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Model filled rubber

Part V *Mechanical properties of rubbery composites*

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Monodisperse size crosslinked polymeric particles of specific chemical compositions, synthesized by emulsifier-free emulsion polymerization, were used as model fillers to study the effect of filler chemical composition on stress-strain behavior of rubbery composites. The modulus, *E* or *G* of filled composites increased while the stress and the strain at break decreased with increasing filler-matrix interactions. Physical crosslinking, either due to particle clustering or a network of filler particles with an adsorbed polymer layer supplemented chemical crosslinking. As a result, the overall crosslink density(chemical and physical) was effectively enhanced. The strength of the physical networks, and hence the stiffness of the composites increases with increasing particle-matrix interactions. However, excessively strong matrix-filler interaction would cause a loss of polymer flexibility at the particle-matrix interface, resulting in a decreased stress and elongation at break of the particle filled composites in the order PS > PMMA > PSVP.

1. Introduction

Striking changes in stress-strain behavior are brought about in the reinforcement of rubber by particulate fillers. Materials which can be used as filler vary extensively with respect to their chemical structures. Mechanical properties of composites are influenced by particle-matrix interactions in the composite [1, 2]. Godard, by investigating polystyrene filled with calcium carbonate with different surface modifications, pointed out that the tensile strength of composites varied mainly with matrix-filler interactions, that is, with the adhesion between filler and matrix and matrix-filler stress transfer mechanism [3]. It was pointed out that the reinforcement of rubber material by silica fillers depends markedly on the extent of interaction between silica surface and polymer matrix, which can be controlled by varying the nature of the silica surface [4].

Optimal reinforcement involves both physical and chemical interactions between filler particles and polymer matrix [2]. Most studies have used industrial fillers with a wide size distribution and unknown surface characteristics. Then, it is not possible to define interactions at the matrix-filler interface under service conditions. As a result, beyond some general agreements, there remains much confusion and controversy [5–15]. Following an investigation of the rheological behavior of suspension of model filled rubbery composites [16], the corresponding completely cured solid composites were tested in tension in order to compare their responses at large deformation after curing. We will use monodisperse size crosslinked polymeric particles of specific compositions, synthesized by emulsifier-free emulsion polymerization, as model fillers. The reinforcement mechanism of rubbery composites filled with particles of varying chemical compositions will be interpreted according to the theory of filled polymer composite.

According to the theory of Bueche [17], it was postulated that strong filler-matrix interactions act as physical crosslinking sites on the filler surface and contribute extra network chains to the filled system.

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

Where $\sigma = f/A$ is the stress, f is the equilibrium force, and A the area of the initial cross-section, κ is Boltzmann's constant and T is the absolute temperature.

$\lambda = \varepsilon + 1$ is the extension ratio, ν_r is the number of network chains(from chemical crosslinking) per unit volume, ν_f is the additional physical crosslinking produced by filler particles. The rubber elasticity theory [18] predicts that the relation between the tensile stress and the elongation ratio, λ, is:

$$\sigma = G(\lambda - 1/\lambda^2) \tag{2}$$

where G is the rubber elasticity modulus based on Equations 1 and 2 the modulus for the filled network can be written as follows,

$$G = (\nu_r + \nu_f)\kappa T \tag{3}$$

Where $\nu = \nu_r + \nu_f$, is the total number of effective crosslinked network chains per unit volume(crosslink density of composites), Based on this theory, the mechanical properties of composites filled with different particles will be analyzed.

2. Experimental

2.1. Materials

Monodisperse spherical particles include: polystyrene (PS), and vinylphenol (VP) modified polystyrene (PSVP), each crosslinked with 2 mole% divinylbenzene(DVB), and poly (methylmethacrylate)(PMMA) crosslinked with 2 mole% ethylene glycol dimethacrylate(EGDMA). These particles, 0.315 um in diameter, were synthesized by emulsion copolymerization in the absence of emulsifier.Details have been reported [19–26]. For the synthesis of crosslinked PS particles, styrene is 99% pure and inhibited by 10–15 ppm 4-tertiary-butylcatechol(4-TBC). Divinylbenzene 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. The monomer and crosslinker were 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. The initiator, potassium persulfate, is certified Fisher Scientific product. A typical recipe for polymerization is 70 g styrene plus divinylbenzene, 700 g water, and 0.16 g(0.845×10^{-3} mole/l) to 0.64 g(3.38×10^{-3} mole/l) potassium persulfate. 650 g of water are added to a reaction flask immersed in a thermostated water bath at temperature of around 95°C. Nitrogen is bubbled through the water and flow continued throughout the reaction. The stirrer is started and agitation speed adjusted to 350 rpm. After 15 minutes, prewashed monomer and crosslinker are added to the flask and allowed to mix for 20 minutes to equilibrate. Potassium persulfate initiator, dissolved in 30 ml of water is added and washed in with another 20 ml water. Polymerization occurs at constant temperature for several hours. Crosslinked PS particles containing 10 mole% vinylphenol(PSVP10) were prepared as follows: distilled water(700 ml), styrene(58.63 g), DVB(3.00 g), and p-acetoxystyrene (10.70 g), and initiator were added to the reactor. The reaction was kept at around 94°C for 4 hours. The resulting particles are 2 mole%DVB crosslinked PS with 10 mole% acetoxy groups(PSAS). Then, the acetoxystyrene residues in PSAS particles were converted to hydroxyl groups by hydrolysis in hydrazine hydrate [19]. The deacetylated resin, now containing free hydroxyl groups, was filtered and washed successively with 75% aqueous dioxane-2M HCl, followed by dioxane-water(1 : 1) and dioxane-methanol(1 : 1) by volume. In the synthesis of PMMA particles, methyl methacrylate(MMA) monomer with assay 98%, inhibited with 25 ppm hydroquinone(HQ), is a product of Fisher Scientific Co. Crosslinking agent, ethylene glycol dimethacrylate, 98% purity, inhibited with 100 ppm hydroquinone monomethyl ether, was purchased from Aldrich Chemical Co. Potassium persulfate was used as initiator. Polymerization was conducted in an internally stirred reaction kettle containing monomer, crosslinking agent, and initiator. The reaction was run for $4 \sim 5$ hours at 80°C, then, the particle latex was filtered, washed with methanol and water, and dried at 80°C for 3 days.

Polysulfide with molecular weight Mw = 8000 g/mole, 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 as follows:

$$\begin{aligned}&\mathrm{HS(C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}S{-}S)_{47}}\\&\quad\mathrm{{-}C_2H_4{-}O{-}CH_2{-}O{-}C_2H_4{-}SH}\end{aligned} \tag{4}$$

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, manganese dioxide was used as purchased. The mechanism of cure is as follows: $2\mathrm{RSH} + (\mathrm{O}) \rightarrow \mathrm{R{-}S{-}S{-}R} + \mathrm{H_2O}$.

2.2. Sample preparation

All compounds contain 30% particles by weight. Since the polysulfide matrix is in a liquid state at room temperature (25°C), dry powder particles were added to the matrix. All samples were prepared by blending at room temperature with an electrically driven mixer, Cole-Parmer, series 4401, RPM 60-700, at a rotor speed of 130 rpm for 30 minutes using a 4-blade mixer. Then, the mixing speed was raised to 300 rpm for 1 hour. 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 again at a speed of 300 rpm for 1.5 hours. The sample was stored at room temperature for two weeks. These procedures proved to be effective in preparing a uniform rubber compound. The catalyst was added to the compound and mixed with stainless steel stirrer for about 7 minutes 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 hours before mechanical tests.

2.3. Mechanical testing

Five dumbbell specimens were cut from a 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

TABLE I Characterization of crosslinked polymeric filler particles

Chemical composition	Diameter (μm)	Crosslink density (mole%)
PS	0.315	2% DVB
PMMA	0.344	2% EGDMA
PSVP10/10%p-vinylphenol	0.315	2% DVB

recording. Samples were extended until fracture. A strain gauge clip-on extensometer, series 2630, from Instron 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 A° of gold and palladium to increase conductivity using a sputter coater, and examined with a Cambridge Stereoscan model 360, scanning electron microscope, at magnifications from 10^2 to 10^4. The filament was LaB6 and the voltage 10 kv.

3. Results and discussion

Monodispersed crosslinked particles were examined by SEM. The particle size was measured and listed in Table I. Particles are monodisperse in size to ± 0.005 μm of any given composition [27, 28]. The functional groups on these particles were identified in FTIR spectra [19]. PS particles showed a standard polystyrene IR spectrum. In PMMA particles, absorption due to the ester group can be found between 1100–1200 cm^{-1} (C—O) and at 2951–2997 cm^{-1} (C=O). For PSVP particles, a transmitance peak at a wavenumber of 3544 cm^{-1} is shown, characterizing the hydroxyl group(—OH) on the molecules. The crosslink density of PS-DVB and PMMA-EGDMA copolymers from the emulsion polymerization was measured by using the equilibrium swelling technique [22, 29]. It was found that for PS-DVB system, at a conversion of 75–80%, the cumulative mole fraction of crosslinks in the copolymer approaches the mole fraction of DVB in the feed for copolymerizations of 2 mole% and 5 mole% DVB with styrene. The conversion of all batches in this research was controlled to around 80% so that the desired crosslink density of the resultant PS particles was obtained. For PMMA particles, it was found that the mole fraction of EGDMA in the monomer feed is approximately equal to the mole fraction of crosslinked units in the MMA-EGDMA copolymer [29]. Here, 2 mole% EGDMA was used to crosslink MMA in the emulsifier-free polymerisation.

Fig. 1 shows stress-strain results measured for composites filled with PSVP(10 mole%VP), PMMA and PS particles, 30 wt.% particles in a polysulfide matrix. Fig. 2 is a fitting of the experimental data to find the rubber elasticity modulus, G. The physical crosslink density, ν_f , was also calculated from Equation 3. Detailed mechanical properties are listed in Table II.

Filled composites all yielded a higher modulus, stress and strain at break than the unfilled rubber.

TABLE II Mechanical properties for composites filled with particles of varying composition

	ε_b (%)	σ_b (Mpa)	ν_f (10^{20} chains/cm^3)	G (Mpa)
Unfilled Matrix	140	1.07	$0(\nu_r = 1.22)$	0.50
PS-2%DVB	410	4.20	1.51	1.12
PMMA-2%EGDMA	230	4.05	1.87	1.27
PSVP(10 %VP)	150	3.65	2.74	1.63

Note: ν_f and ν_γ are calculated from equation $G = (\nu_f + \nu_\gamma)\kappa T$ at 298 K

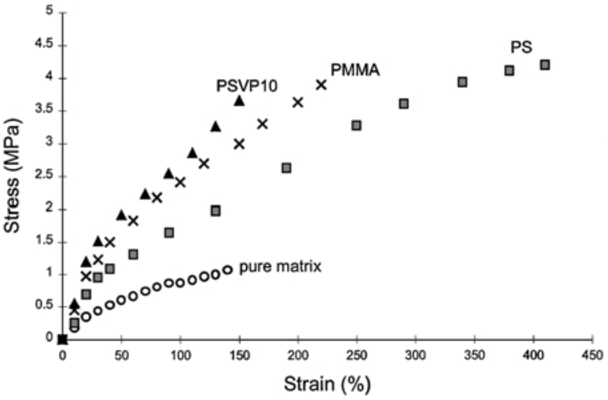

Figure 1 Stress-strain relationship for the cured rubbery composites filled with particles of different chemical composition.

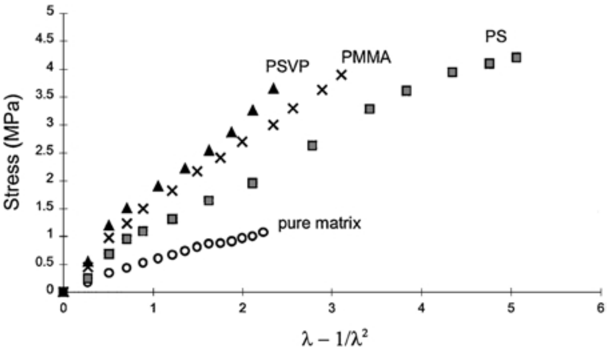

Figure 2 Fitting of experimental data to find the rubber elasticity modulus, G, for the cured composites filled with particles of different composition.

The physical crosslink density, ν_f , and the modulus, G, of composites filled with different particles increased in the order PS < PMMA < PSVP10; while the stress and the strain at break increased in the order PSVP10 < PMMA < PS. That is, the PSVP10(10 mole% VP) filled composite gave the highest modulus, while PS filled composite yielded the highest stress and elongation at break. PMMA filled composite gave intermediate results. SEM microscopy, as shown in Figs 3–6, of fracture surfaces indicated that the unfilled rubber exhibited a smooth layered pattern. At high magnification (5,000 ×), PS particles were nearly free of the matrix, indicating a weaker interfacial adhesion between PS particles and matrix. Most of the particles appeared to be embedded in the matrix in PSVP filled composite, indicating a strong interaction between PSVP10(10 mole%VP) particles and matrix. The fracture morphology of PMMA filled composite appeared to be intermediate between PS and PSVP10

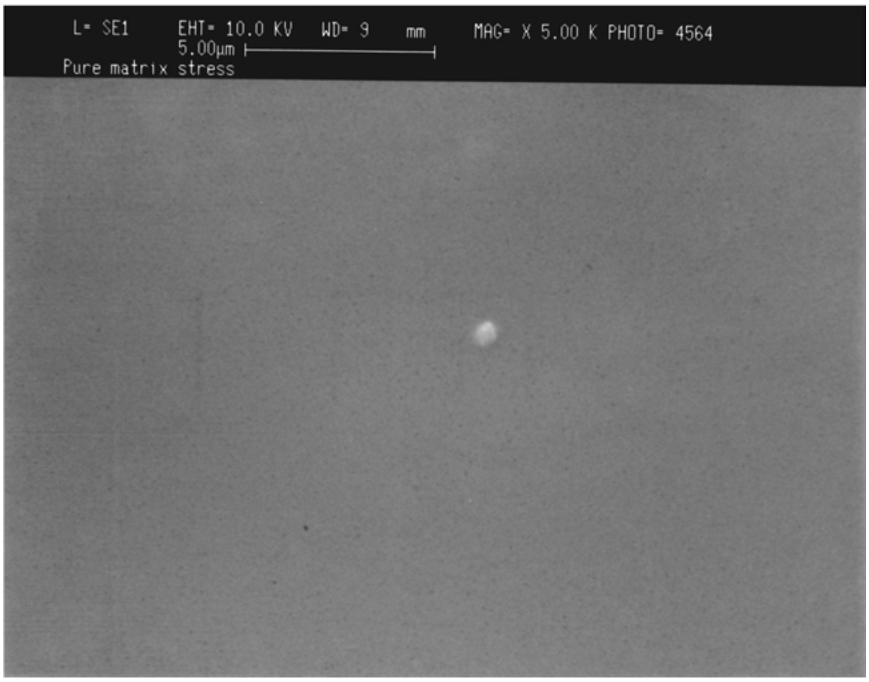

Figure 3 Fracture surface of unfilled rubber, no structure is noticeable in the cured sample (5,000×).

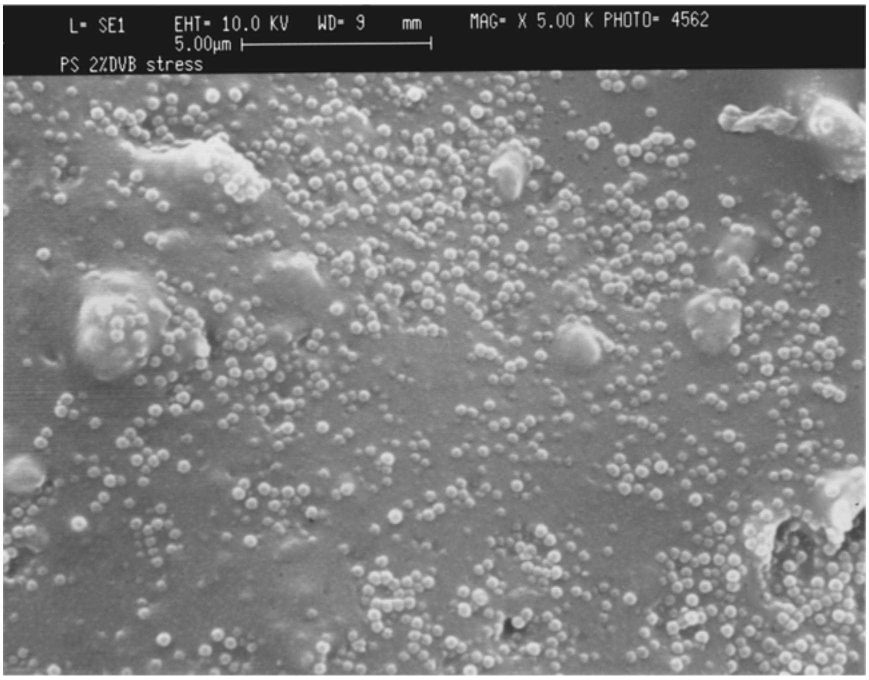

Figure 4 Fracture surface of rubbery composite filled wth PS/2 mole%DVB particles (5,000×). Particle diameter 0.315 μm.

composites. Since no particle fracture was observed, it was inferred that the filled composites begin to fail by debonding at the interface between filler particles and matrix.

The fracture surface morphology as well as the mechanical properties of filled composites is related to particle-particle and particle-matrix interactions in the filled composites. In contrast to the non-polar hydrocarbon long chain structure of traditional rubbers, polysulfide polymers possess a more polar structure with formal and sulfide units in the backbone. In the case of PS particle filled composites, since PS is non-polar, PS particles are not considered to be compatible with the matrix, interaction between PS particles and polysulfide matrix comes from dispersive intermolecular forces. the particle-particle interactions are dominant in PS filled composite. As a result, aggregation takes place by the van der Waals attractive forces between particles [30]. At a critical particle concentration, the aggregates produce a large cluster structure, the matrix material occluded within the particle aggregates or clusters is shielded from deformation and acts as part of the filler [27, 31].

In the PSVP particle filled composites, The polysulfide chains have a strong affinity for the particles through polar or strong hydrogen bonding between

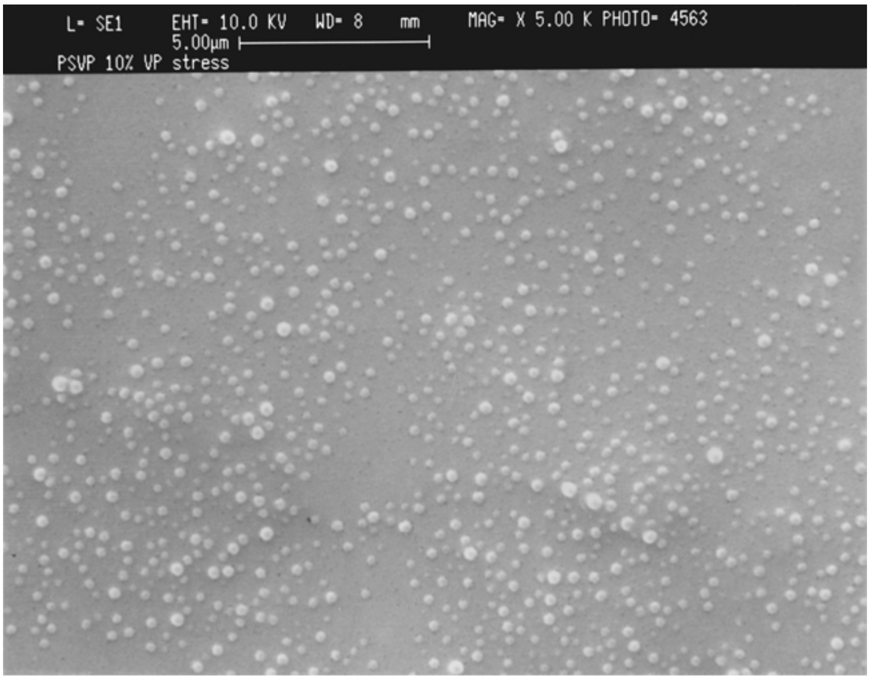

Figure 5 Fracture surface of composite filled with PSVP/2 mole%DVB /10mole%VP particles(5,000 ×). Particle diameter 0.315 μm.

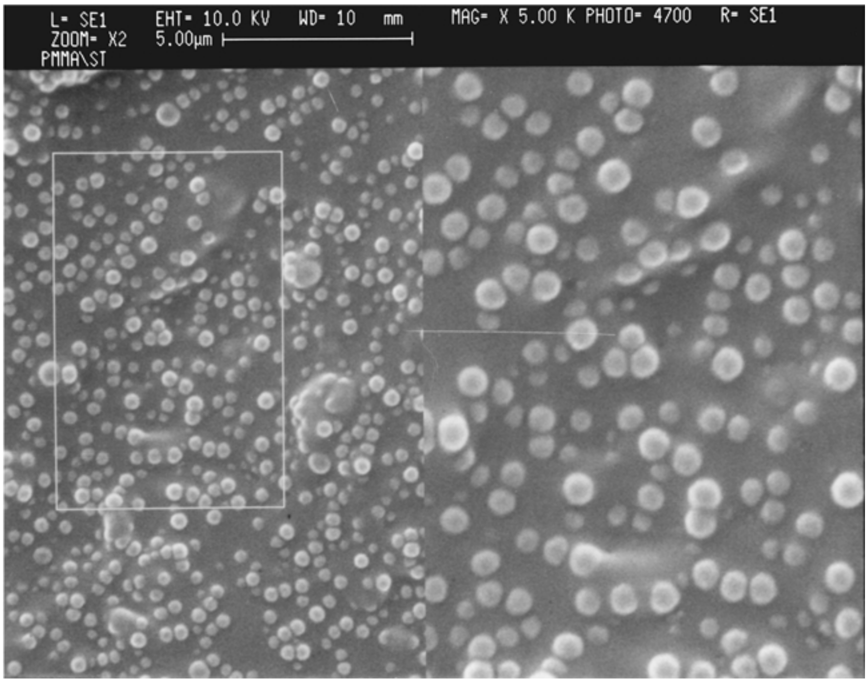

Figure 6 Fracture surface of composite filled with PMMA/2 mole%EGDMA. Diameter 0.3 μm. Magnification: 5,000 × left, 10,000 × right.

PSVP particles bearing hydroxyl groups leading to a dominant particle-matrix interaction. This strong interactions bring about significant matrix adsorption onto the particles. Similarly, in the PMMA filled system, the interaction between PMMA particles and polysulfide matrix comes from both polar interaction and weak hydrogen bonding between carbonyl groups on PMMA molecules and the mercaptan(—SH) groups on the polymer matrix. We suggest that neither particle-matrix nor particle-particle interactions dominate in the PMMA-filled system. However, interactions between PMMA particles and matrix promote an affinity of the matrix to PMMA particles.

With strong particle-matrix interaction, the dispersed particles can be bound together by the matrix. Then, these particles can act as physical crosslinking sites producing a three dimensional continuous network of matrix and fillers. As a result, on the one hand, the polysulfide matrix is chemically crosslinked by vulcanization into a three dimensional network, on the other hand, the filler particles or clusters act as pseudocrosslinks [32, 33]. The overall crosslink density, then, comprises both chemical crosslinking (ν_γ) and physical crosslinks(ν_{f}). Since the dispersive force as in PS filled composite is much lower than polar and hydrogen bonding interactions as in PSVP or PMMA filled composites [15]. The strength of interactions between particles and polysulfide matrix are proposed to be in the following order: PSVP > PMMA > PS. This microstructure of the particle filled composite was also reflected in the suspension rheology [16]. Differences in mechanical properties of rubber compounds stem basically from these interactions.

Umeya, by studying a colloidal suspension, established a relationship between viscoelastic properties and the thickness of the immobilized polymer layer adsorbed on the particle surface [34]. Since interaction between filler and polymer matrix is considered to be responsible for the formation of an immobilized polymer layer on the filler surface, the layer thickness can vary with the strength of the matrix-particle interaction. With increased interfacial interaction, the absorbed layer thickness on the filler particles increases [35, 36]. The adsorption of polysulfide on the filler surface leads to a loss of mobility of the chains. The physical networks (ν_f), and hence, the stiffness of the composites increases with increasing particle-matrix interactions in the order PS < PMMA < PSVP10 (10 mole% VP). Shang also reported that a thicker filler-matrix interface, with a higher work of adhesion(Wa), was obtained by increasing the density of hydrogen bonds at the filler surface. Young's modulus, E, was reported to increase with increasing interfacial adhesion [37].

Although the modulus is increased, the increased effective crosslink density causes a reduction in ductility, leading to lowered stress and elongation at break. Earlier studies had indicated that the strength of composites could be maximized by optimizing interfacial interactions between fillers and polymer matrix [38, 39]. By studying model systems containing terminally brominated liquid polybutadiene matrix, Edwards concluded that the degree of strong bonding desirable in practical vulcanizates appears to be about 0.2 bonding sites per nm^2 of filler surface. An increase, to 0.82 bonding sites/nm^2, produced a reduction in tensile strength and a low elongation at break [2]. In studying the modification of nylon 66 resin by the addition of rubber, Wu pointed out that typical Van der Waals dispersion forces were adequate to obtain toughening reinforcement [40]. Strong interactions between filler and matrix as well as a high concentration of filler increase rigidity in the crosslinked composites. The increased stiffness would yield a reduced elongation at break. In the PSVP10 filled composite, excessively strong matrix-filler interaction immobilizes the polymer layer at the particle surface and causes a reduction in extensibility, since the adsorbed polymer chains can not readily deform to dissipate the applied energy. The increased stiffness of the composite results in a higher modulus, but produces lower strength and elongation at break. However, in the PS filled composite, there are only dispersive Van der Waals forces between particles and matrix, so that polysulfide chain on the filler surface can deform with respect to the particle surface when a high stress is applied. For such composites, more elastic energy is dissipated as surface energy. The toughness is enhanced, and the stress and elongation at break are increased. The interaction between PMMA particles and matrix is intermediate between that for PS and PSVP10 particles and matrix. Therefore, fracture strength and elongation at break increase in the order PSVP10 < PMMA < PS.

4. Conclusions

The mechanical properties of model filled rubbery composites filled with particles of specific chemical composition were investigated in terms of stress-strain behavior. The reinforcement mechanism was analyzed. The filler particles, monodispersed in size, were synthesized by emulsifier-free emulsion polymerization. Based on stress-strain measurement, the mechanical properties of the composites varied with varying interactions between particles and polymer matrix. The modulus, E or G of filled composites increased with increasing particle-matrix interactions in the order PS < PMMA < PSVP10, while the stress and the strain at break increased in the order PSVP10 < PMMA < PS. In PMMA and PSVP filled composites, strong polar and hydrogen bonding exist between particles and matrix. Matrix adsorbed onto the particle surface enhances the crosslink density. In a PS filled composite, interparticle interaction causes particle clustering. These clusters as well as filler particles act as physical crosslinks. As a result, in these filled composites, the overall crosslink density(chemical and physical) was effectively enhanced. The adsorption of polymer matrix onto filler particles increases with increasing interfacial interactions. The strength of such physical networks, and hence the stiffness of the composites increases with increasing particle-matrix interactions. However, excessively strong matrix-filler interaction causes a loss of flexibility of the polymer at the particle surface, resulting in a lowered stress and elongation at break.

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