

Relationship between reagents molar ratio and dispersion stability and film properties of waterborne polyurethanes



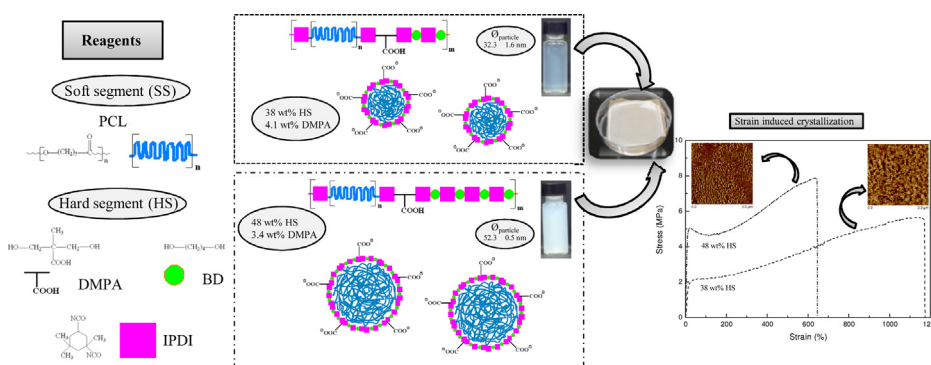
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HIGHLIGHTS

- Waterborne polyurethanes (WBPU) with a broad range of properties were synthesized.
- WBPU visually stable for months with narrow nanoparticles distribution were obtained.
- Strain induced crystallization was observed in low crystalline samples.
- Increasing isocyanate, WBPU with high strength, modulus and deformation were obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmentally-friendly waterborne polyurethanes showing a broad range of properties have been synthesized by the prepolymer method. A macrodiol based on poly(ϵ -caprolactone) diol (PCL) was used as soft segment (SS) and isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA) and 1,4-butanediol (BD) as hard segment (HS). The IPDI/(PCL + DMPA) and PCL/DMPA molar ratio were varied in order to determine the influence of these variables in particle size and stability of dispersions and also in final properties of polymer films. Particle size of the obtained dispersions, determined by means of dynamic light scattering, showed a narrow distribution with small particle diameters. Isocyanate content increase leads to bigger particles due to urethane linkages which restrict chain mobility, whereas DMPA content increase promotes small particles due to higher density of ionic groups. The stable dispersions have been used for films preparation, which have been characterized from the view point of their physicochemical, thermal and mechanical properties, as well as morphology. The increase of IPDI/(PCL + DMPA) molar ratio leads to higher yield stress, stress at break and modulus, maintaining high elongation at break values. Nevertheless, the increase of DMPA content promotes less crystalline soft domains achieving soft segment strain induced crystallization under stress and thus, obtaining higher stress at break and improving elongation at break. Films surface hydrophilicity is predominantly affected by IPDI/(PCL + DMPA) molar ratio, whereas water diffusion depends on DMPA content.

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1. Introduction

The care about environmental issues has been one of the reasons of increasing research and development of waterborne polymer systems for many and different applications. Thus, waterborne polyurethanes (WBPU) have been taking importance during last years. WBPU present the advantage of being synthesized by a solvent-free method which implies low organic compound levels and non-toxicity comparing with conventional solventborne polyurethanes besides presenting lower prices [1]. WBPU are a type of block copolymers which offer the possibility to hierarchically assemble at the nanoscale and develop different morphologies and macroscopic properties [2,3]. They are formed by two blocks; the soft segment (SS) is formed by a macrodiol, whereas the hard segment (HS) generally consists on a diisocyanate and a low molecular weight diol used as chain extender. Both segments result thermodynamically incompatible so that, phase separation takes place leading to a structure consisting on microdomains, which depending on the chemical composition can offer very different properties [4,5].

Apart from environmental advantages, WBPU dispersions present other nice features exhibiting high solid content and high molecular weight, possessing low viscosity [1]. In addition, films with similar properties to conventional polyurethanes can be obtained, such as good chemical resistance, high flexibility, adhesion to many polymers and surfaces and film-forming ability at room temperature. All these characteristics make polyurethanes available in a wide range of fields and applications, like leather and textile finishing, floor coverings, coatings, adhesives, medicine, packaging, construction, automotive, electronics and footwear, among others [6,7,8,9].

Considering the hydrophobicity of polyurethanes, in order to obtain stable aqueous dispersions, ionic groups are incorporated by the addition of a covalently bonded reagent, as internal emulsifier [10]. It is well recognized that a minimum ionic content is required for the formation of stable dispersions, which depends on the type of the ionic species. Recent studies [1,11,12,13] have demonstrated that WBPU dispersions stability and films properties are influenced principally by intrinsic characteristics as ionic groups content, hard/soft segments molar ratio, precursors physicochemical characteristics and structure, and other external factors like the method of synthesis, processing temperature or films preparation procedure, which could affect interactions between hard and soft domains. Nevertheless, there are not many studies that analyze jointly the influence of most of these factors in the stability of the dispersions and the final properties from the microscale to the macroscale of WBPU films prepared exclusively from diols and isocyanate.

Therefore, in this work different diisocyanate/(macrodiol+emulsifier) and macrodiol/emulsifier molar ratios were employed in the synthesis of WBPU with a wide range of properties in order to analyze the effect of composition on dispersions stability and films physicochemical, thermal, mechanical, hydrophilicity and water absorption properties, as well as morphology. For this purpose, WBPU were characterized by dynamic light scattering (DLS), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), mechanical tests, water contact angle (WCA), water absorption study and atomic force microscopy (AFM).

2. Experimental

2.1. Materials

WBPU were synthesized by using a difunctional poly(ϵ -caprolactone) diol (PCL) ($M_w = 2000 \text{ g mol}^{-1}$), purchased from BASF

as soft segment and 1,4-butanediol (BD), provided from Aldrich as chain extender. Both were dried in a rotary evaporator at 50 °C for 4 h. Isophorone diisocyanate (IPDI), kindly provided by Bayer, and dibutyl tin dilaurate (DBTDL), provided from Aldrich, as catalyst, were used as received. 2-Bis(hydroxymethyl) propionic acid (DMPA), selected as internal emulsifier, was supplied by Aldrich being dried under vacuum at 55 °C for 4 h prior to use. Triethylamine (TEA), purchased from Aldrich, was employed to neutralize the ionic groups in the dispersion. Tetrahydrofuran (THF) was used to control the viscosity during the synthesis. TEA and THF were dehydrated with hydranal-molecular Sieve 0.3 nm (water adsorption capacity of 15%), supplied by Fluka, which has been previously dried at 55 °C under vacuum for 1 day.

2.2. Preparation of waterborne polyurethanes

WBPU were synthesized using two-step polymerization procedure varying diisocyanate/(macrodiol+emulsifier) (IPDI/(PCL+DMPA)) and polyol/emulsifier (PCL/DMPA) molar ratios. Preliminary studies were carried out in order to establish the isocyanate/hydroxyl (NCO/OH) groups ratio. Higher molecular weights were measured by gel permeation chromatography increasing NCO/OH groups ratio from 1 to 1.05. The excess of NCO groups ensures the complete reaction with PCL, DMPA and BD, besides the reaction of residual NCO groups with water, resulting in longer chains. Thus, the NCO/OH groups ratio was set at 1.05 for all WBPU. The reaction was carried out in a 250 mL four-necked flask equipped with a mechanical stirrer, thermometer, nitrogen inlet and condenser within a thermostated bath. In the first step, PCL, 0.1 wt% of DBTDL and IPDI were mixed at 90 °C and left to react for 5 h according to kinetic measurements carried out by Fourier transform infrared spectroscopy. Thereafter, DMPA was added and the mixture was allowed to react until the theoretical NCO content was reached. The reaction progress was determined analyzing the NCO content by dibutylamine back titration method (DBBTM) according to ASTM D 2572-97. In the second step, the required amount of BD was added and this step evolution was also verified by DBBTM. Afterwards, the polymer was cooled to 55 °C while viscosity was adjusted adding low amounts of THF. After that, the necessary TEA amount was added with the purpose to neutralize all the carboxylic groups. Thereafter the system was cooled until room temperature and 75 mL of deionized water were added dropwise under vigorous stirring for 15 min. Finally, THF was removed using a rotary evaporator at 60 °C obtaining a dispersion with about 25% solid content. The pH of the resulting dispersions was measured obtaining an average value of 8.12 ± 0.28 . This value is in the range of values found in the literature [3,14], which indicate that carboxylic groups have been successfully neutralized.

Films were prepared by casting 12 mL of WBPU dispersion on leveled (8 cm \times 8 cm) Teflon molds and allowing them to dry in a climatic chamber at 25 °C and 50% of relative humidity during 7 days. The residual water entrapped in films was removed drying in a vacuum oven at 25 °C for 3 days at 800, 600 and 400 mbar, respectively. Reagents molar ratio and hard segment, acid groups and total internal emulsifier contents of the synthesized WBPU are summarized in Table 1. For comparison, neat IPDI–BD block was also synthesized. WBPU samples were named as following, PUX-Y, where the number X denotes the molar composition of diisocyanate, and Y is referred to PCL/DMPA molar ratio. Scheme of polyurethane synthesis is depicted in Fig. 1. Although the internal emulsifier was added in the first step of the synthesis, due to its low molecular weight and taking into account it was added after polyol and IPDI reaction, it might be considered part of hard segment. Dispersions were characterized after their synthesis and films one week after their preparation.

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