Compression Set Property and Stress–Strain Behavior During Compression of Polysulfide Sealants

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ABSTRACT: In this article, mechanical and compression set properties, swelling property, and stress–strain behavior during compression of polysulfide sealants based on different polysulfide resin were investigated. The results showed that molecular weight and cross-linking agent of liquid polysulfide resin had significant influence on mechanical and compression set properties of the sealants. The sealants based on higher molecular weight polysulfide resin had higher mechanical properties. At the same time, lower cross-linking agent in polysulfide resin produced lower cross-link density and higher swelling property, which resulted in higher compression set value of the sealant. However, when different molecular weight polysulfide resins were used in the sealant simultaneously, the testing results indicated that the compression performance of the sealants was significantly enhanced, while mechanical properties of the sealants kept nearly unchanged. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1718–1723, 2010

Key words: polysulfide; sealant; compression

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 oxysalts, which make use of the reducing properties of the thiol group to cause cross-linking. The main reaction procedures were reported by early researchers.[1,2] These cross-linked elastomers derived from liquid polysulfide have wide application in industry, particularly as sealants. They adhere to glass, steel, wood, and concrete, and they have high resistance to the UV radiation and the environment, exhibit good low-temperature properties, low water-vapour transmission, and resist solvents and chemicals.[3,4] There have been many publications on the characterization of polysulfides, cured by metal peroxides,[5–9] reporting the results of thermogravimetry analysis, dynamic mechanical analysis, tensile strength, 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, the structure, mechanical properties, and the modification of polysulfide-based sealant has been studied.[12–16]

Usually rubber compounds exhibit several phenomena, like the ability to retain elastic properties during prolonged action of compression stress and compression set behavior, this loss of resiliency often reduces the capability of elastomertic gasket or seal to perform over a long period of time. Researchers have extensively studied compression set behavior of rubber and rubber compounds, such as styrene-butadiene rubber and nitrile-butadiene rubber.[17,18] However, little work has been done to-date on compression set property and stress–strain behavior during compression of polysulfide sealant.[19] Therefore the aim of this work is to study the compression set and swelling properties, and stress–strain behavior during compression of the sealant based on the polysulfide resin with different molecular weight.

EXPERIMENTAL

Material and preparation of samples

Low-molecular-weight liquid polysulfide resins were supplied by Jiangxi Research Institute of Chemical Industry, China (The main properties of liquid polysulfide resins are listed in Table I). Manganese dioxide (MnO_2), carbon black (SFR black), stearic acid, epoxy resin, and coupling agent were all commercially available materials and were used as received.

The typical compositions of sealants based on different liquid polysulfide resins were listed in Table II. The liquid polysulfide resin, fillers, and curing agent were completely mixed by a mechanical

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TABLE I
The Main Properties of Liquid Polysulfide Resins

Liquid polysulfide resin	JLY121	JLY124	JLY155
Average molecular weight	1000	4000	5000
Cross-linking agent	2%	2%	0.5%
Mercaptan content (—SH)	6.2%	1.6%	1.2%

stirrer and degassed by a Siemens DAC 150FV high-speed mixer by 3000/min. Then the bubble-free mixture was poured onto the mold of PTFE, and cured at 23 ± 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 dimension of 29 ± 0.1 mm diameter and 13 ± 0.3 mm thickness.

Mechanical properties

According to the principles of ASTM D412-98a, the tensile strength and the ultimate elongation were tested using Instron4466 instrument 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.

Swelling measurements

Swelling test (HG/T 3870-2006, China) was performed on 20 × 20 × 2 mm cut specimen by the immersion method in toluene or dichloromethane at 25°C. Then, the test specimen was taken out and blotted with filter paper. Each result was obtained by the test repetition with three specimens.

The swelling ratio is defined as:

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

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 0.001 g accuracy.

Cyclic stress–strain behavior during compression

Cyclic stress–strain behavior during compression measurement was performed on Instron4466 instrument at 23°C. The specimen was placed between steel compression plates (diameter 60 mm and height 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 to 25% of their original thickness, the specimen was relaxed at the same crosshead rate until the stress reverted to 0 MPa. Then the remnant strain was recorded. After that, the specimen was tested in a second compression/unloading cycle. The compression/unloading were performed four times.

Compression set test

Compression set test (ASTM D395) was performed on standard test specimen of cylindrical shape of 29 ± 0.1 mm diameter and 13 ± 0.3 mm thickness vulcanized by 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 7days. After completion of compression, the specimen was removed from the device and allowed to recover for 30 min, after this rest time the final specimen thickness was measured by an electronic digital caliber with 0.01 mm accuracy. Each result was obtained by the test repetition with three samples.

The compression set is defined as:

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

where T_o = the original thickness of the specimen; T_f = the final thickness of the specimen; T_s = the thickness of the spacer bar used.

RESULT AND DISCUSSION

Mechanical properties

The typical formulations of polysulfide sealants based on different liquid polysulfide resins are

TABLE II
Chemical Composition and Mechanical Properties of Polysulfide Sealants Based on Different Liquid Polysulfide Resins

	Samples					
Materials	PSF1	PSF2	PSF3	PSF4	PSF5	PSF6
JLY121	100	0	0	50	50	33.3
JLY124	0	100	0	50	0	33.3
JLY155	0	0	100	0	50	33.3
SFR black	50	50	50	50	50	50
Stearic acid	1	1	1	1	1	1
Plasticizer	15	15	15	15	15	15
MnO_2	10	10	10	10	10	10
Epoxy resin	4	4	4	4	4	4
Coupling agent	2	2	2	2	2	2
Tensile strength (MPa)	3.4	2.4	3.8	3.2	3.6	4.3
Ultimate elongation (%)	101	182	266	182	244	213

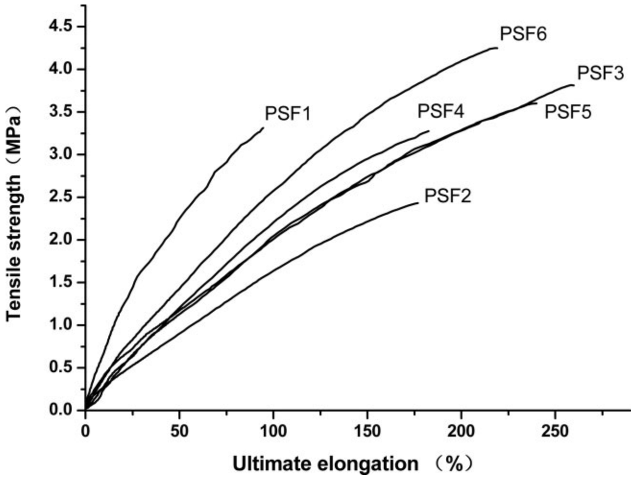

Figure 1 Stress–strain curves of polysulfide sealants based on the different liquid polysulfide resins.

outlined in Table II, and the stress–strain analysis of polysulfide sealants is shown in Figure 1. The tensile properties of unfilled polysulfide sealants are rather poor.[5] However, suitable reinforcement by fillers can lead to products with adequate tensile and elongation properties. The molecular weight of a liquid polysulfide resin before cure also influences the physical properties of the cured polysulfide sealant, and higher tensile strength is obtained with the higher molecular weight liquid polysulfide. The effect of branching (cross-linking agent, i.e., trithiol content) on the tensile strength of polysulfide sealant is relatively low. However, lower branching content always results in higher ultimate elongation.[5] Based on the stress and strain results, it can be seen that the ultimate elongation of sealant increases with the increase in molecular weight of liquid polysulfide, and the sample PSF3 has the best tensile strength and ultimate elongation because JLY155 polysulfide resin has the highest molecular weight and the lowest cross-linking agent. When JLY-121 polysulfide resin and JLY-124 polysulfide resin or JLY-155 polysulfide resin are used in the sealant simultaneously, the testing results indicate that the tensile strength of the sealant does not change significantly.

Swelling properties

TABLE III
The Swelling Percentage of Sealants After Immersion at 25°C for 72 h

Solvent	Samples					
	PSF1	PSF2	PSF3	PSF4	PSF5	PSF6
Toluene	40.6	51.4	61.0	52.7	52.2	48.7
Dichloromethane	76	83.5	92	83	83.5	82

Swelling tests on cured polysulfide sealants were performed on 20 × 20 × 2 mm cut specimen by the immersion method in toluene or dichloromethane 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 sealants after 72 h is outlined in Table III. These data presented are only trends and not absolute as the results depend on the efficiency of cure in polysulfide sealants.[5] From these data, it can be concluded that the swelling percentage of the sealant varies with cross-linking agent in molecular weight of liquid polysulfide resin. The sealant PSF3 has the highest swelling percentage due to the lowest cross-linking agent in JLY155 polysulfide resin. With the same cross-linking agent, JLY121 polysulfide resin-based sealant has the lower swelling percentage than JLY124 polysulfide resin-based sealant. This may be attributed to the higher thiol residue in the sample PSF1, for JLY121 polysulfide resin only has the number–average molecular weight of 1000. It is difficult for all thiol to be oxidized completely. This is the reason that JLY121 polysulfide resin doesn't exclusive used in sealants. When the sealant was prepared from the mixture of liquid polysulfide resins, they exhibited the medium swelling percentage.

Cyclic stress–strain behavior during compression

The cyclic stress–strain behavior under compression/unloading of the sealant cylinder based on different liquid polysulfide resins is shown in Figures 2–7. Two different regions can be identified in these curves. The first region corresponds to high deformation level under lower stress. This plateau covers quite extensive deformation, roughly, starts

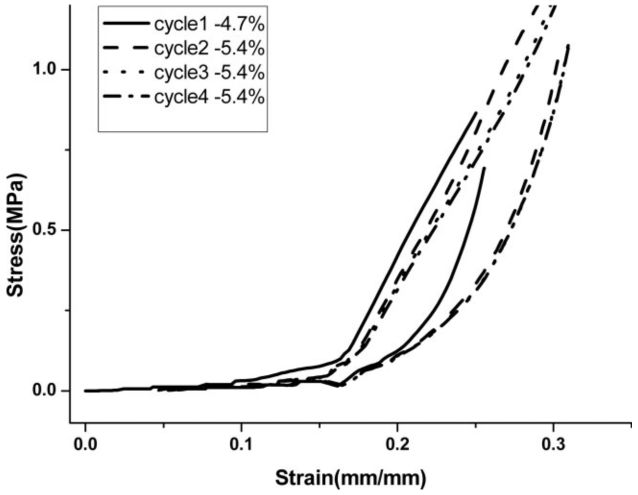

Figure 2 Cyclic stress–strain behavior during compression of the sample PSF1 based on JLY121 polysulfide resin (four times in total, insert: the remnant strain after each cyclic compression/unloading).

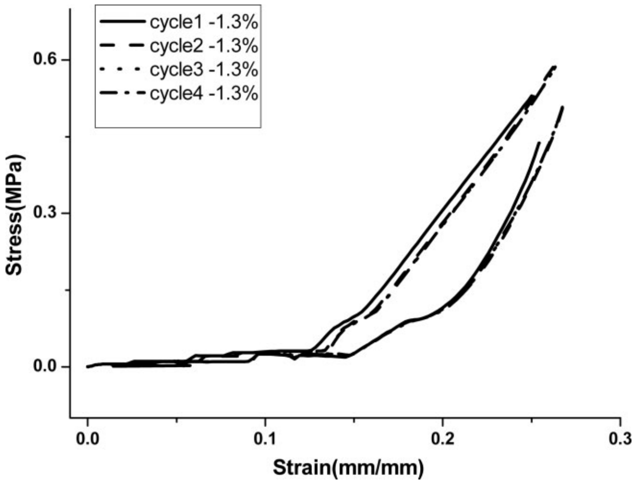

Figure 3 Cyclic stress–strain behavior during compression of the sample PSF2 based on JLY124 polysulfide resin (four times in total, insert: the remnant strain after each cyclic compression/unloading).

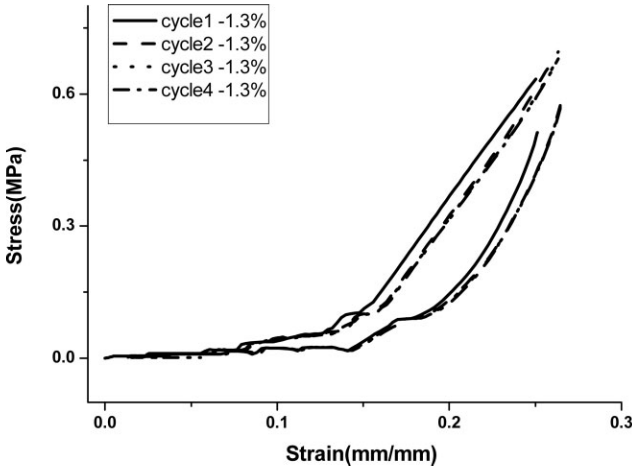

Figure 5 Cyclic stress–strain behavior during compression of the sample PSF4 based on the mixture of JLY124 and JLY121 polysulfide resin(four times in total, insert: the remnant strain after each cyclic compression/unloading).

about 0% strain and goes upto ∼15% strain. In this region, 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. This plateau stress is around 0.02–0.03 MPa depending on different liquid polysulfide resin. After the 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.

By subsequently compressing the same cylinder in another compression/unloading cycle (four times in total), the results are given in Figures 2–7 (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 all of Figures 2–7. A remnant strain of −4.7 or −2.6% is observed after the first unloading for JLY121 polysulfide resin-based sealant (insert in Fig. 2) or JLY155 polysulfide resin-based sealant (insert in Fig. 4), respectively. While JLY124 polysulfide resin-based sealant (insert in Fig. 3) only has a remnant strain of −1.3% after the first unloading. Furthermore, the remnant strain of JLY124 polysulfide resin-based sealant is the same after subsequent cyclic compression/unloading. As for JLY125 or JLY121 polysulfide resin-based sealant, there is a little increase in the later remnant strain. These data indicates that JLY124 polysulfide

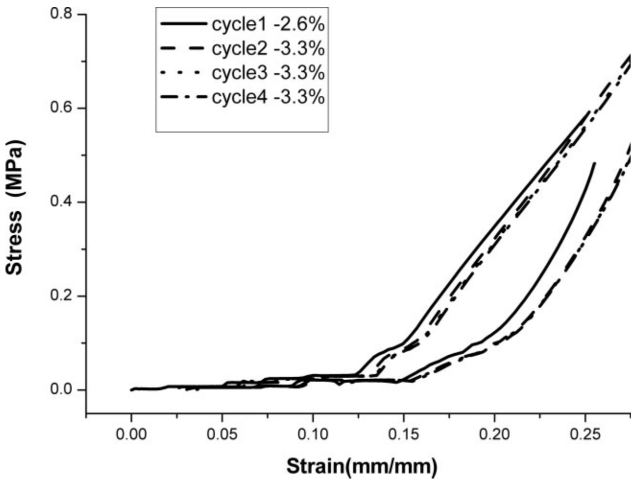

Figure 4 Cyclic stress–strain behavior during compression of the sample PSF3 based on JLY155 polysulfide resin (four times in total, insert: the remnant strain after each cyclic compression/unloading).

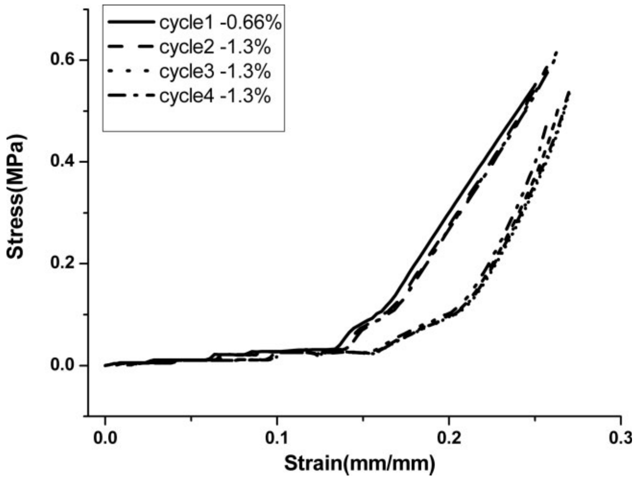

Figure 6 Cyclic stress–strain behavior during compression of the sample PSF5 based on the mixture of JLY155 and JLY121 polysulfide resin (four times in total, insert: the remnant strain after each cyclic compression/unloading).

resin-based sealant has the best compression resistance. Whereas for the sealant based on the mixture of JLY155 and JLY121 polysulfide resin, the remnant strain decrease apparently compared with that of the sealant based on JLY155 or JLY121 polysulfide resin (insert in Fig. 6).

Compression set test

To determine the effect of different liquid polysulfide resin on the compression set of the sealant, the compression set test is carried out. The experimental results are shown in Figure 8. This figure shows the variation of the percentage of compression set against different liquid polysulfide resin-based sealant. From this figure it is clear that in the case of one liquid polysulfide resin-based sealant, JLY124 polysulfide resin-based sealant has the lowest compression set due to higher molecular weight and cross-linking agent in the same time. When the sample is compressed 25% at 23°C for 7 days, PSF1, PSF2, and PSF3 retain 72.5, 55, and 86.8%, respectively. There are two explanations about the relationship of cross-link density and compression set property. One is that, as a result of compression of sealant specimens to definite amount (25% strain), the enormous cross-links may try to resist this compression, which was expressed as increase in the stress of the sealant. During this resistance some cross-links have been broken, so when the load relieved, the number of cross-links responsible for this strain recovery is less than the number of cross-links responsible to resist compression. As a result, the specimen does not recover to its original thickness.[17] On the other hand, to improve compression set properties, it is necessary to prevent chain slipping when compressed. Chain slipping could be decreased by chemically bonding polymer with numerous cross-links.[20] As for polysulfide sealant, the cross-linking density is relatively low, which results in higher retained compression in all samples. Here, the chain slipping is the main factor for compression set. The highest compression set of JLY155 polysulfide resin-based sealant results from the lowest cross-linking agent in the polysulfide chain.

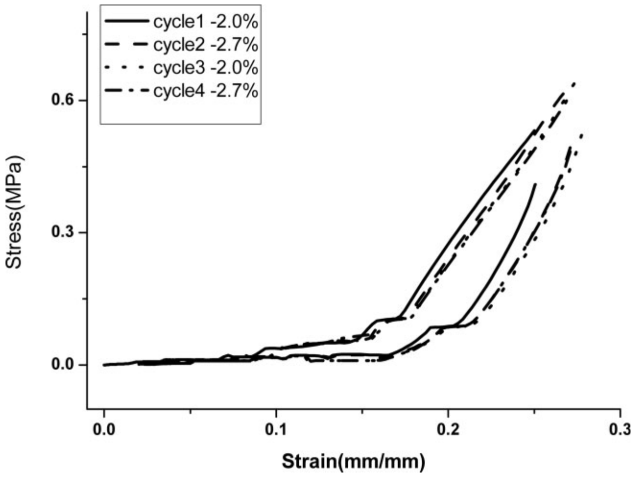

Figure 7 Cyclic stress–strain behavior during compression of the sample PSF6 based on the mixture of JLY124, JLY155, and JLY121 polysulfide resin (four times in total, insert: the remnant strain after each cyclic compression/unloading).

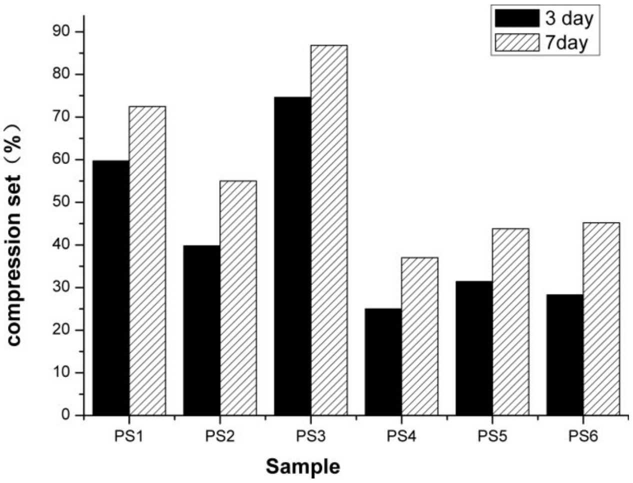

Figure 8 Compression set of polysulfide sealants.

When JLY121 and JLY124, or JLY155 polysulfide resin are used in the sealant, simultaneously the compression set value obviously decreases even compared with that of JLY124 polysulfide resin-based sealant. The mechanism of the decrease in the compression set is not very clear. The reason may be due to the mixture of liquid polysulfide resins with different molecular weight, which could form cross-linking networks of different sizes. Such cross-linking networks may benefit on compression resistance.

CONCLUSIONS

From the current investigation of mechanical and swelling properties, compression set, and cyclic stress–strain behavior under compression of polysulfide sealant, the following conclusions were derived from the experimental results:

1. The sealant based on higher molecular weight polysulfide resin (JLY155 resin) had higher tensile strength.
2. Lower cross-linking agent in polysulfide resin (JLY155 resin) produced higher ultimate elongation and swelling percentage, which resulted in higher compression set value of the sealant.
3. The sealant based on polysulfide resin (JLY124 resin) with higher molecular weight and cross-

linking agent had the lower remnant strain after cyclic compression/unloading and compression set value.

4. When different molecular weight polysulfide resins were used in sealants simultaneously, the testing results indicated that the compression performance of the sealants was significantly enhanced, whereas the tensile strength and ultimate elongation of the sealants changed little.

The effect of filler and other additive loading on the swelling property, compression set property, and stress–strain behavior during compression of polysulfide sealants will be explored in forecoming article.

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