

The Effect of Epoxy-Polysulfide Copolymer Curing Methods on Mechanical-Dynamical and Morphological Properties

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ABSTRACT: *Epoxy – Polysulfide copolymers without or with low amounts of epoxy in their structure have poor mechanical properties in oxidative curing system. To strengthen the mechanical properties of polysulfide elastomer inclusion of epoxy resin (Epon828) as hard segment was studied. FT-IR spectroscopy and rheometry were used to verify the formation of epoxy-polysulfide copolymer. Results obtained from DMTA showed that in different epoxy/polysulfide ratio, the epoxy-polysulfide copolymer had different glass transition temperature (T_g). Gel time and curing behaviors in various ratios of epoxy – polysulfide were investigated using Rheometer and Differential Scanning Calorimeter (DSC). With increasing polysulfide weight percent in epoxy - polysulfide copolymer gel time increased but the enthalpy of cure reaction decreased and the temperature corresponding to exothermic peak was shifted to the higher temperature. Results obtained from DMTA and SEM showed that phase separation of epoxy resin from the copolymer matrix took place.*

KEY WORDS: *Epoxy, Polysulfide, Modification, Mechanical properties, Gel time.*

INTRODUCTION

Polysulfide polymers can be transformed from a liquid state into a solid elastomer, even at low temperatures, which makes its use convenient for adhesives, coatings and sealants. Its success is due to good moisture, solvent and ozone resistance. Curing and cross linking of polysulfide can be affected through the use of chemicals with functional groups capable of oxidizing mercaptan group into disulfide linkage, like inorganic peroxides, dichromates and permanganates or low hardness and high elongation at break [1]. Addition of epoxy to polysulfide develops mechanical and

organic hydro peroxides, but polysulfide elastomers that cured with oxidative agent have low tensile strength, adhesion properties and reduces curring time. the polysulfide provides long flexible or soft segments and epoxy resin provides hard blocks which restricts its compatibility with polysulfide[2,3]. These blocks provide unstable crosslinks at ambient temperatures which dissociate at elevated temperatures to allow the elastomer to flow under pressure [4]. Phase separation can be occurred in epoxy-polysulfide copolymers and was investigated by SEM or DMTA. In epoxy-polysulfide copolymers DMTA

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graph, T_g can be taken as the peak $\tan \delta$ temperature and several peak for a phase separated compound is clearly discernible. To confirm absolutely the presence of separated phase a Scanning Electron Micrograph(SEM) can be used[5-7].

polysulfide could be added from small amounts (as toughening agent) to large amounts as flexible adhesives and hot melt sealants [8].

To develop the properties of Epoxy-Polysulfide copolymers it is necessary to study the mechanism, cure kinetics and matrix morphology. Generally the curing of the epoxy resin is studied by differential scanning calorimetry(DSC). DSC measures the heat flow from a sample as it is heated and provides valuable information on glass transition temperature, onset of cure, heat of cure, maximum rate of cure and degree of cure [9].

Toughening of epoxy resin with various methods was reported in different work [10-13]. Rubber inclusion is one of the most successful methods to modify epoxy resin[14,15]. The Effect of rubber inclusion on DGEBA-based epoxy resin was studied by *Thomas R. et al.* [16]. They resulted that the addition of different weight contents of Carboxyl-Terminated Copolymer of butadiene and acrylonitrile liquid rubber (CTBN) did not change the mechanism of cure but decreased the rate of the reaction in liquid rubber modified epoxies. In similar work the relationship between curing conditions and morphology of carboxyl-terminated poly(2-ethyl hexyl acylate)liquid rubber-modified epoxy have been studied and was shown that the addition of liquid rubber causes a delay in polymerization of the epoxy matrix[17].

In other work The PDMS-modified epoxy resins showed higher early cure reactivity and a lower crosslinking density due to the plasticization and restriction effect of the dispersed PDMS phase, respectively[18].

liquid polysulfide resins have sulfhydryl groups which react with the epoxy resins during cure as a reactive modifier. The polysulfide modified epoxy resin gives a higher strength and better chemical resistance than non reactive elastomeric modifiers [19].

In this work the effect of curing method on mechanical and dynamical properties of polysulfide elastomer was investigated. Also the effect of polysulfide incorporation into the epoxy matrix (as reactive modifier) on curing information (such as heat of cure, onset of cure), glass transition temperature and phase separation of epoxy matrix was studied.

EXPERIMENTAL SECTION

The liquid polysulfide resin used in this study is the mercaptan terminated polymer (G4 grade, $M_n \sim 1100$ gmol $^{-1}$, was purchased from Akzonobel Co., Epoxy resin (Epon828, $M_n \sim 400$ gmol $^{-1}$) with epoxy group content of 5.3 mol kg $^{-1}$ was supplied by Shell Co. Amine hardener (HY564) with amine content of 21.56 mol kg $^{-1}$ was supplied by Ciba Geigy Co.

Diphenylguanidine(DPG), as accelerator, was purchased from Merck Co. . Para quinonedioxime(PQD), was used as curing agent and supplied from Fluka Co. Activated manganese dioxide (MnO_2) was used as curing agent and supplied from Merck Co.

All ingredients of a particular composition, as mentioned in Table 1, were mixed by mechanical stirring for 45 min., at rate of 500 rpm, and temperature of 50 °C, and test specimens were made by casting in the appropriate molds. Time and temperature condition of curing have been brought in tables.

Epoxy and polysulfide resin composition, as mentioned in Table 2, were added into a flask and stirred at rate of 500 rpm for 2 hours at 50°C, then delivered into a vacuum oven to remove entrapped bubbles, the hardener was introduced into the mixture and all components were mixed vigorously for 2 min. Finally the mixture was cast into the Teflon coated molds and placed inside an oven set at 50°C. Time and temperature condition of curing have been brought in Table 2.

Tensile strength (σ), elongation at break (ϵ) and modulus (E) were measured by using an Instron machine (model 122) according the standard method (ASTM D412).

Infrared spectra were recorded on Bruker(Tensor27) for sample E, directly and 20 days after mixing of epoxy-polysulfide at 25 °C, before adding hardener .

Hardness of samples was measured by REX 1600 in Shore A.

Dynamic Mechanical Thermal Analysis (DMTA) was carried out for polysulfide and Epoxy-Polysulfide copolymers by a Dynamic mechanical thermal analyzer (DMA-Triton, tritec2000) according to ASTM E1640-04. with a programmed heating rate of 5 °C/min.

SEM photograph of the gold coated surface was taken, using a vega tscan model scanning electron microscope.

To determination of gel point, Rheological experiments were carried out using a Paar-Physical

Table 1: Formulation and mechanical/dynamical properties of polysulfide compound cured with various oxidative cure systems.

Material / formulation	A	B	C	D	E
G4 resin (g)	100	100	100	100	80
Epon828(g)					20
MnO ₂ (g)			10	6	10
PQD (g)	4	2			
DPG (g)	2	2	2	2	2
σ (MPa)	0.6	0.62	0.89	0.82	0.9
ϵ (%)	170	152	419	190	400
E(MPa)	0.45	0.52	0.55	0.49	0.5
hardness (Shore A)	35	35	35	40	40
Tg(°C)	-45	-45	-40	-42	
Cure time(hr)	72	72	72	72	72
Cure tem.(°C)	55	55	55	55	55

Table 2: Formulation and mechanical properties of polysulfide-epoxy compound cured with amine hardener.

Material/formulation	F	G	H	I	J	K	L	M	N
G4 resin (g)	30	35	40	45	50	55	60	65	70
Epon828(g)	70	65	60	55	50	45	40	35	30
hardener(g)	14	13	12	11	10	9	8	7	6
σ (MPa)	23	21	17	5.1	2.5	1.8	1.2	0.8	0.5
ϵ (%)	5	8	12	25	52	85	120	143	160
E (MPa)	97	52	43	25	17	12	8	5	2
hardness (Shore A)	95	90	87	85	80	71	65	57	50
Cure time(hr)	2	2	2	2	2	2	2	2	2
Cure tem.(°C)	50	50	50	50	50	50	50	50	50

Rheometer (model MCR300) with two parallel-plates. Both plates are from stainless steel, the upper plate having the radius of 25 mm. The upper plate was set at the separation distance of 1 mm. 2 mL of stock solution of the reaction mixture was poured on the lower plate of Rheometer for each determination. The gel point determination was carried out at 100 °C, at frequency of 1 Hz and shear stress Of 0.1 Pa.

In this work the Perkin-Elmer PYRIS 6 differential scanning calorimeter (with indium as reference material) was used to perform calorimetric measurements at heating rate of 10°C/min.

RESULTS AND DISCUSSION

Epoxy-polysulfide interaction

The ideal structure for reactive Epoxy-Polysulfide copolymers comprising a polysulfide molecule capped

with two polyepoxide molecules. This type of copolymer is formed from a stoichiometric excess of oxirane groups over mercaptan groups. The resulting liquid polymer products have no residual mercaptan groups, and have free oxirane groups, which can be opened in chain extension/cross linking reactions using the amine hardener.

FT-IR spectrums of polysulfide-epoxy mixture, directly (A) and 20 days after mixing (B) are given in Fig. 1.

After 20 days, two changes occurred in comparison with immediate-mixed sample spectrum: the -OH stretching vibration at ~3475 cm⁻¹, was strengthened and the -SH stretching vibration at ~2535 cm⁻¹, was weakened. These data revealed that the reaction between mercaptan and epoxide groups of resin had occurred after mixing and continued as time passing. This reaction mechanism is described in Fig. 2.

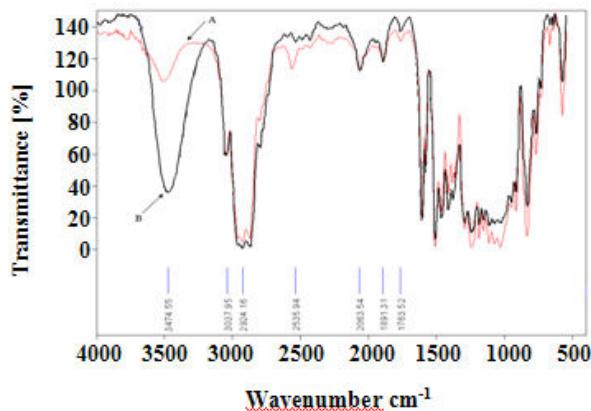


Fig. 1: FT-IR spectra obtained for epoxy-polysulfide mixture directly (A) and 20 days after mixing at 25 °C(B).

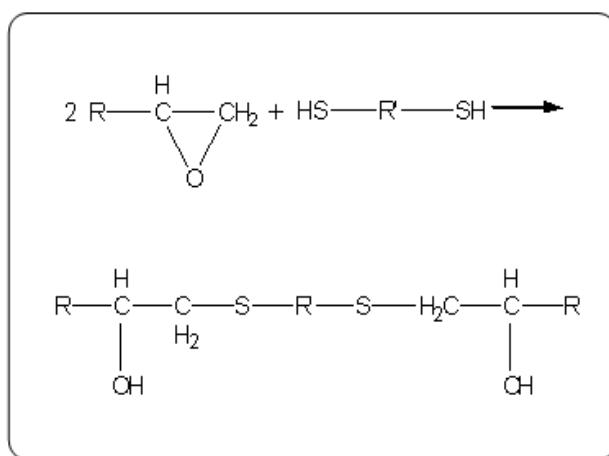


Fig. 2: A typical interaction between epoxy and polysulfide.

Gel time

The gel point is usually defined as the time or the degree of reaction at which the solution no longer remains liquid. Originally qualitative rheological considerations were used to define the gel point. The intercept of loss modulus, G'', and storage modulus G', can be considered as the gel point (Fig 3). The critical region begins with a sudden increase in G' and G'' when G' and G'' intercept, tan δ=1. After intercept, G' becomes greater than G'' and tan δ becomes smaller than 1 [20]. The effect of polysulfide weight percent on the gel time which is illustrated in Fig. 4 shows that the gel time increases with increasing polysulfide weight percent in epoxy-polysulfide copolymers. On the other hand, modification of epoxy leads to a delay in curing. Extending of gel time can be attributed to lower reactivity of the modified epoxy because of chain extension and formation of epoxy-polysulfide copolymer.

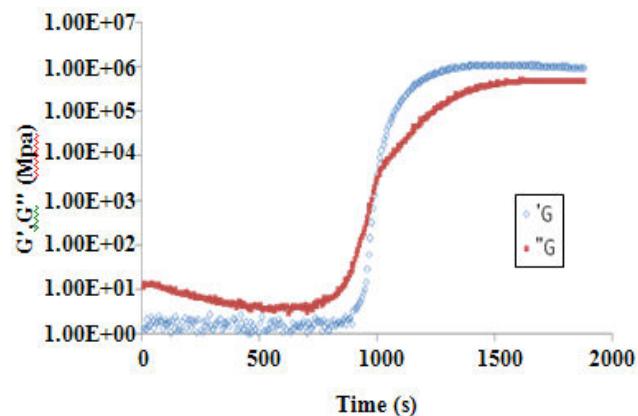


Fig. 3: Variation of storage modulus (G') and loss modulus (G'') versus time at 100 °C for sample I.

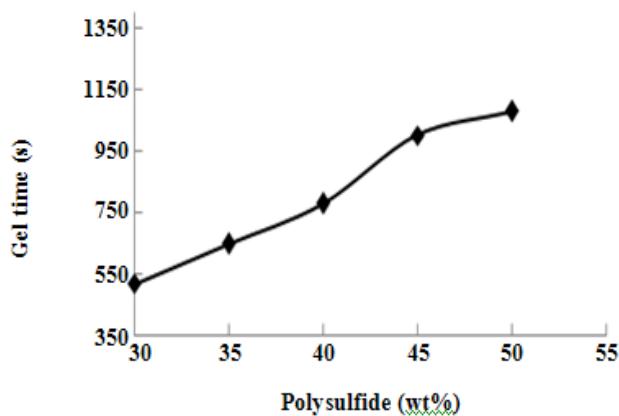


Fig. 4: Gel time behavior of Epoxy-Polysulfide copolymers in various ratios at 100 °C.

Manganese dioxide and para quinonedioxime as oxidative curing agent were used in oxidative curing system. In addition, polysulfide G4, epoxy 828 and HY564 (hardener) were used as formulation materials in copolymerization system. The oxidative curing agents serve as oxygen donor and yield disulfide linkages by linking two thiol groups. Maximum tensile strengths were obtained at a level of 6 phr(part per hundred resin) MnO₂ and 2 phr para-quinonedioxime. Mentioned curing agents had long cure time and were used with 2 phr diphenylguanidine as accelerator. Results showed that oxidative curing agents had no remarkable effect on the mechanical properties and cure time. Although manganese dioxide is effective than para quinonedioxime (Table1).

Therefore it was decided to prepare polysulfide-epoxy copolymer because epoxy serves as hard segment in copolymer chain and Addition of epoxy to polysulfide nearly always

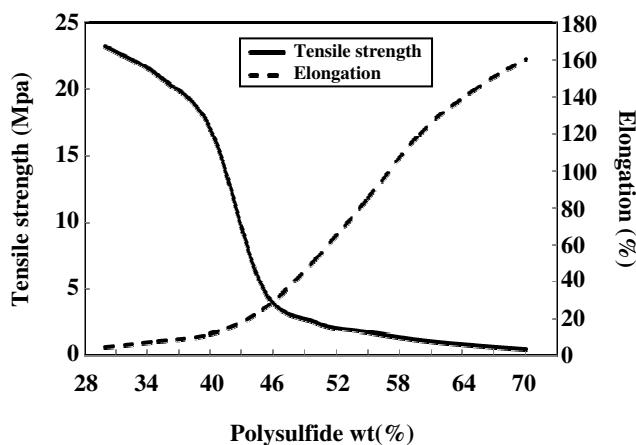


Fig. 5: Variation of Epoxy-Polysulfide copolymers tensile strength and elongation toward polysulfide weight percent.

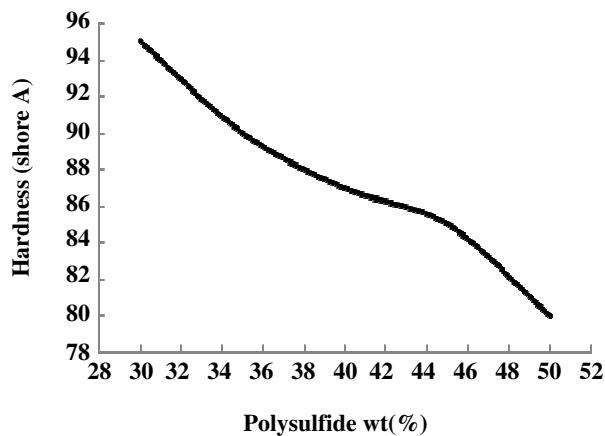


Fig. 6: Variation of Epoxy-Polysulfide copolymers hardness toward polysulfide weight percent

leads to improvement in material properties, particularly the development of mechanical properties (Figs. 5 and 6). Depend on dynamical and mechanical properties that are needed, We prepared epoxy-polysulfide copolymer with different composition because in different epoxy/polysulfide ratio, the epoxy-polysulfide copolymer showed different tensile strength, elongation, hardness, gel time, viscosity and Tg, but epoxy free polysulfide approximately revealed constant mechanical and dynamical properties.

Effect of polysulfide content on epoxy-polysulfide copolymer Cure information

Cure behaviors of Epoxy-Polysulfide copolymers were investigated using Differential Scanning Calorimeter (DSC). The heat of reaction between Epoxy-Polysulfide

copolymers and hardener was measured by integration of the exothermic peaks. Results showed that the curing heat (enthalpy) decreased with increasing polysulfide weight percent in epoxy-polysulfide copolymers, but increasing in polysulfide weight percent caused the temperature corresponding to exothermic peak gradually elevated from 99 °C to 114°C (Fig. 7). The delay in curing was verified by measurement of curing heat flow. As shown in Fig. 8 the temperature of cure onset increased with increasing in modifier content. As mentioned before the delay in curing attributed to chain extension due to epoxy-polysulfide interaction. The traces observed in unprereacted epoxy with 30wt% polysulfide can be related to exothermic reaction between epoxy-polysulfide and epoxy-hardener.

Phase separation and glass transition temperature

Investigating of DMTA graphs obtained from Epoxy-Polysulfide copolymers indicated that phase separation has occurred in copolymer matrix. Two tan delta maxima observed in DMTA spectra indicated the existence of two phases in the sample but in low weight percent of polysulfide (30%) phase separation was not observed (Figs. 9 and 10). The Tg is determined by the tan delta maximum. Predictably, glass transition temperature (Tg) of the Epoxy-Polysulfide copolymers was decreased with increasing polysulfide weight percent in composition. It can be resulted from Fig. 9 the shift of maximum height of tan delta peak to higher quantity can be attributed to the strengthening of viscose behavior. The sample with low tan δ is more elastic than that of the high. Bright section among cured epoxy-polysulfide copolymer Matrix in SEM figures showed morphology that proved phase separation interpreted in DMTA graphs (Fig. 10).

CONCLUSIONS

Oxidative curing agents (Para quinonedioxime, Activated manganese dioxide) have no appropriate effect on the the mechanical properties and cure time. But Addition of epoxy to polysulfide and curing with amine hardener nearly always leads to improvement in material properties, particularly the development of mechanical properties and ductility. Copolymerization of epoxy and polysulfide resin was verified by FT-IR spectroscopy and rheometry. Phase separation of cured epoxy-polysulfide copolymer was detected by DMTA and SEM. And glass transition of

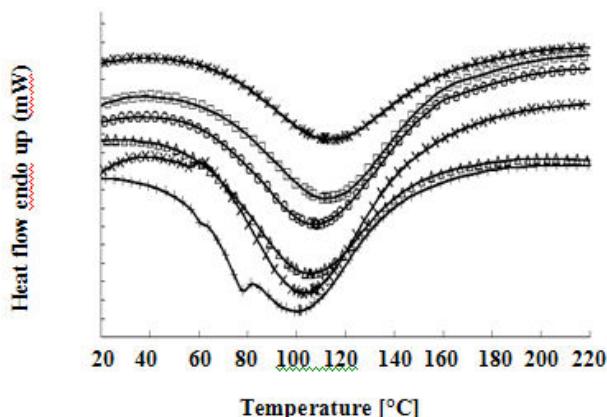


Fig. 7: DSC scan of 30wt% polysulfide in epoxy resin without prereaction(+) and prereacted epoxy with 30(\times),35(Δ),40(\circ),45(\square),50 ($*$) weight percent of polysulfide.

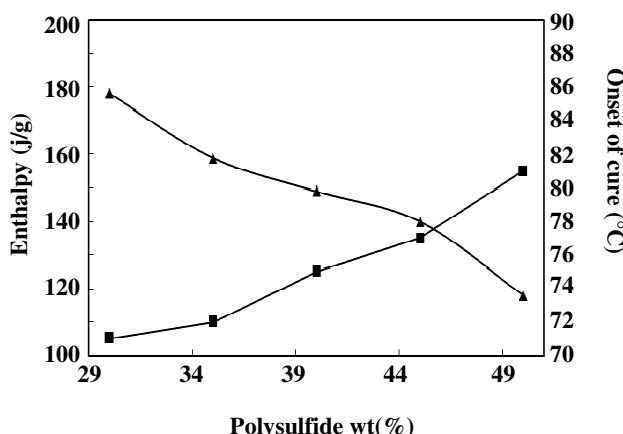


Fig. 8: Variation of enthalpy (▲) and onset of cure (■) versus polysulfide weight percent in Epoxy-Polysulfide copolymer.

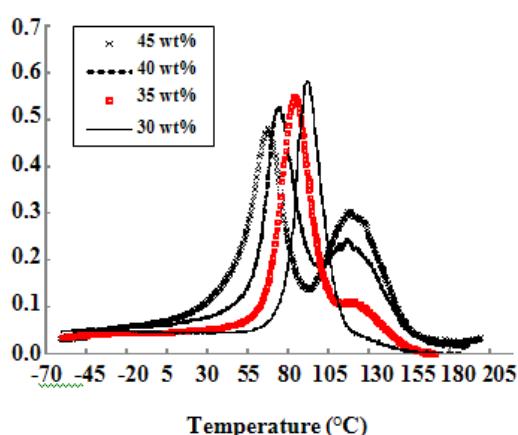
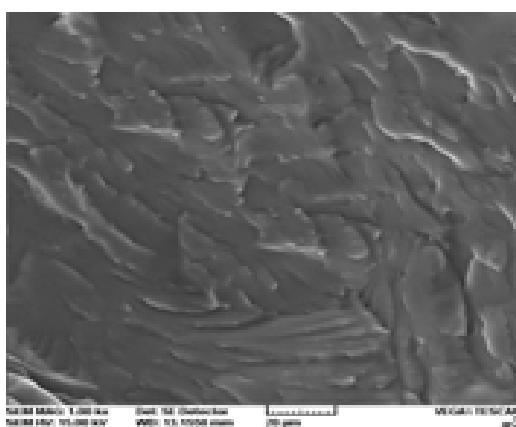
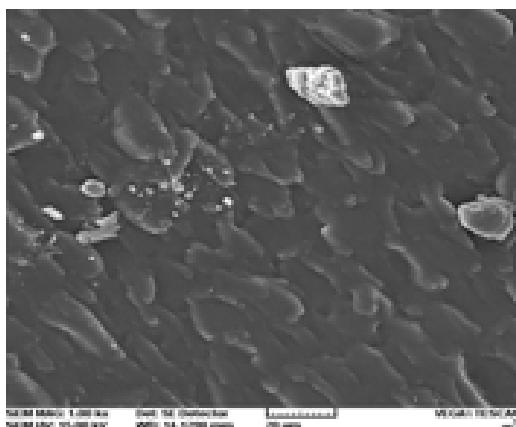


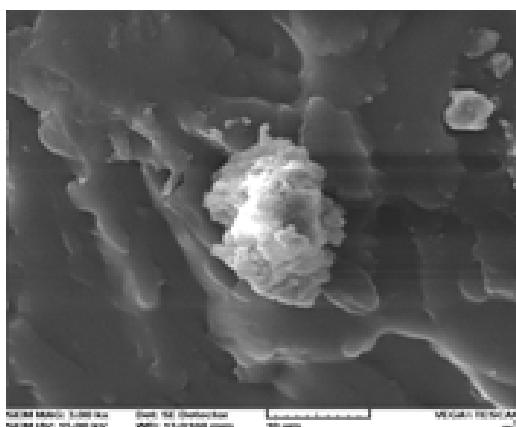
Fig. 9: $\tan \delta$ versus temperature of the Epoxy-Polysulfide copolymers at $T_{cure}=50$ °C.



(a)



(b)



(c)

Fig. 10: SEM figures that obtained from cured epoxy-polysulfide copolymer with 30 (a) and 45 (b , c) weight percent of polysulfide.

epoxy-polysulfide compound was discernible in DMTA graphs. Kinetic study of Epoxy-Polysulfide copolymers by differential scanning calorimetry in dynamical mode showed that cure reaction heat (enthalpy) decreased with increasing polysulfide weight percent in Epoxy-Polysulfide copolymers, but increasing in polysulfide weight percent caused the temperature corresponding to exothermic peak gradually elevated from 99 °C to 114°C.

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