Filler-induced softening effect in thermally aged polydimethylsiloxane elastomers

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An intriguing filler-induced softening effect was observed in filled polydimethylsiloxanes that aged at high temperatures. It was found that the Young's modulus and hardness of the aged filled elastomers first decreased and then increased with filler fraction, remarkably different from those of the fresh samples which always increased monotonically. This softening effect cannot be explained by the original phase structure of rigid particles embedded in a soft matrix. However, due to the notable chain scissions and oxidative crosslinks detected in the aged neat resin, the softening was attributed to a heterogeneous oxidative hardening during the thermal ageing. It is proposed that filler particles behaved as secondary antioxidants to block the local reactions of free-radical crosslinks, effectively producing a soft elastomeric layer around each particle and thus this softening effect. This proposal is consistent with the fact that α-iron oxide, a strong free-radical scavenger, demonstrated the most pronounced softening effect. The proposal was further examined by comparing the mechanical strength at the filler/elastomer interfaces extracted from the wear rate data among the various fillers studied here. It was found that α-iron oxide/elastomer interfaces possess the lowest interfacial strength, in good agreement with the proposed mechanism.

(Keywords: polydimethylsiloxanes; softening effect; thermal ageing)

INTRODUCTION

Owing to their superior thermal stability, silicone elastomers are commonly used for high-temperature applications in many areas of modern industry. In order to improve the mechanical strength, a large amount of inorganic filler is usually incorporated into the resin before moulding for use. Despite the obvious importance, the effects of these added particles on thermal stability and high-temperature mechanical strength of the filled elastomers have rarely been studied.

The general effect of the rigid filler on the elastic properties of filled elastomers that have never been exposed to high temperatures is nevertheless clear. According to the various classic studies, the addition of a rigid filler invariably causes the Young's modulus of the resulting material to increase monotonically with filler fraction. This behaviour has been well documented and explained both theoretically and empirically in the literature, notably by Smallwood[1,2], followed by Guth and Gold[3], who derived the following equation by using an analogy to Einstein's viscosity equation[4,5] for the cases of perfectly dispersed spherical particles in a homogeneous rubber matrix[6–8]:

$$E_1 = E_0(1 + 2.5c + 14.1c^2) \qquad (1)$$

where E_1 and E_0 are the Young's moduli of the composite and the neat resin, respectively, and c is the filler volume fraction. This equation was subsequently modified to include the cases of non-spherical fillers. Later, the popular Kerner equation, developed by elasticity analysis[9,10], was modified and generalized[11–15] to have the following form for filled rubbers:

$$E_0/E_1 = (1 + ABc)/(1 - B\Phi c) \qquad (2)$$

where the Poisson's ratio of the matrix is assumed to be 0.5, and A, B and Φ are material constants. It has been shown that the generalized Kerner equation is equivalent to both the van der Poel equation[16,17] and the Eshelby approach[18–20]. Despite variation in form, these equations describe the same phenomenon: that the Young's modulus of a rubber composite consisting of well dispersed rigid particles in a homogeneous rubber matrix always increases monotonically with filler fraction.

This simple monotonic increase of Young's modulus will no longer be valid, however, if the phase structure of the composite changes. For example, if the elastomers undergo chain scission and oxidative crosslinking in a heterogeneous manner owing to the existence of filler particles, the initial two-phase structure may evolve into a more complicated structure and give rise to a different behaviour of the Young's modulus. Although there are few data in the literature regarding the effect of filler on elastomer ageing, several fillers, notably α-iron oxide, have long been known to the rubber industry as effective free-radical scavengers and have been used extensively. In this paper, several fillers were selected to study their effect on mechanical properties of the filled silicone elastomers before and after thermal ageing. These results were then compared and discussed with the thermal degradation data obtained from chemorheology and with the mechanical strength of filler/matrix interfaces extracted from the abrasive wear results.

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EXPERIMENTAL

A vinyldimethyl-terminated polydimethylsiloxane that can be cured by platinum catalytic reactions (Dow Corning Sylgard 182) was used as the host silicone rubber. The filler was selected from the following group: zinc oxide (density, $\rho = 5.18\,g\,cm^{-3}$); α-iron oxide ($\rho = 5.24\,g\,cm^{-3}$); γ-iron oxide ($\rho = 5.18\,g\,cm^{-3}$); and graphite ($\rho = 2.25\,g\,cm^{-3}$). By scanning electron microscopy, the particles of α-iron oxide and zinc oxide were found to be of irregular shape, but could be approximated as spheres with diameters of around 0.2 and 0.1 μm, respectively. The γ-iron oxide particles are needle-like with average dimensions of approximately 0.1 μm x 10 μm. The graphite particles are platelets with dimensions in the wide range of about 1 μm x (30 ± 20) μm.

The specimens were prepared by first thoroughly mixing the polydimethylsiloxane (PDMS) resin and its curing agents with the filler at room temperature. The final mixture was poured into an open mould in which it was degassed in a vacuum chamber ($\sim$1 Pa) to remove trapped air bubbles. The degassing took from 5 min to 12 h depending on the viscosity of the fluid. After degassing, the mould was sealed and transported into a press where the composite was cured under pressure up to 4 MPa at 170°C for 30 min. The cured specimen was removed and further cured in a convection oven at the same temperature for 1.5 h. Finished specimens had a thickness of approximately 2 mm. For ageing experiments, specimens were stored in the convection oven at 200°C for 25 days before testing.

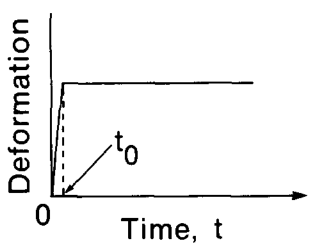
The fully cured sample was cut into strips (6 mm x 60 mm) and tested in an Instron machine to obtain the mechanical data. From the stress–strain curves, the Young's moduli were calculated from the initial slope at ca. 2% elongation. Chemorheology tests[19] were performed by stretching the sample in an environmental chamber attached to the Instron machine at 200°C. For the continuous stress relaxation test, a small strain of 10% elongation was maintained in the sample while the load $f(t)$ was measured as a function of loading time t. For the intermittent stress relaxation, the specimen was deformed intermittently by a train of short pulses of 10% strain $e(t_i)$ and the peak loads $f(t_i)$ corresponding to the strain pulses $e(t_i)$ were measured. The chemorheology tests are illustrated in *Figure 1*. For abrasion tests, a disc of approximately 10 cm in diameter was cut from the cured sample and tested in a Taber Abrader (ASTM C501). The sample was clamped on a circular platen which rotated at a fixed speed ($\sim$60 rev min^{-1}) such that the sample surface was abraded against a pair of abrasive wheels (standard H-18 calibrase wheels), each under a contact weight of 400 g. The wear debris was removed instantaneously by a pair of vacuum nozzles positioned slightly above the sample surface. The weight loss of the abraded sample was measured every 1000 revolutions after gentle cleaning by air flow. The abrasive wheels were refaced after every 1000 revolutions.

RESULTS AND DISCUSSION

Young's modulus and hardness

The Young's moduli of both the fresh and aged samples were measured and are shown in *Figure 2*. The Young's modulus of the fresh samples was found to always increase monotonically with filler fraction, as predicted by equations (1) and (2). However, after ageing at 200°C for 25 days the modulus first decreased and then increased with the filler fraction. The drop of Young's modulus with filler fraction is intriguing, as it has not been reported or predicted before. The modulus reduction, usually reaching approximately 50% of the modulus of the aged neat resin, was observed in all cases for different filler shape and size. Also shown in *Figure 2* is the rapid increase of the neat resin Young's modulus after the same ageing period, indicative of excessive thermal degradation in the neat elastomer during ageing. For convenience of discussion, v_{min} (minimum fraction) is designated as the filler fraction at which the Young's modulus is at a minimum, and v_r (recovery fraction) the filler fraction at which the Young's modulus recovers to a value equal to the aged neat resin modulus, as denoted in *Figure 2*. Obviously, smaller v_{min} and greater v_r indicate a more pronounced softening effect. The v_r values of the non-spherical fillers of γ-iron oxide and graphite were systematically smaller than those of the spherical fillers, but this trend was believed to be the result of smaller percolation thresholds of the elastic stress transfer between non-spherical particles compared to those of the spherical particles. In the sub-group of spherical particles, however, α-iron oxide demonstrated a stronger softening effect than zinc oxide in that its v_{min} value was smaller and v_r greater than those of zinc oxide (v_{min}, 8 wt% *versus* 15 wt%; v_r, 52 wt% *versus* 38 wt%).

(a) Continuous Relaxation



(b) Intermittent Relaxation

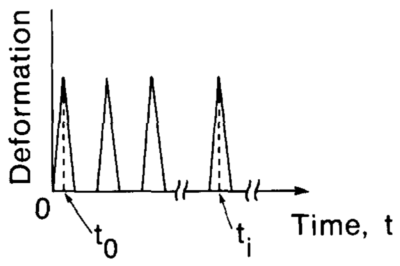


Figure 1 Illustration of the chemorheology tests: (a) continuous and (b) intermittent stress relaxations

Similar behaviour was also observed in the hardness (measured by Durometer shore A) of the fresh and aged filled elastomers (*Figure 3*). Although the variation of hardness with filler fraction was smaller than that of Young's modulus, the relative order of v_r among the tested fillers was perfectly reproduced.

In order to explain this filler-induced softening of the aged elastomers, the initially two-phase structure is obviously no longer working. This is very clear as the two-phase structure of rigid particles embedded in a soft

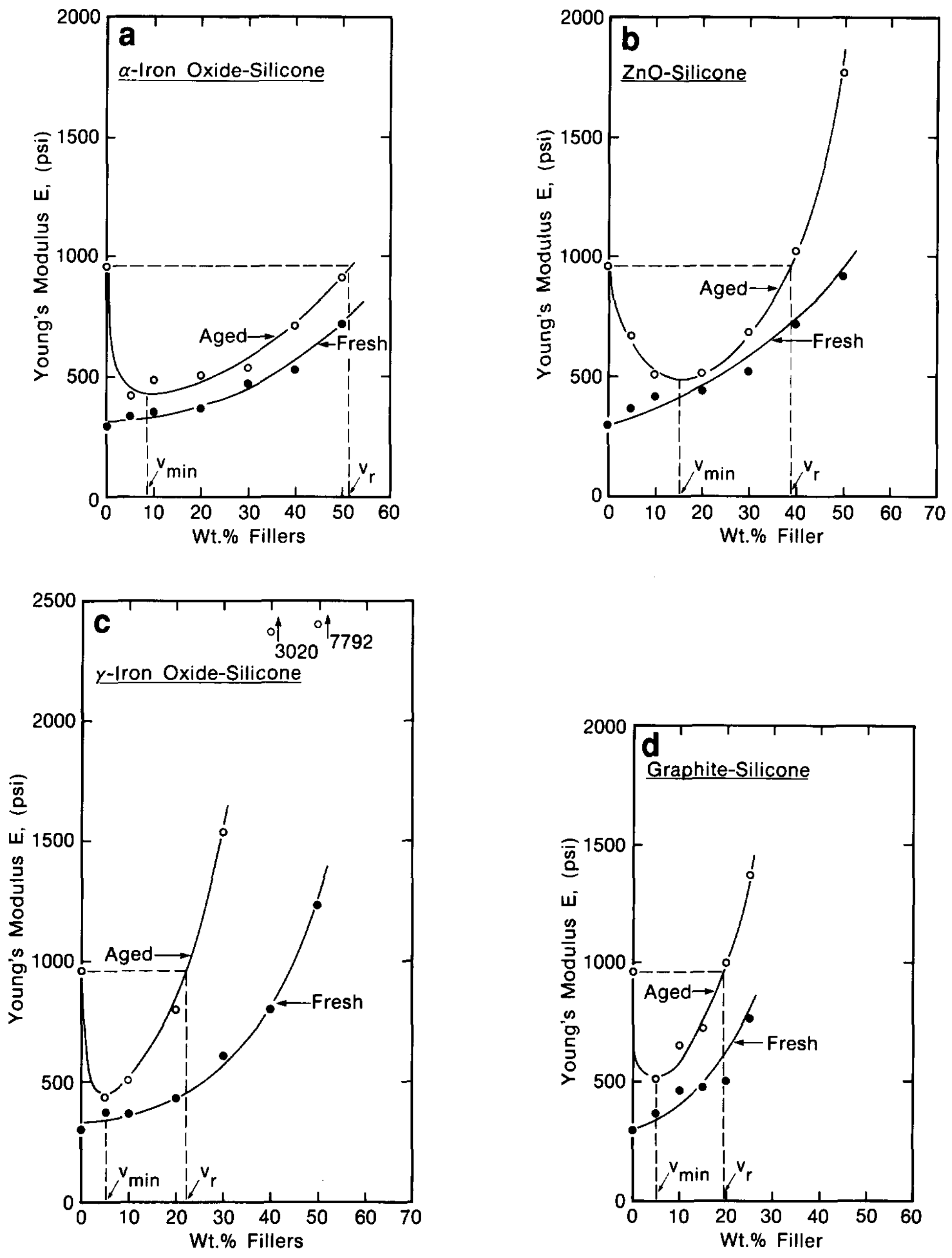


Figure 2 The Young's moduli of the fresh and aged silicone elastomers filled with: (a) α-iron oxide; (b) zinc oxide; (c) γ-iron oxide; (d) graphite

matrix can only produce monotonic modulus increase with filler fraction, as has been thoroughly discussed in the previous sections. To produce the softening effect, the aged composites must have acquired a more complicated structure from thermal ageing. It is proposed that a new elastomeric phase, softer than the hardened matrix, was introduced at the particle/matrix interfaces during thermal ageing due to the local suppression of crosslinking by the filler particles. The change of the phase morphology is shown schematically in *Figure 4*. With this new phase structure, the Young's modulus (tensile deformation) and hardness (compressive deformation) of the filled elastomers can be smaller than those of the aged neat resin; this is because the soft layers can preferentially absorb the deformations applied to the composites since they are the most compliant regions and are located at the stress concentration around the rigid particles. This softening effect could be further enhanced as more filler particles were added. However, when the filler fraction increased to the point that the interparticle spacing became so small that the hydrodynamic effect of rigid filler, described in equations (1) and (2), eventually surpassed the softening effect of the soft interfaces, the Young's modulus and hardness increased monotonically with filler fraction. The transition from the filler-induced softening regime to the filler-induced hardening regime is clearly influenced by the properties (e.g. thickness and softness) of the interfaces. The transition also depends on the magnitude of the percolation threshold of elastic stress transfer between individual particles. Since the non-spherical fillers generally have smaller percolation thresholds, they should have smaller v_r values consistent with the data shown in *Figure 2*.

Haque and Turner[21] have reported observations of the minimum filler fractions, v_{min}, of crosslinked glassy polymers filled with rigid fillers at which the identation hardness showed a minimum. In their system, v_{min} was around 3–5 wt%. They attributed this softening effect to

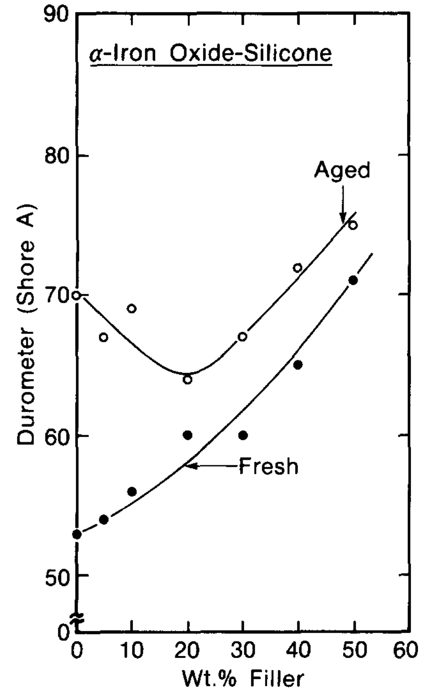


Figure 3 The hardness measured in Shore A of the fresh and aged silicone elastomers filled with α-iron oxide

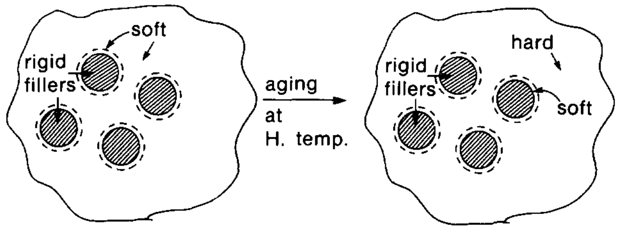


Figure 4 Schematic drawing of the proposed morphology of the filled elastomer before and after high temperature ageing

the increased localized plastic deformation at the stress concentration around the filler particles. Their case is mechanically similar to the deformation of aged filled elastomers. Obviously, the magnitude of $v_{\min}$ should depend greatly on the extent of localized deformations around the filler particles, which in both cases are influenced by the properties of the filler/matrix interfaces.

Thermal degradation

As demonstrated by the rapid increase of Young's modulus and hardness, the neat resin clearly underwent significant degradation after thermal ageing at high temperatures. The thermal degradation process was then investigated by chemical stress relaxations, by which the thermally induced chain scissions and oxidative crosslinking were studied. Following Tobolsky and MacKnight[22], we assumed that the elastomeric chains attained mechanical equilibrium instantaneously upon deformation at the ageing temperature, thus the load $f(t)$ measured could be linked linearly to the crosslink density $\nu_e(t)$ in the sample:

$$f(t)/f_0 = \nu_e(t)RT(\alpha^2 - \alpha^{-1}) \qquad (3)$$

where α is the extension ratio, R is the gas constant, and $f_0 \approx f(t=0)$ is the initial load measured. The measured load $f(t)/f_0$ in an intermittent stress relaxation test will therefore give the instantaneous value of the total crosslinking density $n_e(t)$, which depends on the combined effect of chain scission and oxidative crosslinking from ageing. On the other hand, the measured load $f(t)/f_0$ in a continuous stress relaxation depends only on the number of surviving chains that have successfully avoided chain scission. This is because the new crosslinks created by thermal oxidation in the stretched state cannot share the applied load, except for the cases where excessive crosslinking causes specimen contraction[22]; however, this was not observed in the present experiment. Thus, from the data of intermittent and continuous relaxation experiments, both chain scission and oxidative crosslink density can be measured.

Figure 5 shows the results of chemical stress relaxation obtained with 10% elongation at 200°C, a temperature 320°C above the glass transition temperature of the neat silicone resins. The changes in crosslink density due to reactions of chain scission and oxidative crosslinking were calculated from the data and are shown in *Figure 6*. Evidently, significant chain scission and oxidative crosslinking had both taken place and a net increase of total crosslink density was observed. This observation is consistent with the observed rapid increase of Young's modulus after ageing. The loss of crosslinks from chain scission was large, and the aged resin could

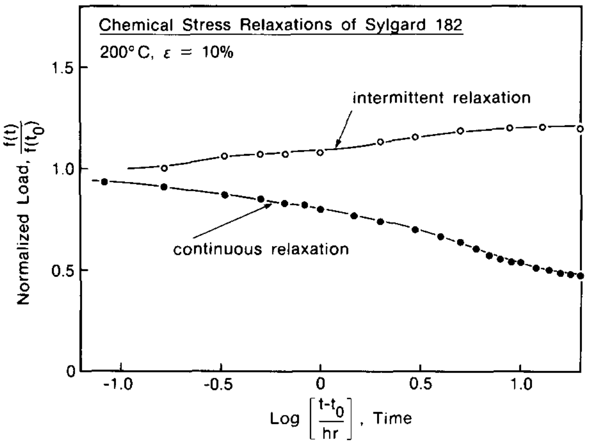


Figure 5 Results of chemorheology tests of the neat silicone resin with 10% elongation at 200°C, where $t_0 \approx 7$ s is the time taken for the crosshead to stretch 10% elongation of the samples

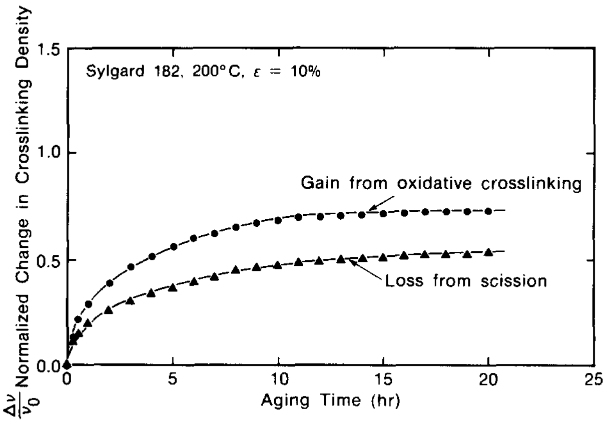
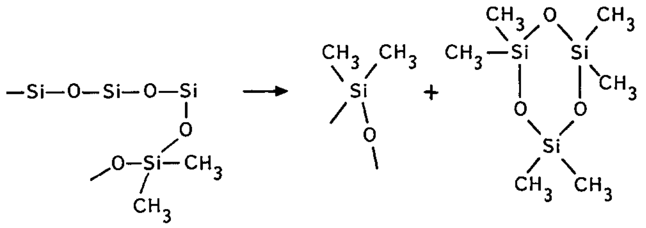


Figure 6 The crosslinking density changes, calculated from the data shown in *Figure 5*, by reactions of chain scission and oxidative crosslinking during ageing

have become significantly softer if oxidative crosslinking was suppressed.

The results shown in *Figures 5* and *6* are consistent with the observations of Atkins *et al.*[23], who reported that the thermal stability of PDMS decreases rapidly at temperatures above 200°C. Grassie and co-workers[24–26] have proposed a degradation mechanism in which cyclic siloxane species can evolve from the thermally aged end-capped PDMS:



This reaction leads to crosslinking loss if the cyclic species contain a long segment of the siloxane backbone. Concurrently during thermal ageing, chain crosslinking takes place in PDMS. Atkins *et al.*[23] have reported that the silicone fluids undergo oxidation when aged in air above 200°C, resulting in an increase in viscosity and the evolution of formaldehyde and formic acid. The increase in viscosity is attributed to the condensation of two or more siloxane radicals, created from the ruptured methyl pendent groups. By the same reaction, additional crosslinks can form between chains, resulting in a material with higher Young's modulus, hardness and tensile strength, but lower elongation at break[22–27], as observed here.

There are few literature data on the exact role of the filler in chain degradation of filled PDMS; however, it is apparent that for filler particles acting as secondary antioxidants and scavenging free radicals locally, chain crosslinking will be suppressed in the neighbourhood of the particles[28,29]. A composite with a soft third phase at the interface between filler and hardened matrix could result and thus cause the softening effect reported here. The free radical scavenging power of the particles obviously has a strong influence on the properties of the soft layers and thus the degree of softening. By u.v. spectroscopy, Gent and Rodgers[30] have shown that iron powder can form a stable species with the mechanically sheared elastomers. Also, α-iron oxide has long been recognized in the rubber industry as an effective secondary antioxidant that can scavenge the free radicals from decomposed methyl groups. Moreover, being a Lewis acid, α-iron oxide can catalyse the hydrolysis reaction and cleave the Si–O backbone[29]. Therefore, in the PDMS filled with α-iron oxide the oxidative crosslinking reaction can be slowed significantly at the vicinities of the α-iron oxide particles during thermal ageing, while the rest of the elastomer is undergoing oxidative hardening. The net result should be a relatively thick soft phase surrounding the individual rigid α-iron oxide particles. Zinc oxide, however, seems to be less effective than α-iron oxide in terms of the free-radical scavenging behaviour as well as of the hydrolysis reactivity, as implied by the work of Gent and Rodgers[30] on elastomer–metal powder systems. Furthermore, the thermal gravimetric results of Dickstein and Lin[31] indicated that the thermal degradation temperature of PDMS filled with α-iron oxide was greater than that of PDMS filled with zinc oxide particles. This is consistent with our observations that the recovery filler fraction v_r of α-iron oxide is much larger than that of zinc oxide.

It may be possible, however, that the mere physical presence of the filler particles is enough to produce a retarding effect on local oxidative hardening at the interfaces. Clearly, for the elastomeric regions immediately next to a thermally inert particle, the probability of forming new crosslinks should be less than that in the bulk of the elastomer, since the rigid particle does not produce free radicals and in fact they can block the diffusion of these crosslinking species. This contribution, however, should be comparable for all the fillers of similar particle geometry.

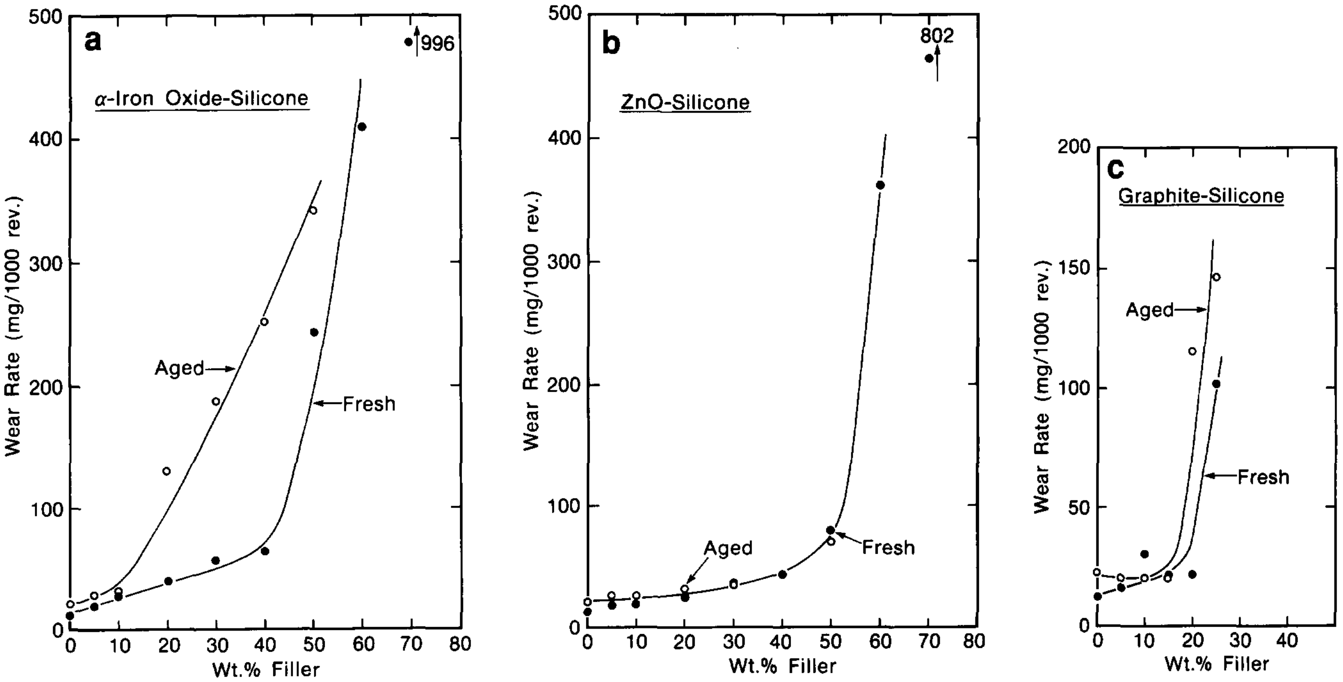


Figure 7 Wear rate *versus* the filler weight fraction for the fresh and aged silicone elastomers filled with: (a) α-iron oxide; (b) zinc oxide; (c) graphite

Wear experiments

The mechanical strength of the elastomer/particle interfaces was probed qualitatively by abrasive wear experiments. It has been shown previously[32,33] that abrasive wear in filled elastomers is controlled by microcavitation and/or microdebonding at the filler/matrix interfaces, the so-called 'damaged zones'. Due to stress overlapping[32], the damaged zones become continuous as filler fraction becomes greater than a critical filler fraction v_c and the wear rate of the filled elastomers in this regime increases very rapidly with the filler fraction. Since the mechanical strength of the interfaces defines the thickness of the damaged zone associated with the individual particles, the magnitude of the critical filler fraction v_c gives an indication of the interfacial strength of the filler/elastomer interfaces. If the interfaces are weakened as a result of significant loss of crosslinks from thermal ageing, the critical filler fraction v_c should decrease.

Figure 7 compares the wear rates of the fresh and aged samples of filled PDMS as a function of the filler fraction for α-iron oxide, zinc oxide and graphite. As expected, two wear regimes divided by v_c are evident. Clearly, the critical filler fraction v_c for α-iron oxide decreases significantly after thermal ageing while the v_c values for the other fillers tested here (zinc oxide, γ-iron oxide and graphite) did not change appreciably; this indicates a much weaker α-iron oxide/elastomer interface than the interfaces in the systems filled with other particles. This is consistent with the observations that the elastomer filled with α-iron oxide demonstrated the most pronounced softening effect. The data also indicate that softening at the interfacial regions for zinc oxide and the non-spherical fillers tested here is large enough to lower the Young's modulus and hardness, but is apparently not enough to produce significant weakening and to decrease the wear resistance appreciably.

CONCLUSIONS

An unusual softening effect due to rigid fillers was observed in thermally aged filled elastomers. The Young's modulus and hardness of the aged filled elastomers were found to first decrease to a minimum and then increase as the filler fraction increased. This softening effect indicates the existence of an interfacial region softer than the bulk matrix located at the particle/matrix interface in the aged samples. This strongly implies that the inorganic fillers can locally suppress the hardening process of silicone elastomers during thermal ageing to produce a large effect on the macroscopic elastic properties of the composites. At the temperature of 200°C, polydimethylsiloxanes were found to undergo significant chain scission and oxidative crosslinking concurrently, due to thermal degradation. Furthermore, consistent with its known behaviour as a free-radical scavenger and a Lewis acid, α-iron oxide demonstrated a more pronounced softening effect than zinc oxide, which had similar particle geometry, and a much weaker filler/matrix interface that also caused a decrease of the critical filler fraction v_c of abrasive wear resistance.

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