Surface dynamics of polydimethylsiloxane rubber

Carlos Alberto Paula Leite
Institute of Physics of the University of Campinas, PO Box 6154, 13083-970
Campinas SP, Brazil

and Ricardo Ferreira Soares, Maria do Carmo Gonçalves and Fernando Galembeck*
Institute of Chemistry of the University of Campinas, PO Box 6154, 13083-970
Campinas SP, Brazil
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The surfaces of polydimethylsiloxane (PDMS) RTV rubber display macroscopic and microscopic (as detected in the atomic force microscope) morphological changes, when heated to 250–280°C, in the presence of air. The separation between adjoining PDMS film surfaces disappears in the same temperature range and the film pieces are effectively soldered, as verified by scanning electron microscopy and by mechanical testing. Mechanical failure of films joined by soldering is cohesive or interfacial, depending on the extent of film ageing, during film preparation. These results are interpreted by considering that PDMS network chains undergo scission, at the above temperatures. As a result, reactive chain segments can migrate at the rubber surface and across the rubber–rubber interface; their recombination forms a new network, from two adjacent networks.

(Keywords: polydimethylsiloxane; surface dynamics; surface morphology)

INTRODUCTION

Dynamic phenomena at polymer surfaces and interfaces have attracted considerable interest in recent years[1,2]. There is a practical motivation for this interest, which is due to problems found in the formation and stability of adhesive joints in which one (at least) of the adherends is a polymer[3,4]. Surface and interface dynamics should also play a role in polymer blend formation[5,6].

There has been considerable progress in the knowledge of the nature and dynamics of polymer surfaces, from both macroscopic and microscopic points of view. Thermodynamic[7], kinetic[8], morphological[9,10], microchemical[11] and spectroscopic[12,13] techniques and concepts have been used to establish useful models for polymer surfaces. Theories for polymer solutions (as applied to polymer–polymer systems) and for polymer chain dynamics (as applied to self-diffusion and interdiffusion) lead to a good understanding of the mechanisms of creation and elimination of surface defects in polymer solids in phenomena such as crack healing and polymer–polymer joining by soldering[14,15].

In this context, crosslinked polymers have a peculiar behaviour. Crosslinking limits chain extension and interdiffusion, for which reason vulcanized rubbers require specific bonding techniques, either by adhesion or by soldering. This may be seen as one particular aspect of the thermostability of these polymers and as one of the factors making their recycling difficult.

In a recent work, thermally activated self-adhesion of the silicone, polydimethylsiloxane (PDMS), to glass and to other hydroxylated surfaces was described[16]. This was ascribed to siloxane chain breaking[17,18], followed by chain-end reaction with silanol, Fe–OH and other groups from the hydroxylated surfaces. Chain-breaking reactions are well known in silicones, and may be followed by other reactions, giving off linear and cyclic oligomers, among other products[19]. Reactive surface groups may trap reactive chain ends, producing stable, covalent bonds across the interface between the silicone network and the adjacent inorganic surfaces. In a broader perspective, these reactions may be seen as just one case of oxane bond dissociation equilibria, which are also important in silica and silicates[20].

The present work describes morphological changes of silicone surfaces and of silicone–silicone interfaces due to exposure to temperatures above 200°C under air. These changes indicate that there is an important activity of mass transfer at these sites.

MATERIALS AND METHODS

The PDMS used throughout this work was prepared using Dow Corning RTV-732 silicone resin. This was dissolved in toluene (10 g resin in 13 ml toluene), homogenized by mild shaking for 15 min and centrifuged at 1500 rev min^{-1} for 3 min in the swinging-bucket rotor of a Sorvall RC-3B centrifuge. Film casting was done by spreading the resin solution over a polypropylene slab ($15 \times 25\ \mathrm{cm}^2$), using a technique commonly used in

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* To whom correspondence should be addressed

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the making of semipermeable membranes[21]. Solvent evaporation and rubber formation took place within a closed chamber made of acrylic sheet and kept at constant temperature (30, 40 or 50 ± 3°C). Films were collected 24 h after solution spreading; their thicknesses were 150 or 300 μm, depending on the spacers used during spreading. Films were aged in the laboratory atmosphere for 2 to 8 days.

Temperature effect on film surface morphology

The films thus prepared were heated for 2 h at the following temperatures, 200, 240, 250 and 280°C, within a furnace whose temperature was maintained within ± 1°C. Temperature chamber decrease was less than 5°C when the chamber was opened, and the set temperature was reached again in less than 5 min, as monitored using a Fluka 2190A meter. Within the furnace, the film pieces were laid over polytetrafluoroethylene (PTFE) film 1 mm thick.

Film surfaces were examined visually, as well as in a JEOL T-300 scanning electron microscope (SEM) and in a Topometrix TMX 2000 atomic force microscope (AFM). Samples for SEM were previously coated with gold, by sputtering. Fracture surfaces were obtained by bending film pieces, under liquid N_2; these were gold-coated and examined in the SEM. Samples for AFM were film pieces (ca. 1 × 1 cm^2), glued to aluminium slabs, which were placed in the instrument sample holder.

Transmission electron microscopy (TEM) of silicone rubber was made on thin sections (ca. 80 nm) cut in a Leica cryoultramicrotome, mounted in a 400 mesh copper grid and observed in a Zeiss CEM-902 instrument.

Silicone–silicone joint formation

Specimens for silicone–silicone joint formation were tie-shaped film pieces (40 × 5 mm^2 in the narrow section), cut across the transverse mirror plane with a doctor blade. The two resulting pieces were partially superimposed, making a 25 mm^2 overlapping area. These joints were laid on a PTFE sheet and heated at 250°C for 2 h, in the same oven as described above. External pressure during joint formation was just atmospheric.

These samples were tested in an EMIC 500 testing machine, at a jaw displacement rate of 50 mm s^{-1}. Force vs. elongation curves were acquired and recorded for each sample in a PC-compatible microcomputer. Measurements taken on five independent samples were averaged, to give each curve presented in the 'Results' section.

RESULTS

The surfaces of silicone film formed in contact with air in the 30–50°C temperature range are visually smooth, but at higher magnification they show an irregular array of elevations and depressions, as seen in *Figure 1*. Their formation is probably associated with two factors: (i) Clustering of silica particles may occur during film formation. A TEM picture of silica particles within silicone rubber is shown in *Figure 2*. These particles make clusters in the same size range as the clear areas in *Figure 1*. Silica is a reinforcing and crosslinking agent added to RTV resins. (ii) Convective (Bénard) liquid circulation, making a cell pattern, may occur during solvent evaporation. The surface formed in contact with the polypropylene film presents small, circular depressions.

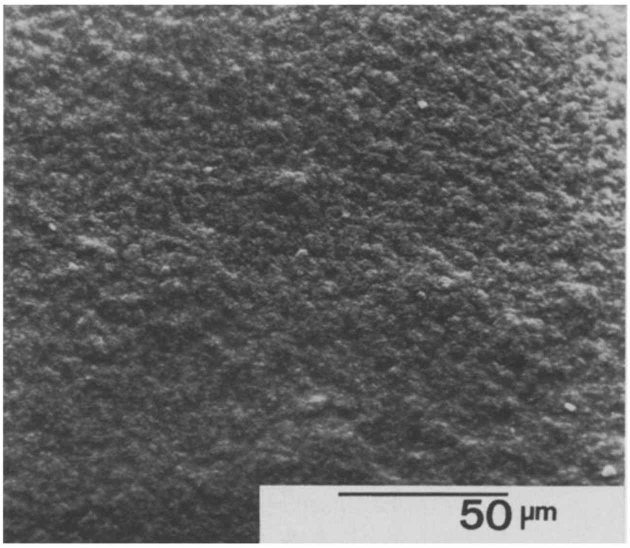

Figure 1 Scanning electron micrograph of a PDMS film surface, as prepared. The features seen in this sample are unaltered by heating up to 280°C

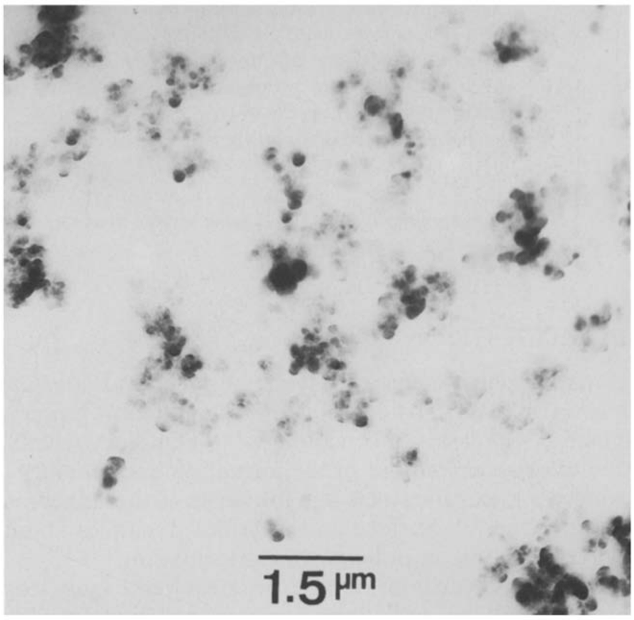

Figure 2 Transmission electron micrograph of a cut from PDMS. The particles seen in the picture are reinforcing silica particles

Upon heating, silicone film surfaces in contact with PTFE acquired a register of the marks found on these (PTFE thick films are made by cutting profiles with rotating knives). However, SEM pictures of the surfaces heated in contact with air did not present any visible changes, and all are as shown in *Figure 1*. In this scale, there are no important morphological changes in the silicone surface.

However, film examination at higher magnification, in the AFM, revealed a marked difference between the pristine film surface and the surface of the film heated at 280°C. The patterns (see *Figure 3*) on the first are linear rather than rounded-off, as in the latter. Maximum height differences are also different: greater than 320 nm in the

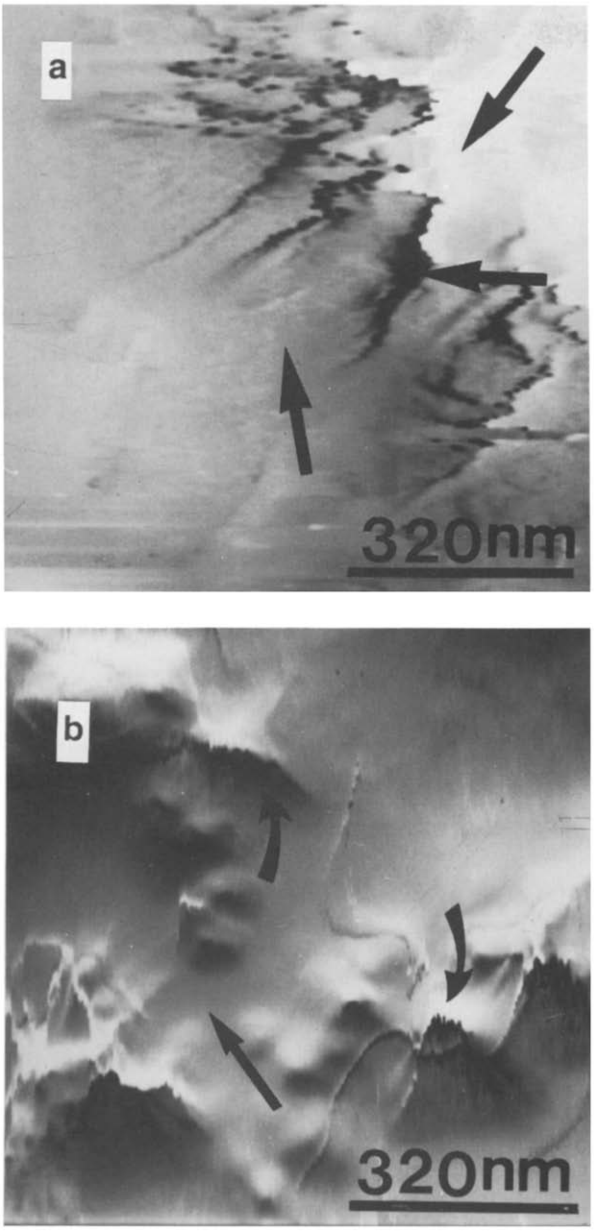

Figure 3 Atomic force micrographs from the surface of PDMS films. (a) As prepared; relative heights of the points indicated by arrows: black = 0, grey = 90 nm, white = 324 nm. (b) After heating to 280°C for 2 h; relative heights: black = 0, grey = 90 nm, white = 253 nm

unheated film, as compared to ca. 250 nm in the heated film. Together, these observations show that mass transfer occurs at silicone surfaces, at the heating temperatures used in this work, at least on a scale sufficient to cause surface morphological changes. The rounding-off of morphological features confirms that the surface acquired an increased fluidity and surface-tension-driven mass transfer could then occur, the net result of which is a decrease in film roughness.

AFM images from polymer surfaces have to be examined with great care, to avoid misinterpretations associated with artifacts induced by the probe. In the present case, probe-induced image artifact damage was easily identified, either as streaks parallel to the probe motion or as small apparent indentations, caused by mechanical vibrations. Surface shading simulation can be done using the instrument software, at various angles. Depending on the chosen angle, probe-induced artifacts are enhanced or weakened. On the other hand, the morphological features described in the previous paragraph were consistently observed in various surface regions of each sample, as well as in repeated scans of the same area. We did not observe irreversible surface damage as described by Meyers and colleagues in polystyrene surfaces[9], probably because ours is a crosslinked polymer, in which morphological changes cannot be induced as easily as in a linear polymer.

Soldering of PDMS rubber surfaces

Silicone–silicone joints formed by the superposition of film pieces, followed by heating at 250°C for 2 h, may be handled, stretched and bent, much as an integral film piece of the same dimensions. Fracture surfaces formed by bending cooled (under liquid N_2) joints do not reveal any indication of the original silicone–silicone interface between the overlapping films, except in a few spots where the two silicone surfaces could not touch each other. This was due to the presence of extraneous particles intercalated between them, as shown in *Figure 4*. For the sake of comparison, a micrograph of another silicone film fracture surface is also shown in *Figure 4*.

Mechanical stability of soldered PDMS joints

Tie-shaped pieces of integral as well as of soldered silicone films were subjected to mechanical testing, under tension. The force–elongation average curves thus obtained are given in *Figure 5* and some measurements taken from the raw data (maximum tension, energy of rupture and maximum elongation) are presented in *Table 1*. This shows that the soldered test pieces have both an elongation and a force at rupture that are ca. 50% of the corresponding data for the integral pieces (except in the case of the film aged for 8 days, before preparing the joint). This means that the cut-and-soldered samples have a significant resistance to tension, as compared to the integral pieces (or else, to test pieces prepared identically but omitting the cutting and heating steps). A small increase in the elastic modulus of the cut-and-soldered samples may be noticed, as compared to the integral test pieces. (Note that, since the curves are the averages of 3–5 individual recordings, the plotted maxima are the points at which the weakest sample in a set failed).

In the bonded test pieces (made with silicone films aged for 2–6 days), the failure site was always a film region in the vicinity of the bonded area. Failure was thus cohesive, not interfacial. This means that cutting and rejoining introduced some weakness in the rubber, but in areas *close* to the joined areas, not *within* them. As of now, the

Table 1 Maximum tension, maximum elongation and energy of rupture for whole silicone films and for cut-and-rejoined films

Sample[a]	Maximum tension ($N mm^{-2}$)	Maximum elongation (mm)	Energy of rupture/area ($N mm^{-1}$)	Thickness (mm)
a	1.8 ± 0.20	319 ± 4	282 ± 25	0.35 ± 0.02
b	1.7 ± 0.30	306 ± 11	266 ± 40	0.33 ± 0.03
c	0.86 ± 0.08	141 ± 20	66 ± 12	0.37 ± 0.02
d	0.86 ± 0.07	140 ± 6	66 ± 5	0.36 ± 0.02
e	0.85 ± 0.04	113 ± 14	94 ± 13	0.33 ± 0.01

[a] As described in the caption of *Figure 5*

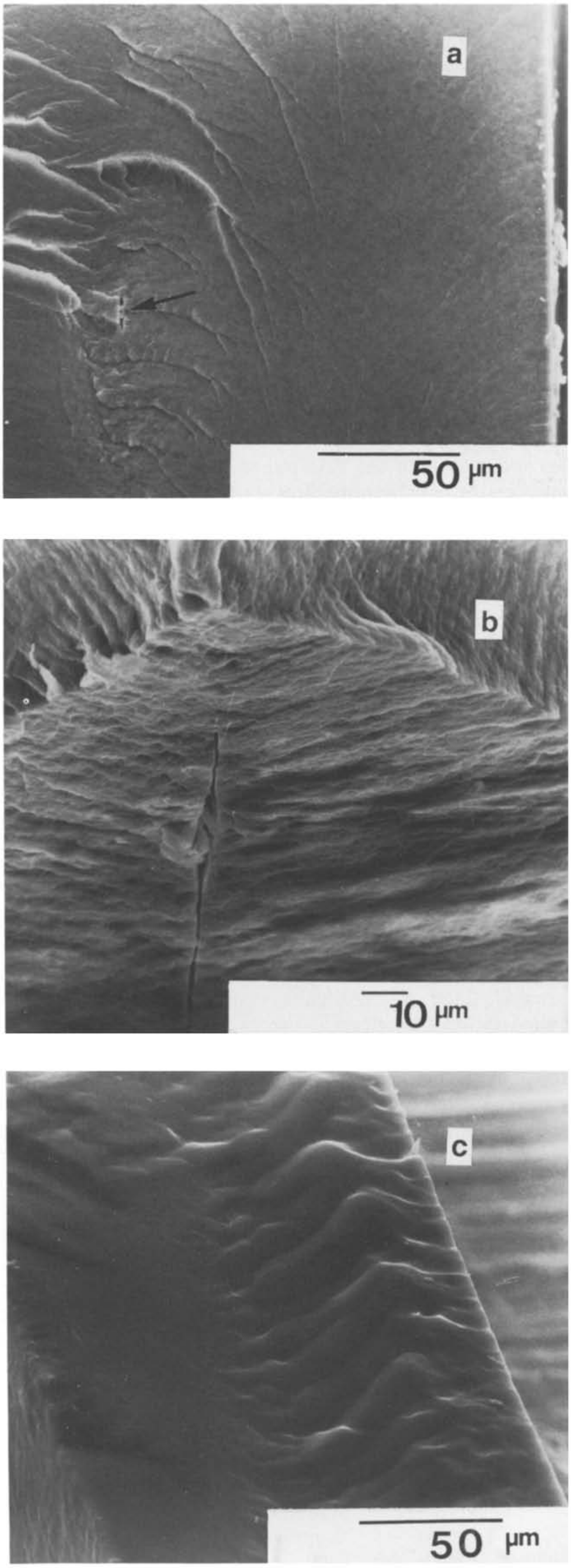

Figure 4 (a) SEM picture of a fracture surface; the fracture was made parallel to the former interface of two soldered PDMS films. The disappearance of the interface is complete, except for the small defect indicated with an arrow. (b) An enlarged view of another soldering defect. An extraneous particle is seen in its interior, which is the probable cause of this defect. (c) View of a fracture surface of an as-prepared PDMS film.

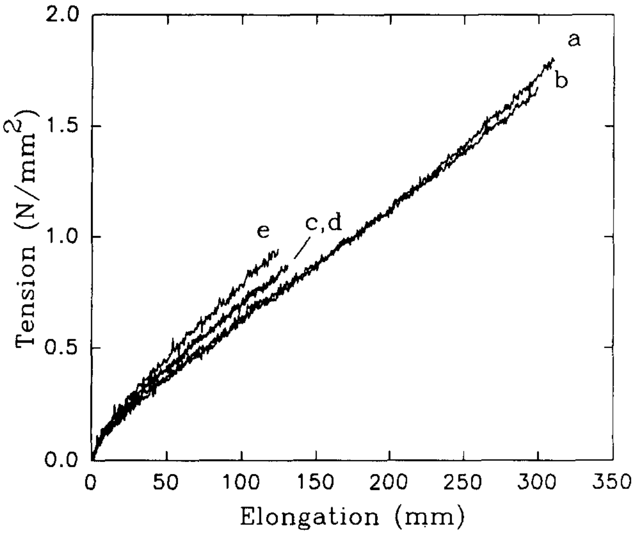

Figure 5 Tension vs. elongation of PDMS films: (a) as prepared; (b) as (a) but heated at 250°C for 2 h; (c, d, e) films cut and rejoined by heating at 250°C for 2 h. Curing times of latter films, after casting: (c) 2 days; (d) 4 days; (e) 8 days

reasons for this peculiar behaviour are not understood, but we recall that mass transfer and interface elimination at the bonding site may introduce some stress in neighbouring areas. Test joints made with films aged for times longer than 8 days had a different behaviour: they showed interfacial failure, instead of the cohesive failure observed in the other cases. However, their tension vs. elongation average curves are otherwise similar to those of the other, less-aged samples.

DISCUSSION

Although this study is limited, silicone rubber surfaces display some characteristics more akin to those of a thermoplastic than those expected for a vulcanized rubber. First, there are both macroscopic and microscopic morphological changes at the silicone surface, taking place when the rubber is heated. Secondly, surface wound healing is possible and even the extreme case of cutting and rejoining by soldering can be done successfully. These phenomena can be understood using the following mechanistic arguments:

(i) In the 250–280°C temperature range, chain-scission reactions take place at a significant rate, as the polysiloxane chains approach a state of equilibrium of the degree of polymerization.

(ii) Reactive chain ends as well as oligomers are formed; both types of produces can diffuse away from their original sites. We recall that chain-end motion in polysiloxanes should be facilitated by 'crankshaft' motions[22] of the backbone.

(iii) In the silicone–air interface, the lightest oligomers evaporate and reactive chain ends recombine, modifying the original network. The weight loss by the PDMS used in this work in thermogravimetric experiments (not shown) is ca. 2%, in this temperature range.

(iv) In the silicone–silicone interface, migrating chain ends and oligomers recombine, extending the two pre-existing three-dimensional networks to previously unoccupied interfacial volume and connecting them. A similar behaviour is found in interfacial crosslinking of immiscible polymer blends[23].

The above-described mechanism has some points in common with the model for the dynamics of reversible networks, developed by Leibler *et al.*[24] and supported by experimental data of Stadler and de Lucca Freitas[25]. However, in the present case there are two important complicating factors: First, the 'stickers' (following the nomenclature of Leibler *et al.*) are terminal groups of the fragmented main chain. Secondly, there is concurrent oligomer formation and migration. However, the success achieved with the current models allows an optimistic forecast regarding a future full treatment of the dynamics of polysiloxane networks at higher temperatures, including their surfaces.

This is the meaning of 'soldering', in the present case: it is the junction of two crosslinked networks, by the opening of some of its links, the formation of translationally mobile link ends and oligo products, their migration to the interface and random recombination, so that the separation between the two original networks is wiped out. We believe that other types of events, such as extensive interdiffusion or the formation of a new phase, do not play an important role in the present case.

At this point, there are many questions arising. Perhaps the most intriguing are related to the possibility of extending the observations made on silicones to carbon-chain vulcanized rubbers. C–C thermal bond dissociation is well known in substituted ethanes with bulky substituents, but in other cases, although the fragment ends recombine reversibly, they do also disproportionate[26–28]. Perhaps, this difficulty may be overcome by adding hydrocarbon isomerization catalysts to the rubber. These could trigger chain-breaking and chain-reforming reactions, thus satisfying the fundamental requisite of the mechanism proposed in items (i) to (iv) above. This mechanism could be useful in countering crack growth in elastomers[29] and, generally speaking, in elastomer recycling.

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