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Novel poly(alkyd-urethane)s from vegetable oils: Synthesis and properties

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ABSTRACT

Triglycerides of palm (*Elaeis guineensis*) oil, soy (*Glycine max*) oil and sunflower (*Helianthus annuus*) oil were converted to monoglycerides by glycerolysis process. The monoglycerides derived from the different oils were reacted with phthalic anhydride at 2:1 monoglyceride-to-phthalic anhydride ratio to obtain novel polyols called alkyd diols. The polyols were reacted with 4,4′-methylenediphenyldiisocyanate (MDI) to produce five novel poly(alkyd-urethane)s (PAU), namely palm oil based poly(alkyd-urethane) (POPAU), soy oil based poly(alkyd-urethane) (SOPAU), sunflower oil based poly(alkyd-urethane) (SFPAU), palm-soy oils based poly(alkyd-urethane) (POSOPAU) and palm-sunflower oils based poly(alkyd-urethane) (POSFPAU). The successful synthesis of the monoglycerides, alkyd diols and poly(alkyd-urethane)s were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR spectroscopy and their morphology were evaluated by scanning electron microscopy (SEM). Further analyses included viscosity, solubility, iodine number testing, gel content, drying time test, thermogravimetric analysis (TGA), crosshatch adhesion tests, impact strength, pencil hardness, chemical and water resistance. Palm oil poly(alkyd-urethane) showed good thermal stability with only 5% weight loss temperature in nitrogen at 270 °C. Improvements in coating performance after blending with sunflower oil or soy oil based alkyd-diols were also observed.

1. Introduction

In the last decade, the depletion of crude oil and increasing oil price have pushed scientists to turn to eco-friendly and cost-effective materials while investigating renewable natural materials as an alternative source of monomers in the manufacturing of polymer (Patel et al., 2008). Vegetable oils are one of the sustainable materials known to be utilized and would usually go through various chemical functionalizations (Khot et al., 2001; Hu et al., 2002; Tanaka et al., 2007; Mosiewicki et al., 2009a,b) in various polymer synthesis processes.

Alkyd resins are tough resinous polymeric materials prepared via an esterification reaction between polybasic acids, polyols and monoacids (commonly fatty acids from vegetable oils or fats) (Parker, 1965). They are widely used and constitute about 70% of the conventional binders used in surface coatings today (Hlaing and Oo, 2008) due to their good attributes such as strength, flexibility, gloss retention, good thermal stability and low price. However, it was reported that alkyd resins possess a few weaknesses such as low water resistance, alkaline resistance and solvent resistance (Williams, 2000). In addition, alkyds have to be diluted in organic solvents prior to application and some of the alkyd resins such as palm oil-based alkyd resins take a long time to dry due to their lower level of unsaturation in the fatty acid chain. To surmount these problems, previous researches were directed to copolymerization of alkyd with acrylate monomers (Akintayo and Adebowale, 2004a; Uschanov et al., 2008), inter-esterification with other oil such as Tung oil (Saravari et al., 2005) and modifications with other chemicals such as natural rubber (Lee et al., 2010a,b). Blending of palm oil based alkyd with other resins such as epoxy was also reported (Issam et al., 2011) to enhance properties of alkyd resins in terms of morphology, viscosity, adhesion, pendulum hardness and impact strength over individual resins.

Owing to the presence of urethane linkages, polyurethanes on the other hand, exhibit faster drying time, better abrasion resistance, toughness, chemical and UV resistance when compared to alkyd resins. Extensive applications of polyurethane can be found in high performance coatings, such as that of automotive appliances and wood industries (Poul, 1996; Swaraj, 1997; Jayakumar et al., 2003; Alam et al., 2004; Dutta and Karak, 2005). It is projected

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that by incorporating urethane linkages into the alkyd backbone, a poly(alkyd-urethane) with enhanced functionality over the individual resins could be produced. To the best of the authors' knowledge, there is no report published on the chemical modification of alkyds by urethane and the consequent effects.

Thus, a series of novel polymers named poly(alkyd-urethane)s were designed by reacting diisocyanates with alkyd diols from two of the abundant vegetable oils: palm oil and soy oil. Palm oil is vegetable oil derived from fruit of oil palms and was selected due to its renewability and abundance mainly in the South East Asian countries such as Malaysia, Indonesia and Africa with a production of 53 metric tons, which occupies 33.98% of total world plant oil productions in the year of 2012 (USDA, 2013a). It has recently seen much demand and received much attention in the synthesis of different polymers or their derivatives such as alkyds (Issam and Cheun, 2009; Ang and Gan, 2012), polyurethanes (Chuayjuljit et al., 2007; Saravari et al., 2007) and bio-diesel fuel (Kalam and Masjuki, 2002; Mohamad and Ali, 2002). The world's most produced vegetable oil is followed by soybean oil with 27.66% of total world's production (USDA, 2013b) which has been seen utilized in the development of IPN (interpenetrating elastomeric networks) (Athawale and Kolekar, 2000; Raut and Athawale, 2000; Athawale and Pillay, 2001).

With sunflower oil as the benchmark, the outcome of synthesized poly(alkyd-urethane)s based on alkyd diol from palm oil and soy oil are hereby discussed with respect to the their relative properties.

2. Experimental

2.1. Material

All purchased chemicals were used as received. Palm oil, soy oil and sunflower oil were purchased from Tesco Stores SdnBhd, Malaysia. Glycerol, toluene and acetone were manufactured by R&M Chemical, UK. Calcium Oxide (CaO) was obtained from Hamburg Chemicals. Phthalic anhydride and 4,4′-methylenediphenyldiisocyanate were supplied by Fluka Chemical, Germany while xylene was manufactured by J. T. Baker SOLUSORB. Ethanol, dimethyl formamide (DMF) and tetrahydrofuran were received from Fisher Scientifik UK Limited. DMF was distilled over calcium hydride before use.

2.2. Preparation of poly(alkyd-urethane)s

Two distinct steps were involved in preparation of alkyd diols. The first step was the reaction between vegetable triglycerides and glycerol. Triglycerides underwent trans-esterification by glycerolysis in the presence of catalyst at an elevated temperature, thus forming monoglyceride. The second major step was the transformation of the monoglyceride to diols with the UNREACTED and TERMINATED hydroxyl groups by reaction with excess phthalic anhydride. The intrinsic type of this reaction was that, the ring opening of phthalic anhydride did not involve any water and this occurred readily at temperature of 180 °C. The alkyd diols were then reacted with the same amount of NCO group of 4,4′-methylenediphenyldiisocyanate, forming urethane bonding, resulting in the formation of the poly(alkyd-urethane)s or PAUs.

2.2.1. Preparation of monoglycerides

A four-necked, round-bottomed flask equipped with mechanical stirrer, reflux condenser, N_2 inlet and addition funnel was charged with 1 equiv. of palm oil and 0.1% CaO powder (by weight) as a catalyst. As the palm oil was heated up to 235 °C, 2 equiv. of glycerol were fed into the system blanketed by nitrogen flow. The reaction was allowed to stand for 3 h. The glycerolysis product, however, may be expected to be consisting majorly of α-monoglyceride (>60%) while minor presence of β-monoglycerides, αα′-monoglycerides, αβ-diglyceride, triglyceride and glycerol was unavoidable (Igwe and Ogbobe, 2000). The reaction was continued until a satisfactory high amount of conversion of triglyceride into α-monoglyceride was ensured whereby, a little sample of monoglyceride was taken out by using a glass rod to test its solubility in ethanol and no emulsion or white spots in the ethanol solution were observed. This reaction produced monoglyceride from palm oil (PO-mono) and substituting soy oil or sunflower oil for palm oil would then produce monoglyceride based on soy oil (SO-mono) and sunflower oil (SF-mono), respectively.

2.2.2. Preparation of alkyd diols

A four-necked, round-bottomed flask equipped with mechanical stirrer, Dean-Stark trap, N_2 inlet and addition funnel was charged with 2 equiv. of PO-mono and 10% xylene (based on weight of monoglyceride). 1 equiv. of phthalic anhydride was added as the temperature of monoglyceride reached 180 °C. The temperature was controlled at 190 °C and the reaction continued for 4 h under a nitrogen blanket. Sample was taken periodically to check the acid number until it fell below 5 mg KOH g^{-1}. Eventually, water and xylene were removed under pressure. Thus palm oil based alkyd diol (PO-diol) was obtained.

Substituting palm oil monoglyceride with the same equivalent of soy oil monoglyceride or sunflower oil monoglyceride would produce soy oil based (SO-diol) and sunflower oil alkyd diol (SF-diol), respectively.

2.2.3. Synthesis of PAU

Into a four-necked, round-bottomed flask equipped with mechanical stirrer, reflux condenser, N_2 inlet and addition funnel was charged 1 equiv. of PO-diol. 1 equiv. of liquid 4,4′-methylenediphenyldiisocyanate (MDI) with DMF was added into the reaction flask through the dropping funnel. The reaction flask was heated up and maintained at 70 °C for 1 h and a half and subsequently increased to 110 °C. The reaction was continued for 12 h with a blanket of nitrogen maintained throughout the reaction. A little sample of PAU was taken out every 2 h for FTIR inspection until all diisocyanate was successfully reacted. The solvent, DMF, was removed under pressure. POPAU was formed, cooled and further analyzed.

The reaction was repeated in the same manner by substituting PO-diol with 1 equiv. of SO-diol or SF-diol to produce SOPAU and SFPAU, respectively. For the synthesis of POSOPAU and POSFPAU respectively, a blend of 0.5 equiv. of PO-diol with 0.5 equiv. of SO-diol or with 0.5 equiv. of SF-diol, was reacted with 1 equiv. of MDI as the way POPAU was produced.

2.3. Instrumentation and measurements

2.3.1. Fourier transform infrared spectroscopic analysis

Chemical compositions of the monoglycerides, alkyd diols and PAUs were evaluated by Fourier Transform Infrared (FTIR) in a Nicolet FTIR Avatar 360 using KBr pellet at wavelengths between 4000 and 400 cm^{-1}.

2.3.2. ^1H and ^{13}C NMR analysis

^1H and ^{13}C NMR spectra of the monoglycerides, alkyd diols and PAUs were obtained using Bruker 400 MHz NMR spectrometer, using DMSO-d_6 as the solvent and TMS as the internal reference.