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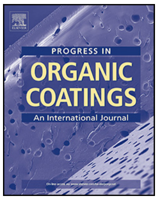

Synthesis and characterization of aqueous (polyurethane/aromatic polyamide sulfone) copolymer dispersions from castor oil

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ABSTRACT

Aqueous dispersions of castor oil-based polyurethane (PUCO)/aromatic polyamide sulfone (APAS) block copolymers (PUCO-co-APAS) were successfully synthesized via a copolymerization reaction. PUCO was prepared by an emulsion polymerization process in four steps, namely isocyanate-terminated prepolymer preparation step ($PUCO_{NCO}$), neutralization step, chain extension step and dispersion step, using castor oil (CO), toluene diisocyanate (TDI), dimethylol propionic acid (DMPA) and ethylene diamine (EDA) as a chain extender. APAS was prepared by a polycondensation reaction between bis(4-aminophenyl)sulfone (in molar excess) and terephthaloyl chloride to produce amino-terminated APAS. Three PUCO-co-APAS were prepared via a copolymerization reaction between the amino-terminated APAS and isocyanate-terminated $PUCO_{NCO}$ prepolymer. APAS, PUCO and PUCO-co-APAS copolymers were characterized using FTIR, ^1H NMR, particle size distribution (PSD), zeta potential (ZP), thermal analysis (DSC and TGA) and GPC. The effect of the copolymerization process on the thermal, chemical, physical and mechanical properties of PUCO films was studied. The obtained results revealed that the mean particle size of PUCO decreased from 80 nm to 46–49 nm after the copolymerization process. Additionally, narrower size distribution was obtained by the copolymerization process. However, the molecular weight increased with increasing the amount of APAS in the copolymer chains. The copolymerized samples showed better thermal stability than PUCO as a result of the stronger hydrogen bonds and the rigid aromatic groups introduced by APAS in the copolymeric chains.

1. Introduction

Segmented polyurethanes (PU) and polyamides (PA) are both excellent polymeric materials that have found many useful applications, such as tubings, footwear, industrial machinery, coatings and paints, elastic fibers, rigid insulations, soft flexible foam, medical devices, and many others [1,2]. The former, which composed of hard and soft segments, are considered as one of the growing industrial markets due to their excellent abrasion resistance, flexibility at low temperature, and excellent chemical, mechanical and physical properties [3–11]. However, one of the problems facing polyurethanes, which obtained by the reaction of a polyol (either polyether or polyester glycols) and diisocyanate, is their dependence on petroleum derivatives [12,13]. Therefore, the efforts are currently directed to replace part or all of the synthetic petrochemical based polyurethanes with the renewable bio-based ones [14–22].

Castor oil (CO) is a low-cost, abundantly available, renewable raw material that has attracted research effort due to its use in coatings, adhesives, paints, sealants and encapsulating compounds [12,23,24]. CO is a triglyceride of fatty acids, in which ricinoleic acid is the major constituent (about 90% of CO). The general structure of ricinoleic acid is $HOOC(CH_2)_7CH{=}CHCH_2CH\mathit{OH}(CH_2)_5CH_3$, with a secondary hydroxyl group that can allow the use of CO as a polyol to synthesize cost-effective and biodegradable PU without further modification [25].

Eco-friendly waterborne polyurethane dispersions (PUDs) have received increased attention as important alternatives to their solvent-based counterparts [26–30]. PUDs consist of linear thermoplastic PU chains that can disperse in water due to the presence of ionic groups in their structure (i.e., polyurethane ionomers). These ionic groups act as an internal emulsifier [11]. PUDs are emerging as a novel chemical technology for eco-friendly adhesives and coatings as they can be used to produce non-toxic, non-flammable coatings with a low volatile organic compound (VOC) content [31].

On the other hand, aromatic polyamides (aramids) are considered to be high-performance polymers, as they maintain their structural integrity and outstanding properties at high temperature [32]. Aramids possess excellent chemical, physical and mechanical

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properties, in addition to superior thermal and oxidative stability [33–35]. However, their rigid backbone structure restricts their fabrication and processing, as well as their potential applications [36]. Therefore, useful attempts have made to improve the processability and increase the overall chain mobility of aramides without affecting their outstanding properties by the incorporation of flexible groups (—O—, —SO_2—, —S—, —C $(CH_3)_2$—), bulky side groups or heterocyclic moieties along the polymer backbone [36].

Polyamides have a similar structure to polyurethanes except for the alkoxyl oxygen in the urethane group [1,4]. Accordingly, polyamides are expected to be compatible with polyurethanes and can modify their properties, especially their thermal properties, as polyurethanes exhibit a low thermal stability [37]. Several papers have investigated PU/PA blends [38–41].

In this work, aqueous polyurethane dispersion was prepared from CO (PUCO) using an emulsion polymerization process. The study aimed to modify the properties of PUCO via copolymerization with APAS, which prepared by a polycondensation reaction of bis(4-aminophenyl)sulfone and terephthaloyl chloride. The effect of the introduction of APAS in the PUCO chains was studied.

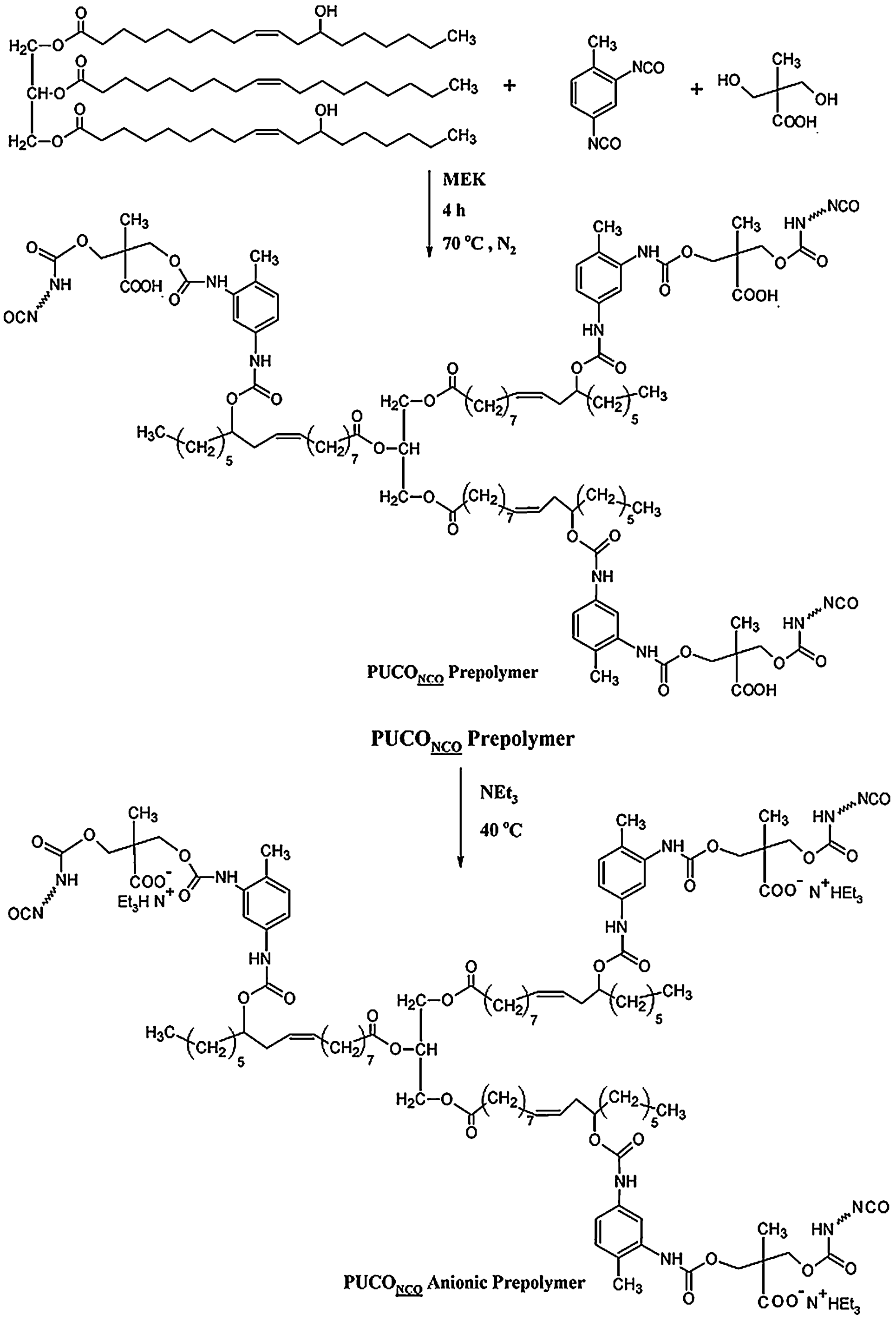

Fig. 1. (a) Synthetic route of PUCO ($PUCO_{NCO}$ prepolymer preparation step). (b) Synthetic route of PUCO (neutralization step). (c) Synthetic route of PUCO (chain extension and dispersion steps).