Relationships between equilibrium swelling in good solvents and the type and concentration of filler

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(Received 12 April 1978; revised 28 June 1978)

The effect of type and concentration of filler on equilibrium swelling of elastomers in solvents has been the subject of numerous investigations. The main aim of these studies has been to shed some light on the interactions which take place between the elastomer and the filler and hence to gain information on possible mechanisms of reinforcement. Along with the experimental work, several groups of investigators have attempted to analyse the problem theoretically; however, these have only been moderately successful. In this paper, it will be shown that the relative modulus or the relative network chain concentration, as a function of filler content for elastomers containing reinforcing fillers can be described using two empirical equations which had been used previously to relate small strain relative modulus and the viscosity of Newtonian suspensions to filler content and hence which appear to be applicable generally.

INTRODUCTION

Measurement of the equilibrium swelling of unfilled elastomers has been widely employed to gain information on the degree of cure. In studies where the effects of both filler type and content on the mechanical behaviour of filled systems are to be investigated, the ideal comparison between the filled and unfilled vulcanizate would be made when both vulcanizates have the same degree of crosslinking. This is all the more true since several studies have shown that the degree of crosslinking has a significant effect on the mechanical behaviour including the failure properties of unfilled vulcanizates[1,2] and there are no reasons to suppose that the effect of degree of crosslinking on mechanical behaviour would be markedly different for a vulcanizate containing a filler. Generally speaking, it is observed that the presence of an active filler reduces the extent of equilibrium swelling as compared to the corresponding gum. However, it is not always clear, in the absence of other information, that the presence of filler has no influence on the number of crosslinks inserted into the system. The relative amount by which the swelling is restricted depends on the 'goodness' of the solvent. For poor solvents only small restrictions are observed whereas with good solvents large restrictions are obtained.

DISCUSSION

Several groups of workers[3–12] have attempted either empirically or theoretically to account for these effects of the type and concentration of filler on the equilibrium swelling of filled vulcanizates; however, such attempts have been only marginally or moderately successful.

Notable exceptions are the work of Rigbi[11] and Sternstein[12] who independently solved the problem, in a rigorous fashion, of the reduction in swelling caused by the presence of an isolated inclusion imbedded in a rubber matrix. The mathematical solution in both cases could not be obtained in closed form but was rather displayed in graphical form. In addition, at attempt was made by Rigbi to extend the results obtained for the isolated particle to the case when several such particles are present. However, in this case, assumptions had to be made about the nature of the distribution of particles within the matrix. For simplicity Rigbi assumed the particles were packed on a cubic lattice.

The results of Rigbi and Sternstein on the swelling behaviour of an isolated spherical inclusion surrounded by a shell of rubber reminds one of the comparable situation which exists with regard to the viscosity of Newtonian suspensions or the relative small strain modulus of a filled vulcanizate. The rigorously deduced limiting law for the relative viscosity of a suspension in the limit of vanishing concentration has been obtained by Einstein[13]. The corresponding limiting law for the relative small strain modulus has been derived by Smallwood[14]. Relationships applicable to higher concentrations have not as yet yielded to solution with the exception of Vand[15] who was able to extend the Einstein result to the case where the effects of doublets on the viscosity of Newtonian suspensions were taken into account.

A rigorous calculation for the effect of the presence of larger aggregates is probably hopelessly complex. Even the rigorous calculation of the properties of a random packed bed of particles has not yet yielded to solution. Hence for real filled systems a description of the relative viscosity[16,17], the relative modulus[2] or the swelling behaviour for finite concentrations must, at the present time, probably rely on the empirical approach.

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* This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration

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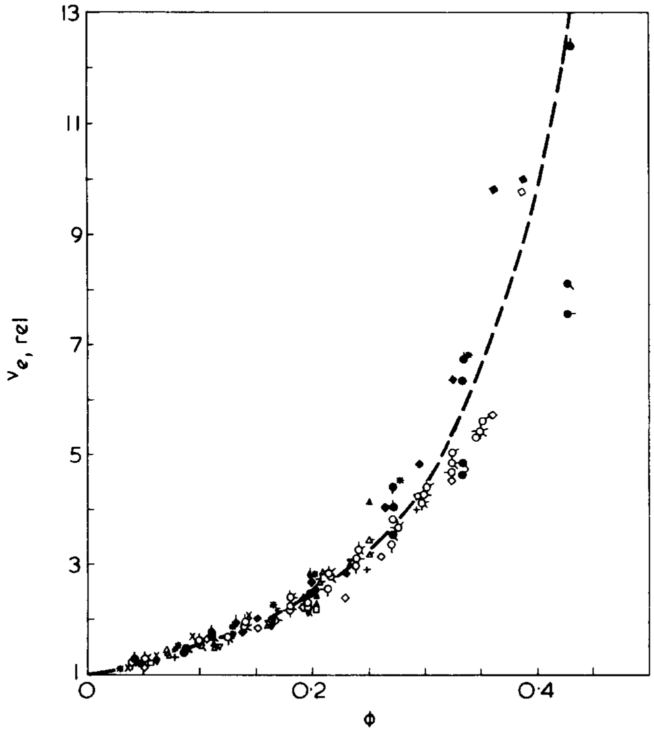

Figure 1 Dependence of relative network chain concentration and volume fraction of filler. △, SAF, ▲, EPC, ■, acetylene, ▽, FEF, □, HAF, ▼, SRF in SBR (ref 3); x, HAF in natural rubber (ref 22); +, HAF in SBR (ref 7): ○ HAF in natural rubber (ref 23). ◇, HAF in natural rubber (by swelling): ◆, HAF in natural rubber (dynamic) (ref 24); *, HAF in natural rubber (ref 5); ●, EPC in natural rubber (ref 25); ⊕, HAF in natural rubber (ref 9). △, SRF and ◈, ISAF in SBR (ref 8). Broken curve is the prediction of equation (2) with $\phi_m = 0.63$

EMPIRICAL RELATIONSHIPS

It has been found that equilibrium swelling behaviour of real systems can be well described over a very wide range of solvent type, filler type, filler concentration, and rubber type by an empirical equation of the Eilers–Van Dijck type[18]. The Eilers–Van Dijck equation was originally proposed to describe viscosity–concentration dependence for slurries. It has been subsequently shown that this general form of equation was also applicable to the viscosity–concentration response up to very high loadings[16] and also to the modulus–filler concentration dependence of filled rubbers[2].

It has been shown previously[2] that the relative response be it relative viscosity, η_r, or relative modulus, G_r, could be described by either of two similar equations: for spherical particles such as glass beads, MT and FT carbon black, etc., the relative response was given by:

$$\eta_r = G_r = \left(1 + \frac{1.25\phi}{1 - \frac{\phi}{\phi_m}}\right)^2 \qquad (1)$$

while for fillers which are composed of permanent aggregates of primary particles such as HAF black, the relative response is given by:

$$\eta_r = G_r = \left(1 + \frac{1.25\phi}{\phi_{\max} - \phi}\right)^2 \qquad (2)$$

where ϕ is the volume fraction of filler in the system and ϕ_m is the maximum volume fraction to which the particles can pack[2]. It is not known why two slightly different equations are necessary depending on the nature of the filler shape; it has, however, been definitely established that two equations are required[2,16,17].

In order to represent equilibrium swelling data for filled rubbers, we set the relative modulus in equations (1) and (2) equal to the relative network chain concentration, $v_{e,\mathrm{rel}}$ which is defined as the apparent network chain concentration calculated for filled system divided by the network chain concentration of the gum. The network chain concentration for the unfilled vulcanizate is calculated in the usual manner using the Flory–Rehner equation[19] with the appropriate value for solvent–polymer interaction parameter, χ_1. The network chain concentration is also estimated using the Flory–Rehner equation and assuming χ_1 is unchanged when filler is present. However, it has been found that the appropriate measure of swelling for filled vulcanizates is ν_2^*, the volume fraction of total vulcanizate in the swollen gel.

We have collected all the swelling data we could find in the literature, (refs 3, 4, 7, 8, 10, 20–24). Generally, information given in the original sources included, nature of the swelling solvent, weight of filler and ν_2. This information was converted to appropriate values of ν_2^* and ϕ. The value of χ_1 was taken either from Kraus'[3] or from Sheehan and Bisio's compilations[20]. If an appropriate value of χ_1 could not be found, the original data were not used.

Figure 1 shows the data for both SBR and natural rubber containing high structure blacks obtained in a variety of solvents and using a variety of curing systems. The symbols employed are listed in the Figure caption along with the original reference; the flags denote variations in the basic recipe as when several curative levels or several solvents were used. The dashed curve is the prediction of equation (2) when $\phi_{\max}$ is assigned a value of 0.63, which is the value appropriate to the random packing of large spheres[25]. As can be seen, the equation describes the experimental data very well. At the higher concentrations there is some deviation from the predicted response but this may be a reflection of the difficulties inherent in mixing large concentrations of active carbon black in unsaturated rubbers.

Of particular interest are the data of Payne[23] who along with measuring the equilibrium swelling of HAF filled natural rubber in n-decane also measured the dynamic behaviour of the dry vulcanizates in shear at 0.1 Hz as a function of the strain amplitude. In the dynamic test, he found that at very small dynamic strains the shear modulus was constant; at intermediate strains the value of the modulus decreases with increasing strain; at very large dynamic strains, greater than about 10%, the shear modulus again levels out and takes on a constant value. The most interesting point here is that the estimate of $v_{e,\mathrm{rel}}$ obtained from swelling (unfilled diamonds in *Figure 1*) is the same as that obtained from the limiting shear modulus obtained at large dynamic strains. The implication is that the same effects which give rise to the decrease in the shear modulus with strain also occur when swelling takes place in a good solvent. We believe that this effort is related almost entirely to dewetting or the separation of the matrix from the filler particle.

An unusual system is HAF filled butyl rubber. Zapp and Guth[26] measured the equilibrium swelling of HAF–butyl vulcanizates as a function of filler content and their data are shown in *Figure 2* as the unfilled circles. Shown as the filled circles are the estimates from the limiting large strain dyna-

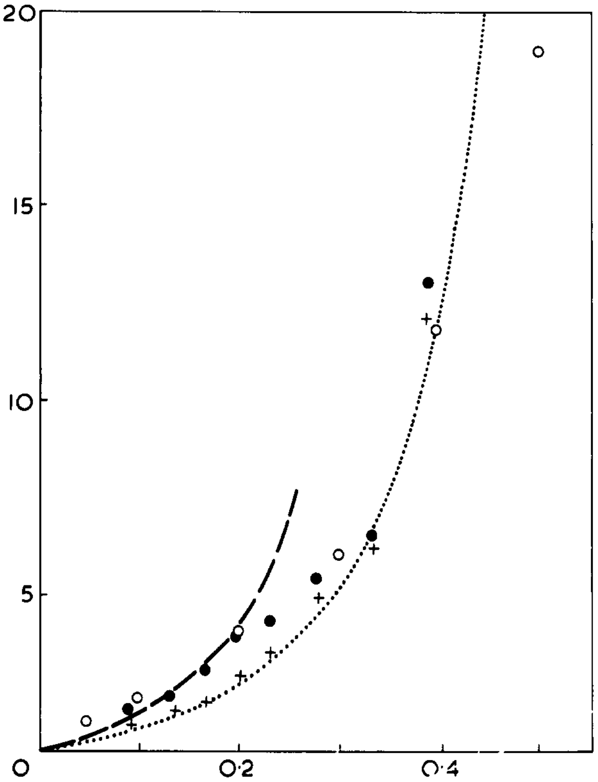

Figure 2 Dependence of relative network chain concentration on filler loading for HAF filled butyl rubber vulcanizates: ○, swelling (ref 27); ●, dynamic behaviour (ref 28). – – – –, Prediction of equation (2) with $\phi_m = 0.43$; . . . . ., prediction of equation (2) with $\phi_m = 0.60$

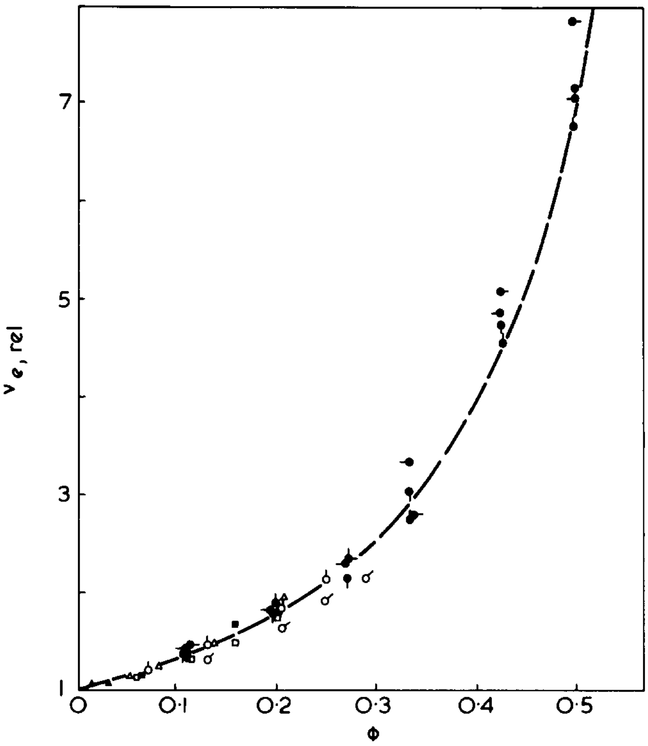

Figure 3 Dependence of relative network chain concentration on filler loading for large size thermal blacks. △, MT in natural rubber (ref 22); □, graphon in SBR; ■, FT in SBR (ref 3); ●, MT in SBR (ref 8); ○, MT in natural rubber (ref 25). – – – –, Prediction of equation (1) with $\phi_m = 0.80$.

mic modulus as reported by Payne for dry samples of the same system[27]. Again as was observed with the natural rubber–HAF vulcanizates, the data obtained from equilibrium swelling are very close to the response obtained in dynamic testing on dry samples at large strains. And again, we believe this effect is due primarily to dewetting.

The broken curve is the prediction of equation (2) taking $\phi_{max} = 0.43$, while the dotted curve is the predicted response when $\phi_{max} = 0.60$. We believe that for low loadings, the value of $\phi_{max} = 0.43$. As the loading is increased a transition occurs and the value of ϕ_{max} changes to 0.60 which is close to the value for the natural rubber–HAF system described in *Figure 1*. Butyl rubber is particularly sensitive to heat treatment and it may be that at the higher loadings sufficient heat is developed during mixing to initiate the heat treatment process. In fact, the crosses shown in *Figure 2* represent the response obtained by Payne[27] from the large strain dynamic testing of heat treated HAF filled butyl rubber and as may be seen, these data can be represented by equation (2) with $\phi_{max} = 0.60$.

When the filler is composed of non-aggregated particles such as the large size thermal blacks the relationship between the relative network chain concentration and the volume fraction of filler is given by equation (1). *Figure 3* shows the behaviour of the relatively non-reinforcing carbon blacks MT, FT and graphon contained in both SBR and natural rubber vulcanizates. The response predicted by equation (1) is shown as the broken curve The value of $\phi_{max} = 0.80$ which is higher than the value expected for the random packing of spheres. However, if dewetting occurs the true value of ϕ_{max} will be lower than the apparent value. For example, if dewetting alone is assumed to contribute a volume increase of 27%, this effect would be sufficient to lower the ϕ_{max} value to 0.63.

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