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Toughening of a Polysilsesquioxane Network by Simultaneous Incorporation of Short and Long PDMS Chain Segments

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ABSTRACT: An effective toughening approach is described in this report. This approach uses a combination of both short and long PDMS segments, simultaneously incorporated into a polysilsesquioxane-based rigid network through chemical bonding at the terminals of these segments. Upon curing, the short chain PDMS remains molecularly dispersed (phase I PDMS) and the long chain PDMS segregates to form silicone rubber particles in situ (phase II PDMS). Proper combinations of phase I with phase II PDMS toughen the network 7−9 times more effectively than the phase I alone at the same total PDMS loading level, while the phase II PDMS alone deteriorates the mechanical properties. The effectiveness of the phase I/II combinations is dependent on the particle size. Submicron-sized particles are more effective than particles of a few microns in diameter. Particles larger than a few tens of microns become ineffective. The size of the particles can be controlled by changing these parameters: the precoupling reaction conditions, the amount of phase II PDMS, the phase II PDMS chain length, and the chain length ratio of phase I PDMS segment to phase II PDMS segments. With appropriate phase I/II combinations, the K_{Ic} is increased by up to 220% and the G_{Ic} by up to 900%, with less loss of elastic modulus as compared with toughening by the phase I alone. It is proposed that the effective engagement of high cross-link density domains into the deformation process by submicron-sized rubbery particles is responsible for the increased fracture toughness.

Introduction

Polysilsesquioxane-based resin networks have gained renewed interest for a range of applications demanding fire/thermal/radiation stability, low dielectric constant/loss, and low moisture absorption. But the brittle nature of these polymers remains as a long recognized problem. Previously we reported the toughening of a organosilesquioxane-based resin by incorporation of triethoxysiloxy-terminated PDMS chains into the resin network.[1] The resin investigated, the Dow Corning 4-3136 resin, was a condensation curable resin prepared from cohydrolyzing a mixture of chlorosilanes and condensing the hydrolyzates to derive an after cure average composition of $(MeSiO_{3/2})_{0.45}(PhSiO_{3/2})_{0.40}(PhMeSiO)_{0.05}(Ph_2SiO)_{0.10}$. Before cure, the resin is a prepolymer of a number-average molecular weight of approximately 1500, according to GPC analysis using a polystyrene standard, and has approximately 2 wt % OH groups. To incorporate the PDMS segments into the resin molecular network, the residue silanol groups on the resin prepolymer were used to react with the triethoxy ends of the PDMS short chains. The short PDMS chains were distributed into the resin network without detectable phase separation. We referred to these modified resins as phase I toughened resins. The best phase I toughening PDMS segments, with a degree of polymerization of 55 and at a level of 10 phr (parts per hundred parts of resin), increased the plane strain critical stress intensity factor K_{Ic} from 0.253 to 0.45 MPa $m^{1/2}$ and the critical strain energy release rate G_{Ic} from 38 to 265 J/m^2. The ultimate strain and the strength of the phase I toughened resin were also substantially increased, but the Young's modulus decreased slightly. The phase I toughening successfully enhanced plastic deformation in the cured resin.

Here we report the toughening of the same resin by phase-separated rubbery particles formed in situ, referred to as phase II toughening PDMS, and by combinations of phase I and phase II toughening PDMS. It has been known that segregated rubbery particles, present in a glassy matrix, alter the stress state at the vicinity of crack tip and introduce mechanisms responsible for higher fracture toughness.[2−10] Under a uniform remote stress field, particulate inclusions of a modulus different from the matrix create a stress concentration which is confined to less than a few diameters away from the surface of the particle. The disturbance of the stress field by the particles may suppress crazing and facilitate yielding, or it may simply induce crazing or yielding in numerous places, instead of just a few when the rubber particles are absent. Because of a mismatch of thermal expansion coefficients between the matrix and the particles, in the matrix compressive stress can be built up in the vicinity of the particles along the tangential directions. Coupled with the tensile stress in the radial direction and the applied tensile stress, this compressive stress will facilitate yielding in the resin matrix.[4] In the particles a negative pressure built up can cause particle cavitation that absorbs additional mechanical energy.[11] The deformation of the particles, much larger than the matrix can endure, stores and dissipates mechanical energy and often bridges the crack surfaces to lower stress concentration.[12] Under certain circumstances debonding of the particles from

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Table 1. Raw Materials

name	supplier	comments
4-3136 resin	Dow Corning Corp.	~ 2 wt % OH
Y-177 catalyst	Dow Corning Corp.	
toluene	Aldrich	reagent grade

Table 2. Triethoxysiloxy-Terminated PDMS

name	targeted DP	actual average DP
FBE	16	16.5
FCE	57	58.9
FDE	246	246
FEE	375	374
FFE	586	586

the matrix also functions as an effective toughening mechanism.[13] In certain matrices the regions of reduced plastic resistance percolate and induce a brittle-to-ductile transition due to a decreased interparticle ligand thickness.[14] In some systems the presence of particles can alter the speed and mode of crack propagation due to their capability to accumulate more energy before fracture.[15] The advantage of using a separated toughening phase in the matrix, as compared with molecularly homogeneous incorporation of toughening agents, is often the much smaller modulus decrease.

For the second phase particles to be effective, the particle type, particle/matrix interfacial interaction, particle size and its distribution, particle concentration, and the relative rigidity of the particles as compared with the matrix have to be in the right range, and a convenient process is needed to control all these parameters. In this paper we will report the formation of a second toughening rubbery phase in a phase I toughened system. The method to form the second phase will be described. The toughening effect of these particles will be discussed as a function of particle size, the presence or absence of phase I rubbers, and particle concentration. A particle−matrix interaction mechanism will be proposed to explain the toughening behavior of the particular rubbery particles of interest.

Experimental Section

Materials. The raw materials used in the experiments, their suppliers, and grades are listed in Table 1. They are used as received without further purification. The Dow Corning 4-3136 resin is a copolymer of cohydrolyzed species of $PhSiCl_3$, $MeSiCl_3$, Ph_2SiCl_2, and $PhMeSiCl_2$ to give an average after cure composition of $(MeSiO_{3/2})_{0.45}(PhSiO_{3/2})_{0.40}(PhMeSiO)_{0.05}(Ph_2SiO)_{0.10}$ with ~2 wt % of residual uncondensed SiOH. The M_n and M_w are 1500 and 2500, respectively. Triethoxysiloxy-terminated PDMS were prepared in the lab. Preparation methods for these triethoxysiloxy-terminated PDMS were documented in an earlier publication.[1] The average degrees of polymerization for these PDMS are listed in Table 2.

Procedures. a. Coupling Reaction of the Functionalized PDMS with 4-3136 Resin Prepolymer. The coupling reaction between the functionalized PDMS and the resin prepolymer can be carried out in two different ways: cocure concurrently with, or precouple before, the curing of the resin. It was found, as reported earlier, that the resin and functionalized PDMS should be precoupled before the resin was cured.[1]

To precouple the resin blocks with the rubber segments, they were dissolved in a toluene solution and heated in the presence of a catalyst, titanium tetrabutoxide. A three-necked, round-bottomed flask equipped with a mechanical stirrer, a condenser, and an electric heating mantle was used. The catalyst level was 0.1−0.2 wt %. An appropriate amount of toluene determined either by the phase diagram or by the need to control the particle size was added to make the resin prepolymer and the PDMS miscible. The reaction temperature was 95 °C, and it was maintained for 28 h. As reported previously, FTIR and ^{29}Si NMR were used to monitor the reaction. The reaction concentration, as discussed later, will have a profound impact on the particle size formed in the resin matrix.

b. Casting Preparation. Special casting techniques have been developed to make sound, void-free castings of condensation cure silicone resins. Details of these techniques were given in a previous publication.[1]

c. Characterization and Mechanical Testing. *(1) SEM.* Freshly fractured surfaces were observed under a Cambridge Instrument Stereoscan 240 SEM. The resin surfaces were coated with a thin layer of gold before observation, and an acceleration voltage of 10−20 kV was used. *(2) Dynamic Mechanical Analysis.* A TA Instrument 2908 dynamic mechanical analyzer was used. The temperature was raised stepwise at 4 °C/min, and at each step the sample was allowed to equilibrate for 2.5 min before data acquisition. Other testing conditions: temperature range, −150 to 400 °C; frequency, 1 Hz; amplitude, 2 μm; sample size, 20 μm by 6 μm by 1 μm. *(3) TGA.* TGA was done both in air and in argon or nitrogen using a TA Instrument model 2950. Temperature was raised at 10 °C/min. (*4*) *Mechanical Testing Sample Preparation.* After curing, the cast plate 0.15 in. (3.8 mm) thick was cut, and four 0.5 in. × 2 in. (12.7 mm by 50.8 mm) specimens were obtained for the three-point bending test and six 0.375 in. × 2 in. (9.5 mm by 50.8 mm) specimens were obtained for the fracture toughness test. The three-point bending test specimens were polished before testing. The following polishing schedule was used: SiC paper grid # 320, 600 (or 800), 1200, 2400, 4000; then alumina dispersion in water: 1, 0.3, and finally 0.05 μm. The polished specimens were dried at 70 °C overnight and conditioned at 20 ± 2 °C for at least 24 h before testing. *(5) Three-Point Bending Test.* The three-point bending test was performed per ASTM standard D 790-92. The support span was 1.5 in. (38.1 mm), and the crosshead rate was 1 mm/min. *(6) Fracture Toughness Test.* The plane strain fracture toughness, K_{Ic}, was obtained following a procedure specified in ASTM D 5045-91a,[16] and the critical strain energy release rate, G_{Ic}, was calculated from K_{Ic} on the basis of LEFM assumptions.[17] The single edge notched geometry was used. A natural precrack was produced by cutting a 0.1 in. (2.5 mm) deep notch at the edge center of the specimen and tapping a razor blade into the notch to initiate a crack and propagate the crack into the center of the specimen. The displacement rate of the test was 10 mm/min.

Results and Discussion

Formation of Rubbery Particles in a Silicone Resin Matrix. One of the unique properties an organosilsesquioxane-based resin has over organic resins is its much superior thermal and thermal oxidation stability. To minimize the compromise on thermal resistance for a toughened system, a thermally stable toughening agent has to be used. Polydimethylsioxane was chosen as the rubbery second phase for this reason. Many ways can be used to incorporate PDMS particles into the resin matrix. Preformed silicone rubber powders are particularly convenient to mix into the resin. A convenient source of these powders is the Dow Corning E powders. But in our experiments no toughening effect was observed from a large number of samples with these powders incorporated. The reason was likely the limited range of particle size and surface functionality that were available and the poor dispersion of these particles to the resin matrix. The diameters of these particles are greater than 2 μm, apparently too large to toughen the silicone resins. The surface of these particles is usually silanol (SiOH) or epoxy functional. Some amino functional silicone rubber particles are also available. All of these surface functional groups proved unsuitable for the 4-3136 resin. These particles also strongly ag-

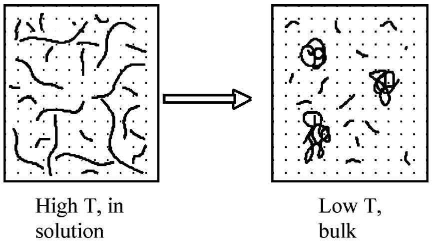

Figure 1. Schematic diagram showing the process of forming second phase rubbery particles.

glomerate, and it is difficult to break up the agglomerates without the use of strong shear force.

In this work a new process was designed to form silicone rubber particles in situ in the silicone resin matrix. This process utilized the difference in miscibility of PDMS segments with the matrix resin caused by the variation of the chain length. Previously, it was demonstrated that relatively long PDMS segments became less miscible with a predominantly silsesquioxane resin matrix, and a precoupling reaction was needed to ensure a homogeneous distribution of the segments in the matrix.[1] The precoupling reaction establishes chemical bonds between the terminals of the PDMS chain and the resin prepolymer. When phase separation was prevented by these chemical bonds, PDMS segments were incorporated homogeneously into the resin network molecular structure. Provided they have the suitable length, these phase I tougheners significantly increase the fracture toughness of the cured resin. If the length of the PDMS segments exceeds a certain limit, however, even chemical bonding at the ends of the chains cannot prevent phase separation. Upon removal of solvent and cooling, these long chain PDMS segments precipitate from the resin matrix to form rubbery particles. The chemical bonding at the ends of these segments provides strong adhesion of the particles to the matrix.

Figure 1 illustrates this process to form second phase particles. The dots in the boxes represent the silicone resin prepolymer, pure or mixed with a solvent; the lines represent the PDMS segments. In the left box short and long lines coexist, representing a mixture of the triethoxysiloxy-terminated phase I and phase II PDMS chains, respectively, both mixed simultaneously with the resin in a solvent. If a part of the short chains is replaced by the longer ones, there is an entropy of mixing loss, which favors phase separation. This can be compensated for by adding more solvent, in this case toluene, or by raising the temperature to obtain a homogeneous solution for an effective coupling reaction of both the short and long PDMS chains to the resin prepolymer. An effective reaction can be done to couple the ends of both the long and short PDMS chains with the resin prepolymer through the condensation reaction between the ethoxy groups (SiOEt) on the PDMS and the silanol (SiOH) on the resin prepolymer. After the reaction, the solvent is removed and the temperature is lowered to allow long chains to phase separate and form second phase particles, while the short phase I PDMS segments stay molecularly incorporated in the network structure. This results in a phase I/II combination toughened resin network. The coupling reaction can also be done with the long chain only, without the short PDMS chain. Then upon solvent removal and cooling only second phase rubbery particles form, without phase I PDMS incorporated into the network structure.

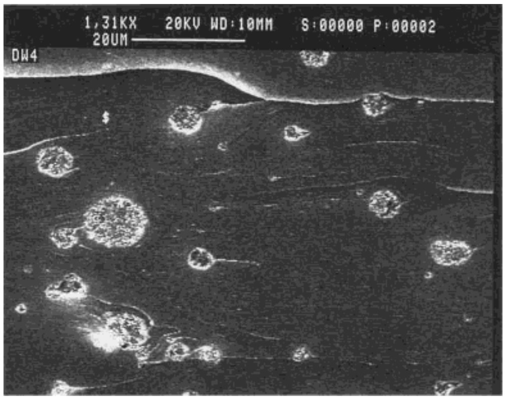

Figure 2. SEM picture of the freshly fractured surface of the 4-3136 resin toughened by a combination of 10 phr of FCE and 2 phr of FFE.

Triethoxysiloxy-terminated PDMS segments of DP 246 (FDE), 375 (FEE), and 586 (FFE) were prepared according to previously published procedures.[1] They were used as the phase II PDMS to form second phase rubber particles. Similarly functionalized PDMS of DP 16.5 (FBE) and 59 (FCE) were also made and used as the phase I PDMS. Through a precoupling reaction, both the phase I and phase II PDMS chains were reacted simultaneously with the 4-3136 resin prepolymer. After the precoupling reaction, the resin−PDMS copolymer was cured and rubber particles were formed in the resin matrix. The size of the rubber particles was controlled by the precoupling reaction conditions, the chain length of the phase II PDMS, the chain length difference between the phase I and the phase II segments, the concentrations of both, and the ratio between their concentrations. An example of second phase particles formed in the cured resin through this process is shown in Figure 2, a SEM picture of the freshly fractured surface of a resin toughened by a combination of 10 phr of FCE and 2 phr of FFE. To prepare this sample, 300 g of 4-3136 resin was dissolved in 572 g of toluene in a 2000 mL flask equipped with a stirrer, a thermometer, and a condenser. The resin/toluene solution was heated to 95 °C, and then 30 g of FCE and 6 g of FFE were added along with 0.67 g of titanium tetrabutoxide. The mixture contained 37 wt % nonvolatile polymers and was heated at 95 °C for 28 h to finish the coupling reaction. To cure the resin, the toluene was removed by drying at 100 °C under a vacuum of 25 mmHg for an hour and then following the curing procedure discussed elsewhere.[1] Phase-separated domains of 3−20 μm were formed in the cured resin. In the absence of the phase II PDMS, 10 phr of FCE was homogeneously distributed in the resin network after the coupling reaction.[1] The use of 2 phr of phase II PDMS successfully induced phase separation and the formation of rubber particles.

Control of Particle Size. Given a particular combination of resin and phase I toughening agent, the particle size can be controlled by varying a number of material and process parameters. These parameters include the chain length of phase II PDMS segments, the concentration of them in the matrix, and the reaction conditions. Table 3 summarizes the particle sizes obtained in samples A through I. In the table where average particle size was given, the particle sizes were measured by taking representative scanning electron microscopy images from a freshly fractured surface of the resin and then averaging the diameters of all

Table 3. Sample Compositions, Precoupling Reaction Concentrations, and Second Phase Particle Size

sample	4-3136[a]	FBE[a]	FEE[a]	FFE[a]	precoupling reaction concn,[b] wt %	particle size, μm
A	100	10	2.5		28.6	0.049
B	100	10	5.0		28.6	0.052
C	100	10	7.5		28.6	1−3
D	100	10	10.0		28.6	1−3
E	100	10	7.5		31.0	∞[c]
F	100	10		2.5	31.0	∞
G	100	10		5.0	31.0	∞
H	100	10		2.5	26.6	12−37
I	100	10		5.0	26.6	20−50

[a] Parts per hundred parts of resin. [b] Reaction conditions: 0.2 wt % Titanium tetrabutoxide, in a toluene solution of the specified total solid content, 95 °C for 28 h. [c] Large scale separated layers.

particles found in the images. To obtain the average particle size, at least 1000 particles were included in the calculation. When particles are fewer than 1000, the minimum to maximum range of particle diameters found in the images is given in Table 3.

The precoupling reaction concentration and the chain length of the phase II PDMS segments are the most influential parameters that determine particle size. The phase II segment concentration also changes the particle size, but the particle size change induced by its variation is much smaller. Regardless of chain length or phase II segment concentration, whenever the precoupling reaction was done at a concentration of 31 wt % in toluene, macroscopic phase separation was observed, and no particles formed in the cured resin matrix. For phase II segments of DP 375, an appropriate precoupling reaction concentration was found to be 28.6 wt %. Under this reaction condition, particles as fine as 40−50 nm in diameter were obtained when the concentration of it was below 5 phr. Particle diameter jumped to 1 to 3 μm when the phase II segment concentration exceeded 7.5 phr. When phase II PDMS segments of DP 586 were used, only large particles were obtained. With a precoupling reaction concentration of 26.6 wt %, also in toluene, particles 12−37 μm in diameter were formed when its concentration was 2.5 phr, while 20−50 μm particles were obtained when 5 phr of it was incorporated into the network.

Submicron-Sized Particle Toughening. The mechanical properties of samples A and B in Table 3, the 4-3136 resins toughened by nanometer-sized phase II particles in combination with a phase I PDMS, are plotted in Figures 3−8. The properties of resins toughened by the phase I alone are also included in the same plots. The phase I PDMS was FBE, and the phase II was FEE, a triethoxylated PDMS of DP 375. In the phase I/II combinations, the amount of FBE was fixed at 10 phr, and that of phase II varied from 2.5 to 5 phr. These two types of segments were prereacted simultaneously with the resin prepolymer in a 31 wt % toluene solution with 0.2 wt % titanium tetrabutoxide. In Figure 3, the lower line represents the effect of phase I alone on the fracture toughness, K_{Ic}, and the upper line the effect of the phase I/II combination. The lower has a slope of 0.0065 and the upper a slope of ~0.05. The phase I/II combination was approximately 8.5 times more effective than the phase I alone. For example, 10 phr of phase I alone prereacted into the resin increased the fracture toughness from 0.25 to 0.33 MPa $m^{1/2}$, and 15 phr of it increased it to 0.340 MPa $m^{1/2}$. If 5 phr of phase II was prereacted with 10 phr of phase I into the resin, the fracture toughness was increased to 0.58 MPa $m^{1/2}$. In Figure 3, the fracture toughness of a resin toughened by the phase II alone is shown as an open circle. When the phase II level was low, it was slightly better than the untoughened resin, but with 10 phr of phase II the resin was too brittle to be tested reliably, and no value is shown in the plot.

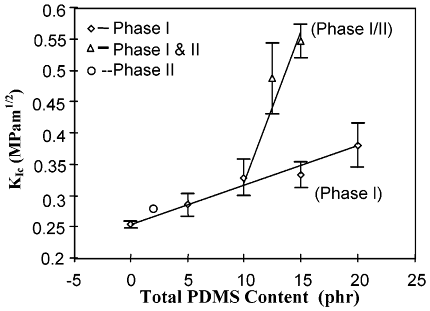

Figure 3. Plane strain fracture toughness, K_{Ic}, of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

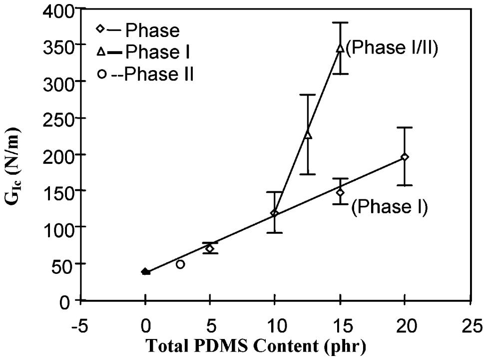

Figure 4. Critical strain energy release rate, G_{Ic}, of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

Figure 4 plots the G_{Ic} values for the same compositions. The lower line has a slope of 7.5 and the upper a slope of 47: the phase I/II combination is 6.5 times more effective in increasing the critical strain energy release rate. Without the phase I PDMS, the phase II alone severely decreased the G_{Ic}. With more than 2.5 phr of phase II alone the samples became so fragile no reliable G_{Ic} measurement was made.

The effect of the two phases on the flexural strain (Figure 5) was more complicated. If both phase I and phase II PDMS or only the phase I PDMS was present, the strain at break increased with total rubber content. If only the phase II particles were incorporated, the resin showed much lower breaking strain at 10 phr of PDMS and some modest improvement at 2.5 phr of PDMS. In Figure 6, flexural strength data are plotted. Both the phase I and the phase I/II combination increased the strength measurably though not monotonically. The phase II alone reduced it quite drastically when a relatively high amount of it was incorporated into the resin. The modulus (Figure 7) showed a down trend with increasing rubber content. The phase I/II combination toughened resins has a slightly higher modulus than the ones toughened by the same amount

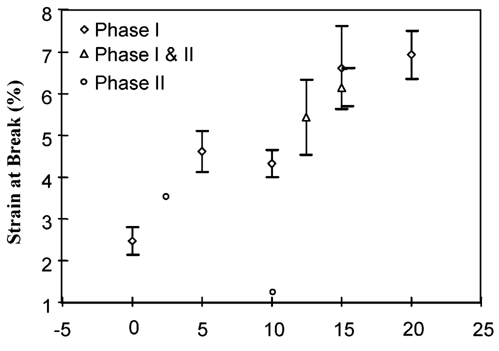

Figure 5. Strain at break of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

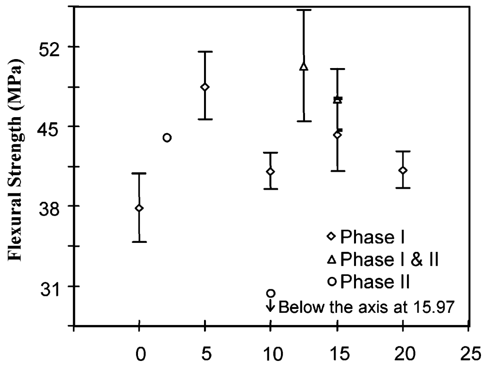

Figure 6. Flexural strength of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

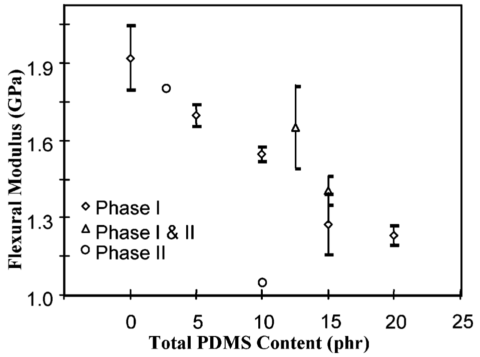

Figure 7. Young's modulus of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

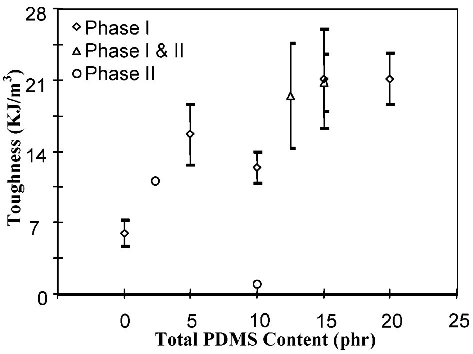

Figure 8. Toughness, measured by the area under the stress−strain curve, of the 4-3136 resin toughened by the phase I PDMS, FBE, alone; by the phase II PDMS, FEE, alone; and by the combinations of 10 phr of FBE with various amounts of FEE. The PDMS content shown in the plot was the total amount of PDMS, including the phase I and phase II.

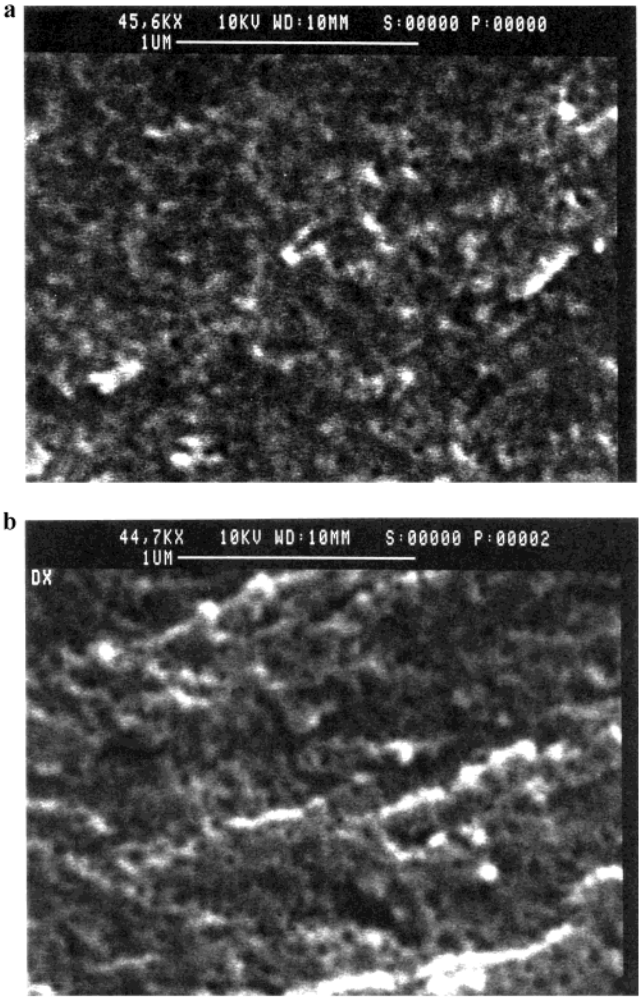

Figure 9. SEM photos of the freshly fractured surfaces of the phase I/II combination toughened resins. The phase I was 10 phr of FBE, and the phase II was (a) 2.5 and (b) 5 phr of FEE.

of phase I PDMS. Again, the 10 phr phase II only material was particularly unattractive. Similarly, the work to fracture shown in Figure 8 increased quite consistently with total rubber content, but the 10 phr phase II alone material was far below the trend line.

Figure 9 shows the SEM images of the freshly fractured surface of the samples A and B. Particles approximately 50 nm in diameter can be seen. Because of differences in thermal expansion coefficients, rubbery particles have a tendency to contract more than the matrix upon cooling from the curing temperature. When a fracture goes through the particles, the constraint exerted by the matrix on the particles is relieved, and the fractured particles contract. On a fracture surface these fractured particles appear indented into the surface and as circular depressions. The particle size was also measured by SAXS, and the two measurements were consistent.

Table 4. Fracture Toughness of the Phase I/II Toughened Silicone Resins with Large Phase-Separated Domains

sample	K_{Ic}, MPa m$^{1/2}$	G_{Ic}, J/m^2
C	0.439 ± 0.019	240.90 ± 31.50
D	0.531 ± 0.046	391.61 ± 50.24
E	0.305 ± 0.014	88.60 ± 13.35
F	0.280 ± 0.025	79.19 ± 11.87
G	0.286 ± 0.028	116.85 ± 13.85
H	0.427 ± 0.024	186.05 ± 27.54
I	0.401 ± 0.021	184.83 ± 28.80

Table 5. Calculated Plastic Zone Size in the Phase I Toughened 4-3136 Resin

toughener	K_{Ic} (MPa m$^{1/2}$)	σ (MPa)	r_y (μm)
none	0.253	37.732	2.4
5 phr of FBE	0.285	48.251	1.9
10 phr of FBE	0.328	40.917	3.4
15 phr of FBE	0.333	44.115	3.0
20 phr of FBE	0.380	41.006	4.6
5 phr of FCE	0.375	43.964	3.9
10 phr of FCE	0.453	48.492	4.6
15 phr of FCE	0.473	43.516	6.3
20 phr of FCE	0.453	35.368	8.7

Large Particle Toughening. As seen in Table 3, the particle size was increased by increasing the precoupling reaction concentration, the length of the phase II rubber chains, or the phase II PDMS content. Fracture toughness values of the 4-3136 resin toughened by a combination of 10 phr of FBE, and large second phase particles are included in Table 4. When large scale phase separation occurs, the fracture toughness value of the resin was lower than the resin toughened by the phase I alone. Samples E−G belong to this category. Better compatiblized systems, H and I, had particle sizes in the range 10−50 μm. They showed a fracture toughness value slightly higher than the resin toughened by the phase I PDMS alone. When the particle size was reduced to 1−3 μm, as in samples C and D, a more observable increase in fracture toughness was measured. However, these large particles are drastically less effective tougheners than the submicron-sized particles discussed earlier.

A Proposed Phase II Toughening Mechanism: Engagement of High Cross-Link Density Domains. It is believed by some authors that for rubber particles to toughen a polymer matrix the size of the stress field disturbance caused by the presence of these particles should be comparable to the scale of the matrix plastic deformation promoted by the particles.[18,19] The plastic deformation induced by a particle occurs in a yielding zone around the crack tip when the crack advances. The Irwin model is often used to estimate the radius of the plastic zone for plane strain condition:[20,21]

$$r_y = \frac{1}{6\pi}\left(\frac{K_{Ic}}{\sigma_{ys}}\right)^2 \tag{1}$$

where r_y is the radius of the plastic zone and σ_{ys} the yield stress. Since a classical yielding has not been observed in the resin, the flexural stress at break is used to approximate σ_{ys}. The values calculated by this method are presented in Table 5. If these calculated results are an indication of the size of the real plastic zone, the plastic zones are small. Considering that the stress field caused by a more compliant particle is probably a few times the diameter of the particle in size, it is reasonable to expect that the most effective particle size is a few times smaller than the plastic zone, i.e., in the submicron range.

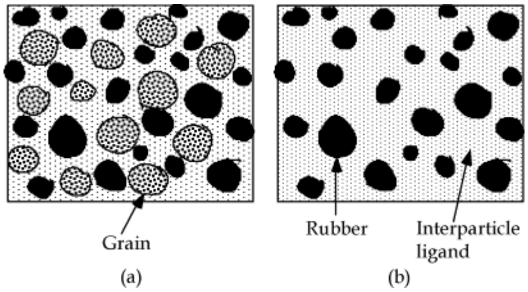

Figure 10. Schematic illustration of the nodules and the second phase particles. (b) is the same as (a) except for the grains which are omitted.

This explanation, although reasonable, offers little insight into the polymer structure−property relationship and no guidance to the design of new resin materials. We propose that the physical origin for the size dependence of toughening effect is in the inhomogeneous distribution of cross-link density, as described below, although direct experimental evidence is lacking.

For highly cross-linked epoxy resins, some researchers attribute the basic features on the fracture surface to grains a few tens of nanometers in size.[22] Similar features were also found on the freshly fractured surfaces of the cured 4-3136 resins, both phase I toughened and untoughened. The size of these “grains” found on the fracture surface is in the range 60−100 nm. These grains and the materials surrounding them are probably areas of different cross-link densities. In a silicone resin such as the 4-3136 resin, this inhomogeneous cross-link density distribution is a result of the resin synthesis process: a prepolymer is first made by condensing most of the SiOH groups on the predominantly trifunctional starting materials; the remaining very small amount of residual SiOH groups are then used to cross-link between these prepolymer molecules to form an extended network. A sketch of such a morphology, with rubbery particles present, is shown in Figure 10.

The grains are higher in cross-link density and stiffer than the surrounding areas. Sometimes they also have differentiable, higher glass transition temperatures and compositional inhomogeneity may also contribute to the mechanical property difference.[23] In a plastic zone several microns in size, strain is concentrated in the more compliant areas surrounding grains. Because of their higher rigidity, grains move but do not deform much, not contributing to energy dissipation. When rubbery particles sufficiently small in size are placed adjacent to these high cross-link density domains, the stress elevation by the rubbery particles help engage these grains and deform them. When large rubber particles are present, the inter-rubbery particle distance is large; the stress elevation can be relieved by the deformation of material between stiff grains and fails to engage those grains. The more effective engagement of high cross-linker density domains in deformation process could be the reason that highly torn inter-rubbery particle ligands were seen in Figure 9. On the fractured surfaces of untoughened and FBE toughened 4-3136 resin, no such features are present.

Dynamic Mechanical Analysis. The dissipation factors measured from a dynamic mechanical measurement for the untoughened, phase I toughened, and

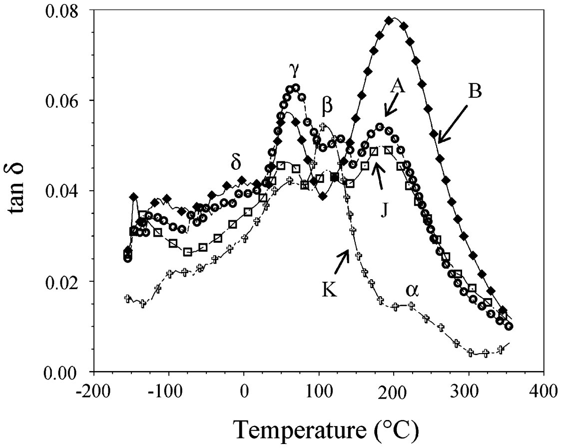

Figure 11. tan δ of the phase I toughened, phase I/II toughened, and untoughened 4-3136 resin: (A, B) the 4-3136 resin toughened by 10 phr of FBE/2.5 phr of FEE and 10 phr of FBE/5 phr of FEE, respectively; (J) 4-3136 resin toughened by 10 phr of FBE; (K) untoughened 4-3136.

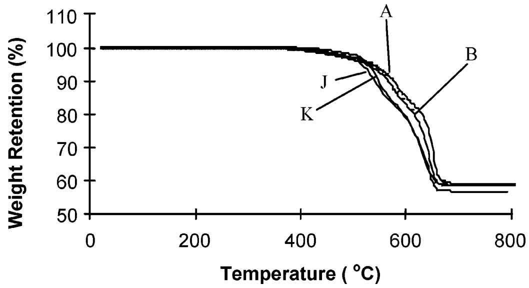

Figure 12. Weight retention in air of untoughened, phase I toughened, and phase I/II toughened 4-3136 resin. For explanation for samples see Figure 11.

phase I/II toughened resins are plotted in Figure 11. For the untoughened resin, four transitions can be observed, with the β and γ transitions being the most prominent. The α peak is small, indicating much less significant mechanical energy dissipation due to the α transition during deformation. The most significant of the changes occurring on the tan δ spectrum after toughening is the very significant enhancement of the α transition peak. Phase I toughening increases its magnitude, and phase I/II toughening enhances it even more. It appears that more effectively engaging this dissipation mechanism in the deformation process is important in toughening the resin network. It is possible that the α transition is due to the high cross-link density domains and this observation is consistent with such a possible assignment.

Thermal Stability. Thermal stability is investigated by TGA, and the results are plotted in Figures 12 and 13. While phase I toughening seems to slightly degrade the thermal stability as compared with the untoughened resin, the phase I/II toughened resins show higher weight loss peak temperatures. The final char yield of the phase I/II toughened resins are very close to that of the untoughened resin, while that of the phase I toughened resin is slightly lower.

Conclusions

Methods were developed to simultaneously incorporate short and long PDMS segments into a predominantly silsesquioxane-based rigid network through chemical bonding at the terminals of these segments. Upon curing, the short chain PDMS remain molecularly dispersed (phase I PDMS) and the long chain PDMS segregates to form silicone rubber particles in situ (phase II PDMS). Proper combinations of phase I PDMS with phase II PDMS toughen the network much more effectively than the phase I PDMS alone at the same loading level. Phase II alone does not toughen the network. The effectiveness of the phase I/II combinations is dependent on the particle size. Submicron-sized particles are more effective than particles of a few microns in diameter. Particles larger than a few tens of microns become ineffective. The size of the particles can be controlled by changing these parameters: the precoupling reaction conditions, the amount of phase II PDMS, the phase II PDMS chain length, and the chain length ratio of phase I PDMS segment to phase II PDMS segments. With appropriate phase I/II combinations, the K_{Ic} is increased by up to 220% and the G_{Ic} by up to 900%, with less loss of elastic modulus as compared with toughening by the phase I alone.

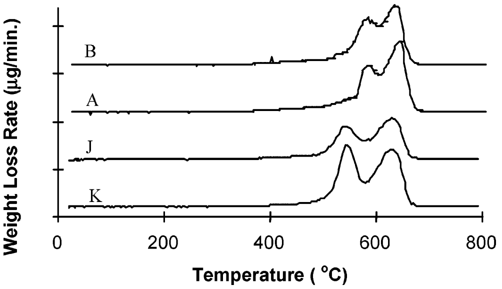

Figure 13. Weight loss rate in air of untoughened untoughened, phase I toughened, and phase I/II toughened 4-3136 resin. For explanation for samples see Figure 11. Vertical axis: 500 per division.

References and Notes

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(23) Unpublished work by the authors: in a cross-linked copolymer of phenylsilsesquioxane (T^{Ph}) and linear PDMS segments, two glass transitions were observed, one for the PDMS segments and one for the T^{Ph} domains. The T^{Ph} domain transition shifted to higher temperatures as the PDMS/T^{Ph} ratio decreased, while that of the PDMS remained at the same temperature.

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