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Model filled rubber IV: Dependence of stress-strain relationship on filler particle morphology

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The addition of monodisperse size crosslinked polystyrene (PS) particles, synthesized by emulsifier-free emulsion polymerization, to polysulfide matrix enhanced mechanical properties of the cured rubbery composites. The modulus, fracture strength, and elongation at break increased with increasing filler volume fraction up to 30 wt% PS particles. The strength and elongation at break decreased with increasing particle diameter from 0.315 to 1.25 μm. The strength at break increased, but the extension decreased, as the particle crosslink density increased from 0 to 5 mol% DVB. Interparticle interactions are dominant and lead to the formation of clusters which form a network structure in PS particle filled composites. Since the number density, as well as the total surface area, of particles increase with decreasing particle diameter, interparticle attractions are enhanced, the tendency for cluster formation increased with decreasing particle size from 1.25 to 0.315 μm. As particle crosslink density was reduced, the porosity and surface roughness of particles increased. Then, the dispersion of particles in the matrix was enhanced and particle agglomeration reduced but more polymer matrix was adsorbed on the particles. These particles or clusters act as physical crosslinks, resulting in an increased total effective crosslink density in the filled composites. © *1999 Kluwer Academic Publishers*

1. Introduction

Reinforcement is essential to the rubber industry. Strength is enhanced in elastomeric materials by the addition of reinforcing fillers, such as carbon black, silica, and $CaCO_3$. It has been reported that reinforcement can be imparted to rubber by any particulate solid of small size with moderate or high surface activity [1–3]. For example, among non-carbon black fillers, Wagner defined "diluent" filler as having particle sizes in the range of 1–8 μm, "semi-reinforcing" filler with diameters from 0.1–1 μm, and reinforcing filler with particle diameters in the range of 0.01–0.1 μm [4].

Mechanical properties of filled rubbers are significantly influenced by filler morphology, such as particle size and microstructure, and surface activity, which determine interparticle and particle-matrix interactions [5–15]. Elucidation of this behavior may be facilitated by studying model filled systems, in which various parameters can be independently controlled. So far, most research involved industrial fillers with a wide size distribution and unknown surface characteristics. Carbon black is the most widely used particle in rubber reinforcement. Carbon blacks are essentially irregular, chainlike, branched aggregates of nodular subunits which are firmly fused together. Thus, the smallest discrete carbon black entity in rubber is always the aggregate, Specific functional groups are often present on their surfaces, such as oxygen on the channel blacks [16]. Then, it is difficult to characterize the polymer-filler interface. It would be highly necessary to study reinforcing fillers of known surface composition and particle morphology in order to determine the interactions between particles and matrix. In this research, we will use monodisperse size crosslinked polymeric particles of specific composition, synthesized by emulsifier-free emulsion polymerization, as model fillers. The reinforcement of rubbery composites filled with particles of varying particle size and surface morphology was interpreted in terms of stress-strain behavior.

2. Experimental

2.1. Materials

Monodisperse cross-linked polystyrene (PS) particles with varying particle size and particle crosslink density were prepared by emulsion polymerization [17–24]. The crosslinking agent is divinylbenzene (DVB). Styrene monomer and divinylbenzene crosslinker are products of Aldrich Chemical Company. Styrene is 99% pure and inhibited by 10–15 ppm 4-tertiary-butylcatechol (4-TBC). Divinylbenzene (DVB) consists of a mixture of 55% meta and para isomers, 42% ethyl vinyl benzene, and 3% diethylbenzene, which is inhibited with ca. 1000 ppm 4-TBC. Styrene and divinylbenzene are stored at 5 °C. The monomer and crosslinker are washed with an equal volume of an aqueous solution of 10% sodium hydroxide for 4 times, followed by deionized water for 4 times, in order to remove the inhibitor before polymerization.

Potassium persulfate and sodium hydroxide are certified Fisher Scientific products. Particles with different crosslink densities were obtained by varying the styrenedivinylbenzene ratio. The particle diameter ranged from 0.315 to 1.250 μm from scanning electron microscopy (SEM). The crosslink density ranges from 0 to 5 mol % DVB. Polysulfide with molecular weight $M_w = 8000$ g/mol, a viscous liquid with specific gravity of 1.29 g/cm^3 25 °C, manufactured by Morton International, Inc., was used as matrix. The polymer molecule also contains 0.5% branched chains. Chemically, polysulfide is a polymer of bis-(ethylene oxy) methane containing disulfide linkages. The polymer is terminated with reactive mercaptan (—SH) groups. The molecular structure is shown below:

$$\mathrm{HS(C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}S{-}S)_{47}{-}}$$
$$\mathrm{C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}SH}$$

Liquid polysulfide polymer was cured by converting mercaptan (—SH) groups to disulfide (—S—S—) bonds. This results in a high molecular weight polymer with elastomeric properties. The curing agents used are oxygen donating materials. In this research, we use manganese dioxide, a fine black powder, as purchased. The mechanism of cure is as follows: $\mathrm{2RSH + (O) \rightarrow R{-}S{-}S{-}R + H_2O}$

2.2. Sample preparation

Since the polysulfide matrix is in liquid state at room temperature (25 °C), dry and powder filler particles were weighed and added to the matrix. All samples were prepared under the same conditions by blending at room temperature with an electrically driven mixer, model Cole-Parmer, series 4401, RPM 60-700, at a rotor speed of 130 rpm for 30 min using a 4-blade mixer. Then, the mixing speed was raised to 300 rpm for 1 h. The dense suspension was transferred onto a sheet of polyethylene film, mixed forcefully back and forth using a flat, stainless steel spatula. Finally, the blend was mixed in the container at a speed of 300 rpm for 1.5 h.

After the base dispersion was prepared, we carefully weighed a specified amount of filled compound into a plastic cup and added activated manganese dioxide ($\mathrm{MnO_2}$) a catalyst concentration of 1.4 wt % $\mathrm{MnO_2}$ was used for all filled composites.

The mixture was blended with a stainless steel stirrer for about 7 min at room temperature. Then, the mixture was transferred immediately into the space between two polyethylene films, with spacers controlling the thickness, and compression-molded with a round, heavy stainless steel bar into the specified thickness. Care was taken to eliminate air bubbles trapped in the mixture. A slab of rubbery material of the required thickness was prepared in this way. The material was then cured at room temperature for 14 days. Specimens were equilibrated at room temperature for at least 24 h before mechanical tests.

2.3. Mechanical testing

Five dumbbell specimens were cut from the cured slab of rubbery material, using a Die C cutter conforming to ASTM dimensions. All specimens were prepared and tested according to ASTM D412-87 specifications. Mechanical testing was carried out at room temperature with an Instron Model 4204 with computerized recording. Samples were extended until fracture. An extensometer was mounted onto the specimen to measure elongation.

2.4. Fracture surface analysis

Scanning electron microscopy (SEM) was used to study the fracture surfaces of filled composites. The surfaces were coated with ca. 200 Å of gold and palladium using a sputter coater to increase conductivity, and examined with a Cambridge Stereoscan model 360, scanning electron microscope, at magnifications from 10^2 to 10^4. The filament used was $\mathrm{LaB_6}$ and the voltage 10 kV.

3. Results and discussion

For the development of high strength, rubber must dissipate large amounts of strain energy near the tip of growing cracks by viscoelastic processes [25]. The presence of filler particles can lead to changes in micromorphology and hence change the observed bulk properties of composite. This may lead to a deviation of the tear path caused by the anisotropy of stress around the crack-tip. For example, at certain concentrations, the particles or particle aggregates can act as physical crosslinks. As a result, strong linkages may exist between rubber chains and reinforcing filler particles. The number and the strength of these attachments and the mobility of the filler particle in the rubber are important factors determining mechanical properties. Very highly stressed chains extended between adjacent filler particles support a much larger than average stress. Since the number of attached chains is proportional to the available surface area of fillers, good dispersion and small particle size are necessary for a highly reinforcing filler.

For uniaxial tension, the Hooke's law is:

$$\sigma = E\varepsilon$$

where E is Young's modulus and corresponds to the initial slope on a stress (σ)-strain (ε) curve.

According to the network theory of reinforcement proposed by Bueche [26, 27], strong filler-matrix interaction makes fillers act as physical crosslinking sites on the filler surface contributing extra network chains to the filled system. In essence,

$$\sigma = (\nu_r + \nu_f)\kappa T(\lambda - 1/\lambda^2)$$

Where κ is Boltzman's constant and T is absolute temperature.

The modulus for the filled network can be written as:

$$G = (\nu_r + \nu_f)\kappa T$$

$\nu = \nu_r + \nu_f$ is the total number of effective crosslinked network chains per unit volume (crosslink density of composites), $\lambda = \varepsilon + 1$ is the extension ratio, ν_r is the number of network chains (from chemical crosslinking) in the unfilled rubber per unit volume and ν_f is the additional crosslinking produced by bonding to fillers. It was assumed that

$$\nu_f = (S/s)\,\phi$$

where, S is the surface area per unit volume of filler and s, the average area per attachment site, ϕ is the volume fraction of filler. Clearly, ν_f is proportional to the volume fraction, the available surface area, the ability to form a cluster structure of fillers. G or E should be enhanced as ν_f increases. The mechanical properties of composites filled with different particles will be analyzed using this theory.

3.1. Effect of particle concentration on mechanical properties

The stress-strain behaviour of composites filled with various particle concentrations is illustrated in Figs 1 and 2. The particulate filler was PS particles, 0.315 μm in diameter, crosslinked with 2 mol % DVB. The filler concentration varied from 0 to 40 wt %. Pure unfilled rubber fractured at low stress and elongation. The composite filled with 10 wt % particles showed a small improvement in strength. The filled composites fractured

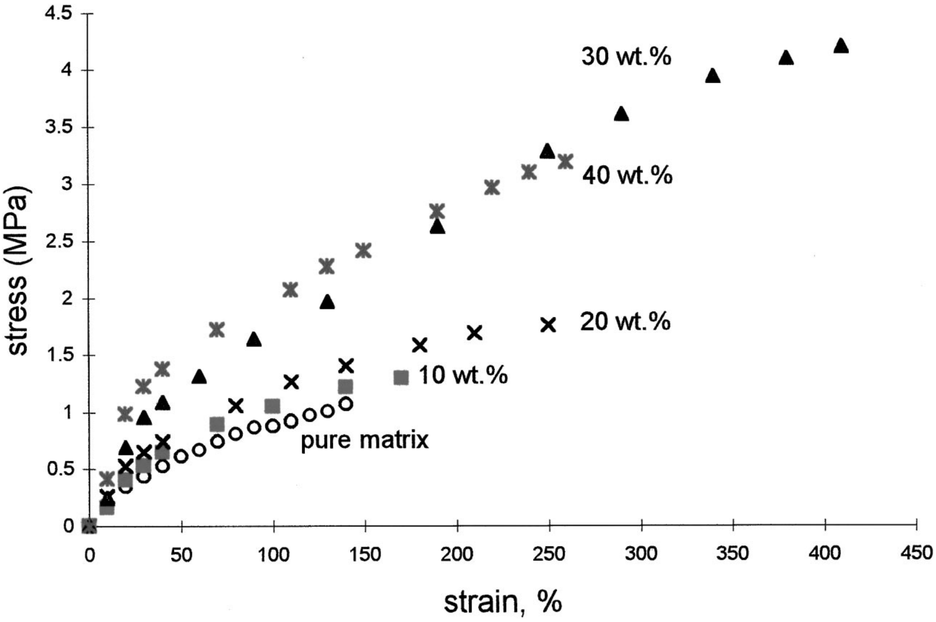

Figure 1 Stress-strain relationship for the cured rubbery composite filled with PS/2 mol % DVB.

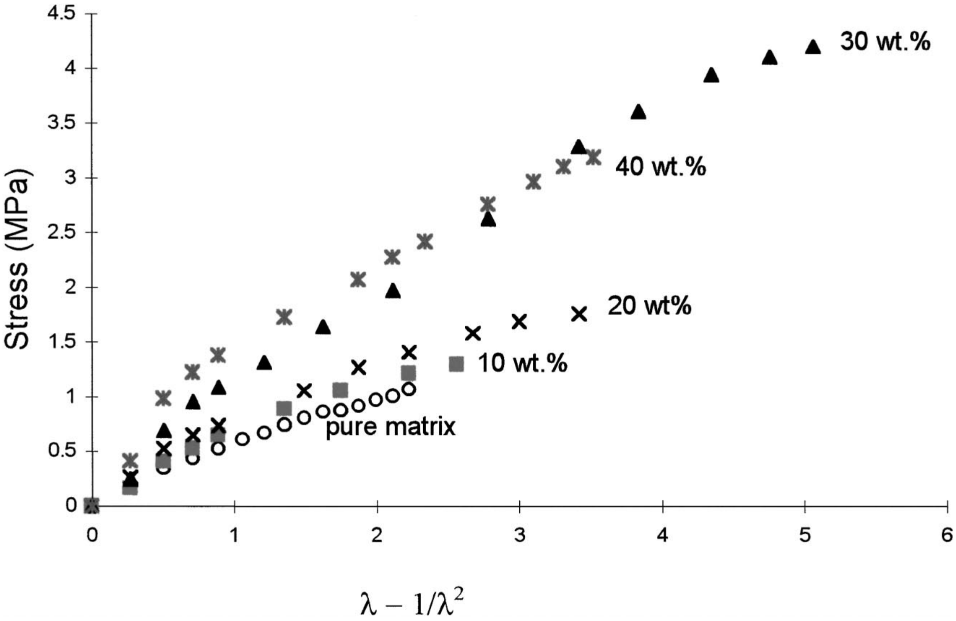

Figure 2 Fitting of experimental data to find the rubber elasticity modulus, G, for the cured composite filled with PS/2 mol % DVB.

TABLE I Mechanical properties for composites filled with PS particles

	ε_b (%)	σ_b (MPa)	ν_f (10^{20} chains/cm^3)	E (MPa)	G (MPa)
Unfilled matrix	140	1.07	0 ($\nu_r = 1.22$)	1.50	0.50
10 wt %	170	1.29	0.29	1.62	0.62
20 wt %	250	1.76	0.61	2.50	0.75
30 wt %	410	4.20	1.51	3.38	1.12
40 wt %	260	3.19	2.91	5.58	1.70

Note: ν_r and ν_f are calculated from equation $G = (\nu_r + \nu_f)\kappa T$ at 298 K.

at increasing stress and elongation, as filler concentration was increased from 10 to 30 wt %. The stress and elongation at break for a composite filled with 40 wt % particles were lower than those with 30 wt % fillers. The modulus, E or G, increased with increasing filler concentration from 10 to 40 wt %. Mechanical properties for the filled rubbers are summarized in Table I.

All filled composites show improved modulus and fracture behavior compared to the unfilled rubber. One mechanism of filler reinforcement is an effective decrease in the cross-sectional area of load-bearing polymer matrix due to the presence of fillers. Some polysulfide molecules attach to PS particles through intermolecular van der Waals forces. As particle concentration increases, the effective amount of matrix subjected to stress decreases. The stress necessary for the composite to fail is therefore increased. On one hand, filler particles can induce microflaws or cavitation to occur harmlessly under extension, and convert large amounts of elastic energy into heat and surface energy. On the other hand, the presence of rigid fillers can cause a crack to deviate or even stop. Under extensional force, fracture starts from the interfaces between particles and matrix. As filler concentration increases, the surface area available for matrix attachment and, therefore, the fracture surface area increases, so that more energy will be required for the composite to fracture. As a result, the fracture is shifted to higher stress and larger elongation in the presence of fillers. We suggested [28] that in a PS particle filled composite, agglomeration of particles takes place by van der Waals interactions among particles. The aggregates form clusters. At a high enough particle concentration, the clusters span all over the compound and produce a three dimensional continuous network. The strength and tendency to form clusters increase with increasing particle concentration. These clusters or aggregates act as physical crosslinking points and the calculated additional crosslinking (ν_f) is increased as filler concentration increased (Table I). As a result, the overall effective crosslink density of composites is enhanced. Since more energy is required for a composite of higher crosslink density to deform or fracture, the modulus and fracture strength of filled rubber increase with increasing particle concentration.

It has been reported that the modulus of filled polymers increased with increasing filler volume fraction [29, 30]. However, at a particle concentration of 40 wt %, the composite fractured at lower stress and elongation than the composite with 30 wt % filler. Although the addition of rigid particles increases the modulus, the composite with 40 wt % filler behaved like a more brittle material showing high modulus, but a low fracture strength and elongation at break. Here, excessive particle attachment and aggregation restrict deformation of polymer chains. Morever, the over “crowding” of filler particles causes poor wetting and weak adhesion between particles and matrix. It follows that in rubber reinforcement, there is an optimum filler concentration. A similar conclusion was also drawn by Furukawa and Ogunniyi in their theoretical and experimental investigations [31, 32]. In our study, at a filler concentration of 30 wt %, the highest strength and elongation at break were obtained. In the following sections, all the composites studied contain 30% filler particles by weight.

3.2. Effect of particle size on mechanical properties

Composites filled with PS/5 mol % DVB particles with diameters varying from 0.315 to 1.25 μm were cured and tested in uniaxial tension. The stress-strain response is shown in Figs 3 and 4. All the composites showed significant improvement in strength and modulus over the unfilled rubber and exhibited similar values of the modulus, E or G. However, the stress and elongation at break decreased as particle size increased. The mechanical properties of composites filled with particles of varying diameter is shown in Table II.

SEM photographs of fracture surfaces of all the filled composites showed rougher fracture surface than pure matrix. Composites containing particles of diameters 0.688 or 1.25 μm showed similar fracture patterns. At a magnification of 5000×, filler particles can be seen protruding and almost free from the matrix. No particle fracture or voids were found in the fracture surfaces. It can be inferred that such composites failed adhesively, starting from the interface between particles and matrix, since only weak dispersive intermolecular forces exist between PS particles and matrix molecules. We suggested [28] that attractive interactions between particles lead to the formation of clusters, and that clusters or aggregates interacted to form network structure. As particle size decreases, particle-particle interaction is enhanced. The forces between particles depend on surface area and the distance between particles. With decreased particle size, we get an increased total surface area and total number of particles. We suggest that larger and stronger clusters were formed in composites filled with PS particles of 0.315 μm diameter than

TABLE II Mechanical properties for composites filled with PS particles of different sizes

	ε_b (%)	σ_b (MPa)	ν_f (10^{20} chains/cm^3)	E (MPa)	G (MPa)
Unfilled matrix	140	1.07	0 ($\nu_r = 1.22$)	1.50	0.50
$d = 0.315$ μm	320	4.14	2.67	3.90	1.60
$d = 0.501$ μm	270	2.74	2.79	4.30	1.65
$d = 0.688$ μm	210	2.38	2.79	4.30	1.65
$d = 1.250$ μm	130	2.19	2.79	4.30	1.65

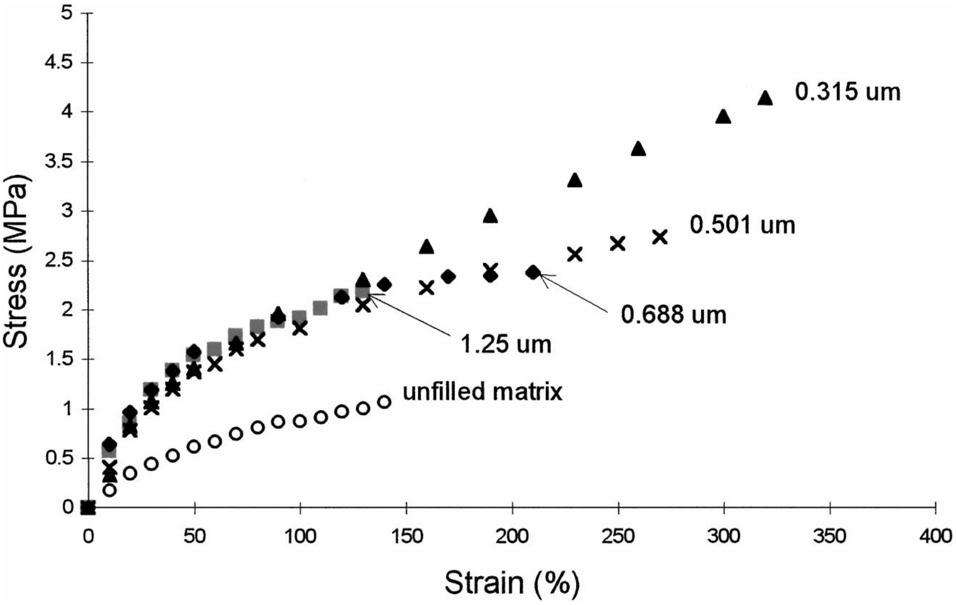

Figure 3 Stress-strain relationship for cured rubbery composites filled with PS/5 mol % DVB particles of varying particle sizes.

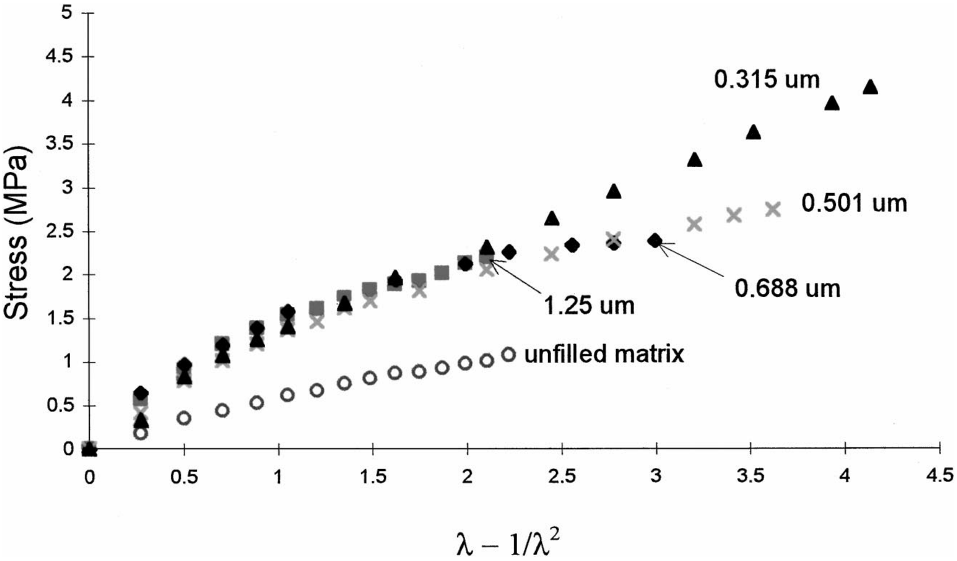

Figure 4 Fitting of experimental data to find the rubber elasticity modulus, *G*, for cured composites filled with PS/5 mol % DVB of varying particle sizes.

in composites with larger PS particles and larger particles were more isolated from one another as SEM microscopy indicated. We conclude that the ability for cluster formation increased with decreasing particle size from 1.25 to 0.315 μm. These clusters act as physical crosslinks, adding to the chemical crosslink density from the vulcanization of polysulfide matrix. The aggregates or clusters are then able to carry a larger fraction of the load than the primary particle and yield a higher fracture strength and elongation at break. Moreover, the rubber matrix occluded within the particle aggregates or clusters, after cured, becomes entangled with the particles. Also, interactions between particles and matrix are strongly dependent on specific surface area. The number density as well as the total surface area of particles increase with decreasing particle diameter. Thus for the smaller sized filler particles, a greater amount of matrix would be adsorbed on the particle surfaces, and the interfacial attachment is enhanced. As a result, the reinforcing effect and the toughness of the composite, as indicated by the area under the stress-strain curve, increase with decreasing particle size.

Another reinforcement mechanism relating to particle size is the effect of cavitation on the mechanical behavior of filled rubbers. It was suggested that the probability of finding a large flaw leading to material fracture under a given stress concentration increases with increasing particle size [33–35]. On the other hand, there are only dispersive forces between PS particles and matrix, and the matrix polymer molecules may be free to move with respect to the particle surface under deformation. Particles with a small enough size, such as 0.315 μm in diameter, may induce microflaws or cavitation without the formation of cracks. This process can convert large amounts of elastic energy into heat and surface energy. Then, it would take higher stress and more energy for the composite containing smaller partcles to deform and eventually fracture. Thus, the strength and elongation at break increase as the particle size is decreased (Table II).

3.3. Effect of particle crosslink density on mechanical properties

Composites filled with PS particles, 0.3 μm in diameter and with crosslink density varying from 0 to 5 mol % DVB, were cured and tested in uniaxial tension. The stress-strain relationships are plotted in Figs 5 and 6. All the particle filled composites showed reinforcement over pure unfilled rubber. The modulus, E or G, for composites filled with particles crosslinked with either 0.5 or 2 mol % DVB is very similar, but slightly higher than that for uncrosslinked particles. Composite filled with particles crosslinked with 5 mol % DVB exhibited the highest modulus. The strength at break increased, but the extension decreased as the particle crosslink density increased from 0 to 5 mol % DVB. Results are listed in Table III.

SEM photographs of fracture surfaces showed that the composite filled with PS/0.5 mol % DVB particles

TABLE III Mechanical properties for composites filled by particles with varying crosslink density

	ε_b (%)	σ_b (MPa)	ν_f (10^{20} chains/cm^3)	E (MPa)	G (MPa)
Unfilled matrix	140	1.07	0 ($\nu_r = 1.22$)	1.50	0.50
0% DVB	570	2.90	1.45	2.75	1.10
0.5% DVB	480	3.25	1.51	3.38	1.12
2% DVB	410	4.20	1.51	3.38	1.12
5% DVB	320	4.14	2.67	3.90	1.60

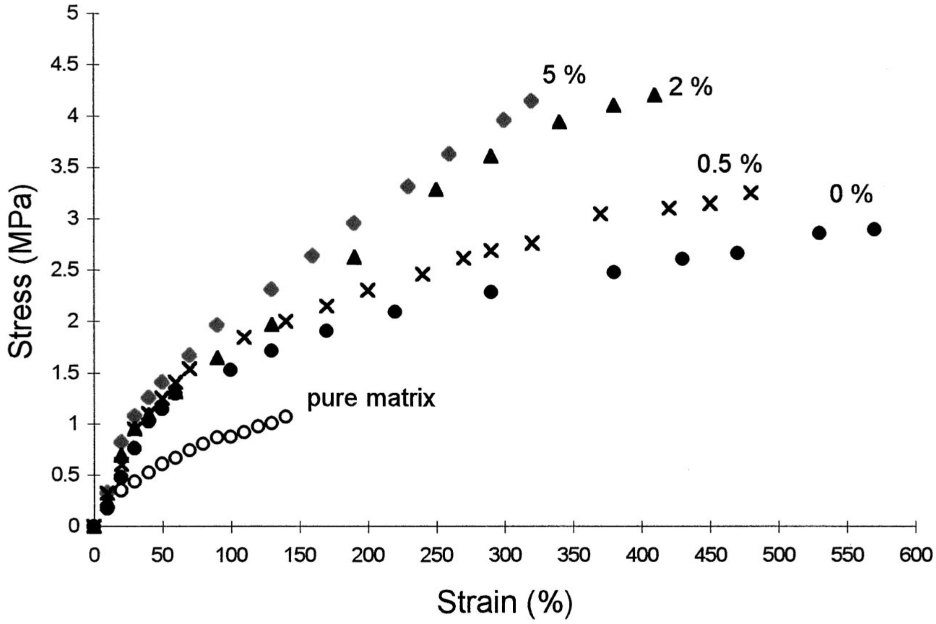

Figure 5 Stress-strain relationship for the cured rubbery composites filled with PS particles of different particle crosslink density. Particle diameter 0.3 μm.

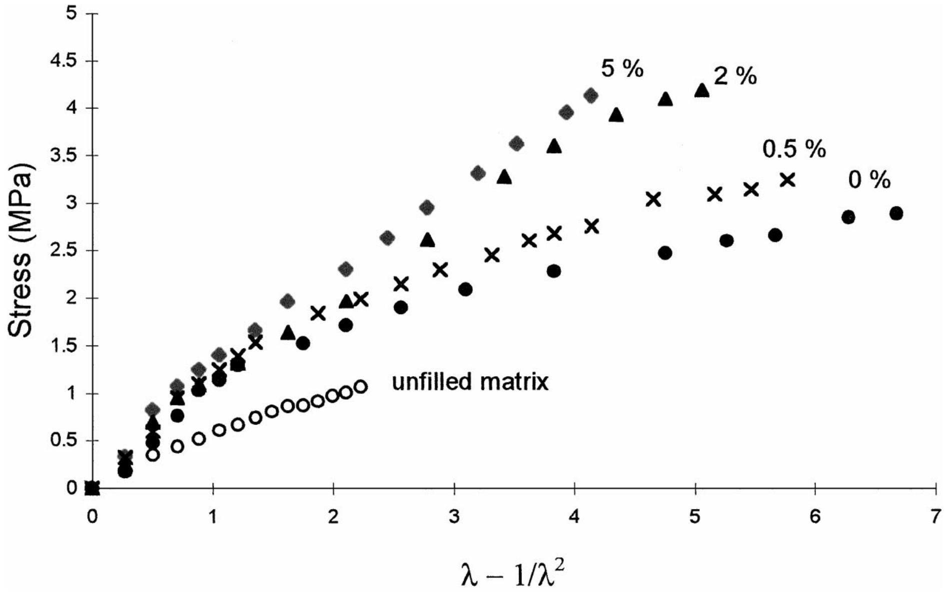

Figure 6 Fitting of experimental data to find the rubber elasticity modulus, G, for cured composites with PS particles of different crosslink density.

had a rough fracture surface. The composite filled with PS/2 mol % DVB particles, at 150×, showed many steps on the fracture surface, indicating that fracture occurred in several planes. In all samples, particles could be seen dispersed over the fracture surfaces at high magnification (5000×). However, the composite filled with uncrosslinked PS particles showed a more uniform dispersion. Clusters or agglomerates are apparent in the composite filled with PS/2 mol % DVB. No particle fracture was observed in these composites.

In PS particle filled composites, attractive interactions between particles lead to the formation of clusters or particle agglomerates. SEM photographs showed that at a crosslink density of 2 or 5 mol % DVB, cluster domains are seen, while in composites filled by PS particles either crosslinked with 0.5 mol % DVB or uncrosslinked, the particles are more isolated from each other in the matrix. We suggest that cluster formation increased with increasing crosslink density from 0 to 5 mol % DVB. We proposed that the microstructure of PS particles crosslinked by DVB was affected by their crosslink density. As the DVB concentration was increased, the porosity and surface roughness of crosslinked PS particles were reduced. When PS particles are mixed with the low molecular weight liquid polysulfide, the matrix molecules diffuse and penetrate into the pores in the filler particles and are adsorbed onto the particle surface, so that a layer of matrix polymer is attached to the particle surface.

Adsorption at the PS particle surface is physical, arising from Van der Waals interactions between particles and polymer matrix. Unlike chemisorption, physical adsorption does not completely restrict the movement of polymer chains relative to the particle surface when high stresses are applied. Polymer chain threads located in or on PS particles can either be pulled out or broken in order to detach from the surface under deformation. We suggest that the porosity and surface roughness of the particles increases as the particle crosslink density decreases, it is reasonable to infer that particles of lower crosslink density, that is, synthesized with a lower concentration of DVB, should have a deeper and more extensive adsorption layer of polysulfide matrix. Composites filled with such particles should deform to a greater extension before rubber molecules are fractured or detached from the particles, yielding a higher strain at break. Thus, the elongation at break increases with decreasing particle crosslink density (Table III). Also, as we reduce the crosslink density of the PS particles, they become increasingly succeptible to swelling by the matrix. Moreover, the surfaces of the particles became rougher as PS chains from the particle protrude into the matrix. If low molecular weight polysulfide chains diffuse and penetrate into the pores in the particles, the dispersion of particles in the matrix is enhanced, and particle agglomeration reduced. Therefore, we infer that particles with sufficently low crosslink density should exhibit lower cluster formation. Stronger cluster networks would be formed in composites filled with PS particles crosslinked with 5 or even 2 mol % DVB. The rubber matrix occluded within particle aggregates or clusters, after cured, is well entangled with the particles. These clusters or particle agglomerates formed in the composite act as physical crosslinks (ν_f), and are able to carry a larger proportion of the load. It follows that the overall effective crosslink density of the composites increases with increasing PS particle crosslink density, since cluster formation increases. As a result, the modulus and fracture strength of the particle filled composites increase as particle crosslink density increases. However, the composites filled with PS particles of higher crosslink density are stiffer and more brittle, so the elongation at break, ε_b, decreases with increasing particle crosslink density (Table III).

4. Conclusions

In this paper, we report on the effect of filler particle morphology on the mechanical properties of model filled rubbery composites. Monodisperse size filler particles of varying particle size and particle crosslink density were synthesized by an emulsifier-free emulsion polymerization and used as model fillers.

The addition of filler to a rubber matrix improves mechanical properties. The modulus, fracture strength, and elongation at break increased with increasing filler volume fraction up to 30 wt % PS particles. The strength and elongation at break decreased with increasing particle size from 0.315 to 1.25 μm in diameter. The highest strength, extensibility, and toughness were obtained for the composites filled with the smallest particles, diameter 0.315 μm. The strength at break increased, but the extension decreased as the particle crosslink density increased from 0 to 5 mol % DVB.

Interparticle interactions are dominant and lead to the formation of clusters, and the clusters or aggregates interact to form a network structure in PS particle filled composites. The number density as well as the total interfacial surface area of particles, and hence the interactions between particles and matrix, increase with decreasing particle diameter. The interparticle interaction and ability for cluster formation increased with decreasing particle size from 1.25 to 0.315 μm. As particle crosslink density was reduced, the porosity and surface roughness of particles increased. Then, the dispersion of particles in the matrix is enhanced as matrix chain diffuse and penetrate into pores in the particles, and particle agglomeration was reduced. Composites filled with particles of lower particle crosslink density should deform to a greater extent before fracturing, yielding a higher strain at break. These particles or clusters act as physical crosslinks, resulting in an increased total effective crosslink density in the filled composites.

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