

The best fit to the data for the 2000/200 samples has been calculated previously⁶ for the composite rod model⁹ using the parameter values $l_c \sim 9$ nm, $E_c \sim 9 \times 10^{10}$ N/m² and $E_a \sim 10^{10}$ N/m². These theoretical lines are shown on *Figure 1* and can be seen to adequately represent the data for all the mixtures.

In summary, the data show that within the approximation of the composite rod model, the modulus of the amorphous layer, E_a , can be assumed constant and equal to 10^{10} N/m².

Effect of γ -irradiation on chemically crosslinked poly(dimethyl siloxane)

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INTRODUCTION

The processes of radiation or chemical crosslinking in poly(dimethyl siloxane) (PDMS) have been extensively studied by many workers¹⁻⁴. The crosslink formation efficiency in PDMS introduced by a chemical agent (e.g. benzoyl peroxide) was found to decrease markedly as the peroxide concentration increased, apparently tending to zero at high values. Therefore it is not possible to obtain high crosslink densities by chemical means. On the other hand the crosslink density of networks formed by radiation can reach very high values. The effect of γ -radiation on rubbers that have already been chemically crosslinked has not been extensively studied. Bopp and Sisman⁵ studied the effect of radiation on natural rubber chemically vulcanized by sulphur. No data have been published for PDMS. In this Note we report the effect of γ -radiation on a series of PDMS samples that have been crosslinked using different amounts of benzoyl peroxide. The effect of temperature on the rate of formation and quality of the networks during the chemical curing has also been studied.

EXPERIMENTAL

The material used in this study was a

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RESULTS AND DISCUSSION

The variation in crosslink density with benzoyl peroxide concentration is shown in *Figure 1*. It is worth pointing out here that the two stage heating (80° and thereafter 150°C) plays an important role especially in the sample quality. Previous curing methods²⁻⁴ in which samples are first held at $\sim 120^\circ\text{C}$ for a few minutes before increasing to $\sim 150^\circ\text{C}$ for 24 h, with or without pressure are not always successful. Bubbles of gas evolved during the crosslinking process are trapped in the network, especially when the sample is thick and the crosslink density high. This can be partly avoided by pressure control but the samples are then not uniform in thickness and their surfaces not smooth. Using the two stage curing the crosslink density seems to be independent of the sample thickness, no bubbles are present for any thickness or any peroxide concentration and the surfaces are extremely smooth with a very high degree of reflectivity.

Following an analysis described elsewhere⁹ the crosslink density $\langle n \rangle^{-1}$ can be expressed as a function of the peroxide concentration C :

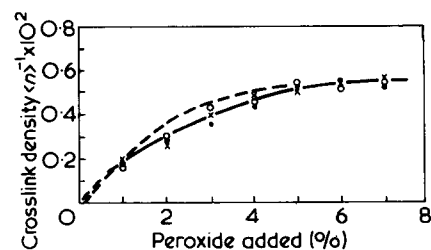


Figure 1 Crosslink density as a function of benzoyl peroxide concentration. —, corresponds to experimental data; - - -, to equation (1). ●, Swelling; ○, ball-bearing indentation; X, extension

linear PDMS 5273-11-1 provided by ICI Ltd with molecular weight 7.7×10^4 as determined by g.p.c. techniques. Benzoyl peroxide was used for the chemical vulcanization. Accurately determined weights of peroxide dissolved in dichloromethane were added to PDMS gum. After thorough mixing the solvent (CH_2Cl_2) and dissolved gases were removed by putting the mixture under vacuum and heating to 44°C (boiling point of solvent $\sim 41^\circ\text{C}$). Square moulds containing the samples were placed in a circulating air oven at 80°C for a few hours. Then the temperature was increased to 150°C and held constant for 24 h.

When the sheets were removed from the moulds they were exposed to γ -radiation in the ^{60}Co facility at Salford University. Doses ranged from 3.5 up to 500 Mrad at rates of 3.5 or 0.01 Mrad/h. The samples were annealed at 50°C for 12 h in order to remove any undesirable crystallinity⁶. The crosslink density was estimated from ball-bearing indentation^{7,8}, extension and swelling measurements^{2,3}. The samples were characterized by the crosslink density $\langle n \rangle^{-1}$, where $\langle n \rangle$ represents the average number of monomer units between crosslinks, because this gives a clear picture of the network at the molecular level. It also has the advantage of providing a common base for comparison of the three types of experimental measurement.

$$\langle n \rangle^{-1} = \alpha C - \frac{\alpha^2 + b}{2} C^2 + \frac{\alpha^3 + 3\alpha b}{6} C^3 \dots \quad (1)$$

or alternatively

$$\langle n \rangle^{-1} = \alpha C - \frac{\alpha^2 + \alpha b}{2} C^2 + \frac{\alpha^3 + 3\alpha^2 b + \alpha b^2}{6} C^3 \dots \quad (2)$$

Equations (1) and (2) correspond to the empirical equations for the probability of crosslink formation, P , per chain and per unit per cent concentration:

$$P = \alpha - bC \quad (3)$$

$$P = \alpha \exp(-bC) \quad (4)$$

respectively expressing formation probabilities decreasing linearly and exponentially with concentration. α and b are constants determined from the experimental data. In this particular rubber the following values have been found to give the best fit of equations (1) and (2) to the experimental data: $\alpha = 1.78 \times 10^{-3}$; $b = 2.94 \times 10^{-4}$ for equation (1) and $\alpha = 9.45 \times 10^{-4}$; $b = 2.15 \times 10^{-2}$ for equation (2). The broken line in *Figure 1* represents the fit to equation (1).

The maximum crosslink density appears to be about 0.54×10^{-2} corresponding to a minimum average of about 200 monomer units between crosslinks. To increase further the crosslink density the samples have been exposed to radiation. The radiation of already

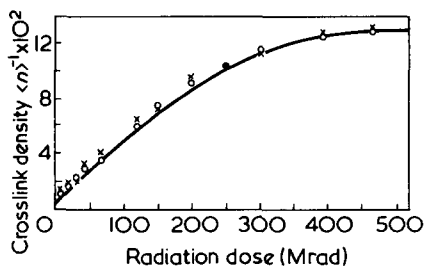


Figure 2 Crosslink density variation with radiation dose. — for pure PDMS. X, \circ PDMS crosslinked by 3% peroxide; X, swelling; \circ , ball bearing indentation

chemically crosslinked rubbers is a useful technique for some practical purposes. It seems to be much easier to control the formation of crosslinks by radiation when the starting material is in sheet form. Samples so prepared were always very clear and extremely uniform in thickness, both of which properties can be controlled more easily in the moulding and vulcanization stage. However the addition of peroxide did cause slight yellowish colouration. This tended to decrease when the samples were subsequently irradiated and in this way the problem of bubble formation was also overcome. This is particularly important when relatively large samples are required, for instance for optical or ultrasonic experiments where good homogeneity is essential. PDMS crosslinked by different peroxide concentrations was exposed to different radiation doses and the crosslink density was estimated as before. *Figure 2* shows the crosslink density as a function of dose for pure PDMS (solid line) and for PDMS previously crosslinked by 3% peroxide. All experimental points are values from swelling and ball-bearing indentation measurements. Because the number of crosslinks introduced chemically is very low in comparison with those by radiation, the difference between data of different peroxide concentrations can fall within the experimental error, especially at higher doses. It can be seen that, in qualitative terms, the data show a similar dependence on dose, but that the chemically treated samples are always slightly above the pure PDMS.

It seems that the radiation-induced crosslinks are simply added to those produced by peroxide. This is borne out by data from the other samples as can be seen in *Figure 3*, a comprehensive diagram in which crosslink density is plotted *versus* peroxide concentration and radiation dose for seven samples ranging from 0 to 6% peroxide concentration. Each of the solid lines corresponds to a sample of given peroxide content and shows the increase in crosslinking with radiation. The broken lines have been drawn parallel to the lowest one, which corresponds to zero dose (*Figure 1*), in order to clarify the graph. With the exception of the lowest, these broken lines do not represent experimental loci, as do the full lines.

In all samples the deviation from the linear dependence of crosslink density on radiation dose occurs at ~ 160 Mrad. The mechanism of formation appears to be the same for the two methods. Thermal decomposition of peroxide leads to free radicals which can in turn induce

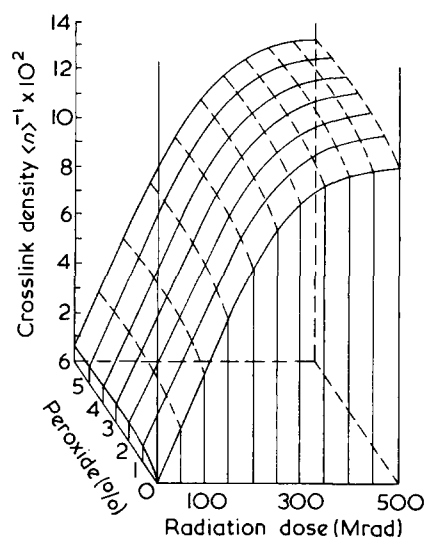


Figure 3 Three dimensional diagram representing the crosslink density of networks formed by a combination of chemical and ^{60}Co γ -radiation curing

the formation of free radicals on the polymer chain thus causing crosslinking. In the case of radiation, the radicals are directly formed on the polymer. Analysis of the evolved gases shows that the radicals are formed by the fracture of Si-C and C-H bonds. The saturation of the crosslinking at high peroxide concentrations and high radiation doses can be explained on a model⁹ that takes into account the constraints on chain flexibility caused by the crosslinks.

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