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Hybrid waterborne polyurethane/acrylate dispersion synthesized with bisphenol A-glicidylmethacrylate (Bis-GMA) grafting agent

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ABSTRACT

New hybrid waterborne polyurethane/acrylate (WPUA) dispersions were synthesized by grafting with bisphenol-A-glycidyl dimethacrylate (Bis-GMA) in order to create chemical bonds between polyurethane and polyacrylate chains. WPUAs were prepared by using prepolymer self-emulsifying method with isophorone diisocianate, poly(tetramethylene ether) glycol, dimethylolpropionic acid, and ethylenediamine in the polyurethanic part, and styrene and *n*-butyl acrylate in the polyacrylate portion. A redox pair system consisting of ascorbic acid and hydrogen peroxide were used as polymerization initiator. The particle size of the WPUA dispersions increased by increasing the Bis-GMA/1,4 butanediol ratio, stable dispersions of negatively charged particles were obtained, and they had low viscosity (around 1.3 mPa.s) in spite of the relatively high solids content (27 wt%). Higher thermal stability was obtained when 50 mol% of chain extension was carried out with Bis-GMA. Using Bis-GMA/BD, instead of HEMA, as grafting agent, allowed obtaining hybrid polyurethane dispersions with the lowest mean particle size and better colloidal stability. Finally, the addition of 35 wt% Bis-GMA increased noticeably the cross-cut adhesion of polyurethane/acrylate coatings to stainless steel.

1. Introduction

Waterborne polyurethane dispersions have emerged as an important alternative respect to solvent-borne adhesives and coatings, because of the environmental problems due to the release of VOCs to the atmosphere. Since 1960s, the patent activity in waterborne polyurethane dispersions has been noticeably increased, as well as more interest in academia on the synthesis, thermal, adhesion and mechanical properties of waterborne polyurethane dispersions [1–3]. In order to improve some properties of polyurethanes obtained from dispersions such as hardness, tensile strength, elongation at break, and solvent and alkali resistance, hybrid physical blends of polyurethane and acrylic or vinyl polymers have been proposed [4,5], interpenetrated networks, hybrids prepared by end-capping [6], and grafting or crosslinking [4,7] of acrylic or vinyl monomers with polyurethane prepolymers. The particularity of the hybrid systems is the presence (grafting or end-capping) or not (physical blends and interpenetrated networks) of anchoring points into the polymer structure.

In grafting and end-capping systems, the double C═C bond acts as anchoring sites that can be located in different parts of the polymer structure. For end-capped polymers, hydroxyethyl acrylate (HEA) [8,9] and hydroxyethyl methacrylate (HEMA) [10–12] are the most common monomers used for synthesizing hybrid polymers. The anchoring points for the hybrid formation are the ends of the polyurethane macromolecule [12] and different kinds of chemical bonds can be obtained, such as dangling chains, polyurethane pendant chains [13], and free polyurethane chains [12]. On the other hand, when the anchoring points are distributed along the backbone of the polyurethane chain, a grafting-like topology can be obtained, facilitating hybridization and crosslinking. This strategy has been less explored in the existing literature. It has been reported the use of unsaturated amine [2-(dimethylamino) ethyl methacrylate] [14] to neutralize the dimethylol butanoic acid (DMBA) moieties and at the same time to incorporate reactive double C═C bonds into the polymer structure; these double C═C bonds were polymerized in presence of methyl methacrylate by using potassium persulfate (KPS) or azobisisobutyronitrile (AIBN) as initiators, leading to the formation of core-shell particles of polyurethane/acrylate hybrid polymer. These hybrid polymers were more hydrophobic than the polyurethane ones.

The polymerization methodology to obtain hybrid systems is essential for obtaining adequate mechanical, chemical and adhesion properties. Most of the reported methodologies involved the emulsion

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[7,8,15,16] and miniemulsion [12,15,17,18] polymerization. However, these methodologies have some disadvantages associated to the use of solvents (for decreasing the viscosity) and the addition of external emulsifiers (for stabilizing the dispersions). Some studies avoiding the use of external emulsifiers have been published [6,19,20]. Xin et al. reported the so-called solvent/emulsifier free method [21] in which the polyurethane prepolymer is dissolved in vinyl and acrylic fluorinated monomers before dispersing in water. The waterborne polyurethane chains can act as dispersing agent which also help to stabilize the aqueous dispersion. In this sense by avoiding the use of solvents the preparation of "green systems" is favored, and by avoiding the use of external emulsifiers improved properties can be obtained. However, the solvent/emulsifier free method has been used only for developing antifouling coatings and the monomers used are environmentally hazardous.

Most of the above described methods of polymerization are based on conventional radical polymerization mechanism. However, the living radical polymerization of polyurethane/acrylate copolymers, e.g. reversible addition−fragmentation chain-transfer polymerization (RAFT) [22] and atom transfer radical polymerization (ATRP) [23], has been proposed. These polymerizations are adequate when tailored macromolecular structures are required. However, they are more difficult of scaling up.

Regarding to the radical initiator system, the use of redox initiator [24] is appropriate as high temperatures are avoided, limiting the destabilization of the colloidal system. In fact, it has been reported that the ascorbic acid/hydrogen peroxide pair allow stable polyurethane/acrylate hybrid particles [17].

In this work, an alternative approach to the auto-emulsifying method is proposed to obtain waterborne polyurethane/acrylate hybrid dispersions made by grafting with bisphenol-A-glycidyl dimethacrylate (Bis-GMA) as anchoring molecule into the polyurethane macrostructure. A redox initiation system of ascorbic acid and hydrogen peroxide is used to promote the hybridization among the urethane and the acrylate chains. In order to leave unreacted terminal NCO groups, the NCO/OH molar ratio was set to 1.30, and the chain extension was produced in two different ways: *(i)* Half of the unreacted terminal NCO groups was reacted with mixture of Bis-GMA/1,4 butanediol (BD) in different molar ratios, and the other half of NCO groups were reacted with an aqueous solution of ethylenediamine (EDA); (ii) Use of hydroxyethyl methacrylate (HEMA) as end-capping agent instead of Bis-GMA/BD. The mass ratio of polyurethane/acrylate was fixed at 60/40 with the acrylic part containing 50/50 styrene/n-butyl acrylate.

2. Experimental

2.1. Materials

Isophorone diisocianate (purity: 99.5%) (IPDI) (Versanat supplied by Evonik, Essen, Germany) and poly(tetramethylene oxide) of molecular weight 2000 g/mol (PTMO), were dried for two hours at 110 °C in vacuum; triethyl amine (purity: 99%) (TEA), 1,4 butanediol 99% (BD), 1-methyl-2-pyrrolidone (purity: 99.5%) (NMP), bisphenol-A-glycidyl dimethacrylate (Bis-GMA), ethylenediamine (purity: 99.5%) (EDA), *n*-butyl acrylate (purity: 99%) (BA), styrene (purity: 99%) (ST), and 2-hydroxyethyl methacrylate (purity: 99%) (HEMA) were purchased from Sigma-Aldrich (Sigma-Aldrich, Missouri, USA) and they were used as received. Dibutyltin dilaurate catalyst (purity: 95%) (DBTDL) (Sigma-Aldrich, Missouri, USA) was dissolved in xylene (10 wt%). Dimethylopropionic acid (purity: 95%) (DMPA, Geo Specialty Chemicals, Indiana, USA) was used as internal emulsifier. L-ascorbic acid (AA) (purity: 99%) and hydrogen peroxide (H_2O_2) with 35% concentration, were supplied by Merck (Bogotá, Colombia) and they were used as received. Deionized water was used as dispersing phase.

2.2. Preparation of the waterborne polyurethane/acrylate dispersions

PTMO, DMPA, NMP (weight ratio 4:1, NMP:DMPA) and DBTDL were placed in 100 mL four-neck reactor, heated up to 90 °C and mechanically stirred at 500 rpm under nitrogen atmosphere. After homogenizing the mixture at 90 °C, IPDI was slowly fed into the reactor allowing react for two hours and the NCO/OH mole ratio in the prepolymer was maintained at 1.30. Separately, for chain extended dispersions, Bis-GMA and/or BD were diluted in 1/4 of the total amount of ST/BA used mixture for hybridization (1:1 wt.% ST/BA). In the case of the end-capped dispersion, all the Bis-GMA and the BD were replaced by the HEMA, following the same procedure. The reactor was cooled down to 60 °C and that mixture was added, allowing react for two additional hours. Then, the acid groups were neutralized with TEA during 30 min and the remaining ST/BA mixture (3/4 of the total amount) was fed into the reactor. The temperature was diminished to 30 °C, the stirring was increased up to 2200 rpm and a solution of EDA in distillated water was added to react with the remaining 50% of NCO groups and the stirring was maintained for one hour. After cooling down to room temperature, an aqueous solution of AA and H_2O_2 was added drop by drop under stirring at 250 rpm, and let react at 30 °C during two hours. The concentrations of hydrogen peroxide and ascorbic acid were fixed at 0.1 and 0.002 M, respectively. Then, the hybrid dispersion was obtained. The nominal solids content for each dispersion was 30 wt% based on the polymer weight fraction. Fig. 1 shows the scheme of the synthesis of the hybrid dispersions, and Table 1 shows the composition of waterborne polyurethane/acrylate (WPUA) dispersions.

2.3. Characterization of the polyurethane/acrylate dispersions

Mean particle size and particle size distribution of the polyurethane/acrylate dispersions were obtained in Nanoplus HD (Particulate systems, Micromeritics Instruments, Norcross, GA, USA). To perform the measurement, a drop of the dispersion was added to deionized water container, 30 scans were carried out, and three replicates were measured and averaged.

The ζ potential measurements of the polyurethane/acrylate dispersions were performed in Zsizer Nano ZS (Malvern Instruments, Worcestershire, United Kingdom). For measurement, 10 μL of dispersion were diluted to 1.0 mL with deionized water. Three replicates were measured and averaged.

pH of the polyurethane/acrylate dispersions were measured at 24 °C in Thermo Scientific Orion 3-Star Benchtop pH Meter (Thermo Scientific, Panda garden, Singapore). Three replicates were measured and averaged.

Brookfield viscosity at 25 °C of the polyurethane/acrylate dispersions was measured in Brookfield LDVE115 viscometer (Brookfield Engineering Laboratories, Middleborough, MA, USA). The measurements were carried out at 100 rpm by using the spindle no. 2.

Surface tension of the polyurethane/acrylate dispersions was performed by using the Du Nouy's ring method in Phywe dynamometer (Phywe System Gmbh, Gottingen, Germany), equipped with a metal ring of 19.5 mm diameter. The dispersion was poured into beaker of 11.0 mL and the ring was placed on the dispersion surface, determining the force (F) necessary to remove the ring. The surface tension (γ) was calculated by using Eq. (1)

$$\gamma = \frac{F}{4\pi r} \tag{1}$$

where r is the radius of the ring. Four replicates were measured and averaged.

The solids content of the polyurethane/acrylate dispersions were obtained by weight difference before and after water removal. About 0.5 g of dispersion was poured on Teflon® plate and heated at 40 °C during 72 h; then, the temperature was increased up to 75 °C and