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# High performance polyurethane dispersion synthesized from plant oil renewable resources: A challenge in the green materials

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ABSTRACT

A series of hyperbranched polyesters were incorporated by the chemical reaction of the dimethylolpropionic acid with trimethylolpropane, pentaerythritol, and glycerol as the core group. The castor oil-based fatty acids were also successfully prepared in order to examine the impact of the biopolyols on the thermo-mechanical characteristics of the hyperbranched waterborne polyurethane. The chemical structure of the polyols and the resulting polymer were characterized. Developing −OH functionality of the polyols the polyurethanes represented an improvement in crosslinking density, leading to increasing $T_g$, tensile modulus, and tensile strength and a decrease in elongation and toughness. Thus, the overall results forward the synthesized HBWPU as a potent sustainable and eco-friendly polymeric material by a simple approach that possesses a higher degree of sustainability over a purely petrochemical route.

## 1. Introduction

Polyurethanes (PUs) comprise an important class of polymeric materials whose properties can be tailored by adjusting its compositions, −NCO/−OH ratio, and the structure of raw materials [1–4]. Because of this, the chemistry of polyurethanes is extensively utilized for various purposes, such as coatings, foams, adhesives, liquid crystals, medical devices, sealants, elastomers, and others [2]. Waterborne polyurethane dispersions (WPU) became one of the most rapidly expanding areas of PU research, which exhibit a lower viscosity at high molecular weight, and great applicability [3]. In addition, they are also eco-friendly nature due to their low content of hazardous pollutants and volatile organic chemicals (VOCs) [4]. The major chemical building block of the WPU dispersions, including di/poly isocyanates, di/polyols, catalysts, chain-extender and others. There are a limited number of polyisocyanates are used in the PU industry, while a variety of polyester and polyether polyols are formulated [5]. Therefore, the nature of selected polyols must be competitive with other formulated soft segments (polyols) and also enable PU product to be cost competitive with other polymeric materials in end-user applications [6]. A general environmental awareness and the soaring price of finite crude oil reserves have triggered a big interest in the exploration of renewable resources, such as starch, sugars, cellulose and natural oils. Natural oils-based polyols are amidst the most promising sustainable building blocks that can effectively replace fossil-fuel-derived polyether and polyester polyols [7]. Vegetable oils are triglycerides mainly consisting of saturated and unsaturated fatty acids. The six very traditional fatty acids are (1) saturated and (2) unsaturated: (1) stearic (C18:0) and palmitic (C16:0) and (2): linoleic (C18:2), oleic (C18:1) and linolenic (C18:3). The structure-property relationships of the resulting polyurethane hugely depend on the kind of triglyceride used [8], the degree of cross-linking and the nature of the isocyanate (−NCO) group [9]. The hydrophobic nature of triglyceride structure of vegetable oils exhibit the final physicochemical properties and hydrolytic stability [3]. In order to utilize vegetable oil-based fatty acids for high-performance PU applications, a variety of specific methods is developed to transform an inexpensive, readily available, renewable feedstock into valuable monomer and other natural feedstock. Some of the methods are epoxidation of carbon-carbon double bonds followed by epoxide ring opening, hydroformylation, hydrolysis, ozonolysis, transesterification, and microbial conversion as well as thiol-ene coupling [3,10]. The modified reactive chemical sites in vegetable oils, widely investigated for the preparation of various structural PU which, impart different properties to the final product.

Most recently, anionic WPU dispersions with uniform particle substances have been synthesized by the reaction of polyisocyanates, internal emulsifiers (dimethylolpropionic acid), and vegetable oil-based polyols from soybean oil, jatropha oil, cashew nut shell oil, castor oil, and rapeseed oil [3,11–13]. The chemically modified WPU films, comprising 50-70 wt% vegetable oil polyols, exhibit chemical and

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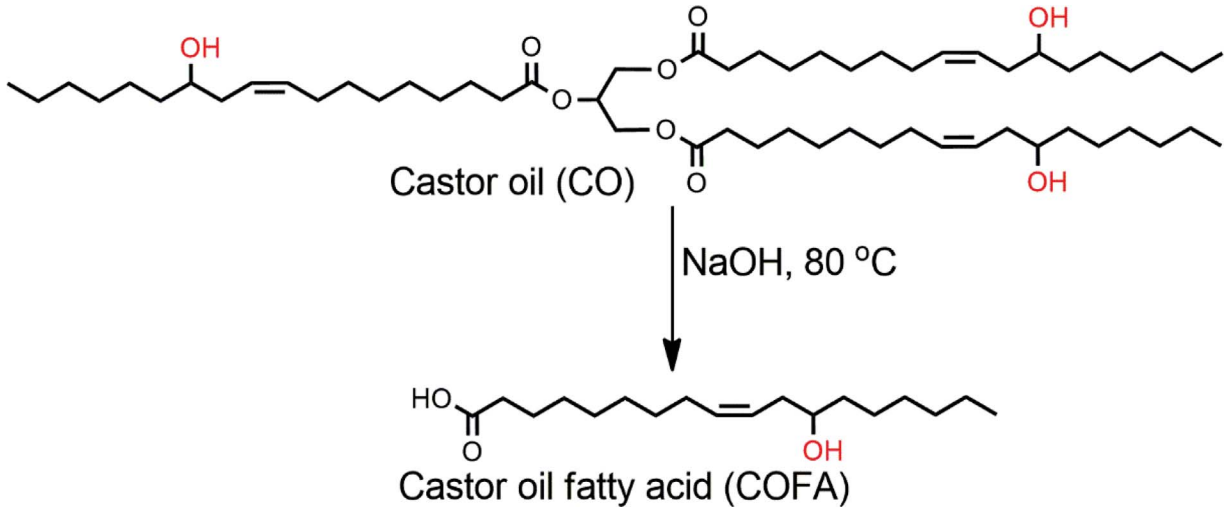


**Scheme 1.** Preparation of castor oil-based fatty acids (COFA).

mechanical properties related to PUs from petroleum based polyols, proposing various promising utilization for these biobased materials. For anionic WPUs, dimethylolpropionic acid (bis-MBA) that incorporates as a chain-extender in the chemical reaction with −NCO, and its carboxylic acid (−COOH) groups in the ionic center provides surface charge to polymer particles, which stabilize the WPU in the water phase. These sources of bis-MBA are also considered non-renewable so that the biocontent of the WPU is limited, although their costs economically non-viable [14].

Among other vegetable oils, castor oils (*Ricinus communis*) contains between 87 and 90% of a hydroxylated unsaturated fatty acid called ricinoleic acid (12-hydroxy-9-octadecenoic acid), and 10% non-hydroxylated fatty acids, largely oleic and linoleic acids [12]. The ricinoleic acids (RA) is one of the few naturally occurring castor oil-based fatty acids (COFA) with an additional 12-hydroxy (−OH) group along with terminal carboxylate groups (−COOH) [15,16]. In addition, castor oil (CO) or RA are possible starting materials to substitute bis-MBA since they are triglycerides composed of three fatty acid chains. Furthermore, CO-based polyols can be saponified into polyhydroxy fatty acids which manifest comparable properties as bis-MBA [14]. Recently, many researchers have focused on the RA-based polyesters were developed by polycondensation or by ring opening polymerization (ROP) from COFA and epoxidized soybean oil (ESBO) using a solvent-free method. Zhang et al. reported ROP reactions of ESBO with COFA using a solvent/catalyst-free method [17]. The resulting polyurethane films had a better thermomechanical property than the polyols obtained from oxirane ring-opening using small molecules. Kiatsimkul et al. initiated high hydroxyl molecular weight polyols from ESBO that were ROP by linoleic acid, RA, and RA estolide without catalysts [18].

Further, the hyperbranched polyester polyols (HBPP) is gaining significant attention for the synthesis of hyperbranched waterborne polyurethane (HBWPU) due to their remarkable physical and chemical properties. The chemical structure of HBPP exhibit many unique properties, such as low melt and solution viscosity, three-dimensional architecture, unentangled structure as well as a substantial amount of functional end-groups which is provided ample scope to form high-performance HBWPU [19]. It has been inscribed that the properties of HBWPU coating formulations containing HBPP polyols are more preferred to direct polyols because of the highly branched polyesters have a significantly lower viscosity than their linear counterparts [20]. In this context, the structure of COFA is interesting because of its architectural similarity with HBPP. A designing of COFA based hyperbranched WPU seems to be an interesting proposition because of significant sustainability and environmental biocompatibility [21]. A few successful attempts on biobased linear and HBPP have been found in the literature. In this investigation, an attempt was made to use this strategy to obtain COFA-based HBWPU.

The purpose of the present work henceforth emphasizes the synthesis of HBWPU using COFA as a branch, generating sufficient cross-linking agent as well as the ionic segment, which is the first attempt in this field as per author's knowledge. Castor oil-based polyols can be saponified into polyhydroxy fatty acid by heating with sodium hydroxide solution. In addition, we report the synthesis of HBPP using bis-MBA with trimethylolpropane as a core molecule. To determine their structural molecular reaction of the resulting COFA and HBPP were characterized by a variety of methods such as nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). Subsequently, the polyols (COFA and HBPP) were used to produce COFA-based hyperbranched WPU and the thermal and physicomechanical properties were analyzed by dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and tensile tests. This work proves that the increased cross-linking density with increasing hydroxyl groups of the polyols, which presented to an extension in physicomechanical properties.

## 2. Experimental section

### 2.1. Materials

Castor oil (CO) (Heritage Store® brand or equivalent) used in this study was purchased from a local grocery store and was dried at 80 °C under the vacuum for 5 h before use. 2,2-bis(hydroxymethyl) propionic acid (bis-MPA, 98%, Aldrich, Milwaukee, WI, USA) were dried in a vacuum oven at 90 °C for 12 h. Isophorone diisocyanate (IPDI, 98%, Aldrich, Milwaukee, WI, USA), titanium (IV) isopropoxide (TTIP, 97%, Aldrich, Milwaukee, WI, USA), triethylamine (TEA, ≥99%, Aldrich, Milwaukee, WI, USA), dibutyltin dilaurate (DBTDL, 95%, Aldrich, Milwaukee, WI, USA), and the dibutylamine (DBA, ≥99.5%, Aldrich, Milwaukee, WI, USA) were utilized without further purification. Methyl ethyl ketone (MEK) were purchased from the Fisher Scientific Company (Mumbai, India). Other chemicals and solvents were applied as obtained without any additional purification.

### 2.2. Saponification of castor oil fatty acid (COFA)

The COFA were prepared by saponification of CO (Scheme 1). Initially, required quantities of CO was saponified into fatty acid with a heating of sodium hydroxide (NaOH) solution in a temperature range of 75–80 °C. After 3 h, the solution was neutralized by hydrochloric acid (HCl). Finally, the resulting COFA was cooled and washed with water