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Synthesis and characterization of a novel internal emulsifier derived from sunflower oil for the preparation of waterborne polyurethane and their application in coatings

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ABSTRACT

A renewable, green and scalable dihydroxy acid was synthesized from sunflower oil and applied as a chain extender in the preparation of waterborne polyurethanes. In order to prepare dihydroxy acid, epoxidized sunflower oil was ring-opened with methanol followed by saponification. Chemical structure of dihydroxy acid verified by FT-IR and ^{1}H NMR spectroscopies. Acetone process was used as a main method for the synthesis of waterborne polyurethane nanoparticles from Poly(1,4-butylene adipate) (PBA) and dihydroxy acid. Particle size and morphology of nanoparticles were investigated by Dynamic Light Scattering (DLS) and Scanning Electron Microscopy (SEM), respectively and confirmed the narrow distribution with small particle diameters of nanoparticles (50–100 nm). The stable dispersion of nanoparticles applied for the preparation of films and subsequent characterizations of their thermal and mechanical properties. The obtained results corroborated that these kinds of novel waterborne polyurethane nanoparticles would be extensively efficient and applicable in coatings.

1. Introduction

Nowadays polyurethanes (PUs) are one of the prominent polymers due to their versatility and unique characteristics and attracted attention of scientists all over the world. PUs are synthesized via polyaddition reaction between isocyanates and polyols and as they are an essential part of modern life and their different applications in plastics, construction industry, automotive, medicinal science, synthetic leather, furniture, coatings, etc. [1–3]. Synthesis of PUs from bio-based materials is of highly importance. Solventborn PUs that are widely used in many industrial fields including coationg, ink, and adhesive, typically are formulated as a 25% solution. One of the huge defects of these systems is the toxic solvents such as dimethylfromamide (DMF), toluene, methyl ethyl ketone (MEK) that are used in the process of their preparation and the deleterious effects of these solvents, because they are volatile and enter the atmosphere as soon as possible [4]. In The United States and European countries, stricter legislation has been imposed to eliminate or decrease the amounts of organic volatile solvents released into the atmosphere; therefore, paint and coating industries for various fibers, primers for metals, caulking materials, adhesives for alternative substrates, emulsion polymerization media for different monomers, associate thickeners, pigment pastes, paint additives and textile dyes should produce environmentally friendly products. Considering this issue, synthesis of waterborne PUs containing carboxylic acid, sulfonic acid, and tertiary amine groups in the presence of environmentally friendly solvent, water, are extremely preeminent in many industries [5–8] that results in decreasing air pollution, improving the aspects of occupational health and lower energy consumption. Additionally, in the procedure of synthesis of waterborne PUs the viscosity is controllable and adjusted [9–13]. The anionic colloidal PUs are synthesized from various polyols, diisocyanates and a dihydroxy acid as a chain extender, which contains an anionic group. Among the well-known dihydroxy acids, dimethylolpropionic acid (DMPA) is the one that is used in most reports and leads to stabilization of polyurethane colloids in the water phase [14]; nonetheless, DMPA is synthesized from formaldehyde through the complex pathway and is considered an expensive material in the industry. Recently, scientists are interested in synthesis of bio-based PUs from the vegetable oils, for they eliminate any concern regarding extensive petroleum resources causing environmental issues [15–20]. Vegetable oils are an excellent raw material for preparation of a range of polymers because they are inexpensive, readily available, and renewable resources [21–23]. These beneficial biomaterials are triglycerides of saturated and unsaturated

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fatty acids [24]. In this study, we designed and synthesized a dihydroxy acid from vegetable oils that can be used as a chain extender in the preparation of waterborne polyurethanes containing (PBA) as polyol. PBA is a biodegradable aliphatic polyester with excellent tensile property and is extensively used as a polyol in polyurethane industry [25–28]. The PBA with high molecular weight is used in polyurethane films and highly expanded foams, while the one with relatively low molecular weight is a basic raw material in polyurethane hot melt adhesives [29]. Herein the sunflower oil (SFO) was epoxidized to prepare diol using methanolysis process and the saponification of diol led to dihydroxy acid. The obtained dihydroxy acid was used as an internal emulsifier in the synthesis of waterborne polyurethane.

2. Experimental

2.1. Materials

Sunflower oil (SFO) was purchased from local supermarket and used without purification, hydrogen peroxide 35%(H_2O_2), formic acid, p-toluene sulfonic acid, methanol, anhydrous manganese sulfate ($MnSO_4$), isophorone diisocyanate (IPDI), 4,4′-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), 1, 4-diazobicyclo[2.2.2] octance (DABCO), dibutyltin dilaurate (DBTL), methyl ethyl ketone (MEK), triethylamine (TEA), adipic acid, Titanium isopropoxide (Ti (i-Pr)$_4$) and 1, 4-butanediol (BDO) were purchased from Merck Co. All materials were used without further purification.

2.2. Synthesis of PBA

The polyester polyols, PBA 1000, was prepared using adipic acid and 1,4-butanediol in the presence of Ti (i-Pr) $_4$ as a catalyst [30]. A 1 l three-necked round bottom flask equipped with a mechanical stirrer, thermometer, and Dean & Stark trap connected to a condenser was charged with 204 g (2.27 mol) 1, 4-butanediol and 300 g (2.06 mol) adipic acid (AA) and Ti(i-Pr)$_4$ heated to 120 °C, while vigorously stirring in order to achieve a clear liquid. Then, by collection of 20, 60 and 68 mL of water as a byproduct in the Dean & Stark trap at 190, 200 and 215 °C after 0.5, 1 and 1.5 h, respectively, the PBA synthesis was monitored. Finally, the acid value was determined according standard titration and reached 3. After slowly reduction of pressure to below 100 mm Hg and increase of temperature to 220 °C and 3 h reaction, 72 mL water was collected and acid value reached to 0.5 by which reaction termination was determined. The resulting transparent liquid was cooled down to room temperature and analyzed by ^{1}HNMR and the average molecular weight of 1000 was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.12 (s, 4H, (CO) OCH2-integration 1), 3.6 (t, 4H, CH_2OH-integration 0.2), 2.53 (s, 4H, CH_2CO-integration 1.01), 1.67 (m, 8H, CH_2CH_2 −integration 2.01).

2.3. Epoxidation of sunflower oil (ESFO)

Epoxidized Sunflower oil (ESFO) have been prepared by the reaction of the carbon double bond (C=C) of sunflower oil and a mixture of formic acid and hydrogen peroxide. Briefly, the sunflower oil (100 g) and formic acid (52 mL) were added to reaction vessel that equipped with a mechanical stirrer and thermometer. The mixture was vigorously stirred for 10 min at 50 °C. Then 115 mL hydrogen peroxide was added dropwise to reaction mixture for more than 1 h for epoxidation of sunflower oil. (Note: 1:2 molar ratio of the hydrogen peroxide: SFO, and 1:1.1 molar ratio of the hydrogen peroxide: formic acid were used). The reaction was continued for 5 h at 50 °C. Subsequently, the mixture was cooled down to room temperature and washed with distilled water to eliminated excess acid and dissolved in dichloromethane to simplify separation of organic phases. The organic layer was dried with manganese sulfate and filtered. Finally, the clear viscous product was obtained after evaporation of dichloromethane using a rotary evaporator.

^{1}HNMR(300 MHz, $CDCl_3$) : δ(ppm) = 5.32(m, 1H, OCOCH), 4-4.3(m, 4H, OCH_2-), 2.9-3.16(m, 2H, O-CH), 2.3(t, 2H, CH_2-CO), 1–2(m, 5 h, CH_2, CH_3)

2.4. Methoxylated sunflower oil (MSFO)

The methoxylated sunflower oil was obtained by the ring opening of epoxide ring with methanol. ESFO (50 g) with p-toluene sulfonic acid as a catalyst were mixed with methanol and refluxed under vigorously stirring at 70 °C for 12 h. The same method used in the separation of ESFO, was used in the purification of MSFO as a product.

^{1}HNMR(300 MHz, $CDCl_3$) : δ(ppm) = 5.32(m, 1H, OCOCH), 4-4.3(m, 4H, OCH_2-), 3.5–4(m, 2H, O-CH, 3H, O-CH_3), 2.3(t, 2H, CH_2-CO), 1–2(m, 5 h, CH_2, CH_3)

2.5. Preparation of *dihydroxy acid (DHA)*

Saponification of methoxylated sunflower oil was carried out in sodium hydroxide solution. Briefly, 100 g MSFO, 50 g sodium hydroxide and 200 mL ethanol were added into 0.5 Liter two-necked round bottom flask equipped with condenser and refluxed for 5 h and the product was neutralized by the addition of hydrochloric acid. Then organic phase was extracted by dichloromethane and washed with saturated sodium chloride solution. After drying over manganese sulfate, DHA with yellowish color was obtained via removal of organic solvent using rotary evaporator.

^{1}HNMR(300 MHz, $CDCl_3$) : δ(ppm) = 3.5–4(m, 2H, O—CH, 3H, O—CH_3), 2.3(t, 2H, CH_2—CO), 1–2(m, 5 h, CH_2, CH_3)

2.6. Synthesis of waterborne polyurethane (WPU)

Waterborne polyurethanes were synthesized by acetone process. The reaction for WPU-3 carried out in three-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer.100 g of PBA (0.1 mol, M_n = 1000 g/mol), 62.7 g of IPDI (0.3 mol), 75.5 g of DHA (0.2 mol) and one drop DBTDL as a catalyst were heated at 80 °C for 2 h. Then, 50 mL methyl ethyl ketone (MEK) was added to reaction mixture for decrease of viscosity and elimination of gelation process and the reaction was continued for 2 h at 80 °C. Then, reaction system was cooled to room temperature, and solution neutralized by TEA (0.24 mol) for 0.5 h. Subsequently, distilled water was added slowly to reaction mixture and was stirred vigorously for 0.5 h. Finally, waterborne polyurethane dispersion was obtained by removal of MEK with rotary evaporator at 50 °C for 0.5 h. Other WPUs have been synthesized in same conditions

2.7. Characterization

^{1}HNMR spectra were recorded on Bruker Avance operating at a frequency of 300 MHz using tetramethylsilane (TMS) as an internal standard and $CDCl_3$ as solvents. Infrared spectra from 400