In situ polymerization of functional monomers in rubbers: 1. Modification of silicone rubbers by a poly(ester thioether amine) based on piperazine

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Modified silicone rubber intended mainly for biomedical applications was obtained by *in situ* polymerization. The process involved swelling of the rubber with a mixture of solvent and monomers, polymerization, and finally evaporating the solvent under reduced pressure. The polymerization system selected was the stepwise hydrogen-transfer polyaddition of 1,4-piperazinediyl diethanethiol to ethylene glycol dimethacrylate, leading to a poly(ester thioether amine). The modified silicone was physically and mechanically characterized by several analytical techniques (Fourier-transform infra-red spectroscopy, differential scanning calorimetry, dynamic mechanical thermal analysis, dynamic contact angle and scanning electron microscopy), and the results obtained were compared with those relative to both the linear guest polymer and the unmodified rubber.

(Keywords: modified silicone rubber; poly(ester thioether amine); hydrogen-transfer polyaddition)

INTRODUCTION

In situ polymerization basically consists of inducing the formation of a new polymer – the guest polymer – inside a preformed polymeric network – the host polymer. It is usually performed in three steps: first, the host polymer is swollen by a monomer, or a mixture of monomers, either undiluted or diluted with a suitable solvent; secondly, the formation of the guest polymer is caused to occur; and finally, the produce is deswollen, cleaned from residual monomers and dried.

The above technique, if compared with other techniques proposed for modifying preformed polymeric materials, e.g. surface grafting, introduces larger proportions of the modifying guest polymer. Moreover, *in situ* polymerization operates in bulk, and therefore it may also influence properties related to the bulk structure of materials.

By selecting the proper monomeric systems, an immense variety of guest polymers endowed with the desired chemical and physico-chemical properties can be introduced, in principle, taking relatively little notice of their physical properties, since it is the host polymer that is responsible for most of the mechanical performance. Moreover, *in situ* polymerization can be performed in already fabricated articles, with little alteration in size and shape.

When dealing with multifunctional guest polymers, *in situ* hydrogen-transfer stepwise polyaddition of amines or functional bisthiols to compounds bearing activated double bonds appears to be the method of choice, owing to the exceptional versatility of this synthetic method, which easily leads to new purpose-tailored polymeric structures (see *Scheme 1*)[1].

The aim of this paper is to relate our results on silicone rubber modification by *in situ* stepwise polyaddition of 1,4-piperazinediyl diethanethiol to ethylene glycol dimethacrylate, as a first example of a wider research project involving different rubbers and different guest polymers.

Silicone rubbers have many important applications[2,3], which would benefit by the introduction into their molecular networks of purpose-tailored chemical structures, without substantially altering their original physical properties. For instance, the introduction by *in situ* polymerization of heavy-metal-ion-complexing polymers belonging to the above-mentioned families[4,5] could lead after complexation to enhanced selectivity towards oxygen in gas permeation, in the same way as the impregnation with low-molecular-weight complexing agents does[6].

The new material obtained, or similar materials, may have a potential also for the preparation of heparinizable articles. This point is based on a wealth of previous results[7-9] on the heparin-complexing properties of

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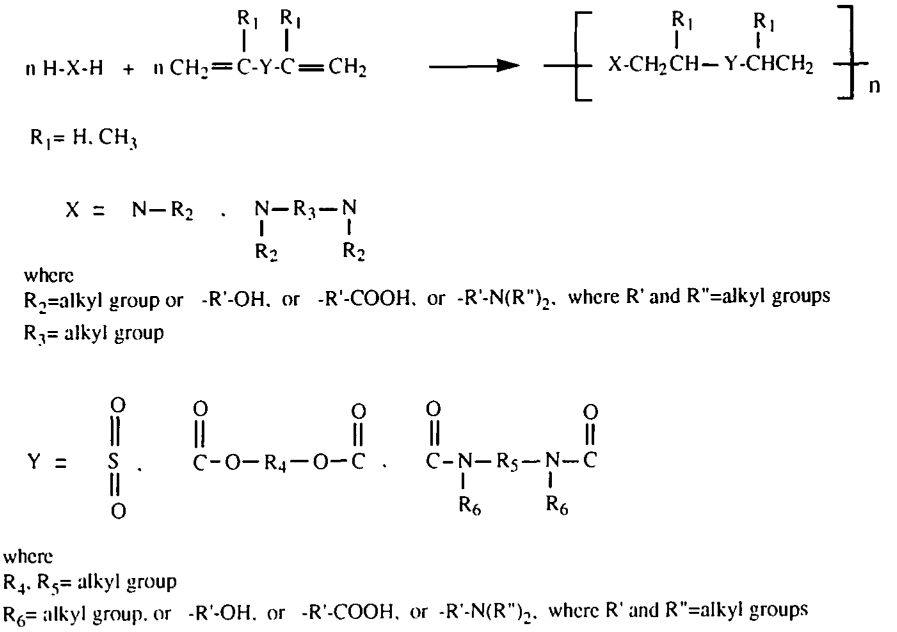


Scheme 1

poly(amido-amine)s, whose general structure is very similar to that of poly(ester thioether amine)s as far as the amine portion, responsible for heparin complexation[9], is concerned.

Moreover, we have recently found that poly(ester thioether amine)s can be easily quaternized when dissolved in organic solvents. Their quaternization products have good antimicrobial activity even against usually resistant species such as *Pseudomonas aeruginosa*[10,11]. We have already gathered experimental evidence that quaternization can also be performed *in situ* on the guest polymer in the modified silicone rubbers described in this article. It is well known that the main drawback of some silicone rubber medical articles, such as permanent catheters, is their proneness to microbial colonization[12]. A substantial improvement in this respect can be reasonably achieved starting from the modification method described in this paper.

EXPERIMENTAL

Instruments

Infra-red spectra were run on a Jasco 5300 *FT*-i.r. spectrophotometer. Viscometric measurements were performed in chloroform, at 30°C, using an Ubbelohde viscometer. Elemental analyses were performed by Redox Co. (Cologno Monzese). ^{1}H n.m.r. were run on a 60 MHz Varian 360A spectrometer, using CDCl$_3$ as solvent and tetramethylsilane (TMS) as internal standard. Differential scanning calorimetry was performed using a Mettler DSC30 thermal analyser, at a scanning rate of 10°C min^{-1}. SEM analyses were performed using a Cambridge Stereoscan 200 scanning electron microscope, equipped with a Link AN-10000 HDS microanalysis probe. The effect of the addition of polymer on the silicone rubber wettability was determined through measurements of the advancing and receding contact angles of modified and unmodified silicone rubber samples, in distilled water, using a Wilhelmy microbalance. Mechanical and dynamic mechanical (d.m.t.a.) properties of samples were verified by using an Instron 4502 dynamometer and a Polymer Laboratories DMTA Mk II dynamic mechanical thermal analyser.

Materials

Silopren HV silicone layers (1 mm thick) were purchased from Bayer and extracted continuously with hot toluene for 2 days, to eliminate low-molecular-weight impurities. Elemental analysis calculated for (SiO(CH$_3$)$_2$)$_n$: C 32.43%, H 8.1%, N 0.00%. Found: C 23.77%, H 6.01%, N <0%. I.r. (cm^{-1}): 2960 (ν_{Si-H}), 1410, 1260 (ν_{Si-C}), 1010 (ν_{Si-O}), 865, 785 (δ_{Si-C}).

Ethylene glycol dimethacrylate, piperazine and ethylene sulfide were purchased from Fluka and used without any purification.

2,2'-Piperazinediyl ethanedithiol (I). Anhydrous piperazine (17.2 g, 0.1 mol) was dissolved in toluene (70 ml). Ethylene sulfide (24 ml, 0.4 mol) was added under inert atmosphere. The reaction mixture was maintained at 80°C, with stirring, for 24 h, and then it was concentrated under reduced pressure. The white solid so obtained was purified by fractional distillation. Yield = 34.02 g (85%), b.p. = 115°C/0.7 mmHg, m.p. = 45.5°C. The pure product was stored under inert atmosphere. Elemental analysis calculated: C 46.56%, H 8.79%, N 13.57%, S 31.07%. Found: C 46.62%, H 8.70%, N 13.04%, S 30.70%. I.r. (cm^{-1}): 2940–2760 (ν_{C-H}), 2550 (ν_{S-H}). ^{1}H n.m.r. (δ, ppm): 2.65 (m, 8H, -S(CH$_2$)$_2$N-), 2.55 (s, 8H, -N(CH$_2$)$_2$N-), 1.15 (s, 2H, -SH).

Polymer (III). First, I (20.64 g, 0.1 mol) was dissolved in toluene (100 ml). Ethylene glycol dimethacrylate (**II**) (19.82 g, 0.1 mol) and t-butyl alcohol (19.82 g) were added to the polymerizing mixture under inert atmosphere. The solution was then maintained at 45°C, with stirring, for 7 days. The crude polymer was purified by precipitation in diethyl ether (500 ml). Yield = 36.41 g (90%). Elemental analysis calculated: C 53.44%, H 7.97%, N 6.92%, S 15.85%. Found: C 52.68%, H 8.07%, N 7.25%, S 16.25%.

I.r. (cm^{-1}): 2940 (ν_{C-H}), 2910 (ν_{C-H}), 1735 ($\nu_{C=O}$), 1459 (δ_{C-H}), 1158 (ν_{C-N}). ^{1}H n.m.r. (δ, ppm): 1.1–1.4 (m, 6H, CH_3), 4.35 (s, 4H, OCH_2CH_2), 2.2–2.9 (m, 22H, all other H).

Silicone–III adduct. First, a 1 mm thick silicone layer (4 × 4 cm^2, 4.607 g), **I** (1.989 g, 9.64 mmol), and **II** (1.912 g, 1.94 mmol) were mixed together in toluene (30 ml). The reaction mixture was maintained under inert atmosphere at 0°C for 2 h, to allow the silicone layer to swell to the maximum extent. The amount of solvent was selected purposely to cover the layer exactly, to avoid excess polymerizing solution. Then it was warmed up to 45°C and maintained at this temperature for 7 days. The silicone layer was then removed from the polymerizing mixture and washed twice with fresh toluene (20 ml). Then it was dried to constant weight under reduced pressure. Yield = 5.5299 g, weight increment = 6.95%. Elemental analysis: C 24.60%, H 6.05%, N 0.51%, S 0.70%. Calculated for 7.4% yield: N 0.51%, S 1.17%. I.r. (cm^{-1}): 2960–2940 (ν_{Si-H}), 2910 (ν_{C-H}), 1735 ($\nu_{C=O}$), 1410, 1260 (ν_{Si-C}), 1158 (ν_{C-N}), 1010 (ν_{Si-O}), 865, 785 (δ_{Si-C}).

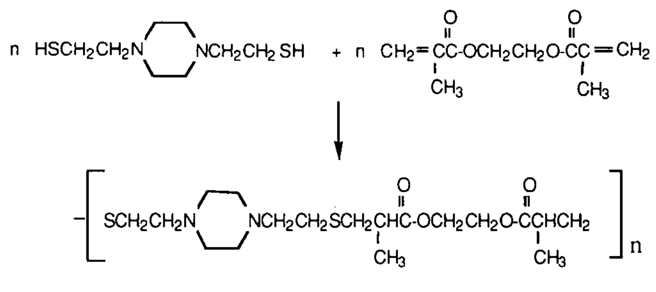
RESULTS AND DISCUSSION

Synthesis

Selection of the system. As pointed out in the 'Introduction', the hydrogen-transfer polyaddition reaction of 2,2′-alkylenediiminodiethanethiols to bisacrylic esters or bismethacrylic esters has several features making it convenient for the purpose of our investigation[13,14].

In particular, it is very versatile, leading to a large variety of polymeric structures all characterized by the presence of quaternizable tertiary amine groups in the main chain[14]. Moreover, it takes place in a number of solvents, including chlorinated and hydrocarbon solvents with high affinity for most rubbers including silicone rubber. The rate of reaction in aprotic solvents, and below room temperature, is usually very slow, but can be increased both by heating and by adding proton-donating substances such as, for instance, t-butyl alcohol[14]. Therefore, it is possible to swell the selected rubber in the cold with the monomeric mixture dissolved in a suitable solvent, before the formation of large macromolecules, which would probably not be absorbed. Polymer formation is then induced by changing the reaction conditions.

The system selected for the present study involves 1,4-piperazinediyl diethanethiol and ethylene glycol dimethacrylate (*Scheme 2*), which on the basis of our previous studies[13,14] was considered representative of the whole polymerization method.



Scheme 2

As a rubber we selected a typical silicone rubber, Silopren HV, density 1.0–1.2 g cm^{-3}, thermal stability up to temperatures higher than 350°C, and containing vinyl groups, in the form of 1 mm thick sheets. Its swelling properties in different solvent systems and under different conditions were investigated first. The results are reported in *Table 1*. It may be observed that both toluene and chloroform provide convenient solvent systems. Toluene was preferred because of its superior chemical stability, and lower volatility.

Polymerization process. The *in situ* polymerization process was performed in two steps. First, the silicone rubber was swollen in a solution of an equimolecular mixture of monomers in toluene containing t-butyl alcohol. The sum of the monomers amounted to 15% (w/v) of the final mixture.

Secondly, the temperature was raised to 45°C, and the reaction mixture remained at this temperature for 7 days. All operations were run under inert atmosphere in order to avoid oxidation of the thiol groups. The final product was isolated by separation from the surrounding liquor, washing by repeatedly dipping into fresh toluene, taking care to have contact times of the order of 1–2 s, and drying to constant weight at 40°C and 0.1 mmHg.

The modified silicone rubber has a milky appearance, in contrast to the unmodified sample, which is perfectly clear. Its poly(ester thioether amine) guest polymer content was determined by elemental analysis and weight-increase determination. All tests indicated a guest-polymer percentage of about 5–7% by weight. The *FT*-i.r. spectrum of the modified silicone shows diagnostic bands typical of both linear poly(ester thioether amine) and silicone matrix (see 'Experimental').

The extractability of the guest polymer was tested by means of a Soxhlet apparatus. The results are reported in *Table 2*. It may be worth while to compare these results

Table 1 Swelling properties of Silopren HV

Solvent	Swelling (% w/w) 25°C	45°C
Diethyl ether	110	–
Tetrahydrofuran	157	–
n-Hexane	129	131
t-Butyl alcohol	52	74
Toluene	167	174
Chloroform	335	335
Toluene/t-butyl alcohol (1:1)	–	131
Toluene/monomer **I** (1:1)	–	133
Toluene/monomer **II** (1:1)	–	163

Table 2 Extractability of guest polymer

Solvent	Release (% w/w) Silopren	Modified Silopren	Guest polymer extracted (%)
Diethyl ether[a]	0.64	2.56	43.3
Chloroform[b]	<0.01	4.48	79.3
Water[b]	<0.01	<0.01	<0.3
Ethanol[b]	<0.01	0.87	15.4

[a] Temperature = 25°C
[b] Temperature = 37°C

Table 3 Solubility properties of poly(ester thioether amine) III

Solvent	Solubility[a] 25°C	45°C
Diethyl ether	i	i
Toluene	s	s
n-Hexane	i	i
Acetonitrile	i	i
Acetone	i	i
Chloroform	s	s
Dioxane	s	s
Dimethylsulfoxide	s	s
Dimethylformamide	s	s
Phosphate buffer pH 8.0	i	i
Acetate buffer pH 4.62	i	i

[a] i = insoluble, s = soluble

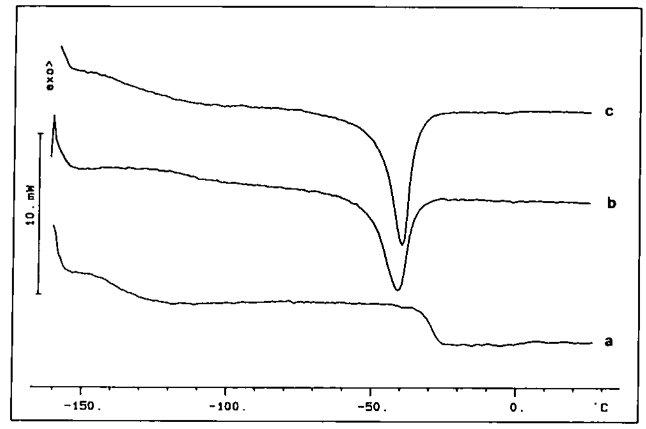


Figure 1 D.s.c. curves of (a) polymer III, (b) silicone rubber and (c) modified silicone rubber

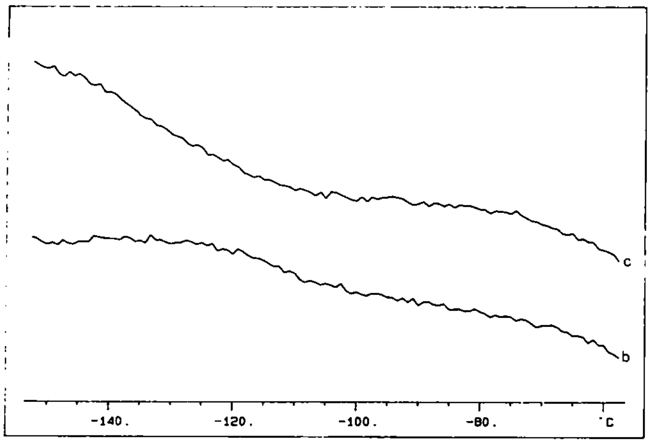


Figure 2 Magnification (× 5) of portion of curves b and c of *Figure 1*

with those of the solubility experiments performed on the free guest polymer (see below). It is apparent that the guest polymer can be extracted only by solvents that are able both to dissolve it and to swell the host silicone rubber, and also in this case with considerable difficulty, as indicated by the long time required to reduce substantially its percentage in the product.

Free poly(ester thioether amine) was present in the mother liquor of the reaction mixture. It was isolated by drying to constant weight as above, and characterized. For comparison purposes, the same polymer was prepared under the same conditions but in the absence of silicone rubber. The two samples were practically identical in all respects. The poly(ester thioether amine) was characterized by the usual techniques (i.r., n.m.r. and elemental analysis). All data were in agreement with the proposed structure. The intrinsic viscosities of all samples, in chloroform at 30°C, ranged between 0.20 and 0.28 dl g^{-1}.

At room temperature, the poly(ester thioether amine) is a sticky, honey-like material freely soluble in several organic solvents, as reported in *Table 3*. From the data reported in this table, it may be observed that the polymer is insoluble in water, but soluble in some aqueous acids.

Physical and mechanical characterization on unmodified and modified silicone rubber

The d.s.c. scan of the piperazine-based polymer, reported in *Figure 1* (curve a) shows a glass transition at around -150 to -120°C, and a second sharper transition centred at -30°C (the nature of this transition is not clear to the authors, being due perhaps to the release of intramolecular interactions). Both of them are always present in successive d.s.c. scans performed on the same sample.

The silicone rubber d.s.c. (curve b) shows the presence of a glass transition, occurring in the range -120 to -100°C, followed by an endothermic melting peak centred at -49°C. *Figure 2* shows a magnification (× 5) of a portion of curves b and c of *Figure 1*, to show in greater detail the T_g of the polymers. The presence of the piperazine-based polymer inside the silicone rubber network is revealed by the decrease of the silicone glass transition region to -145 to -120°C (curve c). The guest polymer higher transition is no longer visible, indicating some constraint effect exerted by the rubber network on the poly(ester thioether amine) flexibility. Moreover, the melting peak of the modified silicone rubber is sharper and slightly displaced towards higher temperatures.

The d.m.t.a. curves clearly confirm the decrease in the silicone rubber glass transition temperature, due to the inclusion of the guest polymer, even though such a decrease appears to be, in this case, only 5–6°C in value. No other significant differences in E' (storage modulus), E'' (loss modulus) and tan δ (damping) curves have been observed.

Tensile mechanical tests performed on both virgin and modified silicone rubber containing a small amount of piperazine-based polymer do not reveal appreciable differences. Elastic modulus, strength and elongation at break are approximately 2.5 MPa, 3.7 MPa and 300% respectively for both materials.

Curves of advancing and receding contact angles in water (h.p.l.c. grade) of both unmodified and modified silicone rubber samples are reported in *Figure 3*. From these curves, it may be reasonably concluded that the presence of piperazine-based polymer does not appreciably affect the silicone rubber wettability, the contact angles being about 100° (advancing) and 57° (receding) for both materials. On the other hand, while repeated immersions of pure silicone rubber samples do not induce any variation in the material contact angle values, the contact angles of the modified silicone increase, after a first immersion, up to 110°C (advancing) or up to 63°

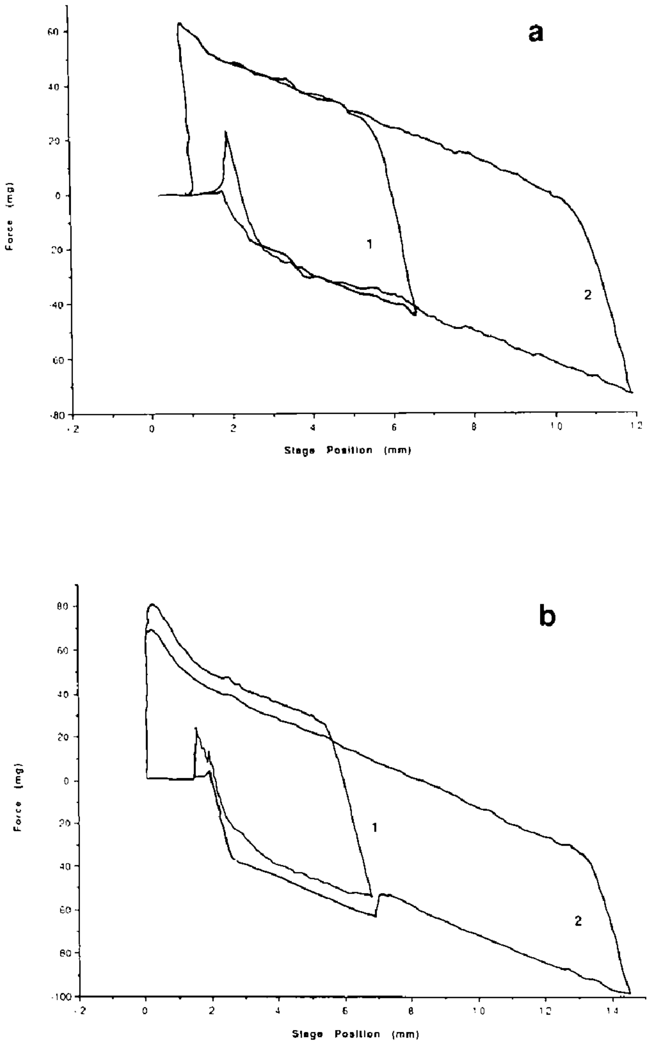


Figure 3 Dynamic contact angle (d.c.a.) curves of (a) virgin silicone rubber and (b) modified silicone rubber in distilled water at room temperature. Numbers 1 and 2 refer to the first and second immersion cycle

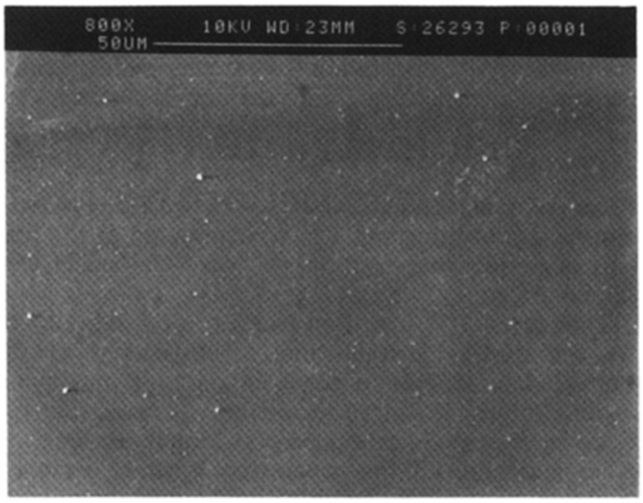


Figure 4 SEM photograph of unmodified silicone rubber

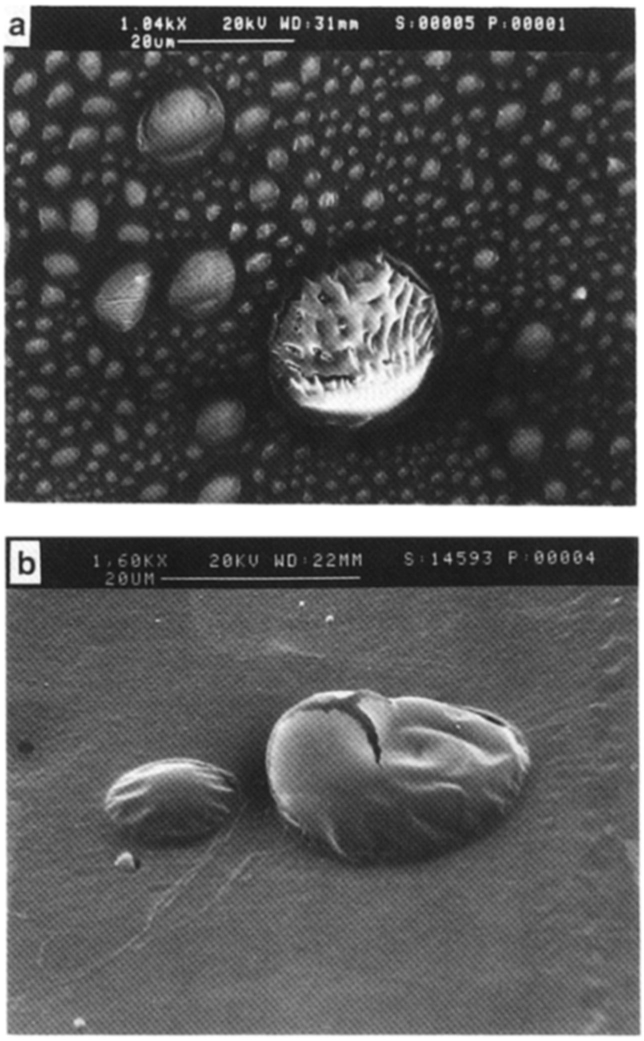


Figure 5 SEM photographs of cross-sections of modified silicone rubber: (a) general view and (b) a bulge fractured by the electron beam

(receding). This effect is clearly shown in *Figure 3b*, for an experiment carried out with the modified silicone rubber. In this experiment the sample was first immersed to 7 mm depth (loop no. 1) and then to 15 mm depth (loop no. 2). The step generated in the resulting force during immersion (lower part of the loop) indicates that some modification occurred in the surface energies of the solid/liquid system. Since the same step was not found during the sample emersion, it could indicate that such modification had already taken place during the first partial immersion.

The SEM micrograph of unmodified silicone surface is reported in *Figure 4*. SEM micrographs of modified silicone surface present numerous protrusions having sizes ranging in the order of a few micrometres. A typical fracture cross-section surface of a modified silicone sample is shown in *Figure 5*. On the other hand, the same protrusions are never shown on the virgin silicone surfaces (related micrographs are not reported here).

This fact, coupled with the observation that the bulges never created negative imprints on the opposite fracture surface of the sample, forced us to interpret them as bubbles probably formed during the sputtering process, which is necessarily performed under high vacuum. Following our hypothesis, the observed bulges are probably formed on the gold layer deposited onto guest polymer bubbles. These, in turn, should be sucked from the inside of the sample during the vacuum treatment. In some cases (see for instance *Figure 5b*), the analysing electron beam causes a bulge to fracture.

Energy dispersion X-ray spectroscopy (EDXS) analysis, performed on modified silicone samples, showed an inhomogeneous distribution of sulfur atoms, which preferentially concentrate onto the bubble surfaces.

CONCLUSIONS

From the results obtained in this work, which, as pointed out in the 'Introduction,' can be considered as the first part of a wider investigation, the following conclusions can be drawn.

The *in situ* hydrogen-transfer polyaddition of 1,4-piperazinediyl diethanethiol to ethylene glycol dimethacrylate provides a convenient way of modifying silicone rubber. It can be reasonably predicted that the scope of this modification process largely exceeds the example provided in this paper, since it can be extended to a number of other alkylenediiminodiethanethiols and bisacrylic or bismethacrylic esters[13,14]. Moreover, cross-linked rubbers other than silicone rubber are probably amenable to the same modification process, provided they swell in suitable solvents. Both points will be investigated in forthcoming papers.

In the present case, the guest polymer is apparently well dispersed within the host polymer, as indicated by a number of physical data (EDXS, d.s.c.).

Mechanical and dynamic mechanical properties of the silicone rubber are not noticeably affected by the modification process. The presence of piperazine-based polymer results in a significant decrease (about 5–7°C) of the silicone rubber glass transition temperature. D.s.c. and d.m.t.a. tests, performed under different conditions, never displayed separate transition phenomena, thus indicating full miscibility of the two polymers in the studied range of composition. No significant differences in the modified and unmodified silicone rubber wettability has been detected.

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