The Effect of Epoxy Resin to Reduce the Compression Set of Polysulfide Sealant

Junsheng Zhang, Zhenghei Wang, Guowei Ding, Yiwu Quan, Qingmin Chen

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

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ABSTRACT: In this article, modified polysulfide sealants with lower compression set were prepared by a simple method of introducing the diglycidyl ether of bisphenol A resin (DGEBA epoxy resin) into sealants. The investigation on reactivity analysis and gel faction test verified that the incorporation of epoxy resin in sealants was just a blending process rather than copolyaddition with polysulfide resin. Stress–strain behavior during compression revealed that the epoxy resin could reduce the compression stress when the sealants were loaded to a certain strain, which effectively lessened crosslink breakages and benefited to compression resistance. Also the rigid phenyl structure in epoxy resin may retard incidental slide between polysulfide chains and prevent interchange reactions between disulfide linkages. The incorporation of 2 phr epoxy resin distinctly reduced compression set of polysulfide sealant from 28.3% to 11.2% after compressed 25% at 23°C for 1 day. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 390–395, 2012

Key words: polysulfide resin; sealant; compression set; epoxy resin

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 cross-linking. 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 sealants,[5–11] reporting the results of thermogravimetry analysis, dynamic mechanical analysis, tensile strengths, hardness testing, thermal stability, and photodegradation of the liquid polysulfide and cured polysulfide. In our earlier work, structure, mechanical properties, and modification of polysulfide-based sealants have been studied.[12–16]

Taking the advantage of lower cost, polysulfide sealants continue to be the dominant part of the elastomeric sealants. However, they are facing strong challenges from silicone and polyurethane-based sealants. One of the reasons is their relatively higher compression set due to incidental slide between chains and interchange reactions between disulfide linkages.[5] Our previous work revealed that fillers,[17] molecular weight and cross-linkage content of polysulfide resin[18] have important effect on reducing the compression set of sealants. In this article, we describe another simple method to reduce compression set by introducing DGEBA epoxy resin into polysulfide sealant.

EXPERIMENTAL

Materials and preparation of samples

Low-molecular-weight liquid polysulfide resins (JLY121: SH% = 6.2 ∼ 7.5%, M_n =1000 ± 200, with 2% mol trithiol; LY124: SH% = 1.6 ∼ 2.0%, M_n = 4000 ± 200, with 2% mol trithiol; JLY155: SH% = 1.0 ∼ 1.4%, M_n = 5000 ± 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 (DGEBA, a low molecular weight liquid diglycidyl ether of bisphenol A with epoxide number of 0.44) and coupling agent (2,3-epoxy propoxy propyltrimethoxysilicane, KH560) were all commercially available materials and were used as received.

Correspondence to: Y. Quan (quanyiwu@nju.edu.cn).

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TABLE I
The Typical Compositions of Polysulfide Sealants

Materials	JLY121	JLY155	JLY124	Plasticizer	MnO_2	SFR black	SiO_2	KH560
Weight (g)	33	34	33	12	8	40	4	1.5

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 ± 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.

Measurement and characterization

Reactivity of polysulfide and epoxy resin

The cure of epoxy resin with liquid polysulfide was evaluated by dielectric analysis (DEA) at a DEA 230/1 Cure Monitor (produced by NETZSCH-Geratebau GmbH, Selb/Bavaria, Germany) controlled by a microcomputer connected to a planar wafer-thin sensor inserted into the reactor. The sensor was inert and has 2 cm × 1 cm in area and 1 mm thick. The electrode configuration was set in the reactor so as to be swept by the axial flow generated by the propeller.

Gel fraction

According to the principles of ASTM D2765-2001, the gel fraction of the cured samples was evaluated by extraction with toluene; the insoluble materials were dried *in vacuo* for 24 h at 60°C and weighed to determine the gel fraction.

Mechanical properties

According to the principles of ASTM D412-98a, the tensile strength and ultimate elongation were measured on an Instron 4466 Universal Materials Testing Machine (Produced by Instron, Norwood, MA) with a speed of 50 mm/min at 23°C. The cured film in 2 mm thickness was cut into dumbbell-shaped specimens. Each result was obtained by the test repetition with three 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, 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.

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.

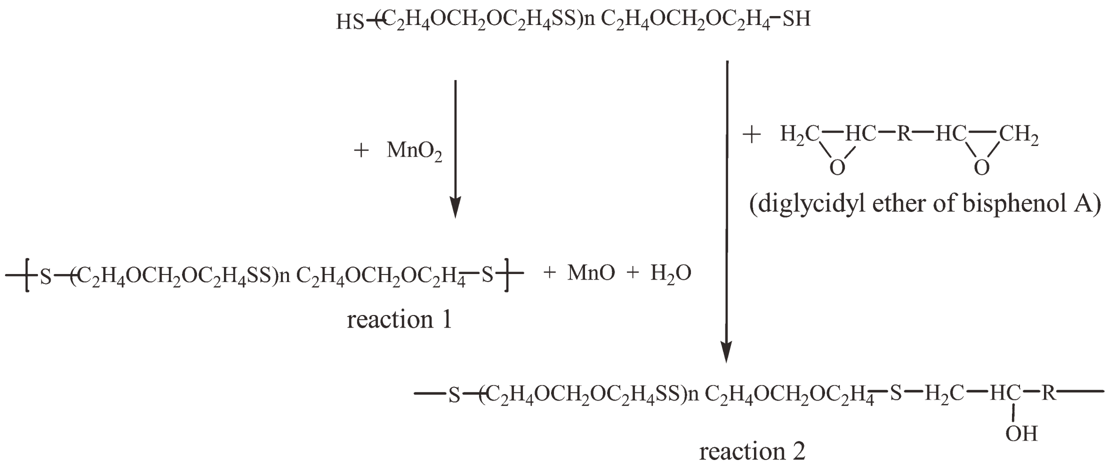
Compression set tests

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 days 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:

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

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.


HS-(C2H4OCH2OC2H4SS)n C2H4OCH2OC2H4-SH
+ MnO2
+ H2C—HC—R—HC—CH2
O
O
(diglycidyl ether of bisphenol A)
S-(C2H4OCH2OC2H4SS)n C2H4OCH2OC2H4-S + MnO + H2O
reaction 1
—S-(C2H4OCH2OC2H4SS)n C2H4OCH2OC2H4-S—H2C—HC—R—
OH
reaction 2

Scheme 1 Oxidation of polysulfide resin by manganese dioxide and copolyaddition reaction between epoxy resin and polysulfide resin.

RESULTS AND DISCUSSION

Reaction

Liquid polysulfide polymers can readily react with epoxy resin (e.g., diglycidyl ether of bisphenol A resin) under basic conditions to form a block polymer (shown in Scheme 1, Reaction 2). So, the lower molecular weight liquid polysulfide resin (e.g., Thiokol LP-3, JLY 121) can be used for epoxy modification. The polysulfide-epoxy block copolymer has significantly higher impact resistance and more flexibility than epoxy. On the other hand, epoxy resin, as well as silane, usually performs as adhesion promoter for polysulfide sealant.[5] In this work, epoxy resin is introduced into polysulfide sealants in order to reduce compression set. In this curing system, two reactions may simultaneously occur (see Scheme 1). One is the oxidation of liquid polysulfide by manganese dioxide (Reaction 1), and the other is the reaction between epoxy resin and polysulfide (Reaction 2). Here, DEA is used for evaluating the reactivity of liquid polysulfide with epoxy resin, or oxidation of liquid polysulfide by manganese dioxide. DEA is based on the study of the electrical response of a polymer, and dielectric cure monitoring is sensitive to the mobility of ions and the rotational mobility of dipole on the polymer molecule in the presence of an electric field. The important information that can be obtained by DEA includes relative viscosity change, cure rate, cure state, and the end of cure,[19,20] in which, the dielectric loss factor (ε'') can be used to determine the degree of cure.[21]

Figure 1 shows typical time variations of dielectric loss factor for model reaction 1 and reaction 2 at 50°C, respectively. Usually, the value of ε'' decreases during the reaction process, for ε'' encompasses contributions from both electronic polarization and molecular reorientation, which are increasing restricted during polymerization progress. However, it can be observed from Figure 1, the ε'' of System 1 increases all the time during oxidation progress of liquid polysulfide, this is because mobility of ions is increasing unlimited during reaction due to release of water in oxidation progress of liquid polysulfide (Reaction 1). The value of ε'' increases rapidly in initial 200 min and reaches the maximum after 500 min, corresponding a gel state. This means most of thiol has been oxidized into disulfide. However, the ε'' of System 2 remains almost unchanged in several hours, which should be decreased if copolyaddition of epoxy and thiol groups occurred. The above investigation reveals that the reactivity of thiol and epoxy is much lower than that of oxidation of thiol by manganese dioxide. It can be concluded that the incorporation of epoxy resin in polysulfide sealant is just a blending process rather than copolyaddition with polysulfide under this experimental condition.

The typical formulations and gel fractions of polysulfide sealants with different epoxy resin loadings

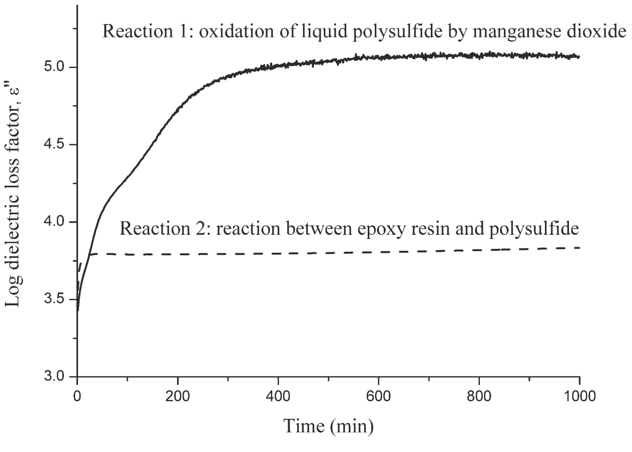


Figure 1 Dielectric analysis for the curing processes of liquid polysulfide by manganese dioxide or epoxy resin.

TABLE II
Gel Fractions of Polysulfide Sealants by Toluene Extraction

Samples	Polysulfide sealant (phr)	Epoxy resin (phr)	Gel fraction (%)
PSF0	100	0	91.09
PSF1	100	1	90.38
PSF2	100	2	89.52
PSF3	100	3	87.96
PSF4	100	4	86.52

are outlined in Tables I and II. Here, sample PSF0 is the typical compositions of polysulfide sealants as shown in Table I, other samples PSF1 ~ PSF4 are polysulfide sealants modified with different epoxy resin loadings. All of the samples used in this study have gel fractions extracted by toluene around 86.5–91%. The main extraction is dibutyl phthalate plasticizer which has been employed in curing agents (e.g., MnO_2). From these data, it can be seen that the gel fraction of sealants varies markedly with the increase of epoxy resin loading. Sample PSF4 has the lowest gel fraction because of high epoxy resin loading. This results from the lower reactivity of epoxy resin with polysulfide sealant, and uncombined epoxy resin is extracted out.

Mechanical properties

The mechanical properties of polysulfide sealants with different epoxy resin loadings are outlined in Table III. The stress–strain curves of these polysulfide sealants are shown in Figure 2. As shown in Figure 2 and Table III, the incorporation of epoxy resin results in improved ultimate elongation and decreased tensile strength. For examples, sample PSF0 has a tensile strength of 5.1 MPa and an ultimate elongation of 209%. With 2 phr additive of epoxy resin, the tensile strength of sample PSF2 decreases to 4.2 MPa, and the ultimate elongation reaches 286%. This also indicates a change in Young's modulus, related to plasticization of epoxy resin in polysulfide sealants, which consists with the results of hardness test. Although DGEBA epoxy resin usually can be regarded as the hard domains, but here the plasticization of the above resin results in gradually lower hardness due to DGEBA is compatible with polysulfide.

TABLE III
Mechanical Properties of Polysulfide Sealants Modified with Epoxy Resin

Sample	Tensile strengh (MPa)	Ultimate elongation (%)	Hardness (Shore A)
PSF0	5.10	209	60
PSF1	4.77	258	58
PSF2	4.20	286	53
PSF3	3.83	333	44
PSF4	3.53	392	40

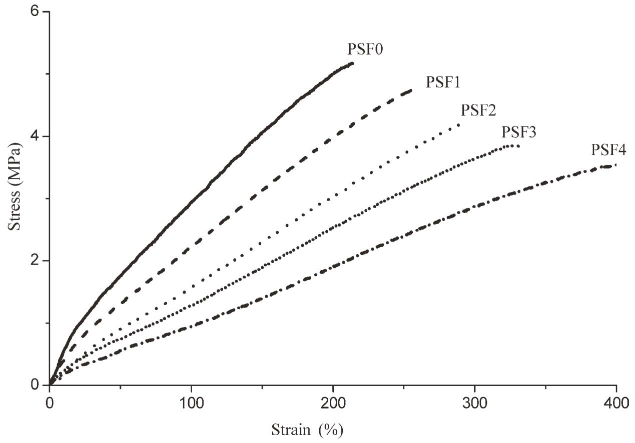


Figure 2 Stress–strain curves of polysulfide sealants modified with epoxy resin.

Dynamic mechanical thermal analysis

The results of DMA analysis for polysulfide sealants are displayed in Figure 3, and the glass transition temperature (T_g) determined from maximum in tan δ and loss modulus (E'') is outlined in Table IV. From Figure 3, it can be seen that the T_g in E'' around $-50°C$ is characteristic of the poly(ethyl formal disulfide) glass transition, and the T_g of sealants varies slightly when modified with epoxy resin. With the increase of epoxy resin content, the glass transition temperature demonstrates a ratherish increasing trend and the store modulus decreases macroscopically (especially above room temperature). The 2–4 phr additive of epoxy resin results in a 1.6–4°C increase in glass transition temperature,

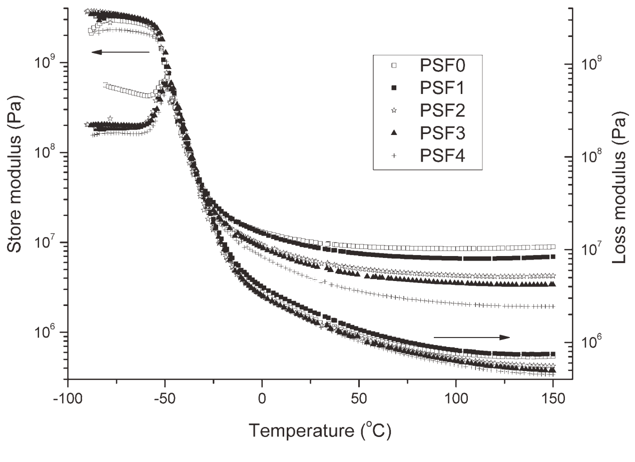


Figure 3 Storage modulus (E') and loss modulus (E'') curves of polysulfide sealants modified with epoxy resin.

TABLE IV
T_g of Polysulfide Sealants Modified with Epoxy Resin

Sample	T_g from tan δ (°C)	T_g from loss modulus, E'' (°C)
PSF0	−41.8	−50.4
PSF1	−40.8	−49.3
PSF2	−40.2	−49.1
PSF3	−38.9	−47.6
PSF4	−37.8	−47.8

which is indicative of good compatibility of polysulfide with epoxy resin. Usually, DGEBA resin helps to improve the storage modulus of sealants due to rigid phenyl structure. However, in this system, the addition of epoxy resin results in a decreased store modulus. The reason is that most of epoxy resin is blended with polysulfide resin instead of copolyaddition, which also has been explained by the facts found in the hardness and tensile strength measurements.

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 4 shows stress–strain curves under lower compression stress of polysulfide sealants with different epoxy resin 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 2.5–4% 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 0.1 MPa despite of different epoxy resin loadings. However, the ultimate deformation in this region also increases slowly with the increase of epoxy resin loading. For example, sample PSF0 has a strain of 2.60% under 0.10 MPa compression stress, while sample PSF2 has 3.21% strain under 0.099 MPa compression stress, and sample PSF4 has a maximal value of 4.15%. 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 epoxy resin loading results in lower compression stress/strain ratio. The results are consistent with those obtained from stress–strain analysis under tension.

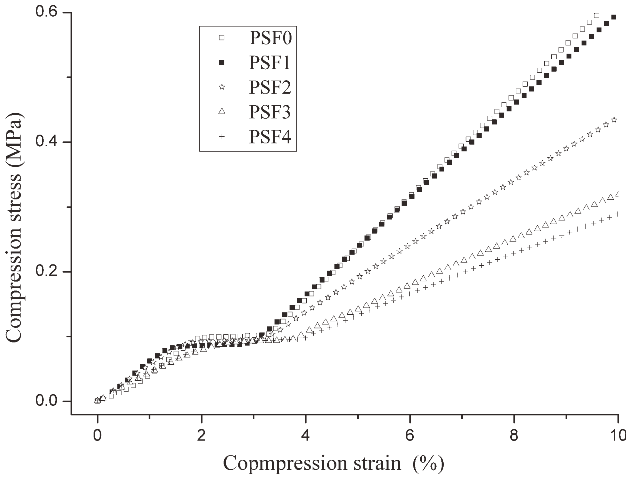


Figure 4 Stress–strain behaviors under lower compression stress of polysulfide sealants with different epoxy resin loadings.

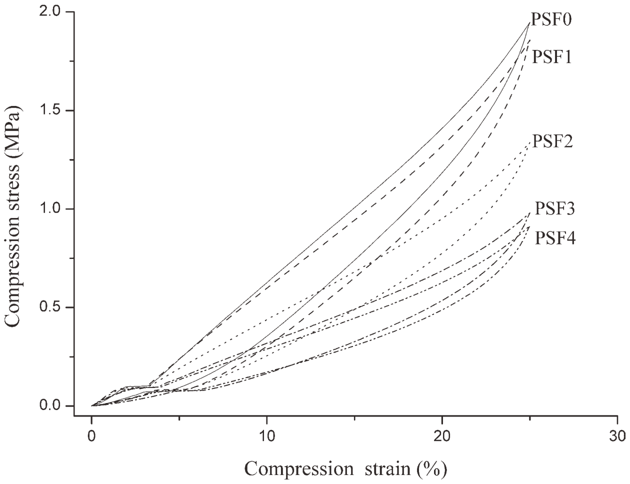


Figure 5 Cyclic stress–strain behaviors during compression of polysulfide sealants with different epoxy resin loadings.

The cyclic stress–strain behaviors under compression/unloading of polysulfide sealant cylinder with different epoxy resin loadings were also 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

TABLE V
Compression Set of Polysulfide Sealants Modified with Epoxy Resin

	Compression set (%)		
Sample	1 day	3 days	7 days
PSF0	28.3	36.3	44.7
PSF1	18.3	24.1	30.8
PSF2	11.2	16.3	24.5
PSF3	11.4	17.2	27.4
PSF4	11.5	17.5	27.1

the stress reverted to 0 MPa. The results are shown in Figure 5. The figure displays that the compression stress decreases with the increase of epoxy resin loading when the specimens are loaded to a strain of 25%, the corresponding stresses are 1.95 MPa, 1.85 MPa, 1.33 MPa, 0.98 MPa, and 0.91 MPa for samples PSF0, PSF1, PSF2, PSF3, and PSF4, respectively. The compression stress decreases by 31% when epoxy resin loading increases from 0 to 2 phr, this may help reduce the compression set of polysulfide sealants (latter discussed).

Compression set test

To determine the effects of different epoxy resin loadings on the compression set of polysulfide sealants, the compression set test is carried out. Table V shows the variations of compression set against polysulfide sealants at various epoxy resin loadings. From Table V, it is shown that the sealants filled with epoxy resin have relatively lower compression set value. The compression set of these materials changes profoundly when epoxy resin loading increases from 0 to 2 weight percent but changes little between 2 and 4 weight percent. For examples, when compressed 25% at 23°C for 1 day, samples PSF0, PSF1, PSF2, PSF3, and PSF4 retain 28.3%, 18.3%, 11.2%, 11.4%, and 11.5% of compression set respectively. The reasons for compression set may be explained as follows[22]: As a result of compression of sealant specimens to a definite amount (25% strain), the enormous cross-links may try to resist this compression which expresses as an increase in the stress of the sealant. During this resistance some cross-links have been broken, so when the load is relieved, the number of cross-links responsible for this strain recovery is less than the number of cross-links responsible to resist compression, so the specimen does not recover to its original thickness. There are two reasons about the effect of epoxy resin on improving compression set properties. One is that, as revealed by analysis of stress–strain under compression, the addition of epoxy resin into sealants reduces the stress when compressed to 25% of their original thickness, which would lessen cross-link breakages and benefit to compression resistance. The other is that the rigid phenyl structure may retard incidental slide between polysulfide chains and prevent interchange reactions between disulfide linkages.

CONCLUSION

Conclusions can be drawn from the above investigations of mechanical properties, DMA, compression stress–strain behavior, and compression set properties of polysulfide sealants. DGEBA epoxy resin additive can significantly enhance compression performance of polysulfide sealant. The incorporation of epoxy resin in polysulfide sealant is blending rather than copolyaddition with polysulfide under this experimental condition, for the reactivity of thiol and epoxy is much lower than that of oxidation of thiol by manganese dioxide. The incorporation of 2 phr epoxy resin results in a slightly higher T_g and distinctly reduced compression set of polysulfide sealant from 28.3% to 11.2% after compressed 25% at 23°C for 1 day. At the same time, the ultimate elongation of sealants increases remarkably from 209% to 286%, while the tensile strength decreases from 5.1 to 4.2 MPa.

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