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Urethane/Siloxane Copolymers with Hydrophobic Properties

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Summary: Different composition polyurethane-siloxane thermoset copolymers obtained from isophorone diisocyanate trimer, poly (caprolactone) triol and hydroxy terminated poly(dimethyl siloxane) were casted over aluminium surfaces. Dynamic mechanical thermal analysis (DMTA) measurements showed that the copolymers presented a phase separated morphology. The water contact angle increased with the siloxane percentage. In addition, for a fixed siloxane percentage, the water contact angle obtained in the air contact generated surface was higher than the one registered in the aluminium contact generated surface, suggesting that the low surface energy siloxane component migrated to the air contact generated surface.

Keywords: block copolymers; phase separation; polysiloxanes; polyurethane

Introduction

The generation of surfaces which present water static contact angles higher than 90°, called hydrophobic, has aroused great interest because properties such as self-cleaning and anti-biofouling are expected.[1,2] Low surface energy materials such as fluorinated polymers and polysiloxanes[3] are hydrophobic and therefore have high water contact angles. However, according to literature the contact angle cannot be increased beyond 120° by a purely chemical process and higher contact angles can only be obtained if the hydrophobic surface is roughened.[4]

In practice, hydrophobic surfaces can be prepared using different methods such as etching and lithography,[5,6] sol-gel processing,[7,8] electrospinning[9,10] and by nanostructuration of block copolymers.[11]

The present paper is devoted to the generation of hydrophobic surfaces by nanostructuration of urethane siloxane block copolymers. The particular surface properties of poly(urethane siloxane) copolymers are obtained through the segregation of incompatible and less polar soft siloxane domains towards the surface to minimize the interfacial tension with air.[12,13,14] In addition, the siloxane domains in the surface generate a roughness that can make the water contact angle increase. These types of surfaces are of special interest as anti-biofouling[15] coatings because they couple the toughness and good adhesion of polyurethanes with the hydrophobic surface properties of polysiloxanes.

Experimental Part

Materials

Aliphatic polyisocyanate Vestanat T 1890 E (IPDI trimer, 70 wt % in butyl acetate) was obtained from Evonik Industries. Polyethylene glycol terminated polydimethylsiloxane (PDMS, Mn = 1000 g mol^{-1}, 20 wt % non siloxane component) was obtained from Gelest Inc. Trifunctional polyol (polycaprolactone, PCL, Mn 900 = g mol^{-1}), dibutyltin dilaurate (DBTDL) and butyl acetate (BA) were supplied by Sigma-Aldrich.

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Coating Preparation

Several synthesis were made changing the relation of the polyols (PCL/PDMS) from 0 to 100 wt % of PCL and keeping constant the NCO:OH ratio 1.1:1.0.

PCL and PDMS solutions in butyl acetate (33 wt % of solids) were introduced in a 100 mL Erlenmeyer at room temperature and mixed for 1 minute under magnetic stirring. Then, the required amount of IPDI trimer and DBTDL (0.1% total solids) were added. Before gelification, the solutions were casted over aluminium pans of 43 mm diameter and kept under environmental conditions for 24 h followed by oven curing at 80 °C for 45 minutes.

Instrumentation

Samples for FTIR studies were prepared on KBr pellets using spin coating (speed 1900 r.p.m for 15 seconds). The spectra were registered on a Nicolet 6700 (Thermo Scientific) FTIR spectrometer. Scanning resolution was 4 cm^{-1} and 10 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 relative humidity). The measurements were made from both sides of the films. The average error of the results (10 measurements were made for each sample) of the upper face (air contact) was 3 ° and 5 ° for the face in contact with the aluminium pan.

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 7–9 mm of width and between 1.5–1.9 mm of thickness. Atomic Force Microscopy (AFM) studies were performed on a Nanoscope IV of Digital Instrument. Experiments were operated under tapping mode in air at ambient conditions.

Results and Discussion

The polymerization reaction of the different samples was monitored by infrared spectroscopy, collecting several spectra before reaching the gel point of the reaction mixture.

Figure 1 (left) shows the scale expanded infrared spectra of sample 70/30 PCL/PDMS. As can be observed, the absorbance of the band at 2200 cm^{-1}, assigned to the isocyanate stretching vibration decreases with the reaction time, which is indicative of

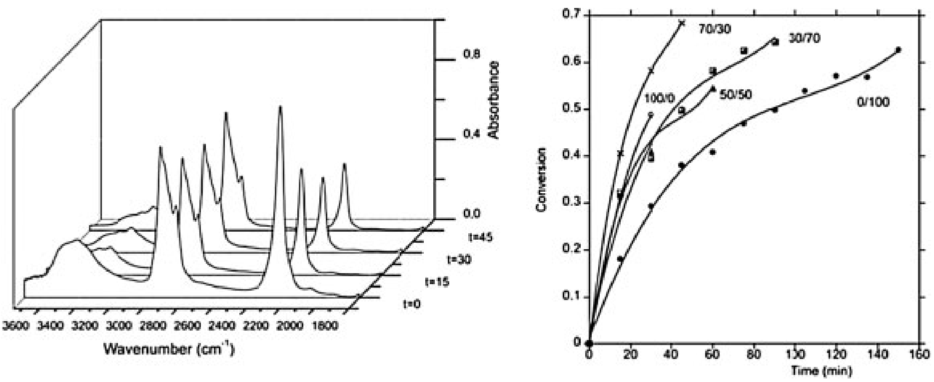

Figure 1.

Scale expanded infrared spectra of sample 70/30 PCL/PDMS vs. reaction time (left) and conversion vs. time (right) for different samples.

the polymerization process. The conversion of the reaction, shown in Figure 1 (right) can be calculated according to equation 1.

$$Conversión = 1 - \frac{(A_{2400}/A_{3000})_t}{(A_{2400}/A_{3000})_{t_o}} \qquad (1)$$

where A_{2240} and A_{3000} are the areas of the absorptions at 2240 and 3000 cm^{-1} at initial time (t0) and time (t) respectively.

As can be observed, as the content of the trifunctional polyol (PCL) in the samples increased less experimental points could be obtained because the gel point was reached at lower conversions. However, comparing the conversion obtained at the same reaction time for different systems, except for the sample containing only PCL (100/0) it seems that the conversion was lower as the PDMS content increased. This result can be explained upon the basis of a lower reactivity of PDMS polyol.

In order to study the microstructure of the samples DMTA measurements were carried out (Figure 2). For PCL/PDMS (0/100) sample, two peaks were observed (named I and III in Figure 2). The lower temperature mechanical loss process (I), located at −95 °C was assigned to the segmental motion of PDMS units.[16] In addition, the strength of this relaxation reduced with the PDMS content, supporting this assignment. The higher temperature segmental loss process at 48 °C (III) was associated to the mixing of the PDMS final Poly(ethylene glycol) end groups with the IPDI trimer. These segments are not compatible with the PDMS units and therefore in (0/100) PCL/PDMS sample two transitions were observed.

For PCL/PDMS (100/0) sample, one main transition (II) was observed at −1 °C, indicating the total compatibility between the PCL and IPDI segments. For the sample containing 30% of PDMS (70/30), the transition assigned to the PCL/IPDI segments (II) shifted towards higher temperatures and for the samples containing higher PDMS contents the transition was not detected, probably because it was overlapped with III. The shift of the II peak can be explained taking into account that there is a partial mixing between the PCL segments and the final Polyethylene glycol groups of PDMS units.

However, the position of the segmental motion of PDMS units (I) did not change with the introduction of PCL in the structure, indicating no discernible mixing between the siloxane units and PCL, and the formation of pure PDMS unit microphases.[17]

Figure 3 shows the water contact angle of the surfaces in contact with aluminium

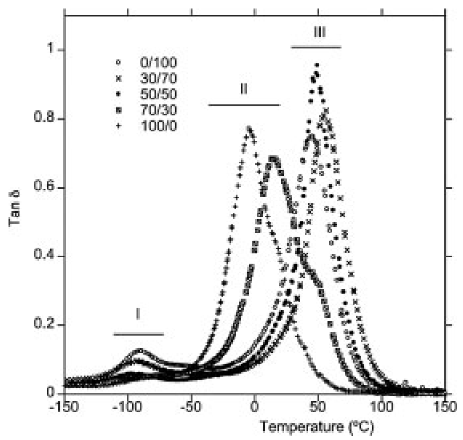

Figure 2.
Tan δ vs. temperature for different samples (PCL/PDMS/IPDI).

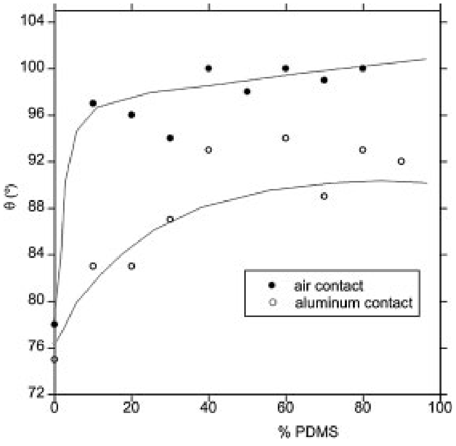

Figure 3.
Water contact angles vs. siloxane content for both faces of the different films.

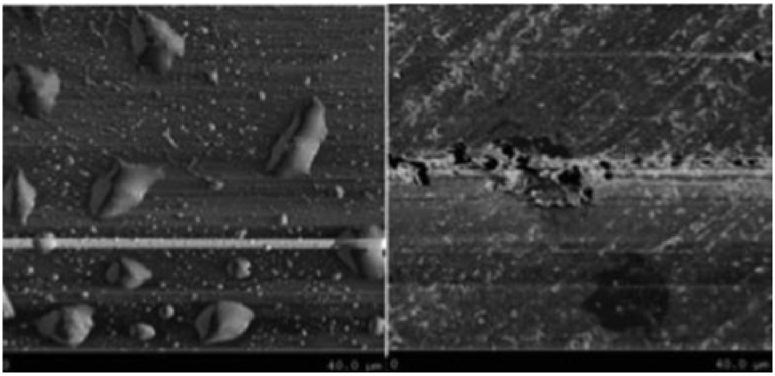

Figure 4.
AFM images (40 × 40 μm) of the 70/30 sample (PCL/PDMS). Air contact (left) aluminium contact (right).

and air for the different composition samples. As can be seen, no PDMS containing sample showed a contact angle near 77 °, characteristic of a hydrophilic surface. However, the incorporation of a 10% of PDMS to the polyol mixture caused an important increase of the water contact angle, especially on the face in contact with air, where the value increased to 96 °, making the surface hydrophobic. Additional increments of the PDMS content did not significantly affect the air contact surface hydrophobicity. Moreover, comparing the data of the contact angles obtained in both surfaces, it is clear that higher angles were obtained in the air contact generated surface what means that there was a higher concentration of less polar siloxane domains in this surface.

In order to compare the morphology of the air and aluminum contact surfaces AFM images were registered (Figure 4).

The AFM image showed a two-phase morphology on the surface obtained in contact with air while a homogeneous surface was observed on the aluminum generated surface. From these results it could be deduced that probably the dispersed phase observed on the surface in contact with air is mainly composed of siloxane domains. This morphology is probably the reason of the higher water contact angle shown by this surface.

Conclusion

The DMTA results of the synthesized urethane/siloxane copolymers showed that the systems were phase separated. The sample containing only the polycaprolactone polyol was hydrophilic but the addition of small quantities of siloxane polyol increased substantially the water contact angle, changing the surface to hydrophobic. The water contact angles obtained on the surfaces generated in contact with air were higher than the obtained on the aluminum contact surface, suggesting that the siloxane content was higher in the air generated surface and evidencing the self stratification of the coating. AFM images supported this hypothesis.

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