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Reinforcement of model filled elastomers: experimental and theoretical approach of swelling properties

J. Berriot, F. Lequeux, H. Montes*, H. Pernot

UMR 7615 Lab de Physico-Chimie Structurale et Macromoleculaire, ESPCI, 10 Rue Vauquelin, 75231 Paris Cedex 05, France

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Abstract

The swelling properties of model filled elastomers consisting of crosslinked polyethylacrylate chains mixed with grafted silica nanoparticles are analysed using a continuous media mechanics approach. We show that the swelling restriction observed in these filled elastomers cannot be simply explained through the increase of the topological constraints density resulting from the interactions at the interface between the particles and the polymer chains. Strong interactions at the particle/matrix interface lead to geometrical constraints which control and restrict the swelling of the polymer network. We propose a model giving an analytical relation between the swelling properties of the filled elastomer, one of the elastomer without particles, and the volume fraction of solid particles. This model describes relatively well the experimental data obtained for varying topological constraint density at the particle surface. © 2002 Published by Elsevier Science Ltd.

Keywords: Polymer networks; Filled elastomers; Swelling properties

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1. Introduction

The addition of fillers in elastomer modifies the mechanical properties of the polymer matrices. Among them, the swelling properties are affected by the presence of particles. Swelling measurement of filled elastomers is a classical test to detect the density of covalent bonds between the elastomer and the particles. However, the interpretation of this measurement is not clear in the literature.

Two kinds of approaches have been developed, in order to account for the variation of the swelling properties versus the particle volume fraction and the anchoring of the elastomer matrix on the particles.

The first one is just based on the following approximation: all the covalent bonds between the elastomer matrix and the solid particles contribute similarly to crosslinkers in the elastomer network. This approach is rather approximate, but is efficient when the distance between the crosslinkers is of the same order as the distance between particles, and it has been applied successfully to the description of the swelling properties, for instance, in the case of silica/PDMS systems [1–5]. However, in most of the filled elastomers, this approach fails, as we will show in this paper.

The other approach consists in making a continuous description of the problem. It is then assumed that the elastomer has the same properties with and without particles. However, since the elastomer is connected to the solid particles, its swelling is restricted by the boundary conditions at the surface of the particles. This second approach is delicate and its description in the literature requires a non-analytical resolution of the mechanical problem [6–8]. This description accounts for the covalent bonds between particles and elastomer via a boundary condition at the particle/matrix interface which is either zero stress (no bounds) or zero displacement (bounds). An empirical model was developed by Kraus [9] predicting the linear variation of the swelling ratio with $\phi/(1-\phi)$ where ϕ is the volume fraction of filler. No analytical expression is given for this slope which is in practice a free parameter varying with the nature of the filled elastomers. Moreover, as the number of topological constraints at the particle/polymer interface is large, no linear dependence of the swelling ratio versus $\phi/(1-\phi)$ is observed [10].

Last, Rehner [11] has developed a model combining the two kinds of approach. The swelling behaviour is described by the density of topological constraints including both the

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* Corresponding author. Tel.: +33-1-4079-4687; fax: +33-1-4079-4686. *E-mail address:* helene.montes@espci.fr (H. Montes).

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crosslinks far from particles and the junction points between the particle and the polymer chains at the interface. But Rehner distinguishes the effects of crosslinks located far from the particles to those of crosslinks located at the particle surface. Thus as the interactions between the particles and the elastomer matrix are strong, the chain segment between two topological constraints is smaller at the interface than in the bulk. Hence, the polymer network does not swell homogeneously through the whole sample: the polymer chains swell less at the interface than far from the particle surface. However, no analytical expression of the swelling ratio versus the particle concentration is deduced.

This paper presents a model which gives an analytical relation between the swelling properties of the filled elastomer, the one of the elastomer without particles, and the volume fraction of solid particles. Then we use this model for analysing the swelling experiments performed on various model elastomers made up of polyethylacrylate chains mixed to grafted silica nanoparticles and for which the crosslinker concentration has been controlled by NMR results [12,13]. We finally discuss the influence of the anchoring density at the particle/matrix interface on the swelling properties.

2. Experimental section

2.1. Sample preparation

2.1.1. Main steps of the filled elastomer synthesis

We will present the main lines of the synthesis which is described with more details in a previous article [14].

Spherical, weakly polydisperse particles of colloidal silica with varying diameter were prepared following the procedure developed by Stöber [15]. Their mean size and polydispersity were characterized by small angle neutron scattering [14].

Filled elastomers were prepared from these colloidal silica solution following the procedure developed by Ford and coworkers [16–19]. At first short silane molecules are grafted onto the silica particle surface. Three kinds of non-polar coupling agents were used: the 3-trimethoxysilylpropylmethacrylate (TPM), the 3-methacryloxy propyl dimethylchlorosilane (MCS) and the acetoxyethyldimethylchlorosilane (ACS). Quantification of the amount of grafted coupling agent was determined by elemental analysis comparing the carbon and silicon contents of the non-grafted and grafted silica particles.

The dispersion of grafted silica particles is first transferred to methanol and then to the acrylate monomers by successive dialysis. Lastly, a photoinitiator (Irgacure, CIBA) (0.1 wt% to monomer) and a crosslinker—the diacrylate butanediol (Lancaster)—are added to this dispersion in order to achieve the polymerization and the crosslinking, respectively. The polymerization and the reticulation of the polyacrylate chains performed under UV illumination occur simultaneously. From each initial solution of grafted silica particles, we have prepared a concentrated silica dispersion in acrylate (around 20% in volume). This parent solution was then diluted with acrylate monomers in order to prepare varying silica concentration samples. Several solutions with varying silica concentrations were then obtained and polymerized. For each silica volume fraction, the concentration of crosslinker was kept equal to 0.3% per mol of acrylate monomers.

2.1.2. Chemical structure of the particle/polymer interface

Chemical structure of the covering. The TPM molecules have three reacting groups which can form a covalent bond either at the silica surface or with other TPM molecules. As shown by ^{29}Si NMR [14,20] there is a polycondensation of the TPM molecules around the silica surface. Thus these TPM molecules form a dense shell around the particles. Moreover, the amount of grafted TPM molecules can be larger than the number of hydroxyl groups at the silica surface.

At the opposite, the MCS and ACS grafts have only one group that can react with the hydroxyl groups. In this case, there is no polycondensation between neighbouring coupling agent molecules. The MCS and ACS grafts form brushes over the particle surface.

The grafting density was measured by elemental analysis. We can deduce the thickness e_G of the grafting layer applying the following relation

$$e_G = \frac{d}{2}\left(\sqrt[3]{1 + \frac{6\Gamma M_{mol}^G}{d\rho^G N_a}} - 1\right) \tag{1}$$

where M_{mol}^G and ρ^G are the molar weight and the density of the graft molecules; N_a, the Avogadro number; Γ, the grafting density and d is the particle diameter.

Interaction of the graft molecules with the polyacrylate chains. Both TPM and MCS coupling agents have one methacrylate group which can react with the acrylate monomers during the polymerisation step. TPM or MCS silica particles are then covalently bound to the acrylate matrix. On the contrary, the ACS coupling agent does not possess such methacrylate ending. The ACS–silica particles are then not connected to the elastomeric network.

In a previous work we have shown that the final silica dispersion state depends on the procedure used to prepare the concentrated silica/acrylate dispersion which is then diluted in order to obtain filled elastomer with varying silica volume fractions [14]. We have prepared several sets of filled elastomers differing by their particle size, the chemical nature of the grafting agent and the concentration procedure. Each set of samples corresponds to reinforced elastomers prepared from the same initial grafted silica solution following the same concentration procedure. Each set of filled materials consists of several samples having volume fraction between 0.06 and 0.2. The dispersion state of the

Table 1
Characteristics of the reinforced sample sets

Set name	Mean silica diameter (nm)	Graft type	Grafting density, Γ (nm^{-2})	$\langle f_{Si}^{N}\rangle^{e}$ (nm^{-2})	Dispersion state[a]	e_G (nm)	e_f (nm)
ACS/H	54	ACS	2	0	Very bad[b]	–	–
MCS_I/C	45	MCS	1.6 ± 0.5	2.25	Good[c]	0.52	1
MCS_II/H	50	MCS	2.8 ± 0.5	1.05	Bad[d]	0.9	-0.5
MCS_III/H	54	MCS	<1	0.15	Bad[d]	<0.35	-5.8
TPM_I/H	50	TPM	3.3 ± 0.5	1.1	Bad[d]	1.07	1.5
TPM_II/H	54	TPM	7.8 ± 0.5	2.7	Bad[d]	2.4	4
TPM_V/H	24	TPM	1.5 ± 0.5	1.05	Bad[d]	1.3	1

[a] From SANS measurements [14].
[b] Presence of large aggregates.
[c] There is an exclusion radius around the particles.
[d] There is the coexistence of any linear aggregates with single particles.
[e] From ^{1}H NMR measurements [12,13].

silica particles has been characterized by small angle neutron scattering. The details are presented in Ref. [14]. As shown below the dispersion quality does not deeply influence the swelling, therefore, we have just indicated in Table 1 the quality of the dispersion by either good, bad or very bad. The label 'good' means that during the polymerization the particles 'repel' one another. Their order in the elastomer matrix is the one of sphere with repulsive interactions. The label 'bad' corresponds to quite disordered arrangement with many particle doublets.'Very bad' refers to samples containing fractal aggregates of particles. In addition, we have performed ^{1}H NMR measurements in order to characterize the elastomeric matrix. The ^{1}H NMR spectroscopy allows to determine the average density of topological constraints ν_{tot} for the polymer chains [12]. ν_{tot} is the sum of three contributions: $\nu_{tot} = (\nu_e + \nu_c + \nu_G)$. The first two contributions are due to entanglements (ν_e) and to the crosslinker molecules (ν_c) as in non-reinforced elastomers. The third one (ν_G) is proportional to both silica particle concentration and grafting density. This third contribution reveals the connections between the particles and the elastomer matrix.

We have deduced the particle functionality $\langle f_{Si}^{N}\rangle$ for each kind of grafted silica particle which is the topological constraint density (ν_G) by silica surface unit. All the characteristics of each set of filled elastomers are reported in Table 1.

2.2. Swelling measurements

The maximum swelling at equilibrium of the polymer networks was determined after extraction of the free chains contained in the filled elastomer. The extraction was performed using the following procedure. Chloroform was used to extract the free chains and to swell the polymer network. The filled elastomer was washed with chloroform during one week. the solvent being replaced three times. The sample was then weighed, immersed in CCl_4 and weighed again in order to determine its equilibrium swelling ratio Q_m which is reached as the weight of the swollen sample does not increase anymore.

Following the literature, this maximum swelling Q_m was defined as the volume of the maximum swollen polymer network divided by the initial volume of the crosslinked polymer chains after extraction of the free chains (Eq. (2))

$$Q_{pol} = \frac{V_{SW} - V_{Si}}{V_D - V_{Si}} \qquad (2)$$

where V_D is the volume of the samples after extraction of the free chains; V_{SW}, the volume of the swollen sample and V_{Si} is the volume of the silica particles dispersed in the sample. The density of the silica particle was taken equal to 2 g/cm^3 [16–19].

3. Theoretical section

When immersed in a good solvent, the elastomer matrix has a tendency to swell. The equilibrium swelling ratio, without the presence of particles, is determined by the balance between the osmotic pressure of the chains and the stretching of the polymeric network. In the presence of particles, the covalent bonds between the particles and the polymer matrix lead to decrease the swelling at equilibrium.

If the particles are not covalently linked to the network, particles do not restrict the swelling of the elastomer network. The network undergoes an isotropic dilation similar to the one of the elastomer without particles. Thus cavities develop around each filler, that are filled with solvent, and the formation of this solvent shell does not restrict the expansion of the elastomer network. Hence the whole sample exhibits a dilation similar to the one observed for an elastomer without filler (Fig. 1).

In the case of an elastomer with solid fillers that are covalently connected to the polymer network, the situation is different. The elastomer cannot sustain an isotropic expansion, as it has to remain connected to the particles. Thus the swelling of the elastomer will be restricted,

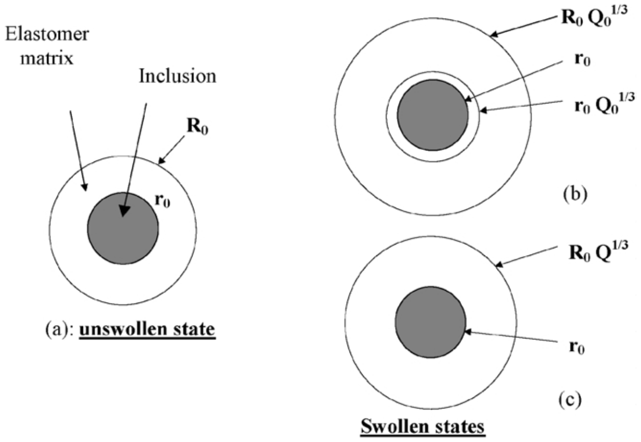

Fig. 1. Schematic representation of the swelling of a polymer layer surrounding a particle. (b) Swelling if there is no adhesion between the particle and the polymer matrix; (c) swelling if there is adhesion.

especially in the vicinity of the particles. On the other hand, very far from the particles, the elastomer will recover its equilibrium swelling. Thus the swelling will be inhomogeneous in the sample. The mechanical problem is complex, because the elastomer contains a given volume fraction of solid particles, and because the relations between the swelling degree of the elastomer, the stress and the strain are non-linear. We will assume that the polymer network can be described by continuous mechanics. This is reasonable in the case of our filled elastomers because the mesh size ξ (6 nm) of the network, is small compared to the distance between particles—higher than 20 nm typically [12,13].

Following the literature, but contrary to previous authors [6–8], we will assume here for sake of simplicity that the elasticity is linear for the elastomer matrix, taking as the reference state the elastomer swollen at equilibrium, in the absence of particles. We will make a self-consistent approximation in order to take into account the particle volume fractions. Then the problem will appear to be a classical problem of elasticity that we will solve. We will obtain a relationship between the swelling degree of the free elastomer and the one of the filled elastomer, as a function of the volume fraction of fillers and the Poisson ratio of the elastomer.

Self-consistent approximation. Let us first assume that there is an homogeneous distribution of particles in the elastomer matrix. We will consider the unswollen state of the system. We can then build the Voronoi tesselation of the mass centre of the particles. Each Voronoi polyhedron corresponds to the points that are closer to the centre of mass of a given particle, than to any other mass centre. They are also called Wigner–Seitz cells in the case of crystalline arrangement. These polyhedra have been shown to possess around 12 or 13 faces. They constitute a space filling structure. The idea of the approximation is to replace each polyhedron by an effective sphere. Each effective sphere will thus contain a core constituted by the filler, and a shell constituted by the elastomer network.

Let the radius of the filler be r_0, the volume fraction of the fillers Φ_f, and the close-packing volume fraction Φ_{cp}. It is reasonable to assume that effective sphere arrangement constitute a close-packing structure. Thus the radius of these spheres R_0 is given by the relation:

$$\frac{R_0}{r_0} = \left(\frac{\Phi_{cp}}{\Phi_f}\right)^{1/3} \tag{3}$$

The elastomer shell has an inner diameter r_0 and an outer diameter R_0 before swelling.

Boundary conditions. If now the system is immersed in a solvent and swells towards its equilibrium, each shell will be constrained by its solid core. The inner boundary condition is the following: the elastomer in the vicinity of the particle will remain at the same position after swelling. The outer boundary condition of the shell is different. If all the spheres have the same diameter, they can swell similarly without restriction at their contacts. More precisely the interface in between each Voronoi polyhedron will just undergo an isotropic dilation. Thus, the boundary condition for the external surface is a zero stress condition.

Strain field. Let us now introduce the displacement field. We will take as the reference state, the situation in which the elastomer would have swollen as it has not been connected to the particles. That corresponds to a shell with an inner diameter $r_0 Q_0^{1/3}$ and an external diameter $Q_0^{1/3} R_0$. The displacement $\mathbf{u}$ is thus equal to zero in this situation. The swelling ratio in this situation—without particle restriction—is Q_0. Let us now introduce the boundary conditions mentioned above. The first condition is that the elastomer at the inner surface of each shell is connected to the particles. In the absence of connector, it would have been equal to $r_0 Q_0^{1/3}$. Because of symmetry the displacement is purely radial (u_r)

To connect the swollen elastomer, we must apply a displacement to the inner cell from $r_0 Q_0^{1/3}$ to r_0. Thus it corresponds to a radial displacement u_r equal to:

$$u_r(r_0 Q_0^{1/3}) = (1 - Q_0^{1/3}) r_0 \tag{4}$$

The external boundary condition is a zero normal stress condition, and thus writes:

$$\sigma_{rr}(Q_0^{1/3} R_0) = 0 \tag{5}$$

This will determine the external radius R_{ex} of the shell swollen at equilibrium, in the presence of the filler. This radius will be the one without the particle minus the displacement of the surface of the shell.

$$R_{ex} = Q_0^{1/3} R_0 - u_r(Q_0^{1/3} R_0) \tag{6}$$

The final swelling ratio Q, in this model, will simply be equal to:

$$Q = \left(\frac{R_{\mathrm{ex}}}{R_0}\right)^3 \tag{7}$$

The elastic problem is thus the problem of a spherical shell with the two boundary conditions mentioned above. The problem has a spherical symmetry and the general solution can be found in classical elasticity books [21]:

The radial displacement writes:

$$u_r = Br + \frac{C}{r^2} \tag{8}$$

where B and C are two arbitrary constants. The radial component of the stress writes

$$\sigma_{rr} = \frac{E}{1-2\sigma}B - \frac{2E}{1+\sigma}\frac{C}{r^3} \tag{9}$$

where E and σ are, respectively, the Young modulus and the Poisson ratio of the swollen polymer.

Thus we have to apply the two boundary conditions (4) and (5), to determine the constants B and C. From the value of B and C, using Eq. (7) it is easy to obtain the final swollen ratio of the filled elastomer:

$$Q(\Phi_{\mathrm{f}}) = Q_0\left(1 - \frac{Q_0^{1/3}-1}{Q_0^{1/3}}\,\frac{3(1-\sigma)}{2(1-2\sigma)+(1+\sigma)(\Phi_{\mathrm{cp}}/\Phi_{\mathrm{f}})}\right)^3 \tag{10}$$

In this expression the swollen ratio of the elastomer Q is smaller than the one of the elastomer without filler. It is given as a function of the volume fraction of filler, the Poisson coefficient of the swollen elastomer, the equilibrium swelling ratio of the matrix alone and the volume fraction at the random close packing.

Let us discuss our approximation. The models of Rigbi [8] and Sternstein [6,7] take into account some non-linearities of the swollen elastomer mechanics but they require non-analytical resolutions of the mechanical equations. As we remain in the frame of linear elasticity, we probably underestimate the unswelling, especially in the vicinity of the particles where the strain and the stress are large.

On the opposite, far from the particles the approaches are similar.

A way to take into account these non-linearities is to replace the boundary condition—in the linear model—by an effective boundary condition, in order to match the exact solution. Here we can slightly shift the radius of the particles, and then replace in Eq. (10) Φ_{f} by $\Phi'_{\mathrm{f}} = \Phi_{\mathrm{f}}(1+e_0/r_0)^3$, where e_0 is a small length. We will see in Section 4 that e_0 is of the order of a few nanometers, and thus our linear approximation will be validated.

In the experiments that we will present, the particles, solvent and polymer are weighted and it is thus convenient to express the swelling ratio as the volume of solvent and the polymer versus the volume of polymer. This ratio Q_{pol} is thus the swelling ratio of the elastomer network alone, and does not take into account the silica particles. This definition is the one commonly used in the literature for the swelling of filled rubbers. The relation between the swelling ratio of the polymer itself Q_{pol}, and of the whole system $Q(\Phi_{\mathrm{f}})$ is simply:

$$Q_{\mathrm{pol}} = \frac{Q(\Phi'_{\mathrm{f}}) - \Phi_{\mathrm{f}}}{1-\Phi_{\mathrm{f}}} \tag{11}$$

Here Φ'_{f} is the corrected silica volume fraction which allows the description of the deformation field induced by the fillers while Φ_{f} corresponds to the effective particle volume.

Finally for systems in which the particles are not covalently connected to the network, the apparent swelling ratio Q_{pol} is just:

$$Q_{\mathrm{pol}} = \frac{Q_0 - \Phi_{\mathrm{f}}}{1-\Phi_{\mathrm{f}}} \tag{12}$$

This apparent swelling ratio of the polymer alone, is larger than the ratio of the polymer alone Q_0, just because there are voids around each particles that are filled with solvent. This solvent in the shell surrounding each particle for the swollen systems, is taken into account and increases the apparent swelling of the polymer as already mentioned by Kraus [9].

Finally, our approach presents the advantage to give a simple expression which relates the swelling of a filled elastomer with the one of the non-reinforced matrix and the particle concentration. A parameter e_0 is let free in order to account for some possible effects of non-linearity, but also for some effects that we will discuss now.

4. Results and discussion

Fig. 2 shows the variation of the ratio Q_{pol}/Q_0 at equilibrium versus silica volume fraction for different series of filled elastomers.

We consider first the filled elastomers for which there is no particle/matrix adhesion. It corresponds to the ACS/H set. We observe that the swelling ratio increases with the silica concentration. We compare the experimental data to the theoretical predictions given by Eq. (12). The theoretical curve in solid line in Fig. 2 agrees reasonably with the experimental data.

Now we consider the samples for which the particles are covalently connected to the elastomer matrix. In this case we have chosen to include in the effective particle volume fraction Φ_{f} the layer composed by the coupling agents which does not swell. This means that r_0 is in this case given by $r_0 = d/2 + e_{\mathrm{G}}$ and the effective particle volume fraction is then $\Phi_{\mathrm{f}} = \Phi_{\mathrm{Si}}(2r_0/d)^3$ where Φ_{Si} is the silica volume fraction. We observed that the swelling restriction increases with the effective silica concentration. We will now

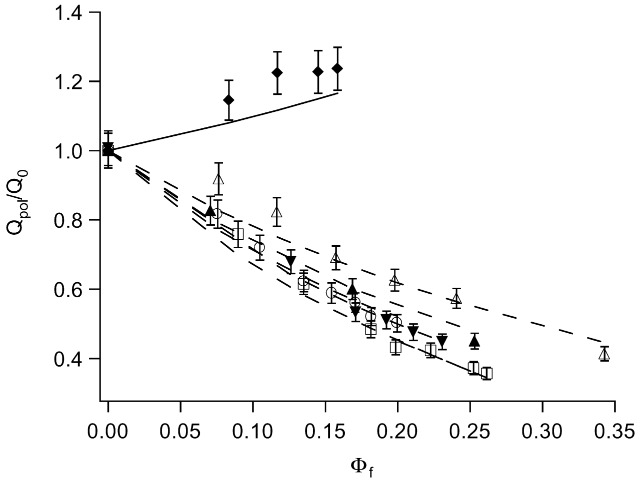

Fig. 2. Variation of the normalized equilibrium swelling ratio Q_{pol}/Q_0 versus effective silica volume fraction Φ_f. (◆) ACS/H; (▲) MCS_I/C; (△) MCS_II/H; (○) TPM_I/H; (□) TPM_II/H; (▼) TPM_V/H. The solid line corresponds to the description given by Eq. (12). The dashed lines correspond to the theoretical fitting given by Eq. (11) and adjusting the value of e_0. The corresponding value of e_0 are called e_f and are given in Table 1.

compare the data to the theoretical predictions given by Eq. (11).

The Poisson coefficient was taken equal to 0.33 which corresponds to the value found by Geisler et al. [22] for elastomer chains diluted in a good solvent and the close-packing concentration was taken equal to 0.64.

The silica concentration dependence of the swelling ratio is well described by our model with the proviso of choosing an appropriate value for e_0. The value of e_0 giving the best description of the experimental curves are called e_f and are given in Table 1 for each sample set. The corresponding curves are plotted in dashed lines in Fig. 2.

Fig. 3 shows the influence of e_0 on the quality of the description for one representative set of samples reinforced with TPM silica. As e_0 is fixed to zero we clearly see that the swelling restriction is underestimated by the model. The deviation of experimental data from the theoretical curve is larger and larger as the silica concentration increases. However, this discrepancy remains smaller than 10%. Thus, e_f results from the corrections due to different effects such as the deformation field, the dispersion state and the influence of the anchoring density at the interface.

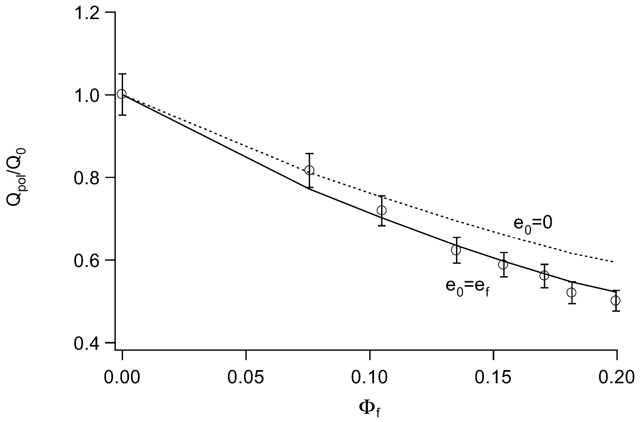

Fig. 3. Influence of the value of e_0 on the theoretical predictions given by Eq. (11). $e_0 = 0$ in dotted line and $e_0 = e_f$ in solid line. (○) experimental data measured on the TPM_I/H samples.

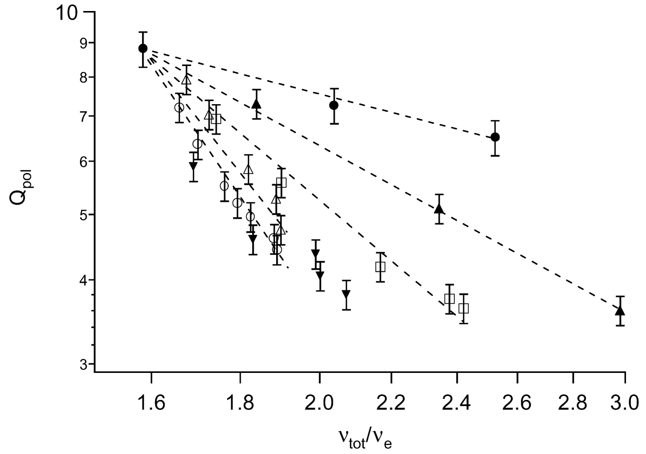

Fig. 4. Variation of the equilibrium swelling ratio versus topological constraint density normalized by the entanglement density ν_{tot}/ν_e. ν_{tot} and ν_e were measured by ^{1}H NMR [7]. (●) non-reinforced ethylacrylate matrix; (▲) MCS_I/C; (△) MCS_II/H; (○) TPM_I/H; (□) TPM_II/H; (▼) TPM_V/H.

Commonly, the swelling restriction of elastomer matrices is attributed to the crosslinks connecting the polymer chains which avoid the extension and the diffusion of the polymer chains. In a previous paper we have measured by ^{1}H NMR the total topological constraint density ν_{tot} of our filled elastomers [12] which includes the covalent bonds due to the crosslinker molecules and those between the particles and the elastomer matrix. In Fig. 4 we have plotted the variation of the equilibrium swelling ratio for pure elastomers with various concentrations of crosslinks versus ν_{tot}/ν_e where ν_{tot} in this case is simply equal to $(\nu_c + \nu_e)$. We have also plotted the data measured on our reinforced poly(ethylacrylate) matrices as a function of ν_{tot}/ν_e with $\nu_{tot} = (\nu_e + \nu_c + \nu_G)$. We clearly observe that the swelling ratio of the filled elastomers are sensibly lower than those of the equivalent unfilled matrices as expressed in term of topological constraint. Thus the swelling restriction does not depend only on the topological constraints.

In these conditions the approximation that the swelling of filled elastomers is controlled by the average mesh size ξ of the polymer network fails.

However, we observe in Fig. 2 that the swelling ratio depends on the structural and chemical features of the filled elastomers such as the dispersion state and the size of the particles, the grafting density or the nature of the coupling agent. In each case the experimental data are well described by our model if we include a polymer layer e_f around the particles which does not swell. All the data superimpose on a master curve if one plots the experimental data versus the corrected volume fraction $\Phi_f' = \Phi_f(1 + e_0/r_0)^3$ as shown in

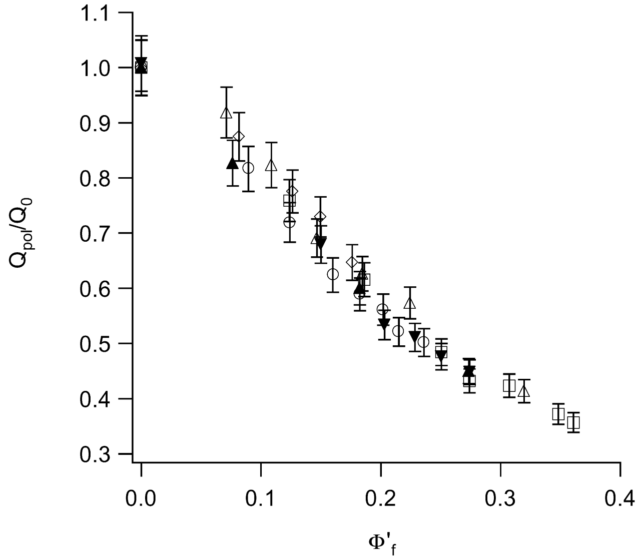

Fig. 5. Variation of the normalized equilibrium swelling ratio Q_{pol}/Q_0 versus the corrected silica volume fraction $\Phi_{\mathrm{f}}' = \Phi_{\mathrm{f}}(1 + e_0/r_0)^3$. (▲) MCS_I/C; (△) MCS_II/H; (○) TPM_I/H; (□) TPM_II/H; (▼) TPM_V/H.

Fig. 5. That means that the swelling ratio is controlled by this single parameter e_{f} whose value is influenced by the structural parameters such as grafting density, particle diameter, dispersion state, etc.

We will successively pick out the effects of these different parameters on the swelling behaviour.

Influence of the dispersion state. We will focus our attention on the swelling behaviour of MCS_I/C and MCS_II/H samples. We observe that the MCS_II/H samples swell more than the MCS_I/C filled elastomers despite a higher grafting density. We can conclude that a worse dispersion state leads to a smaller swelling restriction and then to a lower value for e_{f}.

Influence of the anchorage density. The swelling restriction is strongly controlled by the anchorage density between the particles and the elastomer matrix Considering the samples of sets MCS_II/H, TPM_I/H and TPM_II/H we observe that e_{f} increases with the anchorage density $\langle f_{\mathrm{Si}}^{\mathrm{N}} \rangle$. e_{f} varies from -0.5 to 4 nm. We deduce that the swelling of the polymer layer located between r_0 and $r_0 + \xi$ can be strongly different according to the chemical nature of the coupling agent and the anchorage density $\langle f_{\mathrm{Si}}^{\mathrm{N}} \rangle$. A negative value is observed as the coverage by the graft molecules is partial (samples of the MCS_III/H set). It could be associated to solvent 'hole' at the particle surface located where there is no graft molecules.

The equilibrium swelling ratio of filled elastomers is influenced both by the topological and the geometrical constraints at the particle/polymer interface. But none of these two concepts can separately explain the behaviours observed. The swelling ratio would be overestimated if we consider only the topological constraint density while the variation of the swelling ratio with the grafting density cannot be explained by considering only geometrical constraints. The results measured on our filled elastomer show that there is around the particles a polymer layer whose swelling behaviour is influenced by the covalent bonds at the particle/matrix interface. According to the grafting density and the chemical nature of the coupling agent this polymer layer swells more or less than the elastomer matrix. However, outside this polymer layer, the mechanical constraints control the swelling of a filled elastomer.

The contribution to e_0 due to the corrections of the non-linearities and the dispersion state are negligible. These contributions do not seem to be pertinent to explain the swelling behaviour of our filled elastomers, compared to the effect of grafting on the swelling of the first polymer layer surrounding the particles.

5. Conclusion

We have analysed the swelling behaviour at equilibrium of model filled elastomers composed of crosslinked poly(acrylate) chains reinforced by nanometric grafted silica particles. The matrix/particle interaction was changed by varying the chemical nature of the grafting agent and the grafting density. From previous NMR measurements we have shown that the mesh size ξ of the elastomer matrix far from the particle surface is smaller than the distance between particles. We show in this work that the swelling restriction observed in such filled elastomers is not only controlled by the crosslink density but also by the mechanical constraints at the particle/matrix interface. We propose a model using a continuous media mechanics approach. A free parameter has to be adjusted in order to take into account the non-linearities and the influence of the topological constraints at the particle/matrix interface on the swelling of the polymer chains close to the particle. As a result the influence of the dispersion state on the swelling is weak and negligible compared to the effect of grafting. Moreover, the effect of the mechanical constraints at the particle surface is modulated by the swelling behaviour of the polymer layer located near the interface. This polymer shell of small thickness (<5 nm) swells more or less depending on the grafting density and the chemical nature of the coupling agent.

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