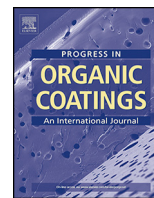




Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



Waterborne hybrid polyurethane coatings functionalized with (3-aminopropyl)triethoxysilane: Adhesion properties

H. Sardon, L. Irusta, A. González, M.J. Fernández-Berridi*

POLYMAT, Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco UPV/EHU, P.O. Box 1072, 20018 Donostia, Spain

ARTICLE INFO

Article history:

Received 22 October 2012
Received in revised form 22 February 2013
Accepted 27 March 2013
Available online xxx

Keywords:

Waterborne polyurethanes
(3-Aminopropyl)triethoxysilane
Adhesion properties

ABSTRACT

Waterborne polyurethanes based on isophorone diisocyanate and two different soft segments, poly(1,4-butylene adipate) and poly(propylene glycol), were end-capped with (3-aminopropyl) triethoxysilane to impart them the ability to crosslink at room temperature. Polyurethanes were synthesized by means of acetone process and stabilized in aqueous medium using dimethylolpropionic acid (DMTA) as internal emulsifier. ¹³C NMR experiments confirmed the insertion of the alkoxy silane. The adhesion properties of the room temperature cured films as a function of alkoxy silane concentration were evaluated. The optimum film formation time and adhesion temperatures were established using the design of experiments (DOE) methodology. The Lap Shear adhesion increased as a function of the alkoxy silane content up to a point, 9.7 wt.% of alkoxy silane, where the adhesion capacity disappeared totally due to the rigidity of the material. Furthermore, both polyester and polyether based systems presented an optimum window, between 5 and 15 wt.% of alkoxy silane, where the synthesized systems promoted good adhesion at high temperatures above 200 °C for more than 24 h.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Waterborne polyurethanes (WPU) are well positioned to find an increasing usage as adhesives, coatings and sealants due to a variety of reasons [1–3]. Polyurethanes themselves offer good adhesion to a number of substrates such as concrete, wood, plastic and glass due to their elasticity and structural properties [4,5]. Furthermore, the release of VOC-s to the atmosphere in these systems is considerably reduced compared to conventionally employed solvent-based systems [6–10].

The main problem for synthesizing WPU-s, compared to other polymers, is the high reactivity of isocyanate groups toward water. Therefore, it is not possible to obtain waterborne polyurethanes by conventional water synthesis methods such as emulsion or suspension polymerization and alternative synthesis have to be employed [5,7,11]. Several processes have been developed for the synthesis of polyurethane water dispersions. The first and probably the most common one in the industry, is the prepolymer mixing process. In the literature, polyurethane aqueous dispersions are almost exclusively obtained in two-step procedure. In the first step, a polyurethane prepolymer is prepared in a non-aqueous system [10,12], which is then in a second step dispersed in water.

Recently, it has been shown that hydrophobic polyurethane dispersions can be synthesized in water in a one step procedure using the miniemulsion process [13].

However, some inferior properties of waterborne polyurethanes such as low mechanical strength, solvent and chemical resistance restrict to some extent their utility for high performance applications [14–16]. Therefore, it is important to modify WPUs with inorganic moieties in order to improve the mentioned properties. These “new” systems are increasing their use due to the synergistic effect between the organic and inorganic phases [17–20]. This synergistic effect can only be observed when good compatibility between phases is achieved [21–23].

In recent publications, waterborne polyurethane dispersions that can cure by means of the hydrolysis and condensation reactions of alkoxy silanes have been synthesized using the “acetone process” [22–24]. In order to obtain these dispersions, the isocyanate end groups of the polyurethane prepolymer dissolved in acetone, react with 3-aminopropyltriethoxysilane (APTES), being incorporated quantitatively in the polyurethane chain. The inserted alkoxy end groups undergo crosslinking reactions at room temperature during the water evaporation process, to form a stable siloxane linked network. The cured polyurethane/siloxane networks, due to their hybrid character, are supposed to present superior properties as coating materials than those presented by non-hybrid polyurethanes. In a previous paper we presented the thermal and mechanical properties of room temperature self-curable hybrid waterborne polyurethanes [25].

* Corresponding author. Tel.: +34 943018194; fax: +34 943015270.
E-mail address: mj.fernandezberridi@ehu.es (M.J. Fernández-Berridi).

The present paper is devoted to describe different adhesion tests of these types of systems. Adhesion to different substrates is an important issue in order to define a good adhesive or coating. The first issue studying adhesion properties is to define what adhesion means as there are many different definitions. In the literature adhesion is related with the strength required to debond a coating or film from a substrate. The adhesion strength can be determined by many different standard test methods (Lap Shear Test, Peeling Test, Pull Test, Scratch Test, etc.) all of them presenting advantages and disadvantages [26–30].

In this work self-curable polyurethanes were synthesized by means of the acetone process employing an alkoxy silane to promote the crosslinking at room temperature. This manuscript reports the variations of the adhesion properties as a function of APTES content. Two series of isophorone diisocyanate (IPDI) based polyurethanes were investigated (a) polyester based polyurethane (being the polyester semicrystalline) and (b) Polyether based polyurethane (being the polyether amorphous). In both cases 2-bis(hydroxymethyl) propionic acid (DMPA) was employed as internal emulsifier. The Peel and Lap Shear Tests were selected in this study taking into account the nature and the possible applications of the polyurethanes as well as the Shear Adhesion Failure Temperature (SAFT) Test for defining the maximum usage temperature of the synthesized adhesive. Before carrying out the adhesion measurements, an experiment design (DOE) was defined in order to determine the best experimental conditions (temperature of adhesion, time of exposure before adhesion, etc.) to obtain a good adhesion.

2. Materials and methods

2.1. Materials

Isophorone diisocyanate (IPDI), 2-bis(hydroxymethyl) propionic acid (DMPA), 1,4-butanediol (BD), poly(1,4-butylene adipate) end capped diol (PBAD) (M_n 1000 g mol⁻¹), poly(propylene glycol) end capped diol (PPG) (M_n 1000 g mol⁻¹) triethylamine (TEA), dibutyltin diacetate (DBTDA), (3-aminopropyl) triethoxysilane (APTES), acetone, acetone d-6 and potassium bromide (KBr) were purchased from Aldrich Chemical Corporation. All materials were used as received.

2.2. Preparation of room temperature self-curable silanized hybrids WPU films

Two series of silanized hybrid WPUs were synthesized as described in a previous work [22]. The preparation of the WPU hybrids was divided into three main steps: (a) synthesis of the polyurethane prepolymer, (b) functionalization of the prepolymer and (c) emulsification. Table 1 shows the amount of reagents used in the different reactions.

Table 1
Amount of reagents employed for the preparation of both series of silanized WPUs.

Name	APTES (wt.%)	PBAD (mmol)	PPG (mmol)	IPDI (mmol)	DMPA (mmol)	TEA (mmol)	APTES (mmol)	BD (mmol)
PBAD_0	0	45	–	113	22	30	0	46
PBAD_5.0	5.0	45	–	113	22	30	19	37
PBAD_9.7	9.7	45	–	113	22	30	38	27
PBAD_14.0	14.0	45	–	113	22	30	57	18
PBAD_18.4	18.4	45	–	113	22	30	82	5
PPG_0	0	–	45	113	22	30	0	46
PPG_5.0	5.0	–	45	113	22	30	19	37
PPG_9.7	9.7	–	45	113	22	30	38	27
PPG_14.0	14.0	–	45	113	22	30	57	18
PPG_18.4	18.4	–	45	113	22	30	82	5

2.3. Preparation of the cured films for analysis

The curing process of these polyurethane dispersions was carried out in a Teflon mold in a controlled temperature room at $21 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity, as described in a previous work [22]. 30 mL of both series of synthesized polyurethane dispersions containing 30 wt.% of solids were poured into a circular 15 cm diameter Teflon mold. The dispersions were self-cured at room temperature for one week and after demolding, the films were stored for an extra week at 30°C under vacuum.

2.4. Instrumentation

¹³C liquid Nuclear Magnetic Resonance (NMR) was used to determine the structure of the synthesized polymers and verify the insertion of APTES. The spectra were obtained in a Fourier Transform Bruker 300 MHz spectrometer (model Avance 300 DPX). 0.75 mL from the reactor was charged into the NMR tube and a small amount of deuterated acetone was added. TMS was used as internal standard.

The crystallinity of the synthesized systems was studied by differential scanning calorimetry (DSC). In order to avoid the thermal history effect, the cured films were preheated to 150°C for 5 min and then kept for one week at room temperature, before performing the heating ramp from -80°C to 150°C at $10^\circ\text{C min}^{-1}$ under N₂ atmosphere. All the DSC thermograms were carried out using a TA Instrument Q 2000 apparatus.

2.5. Adhesion properties

The adhesive performance of the produced self-curable polyurethanes (Lap Shear Test, Peel strength, and Shear Adhesion Failure Temperature) was evaluated.

a) *Lap Shear Test* was carried out using an Instron 5569 machine, at $23 \pm 2^\circ\text{C}$ and at $50 \pm 5\%$ relative humidity. The polyurethane adhesive was applied onto the faces of two metallic panels that were clamped to the jaws of an Instron Tensile Tester. The adhesion values were obtained from pulling the panels following the ASTM D3163 standard. The procedure used to perform the Lap Shear Test was as follows: First 30 wt.% of the polyurethane dispersion was applied using a roller applicator of 200 μm onto a 3 cm × 10 cm metallic panel. Subsequently, the samples were prepared under two different experimental conditions: In the first one the adhesive was deposited onto the two panels and dried for 10 min before the panels were attached them using a pressure of 10 MPa at room temperature for 15 min to improve the contact. In the second one the sample on the panels was left drying at room temperature for 120 min before the two metallic panels were attached at a pressure of 10 MPa at 90°C for 15 min. Afterwards, the samples were kept at room temperature for 14 days before performing the measurements. Finally, after

Download English Version:

<https://daneshyari.com/en/article/10398013>

Download Persian Version:

<https://daneshyari.com/article/10398013>

[Daneshyari.com](https://daneshyari.com)