Effect of filler on network behaviour at high elongation

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INTRODUCTION

The reinforcement of elastomers with particulate fillers is a process of great practical and technological importance. The object of reinforcement is mainly to improve the tensile properties, the moduli, and the abrasion resistance of rubbers.

In spite of the existing data concerning stress–strain measurements of reinforced networks[1–7] even at high elongation, little work has been done in exploiting the filler presence in order to explain the main features observed. A general treatment to study the stress–strain behaviour of reinforced networks is to use relations based on a statistical theory for unfilled networks introducing a filler-concentration-dependent elastic modulus[6,8]. Unfortunately the applicability of the empirical and theoretical expressions for the elastic modulus is very limited since there are considerable deviations from the experimental data, mainly at high concentrations. Details of the existing formulae for reinforced rubber can be found in the Kraus review[8].

Although the stress–strain relationship of a reinforced network looks like being a complicated one, plots of $\phi = f/2(\lambda - \lambda^{-2})$ against λ^{-1}, where f is the stress referred to the original (unstressed) cross-sectional area and λ is the extension ratio (l/l_0), l_0 and l being the length of the specimen in the unelongated and elongated states, are very similar for unfilled and filled networks. At low and moderate extensions the behaviour of an unfilled network can be described in terms of two constants C_1 and C_2 by the formula

$$\phi = \frac{f}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \qquad (1)$$

The same equation can be used also in the case of filled networks[2], where C_1 is related to the number of the ordinary network chains and of the additional chains produced by bonds to the filler.

At high elongation, however, departures from equation 1 occur and each curve goes through a minimum; thereafter ϕ increases rapidly with further extension.

The occurrence of an upturn in the stress–strain isotherms of rubbers at relatively high extensions is a well known phenomenon and two interpretations for it have been suggested. The first introduced by Flory[9] is based on the strain-induced crystallization[10,11] and the second is based on the limited chain extensibility of networks[12,13].

The purpose of this note is first, to provide experimental data supporting the interpretation that the onset of the upturn in the conventional stress–strain isotherms of filled networks is associated with some sort of 'non-Gaussian' behaviour, second to introduce a qualitative relationship between either the elongation λ_{min} at which the stress goes through a minimum or the λ^* at which the deviation due to finite extensibility reaches a value of 2.5% of C_1[14] and the filler concentration.

EXPERIMENTAL

The PDMS used in this study was kindly provided by ICI (S273-11-1). The molecular weight was 7.7×10^4 as determined by g.p.c. techniques. Samples used were cut from sheets of vulcanized PDMS rubber about 0.1 cm thick. The sheets were prepared by mixing 1.5 parts by weight of benzoyl peroxide dissolved in dichloromethane with 100 parts by weight of linear PDMS. After a thorough mixing the mixture was put under vacuum for several hours in order to remove the dissolved gases which normally exist in commercially available siloxanes and the solvent (CH_2Cl_2) which is evaporated easily due to the low boiling point (~41°C).

Different amounts of fine silica were used (also provided by ICI (Aerosil 200)). The spherical filler particles have an average diameter of 12 millimicrons and a surface area 200 ± 25 m^2/g.

Vulcanization was carried out by heating under pressure at 1.3 tons/in^2 for 15 min at 130°C followed by 24 hours at 150°C in an air circulating oven.

Stress–strain measurements were made in simple extension on shaped specimens having approximate dimensions $3.0 \times 0.32 \times 0.1$ cm at the free area cut from the sheets using a suitable die. Reference lines for the length measurements were marked on the central portion of each sample. The length between the two marks was then measured to ±0.01 mm with a cathetometer.

The stress–strain isotherms were obtained in the usual manner[15,16] at room temperature (~23°C) and under nitrogen atmosphere. The applied force was increased in stepwise fashion and the elongation measured at a time interval after application of the load, when no further detectable variation was observed.

The crystallinity of the samples under stress was examined by X-rays. A Phillips apparatus at 40 kV and 20 mA with $\lambda_{C\alpha} = 1.42$Å was used, and two flat-film cassettes were placed in the forward and in the back-reflection position[17]. The samples were loaded at room temperature at elongations corresponding to their particular λ_{min} for each filler concentration.

RESULTS AND DISCUSSION

Stress-elongation measurements as above mentioned for PDMS networks with different filler concentration are illustrated in *Figure 1*, where the function $\phi = f/2(\lambda - \lambda^{-2})$ is plotted versus λ^{-1} at room temperature (~23°C). All of the curves show that at low and moderate extensions there is a region where the stress–strain behaviour can be described in terms of the two parameters C_1 and C_2 (equa-

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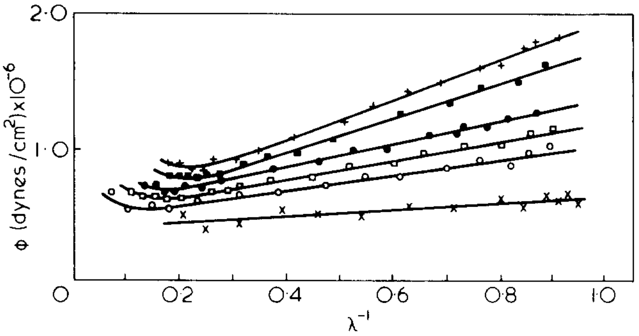

Figure 1 'Mooney' plot of stress-elongation data for different filler concentration (X 0%, ○ 0.5%, ■ 7.5%, ● 10%, □ 12.5% and +15% per weight) at room temperature

tion 1). At higher extensions (smaller λ^{-1}) departures occur and each curve goes through a minimum, the value of ϕ thereafter increasing with further extension. *Figure 1* also shows that both λ_{min} and λ^* correspond to larger values of λ^{-1} for more highly filled networks, and that C_2 expressed by the slope of the straight lines increases with the filler concentration.

Approximate estimates of λ^* and λ_{min} from *Figure 1* are plotted in *Figure 2*. Both λ^* and λ_{min} are seen to decrease linearly with increasing filler concentration. Almost the same dependence was found in the data for natural rubber networks reinforced with black carbon reported by Mullins and Tobin[5].

The reinforcement effect of PDMS is attributed to additional crosslinks according to Bueche[1] or to physical mechanical effects according to Charlesby and coworkers[3]. Since both mechanisms seem to be equally possible one can accept both of them to occur in any percentage, a fact which does not change the reinforcement effect to be used in explaining the upturn of the stress–strain curves when interpreted in terms of the finite chain extensibility.

Let us assume a simple picture of a reinforced network. There are the usual crosslinks between chains, extra crosslinks between network chains and filler particles and relatively weak physical forces between chains and filler. Since the average chain length becomes shortened by the introduction of extra crosslinks, the values of extension ratio λ^* at which the chain-limited extensibility starts to be important are lower for higher filler concentration, in agreement with the experimental results. It is also necessary to consider the influence of the extra crosslinks, and the physical forces between the chains and the filler, on the onset of crystallization. On one hand extra crosslinks and physical forces reduce the chain mobility[18], they impede, to a certain extent, the relative displacement of chain segments required for the formation and growth of nuclei; on the other hand the presence of the filler reduces the amount of deformable material per unit volume, hence the rubbery component must sustain a higher local strain for a given macroscopic strain. This will result possibly in a greater tendency to crystallize as the filler concentration increases. The first of these two competitive factors appears to be predominant for PDMS networks. The absence of any crystallization in the X-ray patterns of the stressed filled networks at elongations $\lambda = \lambda_{min}$ obtained by the authors can be considered as direct experimental evidence supporting this conclusion. At higher elongations the effect of crystallization on the stress–strain behaviour of the networks could be important even though superimposed on that due to finite chain extensibility.

Diagrams such as *Figure 2* can be useful in predicting approximate values of λ^* or λ_{min} if an extrapolation to zero filler concentration assumed is valid. For the chemically crosslinked PDMS with a crosslink density $\langle n\rangle^{-1} = 0.28 \times 10^{-2}$ [15] ($M_c = 26\,400$), where $\langle n\rangle$ is the average number of monomer units between crosslinks, λ^* and λ_{min} must be approximately 7.5 and 9 respectively (extracted from *Figure 2* by extrapolation to zero concentration). Therefore, for a PDMS network with crosslink density in this region deviations from the straight line of the stress-elongation curves (*Figure 1*) could be expected at elongation λ not lower than 7.5. Such high elongations are extremely difficult to obtain for PDMS networks formed chemically or by γ-irradiation, since the elongation breaking point is lower. Based on these figures the deduction of Mark, Kato and Ko[11] that the failure to observe any upturn in the stress at high extensions (5.4 for PDMS and 7.4 for poly(ethyl acrylate) at 50°C and 30°C) strongly supports the idea that the upturn is due to strain-induced crystallization and not to the limited network extensibility, should be reconsidered.

It so happens that the region of study in which the non-Gaussian theory based on the limited chain extensibility becomes relevant coincides roughly with the region where crystallization develops. The behaviour of rubbers at high extensions has been comparatively little investigated so that a clear description of the sequence of the two phenomena namely crystallization and non-Gaussian behaviour – and their relative importance is still not clear. The two different interpretations have been supported by a number of investigations and have been extensively discussed in many papers.

It is worthwhile to mention here the work of Smith, Greene and Ciferri[19], using X-ray diffraction and other methods of detecting the onset of crystallinity, which has shown quite definitely that the initial upturn in the force-extension curve is a genuine non-Gaussian effect, unrelated to crystallization, though at higher extension complications associated with crystallization were observed.

Further experimental data on different filled networks focussing attention on the strain determination at which crystallization starts to be apparent should be very useful.

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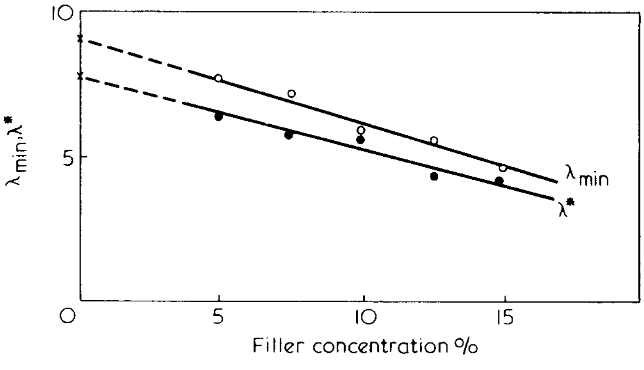

Figure 2 Plot of λ^* and λ_{min} of PDMS networks against filler concentration

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Letters

Observations of charge on nascent poly(vinyl chloride) particles in monomer

In the early stages of the polymerization of vinyl chloride (VCM) within monomer droplets, the precipitated polymer forms particles which are colloidally stable. We describe here an experiment to determine whether electrostatic charge resides on the surface of the particles.

A stainless steel pressure vessel, designed for measurement of surface and interfacial tensions of pendent drops of liquid VCM, was modified to enable an electrode to be introduced into a vinyl chloride drop. A gold-plated, needle-shaped electrode was insulated in a PTFE block, leaving only the tip protruding, and mounted in the top of the pressure cell. A 'D'-shaped steel plate (0.4 mm thick), with a 3 mm hole drilled through, was mounted 3 mm below the electrode tip. Water and liquid VCM were introduced into the cell through a glass capillary tube (0.5 mm bore, 6 mm O.D.) fitted to a non-return ball valve in the base of the cell. The electrode, glass capillary and hole in the plate were vertically aligned, the plate being 4.5 mm above the tip of the capillary. All steel surfaces within the cell had previously been gold-plated.

The cell was first filled with water until the level was above the top of the observation windows, then pressurized with nitrogen (~13 bar). Liquid VCM, containing 0.2% w/v dicetyl peroxydicarbonate as initiator, was then admitted, forming pendant drops at the capillary tip before detaching and rising to the water surface. By varying the drop size and rate of admission of VCM, it was possible to pass drops through the hole in the plate and trap them between the plate and electrode. In this way an isolated conical drop (volume ~0.03 cm^3) was held between the plate and electrode tip as shown in *Figure 1*. Polymerization was initiated within this drop by heating the cell in a current of hot air. After 90 min, when the cell temperature was 48°C, the drop became turbid and heating was stopped. Polaroid photographs of the drop were taken throughout the experiment (magnification x 5) and, 10 min after heating stopped, a photograph showed that the suspended PVC particles had sedimented sufficiently to leave a clear layer of monomer at the top of the drop. Potential differences of ±1.5 V were then applied between the electrode and the plate and movement of the dispersion/monomer boundary

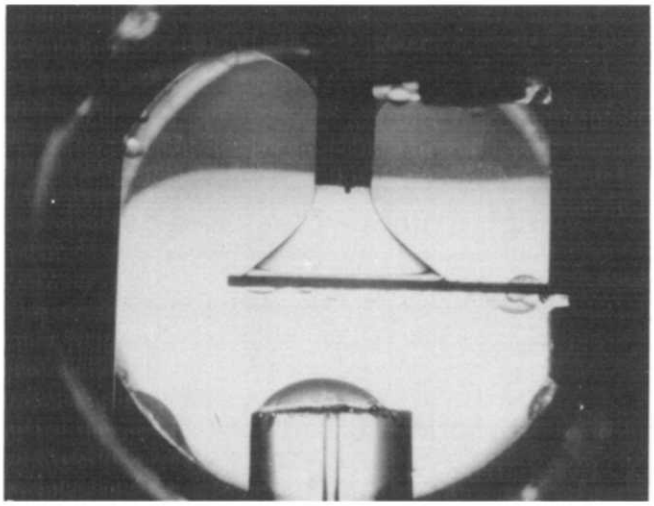

Figure 1 Monomer droplet held between electrode tip and plate in an aqueous medium

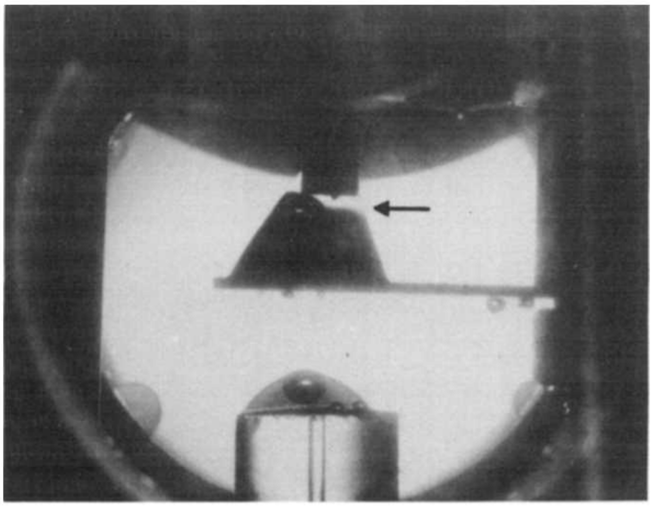

Figure 2 Movement of dispersion/monomer boundary (indicated by arrow) from electrode tip on application of −1.5 V to the electrode tip

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