Effect of Filler on the Compression Set, Compression Stress–Strain Behavior, and Mechanical Properties of Polysulfide Sealants

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ABSTRACT: In this work, investigations were made on the mechanical properties, stress–strain behavior during compression, swelling and compression set properties of polysulfide sealants at different carbon black and silicon dioxide loadings, and dynamic mechanical thermal analysis was also presented. The results reveal that carbon black filler indeed has significant effects on reinforcing mechanical properties of polysulfide sealants. Increasing carbon black loading improves the tensile strength of sealants promptly, but compression performance increases slowly. The simultaneous use of carbon black and silicon dioxide filler in polysulfide sealants hardly changes the tensile strength of sealants, whereas the ultimate elongation and compression performance of sealants are enhanced remarkably. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2001–2007, 2011

Key words: polysulfide; sealant; compression; filler

INTRODUCTION

Low-molecular-weight polysulfide polymers bearing thiol end-groups have been produced since 1940. These liquid polysulfide polymers can be cured by metal peroxides and other metal oxy-salts, which make use of the reducing properties of the thiol group to cause crosslinking. The main reaction procedures were reported by the early researchers.[1,2] These crosslinked elastomers derived from liquid polysulfide have found wide applications in industry, particularly those used as sealants. They are marked by their adherence to glass, steel, wood, and concrete, their good low-temperature properties and low-water vapor transmission, and their high resistance to UV radiation and the environment.[3,4] Many publications can be found on the characterization of polysulfide cured by metal peroxides,[5–9] reporting the results of thermogravimetry analysis, dynamic mechanical analysis, tensile strengths, and hardness testing. Thermal stability and photodegradation of the liquid polysulfide and cured polysulfide were also studied by Mahon et al.[10,11] In our earlier research work, structure, mechanical properties, and modification of polysulfide-based sealants have been studied.[12–16]

Usually, rubber compounds exhibit several phenomena like the ability to retain elastic properties during prolonged action of compression stress, compression set behavior, and this loss of resiliency often reduces the capability of elastomeric gasket or seal to perform over a long period of time. Researchers have extensively studied compression set behavior of rubber[17–18] and rubber compounds filled with SiO_2 and carbon black.[19,20] However, little work has been done to date on the compression set properties and stress–strain behavior during compression of polysulfide sealants.[21] It has been found recently that molecular weight and crosslinkage content of polysulfide resins have important effect on the compression set properties and compression stress–strain behavior of sealants.[22] Furthermore, when a combination of different molecular weight polysulfide resins is used in the sealants simultaneously, the compression performance of sealants is significantly enhanced. This work is to study the effects of carbon black and silicon dioxide filler on compression set properties, stress–strain behavior during compression. The results reveal that the loading of fillers has significant effects on the compression and mechanical properties of polysulfide sealants; however, only sealants prepared from a combination of fillers have lower compression set and optimal mechanical properties simultaneously.

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TABLE I
Effect of Fillers on the Mechanical Properties of Polysulfide Sealants

	Samples								
Materials weight (g)	PSF01	PSF02	PSF03	PSF04	PSF05	PSF06	PSF07	PSF08	PSF09
JLY121	50	50	50	50	50	50	50	50	50
JLY155	50	50	50	50	50	50	50	50	50
Plasticizer	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
MnO_2	10	10	10	10	10	10	10	10	10
Epoxy resin	2	2	2	2	2	2	2	2	2
Coupling agent	1	1	1	1	1	1	1	1	1
SFR black	0	20	30	40	50	60	40	40	40
SiO_2	0	0	0	0	0	0	2	4	6
Tensile strength (MPa)	1.29	2.31	2.80	3.23	3.34	3.74	3.05	3.07	3.13
Ultimate elongation (%)	321	332	300	291	275	231	385	396	367
Adhesive strength to steel substrate (MPa)	1.07	2.54	2.59	3.55	3.66	3.73	3.46	3.64	3.89

EXPERIMENTAL

Materials and preparation of samples

Low-molecular-weight liquid polysulfide resins (JLY121: SH% = 6.2–7.5%, $M_n = 1000 \pm 200$, with 2% mol trithiol; JLY155: SH% = 1.0–1.4%, $M_n = 5000 \pm 400$, with 0.5% mol trithiol) were supplied by Jingxi Research Institute of Chemical Industry, China. Manganese dioxide (MnO_2), carbon black (SFR, N774), silicon dioxide (SiO_2), stearic acid, epoxy resin (a low-molecular weight liquid DGEBA with epoxide number of 0.44), and coupling agent (2,3-epoxy propoxy propyltrimethoxysilicane) were all commercially available materials and were used as received.

The typical compositions of polysulfide sealants based on different fillers are listed in Table I. The liquid polysulfide resins, fillers, and curing agents were fully mixed by a mechanical stirrer and degassed by a Siemens DAC 150FV high-speed mixer by 3000/min (produced by Hauschild, Herrliberg, Germany). Then the bubble-free mixture was poured onto the mold of PTFE and cured at 23°C ± 2°C for 10 days. The specimens for the tensile strength measurement are 2.0 ± 0.2 mm in thickness. The specimens for compression set test and stress–strain behavior during compression measurement have the dimensions of 29 ± 0.1 mm diameter and 13 ± 0.3 mm thickness.

Mechanical properties

According to the specifications of ASTM D412-98a, the tensile strength and ultimate elongation were tested using Instron 4466 Universal Materials Testing Machine (produced by Instron Co., Norwood, MA) on dumbbell-shaped specimens. The specimens were tested at 23°C using a crosshead speed of 50 mm/min. Each result was obtained by the test repetition with three specimens.

The adhesive behavior was studied by the lap shear test. The substrate used was commercial stainless steel. The steel treatment consisted of three steps: (1) the surface was abraded with a piece of abrasive paper with 100 meshes, (2) then the surface was cleaned by a solvent wiping with acetone, and (3) the surface was dried with dry air. After the surface treatment, the steel pieces (100 mm × 25 mm × 2 mm) were assembled into lap shear joints with 12.5 mm of overlap length. The prepared samples were stored at 50°C for 48 h before being tested. The adhesive strength was tested on the Instron 4466 instrument at a crosshead speed of 5 mm/min. Each result was obtained by repeating the test with five specimens.

Dynamic mechanical thermal analysis

All dynamic mechanical thermal analysis (DMA, tension mode) was carried out using a DMA + 450 (produced by 01 dB; Metravib Co., France). The dimensions of the samples were 20 mm × 18 mm × 1 mm. The frequency was fixed at 10 Hz. The samples were heated at a nominal rate of 3°C/min from −100°C to + 150°C.

Swelling measurements

The swelling test (HG/T 3870-2008 China) was performed on a 20 mm × 20 mm × 1 mm cut specimen by immersion in toluene at 25°C. Thereafter, the test specimen was taken out, blotted with a piece of filter paper, and weighed. Each result was obtained by repeating the test with three specimens.

The swelling ratio is defined as:

$$Q\% = (M_t - M_0) \times 100/M_0$$

where M_0 and M_t are the mass of the test piece before swelling and after immersion respectively, and the mass of the specimen is measured by electronic digital balance with an accuracy of 0.001 g.

Stress–strain behavior during compression

Stress–strain behavior during compression measurement was performed on the Instron4466 instrument at 23°C. The specimen was placed between steel compression plates (with a diameter of 60 mm and a height of 15 mm) during the compression. All measurements were performed in displaced control at the crosshead rate of 10 mm/min. When the percentage of the compression reached 25% of their original thickness, the specimen was relaxed at the same crosshead rate until the stress reverted to 0 MPa.

Compression set tests

Compression set tests (ASTM D395) were performed on standard test specimens vulcanized using compression mold method. The test specimens were placed between the plates of the compression device with the spacers on each side of it, allowing sufficient clearance for bulging of the rubber when compressed. The bolts shall be tightened, so that the plates are drawn together uniformly until they are in contact with the spacers. The percentage of the compression employed is 25% of the original thickness. Then the assembled compression device was placed at 23°C for 3 or 7 days. After the completion of the compression, the specimen was removed from the device and allowed to recover for 30 min, after this thickness of the final specimen was measured by an electronic digital caliber with 0.01 mm accuracy. Each result was obtained by repeating the test with three samples.

The compression set is defined as:

$$\text{Compression set } (\%) = [(T_o - T_f)/(T_o - T_s)] \times 100$$

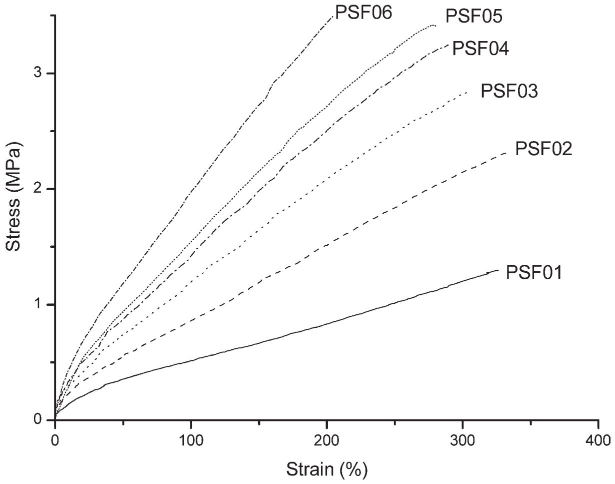

Figure 1 Stress–strain curves of polysulfide sealants based on different carbon black loadings.

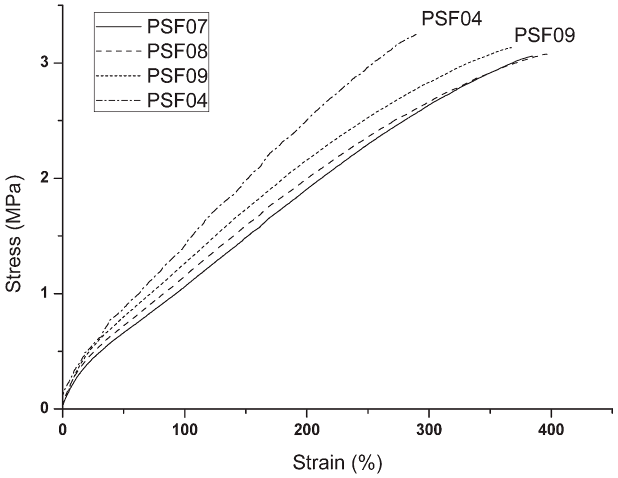

Figure 2 Stress–strain curves of polysulfide sealants based on a combination of carbon black and silicon dioxide filler.

where T_o is the original thickness of the specimen, T_f the final thickness of the specimen, and T_s the thickness of the spacer bar used.

RESULTS AND DISCUSSIONS

Mechanical properties

The typical formulations and mechanical properties of polysulfide sealants with different carbon black and silicon dioxide filler loadings are outlined in Table I. The stress–strain curves of those polysulfide sealants are shown in Figures 1 and 2. The carbon black is most commonly used in polysulfide sealants. Filler reinforcement of polysulfide sealants significantly increases the tensile strengths of polysulfide sealants. The tensile strength and the adhesion to stainless steel of unfilled polysulfide sealants are rather poor.[5] As shown in Figure 1 and Table I, sample PSF01 only has a tensile strength of 1.29 MPa and an adhesive strength of 1.07 MPa. The tensile strength of these materials changes profoundly when carbon black loading increases from 0 to 40 wt % but changes slightly between 40 and 60 wt %. With 40 or higher weight percent carbon black loading, the tensile strength of the samples reaches over 3 MPa, and the adhesive strength increases from 1.07 to 3.55 MPa, a remarkably relative increase of 230%. However, the ultimate elongation of samples decreases slowly with increasing carbon black loading. On the other hand, silicon dioxide with nanometer dimension is often used in sealants as a thixotropic agent. The testing results show that samples PSF04, PSF07, PSF08, and PSF09 with the same carbon black loading have similar tensile strengths around 3 MPa. However, the ultimate elongation of the samples increases obviously when filled with silicon dioxide. Samples PSF07, PSF08, and PSF09 have

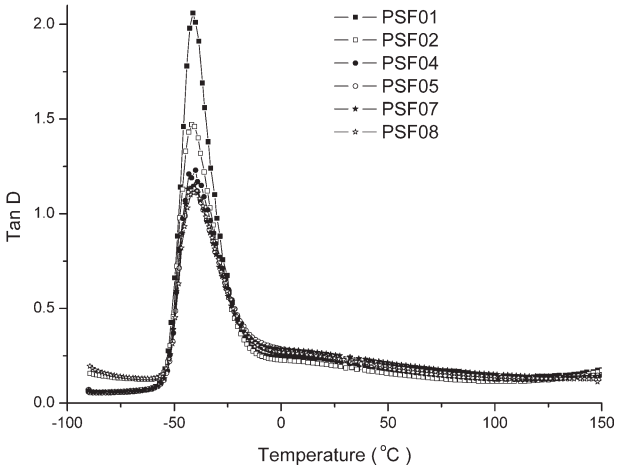

Figure 3 Loss factor curves for polysulfide sealants in DMA analysis.

the ultimate elongation of 385%, 396%, and 367%, respectively, while the sample PSF04 only has 291%. The results indicate that nanometer dimension silicon dioxide is more compatible with polysulfide resin than carbon black and helps improve the ultimate elongation of the sealants effectively. This results from the large numbers of hydroxyl groups on the surface of SiO_2 particles and hydrogen bonds formed between SiO_2 particles and ether groups of polysulfide resins. Here, sample PSF08 has the highest ultimate elongation. With more SiO_2 filler added, the ultimate elongation decreases again due to too much crosslinking.

Dynamic mechanical thermal analysis

The results of DMA analysis for polysulfide sealants are displayed in Figures 3 and 4. From the figures, it can be seen that the glass transition temperatures of polysulfide sealants vary little when filled with different filler loadings. With the increase of carbon black and SiO_2 content, the damping ratios (tan D) of sealants demonstrate a decreasing trend and store modulus increases macroscopically. It is known that the damping ratio of the composite materials reflects the materials' dissipation of energy, which mainly depends on the value of the interaction force multiplied by the slipping displacement.[23] Here, sample PSF01 has a value of tan D as high as 2.06, whereas samples PSF02 and PSF04 only have values of 1.47 and 1.21, respectively. After the addition of carbon black, the interaction force between the particles and polysulfide resins decreases the slipping displacement. The energy dissipation is accordingly reduced and the damping ratio decreased. The further addition of SiO_2 results in a lower damping ratio due to the interaction force between SiO_2 and polysulfide resin. In general, a large slipping displacement occurs in the poorly bound polysulfide sealant samples and results in a high-damping ratio. These conclusions indicate a relatively higher compression set value tested later.

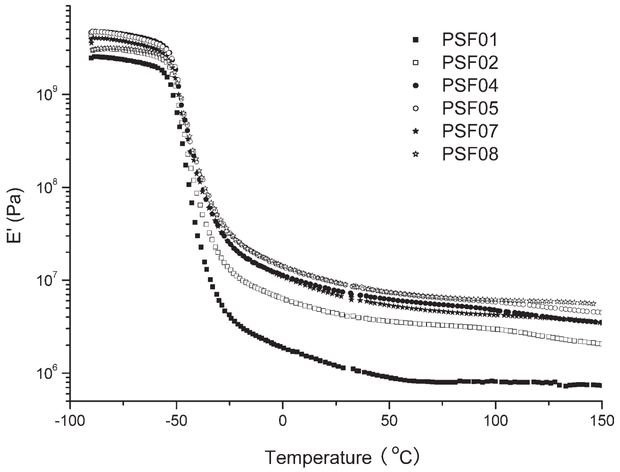

Figure 4 Storage modulus curves of polysulfide sealants in DMA analysis.

Swelling properties

Swelling tests on cured polysulfide sealants were performed on a 20 mm × 20 mm × 1 mm cut specimen by immersion in toluene at 25°C. The equilibrium of solvent absorption was established in 72 h. With more immersion time, the weight did not increase any more for all specimens. The swelling percentage of the sealants after 72 h is outlined in Table II. The presented data are only trends and not absolute, because the results are dependent on the efficiency of cure in polysulfide sealants.[5] From these data, it can be concluded that the swelling percentage of the sealants varies markedly with the increase of carbon black loading. As a result, sample PSF06 has the lowest swelling value because of high-carbon black loading. Addition of filler loading to rubbers has long been known to reduce swell, and this is attributed to the lower volume fraction of polymer, which is available to the swelling agent.[24,25] Moreover, the addition of silicon dioxide

TABLE II
The Swelling Percentage of Polysulfide Sealants After Immersion in Toluene at 25°C for 72 h

Samples	Carbon black (phr)	Silicon dioxide (phr)	Swelling ratio (Q%)
PSF01	0	0	113.56
PSF02	20	0	84.41
PSF03	30	0	74.78
PSF04	40	0	68.74
PSF05	50	0	67.45
PSF06	60	0	59.02
PSF07	40	2	66.37
PSF08	40	4	64.00
PSF09	40	6	63.15

filler also helps reduce swelling ratio due to the same reason.

Stress–strain behavior during compression

Stress–strain behavior during compression measurement was performed on Instron4466 instrument at 23°C. The specimen was placed between steel compression plates (60 mm in diameter and 15 mm in height) during the compression. Figure 5 shows stress–strain curves under lower compression stress of polysulfide sealants based on different carbon black loadings. Two different regions can be identified in these curves. The first region corresponds to the high-deformation level under lower stress. This plateau roughly starts about 0% and goes up to 2–5% strain. In this region, the higher deformation level suggests a new microstructure settling. Pronounced changes in the morphology occur due to plastic flow. The resistance to plastic deformation is correlated to the strength of all interactions inside the material, and this plateau stress is around 0.034 MPa despite of different filler loadings. However, the ultimate deformation in this region decreases slowly with the increase of carbon black loading. For example, sample PSF01 has a strain of 5.07% under 0.0339 MPa compression stress, whereas sample PSF06 has only 2.28% strain under 0.0345 MPa compression stress, and sample PSF04 has a medium value of 3.06%. This means that carbon black can help withstand the plastic flow in polysulfide sealants. After this transition, the plateau ends when the stress starts to increase progressively, going into the second region. Here, good linearity between applied stress and strain undergone can be observed and higher carbon black loading results in higher compression stress/strain ratio. Similar phenomena are found in compression stress–strain curves of sealant based on a combination of carbon black and dioxide silicon as shown in Figure 6. The addition of silicon dioxide also has effects on the decrease of plastic deformation in the first compression region under a low-compression stress of 0.035 MPa.

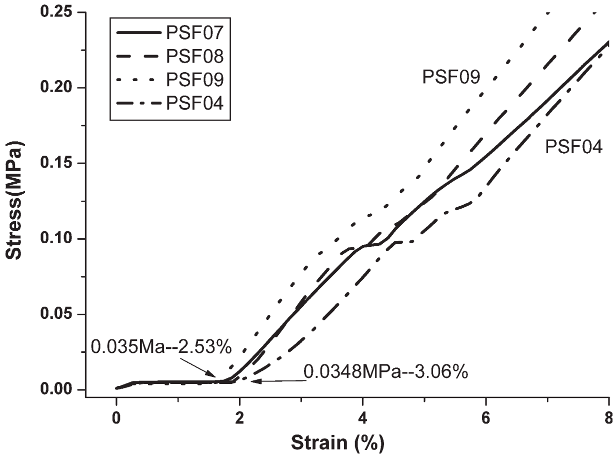

Figure 6 Stress–strain behaviors under lower compression stress of polysulfide sealants based on different silicon dioxide loadings.

Cyclic stress–strain behavior during compression measurement was also performed on Instron4466 instrument at 23°C. All measurements were performed in displaced control at the crosshead rate of 10 mm/min. When the percentage of the compression reached 25% of their original thickness, the specimens were relaxed at the same crosshead rate until the stress reverted to 0 MPa. The cyclic stress–strain behavior under compression/unloading of polysulfide sealant cylinder based on different carbon loading is shown in Figure 7. The figure displays that the compression stress increases with the increase of carbon black loading when the specimens are loaded to a strain of 25%, the corresponding

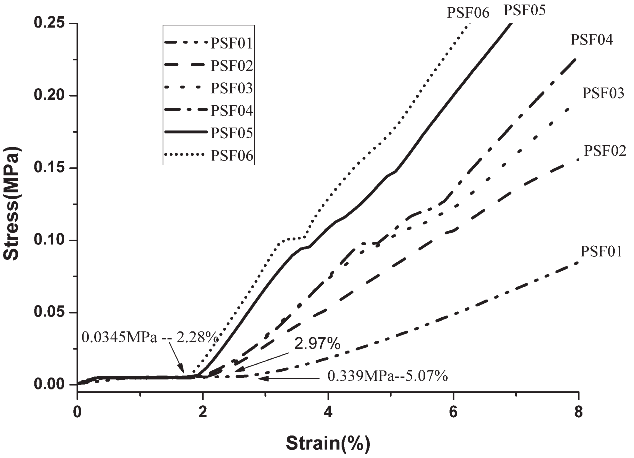

Figure 5 Stress–strain behaviors under lower compression stress of polysulfide sealants based on different carbon black loadings.

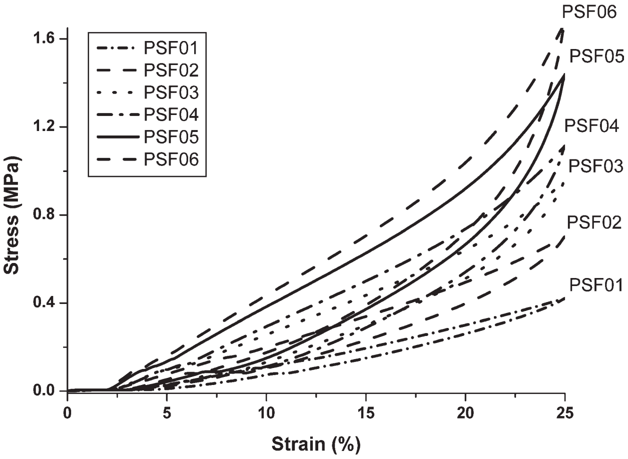

Figure 7 Cyclic stress–strain behaviors during compression of polysulfide sealants based on different carbon black loadings.

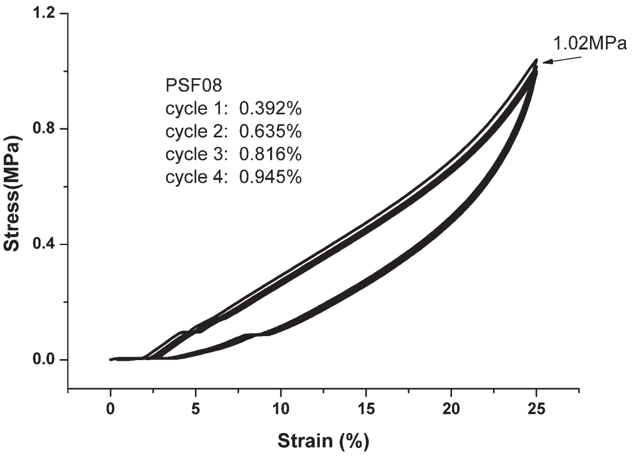

Figure 8 Cyclic stress–strain behavior during compression of sample PSF08 (four times in total, insert: the remnant strain after each cyclic compression/unloading).

stresses are 0.42, 0.70, 0.96, 1.14, 1.44, and 1.68 MPa for samples PSF01, PSF02, PSF03, PSF04, PSF05, and PSF06, respectively. The results are consistent with those obtained from stress–strain analysis under tension. To study the effects of silicon dioxide filler on stress–strain behavior during compression of polysulfide sealant, we simultaneously compressed samples PSF08 and PSF04 cylinders in compression/unloading cycle (four times in total), the results are shown in Figures 8 and 9 (insert: the remnant strain after each cyclic compression/unloading). It is clear that an irreversible compression/unloading behavior is observed, and a partial hysteresis curve is obtained in both Figures 8 and 9. A remnant strain of 0.392% or 0.377% is observed after the first unloading for sample PSF08 (insert in Fig. 8) or PSF04 (insert in Fig. 9), respectively. After subsequent cyclic compression/unloading, there is a little increase in the later remnant strain for both samples. We believe that the partial hysteresis curve has something with plastic flow of materials under compression. However, it is found that the compression stress is different when the specimens are loaded to a strain of 25%. The corresponding stresses are 1.14 MPa for sample PSF04 and 1.02 MPa for sample PSF08, respectively. The stress decreases by 10% even if silicon dioxide loading increases from 0 to 4 phr, this may help reduce the compression set of polysulfide sealants (latter discussed).

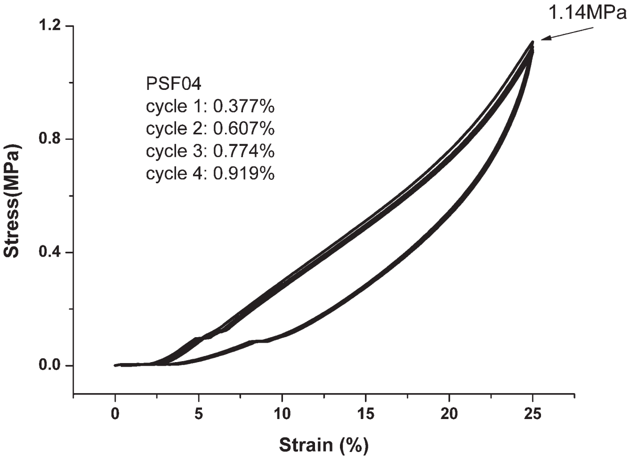

Figure 9 Cyclic stress–strain behavior during compression of sample PSF04 (four times in total, insert: the remnant strain after each cyclic compression/unloading).

Compression set test

To determine the effects of different filler loadings on the compression set of polysulfide sealants, the compression set test is carried out. Figure 10 shows the variations of compression set against polysulfide sealants at various carbon black and silicon dioxide loadings. From Figure 10, it is shown that the sealant filled with more carbon black filler has relatively lower compression set value. Carbon black functions as a physical crosslinking agent, which helps improve crosslink density and reduce compression set. For example, when compressed 25% at 23°C for 3 days, samples PSF01, PSF02, PSF03 PSF04, PSF05, and PSF06 retain 85.6%, 80.5%, 73.1%, 64.4%, 65%, and 57% of compression set, respectively. The reasons for compression set may be explained as follows[17]: as a result of compression of sealant specimens to a definite amount (25% strain), the enormous crosslinks may try to resist this compression, which expresses as an increase in the stress of the sealant. During this resistance, some crosslinks have been broken, so when the load is relieved, the number of crosslinks responsible for this strain recovery is less than the number of crosslinks responsible to

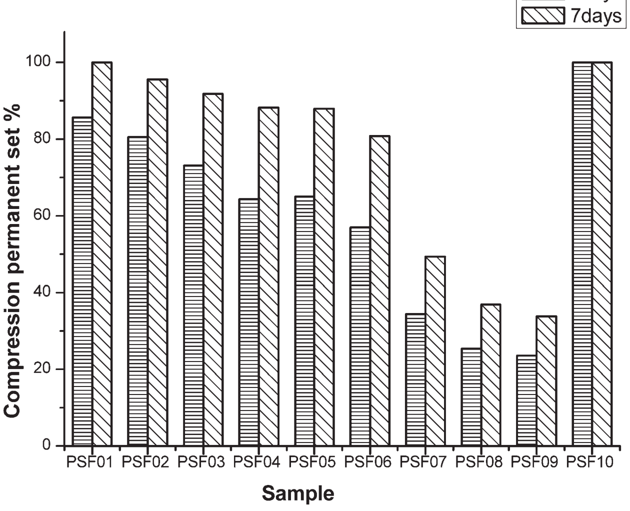

Figure 10 Compression set of polysulfide sealants filled with carbon black and silicon dioxide.

resist compression, and so the specimen does not recover to its original thickness. Although higher carbon black loading produces more crosslinks, it also brings about an increase in the stress of the sealant, which would result in more crosslink breakages and increase compression set. As a result, even if filled with 60 phr carbon black, sample PSF06 still has a high-compression set value of 80.8% when compressed 25% at 23°C for 7 days.

However, when carbon black and silicon dioxides are used in the sealants simultaneously, the compression set value obviously decreases. For an instance, sample PSF08 only has a compression set value of 36.9% when compressed 25% at 23°C for 7 days, and the compression set value is less than half that of sample PSF04. There are two reasons about the effect of silicon dioxides filler on improving compression set properties. One is that, as a result of nanometer filler, silicon dioxides effectively prevent polysulfide chain slipping with numerous crosslinks when compressed. Moreover, as revealed by analysis of stress–strain under compression, the addition of silicon dioxides into sealants reduces the stress when compressed to 25% of their original thickness, which would lessen crosslink breakages and benefit on compression resistance. However, as controlled, polysulfide sealant solely filled with silicon dioxide (sample PSF10) shows very poor compression resistance. This result reveals that the polysulfide sealants prepared using a combination of carbon black and silicon dioxide filler have better compression performances.

CONCLUSIONS

Conclusions have been drawn from the above investigations of mechanical properties' DMA, swelling, and compression set properties, and compression stress–strain behavior of polysulfide sealants. Carbon black filler can significantly reinforce the tensile and adhesive strengths of polysulfide sealants. With increasing carbon black loading, the tensile strength of sealants is improved promptly from 1.23 MPa to 3.7 MPa, but the compression performance increases slowly. However, when a combination of carbon black and silicon dioxide fillers is used in the sealants simultaneously, the tensile strength of sealants undergoes little change, whereas the compression performance of sealants is enhanced remarkably for silicon dioxide functions to enhance crosslinks and reduce the stress under compression, which helps reduce compression set. Based on the 40-phr carbon black loading, the addition of 4-phr silicon dioxide helps decrease the compression set value of polysulfide sealants from 88 to 37% after compressed 25% at 23°C for 7 days.

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