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Influence of particulate fillers on the indentation hardness of a glassy cross-linked polymer

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The indentation hardness of a glassy cross-linked network was decreased to a minimum value by a low volume fraction (0.03 to 0.05) of each of six fillers having rigid particles varying in size and surface. This "minimum" effect was eliminated after specimens were more highly cross-linked by prolonged exposure to γ-rays. These results are consistent with an earlier suggestion that filler particles act as stress concentrators which may cause increased localized plastic deformation and hence a decreased indentation hardness. In the case of larger particles, morphological evidence of localized plastic deformation was obtained by fractography.

1. Introduction

A number of theories have been reviewed all of which predict a monotonic increase of the elastic modulus of a polymer with increasing volume fraction of a rigid particulate filler [1–3]. Against this background, it was surprising to find a system in which both the Vickers hardness number and yield stress went through a minimum value at a low volume fraction of filler (0.05). A clue was provided by fractographic evidence of localized plastic deformation originating at individual filler particles. It was suggested that the filler particles are sites of localized plastic deformation because they act as stress concentrators [4–6].

A puzzling aspect of the suggestion about stress concentration is that it would seem to imply a general effect. Yet, generally, no such effect has been noted in numerous reports on fillers in polymers. Guth [7] did mention a possibly related observation that low volume fractions of a filler may decrease the tensile strength of rubber, but gave no details. Then, again, the toughening of rigid polymers with a rubber microphase might be regarded as a related phenomenon but involving particles which are softer than the matrix [8, 9]. Analogies of this kind make further work desirable to explore the range of conditions in which the "minimum" effect occurs. In the present work the previously studied cross-linked polymeric matrix, made by photopolymerization of dimethacrylate monomers, was retained because of its practical importance in the restoration of teeth. Some modification of the matrix is made by increasing cross-link density by γ-irradiation. However, the main purpose of the present work was to extend the investigation to include additional fillers.

2. Experimental procedure

Two dimethacrylate monomers, i.e. a stoichiometric adduct of bisphenol-A and glycidyl methacrylate, bis-GMA (75 wt %) and triethylene glycol dimethacrylate (25 wt %) were mixed (Polysciences, Warrington, Pennsylvania) dl-Camphoroquinone (0.2%) and *N,N*-dimethylaminoethyl methacrylate (0.1%) were added as photosensitizers (Aldrich, Milwaukee, Wisconsin). The mixtures were used within 3 days, after storage in the dark. Weighed filler was spatulated into the monomer in stages, with intermittent heating, to give a smooth paste which was degassed in vacuum. Generally a pestle and mortar were used for spatulation, but for more direct comparison with a previous procedure some pastes were mixed using a glass rod [6]. Sedimentation was negligible because of the high viscosity of bis-GMA. Some characteristics of the fillers are given in Table I. Two of the fillers had been treated with a silane coupling agent. For comparison, this was removed by "ashing", i.e. by heating until thermal decomposition of the silanated surface was complete. The hydroxyapatite was made by crushing a sintered specimen.

Freshly prepared mixtures were confined with transparent adhesive tape, at the lower end, in holes (length = 7.0 mm, diameter = 5.5 mm) drilled through a block of polytetrafluorethylene. The mixtures were exposed (60 sec) from one side to visible light (400 to 600 nm) at an incident intensity of 1200 W m^{-2} (Command Lamp, Sybron Kerr, Romulus, Michigan). After polymerization specimens were exposed for a further 60 sec from the other, previously unexposed, end. They were stored for several days at room temperature before testing.

Hardness measurements were made using a Vickers diamond pyramidal indentor (Kentron Hardness Tester) on specimens polished to 0.3 μm. A load of 600 g was applied for 60 sec and produced indentation diagonals of length 0.15 to 0.3 mm, sufficient to avoid

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TABLE I Characteristics of fillers

Name	Source	Surface treated	Density ($g\,cm^{-3}$)	Particle size (μm)
Lithium aluminium silicate	L.D. Caulk Co. Milford, Delaware	yes	2.6	< 50
Lithium aluminium silicate	as above	no (ashed)	2.6	< 50
Silica (IMSIL A-10)	Illinois Minerals Cairo, Illinois	yes	2.65	< 20
Silica (IMSIL A-10)	as above	no (ashed)	2.65	$< 20 \times 10^{-3}$
Tribasic calcium phosphate (C127)	Fisher, Fair Lawn, New Jersey	no	3.2	$< 60 \times 10^{-3}$
Hydroxyapatite	Calcitek, San Diego, California	no	3.2	$< 60 \times 10^{-3}$

variations due to particulate microstructure. The surface zone was softer because of retardation of polymerization by oxygen. Hardness values were determined from six indentations on specimens which had been ground to their mid-section before polishing.

Fracture surfaces, made by bending notched specimens [6], and also polished surfaces were coated with a gold–palladium alloy and examined by scanning electron microscopy (SEM, ETEC U-1, Perkin Elmer, MD).

In some experiments polished photopolymerized specimens were γ-irradiated in air using a ^{137}Cs source: dose rate = $0.8\,Mrad\,h^{-1}$; ambient temperature = 40° C. These specimens were removed periodically from the source and further hardness measurements were made. The specimens were repolished in order to demonstrate that there was no difference between surface and bulk hardness.

3. Results

The size and shape of the larger filler particles could be judged by SEM examination of polished surfaces of photopolymerized specimens. Results for the silicate fillers were similar to those reported previously [6] and are not reproduced here. Hydroxyapatite particles are shown in Fig. 1a. Occasionally a gap was seen between the particles and the polymeric matrix. This was on the side remote from the direction of polish and is, predominantly, an artefact of polishing. The hydroxyapatite particles include small voids (Fig. 1b). No microstructure could be detected for the colloidal particles of silica or for the tribasic calcium phosphate.

Fracture surfaces show that large filler particles can initiate formation of a linear feature on the side which was remote from the advancing crack during fracture (Fig. 2). In the case of the fillers of colloidal dimensions there is evidence of aggregation (Fig. 3). Aggregates may cause formation of linear features (Fig. 3b) and also parabolic markings (Fig. 3c).

Plots of hardness number against volume fraction of filler are shown in Figs 4 to 6. A standard deviation bar is shown except in cases where this is smaller than the symbol used to represent the mean value. Despite variations in particle size, shape, and surface, all six fillers gave composites with a minimum in indentation hardness at a volume fraction in the range 0.03 to 0.05. However, the decrease in hardness varies considerably, from 5 to 34%.

Hardness can be increased by γ-irradiation to a plateau value which is the same for unfilled specimens and for specimens containing a small amount of the silanated silicate (Fig. 7).

The results in Fig. 7, for unirradiated specimens,

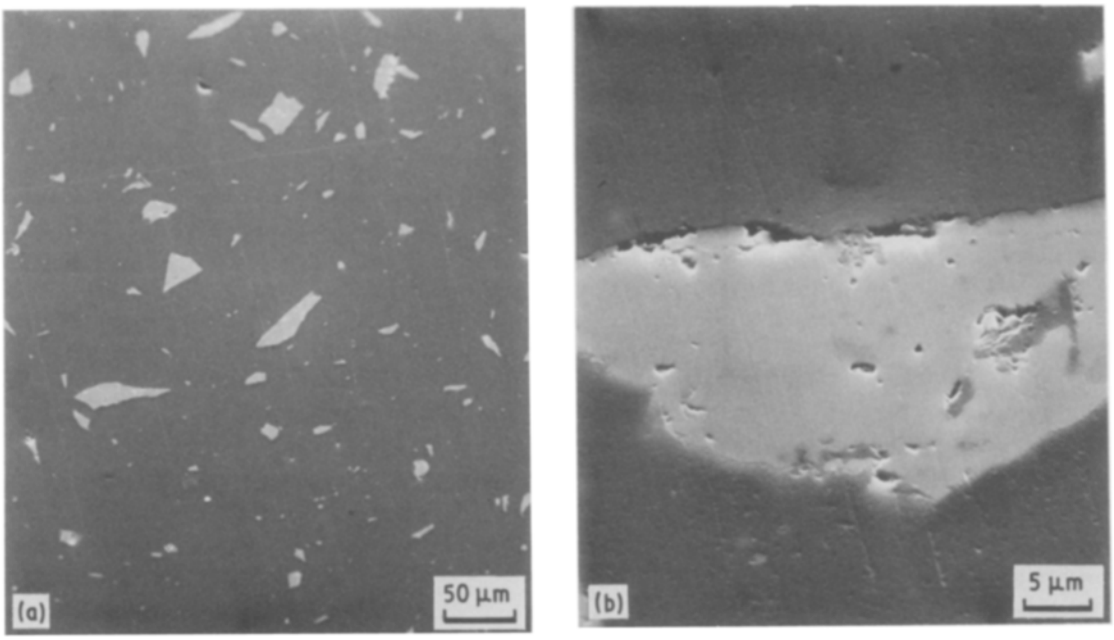


Figure 1 Polished sections for polymerized specimens containing hydroxyapatite (volume fraction = 0.05).

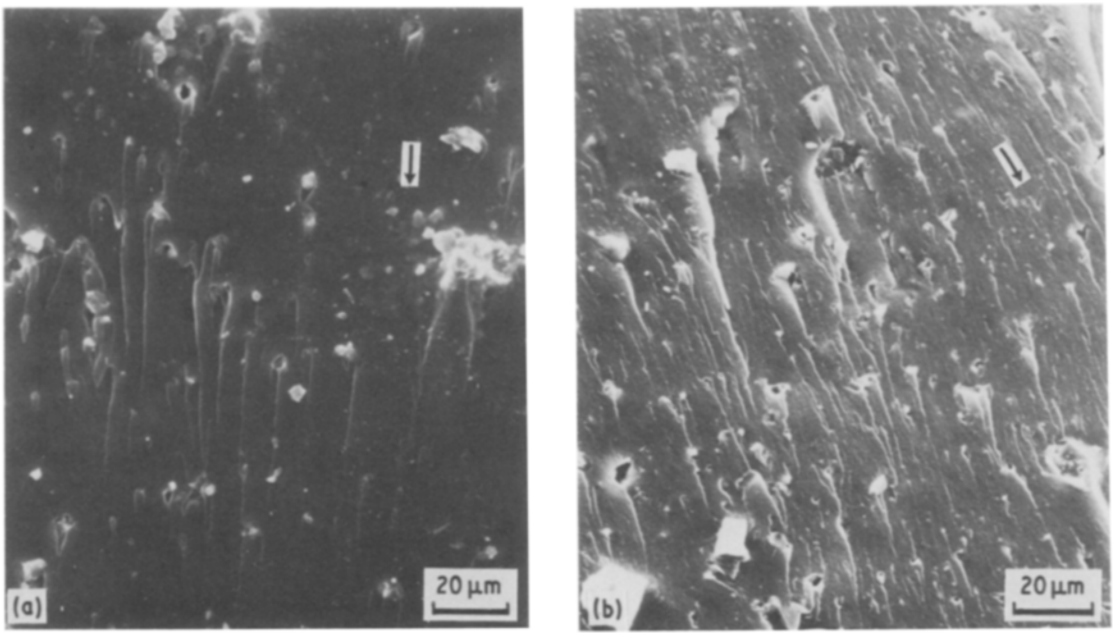
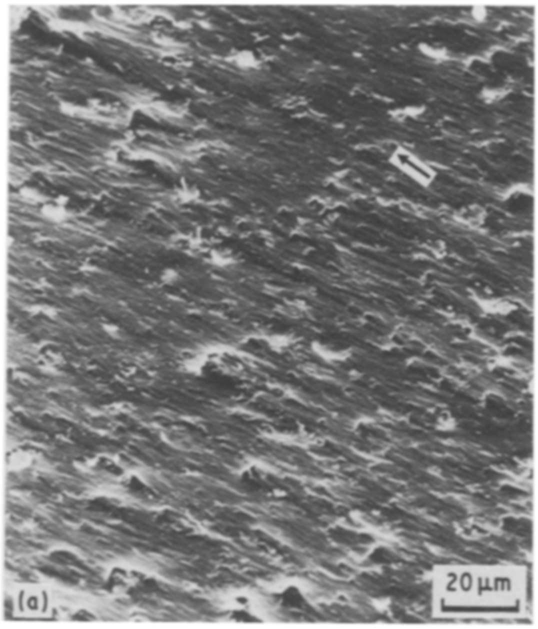


Figure 2 Fracture surfaces of specimens containing large particles (up to 60 μm): volume fraction of filler = 0.03; (a) unsilanated silicate; (b) hydroxyapatite.

also provide evidence that results are insensitive to the method of mixing (Table III). Earlier results have been included in Table III but they are not strictly comparable because specimens were conditioned at a higher temperature before testing, i.e. at 40° C.

4. Discussion

When a material is strained, a rigid inclusion may act as a stress concentrator [10]. In the case of linear polymers in the glassy state, it has been found that a tensile strain may result in yielding accompanied by stress-whitening due to crazing [11]. Yielding was initiated in polystyrene even at the lowest volume fraction (0.08) of filler which was studied [12]. In contrast, yielding was not reported in earlier studies which were of a similar kind, but which involved a cross-linked (epoxy) glassy network [13]. Such a difference is not



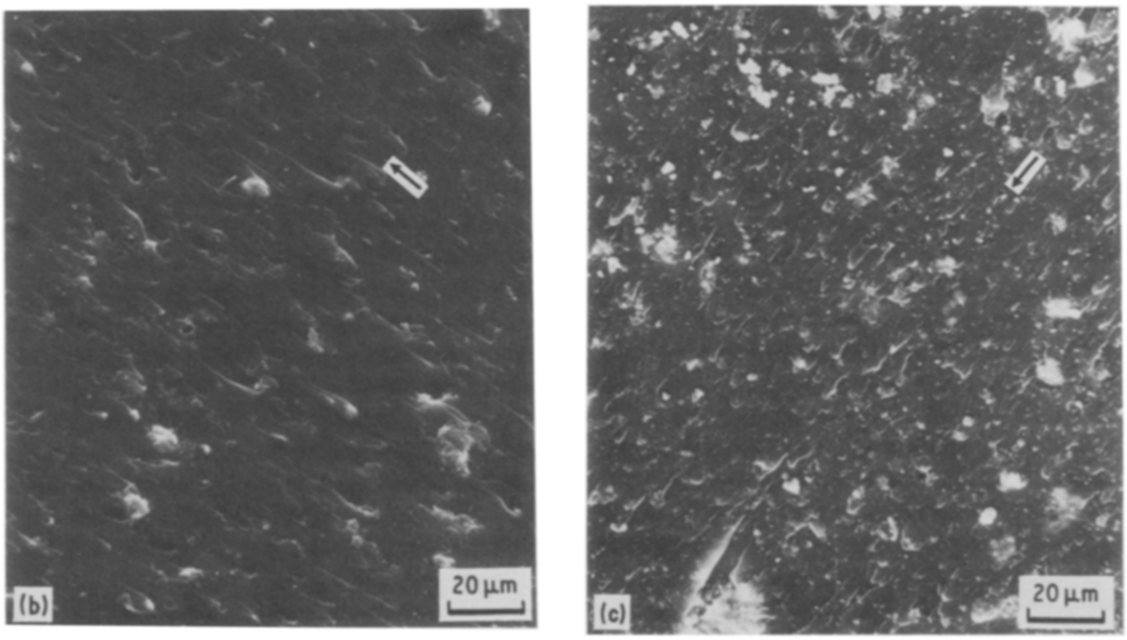


Figure 3 Fracture surfaces of specimens containing small particles (< 20 nm): volume fraction of filler = 0.03.

TABLE II Influence of fillers on Vickers hardness number

Filler	Volume fraction at minimum	% Decrease in VHN*
Silicate (surface treated) [6]	0.03–0.05	10
Silicate (surface treated)	0.05	34
Silicate (ashed)	0.05	7
Silica (surface treated)	0.03	16
Silica (ashed)	0.03	18
Tribasic calcium phosphate	0.03	13
Hydroxyapatite	0.03	5

*100[VHN (no filler) − VHN (at minimum]/VHN (no filler).

unexpected, inasmuch as crazing depends on long-range macromolecular movements which are limited by cross-linking [14]. How is yielding possible in the case of the cross-linked networks studied in the present work? One possibility is that a localized failure occurs by separation at the interface between filler particles and the polymeric matrix, i.e. by dewetting [2, 15]. However, no evidence was found for such an effect. For example, no increase in turbidity was observed after yielding, such as might be expected from the presence of voids. Neither does it seem likely that dewetting would occur with each of the fillers investigated, especially in those cases where the particle surface had been treated with a silane coupling agent chosen to promote bonding to the polymeric matrix. A second possibility is that yielding might occur by simple localized microcracking, such as has been observed in some brittle materials tested for indentation hardness [16], but this was not detected experimentally. Therefore, a third possibility seems more likely that, notwithstanding cross-linking, plastic deformation of the matrix does occur because of stress concentrations in the vicinity of filler particles. Fractographic evidence for such localized plastic deformation is obtained in the case of large filler particles which exhibit rounded fibrous features which have been attributed previously to a process involving localized plastic deformation [17] (Fig. 2).

The possibility of localized plastic deformation seems less surprising in the light of evidence that the networks considered here are not highly cross-linked throughout. Rather they seem to comprise more highly cross-linked particles in a lightly cross-linked matrix [18]. This matrix can be cross-linked more highly by exposure to γ-rays, as evidenced indirectly by an increase in indentation hardness. Eventually, at the highest dose, there was no difference in hardness between specimens made with and without filler. This finding is consistent with the idea that the softening effect is limited to lightly cross-linked networks. However, this idea could not be extended further to account for the considerable variations in the degree to which hardness is depressed, as shown in Table II. Presumably there are other uncontrolled variables which predominate.

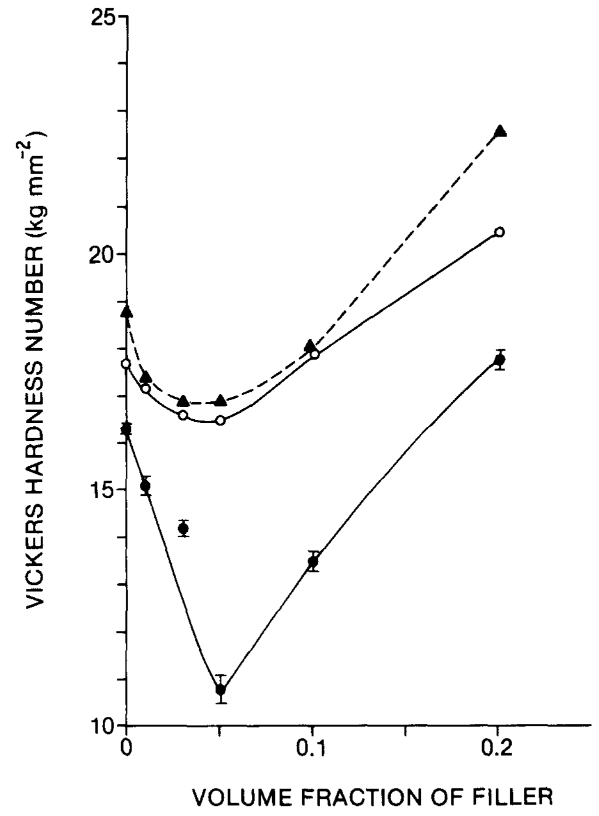


Figure 4 Influence of a silicate filler on Vickers hardness of a polymeric network: (●) silanated lithium aluminium silicate; (○) unsilanated lithium aluminium silicate (▲) silanated lithium aluminium silicate, from [5].

The most striking uniformity found in the present work is that the minimum value of hardness occurs in a narrow range of volume fractions of filler, even though wide variations were made in particle size and surface characteristics (c.f. Table I and II). Apparently neither shape factors of the more or less isometric particles listed in Table I, nor the degree of particle–matrix bonding is especially important. What is important is that eventually, for all the fillers, the yielding associated with isolated particles is offset by a normal hardening mechanism. Some quantitative insight might be sought by consideration of various theoretical equations which predict the dependence of a property (P), such as viscosity or elastic modulus, on the volume fraction (ϕ) of rigid particles; for example Equation 1, in which P_0 is the value of the property for

TABLE III Influence of mixing procedure on hardness, using silanated silicate (volume fraction = 0.03)

VHN, without filler	Stirring rod		Pestle and mortar	
	VHN (kg mm^{-2})		VHN (kg mm^{-2})	
	18.8 ± 0.1	16.0 ± 0.1	16.3 ± 0.1	15.5 ± 0.2
% Decrease in VHN	10	18	13	14
Source (Fig.)	1 [5]	7b	4	7a

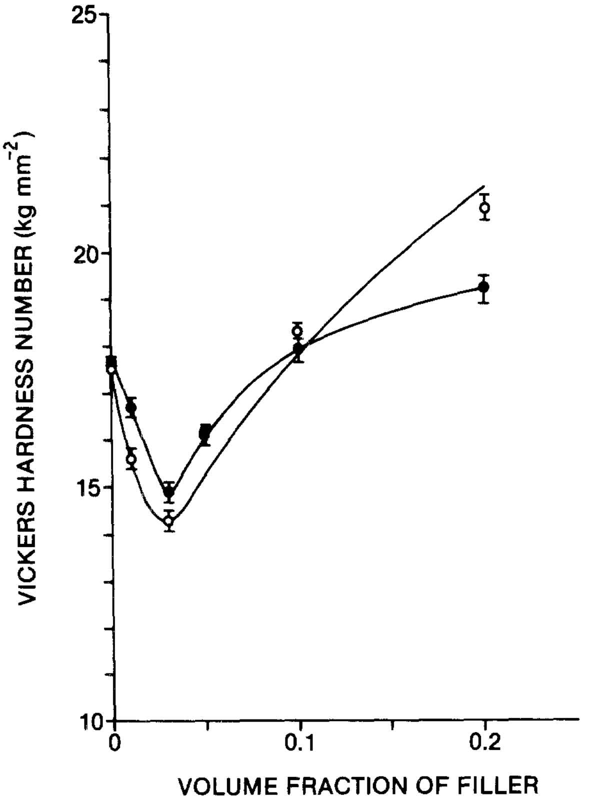


Figure 5 Influence of a silica filler on Vickers hardness of a polymeric network (●) silanated silica (○) unsilanated silica.

the unfilled polymer and A and B are coefficients which include a dependence on shape factor and on particle–matrix bonding.

$$P = P_0 (1 + A\phi + B\phi^2) \quad (1)$$

The particles may be supposed to be acting independently in the region where the contribution from the square term is negligible, i.e. where P/P_0 has a linear dependence on ϕ. Reference to viscosity data indicates this region to be $\phi \leqslant 0.07$ [19]. The minimum in hardness is observed at a lower value i.e. $\phi = 0.03$ to 0.05 (Table II). Presumably it would be more pertinent

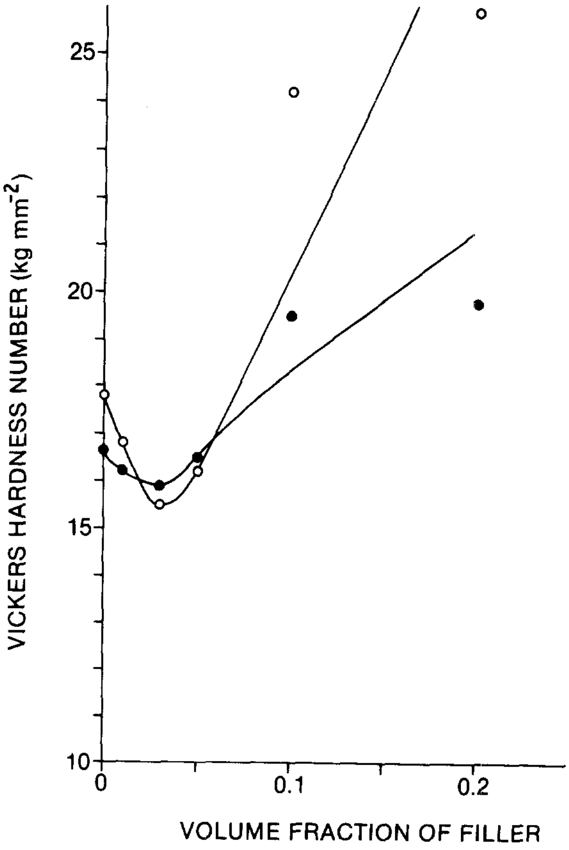


Figure 6 Influence of calcium phosphate fillers on Vickers hardness of a polymeric network: (●) hydroxyapatite (○) tribasic calcium phosphate.

to make this comparison by reference to elastic modulus data but these appear to be too imprecise.

5. Conclusions

1. The indentation hardness of a cross-linked network has a minimum value at a volume fraction of filler in the range 0.03 to 0.05.

2. The minimum was found for all six fillers investigated, despite wide variations in the size of the

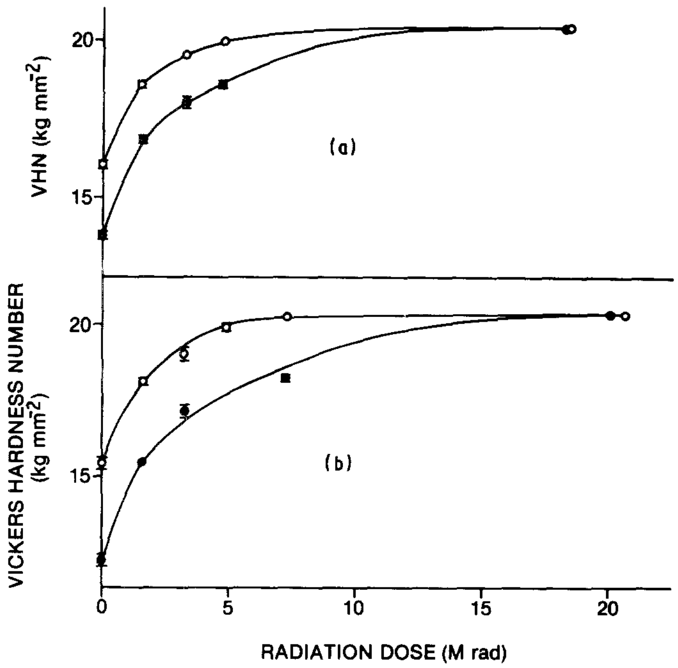


Figure 7 Influence of γ-irradiation on Vickers hardness of polymeric networks, with and without a filler: (a) mixed with pestle: (b) mixed with stirring rod. (○) Without filler (●) with 3 vol % silanated silicate filler.

particles and in the nature of their surfaces. To this extent, the effect appears to be general in respect of filler variations.

3. The effect is not general in respect of properties of the network. It is not observed in specimens which have been cross-linked more highly by γ-irradiation.

4. Results are consistent with the idea that particles act as stress concentrators which may result in localized plastic deformation and, thereby, to a decreased indentation hardness.

Acknowledgements

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