STABILITY OF TRIETHOXYSILANE TERMINATED WATERBORNE POLYURETHANE NANOPARTICLES

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The water-based systems are gradually dominating most of the coating market as a consequence of their lower toxicity comparing to the organic borne systems. According to this, in the last decades aqueous polyurethanes (PU) [1,2] have grown commercially due to environmental reasons. Polyurethane materials demonstrate a unique combination of performance properties, including excellent abrasion resistance, flexibility, hardness and many other that make then suitable for a lot of useful products including coatings, adhesives and sealants.

Several processes have been developed for the synthesis of polyurethane dispersions. One of the most used is the "acetone process". In that system, the polyurethane is synthesized in a low boiling point solvent (usually acetone). The synthetic procedure is similar to the one used in the traditional formation of polyurethanes, but a part of the chain extender is replaced by a functionalized diol that improves water dispersability. After that, water is added drop wise to the polymeric solution, giving rise to a fine polyurethane dispersion. Finally the acetone is removed by distillation and the aqueous polyurethane dispersion is obtained. Figure 1 shows a scheme of the described process.

Because most commercial aqueous PU-s are linear thermoplastic polymers, the mechanical properties and solvent resistance of these systems is lower than the obtained in crosslinked two pack solvent based PU-s. Many ways of crosslinking waterborne PU-s have been studied. In recent publications [3], PU prepolymer dispersions have been reacted with alkoxisilane containing compounds in order to get a moisture curable PU. These systems display good adhesion to different substrates and improved mechanical properties because of the presence of the inorganic domains. However, the incorporation of the alkoxisilane end groups can reduce the stability of the PU dispersion.

In this work different waterborne polyurethanes were synthesized by means of the acetone process. Isophorone diisocyanate (IPDI), Polyester end capped diol (PBAD), 2,2-bis(hydroxymethyl) propionic acid (DMPA), triethylamine, 1,4-butanediol, sodium hydrogen carbonate ($NaHCO_3$) and a tin catalyst were used for the synthesis of the waterborne polyurethanes.

In addition some of those polymers were reacted with 3- aminopropyltriethoxysilane (APS). The amine group can react with the isocyanate group, giving rise to urea groups. Different reactions were performed using variable amounts of APS. Figure 2 shows the infrared spectra of the obtained polymers.

As can be seen in Figure 2, the modified polymers show a new band (1630 cm^{-1}), attributable to urea groups, whose intensity increases with APS concentration. These results confirm that the APS has been covalently linked to the PU chain.

However, APS ethoxysilane groups are highly reactive and in the presence of water are prone to hydrolyze. Although during the polymerization process in acetone there is not hydrolysis thanks to the nitrogen inlet, when water is added and the phase inversion starts, the ethoxy groups, coming from the APS, hydrolyze and can condense between them forming a network and making the dispersion less stable.

In order to check the stability of the dispersion, Dinamic light scattering (DLS) measurements were carried out during the phase inversion to monitorize the diameter of the obtained particles (Dp). The obtained results have shown that the addition of APS increases considerably the diameter of the particle and therefore, decreases the dispersion stability.

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References:

[1] A. K. Nanda, D. A. Wicks, Polymer, 47 (2006) 1805-1811.
[2] H. T. Jeon, M. K. Jang, B. K. Kim, K. o Kim, Colloids and Surfaces A: Physicochem. Eng. Aspects, 302 (2007) 559-567.
[3] S. Subramani, J. M. Lee, J. Y. Lee, J. H. Kim, Polym. Adv. Technol, 18 (2007) 601-609.

Figure 1. Scheme of the formation of water borne polyurethane

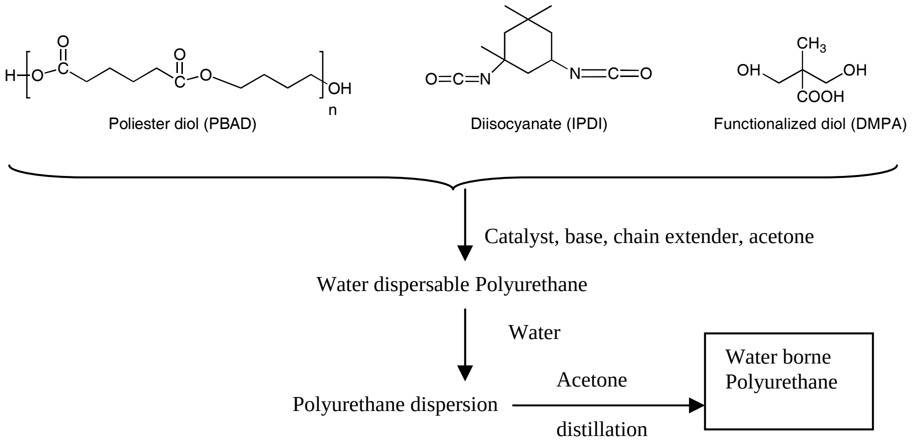

Figure 2. FTIR spectra for different polyurethanes