



Preparation and characterization of waterborne polyurethane/silica hybrid dispersions from castor oil polyols obtained by glycolysis poly (ethylene terephthalate) waste



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ABSTRACT

Castor oil polyols (COLs) have been synthesized from glycolized oligoester polyol in order to produce waterborne polyurethane (WPU)/silica hybrid dispersions. Soft drinks poly(ethylene terephthalate) (PET) bottles were depolymerized by glycolysis with different molar ratio of poly(ethylene glycol) (PEG 400), in the presence of zinc acetate as catalyst. The obtained glycolized products were reacted with castor oil (CO) to attain castor oil polyols by the process of transesterification. Five castor oil polyols were used with hydroxyl values of 255, 275, 326, 366 and 426 mg KOH g⁻¹. Several castor oil-based, polyurethane/silica hybrid dispersions having soft segment content of 39.6% to 28.2% and two concentrations of SiO₂ nanoparticles (0.5 and 1.0) have been prepared.

The incorporation effect of SiO₂ nanoparticles into the PU matrix and the hydroxyl functionality of the COLs on the thermal and mechanical properties of resulting polyurethane films has been examined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis (TG) and measurement of the mechanical properties. The degree of phase separation (DPS) between oxide nanoparticles and hard segment, and particle size in the polyurethane, depends to some extent on nanosilica content and the hydroxyl functionality of the polyols employed in the polyurethane preparation process.

Thermal stability of obtained hybrid materials depends on the hydroxyl functionality of the COLs and nanosilica content. The $T_{10\%}$ and $T_{50\%}$ (the temperature where 10 and 50% weight loss occurred) of WPU films decreased with the rise of OH functionality of castor oil polyols, caused by the increase of hard segment content. Glass transition temperature increased with increasing OH functionality and SiO₂ content. The hardness, adhesion and gloss quality of the polyurethane films were also determined with a view to assessing the effect of mole ratios of PET to glycol in glycolized products, the hydroxyl functionality and the SiO₂ content.

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1. Introduction

Waterborne polyurethanes, as non-toxic materials, have been abundantly used as environment friendly coatings and adhesives having presented excellent abrasion and chemical resistance, flexibility as well as fabrication versatility. However, waterborne polyurethanes have some shortcomings especially on the part of poor resistance to high temperature and medium mechanical performance [1]. The incorporation of inorganic nanoparticles e.g.

SiO₂, TiO₂, ZnO and Al₂O₃ into waterborne polyurethanes is one of several methods widely used to improve their thermal stability, mechanical and physical properties. Fumed silicas are often used with polyurethane adhesives to improve their physico-mechanical properties [2]. Silica nanoparticles offer potential for waterborne polyurethane reinforcement, because silanol groups on the surface of nanosilica might interact with the hard and/or soft segments of polyurethane thus supporting dispersion of the nanosilica in the polyurethane backbone [3].

Polyester polyols are the preferred raw materials for the production of polyurethanes. Chemical depolymerization of poly(ethylene terephthalate) (PET) waste is one of several ways of obtaining polyester polyols. The recycling of large quantities of

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PET-based products via chemical transformation provides an ecologically sensitive means by which polymers can be developed [4].

Recycled polyol products obtained by a conventional PET glycolysis process using short-chain diols (e.g. diethylene glycol) have several disadvantages which limit their use in many applications. During the glycolysis of PET, unwanted cyclic oligomers are commonly present in the final product. These cyclic oligomers reduce the functionality and hydroxyl number of the polyols, which is undesirable for its further application as a raw material for polymerization. Beneš et al. carried out PET waste glycolysis using castor oil [5]. They found the presence of long acylester chains in castor oil molecules which suppressed cyclic oligomer formation with these structures not being found in the final product. On the other hand, castor oil, especially its mixture with ZnAc catalyst, exhibited a high sensitivity towards thermal decomposition above 240 °C. However, there are several studies dealing with the synthesis and characterization of polyurethane dispersion [6], unsaturated polyester resin [6–8], and melamine formaldehyde resin [4] based on glycolized products.

Vegetable oils have a number of excellent properties which could be utilized in producing valuable polymeric materials. The low hydroxyl number of castor oil (CO) causes a poor performance of the obtained polymer materials. The other disadvantage is structural irregularity of CO due to steric hindrance offered by the long pendant fatty acid chains during polyurethane formation, resulting in poor mechanical properties. One way to increase the hydroxyl value is via transesterification [9]. Valero and Gonzalez [10] studied the preparation of polyurethane adhesive using polyol obtained from castor oil modified by the process of transesterification reaction with pentaerythritol. They used the method of matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy to determine the components of CO pentaerythritol alcoholysis product. They concluded that a mixture of the transesterification process consisted mostly of monoacylglycerol while the diacylglycerol was present in minor proportions. The other way to increase the mechanical properties of polyurethanes is to add nano-reinforcement such as exfoliated clay, carbon nanotubes, carbon nanofibers, exfoliated graphite (graphene), and nanocrystalline metals to prepare nanocomposites that have improved properties [11]. On the other hand, incorporation of inorganic nanosilica fillers into polyurethane dispersions to form nanostructured films has become an effective strategy to enhance properties of waterborne polyurethanes.

In this work, PET recycled from post-consumer soft-drink bottles was depolymerized by glycolysis in excess poly(ethylene glycol) with molecular weight 400 (PEG 400) [12]. The glycolysed product was used to synthesize polyester polyols by a transesterification method with castor oil. These polyester polyols contain hydroxyl and ester functionalities and were used as base materials along with nanoparticles as inorganic filler in the formation of waterborne polyurethanes.

In this paper, three stages of polyurethane/silica hybrid dispersion synthesis were applied: the first, glycolysis of PET using different molar ratio of PET repeating unit to poly(ethylene glycol) PEG 400 (1:2, 1:5 and 1:10); the second, transesterification of the oligoester polyols with different weight ratio of oligoester polyol to castor oil (1:10 and 1:15); the third, preparation of waterborne polyurethane/silica hybrid dispersions. Anionic polyurethane/silica hybrid dispersions were prepared using isophorone diisocyanate (IPDI), glycolized products, and dimethylolpropionic acid (DMPA) as a potential ionic center which enables water dispersibility and solutions containing fumed silicas as reinforcing agent.

The possibility of altering the weight ratio of glycolized oligoester polyol to castor oil by transesterification processes with polyester products so as to fine-tune the properties of polyurethane/silica hybrid dispersions based on castor-oil polyol and

fumed silicas remain relatively unexplored in polyurethane chemistry. For these reasons, we have tried to compare the properties of polyurethane/silica hybrid dispersions, based on fumed silicas as reinforcing agent, prepared from polyester polyol based on different weight ratio depolymerized oligoesters to castor oil. The effect of different contents of fumed silicas and polyurethane/silica hybrid dispersions based on recycled polyester polyol on adhesive properties has not to date been considered.

2. Experimental

2.1. Materials

Hydrophilic nano silica (Aerosil 380) used in this work, having a specific surface area of $380 \pm 30 \text{ m}^2/\text{g}$ and particle diameter of 7 nm, was obtained from Evonik Degussa GmbH Company (Essen, Germany).

Postconsumer waste PET bottles were procured from a local market. After removing caps and labels, bottles were cut into approximately 1 cm^2 pieces. Before the bottles were cut, they were washed with soap and methanol in order to remove adhesive materials, dried at room temperature and then dried for 24 h at 120 °C to eliminate moisture. Poly(ethylene glycol) (PEG 400, 99 wt% purity) and castor oil were purchased from Merk-Schuchardt (Hohenbrunn, Germany). Zinc acetate (Kemika, Zagreb, Croatia), was used as the catalyst for the depolymerization of PET.

Saturated polyester polyols prepared by transesterification of glycolized oligoesters and castor oil were dried and degassed in a vacuum oven at 70 °C and under 60 kPa for two days. Analytical reagent grade stannous octoate, purchased from Merk-Schuchardt (Hohenbrunn, Germany) was used as a transesterification catalyst. Isophorone diisocyanate (IPDI, 98 wt% purity) and bis(hydroxymethyl) propionic acid (DMPA), were used without further purification and were supplied by Sigma-Aldrich Co., USA. Dibutyltin dilaurate (DBTDL) was supplied by Bayer (Leverkusen, Germany). 1-methyl-2-pyrrolidone (NMP), methyl ethyl ketone (MEK) and triethyl amine (TEA) of analytical reagent grade were received from Merk-Schuchardt (Hohenbrunn, Germany).

2.2. Glycolysis of PET

Small pieces of PET waste (5 g), equivalent to 0.026 mol repeating unit ($\text{mol.wt. } 192 \text{ gmol}^{-1}$) were added to 20.8 g, 52 g and 104 g PEG ($\text{mol.wt. } 400 \text{ gmol}^{-1}$), such that the molar ratio of PET repeating unit to glycol was 1:2, 1:5 and 1:10 respectively. These mixtures (with different molar ratio PET/glycol) and 0.5 wt. % zinc acetate (based on weight of PET as catalyst) were added into a four-neck flask, which was fitted with a mechanical stirrer (100–150 rpm), a reflux condenser, nitrogen inlet (gas flow of 40 mL min^{-1}) and temperature controller. This reactor was immersed in an oil bath and the content of the reaction kettle was heated at 190 °C for 2 h, subsequently the temperature was raised to 210 °C until all the solids disappeared [12].

The obtained glycolized oligoester polyols were analyzed by hydroxyl value (HV) determination according to the conventional acetic anhydride/pyridine method. About 2 g of sample were accurately weighed and added to a 25 ml acetylating solution, containing 3/125 (vol/vol) pyridine and acetic anhydride, in a glass reactor. The reactor was fitted with a reflux condenser and magnetic stirrer (450 rpm) and then heated in a boiling water bath for 2 h. The reaction mixture was then hydrolyzed with 5 ml of distilled water and the mixture then cooled to room temperature. After adding of 25 ml methanol in another flask, the resulting solution was titrated against 0.5 M KOH standard using

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