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Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica: 3. Morphology and mechanical properties of reinforced films

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Films were prepared through coalescence of latexes of poly(ethyl acrylate) encapsulating nanoparticles of silica. Two kinds of silica have been used for the preparation of the latexes: one of them has been functionalized by treatment with methacryloylpropyltrimethoxysilane, and the other has not. The molecular and colloidal properties of the latexes were described previously. In both cases the resulting films are fully transparent up to a high silica content. Small-angle X-ray scattering gives evidence that a good dispersion of the filler is obtained when encapsulated functionalized silica is involved in film formation. On the other hand, small agglomerates are present in the elastomeric material when non-functionalized silica is employed; their size is estimated from scanning electron microscopy. The mechanical properties of the two series of films are strongly different, as shown by either stress–strain experiments or from dynamic mechanical measurements. Very high elongations at break are obtained when the silica is functionalized, so that a part of the polymer is covalently bound to it as tight loops. To account for these properties, a qualitative model is proposed and some validation experiments are described.

(Keywords: encapsulated silica; poly(ethyl acrylate) latex; reinforced films)

INTRODUCTION

There is a growing interest in hybrid materials containing both inorganic and organic parts dispersed at the molecular level or as nanometric domains. Three main approaches have been used. In the first one, precursors of inorganic particles are introduced in a polymer film. This approach was mainly used as a way for elastomer reinforcement. Typically tetraalcoxysilane is allowed to diffuse inside the film and then diffusion of moisture causes hydrolysis and polycondensation to form nanometric silica particles. This has been studied thoroughly and the main features of this work have been reviewed recently[1]. The second approach is the 'ceramer' technique. Typically tetraalcoxysilane is reacted with telechelic oligomer or polymer carrying reactive OH end groups, in the presence of some water and catalyst. A variety of materials from organic polymer reinforced with small silica particles to silica gel with inclusion of soft elastomeric segments can be prepared. Alumina or zirconia may be used instead of silica; the elastomer materials are chiefly polybutadiene, polydimethylsiloxane and poly(tetramethylene oxide). A recent review has been given by Wilkes[2], while detailed mechanistic studies were published by Surivet *et al.*[3,4].

The third approach, followed in our series of papers, consists of encapsulating inorganic materials by an organic polymer. Among the different routes of that approach, emulsion polymerization in the presence of nanometric silica particles is able to give hybrid particles in the submicrometre range. We have followed that route, first described by Yamaguchi *et al.* for calcium carbonate[5] and later on by Hergerth for silica[6]. The success of this process, in addition to an excellent dispersion of the silica in the water medium, needs a certain number of conditions to be fulfilled. The monomer must be hydrophilic enough, and the surface of the silica must be well balanced for its hydrophilic character (good dispersion in the water) and its hydrophobic character (sufficient adsorption of the monomer). This is governed by both the composition of the functional groups of the silica surface, and the structure of the non-ionic surfactant—which may be adsorbed as admicelles but must not be present in the water as micelles. Care must be taken so that there are no monomer droplets in the medium in order to avoid the formation of a polymer latex in addition to the organic phase encapsulating the silica. These conditions have been illustrated in previous papers[7–9]. A part of the polymer is covalently bound to the silica, when the latter has been treated so that functional groups reactive in radical polymerization have been anchored onto its

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surface. The present paper is devoted to the study of the mechanical properties and tries to explain the differences observed when the initial silica has been functionalized or not.

EXPERIMENTAL

Materials

The materials used, silica and poly(ethyl acrylate) latexes encapsulating silica, have been described in previous papers[7,9]. In addition, silica (Degussa's Aerosil 200) has been functionalized with propylthioltriethoxysilane (PTTS) as has been done for functionalization with methacryloylpropyltrimethoxysilane (MPTMS). With that modified silica, encapsulation by emulsion polymerization of ethyl acrylate was carried out so as to include 6% silica in the latex.

Film formation

The latexes were first concentrated to 15% solids content and then spread onto siliconed glass plates. After water evaporation, the films were matured at room temperature for three weeks. The thicknesses of the films were less than 1 mm.

Morphological measurements

After having fractured the film at liquid-nitrogen temperature, the fracture faces were analysed by scanning electron microscopy after they were covered by a thin layer of gold (5 to 10 nm) under vacuum.

Small-angle X-ray scattering (SAXS) experiments were carried out using a rotating X-ray generator with copper target ($k = 0.154$ nm). The experimental set-up includes two orthogonal mirrors in order to obtain a point collimation and a linear position-sensitive proportional counter. SAXS curves were recorded in the angular range 9×10^{-4} rad $< 2\theta < 3 \times 10^{-2}$ rad where 2θ is the scattering angle.

Mechanical properties

Mechanical stress applied to a material results in two types of response, depending on the amplitude of the stress. The first consists of using large strain, thus leading to the study of the behaviour law. An Instron machine (1 kN cell) was used for tensile tests with dumbbell-like specimens have a standard size (50 nm total length, 12×3 mm^2 in the useful part). The force F was measured as a function of cross-head displacement ΔP and results were presented as conventional stress $\sigma = F/S_0$, (S_0 initial cross-section) *versus* elongation $\lambda = (l_0 + \Delta l)/l_0$ (l_0 initial length). Attention was paid to the slope at the origin $(d\sigma/d\lambda)_{\lambda=1}$.

The second type of response obtained without any modification in microstructure or in morphology is involved in mechanical spectroscopy. A new version of a mechanical spectrometer particularly suited for thin specimens was developed in our laboratory[10] and is now available from Metravib (Ecully, France). It consists of a forced oscillation pendulum working in the temperature range 100–700 K and frequency 5×10^{-5} to 5 Hz. The strain is less than 10^{-4} so that the viscoelastic properties are measured in their non-dependent strain amplitude range. One of the main interests of such a set-up is in its capability to deliver information about modulus variation even for a drop in storage modulus of four orders of magnitude. Thus, the dynamic modulus $G^* = G' + iG''$ was measured as a function of temperature in order to observe the main (α) mechanical relaxation, the rubbery plateau and the beginning of the flow of chains.

RESULTS

Morphology of the films

In both sets of experiments, when the silica content is not higher than 20% (weight), the films are fully transparent, which shows that there are no large aggregates of silica particles. In the case of functionalized silica, SAXS confirms this statement, as shown in *Figure 1*, where the plot of ln $I(q)$ *versus* ln q displays a smooth curve with a slope near -4 at high values of q. However, the Guinier plot (*Figure 2*) tends to support some polydispersity in the particle size with two families of particles with radii of 18 and 38 nm respectively for the largest silica contents.

This fact is confirmed by a more advanced analysis. In effect for a system with spherical particles, the correlation function is given by:

$$\gamma = \int_R^\infty D_v(D)\gamma_D(R)\,dD \qquad (1)$$

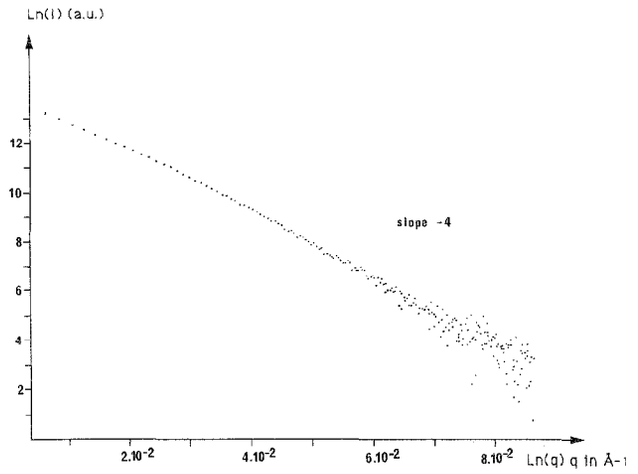

Figure 1 SAXS diagram of films from latex containing 6% of functionalized silica

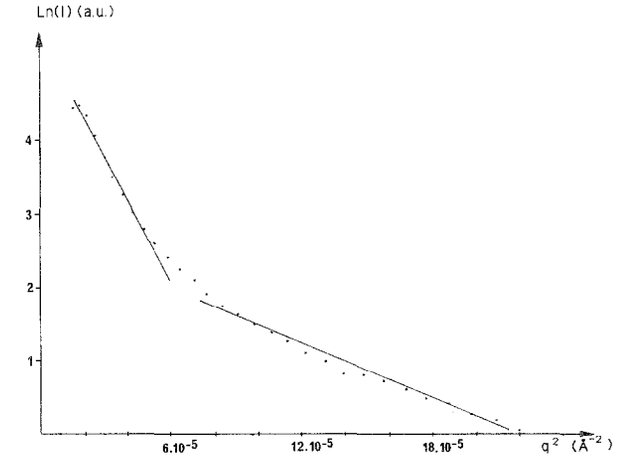

Figure 2 Guinier plot of SAXS of film from latex containing 6% of functionalized silica

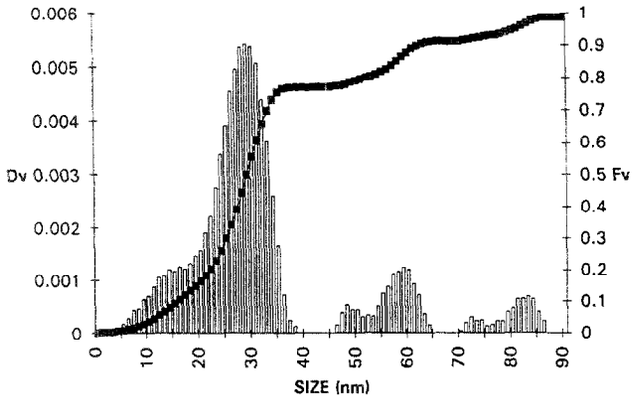

Figure 3 Differential (D_v) and integral (F_v) size distribution of particles in films containing 6% of functionalized silica

where $\gamma_D(R)$ is the correlation function of a sphere of diameter D; $\gamma_D(R)$ can be written:

$$\gamma_D(R) = 1 - \frac{3R}{2D} + \frac{R^3}{2D^3} \qquad O \leq R \leq D$$

Solving equation (1) for $D_v(D)$ one finds:

$$D_v(D) = -\frac{D^3}{3}\frac{\mathrm{d}}{\mathrm{d}D}\frac{\gamma(D)}{D}$$

The method of calculation used is described in ref. 11. *Figure 3* shows the size distribution of particles for 6% silica content; most of particles have a size smaller than 35 nm. A few of them have a greater size, which would correspond to two or three clustered silica particles.

Some differences are observed when the silica has not been functionalized. When the silica content is high, two correlation peaks are clearly observed (*Figure 4*), corresponding, according to a simple Bragg law, to a 30 nm distance. This value is approximately the diameter of non-functionalized silica particles. However, the slope for high q values remains near -4. For lower silica amounts, the two peaks remain visible at the same place. It may be concluded that there are some agglomerates with enough silica particles to give rise to correlation peaks.

The results from SAXS are well confirmed by scanning electron microscopy (SEM). The corresponding micrographs for typical films from the two series are shown in *Figures 5* and *6*. Clearly the fracture face is smoother in the case of functionalized silica. Small holes are visible with size between 200 and 500 nm for the non-functionalized silica-containing film, and only around 100 nm for the more dispersed silica. The aggregation number should be respectively about 10 particles (22 nm initially), and 2–3 in the case of functionalized silica (37 nm initially).

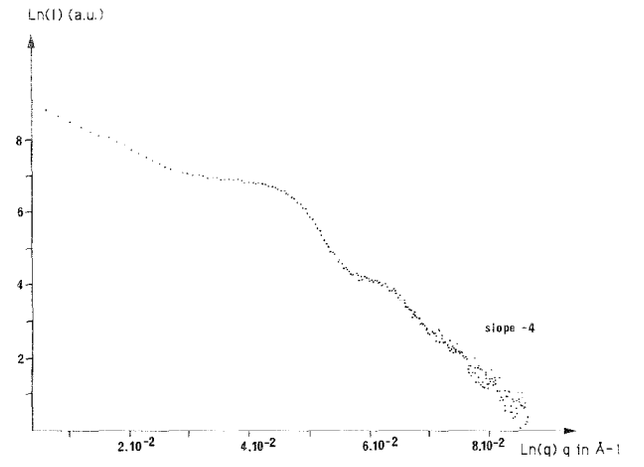

Figure 4 SAXS diagram of films from latex containing 33% of non-functionalized silica

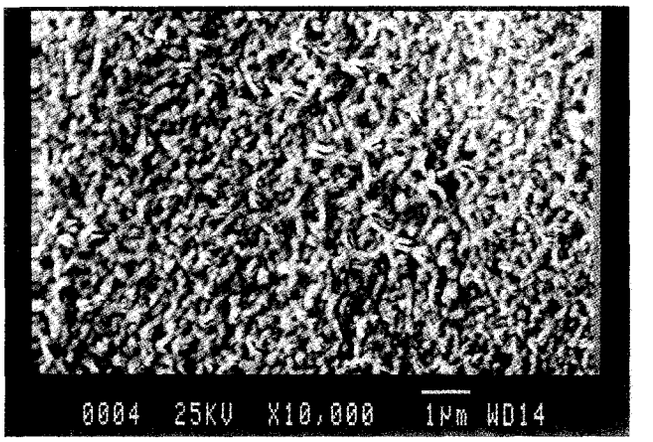

Figure 5 Scanning electron micrograph of the fracture surface of a film from latex containing 6% of non-functionalized silica

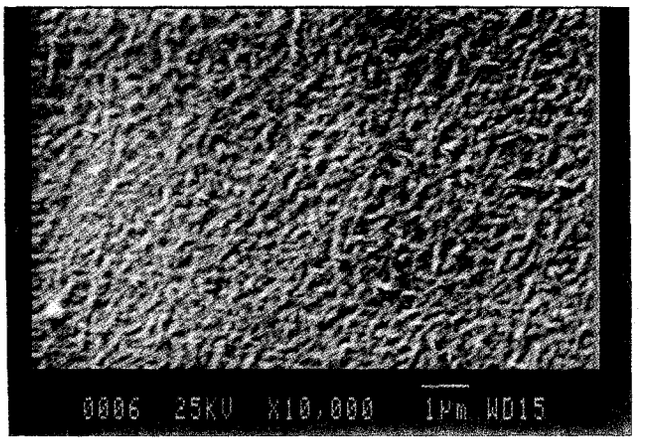

Figure 6 Scanning electron micrograph of the fracture surface of a film from latex containing 6% of functionalized silica

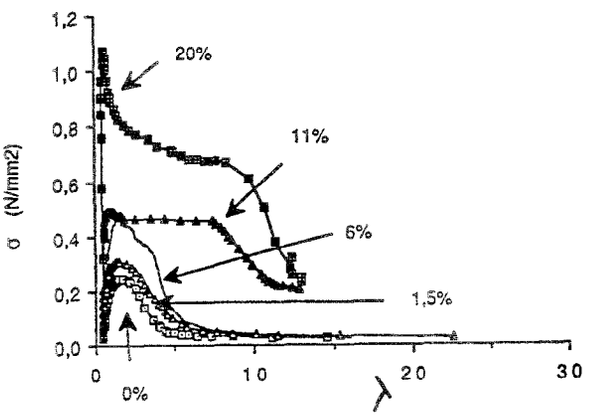

Figure 7 Stress–strain curves of film containing non-functionalized silica. Elongation rate 12 mm min^{-1}

Mechanical properties

Figure 7 illustrates the conventional stress–strain curves obtained in elongation experiments with the films containing non-functionalized silica. A strong reinforcement effect of the silica is observed upon increasing the amount of silica, as shown by the values of the slope at the origin reported in *Table 1*. A yield point is observed at values increasing also with the silica content. After that, a plastic behaviour is observed when the silica content is high, as a plateau value followed by a decrease of the stress σ before rupture, which takes place at rather high elongation ($\lambda = l/l_0$ from 12 to 20). It is interesting to note the reversibility of the initial part of the curve, up to $k = 1.5$.

A totally different behaviour is obtained when the films include functionalized (and then polymer-grafted) silica (*Figure 8*). Again, there is an elastic initial part of the stress–strain curve, also reversible. However, a non-linear plastic deformation is obtained up to very high elongation, where the material behaves like a crosslinked elastomer. Rupture takes place finally at an elongation increasing with the silica content (from $\lambda = 8$ to 35), preceded by a limited decrease of the stress. The slope at the origin and the yield stress at the end of the elastic stage are reported in *Table 2*.

Table 1 Slope at origin and yield stress of films from latex containing non-functionalized silica

Silica (%)	Slope at origin (N mm^{-2})	Yield stress (N mm^{-2})
0	0.5	0.26
1.5	0.7	0.30
6.0	5.2	0.45
11.0	6.0	0.50
20.0	29.3	1.08
33.3	105.5	11.22

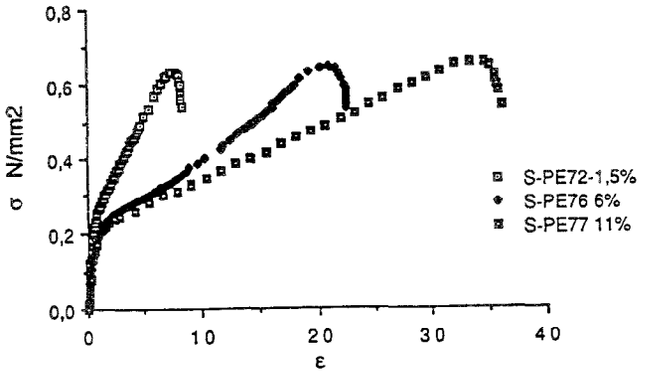

Figure 8 Stress–strain curves of film containing 1.5% (⊡), 6% (■) or 11% (□) functionalized silica. Elongation rate 12 mm min^{-1}

Table 2 Slope at origin and yield stress of films containing functionalized silica

Silica (%)	Slope at origin (N mm^{-2})	Yield stress (N mm^{-2})
0	0.5	0.26
1.5	1.4	0.63
6.0	1.5	0.65
11	5.0	0.67

The main differences between the two sets of samples do not come from the slope at the origin or from the yield stress values; both are comparable for the same amounts of silica. The main differences are observed after the elastic stage.

The previous data correspond to experiments with rather slow elongation rate (12 mm min^{-1}). At high rate (500 mm min^{-1}), the same kinds of behaviour are observed with the two sets of films. However, rupture takes place generally at smaller elongation, chiefly when the reinforcement effect is higher (higher amounts of silica) (*Figure 9*). This is obviously due to the fact that, at low elongation rate, the system is close to equilibrium conditions, allowing flow of chains to take place.

Dynamic mechanical spectrometry was carried out at 0.316 and 1 Hz (*Figure 10*) in the temperature range from 100 to 450 K, using three films: one is from poly(ethyl acrylate) latex without silica ($M_w = 182\,000$), and the two others contain 6% of silica, either functionalized or not. The corresponding molecular weights M_w of the extractible polymer (not covalently linked to the silica) are 286 000 (functionalized) and 261 000 (non-functionalized). In all cases the modulus G' is first slowly decreasing and then drops suddenly, due to the main mechanical relaxation. A rubbery plateau is observed

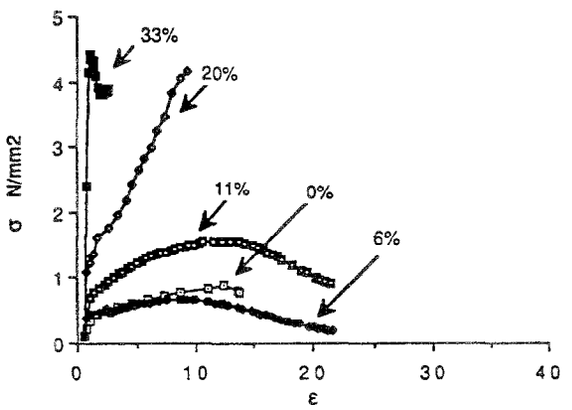

Figure 9 Stress–strain curves of film containing non-functionalized silica. Elongation rate 500 mm min^{-1}

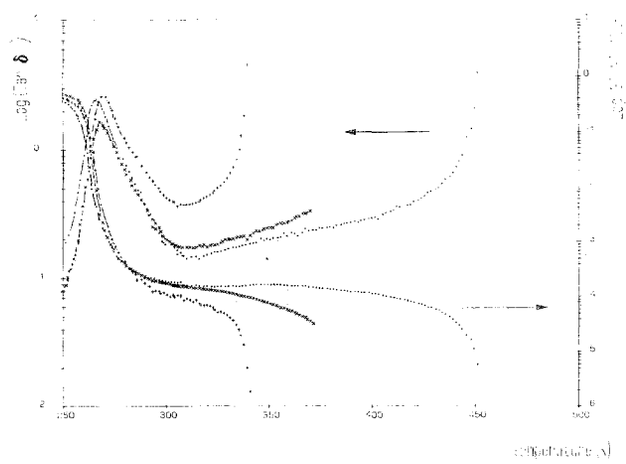

Figure 10 Storage modulus and log(tan δ) *versus* temperature for films without silica (+), and with 6% silica either functionalized (●) or not (×)

after T_a, which is very short for the non-reinforced film, a little more extended (30 K) for the film with non-functionalized silica, and much wider (70 to 110 K) for the third one. These large differences in the rubbery plateau cannot be explained easily on the basis of the small differences in the molecular weight of the grafted polymers. After the rubbery plateau, the modulus finally drops at about 450 K in the third case, which shows that the material is not really crosslinked, as the stress–strain curves might tend to suggest. Another reason to rule out a crosslinking phenomenon is the behaviour of the films in the presence of good solvents of the polymer. In the case of non-functionalized silica, the film is immediately destroyed and pure silica is easily separated from the polymer solution. On the other hand, the films from the functionalized silica remain coherent for about 10 min, but the grafted silica can also be separated from the polymer solution after some time.

The curves for tan δ are quite similar for the three films except for a shoulder of the α peak near 250 K for the most reinforced material.

Another way to obtain information about the rubbery behaviour is to observe the strain recovery after a tensile test. *Figure 11* shows that this recovery is more complete with the material containing 6% of functionalized silica than with the second material including the same amount of non-functionalized silica. In other words, the rubbery behaviour is pronounced with the former although the stress (strain) is higher, while the latter material is more sensitive to chain flow (permanent strain).

DISCUSSION

The reinforcement effect of encapsulated silica is better than the effect that can be obtained by simply mixing the latex and silica, whether it is functionalized or not. This can be demonstrated by comparing the stress–strain curves obtained with the simple mixture (*Figures 12* and *13*) with those of the films from latex containing silica. In the case of non-functionalized silica, the improvement may be simply correlated with the better dispersion state of the silica.

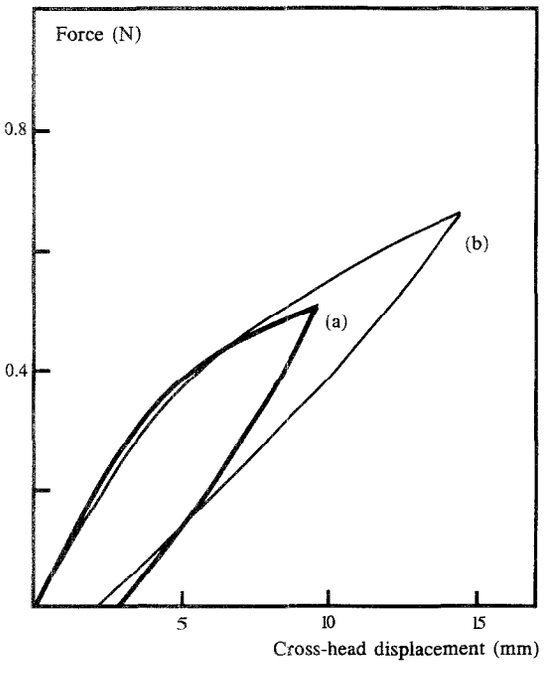

Figure 11 Conventional stress–strain curves for films with 6% silica, either functionalized (b) or not (a)

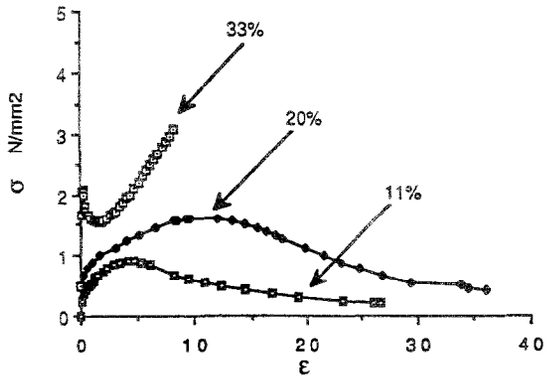

Figure 12 Stress–strain curves of film from mixture of poly(ethyl acrylate) latex and non-functionalized silica. Elongation rate 500 mm min^{-1}

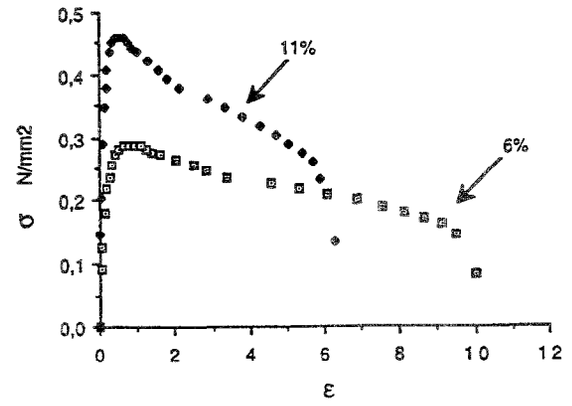

Figure 13 Stress–strain curves of film from mixtures of non-reinforced latex and functionalized silica. Elongation rate 500 mm min^{-1}

Even if the dispersion state is somewhat better in the case of the functionalized silica, another explanation is obviously necessary. In this case, a part of the polymer is actually grafted onto the silica, through copolymerization with the anchored methacrylate group of the coupling agent. This grafting process takes place early during emulsion polymerization, and involves about one-third of the poly(ethyl acrylate) when the amount of silica is 6%. The remaining part of the polymer is non-grafted with a rather high molecular weight ($M_w = 286\,000$). This non-grafted polymer is strongly compressed in the interstices between elementary silica nodules (13 nm diameter) inside the silica particle (37 nm diameter) or in a thin shell (4.5 nm thickness) around the silica particle. This compressed state can be evaluated by considering that the radius of gyration of the polymer in a good solvent (toluene) is 41 nm (ref. 9). It can be expected then that the non-grafted polymer is strongly entangled by itself and also around and in the tight loops of the polymer grafted onto the silica elementary nodules. Then, when the latex is allowed to coalesce during the film-forming process, the non-grafted polymer is expected to expand and then diffuse around to

make new entanglements with polymer molecules from the neighbouring silica particles. Finally, the polymer that occupies the space between the silica particles is strongly entangled first with the loops of the polymer grafted onto the particles, and then with the other non-grafted polymer molecules. This state of tight entanglement can explain the high resistance to flow demonstrated by the long rubbery plateau observed in the dynamic mechanical spectroscopy experiments. The usual explanation of the relationship between the length of the plateau and the molecular weight of the polymer cannot be useful to explain the large differences for the two reinforced films. The molecular weights are similar, with a 10% difference only, while there is a factor of almost 3 for the length of the plateau. In the case of stress–strain experiments, the disentanglement process needed for chains to flow should involve a high stress. Most probably the strength of the links between the non-grafted polymer chain is lower than the one corresponding to the entanglements with the tight loops of the grafted polymers. Then it may be suggested that the polymer chain remains attached to the silica particles and may be fully extended up to the point where the last entanglements with other non-grafted polymer disappear just before rupture (*Figure 14*). The trend to the permanence of the links with the loops can give a coherent explanation for the elastomeric properties of the films with a behaviour similar to that of crosslinked materials: quasi-reversibility of the elongation up to high values and increasing stress with increasing elongation.

The small period of creep observed in the stress–strain curves before rupture is probably linked with the polydispersity of the polymer: rupture takes place when the longest molecules are about fully extended.

Two experiments have been carried out to check the above explanation. In the first one, the non-grafted polymer was extracted with toluene and a film was cast from the toluene solution containing the silica encapsulated by the grafted polymer. In a second experiment, the coupling agent used to functionalize the silica was PTTS (carrying a thiol function), which is a transfer agent in radical polymerization, instead of a comonomer. Then the polymer is grafted by a transfer process and is attached to the silica just by one point; it cannot make loops. Stress–strain experiments were carried out with films from these two experiments and the results are illustrated in *Figures 15* and *16*. In both cases, the outstanding mechanical properties displayed in *Figure 8* were not obtained. In the first case, owing to the extraction process, tight entanglements with loops are no longer present and, in addition, the non-grafted polymer was not compressed in a good solvent. In the second case, there were no loops, even if entanglements

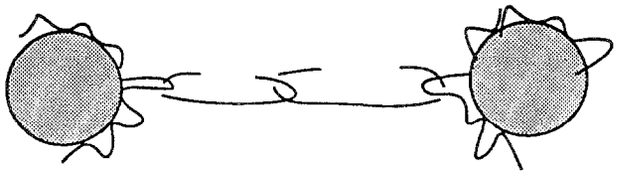

Figure 14 Schematic description of elongated film showing grafted silica and entanglements of non-grafted polymer molecules in between themselves and also with loops of grafted polymer

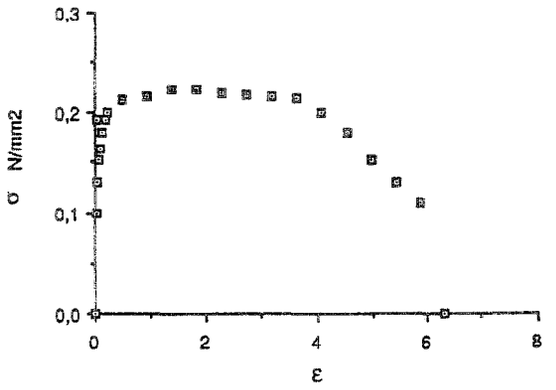

Figure 15 Stress–strain curves of a film cast from the toluene solution of non-grafted polymer and containing the grafted silica (silica content 6%). Elongation rate 10 mm min^{-1}

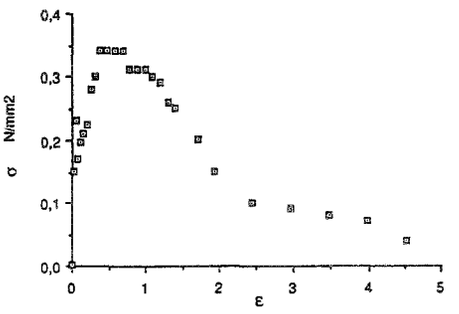

Figure 16 Stress–strain curve of a film from a latex prepared by emulsion polymerization of ethylacrylate in the presence of 6% silica functionalized with propylthioltriethoxysilane

of non-grafted polymer is possible. These two last experiments demonstrate the major importance of the loops of the grafted polymer, which govern the mechanical properties of the film from the latex of the encapsulated functionalized silica.

CONCLUSION

The functionalization of silica with a silane coupling agent carrying a polymerizable methacrylic group allows one to graft onto it rather large amounts of polymer, when the material is used as a nucleating agent in an emulsion polymerization. There results a latex able to give films which display remarkable mechanical properties similar to those of vulcanized elastomers reinforced with solid particles. However, the material is not crosslinked. The polymer that has not been grafted participates in two kinds of entanglements: A first set involves polymer molecules coming from different particles and is formed during the coalescence process of film formation. The second set, which is expected to be stronger and tighter, involves both the non-grafted polymer and the tight loop system formed around the particles by copolymerization of the methacrylic groups of the coupling agent and the growing polymer. Upon elongation of the film, the set of entanglements involving the loops is expected to remain, while the non-grafted polymer can be elongated extensively and quasi-reversibly up to near the rupture process, which takes place when the first set of entanglements disappears.

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