

Studies of Interaction in Silica/Styrene-Butadiene Copolymers

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Synopsis

Adsorption, bound rubber, mechanical properties, and electron microscopy determinations were carried out in silica/styrene-butadiene copolymers. These studies reveal equivalent trends with varying copolymer composition. Thus, when the copolymer is richer in styrene, adsorbance and bound rubber increase, the stress softening effect becomes more remarkable, and silica is more uniformly dispersed in the elastomeric matrix. These results indicate that polymer-filler interaction becomes stronger when the content of styrene in the elastomer is increased. This interaction does not appear to be explicitly reflected in the other mechanical properties studied.

INTRODUCTION

Filler reinforcement of elastomers is of great importance from the practical point of view. Consequently, it is not surprising that a great deal of research effort has been dedicated to this subject.¹⁻³ Among the different ways to study reinforcement of elastomers, an important approach has been to study the effect of varying the physicochemical nature of the filler surface and to follow how the change in the filler-polymer energetics (i.e., the filler-polymer interaction) influence the properties of the filler-elastomer composite. However, the real nature of the interaction mechanism of the macromolecule with the active sites of the pigment surface and how this interaction is related to any specific property are not yet well known.

Adsorption of polymers at the solid-solution interface and bound rubber determinations are methods broadly used to describe polymer-filler interaction. In this direction, attempts to relate adsorption studies with bound rubber and filler reinforcement of elastomers have been reported in the literature.^{4,5}

In the present work, we have chosen the system silica/styrene-butadiene copolymers; and, keeping constant the chemical nature of the filler, we have taken copolymers of different compositions and carried out adsorption, bound rubber, mechanical properties, and electron microscopy determinations, with the purpose of winning a better insight of the polymer-filler interaction and its influence on the reinforcement phenomenon.

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EXPERIMENTAL

Materials

Characterization data for the five commercial polymers used in the present work are given in Table I. The copolymer composition was estimated from the height of the integral step of the NMR spectrum corresponding to the aromatic protons of styrene residues (δ 6.5 and 7.0 ppm) and those from the olefinic protons of butadiene (δ 5.0 and 5.4 ppm). The number-average molecular weight (\bar{M}_n) was measured by means of a membrane osmometer (Hewlett-Packard, model 502) in toluene at 37°C. Aerosil silicas, with BET surface areas of 130, 200, 300, and 380 m²/g (Degussa specifications) were heated in vacuo at 110°C for 24 h and stored in desiccators before use.

Adsorption

Adsorption measurements, using carbon tetrachloride (Merck P.A.) as solvent, were made by pipetting 25 mL polymer solution of known concentration (ranging from 1.0 to 8.0 g/L) onto a known mass of dried adsorbent (ca. 200 mg) which was then dispersed by gentle ultrasonic irradiation. The container was closed and then slowly agitated in a horizontal plane in a thermostat bath at 25.0 \pm 0.5°C for 36 h. After the adsorption period was completed, the supernatant solutions were centrifuged at 4000 rpm for 20 min, and these solutions were passed through membrane filters (Millipore, with an average pore size of 0.22 μ m) to remove any suspended silica. Then, the supernatant concentrations were determined gravimetrically. Separated measurements by infrared quantitative spectroscopy were in good agreement with the gravimetric determinations. Samples and blanks were always taken in triplicate.

Bound Rubber Measurements

Silica (Aerosil 300) and each of the available rubbers (BR, SBR-1, and SBR-2), in a proportion of 0 to 50 pphr (parts per hundred rubber), were mixed on a lab roll mill at 50°C. For the purpose of bound rubber calculation, the exact amounts of silica incorporated in each rubber compound were measured gravimetrically by calcination. Strips of about 0.5 g filled rubber were placed in a closed and tared envelope made of quantitative filter paper (Watman No. 42). Then, each sample was immersed in 75 ml toluene for 72 h at room temperature, prior to

TABLE I
Characterization of the Polymers

Polymer	Wt % styrene in copolymer	$\bar{M}_n \times 10^{-5}$
BR ^a	0	1.41
SBR-1	27	1.54
SBR-2	45	1.73
SBR-3	70	1.61
PS ^b	100	1.40

^a Homopolystyrene.

^b Homopolybutadiene.

drying and reweighing to estimate the amount of unextractable rubber (bound rubber). Samples of pure rubber were subjected to the same procedure in order to have blank measurements of the gel content. This is important in order to check on any effect that rubber mastication may bring about. Samples and blanks were always taken in triplicate.

Mechanical Properties of the Vulcanizates

Rubber compounds of the same elastomers used for bound rubber were prepared on a lab roll mill at 50°C. The following recipe was used: rubber, 100; silica (Aerosil 300), 0–50; stearic acid, 2; sulfur, 3; tetramethylthiuram disulfide, 2.25. Zinc oxide was omitted in our formulation because this substance may tend to react with the most active sites of the silica surface, giving rise to poor properties of the vulcanizates.⁶

Monsanto rheometer curves of these rubber compounds were obtained at 160°C, and from these curves the time to achieve 90% total developed torque, $t_c(90)$, was chosen as the cure time. With this information, the compounds were hot pressed and vulcanized at 160°C for periods of time specified in Table IV. Standard ASTM methods were used wherever applicable to determine the physical properties of the vulcanizates. Young's modulus was determined as the initial slope of the stress-strain curve obtained at a strain rate of 50 cm/min in an Instron tester. The deformation was measured with an extensometer.

The stress-softening behavior was studied with similar dumbbell specimens (die C) in the Instron machine. The sample was stretched to 50% deformation and returned to the unstressed state. The specimen was immediately stretched again to 100%. This procedure was repeated with increasing increments of 50% extension, up to 400% wherever possible. The stress-softening effect was determined as the decrease in the work of stretching between the first and second pulls to a given strain. The work of stretching is given by the area under the stress-strain curve and was measured directly on the Instron charts with a planimeter. In this study, the stress-softening is expressed as the percentage of initial strain energy loss caused by prestressing at a given strain:

$$\Delta U = \frac{U_1 - U_2}{U_1} \times 100 \quad (1)$$

The reported values are the average of the results of nine different samples.

Microscopy

Observation of the degree of dispersion of silica in elastomeric matrixes was carried out by transmission electron microscopy. Thus, from the same filled rubber compounds used for bound rubber studies, thin sections about 500–600 Å thick were cut with a Sorvall cryoultra microtome (du Pont, model MT 2-B) at temperatures below the glass transition temperature of the elastomers. These thin sections were transferred to copper electron microscope grids covered with carbon films 15–20 Å thick. Then, the samples were examined with a high-resolution transmission electron microscope (Philips, model TEM-201).

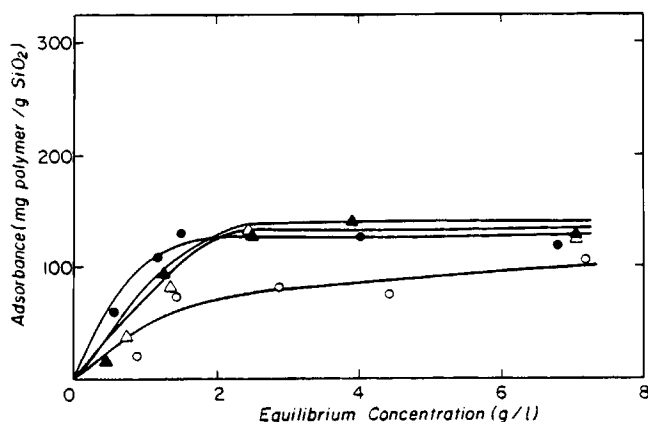


Fig. 1. Adsorption isotherms for SBR-1 adsorbed on Aerosil silicas from CCl_4 at 25°C : Aerosil 130 (\circ), 200 (\bullet), 300 (Δ), and 380 (\blacktriangle).

RESULTS AND DISCUSSION

Adsorption

Adsorption from dilute polymer solutions onto nonporous adsorbents is normally rapid. The adsorption of SBR-3 from carbon tetrachloride onto silica was measured at intervals ranging from a few hours to five days, and the level of adsorption remained constant after 12 h. In the light of these observations, a period of 36 h of contact was set for all polymer/silica systems used in the present work. This should be adequate to ensure equilibrium.

Figures 1 and 2 show equilibrium adsorption isotherms for a styrene-butadiene copolymer (SBR-1) and for polystyrene (PS), adsorbed on four different Aerosil silicas from carbon tetrachloride. As can be seen in these figures, slightly different characteristics in the shape of the isotherm are observed for a low-content styrene copolymer as SBR-1 (Fig. 1) and for polystyrene itself (Fig. 2). Thus, isotherms obtained with polystyrene (or with copolymers of high styrene content as SBR-2 and SBR-3) tend to show steeper initial regions than the ones obtained

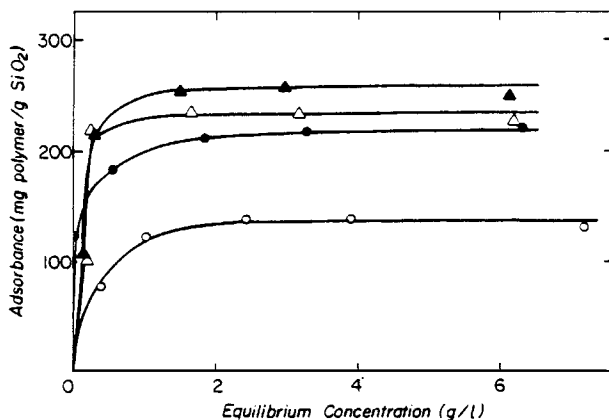


Fig. 2. Adsorption isotherms for PS adsorbed on Aerosil silicas from CCl_4 at 25°C : Aerosil 130 (\circ), 200 (\bullet), 300 (Δ), and 380 (\blacktriangle).

with polymers of low or no styrene content, such as SBR-1 (Fig. 1) and BR. In both cases, the isotherms flatten out to a plateau region where there is very little further increase in adsorption as the concentration in the bulk continues to rise. The gradient of the rise to the plateau was taken by Rowland and Eirich⁷ to be proportional to the strength of the polymer surface bond, the gradient being steeper for strong polymer-surface interactions. According to this criterion, our results would suggest a stronger interaction for polymers with high styrene content than for polymers with low or no styrene content.

Plateau adsorptions (A_{∞}) for the 20 polymer-silica systems here studied are given in Table II. Keeping in mind that the molecular weights of the polymers are approximately the same, these results show that the gravimetric adsorption (mg/g SiO₂) rises when the content of styrene in the polymer is increased. One might think that the pendent phenyl group should play an important role in the tendency of the gravimetric adsorption to increase. And effectively, considering molar adsorption (i.e., by dividing the gravimetric adsorbance by the mean molecular weight of the monomer units), this systematic trend is removed for the higher styrene-content polymers. However, it should be taken into account that changes in the polymer solubility, as the styrene content in the polymer increases, might affect the level of adsorption influencing the observed trends.

Our results are in agreement with competitive adsorption of homopolystyrene and homopolybutadiene on silica,⁸ where it was clearly shown that from an equivalent mixture of these polymers preferential adsorption of polystyrene occurs.

Results from Table II also show that A_{∞} tends to increase when the surface area of the silica increases. Similar trends have been reported for other elastomer-filler systems.^{5,9}

Bound Rubber

Results of bound rubber (i.e., unextractable rubber) given in Table III are expressed as a percentage related to the initial rubber (%) or relative to silica content (g/g SiO₂). These values were corrected for gel content (0.8, 1.1, and 8.6% for BR, SBR-1, and SBR-2 rubbers, respectively) measured as already described in the experimental section. As can be seen in Table III, bound rubber varies with silica loading. Thus, the percentage of bound rubber rises when the silica content is increased. However, it is interesting to note that the relative amount of bound rubber (g/g SiO₂) tends to decrease for rubber compounds with higher silica contents. This latter tendency may be attributed to the possible

TABLE II
Plateau Adsorption (A_{∞}) of Styrene-Butadiene Copolymers Adsorbed on Aerosil Silica from CCl₄ at 25°C

Type of Aerosil	A_{∞} mg polymer/g SiO ₂				
	BR	SBR-1	SBR-2	SBR-3	PS
130	76	106	105	102	137
200	76	129	174	171	229
300	59	134	180	196	235
380	92	141	191	207	259

TABLE III
 Bound Rubber as a Function of Silica Content

Silica content, pphr	Bound rubber					
	BR		SBR-1		SBR-2	
	%	g/g SiO ₂	%	g/g SiO ₂	%	g/g SiO ₂
10	11.6	1.16	10.6	1.06	12.1	1.21
20	13.2	0.66	14.3	0.72	16.6	0.83
30	14.2	0.47	17.7	0.59	26.5	0.88
40	15.0	0.38	18.4	0.46	23.0	0.58
50	16.8	0.34	27.7	0.54	35.3	0.71

formation of bigger silica aggregates, as shown in Figures 7(a) and 7(b), when the amount of silica in the rubber compound is increased, so that as a consequence relatively fewer anchoring sites become available for the polymer segments. As an analogy to the adsorption results, the bound rubber level, at similar silica loadings, increases when the polymer becomes richer in styrene. Although the intrinsic differences between these two methods would not allow a direct quantitative comparison, the mentioned trends point out that both methods are in good agreement and are suitable for describing the polymer–filler interaction. Thus, this interaction would be stronger for copolymers with higher styrene contents.

Pliskin and Tokita¹⁰ have proposed a model for bound rubber in which they separated what they considered truly adsorbed rubber from insoluble gel, which may be formed during the process of dispersing the filler in the elastomer. Based on bound rubber data, they developed an equation by which they claim it is possible to estimate the layer thickness (ΔR_0) of the elastomer adsorbed on the filler surface. Thus,

$$[\text{B.R.}] = \Delta R_0 f \left(\frac{\phi \rho A}{1 - \phi} \right) + G \quad (2)$$

where [B.R.] is the fraction of apparently bound rubber (i.e., g insoluble polymer/g polymer in the composite), f is the fraction of total surface area of filler which is exposed to soluble gum, ϕ is the volume fraction of filler in the composite, ρ is the density of the filler particles (g/cm³), A is the specific surface area of the filler (cm²/g), and G is the fraction of gel in the gum.

These authors¹⁰ pointed out that the value of ΔR_0 obtained from eq. (2) could be taken as a measure of polymer–filler interaction, and that for a fixed surface activity of the filler the equilibrium value of ΔR_0 should depend only on the properties of the elastomer and not on the specific area or concentration of the filler.

In the present work, trying to observe if there is any effect on the adsorbed layer thickness when the chemical composition of the copolymer is varied while the filler is kept the same, the results of bound rubber were evaluated using eq. (2). Taking $\rho = 2.19$ g/cm³ and $A = 3 \times 10^6$ cm²/g for silica, values of $\Delta R_0 = 5.7$, 15.2, and 25.3 Å were obtained for BR, SBR-1, and SBR-2, respectively. This trend suggests that the thickness of the adsorbed polymer layer is bigger when the content of styrene in the copolymer is increased.

However, it should be pointed out that these values of ΔR_0 appear to be underestimated, especially when compared with results in the range of 200–800 Å

found for the adsorbed layer thickness of polymers at the θ -condition.^{11,12} Furthermore, assuming that in the unfilled elastomer the polymer chains adopt the same dimensions as in the θ -state (100–200 Å for the radius of gyration), the calculated values of ΔR_0 would imply a very drastic deformation of the polymer coil in order to form the bound rubber layer.

The extremely low values of ΔR_0 calculated from eq. (2) can be explained by the fact that this equation is obtained from a very simplified treatment in which the bound rubber is assumed to be coated out on the filler surface as a dense layer of thickness ΔR_0 .

Mechanical Properties and Stress Softening Behavior

Table IV contains the results of several physical properties of the vulcanizates. From the cure time values, $t_c(90)$, it can be observed that the crosslinking reaction becomes slower when the silica content increases. This has been attributed to the retarding effect of the acidic silanol groups of the filler on the vulcanization reaction.¹³ Another possible explanation is that even at the cure temperature, silica would remain as a very rigid phase that immobilizes the polymer chains and consequently slows down the vulcanization process. On the other hand, the cure times are longer when the styrene content in the polymer is increased. This reflects the fact that there are fewer unsaturated units able to carry out the crosslinking process in the polymer.

For the purpose of characterizing the polymer–filler interaction by means of

TABLE IV
Physical Properties of Rubber Vulcanizates

	Silica, pphr					
	0	10	20	30	40	50
<i>BR Properties</i>						
Cure time $t_c(90)$, min	14	14	17	25	31	40
Tear, die B, KN/m	4.7	19	18	32	62	42
Hardness, Shore A	52	54	64	77	80	89
Young's modulus, MPa	1.9	2.4	5.5	12	18	25
300% Modulus, MPa	—	2.9	2.9	4.7	8.7	7.8
Tensile strength, MPa	1.1	3.2	4.8	8.3	16	10
Elongation at break, %	89	350	480	470	530	390
<i>SBR-1 Properties</i>						
Cure time $t_c(90)$, min	23	31	40	59	83	110
Tear, die B, kN/m	8.8	13	26	39	59	64
Hardness, Shore A	50	57	66	75	81	90
Young's modulus, MPa	3.2	5.8	8.0	14	24	52
300% Modulus, MPa	—	2.1	3.5	5.7	6.9	12
Tensile strength, MPa	1.3	4.8	12	18	24	24
Elongation at break, %	250	490	600	580	610	470
<i>SBR-2 Properties</i>						
Cure time $t_c(90)$, min	27	33	79	100	120	160
Tear, die B, kN/m	9.1	13	20	38	46	60
Hardness, Shore A	48	49	57	67	77	85
Young's modulus, MPa	1.2	1.9	2.8	6.6	12	27
300% Modulus, MPa	1.6	2.0	3.3	6.2	9.0	13
Tensile strength, MPa	2.3	6.7	12	19	22	23
Elongation at break, %	390	550	570	520	500	460

the mechanical properties, it would be necessary to compare the values of these properties in the rubber compounds with different silica contents but at the same cure level. However, it is not possible to measure with reasonable accuracy the true crosslink density in filled elastomers because of the influence of the filler itself on this parameter. We have chosen to vulcanize all the compounds to the $t_c(90)$ time, as determined by torque measurements by means of a disk rheometer. This criterion of cure implies that the cure level achieved by each elastomer is independent of filler content, which only would slow down the crosslinking process.

We have also obtained rheometer curves of filler-rubber compounds at 160°C without vulcanizing agents and, although the torque levels were higher with increasing amounts of silica, they do not show any remarkable change with time. This fact suggests that no appreciable physical reticulation would influence the $t_c(90)$ determinations. But in any case, in order to minimize possible differences in the crosslink density due to the adoption of the $t_c(90)$ criterion, and to be able to compare the trends in the properties of different elastomers with varying filler content, it becomes necessary to observe the relative or percent changes of these properties rather than the absolute results.

It is our interest to try to characterize how the change in the polymer-filler interaction is reflected in the mechanical properties of the rubber vulcanizates. However, the question arises in which property the influence of this interaction can be explicitly studied.

Figure 3 shows the trend in the Young's modulus of filled elastomers (relative to the Young's modulus of the unfilled elastomers) when the silica content in these rubber composites is increased. It can be observed that, with the exception of the 50 pphr values where the relative Young's modulus does increase with the styrene content in the polymer, the trend is approximately the same for the three rubbers. This can be explained by considering that the increase in the modulus is mainly due to the increasing amounts of the high-stiffness silica phase rather than by the characteristics of the low-stiffness elastomer phase or the type of polymer-filler interaction.

From adsorption and bound rubber results, it might be expected that the elastomers with the higher styrene contents would show more remarkable im-

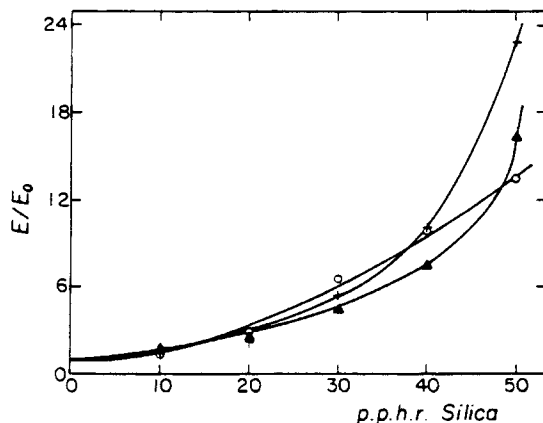


Fig. 3. Relative Young's modulus as function of silica content and copolymer composition: (O) BR; (▲) SBR-1; (+) SBR-2.

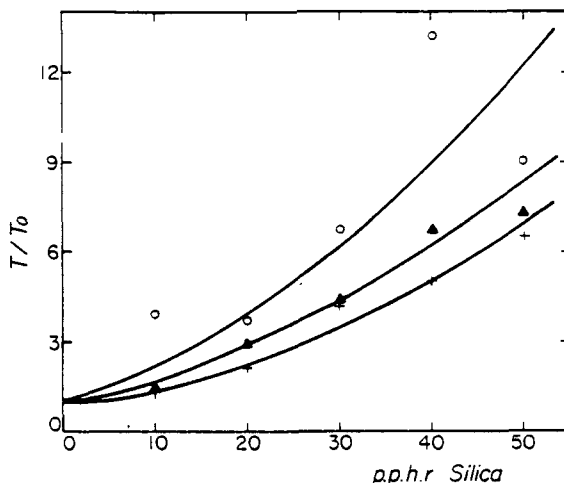


Fig. 4. Relative tear strength as function of silica content and copolymer composition: (○) BR; (▲) SBR-1; (+) SBR-2.

improvements in their physical properties with increasing silica content. However, this is not the case for properties such as tear strength, as shown in Figure 4, and other properties listed in Table IV. Thus, it would appear that the differences in the strength of polymer-filler interaction, shown by adsorption and bound rubber results, are not directly reflected in the improvement of these properties.

Figure 5 shows a family of stress-strain curves as result of a typical stress softening experiment. The stress softening or Mullins effect¹⁴ is expressed as the decrease in the work necessary to deform the material to a given strain after this material has been prestressed to the same strain. Figure 6 shows the results of stress softening plotted as a function of silica content and strain level of prestressing. Curves corresponding to the unfilled elastomers are not presented because they did not show any significant softening effect. These results show that stress softening becomes greater when the content of silica in the composite is increased. On the other hand, if we compare results for the same silica content

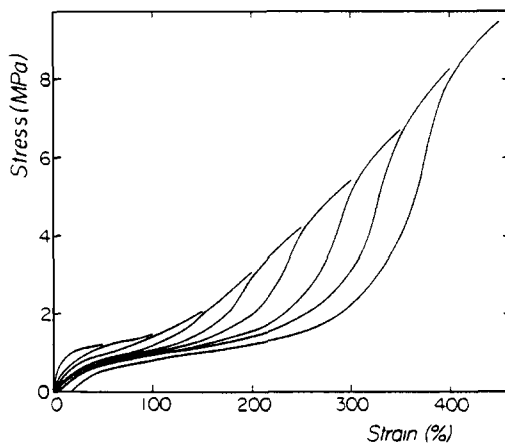


Fig. 5. Stress softening curves of SBR-1 vulcanizate containing 30 pphr silica.

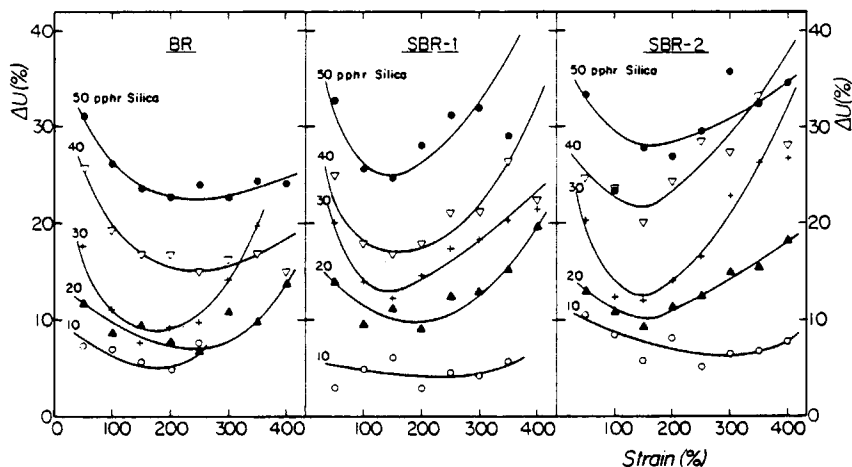


Fig. 6. Percentage of initial stress energy loss as function of elongation and silica content.

and strain level, a tendency for greater stress softening when the rubber becomes richer in styrene is also observed.

Stress softening behavior may be explained by means of two general mechanisms: the breakdown, by stressing, of silica agglomerates formed during mixing and molding¹⁵ and/or the displacement or separation of polymer segments adsorbed at the silica surface¹⁶; cleavage of polymer chains may also occur.

A greater polymer-filler interaction would mean a higher energetic barrier to be overcome in order to separate or displace the polymer segments from the filler surface. Consequently, a higher softening effect due to separation of polymer segments when the styrene content in the copolymer is increased is to be expected. Thus, the results of stress softening as shown in Figure 6 would suggest a greater polymer-filler interaction on increasing styrene content.

The fact that the difference in the softening effect between the three elastomers is not, in any case, very high may be explained by considering that an enhanced interaction would also cause a better filler dispersion and smaller agglomerates.

From another point of view, reticulation of silica in the rubber matrix will be favored by greater mobility of the polymer chains, in other words, with a bigger difference between experimental temperature and glass temperature, $T - T_g$. This difference increases as the styrene content in the copolymer decreases. Thus, the part of the softening effect due to aggregate breakdown would be smaller for the rubber with the higher content of styrene units. The observed experimental trend suggests that the softening effect is mainly due to the separation, by stressing, of the polymer chains adsorbed on the filler surface.

Microscopy

Transmission photomicrographs of thin sections of SBR-1 and SBR-2 composites obtained as described in the experimental section are presented in Figure 7. Control photomicrographs, taken from unfilled rubber and from pure silica, allow one to say that the dark areas in the pictures of Figure 7 correspond to silica aggregates. When Figures 7(a) and 7(b) are compared, it is observed that the size of the aggregates is bigger for the composite with the higher silica loading, as was already discussed.

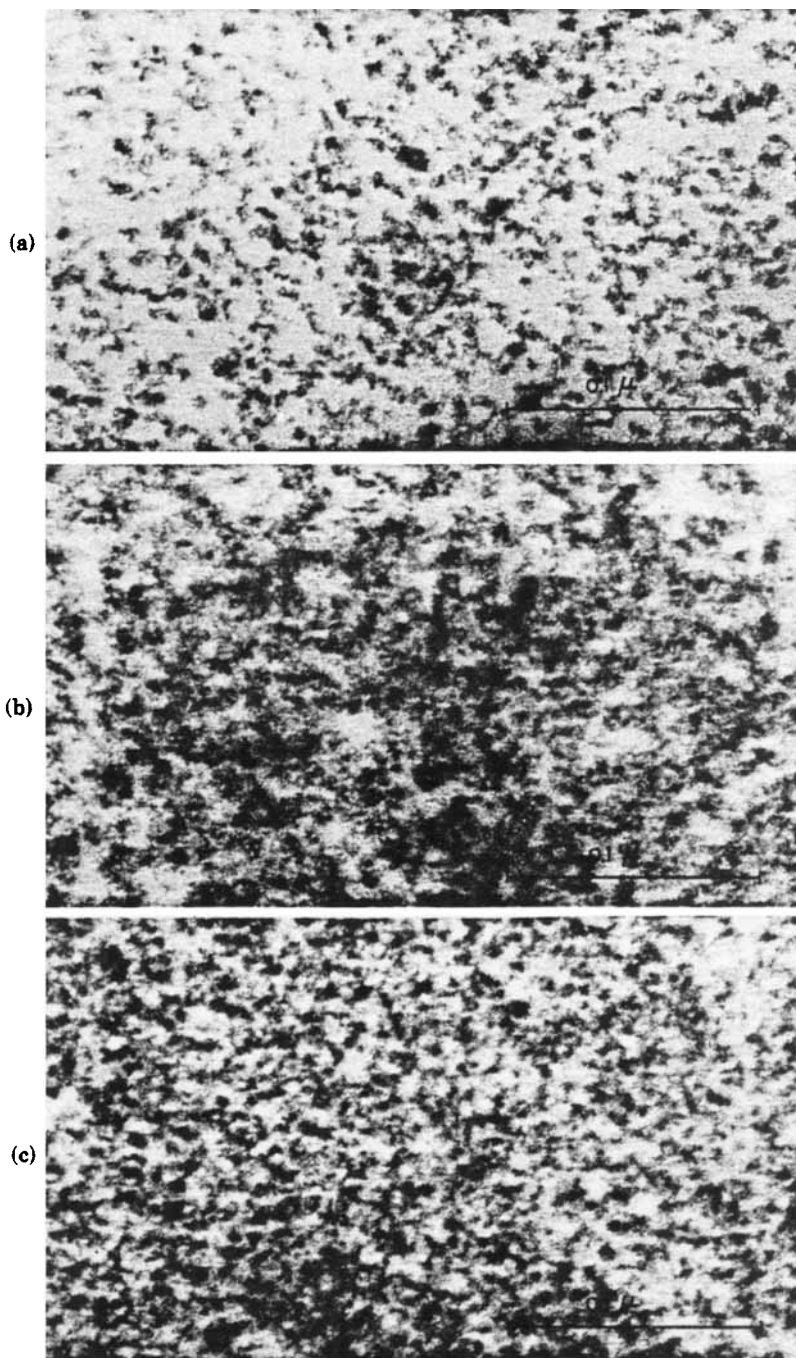


Fig. 7. Transmission photomicrographs from thin sections of rubber composites: (a) SBR-1, 10 pphr silica; (b) SBR-1, 50 pphr silica; (c) SBR-2, 50 pphr silica.

Figures 7(b) and 7(c) show that silica aggregates in the SBR-2 composite are of smaller size and more uniformly distributed than silica aggregates in the SBR-1 composite. Then, in addition to the fact that SBR-2 is a more rigid polymer matrix (smaller $T - T_g$ difference), the stronger polymer-filler interaction for SBR-2 in relation to SBR-1 (as demonstrated by adsorption, bound rubber, and

stress softening) leads to a higher level of adsorption and consequently to a better dispersion of the silica in the polymer richer in styrene. Voet et al.¹⁷ also found a better dispersion of silica in SBR rubbers when the polymer–filler compatibility was improved by the use of coupling agents.

CONCLUSIONS

It was found that when the styrene content in the elastomer increases, the values of maximum adsorbance and bound rubber rise, the stress softening effect is more remarkable, and the dispersion of silica in the elastomer composite is more uniform. These results point out that polymer–filler interaction is stronger when the copolymer is richer in styrene. This may be explained by the fact that silicon, an element of the third row of the periodic table, has an empty 3d orbital which may interact with the aromatic π -electrons of the styrene units. Then, it is to be expected that any property which may be related to the process of anchoring polymer chains on the silica surface would be enhanced if more styrene units are present in the polymer.

Stress softening phenomena appear to reflect polymer–filler interaction, as adsorption and bound rubber do. However, other determined mechanical properties in the vulcanized elastomer did not show any trend with copolymer composition that would indicate any remarkable improvement on filler reinforcement by polymer–filler interaction.

The effect of filler–polymer van der Waals interaction forces on the mechanical properties of rubber compounds is not as dramatic as the effect caused by modification of polymer–filler interaction by the use of coupling agents.¹⁸ In the latter case, real formation of rubber-to-filler grafts is involved resulting in a large improvement of the mechanical properties.

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