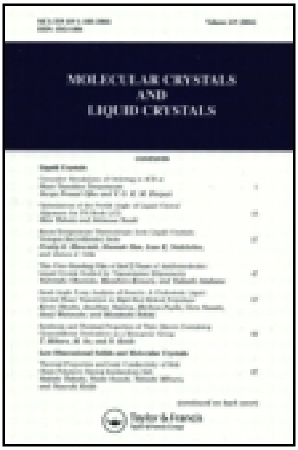

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3D Soft Microlithography in Segmented Anisotropic Urethane/Urea Elastomers

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In this work we describe a way to readily transfer 2D pictures from a mask to 3D structures on flexible free standing urethane/urea substrates. The resultant 3D picture can easily be erased/rewritten or permanently imprinted in the elastomer. The 3D microstructures are induced by UV radiation and can be revealed by application of a mechanical field or by immersing and drying the elastomer in an appropriate solvent. The film casting conditions induces an orientational order of the segregated soft and hard parts of the copolymer that is enhanced by UV radiation which is thought to make up the anisotropic structure that is responsible for the features observed. The copolymer is prepared by extending a poly(propylene oxide)-based triisocyanate terminated prepolymer (PU) with poly(butadienediol) (PBDO; 40% wt).

Polarising Optical Microscopy (POM), Small Angle Light Scattering (SALS) and Atomic Force Microscopy (AFM) were used to evidence the different nano and micromodulated structures that develop in urethane/urea elastomer. The

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measurements were performed before and after applying a mechanical field and after immersion and drying the sample on toluene.

Keywords: AFM; elastomers; SALS; soft lithography; urethane/urea

INTRODUCTION

The improvement of micro and nano patterned surfaces has been extensively explored for applications ranging from biosensor technology [1,2] to tissue engineering [3,4]. Soft lithography methods were developed and opened new routes to obtain high-quality patterns and structures that allow the realization of advanced organic flexible devices [5]. Recently, obtained 3D structures with urethane/urea membranes [6] made them potential materials for these applications.

Preparation of free standing films from urethane/urea copolymers, synthesised by extending a polypropylene oxide-based tri-isocyanate-terminated prepolymer with polybutadiene diol, was first reported in order to prepare pervaporation membranes with improved permeation performance that suit requirements of particular applications [7,8]. The elastomers were characterised with different spectroscopic techniques [9,10], dynamic mechanical thermal analysis and solvent swelling measurements [7]. An assessment of segregation effects was able through the estimation of different types of hydrogen bonds that can occur between the hard and the soft segments present in the copolymers [9]. Related to the casting conditions and UV irradiation a finite orientational order was associated to the development of instability-driven mechanico-optical effects observed in these polymers [11]. In fact a mechanical stress was found to induce two macroscopic states in the elastomer, a transparent (on) and a translucent (off) one. The intense scattering exhibited by the sample in the off state condition was due to a periodic pattern (bands) that developed with the wave vector parallel to the axis of the initial uniaxial applied stress. The process of band formation was completely reversible in cycles of increasing and decreasing strain ratios [12]. The studies performed after these observations focused on the nano and micromodulation of the bands observed in the off state [6,13]. It was found that periodic 3D patterns could be obtained in the polymer surface and microtuned by applying/removing the external mechanical field upon different directions [6]. More recently the UV irradiation and the relative content of the prepolymers involved in the synthesis of the copolymer were found to have a fundamental role on the development, stability and tuning of the structures observed for this kind of free standing elastomers [13]. The 3D anisotropic structures obtained open new applications perspectives for these anisotropic urethane/urea elastomers in soft lithography.

In this work a new microlithography procedure is presented based on the patterns that develop on the surface of a film obtained from a ratio of 40PBDO/60PU. We used Polarising Optical Microscopy (POM), Small Angle Light Scattering (SALS) and Atomic Force Microscopy (AFM) to evidence the different nano and micromodulated structures that develop in urethane/urea elastomer solid free standing thin film that was selective exposed to UV radiation and submitted to a mechanical field and/or extracted with toluene.

1. EXPERIMENTAL

The sample is a 120 μm thick free film prepared from polypropylene oxide based isocyanate terminated triol prepolymer and polybutadienediol, in the amount of 40% by weight of PBDO.

The PBDO is supplied by Aldrich and the PU is acquired from Portuguese petrochemical industry (CPB). The synthesis of these elastomeric films was performed according to the procedure described elsewhere [11] and modified by the following:

(1) The prepolymers were dissolved in toluene, under appropriate conditions with a solid content of 40%wt and the reaction, under nitrogen atmosphere, was allowed for at least 30 min; (2) The mixture was then casted and sheared by moving a casting knife at a controlled shear rate ($v_1 = 5$ mm/s). The final thickness of the film, after casting and cure, was measured using a Mitutoyo digital micrometer. The sample was cut in several parts and exposed to unpolarised ultraviolet radiation ($\lambda = 254$ nm) for two days through a printed silk paper (with the printed letter E) that was used as a mask (see Fig. 2). The extraction of the film after UV irradiation was done with toluene in a soxhlet apparatus, during 28 hours and dried in an oven at 70–80°C for at least 72 h.

The SALS data was obtained with a green ($\lambda = 543.5$ nm) helium neon laser equipped optical bench. The SALS patterns were recorded with the help of a CCD video camera.

AFM was used in order to perform quantitative measurements of topographical features of the solid film, before and after swelling in toluene. A Dimension 3100 SPM with a Nanoscope IIIa controller from Digital Instruments (DI) was used for the AFM measurements. These were performed in tapping mode™ under ambient conditions. A commercial tapping mode etched silicon probe from DI and a $90 \times 90\,\mu m^2$

scanner were used. The optical microphotographs were taken using an Olympus polarising microscope equipped with a photo camera.

2. RESULTS AND DISCUSSION

The idealized chemical structure of the elastomer studied in this work is represented in Figure 1. The network obtained has two kinds of nets that consist of urethane and urea links. The urethane chemical link results from the reaction of the three ended groups of polypropylene oxide-based isocyanate-terminated triol (PU) with polybutadiene diol (PBDO) hydroxyl groups. The urea net corresponds to the reaction of the excess PU isocyanate groups with moisture.

Figure 2 shows the schematic diagram of the microlithography method used to modify the surface of the free standing elastomer obtained after casting and curing for at least 72 h by atmospheric moisture (Sample I). Sample II was obtained from Sample I after being exposing to UV radiation. A photomask, made from silk cellulosic paper imprinted with a capital E black ink letter, was used to create

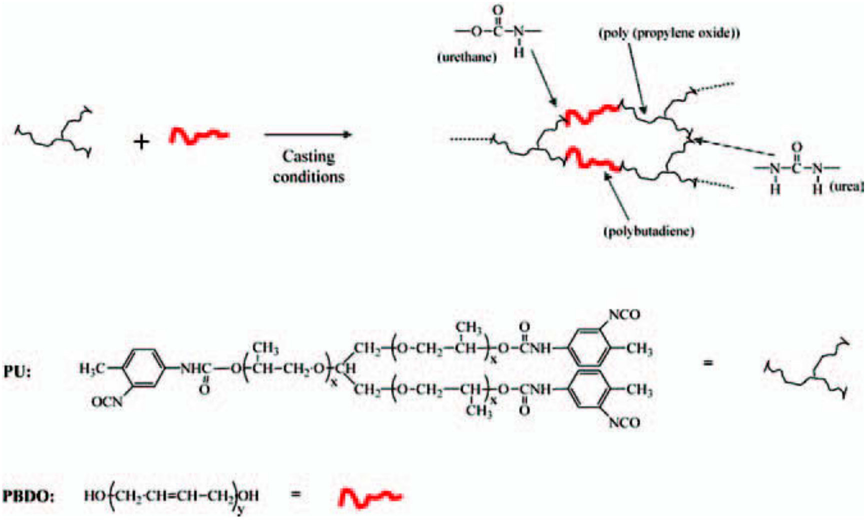

FIGURE 1 Idealized chemical structure of the initial film obtained from 60 wt% of polypropylene oxide-based isocyanate-terminated triol (PU) and 40 wt% of polybutadiene diol (PBDO). The urethane linkages result from the chemical reaction of PU isocyanate end groups with the PBDO hydroxyl groups, catalysed by dibutyltin dilauryate (DBTDL). The urea net corresponds to the reaction of the excess PU isocyanate groups with moisture.

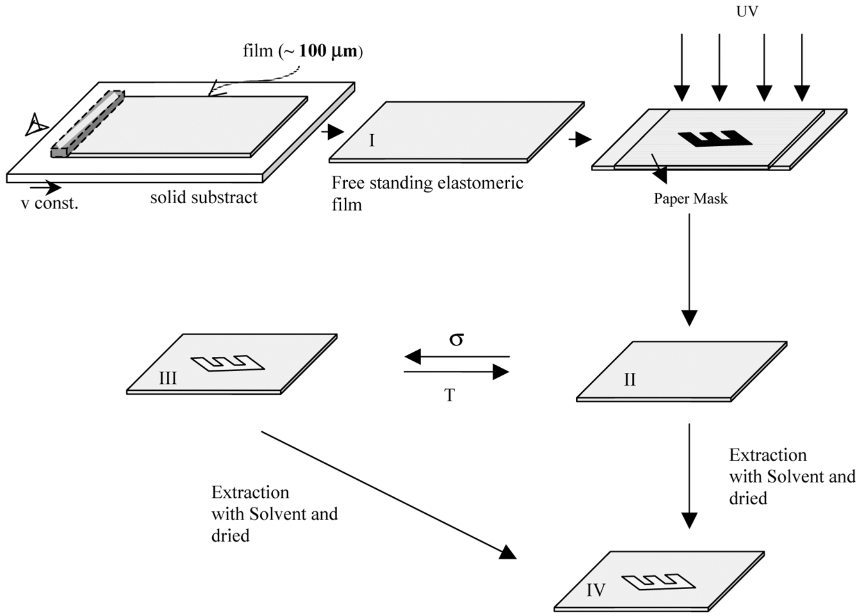

FIGURE 2 Schematic diagram of the microlithography surface modification method. Sample I corresponds to elastomeric samples that were removed from the solid substrate after 72 h of curing by atmospheric moisture. Sample II is the sample after being exposed to UV radiation ($\lambda = 254$ nm) for two days. Sample III is Sample II after applying and removing a mechanical shear stress (σ) perpendicular to the direction of the casting rate, at room temperature. Sample III can be converted in Sample II by increasing the temperature (T) from room temperature to 60°C. Sample IV is Sample II after performing the extraction in toluene and dried.

a picture in the surface. After UV radiation and removing the mask Sample II resembles to Sample I. UV radiation promotes new cross links in the network between the hard (urethane and urea links) and the soft (polybuthadiene and polypropylene) segregated parts of the copolymer [11] and a credible explanation for the results obtained can emerge from the fact that a mesophase can be present in these systems through the mechanism of molecular segregation which is well known to give rise to mesogenic behaviour in copolymers systems [12].

Two kinds of procedures should be made in order to see the three dimensional picture imprinted. Sample III represents the first procedure used and was obtained from Sample II after applying and removing a mechanical shear stress (σ) perpendicular to the direction of the casting rate, at room temperature. Sample III can be converted in Sample II by increasing the temperature (T) from room temperature to up to 60°C [14]. Another way to reveal the picture imprinted is represented by Sample IV. This sample can be obtained from Sample III or/and Sample II after performing the extraction in toluene and drying.

The 3D topography images of the surfaces are shown in Figure 3. Surfaces of Samples I and II (A) are characterised by a mean roughness

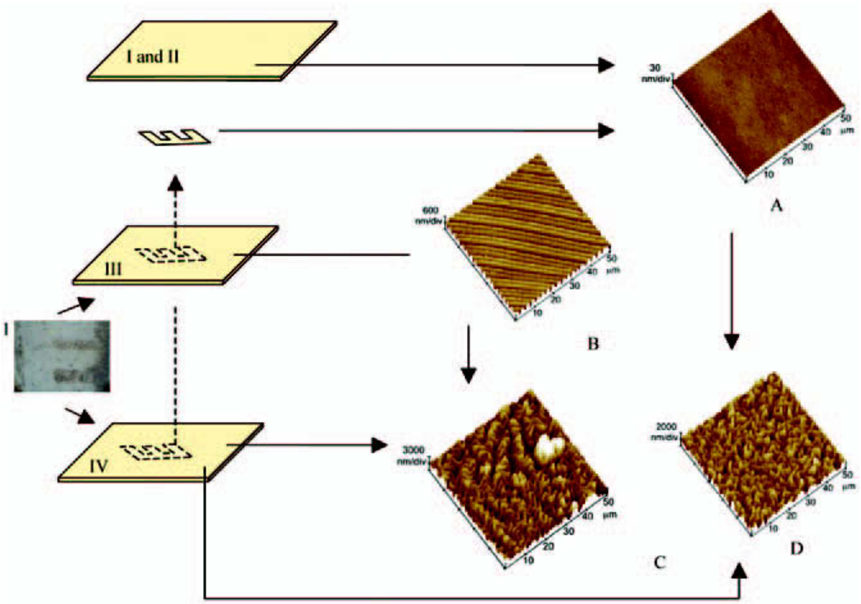

FIGURE 3 3D topography images ($50 \times 50\,\mu m^2$) of the surfaces of the 40%wt. PBDO initial film and after the microlithography process. Surfaces of Samples I and II (A) are characterised by a mean roughness value of Ra = 0.59 nm, this morphology remains in the picture imprinted in the mask, micro photograph 1 (E) (4x) taken between parallel polars with transmitted light. Surface of sample III (B), irradiated and with mechanical treatment, is characterised by a spatial periodicity along the direction of the mechanical shear stress applied. Within this periodicity peaks are grouped in pairs. Each pair is characterised by a spatial periodicity of $4.5 \pm 0.1\,\mu m$. The height difference between subsequent pairs is 42 ± 10 nm with a constant peak-to-valley height 290 ± 30 nm. Surface of Sample IV, irradiated and extracted in toluene and dried, presents two kinds of morphologies depending on being extracted from Sample II (D) or III (C). Sample II (D) surface is corrugated, with features µm-sized in all axes, resulting in a dramatic increase of the overall mean roughness value to Ra = 220 nm. The sample III (C) reveals a preferential direction alignment of the features.

value of Ra = 0.59 nm. This is the morphology that was always found in the picture that was printed in the paper mask (in our case a capital E letter). Surface of sample III (B) irradiated and subjected to mechanical treatment, is characterised by a spatial periodicity along the direction of the mechanical shear stress applied. Within this periodicity peaks

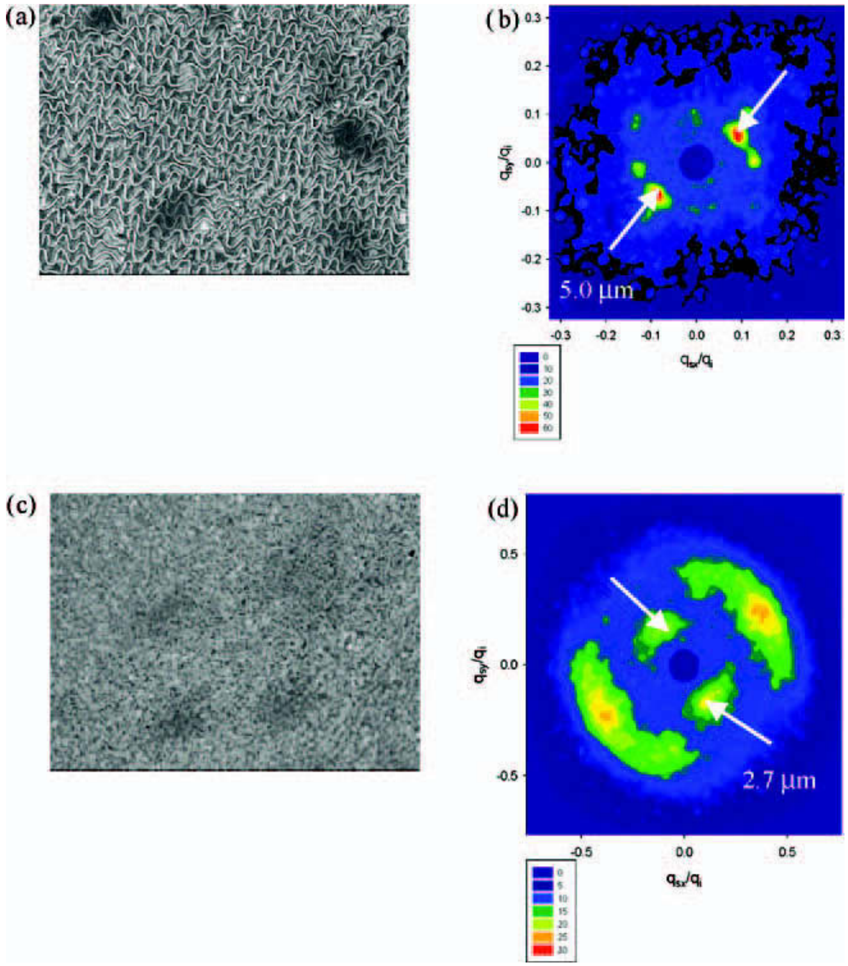

FIGURE 4 Polarized Optical Microscopy (POM) images a) and c) and Small Angle Light Scattering (SALS) patterns b) and d). Sample IV a) and b), after being subject to a mechanical shear stress, extraction with toluene and dried (AFM image Fig. 3 (C)). Sample IV c) and d), after extraction with toluene and dried (AFM image Fig. 3 (D)).

are grouped in pairs. Each pair is characterised by a spatial periodicity of 4.5 ± 0.1 µm. The height difference between subsequent pairs is 42 ± 10 nm with a constant peak-to-valley height 290 ± 30 nm. Surface of Sample IV, irradiated and extracted in toluene and dried, presents two kind of morphologies depending if it is extracted from Sample II (D) or III (C). Sample II (D) surface is corrugated, with features µm-sized in all axes, resulting in a dramatic increase of the overall mean roughness value to Ra = 220 nm. Sample III (C) reveals a preferential packing of the long corrugated line-like structures that is in average along the same direction of the bands observed for sample B that is the precursor state of sample C.

Figure 4 shows Polarized Optical Microscopy (POM) images and Small Angle Light Scattering (SALS) patterns of Sample IV, in the region outside the letter imprinted and with the same magnification as in AFM pictures. Figure 4 a) and b) corresponds to sample D of Figure 3 and Figure 4 c) and d) represents sample C of Figure 3. The POM images (Fig. 4 a) and c)) obtained with the microscope focused near the surface reveals a texture of long corrugated line-like structures. For sample IV obtained from Sample III a texture with packed sinusoidal curves can be observed. The direction of the imposed stress (see Fig. 3 State B) seems to be imprinted in the morphology of the dry sample surface after immersion in the solvent.

The spacing between the structures observed for Sample IV (D) shows periodicity of about 2.7 µm (in agreement with AFM results) and the SALS reveals two well defined periodicities: 1. one corresponding to that observed by POM and AFM and clearly indicated in Figure 4 d); 2. another one (about 1.3 µm) not observed by AFM or in POM image that could be attributed to bulk effects.

The spacing between the structures observed for Sample IV (C) is between 2.3–2.8 µm in the organized areas measured by AFM and shows a tendency to increase to 4 µm in the disordered regions. This value is in the same order of magnitude of the value found with SALS (5 µm). For both samples the discrepancies observed between AFM and SALS results can be ascribed to bulk effects.

4. CONCLUSIONS

In this work we describe a new way of 3D microlithography the surface of transparent flexible elastomeric urethane/urea films, depending on the exposure to UV radiation, through the application of a mechanical field and extraction with a selected solvent. The shape and size of the micro patterns can be modulated depending on the processing conditions. The imprinted picture shows a dynamic behaviour; it can be read, erased or remain for at least months in the surface of the elastomer. The message can also be imprinted and remain unread for months unless a mechanical field is applied or the sample is immersed in a selected solvent.

Further work is in progress in order to study the fundamental questions raised by this kind of soft material and to establish a systematic route to control the periodicities and amplitude of the relief structures in order to be used systematically in lithography and as scaffolds for tissue engineering.

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