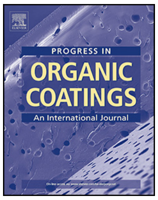
Progress in Organic Coatings 77 (2014) 798–802

Contents lists available at ScienceDirect

Progress in Organic Coatings

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



Microphase separation and hydrophobicity of urethane/siloxane copolymers with low siloxane content

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ARTICLE INFO

Article history:
Received 19 April 2013
Received in revised form
21 November 2013
Accepted 7 January 2014
Available online 31 January 2014

Keywords:
Polyurethane–siloxane thermoset copolymers
Phase separation
Contact angle
Hydrophobicity

ABSTRACT

Polyurethane–siloxane thermoset copolymers were obtained from Isophorone diisocyanate trimer, Polycaprolactone triol and 10% of hydroxy terminated Polydimethyl siloxane. The copolymers showed a phase separated structure that depended on the conversion of the reaction and casting temperature. The different samples obtained had water contact angles higher than 90°. Moreover the contact angle values presented a maximum at intermediate reaction conversion. Although FTIR measurements showed that siloxane concentration at the surface increased with reaction time, the maximum contact angle value was related to the higher roughness calculated from AFM images. DMTA results confirmed that the phase separation was higher at intermediate conversions.

1. Introduction

Segmented polyurethanes present unusual properties directly related to their two-phase microstructure. This microstructure is a consequence of the thermodynamic incompatibility between the hard and soft segments [1,2].

The introduction of nonpolar macrodiols such as Polydimethylsiloxane [3–5] in the polyurethane backbone gives rise to nanostructured surfaces that can be used to generate hydrophobic materials [6–8]. Surface composition analysis of block and graft copolymers containing Polydimethylsiloxane (PDMS) segments has shown that PDMS predominates on the surface due to its immiscibility with other polyurethane components and its low surface energy [9–12]. This type of surfaces is of special interest because they have shown to be effective in reducing the interactions associated with biofouling [13,14]. PDMS elastomers with well-defined microtopographical features inhibit the settlement of fouling organisms [15–17] and this is important since copper and tributyltin (TBI) boat paints, used to prevent fouling, cause particular environmental damage.

In a previous work [18], we reported the synthesis and surface hydrophobicity (via water contact angle measurements) of a series of copolymers obtained from Isophorone diisocyanate (IPDI), Polycaprolactone triol (PCL) and different amounts of hydroxy terminated Polydimethylsiloxane. It is interesting to note that the addition of small quantities of Polydimethylsiloxane increased substantially the water contact angle without considerable modification of the polyurethane chemical structure. Additional increments of the PDMS content did not affect the surface hydrophobicity.

Bearing in mind these results, the present work is devoted to enhance the surface hydrophobicity of a copolymer containing 10% of siloxane units. Following Webster [10,11,19] methodology, Acetylacetone was added to the formulation in order to control the phase separation of the copolymer, while trying to elucidate the role of the surface microstructure on the hydrophobicity.

2. Experimental part

2.1. Materials

Aliphatic Polyisocyanate Vestanat T 1890 E (IPDI trimmer, 70 wt% in Butyl acetate) was obtained from Evonik Industries. Polydimethylsiloxane terminated in Polyethylene glycol (PDMS, Mn 1000 g mol^{-1}, 20 wt% non siloxane component) was supplied by Gelest Inc. Trifunctional polyol (Polycaprolactone, PCL, Mn 900 g mol^{-1}), Dibutyltin dilaurate (DBTDL), Butyl acetate (BA) and Acetylacetone (AA) were supplied by Sigma-Aldrich.

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http://dx.doi.org/10.1016/j.porgcoat.2014.01.006

2.2. Coating preparation

In order to prepare coating formulation PCL (81 g, 9 mmol) and PDMS (1 g, 1 mmol) solutions in Butyl acetate (33 wt% of solids) were introduced in a 100 mL Erlenmeyer at room temperature and mixed for 1 min under magnetic stirring. The equivalent ratio between both polyols was 90:10 PCL:PDMS. Then, 10.13 g (10.6 mmol) of IPDI trimmer, NCO:OH equivalent ratio 11:10 and different amounts of AA were added. Finally DBTDL (19 mg, 0.03 mmol) was added to start the reaction.

At a variety of reaction times, between 15 min and 24 h, the solutions (4 mL) were casted over aluminium pans of 43 mm diameter following two methods. In the first one the coating was kept under room conditions for 24 h. In the second one, the coating was kept at 50 °C for 24 h on a hot plate in a fume hood. In both cases, this was followed by oven curing at 80 °C for 45 min.

2.3. Instrumentation

Samples for FTIR studies were prepared on KBr pellets using Spin Coating (speed 1900 rpm for 15 s [Spin Coater SCC-200]). The spectra were registered on a Nicolet 6700 (Thermo Scientific) FTIR spectrometer. Scanning resolution was 4 cm^{-1} and 10 scans were taken. Attenuated Total Reflectance (ATR) experiments were carried out using an ATR objective (Thermo Electron Corp. Infinity Reflachromat) provided with a Germanium crystal mounted on a microscope (Nicolet Continuμm FT-IR microscope) attached to FTIR spectrometer. A MCT detector was used. The ATR measurements were recorded at a resolution of 8 cm^{-1} and 64 scans were taken.

The contact angle measurements were performed in an OCA20 Instrument at Static Mode, in a room with controlled temperature and humidity (25 °C and 55% of respectively). The measurements were made by pouring a drop of 10 μL of distilled water over the surface and replicating five times for each point.

Dynamic mechanical properties were analyzed in a Polymer Laboratories Mark III Dynamic Mechanical Analyzer DMTA in single cantilever mode. Scans of temperature from −150 to 150 °C at a frequency of 1 Hz, using a displacement of 0.050 mm and a heating rate of 4 °C min^{-1} were carried out in bending mode, employing samples with dimensions of 5 mm length, between 7 and 9 mm of width and between 15 and 19 mm of thickness.

Atomic Force Microscopy (AFM) studies were performed in a Multimode Nanoscope IV of Digital Instruments. Experiments were operated under Tapping mode in air at ambient conditions. Samples for AFM studies were prepared by casting over glass surface. Topographical and Phase images of 20 μm × 20 μm were obtained.

3. Results and discussion

The polymerization reaction resulting from a variation in AA percentage was monitored by infrared spectroscopy, and several spectra collected before the gel point of the reaction mixture was reached.

Fig. 1 shows the infrared spectrum of the sample obtained after 240 min of reaction. The absorbance of the infrared band at 2240 cm^{-1} assigned to the isocyanate stretching vibration, whose relative concentration decreased during the polymerization process, was used to calculate the conversion as described in a previous paper [18].

In order to calculate the conversion, the absorption of the isocyanate band was normalized with a band that did not change during the polymerization process. The C–H stretching band was selected for this purpose. The conversion of the reaction can be calculated according to Eq. (1)

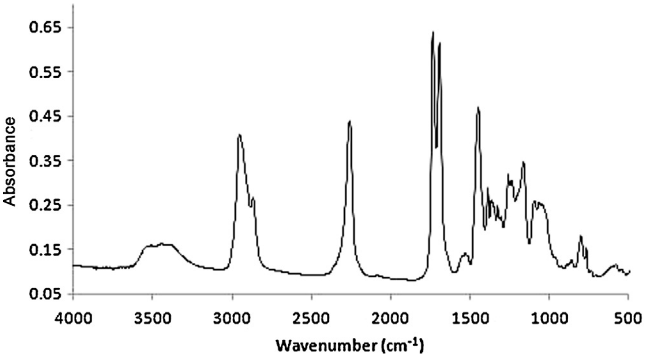

Fig. 1. Infrared spectrum of the sample obtained after 240 min of reaction.

$$\mathit{conversion} = 1 - \frac{\left(A_{2240}/A_{3000}\right)_t}{\left(A_{2240}/A_{3000}\right)_{t_0}}$$

where A_{2240} and A_{3000} are the areas of the absorptions at 2240 and 3000 cm^{-1} at initial time (t_0) and time (t), respectively.

The conversion for samples containing different Acetylacetone (AA) concentration is shown in Fig. 2 As can be observed, the conversion increased with the reaction time. However, regardless of Acetylacetone concentration, the maximum value was always lower than 0.6. Nevertheless, only in the case of the system containing 10% of Acetylacetone (AA) was it possible to monitor the reaction for longer before the product gelled. This result proves that the Acetylacetone reduces the reaction rate and therefore the gel point is reached at longer reaction times. This fact can be explained upon the basis of the complexation of Acetylacetone with the Stannous catalyst, which decreases the catalytic effect of DBTDL [20]. Similar conversions were obtained in literature [19].

As we are interested in preparing films at different reaction conversions, the subsequent experiments were performed using 10% of Acetylacetone because this percentage delays the reaction for one day offering the possibility of controlling the conversion of the reaction.

Thus, a series of films containing 10% of AA were prepared from samples taken at different reaction times and water contact angle measurements were performed. Fig. 3 shows the values of the contact angle for films obtained at room temperature and at 50 °C as function of the reaction time.

As can be observed, in both temperatures all films showed contact angles higher than 90°, which means that this surface was hydrophobic. No significant differences were observed between

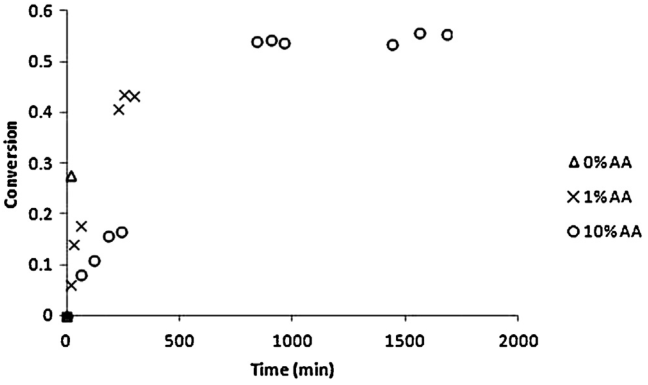

Fig. 2. Conversion vs. time for samples containing different Acetylacetone (AA) concentration.