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One-pot synthesis and physicochemical properties of high functionality soy polyols and their polyurethane-Urea coatings

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ABSTRACT

This paper explores a new approach for the synthesis of highly functional soy polyol (SP) from soybean oil (SBO). A two-step continuous route has been reported for the development of renewable polyols and their polyurethane/urea (PU-Urea) coatings. The methodology includes epoxidation of oils and subsequent hydroxylation to produce polyols. The SBO and SP were characterized by different spectroscopic techniques such as ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, Gel permeation chromatography (GPC), Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA), and rheological properties were also determined. Through the present approach, we were able to achieve hydroxyl number for SP as high as 231.3 mg KOH/g. Additionally, the relative conversion of epoxide value as 0.001% and iodine value under 1.35 (g of I_2 100/g) are superior to the past reports. Different PU-Urea coatings obtained by utilization of the high functionality SP, exhibited excellent thermo-mechanical and solvent resistances. It was found that the molecular design of polyisocyanate and functionality of polyol plays an important role on performance properties of the coatings. The coatings were also evaluated for their in-vitro degradation, contact angle and chemical resistance properties. We observed high glass transition (T_g 171.8 °C), superior cross-linking density of the PU network, chemical resistance and lower degradation rates. The present work can provide an insight on the design and development of high functionality bio-polyols and their PU-Urea coatings.

1. Introduction

The utilization of materials from renewable resources is of expanding significance as the world's leading industries and manufacturers seek to replace declining petrochemical-based raw materials with agricultural-based materials. Sustainable acceptance of polymeric materials from renewable, agricultural raw materials is also demands because they represent a high-tech use for conventional agricultural materials. Polyols are traditionally produced from petroleum-based materials which are expensive, not energy efficient and environmentally friendly (Lu and Larock, 2009; Hu et al., 2014). Hence, in recent years, research has been focused on substitutes, non-petroleum based polyols that are renewable, less expensive and more eco-friendly. Bio-polyols can be obtained from agricultural products like vegetable oils, wood, carbohydrates (cellulose and starch) and lignine. Predominantly, the bio-polyol from vegetable oil is one of the best alternative methods for this purpose (Stanton, 1959; Allauddin et al., 2013; Sherringham et al., 2000). The triglycerides can be converted to hydroxyl functional compounds which are used in coatings, adhesives, elastomers, foams and composites (Cunningham and Yapp, 1974; Bussell, 1974; Hodakowski et al., 1978; Salunkhe et al., 1992; Trecker et al., 1976; Pfister et al., 2011; Gunstone, 1996).

PU-Urea coatings have found versatile applications in the protective coatings' industries mainly because of their abrasion resistance, flexibility, mechanical strength, toughness, thermal insulation of buildings, chemical and corrosion resistance. Consequently, PU coatings are preferred as coatings of choice for various applications which include industrial maintenance, automobile finishing and chemical resistant coatings (Wicks et al., 1999; Stoy and Freitag, 1996; Mannari and Massingill, 2006). PUs from renewable resources especially using vegetable oils are gaining popularity because of possibility of various functional properties arising out of the applications of innovative chemistry and modifications of unique backbone structure of vegetable oils. In particular the unsaturation in the backbone is of interest since various reac-

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tions could be performed to obtain high functionality (OH number) bio-based polyols which react with different diisocyanate to get PUs. Generally, oils are converted into polyols by different methods such as a) oxidation of double bonds (Geiger et al., 2011), b) insertion of epoxy groups at unsaturation positions and successive cleavage of oxirane ring using enzymes, hydroxyl groups, water, organic/inorganic acids, and hydrogenation (Swern et al., 1944; Findley et al., 1945; Petrovic et al., 2000, 2002a; Guo et al., 2000a), c) introduction of hydroxyl functionality by ozonolysis of double bonds (Frankel and Thomas, 1972; Frankel, 1976; Petrovic et al., 2005), d) transesterification of oils (Wright et al., 1944; Freedman et al., 1986), and e) Microbial conversion (Hou, 1995) are being implied to develop polyols. Epoxidation is one of the most commonly employed reactions for commercial production of polyols. Plant oils are preferably epoxidized by in situ performic acid procedure at industrial scale, but still an active area of research. Epoxidation of plant oils can be achieved by different methodologies (Findley et al., 1945; Rangarajan et al., 1995; Sonnet et al., 1995) by using peracetic acid, epoxy and H_2O_2. Petrovic and co-workers‘ reports (Zlatani et al., 2004; Petrovic et al., 2003; Guo et al., 2002; Guo et al., 2000b) have performed many studies to prepare vegetable oil based polyols using epoxide ring opening reactions and have explored their use in PUs. They have reported polyols with maximum hydroxyl (OH) number 247 mg KOH/g by epoxidation and ring opening with methanol. They have also reported polyols with OH number 180–230 mg KOH/g using various catalysts such as Rh, Co, hydrochloric acid and hydrobromic acid. In the literature reported so far the hydroxyl groups have been introduced through a two-step synthetic procedure. The first step is the epoxidation of the —HC=CH— sites with HCOOH and H_2O_2 while the second step is the epoxy ring opening with mono/multi-functional hydroxyl groups, amines, halides and inorganic/organic acids. The effect of OH:NCO ratio and the different polyisocyanate structures on the properties of PU-Urea coating films have been reported (Guo et al., 2006; Petrović et al., 2002; Pan and Webster, 2012; Corcuera et al., 2011; Javni et al., 2003).

In our study, we have prepared high functionality soy polyols by one-pot synthesis using the $HCOOH/H_2O_2$ method. The soy polyols were prepared by the epoxidation of soybean oil (SBO) at 60 °C. The effect of mole ratio and time on the epoxide value of the SBO oil has been studied. The physicochemical and melt viscosities properties of the SBO oil and its polyols were also measured. The obtained soy polyol was then reacted with different polyisocyanates HDI, MDI, IPDI, H_{12}MDI and IPDI-Trimer at OH:NCO mole ratio of 1:1.2 to get PU-Urea coating films. The structural influence of the different polyisocyanates structures on the thermal, mechanical, and degradation properties of the coating films (PU-Urea) were studied for synthesized soy polyol. The coatings were also evaluated for its in vitro degradation, contact angle and chemical resistance properties.

Table 1
Properties of SBO and SP.

Property	Soybean oil	Soy polyol
Acid value(mg KOH g^{-1})	0.16	1.15
Iodine value(g of I_2 100/g)	132.14	1.22
Saponification value(mg KOH g^{-1})	191.15	191.19
Peroxide value(mg kg^{-1})	3.89	4.31
Density (g cm^{-3})	0.923	
Specific gravity	0.924	
Hydroxyl value(mg KOH g^{-1})	–	231.3
Viscosity* at 25 °C (mPa–s)	20	43750
Moisture content (%)	0.33	0.85
Epoxide value	–	0.0009
Molecular weight**	871.7	–

2. Experimental

2.1. Materials

Refined Soybean oil (SBO) was procured from the local market and used without any further purification. Its characteristic values such as acid number and physical properties were measured by standard methods and are tabulated in Table 1 and Table 1S in supporting information. 30% Hydrogen peroxide (H_2O_2) was procured from S.D. Fine Chemicals Pvt., Ltd., Mumbai, India. Formic acid (HCOOH), Sulfuric acid ($H_2SO_{4)}$ was procured from Ranbaxy Pvt., Ltd., Delhi, India. 1,6-Hexamethylene Diisocyanate (HDI), Isophorone Diisocyanate (IPDI), Dicyclohexylmethane-4,4′-diisocyanate (H_{12}MDI) and Dibutyltin dilaurate (DBTDL) (Aldrich, USA). IPDI- Trimer (Tolonate^{TM} IDT 70 B) was procured from Perstorp group, India. Methylene diphenyl diisocyanate (Desmodur-VL) was purchased from Bayer Material Science. All other chemicals were extra pure grade and used without any purification.

2.2. Synthesis of soy polyol (SP)

SBO (250 gr, 0.286 mol), HCOOH (33.3 mL, 0.86 mol) and H_2SO_4 (2.53 mL, 2% wt of the HCOOH and H_2O_2) were placed in a four necked round bottomed flask (RBF) equipped with a dropping funnel, mechanical stirrer, thermometer and cold water condenser. The RBF was immersed in the cold water bath and drop wise addi-

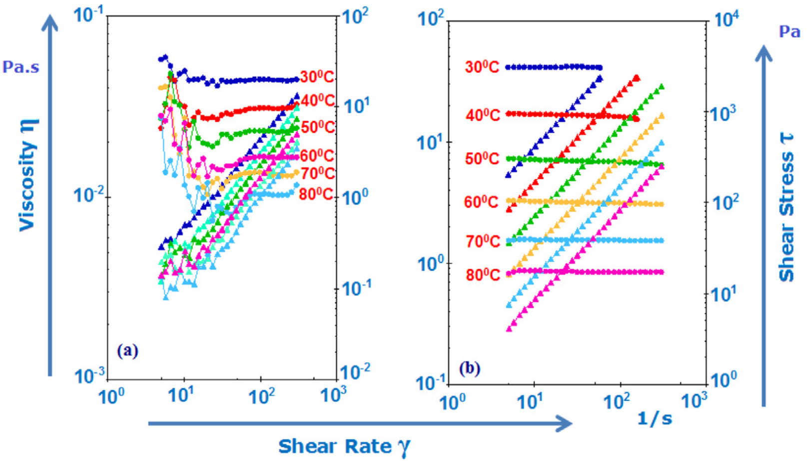

Fig. 1. Typical rheological curves of (a) SBO and (b) SP.