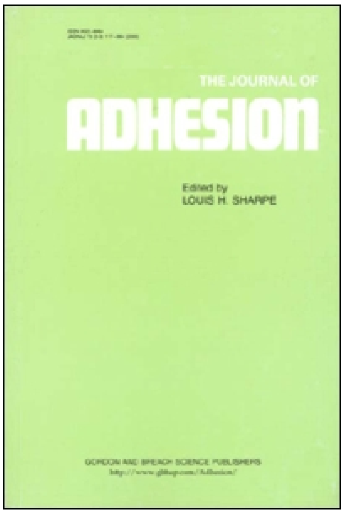

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Effect of Ammonia on Silicone Rubber—Glass Adhesion

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The adhesion energy between silicone rubber and glass has been obtained from the Johnson, Kendall and Roberts' test. The specific effect of ammonia on the quasi-equilibrium value has been studied as a function of the degree of crosslinking of the elastomer. For PDMS networks with lower molecular weight between crosslinks, the effect is more pronounced but completely reversible. This has been related to the increase in the non-dispersive part of the surface energy of the silicone due to the imbibed ammonia. In incompletely crosslinked hydroxyl-terminated PDMS, ammonia has a catalytic effect and is responsible for chemical bonding between the unreacted hydroxyl groups of the PDMS and the hydroxyl groups on glass.

KEY WORDS silicone rubber; glass; ammonia; adhesion; quasi-equilibrium; degree of crosslinking.

INTRODUCTION

Ammonia affects various properties of silicone elastomers. The ammonia action on silicone rubber seems to be a highly specific and rather complex process. In silica-filled silicone rubber, ammonia can both cleave hydrogen bonds on swelling or under mechanical stress[1,2,3] and activate their formation between isolated silanols of the silica filler surface and polysiloxane polymers.[4] Ammonia was also found to catalyze hydrolytic decomposition of very lightly crosslinked poly(dimethylsiloxane) (PDMS) under relatively mild conditions[5] and to promote the auto-adhesion of the lightly cured PDMS and its adhesion to glass and other polar surfaces.[6]

An estimation of the adhesion energy between rubber and a transparent rigid flat substrate, such as glass, can be obtained by using the Johnson-Kendall-Roberts (JKR) method.[7] We have recently studied the effect of crosslinking level in endlinked, silanol-terminated, PDMS on silicone rubber-glass adhesion energy near equilibrium conditions by the JKR method.[8]

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In this study, we report our experimental findings concerning the effect of ammonia vapour on the formation of the silicone rubber-glass interface with respect to the properties of PDMS networks. A tentative explanation of some experimental observations is offered in terms of increased polarity of silicone rubber due to the imbibed ammonia and chemical reaction at the rubber-glass interface.

EXPERIMENTAL

Materials used, sample preparation, characterization of their network structure by toluene swelling (see Table I), determination of adhesion energy in a rubber-glass system and contact angle measurements were described in our previous paper.[8]

In this study, we used the contact-forming JKR adhesion experiment with a thin glass coverslip placed on top of a silicone rubber hemisphere. The energy of adhesion, W_F, is calculated from the size of the contact area at quasi-equilibrium conditions.[7,8]

When testing the ammonia action, the assembled rubber hemispheres topped with glass plates were used for the determination of W_F in air and then placed in a closed dessicator containing an open beaker with ammonium hydroxide. The radius of the rubber-glass contact area was measured in air 30 seconds after removal of the samples from the dessicator.

The maximum time of exposure to ammonia atmosphere was 8 days at room temperature which ensured the equilibrium effect of ammonia in PDMS samples. The crosslink density of silicone rubber hemispheres was then checked by equilibrium toluene swelling[8] and no effect of such ammonia exposure on PDMS network characteristics was found in all samples.

Contact angles of water and diiodomethane on the silicone rubber surface were measured and the reversible energies of adhesion, W_0, were calculated as a function of time of ammonia desorption in air for samples previously exposed to ammonia vapour for 8 days.

TABLE I
Properties of endlinked silanol terminated PDMS
(crosslinked by tetraethoxysilane on catalysis by stannous 2-ethyl hexanoate)[8]

Sample	M_n[c] (g/mole)	End-group ratio[d]	Sol fraction[b] (%)	V_2[b]	M_c (g/mole)
A-1	2 900	0.9	4.4	0.327	5 900
A-2	2 900	1.8	4.9	0.364	4 400
A-3[a]	2 900	1.8	4.3	0.440	2 500
B-1	12 500	0.7	9.1	0.135	43 300
B-2	12 500	1.0	9.6	0.223	17 800
C-1	23 200	0.7	8.6	0.109	63 600
C-2	23 200	1.4	6.8	0.180	24 500
D-1	46 600	0.6	22.2	0.067	136 000

[a] crosslinked in air at atmospheric pressure (other samples crosslinked under vacuum)
[b] obtained from equilibrium toluene swelling
[c] of original PDMS polymer
[d] OH_{TEOS}/OH_{PDMS}

RESULTS AND DISCUSSION

An increase in the contact adhesion energy W_F (Figure 1) was observed when the assembled silicone rubber hemisphere-glass plate samples where placed in the ammonia atmosphere. The contact adhesion energy reached a plateau in 20 to 60 hours of exposure to ammonia vapour at room temperature. The absolute increase in the adhesion energy due to the ammonia action depends on the molecular weight M_c between crosslinks as is obvious from Fig. 1, where results for samples A-1, B-2 and C-1 (see Table I) are displayed. As M_c decreased, the increase in energy of adhesion due to the ammonia action was much more pronounced.

The effect of ammonia imbibed in silicone rubber on its surface energy was checked by measuring contact angles of water and diiodomethane drops on silicone rubber sheets at various intervals after removing the rubber samples from 8 days exposure to ammonia atmosphere. The contact angle of diiodomethane was not affected by the imbibed ammonia. A constant value of 68° was measured in all conditions of the experiment, which means that the dispersive part of the surface energy of silicone rubber $\gamma_S^D = 25$ mJ/m^2 [8] is stable even under ammonia vapour.

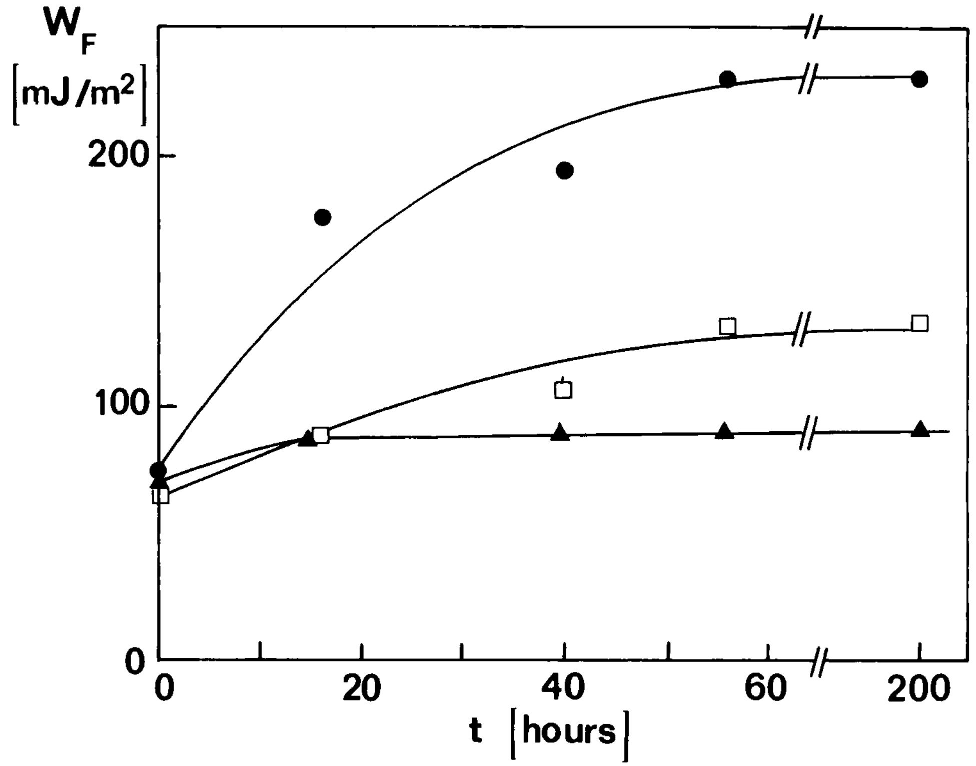

FIGURE 1 Effect of ammonia vapour on the energy of formation of the contact as a function of time of exposure for samples A-1 (●, $M_c = 5900$ g/mole), B-2 (□, $M_c = 17800$ g/mole), and C-1 (▲, $M_c = 63600$ g/mole).

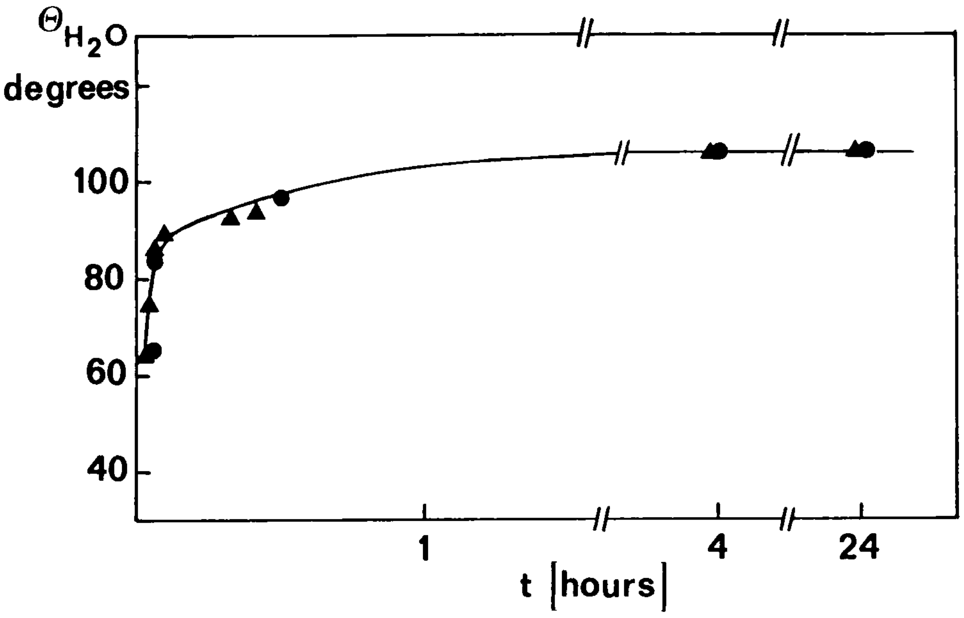

FIGURE 2 Change of the contact angle of water on silicone rubber surface as a function of time of desorption of ammonia for samples A-1 (●, $M_c = 5900$ g/mole) and C-1 (▲, $M_c = 63600$ g/mole). The samples were placed in ammonia vapour for 8 days before the experiment.

On the other hand, the contact angle of water was strongly decreased from the original 106°[8] to 64° by ammonia absorbed in silicone rubber. But as the ammonia desorbed from the elastomer in the laboratory atmosphere, the contact angle of water increased and returned to its original value of 106° within about 4 hours at room temperature, as shown in Figure 2. The decrease of the contact angle of water, along with the constant dispersive component of the surface energy, indicates an increase in polarity of the silicone rubber surface by the absorbed ammonia, which can also be expressed by a rise of the polar component of the surface energy of silicone rubber from 0.17 mJ/m^2 [8] to 16.1 mJ/m^2 after 8 days in contact with ammonia vapour at room temperature.

The increase of polarity due to the presence of ammonia in the PDMS network and the subsequent increase of the reversible adhesion energy, W_0, was completely reversible on evaporation of ammonia at room conditions, as evidenced by Figure 3, where W_0 is plotted as a function of time of ammonia desorption in air for samples A-1 and C-1 (see Table I). There is no difference between two samples with various values of M_c (5,900 and 63,600). The effect of ammonia absorption and desorption on the reversible adhesion energy, W_0, does not depend on molecular weight, M_c, between crosslinks in silicone rubber. The increase in polarity of the silicone rubber surface due to the imbibed ammonia seems to be a purely physical process which accounts for the observed increase of adhesion energy between silicone rubber and glass under ammonia atmosphere.

A similar reversible effect of ammonia on the contact adhesion energy, W_F, was

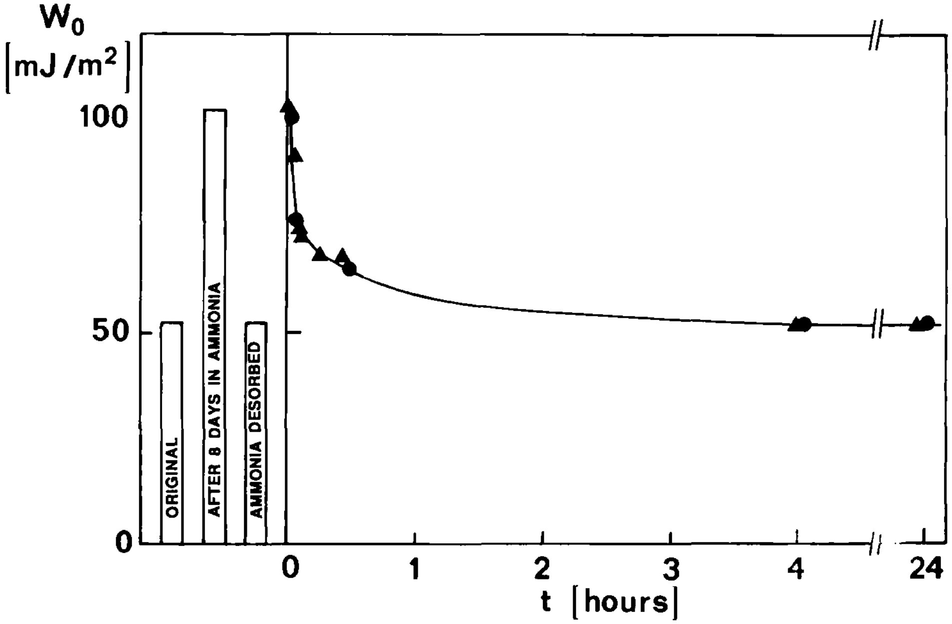

FIGURE 3 Change of reversible energy of adhesion as a function of time of desorption of ammonia for samples A-1 (●, $M_c = 5900$ g/mole) and C-1 (▲, $M_c = 63600$ g/mole). The samples were placed in ammonia vapour for 8 days before the experiment.

observed in silicone rubber hemisphere—glass coverslip samples that were placed in air after a one-day exposure to ammonia atmosphere, as is illustrated in Figure 4 for samples A-2 and C-2. In this case, however, the effect of ammonia on W_F was affected by M_c. This effect cannot be explained only by the increase of the surface polarity of silicone rubber due to the absorbed ammonia, which is the same in various PDMS networks (see Fig. 3).

The effect of M_c on the contact energy of adhesion, W_F, for different PDMS networks (see Table I) exposed to ammonia vapour for 8 days at room temperature is clearly shown in Figure 5. The original values of W_F in air are also plotted and show a very slight dependence, if any, on PDMS crosslink density.[8] It seems that two regions according to the M_c values in the PDMS networks can be distinguished in Fig. 5. In samples with M_c lower than 30,000 g/mole there is a strong increase of the effect of imbibed ammonia on W_F with crosslink density. In lightly crosslinked PDMS networks with M_c higher than 30,000 g/mole, the effect of ammonia on W_F is not very strong and does not seem to be critically dependent on the crosslink density of the silicone rubber.

To test the reversibility of the ammonia effect on the contact energy of adhesion between silicone rubber and glass we stored silicone rubber hemisphere—glass samples at first in ammonia vapour for 8 days and then in the laboratory atmosphere for 4 months. The results of the measured energy of adhesion after removal of all ammonia again divided the PDMS networks into two groups, as can be seen in

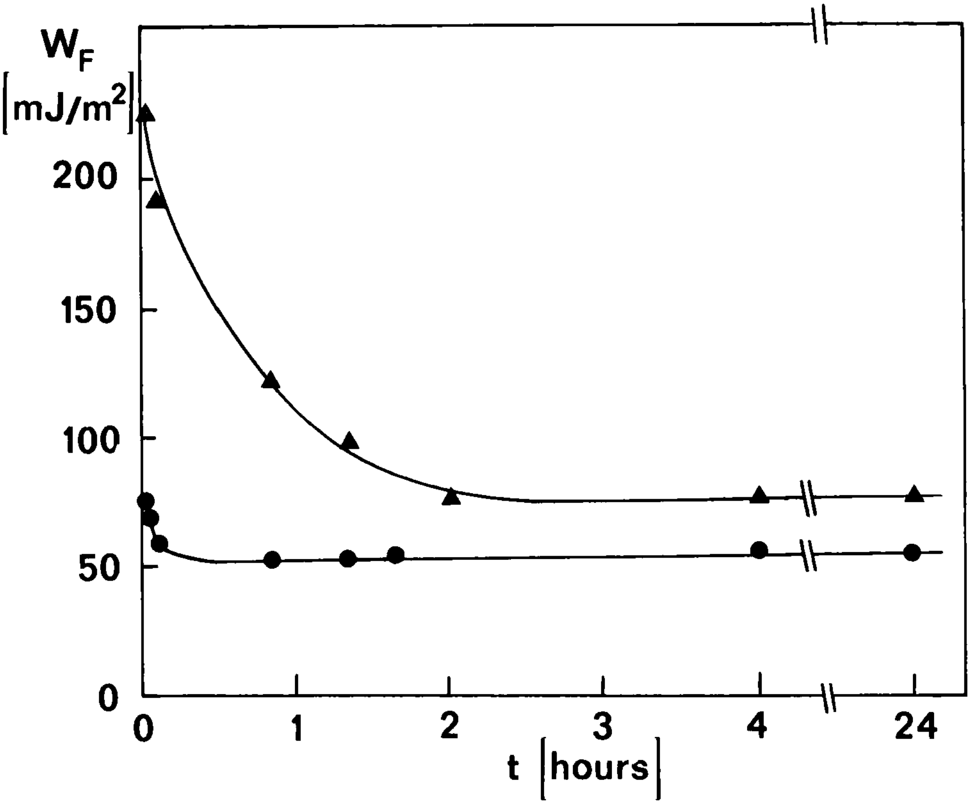

FIGURE 4 Change of the energy of adhesion involved in the formation of the interface as a function of time of desorption of ammonia for samples A-2 (▲, $M_c = 4400$ g/mole), and C-2 (●, $M_c = 24500$ g/mole). The samples were placed in ammonia vapour for 1 day before the experiment.

Figure 6, where the decrease of adhesion energy, W_F, due to the desorption of ammonia from silicone rubber is plotted as a function of M_c. The contact energy of adhesion, which had increased in ammonia vapour in samples with M_c lower than 30,000 g/mole, returned to its original values after ammonia removal. Thus, the effect of ammonia is fully reversible in the more crosslinked PDMS networks. The increase of W_F in ammonia vapour is equal to the decrease after ammonia removal as is shown in Fig. 6, in which the results of the variation of W_F consequent to absorption and desorption of ammonia are compared.

A quite different situation was observed in samples with M_c higher than the limiting value of 30,000 g/mole. Here we found a relatively small effect of the imbibed ammonia but this effect was stable with no variation of W_F after removal of ammonia from the rubber. Moreover, only in those three samples with M_c higher than 30,000 g/mole, the glass coverslips fused together with silicone rubber over the time of the experiment, thus clearly indicating a chemical reaction across the interface. This was not the case in samples with a higher crosslink density, where the reversibility indicated a physical process only.

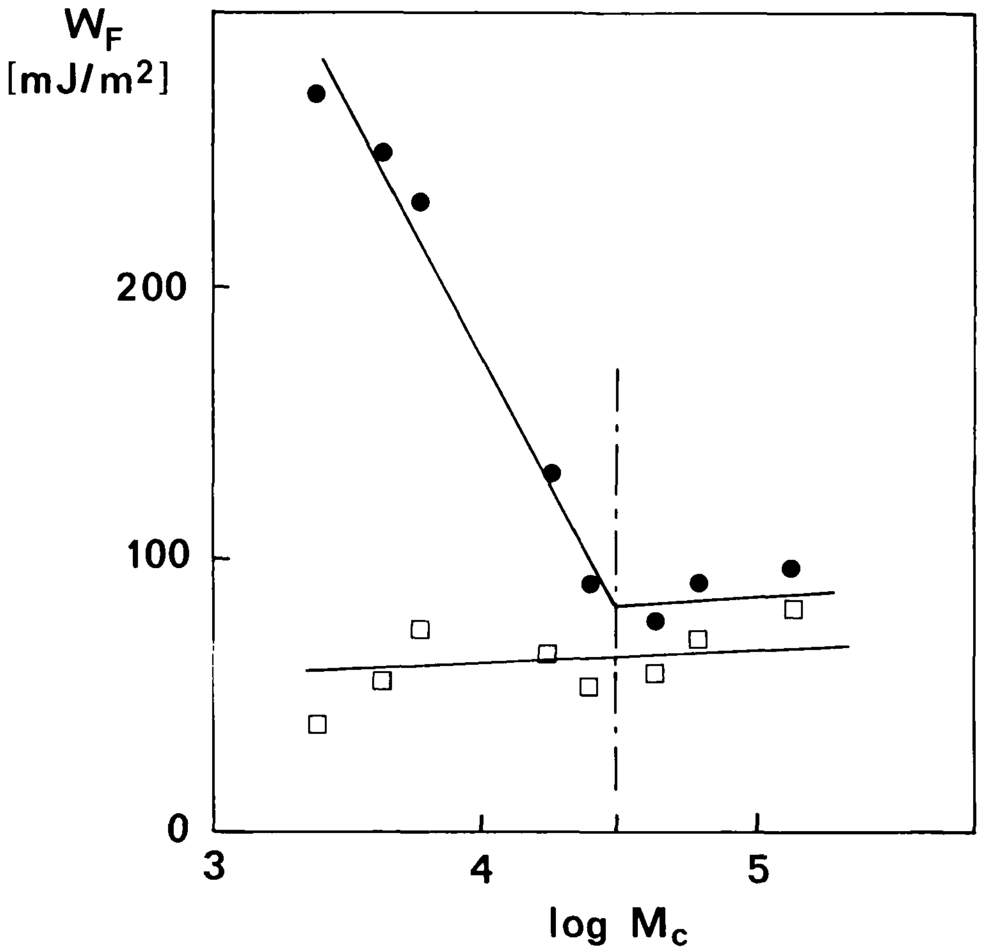

FIGURE 5 Effect of molecular weight, M_c, between crosslinks in silicone rubber on the energy of formation of the glass/silicone rubber interface in air (□) and in ammonia vapour (●).

The samples with very high M_c values, *i.e.* B-1, C-1 and D-1 were prepared with lower than stoichiometric quantities of the crosslinker (see Table I). Therefore, the resulting networks were not fully crosslinked (endlinked) and could contain free unreacted silanol end-groups on PDMS. These end-groups could react, under the catalytic effect of ammonia, with hydroxyl groups of glass.

When removing the glass coverslips from the incompletely crosslinked silicone rubber hemispheres after 8 days in ammonia vapour and 4 months in air, we experienced the cohesive failure of the silicone rubber at the contact area with glass. The situation resembled the spontaneous adhesion between PDMS lightly crosslinked by a peroxide and quartz or glass substrates under catalysis of ammonia vapour, as reported by Gent and Vondráček.[6] They also observed the effect of molecular weight, M_c, between crosslinks on the adhesive behaviour of silicone rubber. Contrary to our present findings, the development of adhesion was less pronounced

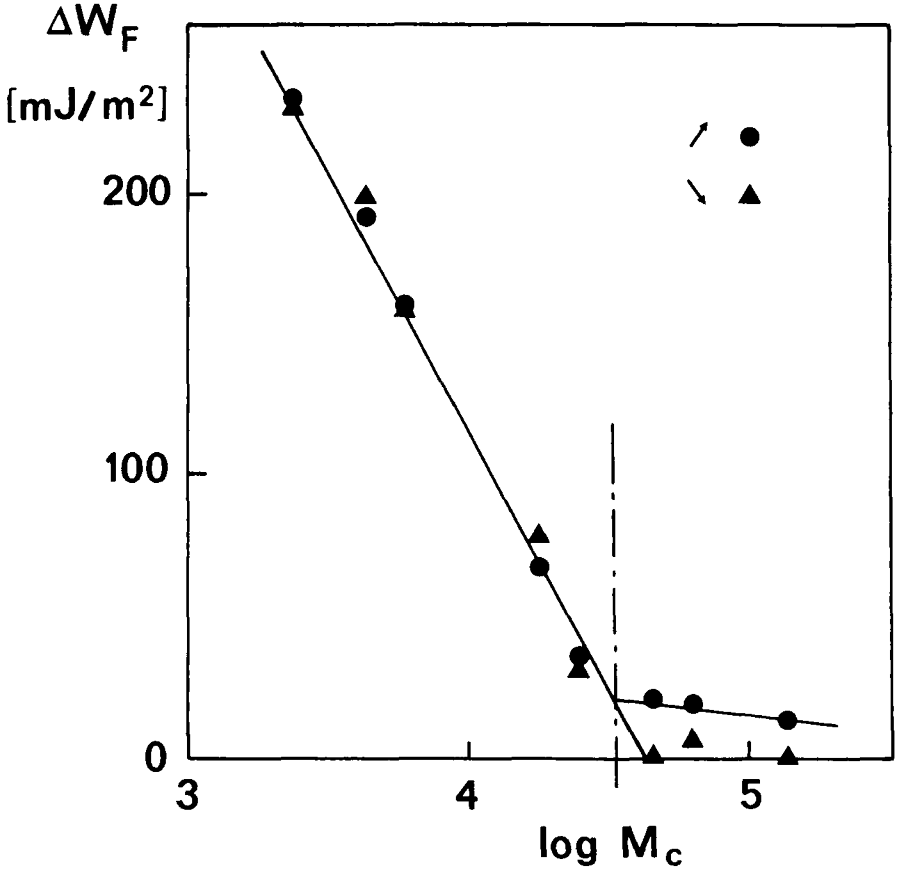

FIGURE 6 Variation of the energy of formation of the glass/silicone rubber interface on absorption (▲) and desorption (●) of ammonia vapour as a function of molecular weight, M_c, between crosslinks.

as M_c decreased. This effect was, however, connected with a higher susceptibility of the less crosslinked PDMS to its hydrolytic decomposition or rearrangements.

Our present experimental observations do not allow one to explain the effect of M_c on the ammonia-induced increase in energy of adhesion between PDMS networks and glass substrates. Some additional experiments will be needed to provide evidence which allows one to offer a mechanism responsible for this effect.

CONCLUSION

Ammonia vapour has been shown to increase the contact energy of adhesion between poly(dimethylsiloxane) networks and a glass surface. The effect of ammonia on the energy of adhesion is more pronounced in PDMS networks with lower M_c. The imbibed ammonia increases the polar component of the surface energy of silicone rubber while the dispersive part remains unchanged. The effect of ammonia on the surface energy of silicone rubber does not depend on M_c. In incompletely crosslinked hydroxyl-terminated PDMS, ammonia has been found to cause chemical interlinking between the rubber and the glass substrate. It is suggested that the unreacted hydroxyl groups in PDMS undergo chemical bonding, under ammonia catalysis, with hydroxyl groups on glass. This again points to a specific effect of ammonia vapour on the behaviour of poly(dimethylsiloxane). The presented results support an idea that minor structural changes in polymeric materials or mild external effects can result in major changes in their adhesive behaviour.

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