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Role of the interactions between carbonate groups on the phase separation and properties of waterborne polyurethane dispersions prepared with copolymers of polycarbonate diol

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ABSTRACT

Different aliphatic waterborne polyurethane dispersions (PUDs) were synthesized by using different polyols (M_w: 1000 Da) of randomly copolymerized polycarbonate diols with hexamethylene and pentamethylene (C6–C5), tetramethylene (C6–C4) and trimethylene (C6–C3); these copolymers differed in the length of the methylene groups and the structural regularity due to the combination of even and odd units. Brookfield viscosity, extent of particle crowding and broadening of the particle size distribution of the PUD synthesized with C6–C4 polyol followed a different trend than for the other because of the even number of methylene units in the polyol. The PUDs showed monomodal particle size distribution which was narrower in C6–C4 (i.e. the dispersion with higher structural regularity) and the mean particle size decreased by decreasing the length of the methylene unit of the copolymer.

The properties of the polyurethanes were affected by the phase separation between the hard and soft segments, the more regular packing of even methylene units in the copolymer and the crystallized polar segments due to carbonate groups. Thus, the glass transition values of the soft segments in the polyurethanes were similar because of the more regular packing of even methylene units in C6–C4 polyol and the crystallized segments produced by interactions of carbonate groups. PU(C6–C5) and PU(C6–C4) showed similar degree of phase separation, the higher degree of phase separation corresponded to PU(C6–C3). Furthermore, the crystallinity of the polyurethanes increased with decreasing the number of methylene units in the polyol, but PU(C6–C4) was the most crystalline because of the more regularly packed even methylene groups in the polyol chain. The thermal stability of the polyurethanes increased from PU(C6–C5) to PU(C6–C3) because the more net interactions between the carbonate groups in the soft segments. The lower was the number of methylene groups between carbonate units in the copolymer, the higher was the elastic modulus of the polyurethanes. The tensile strength and elongation-at-break values of the polyurethanes increased by increasing the number of methylene groups between carbonate units in the copolymer. Finally, the peel strength was maximal in the joint made with PU(C6–C5) and the shear strength was the highest in the joint made with PU(C6–C3), in agreement with the variation of the viscoelastic and mechanical properties of the polyurethanes.

1. Introduction

Aqueous polyurethane dispersions (PUDs) are expanding their applications as coatings and adhesives because of their versatile chemistry and environmental regulations concerning the removal of organic solvent emissions. PUD consists in linear thermoplastic polyurethane chains dispersed in water due to the presence of ionic groups in the structure (i.e. polyurethane ionomer) which act as internal emulsifier [1]. Typically, an NCO-ended prepolymer ionomer is first prepared and later dissolved in acetone. Afterwards, a chain extender, such as diamine, is added to react with the terminal NCO groups to increase the molecular weight. For allowing the polyurethane being dispersible in water, the organic solvent is removed to obtain the aqueous polyurethane dispersion.

The properties of the polyurethane ionomers are determined by the interactions between the hard and soft segments and between

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the ionic groups [2]. Recent studies [3–20] demonstrated that the ionic group content, solids content, segmented structure, molecular weight of the polyol, the type of chain extender and the hard/soft segments ratio determined the PUDs properties. However, there are few studies dealing with the influence of the composition of copolymers of polycarbonate diol on the properties of the polyurethanes [21–25] and, to the best of our knowledge, there are few publications dealing with polyurethane dispersions [22,26,27].

Polycarbonate diols are produced by reaction between an alkyl diol and a dialkyl carbonate by using a catalyst [28,29]. Because of its chemical nature characterized by high polarity and strong carbonate bond, the polyurethanes prepared with polycarbonate diols can be expected to possess good mechanical properties and important degree of phase separation.

Recently Liu et al. [27] prepared a series of waterborne polyurethane (WPU) dispersions by a pre-polymer process using isophorone diisocyanate, 1,6-hexamethylene diisocyanate and polycarbonate diols with different molecular weight (1000–2000 Da) and molecular structure (copolycarbonate C5–C6 and polycarbonate of 1,6 hexanediol), and they showed that the mean particle size, thermal stability, crystallinity, mechanical properties and hydrophobicity increased and the particle distribution decreased with the increase of the molecular weight of the polycarbonate diols. Moreover, copolycarbonate-based WPU dispersions showed smaller particle size, wider particle size distribution, lower viscosity, better hydrophilicity and crystallinity than homopolycarbonate-based WPUs, but lower thermal stability, lower flexibility, and smaller mechanical properties. The change in those properties was ascribed to the less regularity of C5–C6 copolycarbonate which was balanced by higher polyurethane chain flexibility as compared with C6 homopolycarbonate, and furthermore the C5–C6 copolycarbonate owned stronger polarity.

Kojio et al. [23] prepared a series of aliphatic polycarbonate diols with various methylene numbers as soft segments for the synthesis of polyurethane elastomers, and they found that the degree of microphase separation of the polyurethanes became first weaker and then stronger with increasing the number of methylene groups of polycarbonate diols, the threshold carbon number for the degree of microphase separation was six. Furthermore, Young's modulus of the polyurethanes increased with an increase in the methylene number due to the degree of microphase separation and the ease of packing of the polycarbonate chains. In a more recent paper, Kojio et al. [30] established that the mechanical properties of thermoplastic polyurethane elastomers based on either polyether or polycarbonate diols were controlled by restriction of the crystallization of the soft segments. The values of the glass transition temperature of the soft segments increased with increasing C4 composition ratio in the polycarbonate diol copolymer giving stronger degree of phase separation. This behaviour was ascribed to the lower chain mobility of polycarbonate diol with high C4 composition ratio. Furthermore, the introduction of the C4 unit in the polycarbonate diol copolymer improved the heat resistance on account of the increased content of carbonate groups, and furthermore Young's modulus of the polyurethanes increased by increasing in the C4 composition ratio of the copolymer due to the increase in the hard segment content, the degree of microphase separation and stiffness of polycarbonate diol.

Casetta et al. [31] reported the effect of side methyl groups of the polycarbonate diols on the mechanical properties of polyurethanes and they found that the values of the glass transition temperatures were lower than for polycarbonate diols with methyl side groups. On the contrary, the change in the mechanical properties exhibited similar values that these found by Kojio et al. [30] concluding that the introduction of different methylene chains between carbonate groups by random copolymerization was an effective method to improve the mechanical properties of the polyurethanes.

Table 1
Hydroxyl values and molecular weights of the copolymers of polycarbonate diol.

Property	C6–C5	C6–C4	C6–C3
OH value (mg KOH/g)	105.0	111.0	111.5
M_w (Da)	1069	1011	1006

To the best our knowledge, there are not studies in the existing literature considering the influence of adding copolymers of polycarbonate diol of different composition on the properties of aqueous polyurethane dispersions and on their structure–properties relationship. Therefore, in this study different waterborne polyurethane dispersions were prepared with copolymers of polycarbonate diol of different compositions, i.e. copolymers of polycarbonate diol with hexamethylene (C6) and pentamethylene (C5) or tetramethylene (C4) or trimethylene (C3) units between carbonate groups, and their structural, thermal, viscoelastic and adhesion properties were characterized.

2. Experimental

2.1. Materials

Copolymers of polycarbonate diols with molecular weight around 1000 Da (supplied by UBE Chemical Europe, Castellón, Spain) (Table 1) were randomly copolymerized by using an appropriate catalyst. Three copolymers were prepared with hexamethylene (C6) and pentamethylene (C5) or tetramethylene (C4) or trimethylene (C3) units between carbonate groups. These copolymers are composed of different repeating structural units (carbonate groups plus methylene units varying in the length, and hence in their mass), connected randomly, and their content is given by the molar ratio. Thus, the molar ratio of 1,6 hexanediol to 1,5-pentanediol in C6–C5 is 50:50, the molar ratio of 1,6 hexanediol to 1,4 butanediol in C6–C4 is 70:30, and the molar ratio of 1,6 hexanediol to 1,3-propanediol in C6–C3 is 50:50. The structure of the copolymers of polycarbonate diol is shown in Fig. 1. The three copolymers of polycarbonate diol are liquid at room temperature and their hydroxyl values and molecular weights are very similar (Table 1).

The diisocyanate used was isophorone diisocyanate (IPDI, 98% purity) (mixture of *cis*/*trans* isomers) (supplied by Aldrich, Barcelona, Spain) which is liquid at room temperature. Diethyleneglycol (DEG, 99% purity) and dimethylolpropionic acid (DMPA, 98% purity) (both supplied by Aldrich, Barcelona, Spain) were used as short diol and internal emulsifier, respectively, without further purification. Triethylamine (TEA, 99% purity) was used as neutralization agent, and monohydrated hydrazine (HZ, 99% purity) (both supplied by Fluka, Madrid, Spain) was used as chain extender. Deionized water was used as dispersing phase, and high purity acetone (99.5% purity, Aldrich, Barcelona, Spain) was also used.

2.2. Synthesis of the waterborne polyurethane dispersions

The aqueous polyurethane dispersions were prepared by means of the acetone method by reacting an isocyanate, different

HO-CX-O(CO)O-CX-O(CO)O-CX-OH

CX = $-(CH_2)X-$ X = 3, 4, 5 or 6

-C5-O(CO)O-   *M_W : 130 Da*
-C4-O(CO)O-   *M_W : 116 Da*
-C3-O(CO)O-   *M_W : 102 Da*

Fig. 1. Chemical structure of the copolymers of polycarbonate diol.