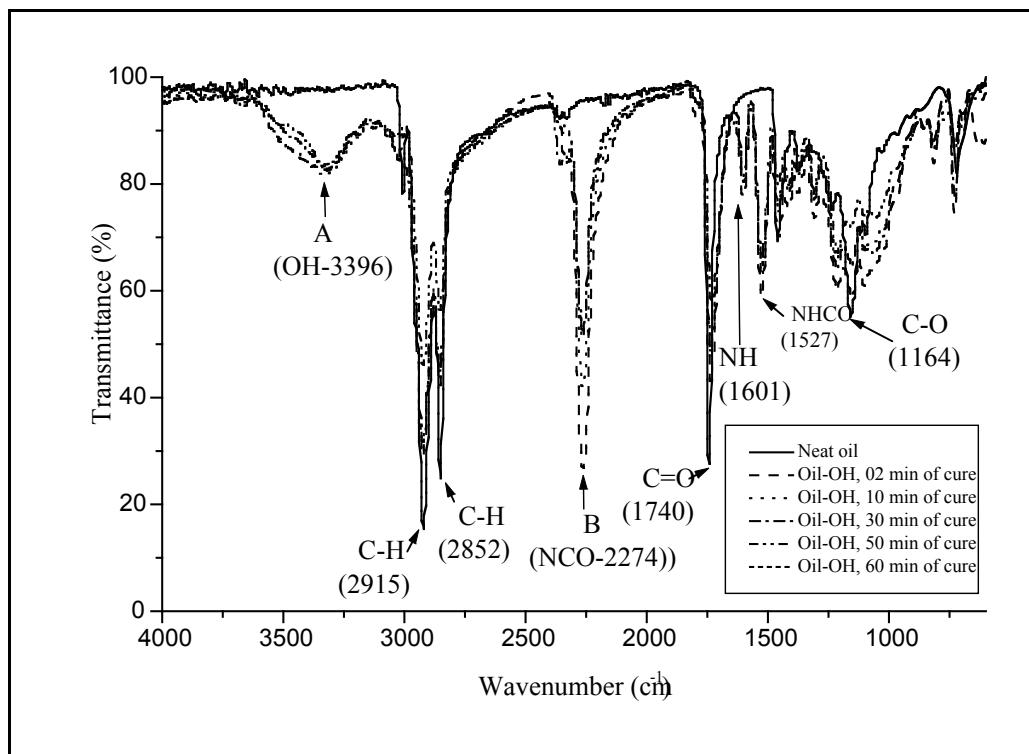
Figure 1: FT-IR spectra of unmodified rapeseed oil, hydroxylated rapeseed oil and MDI polymerised hydroxylated rapeseed oil

Three absorption bands A, B and (Fig. 1) were selected to monitor the polymerisation reaction. The ratio of the percentage absorption of B:A were calculated and plotted in Figure 2 against reaction time by integrating area under the curve representing the O-H and isocyanate group bands, respectively. The integration of the bands provides a simple technique for quantitative analysis of each functional group. A characteristic decrease in the ratio of intensity of NCO:OH is observed (Fig. 2). Similar analogies were propounded by Chao et. al. 1998 when studying the synthesis and physical properties of fire-resistant polyurethane ionomers and by Tsai *et. al*.

(2008) when analysing the infrared of moisture curable polyurethane resins. The method used in this work is viewed useful particularly in industry where quick and accurate results are needed for quick interventions.

The decrease in the un reacted isocyanate is observed with increase in the reaction time by studying the ratio of band B:A (Fig. 1) illustrated in Figure 2. Close observation of Figure 2 provided average reaction time of between 45 minutes. It therefore implies that the optimum cure time of the rapeseed oil based resin is between 40 - 50 minutes.
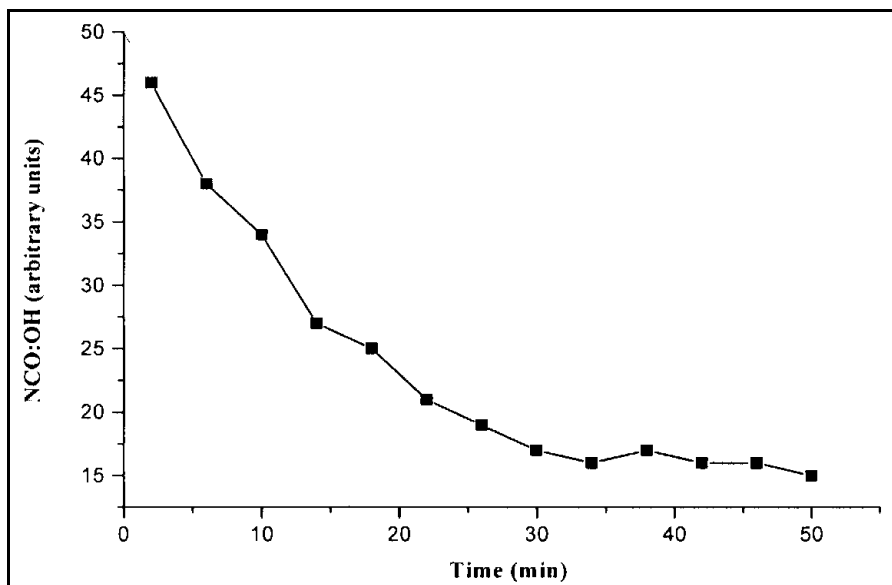
Figure 2:   The ratio of the change of isocyanate to hydroxyl groups with respect to reaction
time

TG analysis

Figure 3 shows the rate of weight loss of the polymerisation of RASOR in nitrogen at different temperatures. The maximum rates of mass loss were determined from Figure 3 for resins undergoing polymerisation in the thermogravimetry furnace for samples reacted at constant temperature. However, only representative curves are shown in Figure 3 while rates of mass loss of all the samples studied is plotted in Figure 4.
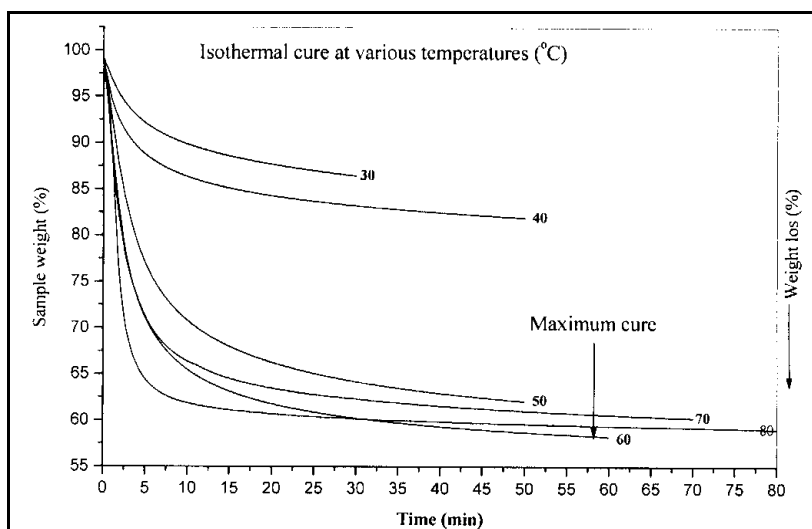

Figure 3:   The thermogravimetry isothermal cure of various temperatures

Figure 3 shows curves exhibiting high initial rate loss at higher temperatures and that the optimum rate loss is attained around 45 minutes of reaction time and that the optimum temperature of cure is 60 °C.
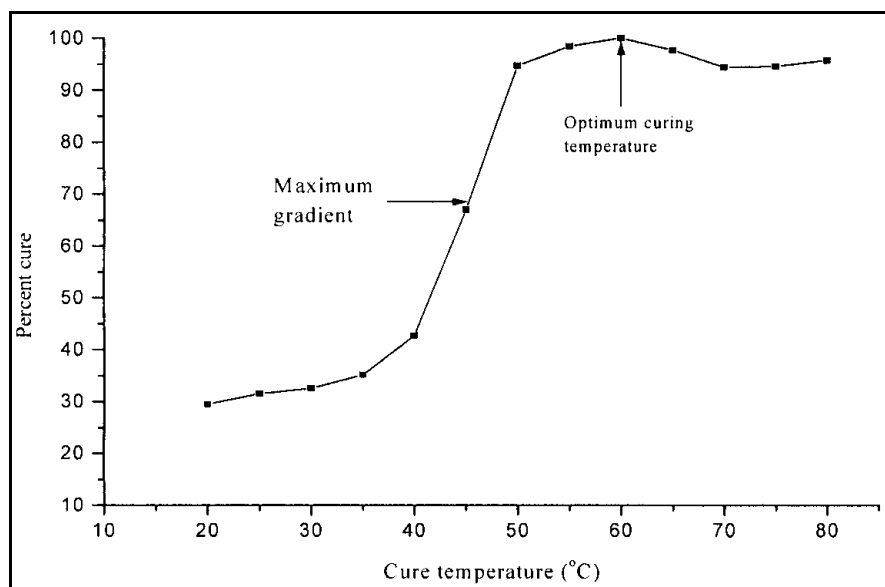

Figure 4:   Isochronal degree of conversion of RASOR against cure temperature.

Figure 4 is a plot of relative percentage cure after 60 minutes cure segments, exhibiting a plateau between the two stages of mass loss which is the most efficient cure temperature as defined by the maximum mass loss, and the apparent onset of degradation. It is believed that the optimum cure temperature occurs at 60 °C. Greenberg and Kamel 1977 used a similar approach to study the kinetics of anhydride formation in poly (acrylic acid) composites. Maximum weight loss occurs at the optimum curing temperature at 100% degree of conversion.

Under ideal conditions the weight loss is equivalent to the enthalpy loss by differential scanning calorimetry as a measure of the degree of conversion (Prime 1997). Maximum rate of conversion occurs at the highest gradient of the cure curve (Fig. 4). It has been reported that the resin attain lowest viscosity at highest rate of conversion (Michaeli and Kamps 2007). In composite processing the flowability of the resin is optimum at lowest resin viscosity (Michaeli and Kamps 2007). It is expected, therefore, that the resin's ability to effectively wet the reinforcement is expected to be effective at higher temperature of curing where it would exhibit lowest viscosity before the onset of cure. Thermoset exhibit low viscosity at high temperatures prior to cross linking (Michaeli and Kamps 2007). This allows easy followability and in composites it facilitates fibre wetting critical for a coherent interface

CONCLUSIONS
In this study it has been demonstrated that the FT-IR and TGA can be used to monitor the *in situ* cure characteristics of ROSAR. It has also been observed that both FT-IR and TGA provided the same cure time of the resin. The reactivity of the isocyanate increases as the processing temperatures are increased. It is important to note that the

cure analysis undertaken in this study covered both the initial rapid cross linking and the post cure stage of the resin. The lower cure time reported using the TG method compared to FTIR value is due to the fact that the TG was run above room temperature. This implies that temperatures above 20 °C facilitates cure of the polyurethane resin reported in this work. A study of the cure characteristics is useful for the prediction of the temperature distribution and time for material processing. The use of RASOR, which is renewable as a feedstock for polymer production has environmental benefit and provides prospects for increased agriculture.

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