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Eco-economical polyurethane wood adhesives from cellulosic waste: Synthesis, characterization and adhesion study

Deepak Mishra, Vijay Kumar Sinha *

Industrial Chemistry Department, V. P. & R. P. T. P. Science College, Vallabh Vidyanagar, Gujarat 388120, India

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ABSTRACT

This study reports the preparation of polyurethane adhesives using polyols obtained from cellulosic waste and detailed study on its adhesive strength in wood joints. Keeping in view the environmental hazards related to the huge paper-waste generation across the world, low-viscosity polyols have been prepared using magazine paper waste and vegetable oils with different physicochemical properties and were used to prepare two-component polyurethane adhesives for wood bonding. Polyurethane was analyzed by FTIR spectroscopy and TGA was used for the analysis of thermal properties. The adhesive strength was measured and compared with commercially available adhesives under different environmental conditions. The synthesized adhesive with NCO/OH ratio of 1.2 and curing time of 5 days was found to be superior to the commercial adhesives Fevicol™ and Araldite™ when compared simultaneously for the single-lap shear strength in different environmental conditions.

1. Introduction

Huge amount of waste is generated across the world as a result of increased consumption of paper due to globalization, population outburst and standard of living of people, especially in developing countries and in foreseeable future the trend is not going to slowdown either. Large junk of cellulosic waste generated in form of paper products like stationary, carry bags, magazines and packaging in turn presents greater difficulties for its disposal with related harm to environment and due to the same reason, different ways to use cellulosic waste has been studied [1]. Research to utilize the paper waste is needed as according to one of the studies on paper-waste generation in different parts of the world, the per capita consumption in India is approximately 3 kg of paper each year as compare to Japan and USA which is 234 and 294 kg, respectively [2]. But, as India is world's second most populated country in the world, the total amount is correspondingly large.

As petroleum oil resources are becoming increasingly scarce and expensive to obtain, researchers have sought different resources and technologies to produce polymers and one of these includes polyurethane (PU) polymers. Polyurethane (PU) has gained considerable attention due to its superior qualities like excellent strength and chemical resistance, but its production from fossil-fuel-based polyols and non-biodegradability is an issue. The synthesis of PU is based on the reaction of isocyanates with compounds containing active hydroxyl groups such as polyols [3]. Polyol precursors obtained from renewable resources have generated great interest among researchers. With the increasing importance of renewable resources, polyols obtained from agricultural waste [4,5], saw dust [6], epoxidized methyl oleate [7] and canola oil [8] have been reported. Researchers are increasingly giving preference to the use of natural resources, especially the triglyceride oils as an alternative feed stock to replace the petroleum-based monomers [9–11]. With much interest in castor oil [12] because of its low cost and purity compared to polyols produced from vegetable and animal fats [13], it has attracted attention in recent past. Cardanol, obtained as a by-product of the cashew industry, is also a valuable and economic resource to develop polyurethane [14]. Doubtless, the uses of natural resources have given a good platform to produce precursors for polyurethane.

In 1968, Goodyear introduced the first structural adhesive for fiberglass reinforced plastic (FRP) which was used for truck hoods. Since then polyurethane adhesives have gained high importance and have been used to bond numerous substrates including glass, wood and plastics. Polyurethane adhesives perform excellently for adhesive properties, heat resistance, chemical resistance and fast curing. As use of natural and renewable resources to obtain PU adhesives gives several advantages over conventional petroleum oil-based PUs, studies related to the development of environmentally friendly and bio-based wood adhesives [15,16] have gained more importance and the synthesis of wood adhesives using chemical modification of soy protein [17], kraft lignin [18] and

* Corresponding author. Tel.: +91 9228 341432; fax: +91 2692 235207.
E-mail address: drvijaysinhavvn@yahoo.com (V. Kumar Sinha).

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coffee bean shell [19] have been reported. Due to these reasons, polymer research has been focused on the use of agricultural and household waste utilizations, minimizing the pollution and developing eco-friendly processes.

Waste paper is a rich source of cellulose and can be de-inked by the combination of chemical and mechanical processes [20]. The present study deals with the feasibility to use cellulosic waste and vegetable oils to obtain polyols which in turn was used to prepare valuable and low-cost polyurethane adhesives.

2. Experimental

2.1. Materials

Magazine paper waste was collected from the local market (Vallabh Vidyanagar). *p*-Toluenesulfonic acid (PTSA) (recrystallised before use) and sulfuric acid (S.D. Fine Chem. Ltd., Mumbai, India) were used as catalyst. Ethylene glycol (S.D. Fine Chem. Ltd., Mumbai, India) and acetone (Merck, Mumbai, India) were used for glycolysis and as solvent, respectively. Double-filtered castor oil (having hydroxyl value of 165), soy oil and rice-bran oil were obtained from local market. Toluene diisocyanate adduct (TDI), containing 13.5% free NCO, was kindly supplied by Synpol Ltd., Gujarat, India. Dibutyltin dilaurate (DBTDL, Merck, Mumbai, India) was used as catalyst.

2.2. Methods

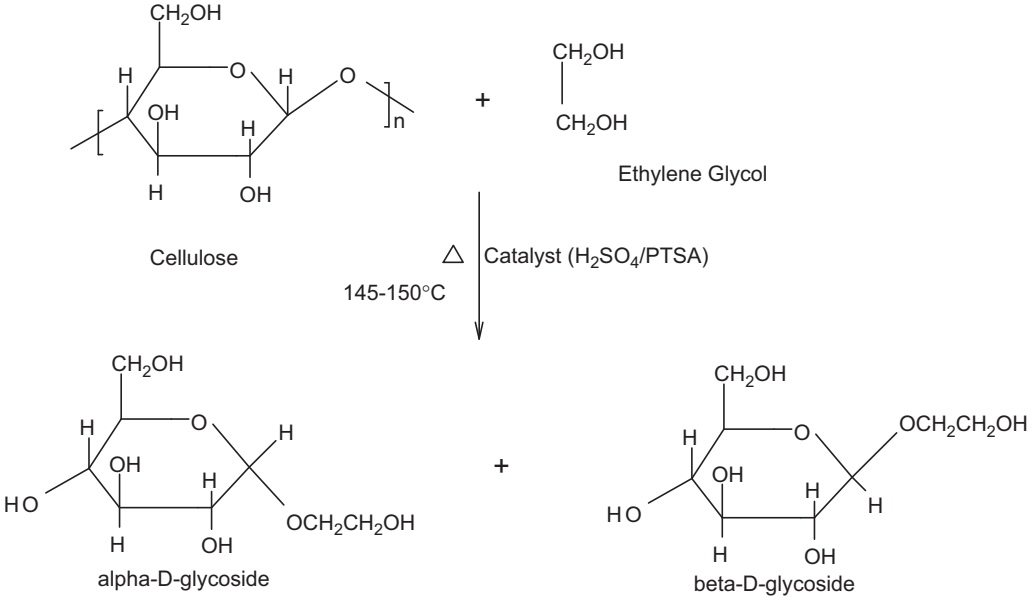
Hydroxyl values and acid values of the polyol were obtained according to the standard methods (No. 6.2.9 and 6.2.11) [21]. The viscosity of the polyols was determined using a Brookfield viscometer (RVT standard, Spindle No. 2 at 100 rpm). The colour of the polyols was obtained by using the Gardner colour comparator. FTIR spectroscopy analyses were carried out using Perkin–Elmer Spectrum GX FTIR system, England, using KBr cell. The moisture content was determined by means of a Karl–Fischer titrator. Lap shear strength of adhesives was measured using single-lap shear joints of two wood specimen on Universal Testing Machine (UTM), LR 30 K Plus, Lloyd Instruments Ltd., Hampshire, U K, at pulling rate of 5.0 mm/min. Optimized reaction methods have only been stated wherever required. Thermogravimetry analysis (TGA) was carried out on Pyris-1 TGA, Perkin–Elmer, Norwalk, CT, USA, heating rate: 10 °C/min. with the 1 mg of the sample.

2.3. De-inking and glycolysis

De-inking of cellulosic waste was done at ambient conditions in two steps:

(i) Partial de-inking with detergent (Ariel, Procter & Gamble), and (ii) complete de-inking with alkali solution. The first step removes the dust and ink from the paper surface whereas the second step swells the paper to remove the absorbed ink. Waste paper were cut into small pieces of 20cm × 40 cm and soaked in detergent solution for 20 h at 25–30 °C followed by stirring for 24 h and washed several times with fresh water to remove the detergent. The resultant mass was treated with 1.5% NaOH solution with stirring for 5 h at 25–30 °C and filtered with repeated washes of water to remove the alkali from the solid mass. The filtrate was checked with pH indicator strip, until the pH of 7 was obtained. De-inked paper was dried in vacuum oven at 90 °C for 24 h. The de-inked mass obtained was 91 g/100 g of waste paper and the dried product was stored in air-tight plastic bags.

A three-necked flask equipped with stirrer, nitrogen inlet, contact thermometer (accuracy of ± 0.01 °C), vacuum line and reflux condenser were charged with 150 ml of ethylene glycol along with 0.5% (w/w) catalyst, i.e. PTSA or H_2SO_4. Traces of moisture were removed by heating the mixture at 85 °C using a electric-heating metal under nitrogen flow and reduced pressure of 100 mmHg; 5 g of de-inked paper was added and the mixture was heated at 145–150 °C for 2.5 h. After reaction, the remaining catalyst was neutralized with barium hydroxide. A light-brown thick liquid was extracted from the residue using acetone which was then vacuum filtered through Whatman filter paper (No. 1). Acetone and unreacted ethylene glycol was distilled off at 150 °C and a reduced pressure of 125 mmHg for 15 min. The mixture obtained contains α-D-glycoside and β-D-glycoside [22] (Scheme 1). The glycoside product obtained was used to synthesize ;the polyols.



Scheme 1