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Influence of the solids content on the properties of waterborne polyurethane dispersions obtained with polycarbonate of hexanediol

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ABSTRACT

Waterborne polyurethane adhesives are an interesting alternative to the current solvent-borne polyurethane adhesives used in the industry. Different aliphatic waterborne polyurethane dispersions (PUDs) with different solids content were synthesised by reacting isophorone diisocyanate (IPDI) with a polycarbonate derived from hexanediol via the acetone method. The PUDs were characterised by Brookfield viscosity, pH, particle size, transmission electron microscopy (TEM) and solids content measurement. The dry polyurethane films were characterised by ATR-IR spectroscopy, plate–plate rheology, differential scanning calorimetry (DSC) and thermal gravimetry (TGA). Their adhesion was evaluated from T-peel tests of flexible PVC/waterborne polyurethane dispersion/flexible PVC joints and single lap-shear tests of aluminium/waterborne polyurethane dispersion/aluminium joints.

The PUDs showed bimodal particle size distribution. The mean particle size of the PUDs decreased by increasing their solids content but the particle size distribution of the PUDs increased by decreasing their solids content. As the solids content increased the Brookfield viscosity of the PUDs increased due to lower mean particle size where particle crowding was favoured, the PUD having 44 wt% solids content was an exception (higher particle size but lower polydispersity). On the other hand, the increase in the solids content increased the hard segments content and the degree of phase separation of the polyurethanes. The greater the solids content of the polyurethanes, the lower their glass transition temperatures values and the lower the elastic moduli. Adhesive strength under peel stresses were not affected by the solids content in the polyurethanes but the single lap-shear strength values decreased by increasing the solid contents in the polyurethanes due to lower hard segments content.

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1. Introduction

Waterborne polyurethane dispersions (PUDs) have an increasing interest in adhesives and coatings industry due to environmental, health and safety issues. Indeed, the development of PUDs formulations is primarily motivated by the need of controlling the emission of volatile organic compound into the atmosphere and also because of the superior properties of these polymers when compared to the similar ones in organic solvents [1].

PUDs are mainly used as flexible coatings for textiles, hard coatings for wood and metallic surfaces, and as adhesives in shoe and laminating industry. The structure of the PUD consists of linear thermoplastic polyurethane chains dispersed in water due to the presence of ionic groups in their structure (i.e. polyurethane ionomer), which act as internal emulsifiers. Typically an

NCO-tipped prepolymer ionomer is first prepared, which is readily dissolved in acetone. Afterwards, a chain extender, such as a diamine, is added to react with the terminal NCO groups to increase the molecular weight. To make the resulting polyurethane dispersible in water, the acetone is removed to obtain the aqueous polyurethane dispersion.

The properties of the polyurethane ionomers are mainly determined by the interactions between the hard and soft segments, and by the interactions between the ionic groups [2]. Recent studies [3–15] demonstrated that the ionic group content, solids content, segmented structure, molecular weight of the macroglycol, the type of chain extender and the hard/soft segments ratio, determined the PUDs properties. However, there have been few studies dealing with the synthesis and characterisation of polyurethanes based on polycarbonate diols [16–22] and, to the best of our knowledge, there are few publications dealing specifically with polyurethane dispersions [11,23].

Polycarbonate diols (PCD) have been extensively used to manufacture biocompatible biomaterials with good mechanical properties. The use of a polycarbonate diol, compared to use of

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polyester and polyether polyols, imparts better hydrolysis resistance, improved ageing and oil resistance, better mechanical properties, better low temperature properties and increased weathering and fungi resistance of the resulting polyurethanes [11,24].

Polycarbonate diols are produced by reaction between an alkyl diol and a dialkyl carbonate by using a catalyst [25,26]. Because of the polycarbonates chemical nature is characterised by high polarity and a strong carbonate bond, it may be expected the resulting polyurethanes will have good mechanical properties and more noticeable degree of phase separation.

Little effort has been paid on the influence of the solids content on the properties of waterborne polyurethane dispersions. To the best of our knowledge, there are three studies only [23,27,28] which have considered the synthesis and characterisation of aqueous polyurethane dispersions derived from different polyols having different solids content. Jung et al. [27] and Lee and Kim [28] synthesised waterborne polyurethane dispersions using a poly(tetramethylene glycol) with different solids content (from 30 to 50 wt%). They concluded that the particle size increased as the solids content of the polyurethane dispersions increased and their viscosities were also affected by the solids content. However, the mechanical and dynamic mechanical properties of the polyurethane films were not affected by the solids content. Madbouly et al. [23] also studied the effect of the solids content (from 24 to 46 wt%) on the properties of aqueous polyurethane dispersions obtained from a polyester polyol and isophorone diisocyanate. They found that the viscosities of the dispersions increased by increasing their solids content and the rheological properties of the polyurethane films were also strongly influenced by the solids content. On the other hand, they found that the solids content of the polyurethane dispersions affected their morphology as network structures, with a unique periodicity and phase connectivity being obtained.

Considering the lack of studies in the existing literature and the contradictory results previously obtained, in this study reported here, several aqueous polyurethane dispersions synthesised from polycarbonate derived from hexanediol, having different solids content were prepared. The aim was to establish the influence of the solids content on the structure-properties relationship in polyurethane adhesives, including their adhesion properties. To the best of our knowledge, this is the first contribution in the existing literature that analyse the influence of the solids content on the properties of polyurethane dispersions obtained with polycarbonate diol.

2. Experimental

2.1. Materials

The aqueous polyurethane dispersions were prepared by means of the acetone method by reacting an isocyanate, a macroglycol, an internal emulsifier and a chain extender. Polycarbonate of hexanediol ($M_w=1011$ Da) (supplied by UBE Chemical Europe, Castellón, Spain) was used as the macroglycol, and it was dried at 80 °C and 5 Torr for 3 h before use.

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 the short diol and internal emulsifier, respectively, without further purification. Triethylamine (TEA, 99% purity) was used as the neutralization agent, and monohydrated hydrazine (HZ, 99% purity) (both supplied by Fluka, Madrid, Spain) was used as the

chain extender. Deionised water was used as dispersing phase, and high purity acetone (99.5% purity, University of Alicante, Spain) was also used.

2.2. Synthesis of the waterborne polyurethane dispersions

Four aqueous polyurethane dispersions were prepared using an NCO/OH ratio of 1.5. The solids content of the dispersions was varied between 37 and 44 wt%. The DEG content was set to 0.5 wt% and that of DMPA was set to 5 wt% (both with respect to the prepolymer weight).

The macroglycol, IPDI, DEG and DMPA were added to a glass jacketed reactor equipped with a mechanical stirrer to obtain a prepolymer. The reaction was carried out at 80 °C under nitrogen atmosphere. When the amount of residual NCO groups reached the desired value (obtained by *n*-dibutylamine titration), the prepolymer was dissolved in acetone at 45–55 °C by continuous stirring at 450 rpm until complete dissolution. This solution was then dispersed into a triethylamine (TEA) aqueous solution to neutralise the carboxylic acid moieties in the DMPA.

Afterwards, the chain extender (hydrazine) was added to avoid the reaction between the unreacted NCO groups and the water, because of the preferential reactivity of the NCO groups with amines. The polymer was dispersed in water at 900 rpm and the residual acetone was removed in a Rota Vapour unit at 50 °C and 300 mbar for 1 h.

2.3. Preparation of the polyurethane films

Some properties of the polyurethanes were measured using solid films, which were prepared by placing about 100 cm³ of polyurethane dispersion in a Teflon mould and allowing a slow evaporation of the solvent at room temperature for 72 h. Afterwards, the polyurethane was dried at 40 °C for 8 h to allow the complete removal of water. Films obtained were about from 0.7 to 0.9 mm thick.

The nomenclature of the polyurethanes is given in Table 1 and it consists in the capital letters PU followed by the value of the solids content.

2.4. Experimental techniques

2.4.1. Characterisation of the waterborne polyurethane dispersions

pH measurement. About 25 ml waterborne polyurethane aqueous dispersion was placed in a beaker. The pH values of the polyurethane aqueous dispersions were measured at 20 °C in a pHmeter using a silver reference electrode model HI 8418 (Oakton Instruments, Vernon Hills, USA). The pH was calculated as the average of three experimental determinations.

Particle size distribution. The mean particle size and the particle size distribution of the polyurethane dispersions were measured in a Coulter LS230 system (Beckman Coulter Inc., Miami, FL, USA), provided with laser diffraction and polarised light detectors. A small amount of aqueous polyurethane dispersion was added into the deionised water tank. The statistical model used to obtain the particle size distribution assumes that the particles are

Table 1
Nomenclature and some properties of the waterborne polyurethane dispersions.

Nomenclature	Solids content (wt%)	pH	Brookfield viscosity (mPa s)
PU37	37.4 ± 0.3	8.3	40.8
PU39	39.2 ± 0.2	8.3	40.9
PU42	42.5 ± 0.2	8.3	63.7
PU44	43.8 ± 0.6	8.4	33.1

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