Study of waterborne polyurethane materials under aging treatments. Effect of the soft segment length

Anny C. Ospina[a], Víctor H. Orozco[a,*], Luis F. Giraldo[a], Mónica Fuensanta[b], José Miguel Martín-Martínez[b], Noemi Mateo-Oliveras[b]

[a] Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia
[b] Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain

ABSTRACT

Coatings made of waterborne polyurethane dispersions are a promising alternative to solvent-borne ones but their mechanical and thermal properties under harsh outdoor conditions such as high temperature and humidity are somewhat limited. In this work saturated polyesters (PBA) with different molecular weights (800–2600 g/mol) were synthesized by reacting adipic acid with 1,4 butanediol. These polyols, an internal emulsifier, and an aliphatic diisocyanate were used as raw materials to synthesize polyurethane (PU) aqueous dispersions with solids contents of 29–38 wt%. The increase of the molecular weight of the polyol decreased the mean particle size of the PU dispersions from 308 to 78 nm.

Polyurethane (PU) films were obtained by water evaporation of the PU dispersions and they were annealed at 80 °C for 2 h. Accelerated aging studies were performed by submerging the PU films in the water at 80 °C for 2 h. The PU films synthesized with the polyols with lower molecular weight exhibited enhanced phase miscibility, giving place to storage and loss moduli of similar magnitudes in a wide temperature range and they were less susceptible to hydrolytic degradation. Microphase miscibility was favored when shorter polyols are used. Contact angle measurement and cross-hatch adhesion test on PU coatings placed on stainless steel plate, before and after annealing and water aging were carried out. All PU coatings retained the adhesion to the substrate after aging, the PU coatings synthesized with shorter polyols exhibited enhanced adhesion.

1. Introduction

Polyurethanes (PUs) are versatile polymers because of their wide range of physical, chemical, and mechanical properties, and their suitable performance and durability. The PUs are widely used in furniture, construction, packaging, footwear, bedding, paints, sealants, coatings and adhesives industries, among others [1]. In most of these applications, good adhesion of the PUs is an essential property, particularly for coatings in which high abrasion resistance, good hardness, elastomeric properties and high flexibility at low temperature are important [2].

Waterborne polyurethane dispersions are emerging in the adhesives and coatings industry because of the need of replacing the solvent-borne polyurethanes that contain volatile organic compounds (VOC´s), owing to the currently stricter environmental legislation. In fact, the European Parliament has demanded the compulsory reduction in the use of VOCs (Directive 2004/42/CE) especially in paints, varnishes, and adhesives [3,4]. One way to fulfill this requirement is the use of waterborne dispersions as raw materials for adhesives and coatings

formulation. Furthermore, it has been demonstrated that the performance of waterborne dispersions as coatings or adhesives is similar or even better than the one of the solvent-borne formulations [5–7].

PUs exhibit structure-property relationship and therefore, their properties, including adhesion, can be designed and modulated by selecting the adequate composition and method of synthesis. The properties of the waterborne polyurethane dispersions are determined by the method and conditions of synthesis [4] but mainly by the nature and molecular weight of the raw materials (polyol, isocyanate, chain extender, etc), the amount and distribution of hard to soft segments [8,9], and the pendant group in the internal emulsifier, among other. On the other hand, the glass transition temperature (T_g) and phase miscibility of the polyurethanes are affected by the molecular weight and the hard segment content of the polyurethane [10,11].

Resistance against environmental agents such as humidity and high temperature is important in coatings because their degradation may cause unwanted alterations in adhesion and mechanical properties. The water absorption on to polymer bulk affects the glass transition

---

* Corresponding author.
E-mail address: hugo.orozco@udea.edu.co (V.H. Orozco).

temperature in certain polymers [12,13] leading to plasticization [14]. Furthermore, the formation of hydrogen bonding between absorbed water and soft or hard segment domain in PUs may contribute to deterioration and aging [15], these also depend on the hard to soft segments ratio, and the shape, size and distribution of the crystalline domains. The influence of the percentage of amorphous domains, and the intramolecular and intermolecular hydrogen bonds on the thermal and mechanical properties, on the aging resistance and the extent of retained water, and on shape memory functionality of PUs have been studied elsewhere [8,14]. The increase of the amorphous domains promotes water sorption due to easier penetration into the internal structure of the polymeric chains, i.e., the hard segment domains act as a tortuous path for the diffusion of water into the PU bulk. On the other hand, it has been demonstrated [15] that the hydrolytic degradation shortens the soft segment chains, reduce the molecular weight, and affect the hydrogen bond interactions in the PUs, all of which cause a deterioration of their properties [15].

Pretsch et al. [14] have proposed a degradation model for poly (ester urethane) aged in hot water for 21 days. Initially, there is an induction step (0–2 days) in which the water diffuses into the hard and soft segments, the latter one seems to be hydrolyzed in a reversible way but the hard segments are not affected; the induction step lead to reduced moduli but the elongation at yield and the shape memory functionality remain unaffected. On the other hand, the extent of hydrolytic degradation increased by increasing the water sorption and when less crystalline was the polyurethane backbone [14]. Furthermore, the solid PU coatings obtained from waterborne polyurethane dispersions may contain some retained water into the structure owing to the residual water or humidity of the environment, PUs made with polyester polyol can absorb water in the bulk which accumulates between the interstices of the polymeric chains.

A current challenge in the industry is to develop coatings and adhesives with excellent stability to high relative humidity and temperature while their VOC contents are reduced. Changing the hard to soft segment ratio is possible to understand the characteristics that improve the aging resistance of the films. Therefore, in this study, aqueous polyurethane dispersions were obtained by using DMPA internal emulsifier, IPDI diisocyanate and poly (1,4 butylene adipate) - PBA- polyols of different molecular weights. Their structure and adhesion properties before and after accelerated aging by immersion in water at 80 °C for 2 h have been studied.

2. Experimental

2.1. Materials

Adipic acid of 99.8% purity (BASF, Bogotá, Colombia), 1,4 butanediol of 99% purity (Sigma Aldrich, Bogotá, Colombia), and butyl stannic acid of 95% purity (FASCAT 4100, Arkema, Colombes, France) were used for the synthesis of the new polyester polyols.

Dimethylolpropionic acid of 98% purity -DMPA- was kindly supplied by GEO Specialty Chemicals (Pennsylvania, USA), isophorone diisocyanate (IPDI) of 98% purity (Evonik, Medellín, Colombia), butyl stannic acid (FASCAT 4100, Arkema, Colombes, France), and N-methyl pyrrolidone of 99% purity (NMP, Merck, Bogotá, Colombia) were used for the synthesis of the waterborne polyurethane dispersions.

2.2. Synthesis of the polyester polyols (PBAs)

Poly(1,4 butylene adipate) polyols -PBA- (Fig. 1) of different molecular weights (800–2600 g/mol) were synthesized by reacting 1,4 butanediol and adipic acid in the presence of 0.09% m/m butyl stannic acid catalyst. The general reaction to obtain the polyester is shown in Fig. 1. The 1,4 butanediol to the adipic acid molar ratio (OH/COOH) was set to 1.05 for having controlled excess of 5% of hydroxyl groups during synthesis to ensure that the polyester chains contain OH groups at the head and the tail.

The monomers and the catalyst were loaded in a 100 mL three-neck round bottom flask under a continuous nitrogen flow of 10 mL/min and under magnetic stirring at 450 rpm. The reactor was heated from room temperature up to 180 °C (heating rate: 2.4 °C/min) and this temperature was maintained during the reaction. The kinetics of the polymerization was monitored by quantifying the amounts of acid groups during the course of the synthesis according to ASTM D4274-05 standard [16]. The polyesters were cooled down to 60 °C and poured into a clean 60 mL glass container. The polyesters were solid at room temperature and were heated at 90 °C for 1 h before using to remove residual water. The polyesters were characterized by infrared spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR), gas permeation chromatography (GPC) and differential scanning calorimetry (DSC).

2.3. Synthesis of waterborne polyurethane dispersions (PUDs)

The PUDs were synthesized with PBA polyester polyol, 4 wt% DMPA (with respect to the total mass of all monomers) internal emulsifier, IPDI aliphatic diisocyanate, and five drops of a solution at 10%wt of dibutyltin dilaurate in xylol. An NCO/OH ratio of 1.7 was used. Due to the low solubility of DMPA in the reactants, a small amount of N-methyl pyrrolidone - DMPA/NMP = 1:3 (wt/wt) - was added.

The catalyst was pre-dissolved in NMP and together with the polyester polyol and DMPA were poured into a 100 mL three-neck reactor under nitrogen atmosphere (10 mL/min) at the constant mechanical stirring of 400 rpm. The reactants were heated up to 90 °C, and once the temperature was reached, IPDI was added. The reaction progress was monitored by collecting small amounts of the reactants mixture at different times and determining the NCO content by n-dibutyl amine titration according to ASTM D2572-97 standard [17]. Depending on the molecular weight of the polyol, about 40–120 minutes of the reaction was needed for reaching constant free NCO groups content, i.e., all hydroxyl groups of the polyester were consumed. Afterward, the temperature was lowered to 60 °C and the acid groups of DMPA were neutralized with triethylamine at 600 rpm for 30 min. Then, the temperature was decreased to 30 °C and the dispersion of the polyurethane in water was carried out by increasing rapidly the stirring speed to 2400 rpm and maintaining the stirring at 30 °C for one hour; the amount of added water was the needed to get a dispersion with a solids content of 30 wt%.

Some properties of the polyurethanes were measured in PU films that were obtained by drying the dispersions at 50 °C, over polytetrafluoroethylene plates during 20 h.

2.4. Experimental techniques

ζ potential and particle size distribution analysis. The zeta-potential values and the particle size distributions of the waterborne polyurethane dispersions were carried out in Micromeritics Nanoplus 3
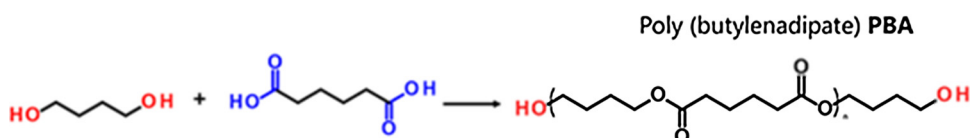

Poly (butylenadipate) PBA

Fig. 1. Scheme of reaction to obtain poly(butylenadipate).