Investigating the Effect of Modifier Chain Length on Insulation Properties of Polysulfide Modified Epoxy Resin

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ABSTRACT: *Polysulfide resins, with trade name of G4 and G112, with short and long chain lengths respectively, were used as reactive modifiers to toughen epoxy resin. The effects of molecular weights of G4 and G112 on impact resistance, dielectric constant, thermal conductivity as well as decomposition heat and adhesion properties of toughened epoxy were investigated. The impact strength and the dielectric constant of epoxy resin were enhanced by increasing of polysulfide so that the effect of the G112 is higher than the G4. For the same weight percent of G4 and G112, the G112 modified epoxy resin has lower Cure enthalpy than the G4 modified epoxy resin. Addition of modifier with long chain up to 10 weight percent was also leaded to higher bond strength with aluminum sheets. also, It is observed that the thermal conductivity of epoxy decreasing with incresing modifier chain length.*

KEY WORDS: *Epoxy, Polysulfide, Insulation properties.*

INTRODUCTION

Cracking during mechanical loading or thermal cycling is a well-known phenomenon, which occurs with many liquid epoxy resin system. In both cases, the epoxy resin creates stresses because it is in contact with materials, which have thermal expansion coefficients approximately 0.1 that of the resin. Many epoxy resins are toughened in order to improve crack resistance [1]. There are several methods for toughening of epoxy resins on the basis of the structure-property relationships [2-5]. The traditional chemical methods can be classified as: (1) chemical modification of rigid epoxy backbone to a more flexible structure; (2) lowering the crosslink density by increasing the molecular weight; and (3) decreasing the functionality of the curing agents. Among these approaches, the incorporation of rubbery phase into the epoxy matrix is the most common method. Rubber modified epoxy resins are successful with adhesives, which have been characterized with respect to their fracture behaviour and adhesive bonds. The advantages of liquid rubber as a modifier include its solubility in the base epoxy resin and formation of a homogeneous solution [6,7].

Table 1: Formulations of toughened epoxy with two different modifiers.

EP8	EP7	EP6	EP5	EP4	EP3	EP2	EP1	EP0	Material/formulation
-	-	-	-	20	15	10	5	-	G4 resin (g)
20	15	10	5	-	-	-	-	-	G112 resin (g)
80	85	90	95	80	85	90	95	100	Epon828(g)
10	11	12	13	10	11	12	13	14	Hardener(g)
50	50	50	50	50	50	50	50	50	Curing temp.($^\circ$C)
2	2	2	2	2	2	2	2	-	Curing time (hr)

Wilford and coworkers [8,9] reported that the touhgening of epoxy resin by liquid polysulfide can improve adhesion properties and flexibility. *Abdouss et al.* [10] investigated the effects of polysulfide modifier on mechanical and morphological peoperties of epoxy resin. They reported that addition of polysulfide into epoxy can form epoxy–polysulfide copolymer. For different epoxy/polysulfide weight ratios, the epoxy-polysulfide copolymer showed different tensile strength, elongation, hardness, gel time, viscosity and glass transition temperature (T_g) [10]. *Abdouss* and coauthors [11] have also studied phase separation and T_g of polysulfide modified epoxy resin. *Agrawal et al.* explored [12] heat resistance, brittleness temperature, plasticizer absoption, oxygen index and other dynamical-mechanical properties of polysulfide modified epoxy resin. The ultimate properties of modified epoxy resin are strongly dependent on the final morphology of the blends, curing conditions, composition and molecular weight of the modifier. Maximum toughness can be acheived in blends that are miscible in the uncured state. The immiscibility depends mainly on the high molecular weight and semicrystalline nature or the chemical makeup of the resins. Thus, low molecular weight resins with reactive functional groups or with large side groups attached to main chain can be used as modifiers for epoxy resin [13-15].

Morell et al. studied [16] thermal expansion coefficent and impact strength of epoxy resin hydroxy-functionalized HyperBranched Poly (HBP) (ester-amide) with different molecular weights. They found that thermal expansion coefficent of modified epoxy with HBP in the glassy and rubbery states decreases by increment of the percent weight of HBP. For the presence of high molecular weight of modifier, the reduction of thermal expansion coefficent is higher [16].

Thermal and mechanical properties of modified epoxy resins are very sensitive to the chemical and stractural nature of epoxy resins, modifier and crosslinker. Thermal decomposition kinetics of rubber modified epoxy resins were investigated elsewhere [17-20]. Ordinarily inclusion of rubber as modifier into epoxy resins accompany with reduction of thermal stability and decomposition point because crosslinking density is decreased. It should be mentioned that reducing of decomposition temperature is proportional to decreasing of crosslinking density in epoxy structure.

In another study, The authors have attempted to measurment thermal conductivity using an epoxy resin modified with different aliphatic diols in order to vary the cross-link distance. The thermal conductivity was measured in the temperature range 0.5- 80 K for a set of specimens with different diol chain lengths and using different catalysts. [21].

The purpose of this work is to study the effects of two grades of polysulfide resins G4 and G112 as reactive modifiers with different molecular weights on mechanical and thermal properties of epoxy resin. Different properties of toughened epoxy resin are invetigated, i.e. the effect of modifier molecular weight on impact resistance, thermal expansion coefficient, thermal conductivity, decomposition temperature and adhesion properties.

EXPERIMENTAL SECTION

The liquid polysulfide resins used in this study are the mercaptan terminated polymer (G4 grade, M_n~1100 g/mol, G112 grade, M_n~4000 g/mol), which were purchased from Akzonobel Co. Epoxy resin (Epon828, M_n ~400g/mol) with epoxy group content of 5.3 mol / kg was supplied by Shell Co. Amine hardener (HY564) with amine content of 21.56 mol / kg was supplied by Ciba Geigy Co.

As mentioned in Table 1, epoxy and polysulfide resins were added into a flask and stirred at rate of 500 rpm for 2 hours at 50°C to prepare samples. Prereaction

of samples was performed at 25°C for 14 days. The prepared samples were inserted into a vacuum oven to remove entrapped bubbles. Finally, hardener was introduced into the mixture and all components were mixed vigorously for 2 min.

Tensile strength, elongation at break and modulus were measured by using an Instron machine (model 122) according the standard method (ASTM D638). Dumbell shaped specimens were prepared in a mold. The specimens were then clamped in the jaws of the machine and tension was applied at the constant rate of 50 mm/min.

The samples for thermal conductivity measurements were cut into disk shapes with a 1-cm diameter and a 1-mm thickness. The thermal conductivity was evaluated with the Laser Flash Thermal Diffusivity (LFTD) method. The LFTD method is based on the application of a high intensity and short-duration heat pulse to one face of a parallel-sided test piece and the monitoring of the temperature increase on the opposite face as a function of time. The thermal diffusivity of the sample (α) is then calculated according to the following formula: $\alpha = 0.139 L^2 / t_{1/2}$ where L is the thickness of the specimen and $t_{1/2}$ is the time from the initiation of the pulse until the rear face of the test sample reaches one-half of its maximum temperature. The LFTD method measures the thermal diffusivity and specific heat capacity of the sample. The thermal conductivity of the sample (k) is determined as follows: $K = \alpha \rho C_p$ where C_p is the specific heat capacity and ρ is the density of the sample. Density of solid sample sheets was determined using the rule of mixture.

The LINSEIS (model STAPT1600) Differential Thermal Analysis (DTA) apparatus was uesd to determinate the thermal decomposition enthalpy of unmodified and modified epoxy resin in inert (nitrogen) atmosphere with the temperature program of 10°C/min.

The Izod unnotched impact test was carried out using an impact tester with striking velocity 3m/s according to ASTM D4812. Impact test samples were prepared in dimension of $0.5 \times 1 \times 7$ cm^3 . In this work the Perkin-Elmer PYRIS 6 differential scanning calorimeter(with indium as reference material) was uesd to perform iso thermal calorimetric measurements .

Single lap shear strength was determined for aluminum-aluminum bonds according to ASTM D-1002 standard using treated aluminum sheets of size 12×2.5 cm^2

with an overlap of 2.5 cm. The adhesive formulation was applied uniformly on both surfaces. Samples were mated and cured at 50°C for 3 days. The adhesive thickness was approximately 0.03 mm. The joint strength was measured in an Instron testing machine (model 122) with the crosshead speed of 20mm/min at 25°C. The procedure for the surface treatment of aluminum sheets includes the following steps:

1) The aluminum sheets was washed with acetone thoroughly, then placed in an air-forced oven, and dried at 50°C for 2h.

2) The acetone cleaned aluminum was treated with multifunctional isocyanate primer (desmodur RE) and dried in the mentioned oven at 50°C for 10 min.

The dielectric properties of the neat and the polysulfide containing epoxy systems were tested using a broadband dielectric spectrometer at the platinum (Pt) electrode at room temperature and a frequency range of 1 MHz. The experiment was repeated four times under the same conditions.

The flat free surfaces of the samples were used for measurement of contact angles. The measurements, using ultrapure water as probe liquids, were performed on an OCA20 contact angle measurement instrument (Hysics Co.) at room temperature.

RESULTS AND DISCUSSION
Reactive modification

The ideal structure for reactive polysulfide modified epoxy resin consists of a polysulfide molecule capped with two polyepoxide molecules. This type of copolymer is made from a stoichiometric excess of oxirane groups over mercaptan groups. However, the resulting liquid polymer products have no residual mercaptan groups. Meanwhile, they contain free oxirane groups, which can be opened in chain extension/cross linking reactions using the amine hardener. This reaction mechanism is described in Fig. 1.

Impact and mechanical properties

The effect of adding polysulfide rubbery phase on impact strength of epoxy resin is illustrated in Fig. 2. Impact resistance is a useful method for the evaluation of the toughness or brittleness. As seen in Fig. 2, the impact strength of epoxy resin is increased by addition of polysulfide but the trend of elevation is high in the

Table 2: Mechanical and thermal properties of polysulfide toughened epoxy resin.

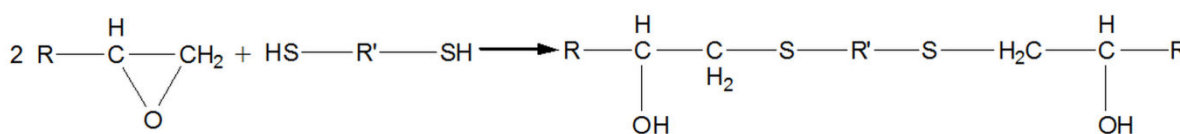| EP8	EP7	EP6	EP5	EP4	EP3	EP2	EP1	EP0	Properties/Sample
27.36 ±0.7	32.7 ±0.6	30.2 ±0.5	28.5 ±0.7	62.39 ±0.5	63.2 ±0.4	65.2 ±0.6	62.8 ±0.6	61.7 ±0.3	Tensile strength(MPa)
2.85 ±0.1	2.5 ±0.1	2.3 ±0.1	2.1 ±0.2	4.5 ±0.15	3 ±0.1	4 ±0.2	3.2 ±0.1	2.1 ±0.1	Elongation @ break(%)
0.94 ±0.07	1.1 ±0.06	1.16 ±0.05	1.2 ±0.05	1.24 ±0.06	1.3 ±0.08	1.4 ±0.05	1.49 ±0.07	1.56 ±0.08	Modulus(GPa)
17.5	18.4	16.5	13.2	13.2	14.6	15.6	12.67	8.75	Impact resistance (kJm^{-2})
0.2	-	-	-	0.25	-	-	-	0.28	Thermal conductivity(W/mk)
EP8	EP7	EP6	EP5	EP4	EP3	EP2	EP1	EP0	Properties/Sample
1.25				1.34				1.37	Specific heat capacity(J/g°C)
0.12	-	-	-	0.14	-	-	-	0.16	Thermal diffusivity(mm^2/s)
4.01 ±0.1	4.26 ±0.1	3.8 ±0.2	3.5 ±0.15	2.7 ±0.2	3.25 ±0.2	4.46 ±0.2	3.1 ±0.1	2.4 ±0.1	Lap shear strength (MPa)
4.2	-	-	-	3.9	-	-	-	3.5	Dielectric constant(ε)
-	24	-	20	-	26	-	27	44	Decomposition heat(µVs/mg)$_{DTA}$

Fig. 1: A typical interaction between epoxy and polysulfide.

presence of higher molecular weight of modifier, i.e. G112 polysulfide resin. The formulations containing 10 wt% G4 and 15 wt% G112 have higher impact strength and mechanical properties (Table 2). G112 modified epoxy resins have lower tensile stength than those modified with G4 (Fig. 3). Because the reduction in concentration of reacting functions, i.e. addition of rubbery resin with long polymer chain(G112) causes lowering in crosslinking density of epoxy matrix during the cure polymerization reaction. The curing of epoxy resins in the presence of polysulfide modifiers produces block copolymer structures in which one "block" is the crosslinked epoxy/amine network and the other "block" is the linear modifier segment. As shown in Table 2, Toughness properties of G4 modified epoxy systems were beter than that of modified with G112. Because of small size molecules, G4 polysulfide as a plasticizer can occupy the free volume of epoxy netwok.

Decomposition heat

The thermal decomposition of cured epoxy resin proceeds in two or more steps, which depend on its molecular structure. Evolution of water is believed to take place in the first step (~300°C). Acetone, carbon dioxide, hydrogen cyanide and aliphatic hydrocarbons are also evolved at higher temperatures [20]. The area under a DTA peak is the enthalpy change during decomposition (Fig. 4) and is not affected by the heat capacity of the sample. As shown in Table 2, the heat changes of decomposition phenomenon are decreased with increasing polysulfide modifier. When the weight percents of G4 and G112 are the same, the decomposition heat of G4 modified epoxy resin is higher than the G112 modified epoxy resin.

Thermal Diffusivity analysis

Figs. 5-7 show the thermal diffusivity plots for samples of EP0,EP4 and EP8.The modification of
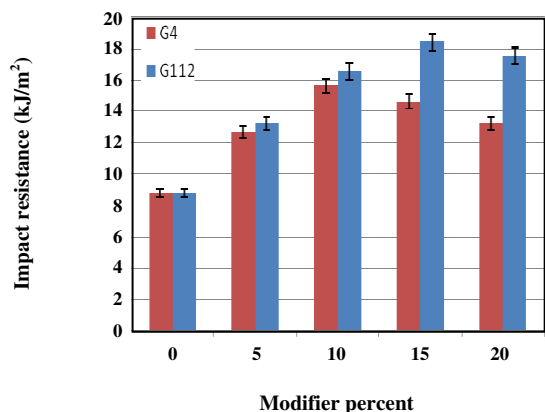
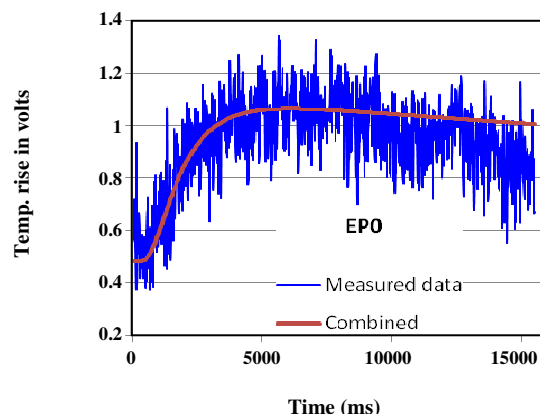**Fig. 2: Impact resistance of G4 and G112 polysulfide modiied epoxy resins versus modifier percent.**

Fig. 5: The monitoring of the temperature increase on the opposite face as a function of time in sample EP0.
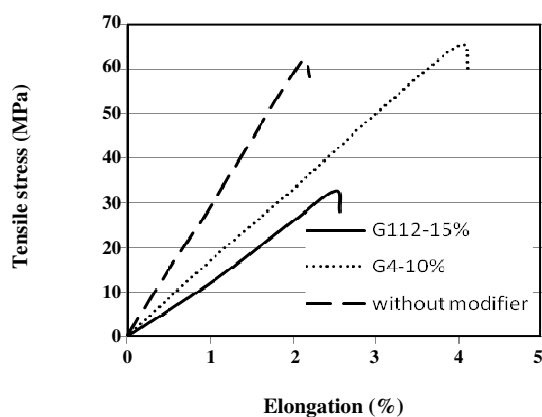

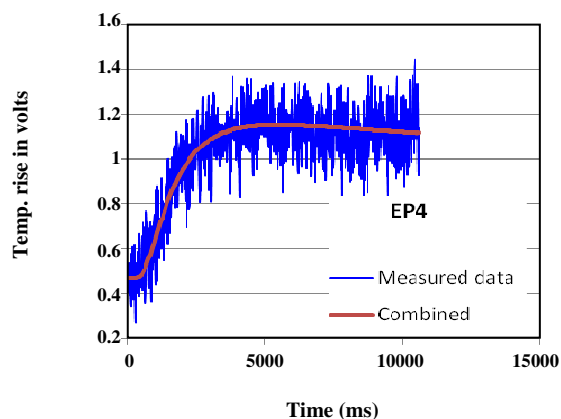**Fig. 3: Stress-strain curves of unmodified and polysulfide modified epoxy resin.**

Fig. 6: The monitoring of the temperature increase on the opposite face as a function of time in sample EP4.
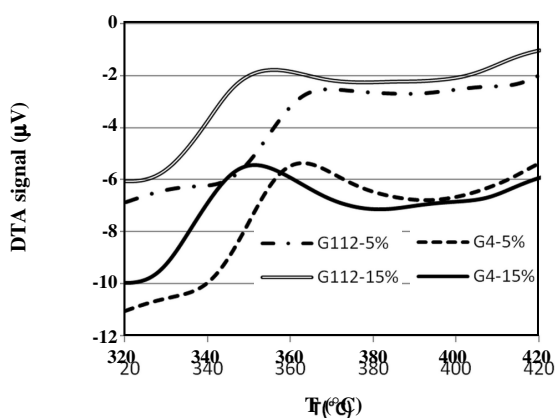

Fig. 4: Comparison of the effects G4 and G112 modifiers on thermal decomposition of epoxy resin.
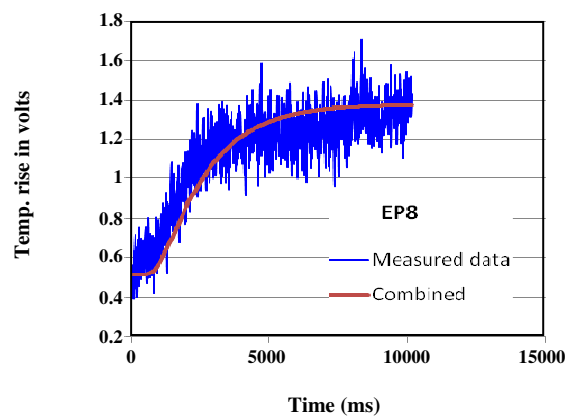

Fig. 7: The monitoring of the temperature increase on the opposite face as a function of time in sample EP8.

epoxies with different polysulfide modifier leads to changes in thermal conductivity (Table 2). Increasing the modifier chain length Decreases the value of the thermal conductivity. The G112 modified epoxies show lower thermal conductivities than the G4 modified epoxies, likely due to the lower crosslink densities.

Curing enthalpy

Isothermal heating study was performed at temperatures of 80°C. Using Differential Scanning Calorimetric (DSC). The analysis is based on the assumption that the heat generated during the epoxy curing reaction is equal to the total area under the heat flowe-time curve. The heat of reaction between Epoxy-Polysulfide copolymers and hardener was measured by integration of the exothermic peaks (Fig. 8). Results showed that the curing heat (enthalpy) decreased with increasing polysulfide into Epoxy resin. The reduction in curing heat attributed to chain extension due to epoxy-polysulfide interaction. As shown in Fig. 8 the G112 modified epoxy has lower curing enthalpy than that modified with G4 at the same modifier weight percent. Chain length of G112 modifier is higher than G4 and its reaction with epoxy resin leads to extended and sedentary polymeric chains.

Static Contact Angle and adhesion properties

The contact angles of unmodified and polysulfide modified epoxy resin were measured with water as probe liquids. The results are shown in Fig. 9. The contact angle of the pure epoxy was measured with water at approximately 72°. With the incorporation of polysulfide into the epoxy systems, the contact angles dramatically decreased with increasing polysulfide content. The decreased surface contact angles indicate that the hydrophilic properties of the materials is significantly improved, which can be attributed to the polysulfide network having high surface energy and showing hydrophilicity. G4 and G112 approximatly showed the same effect on suface energy of modified epoxy.

The effects of incorporation of each polysulfide adhesion strength of modified networks are shown in Fig. 10. The results show that adhesive strength is improved with respect to unmodified one for each sample, which depends on weight percent of the polysulfide. The maximum adhesion strength is obtained at 10 wt% of G4
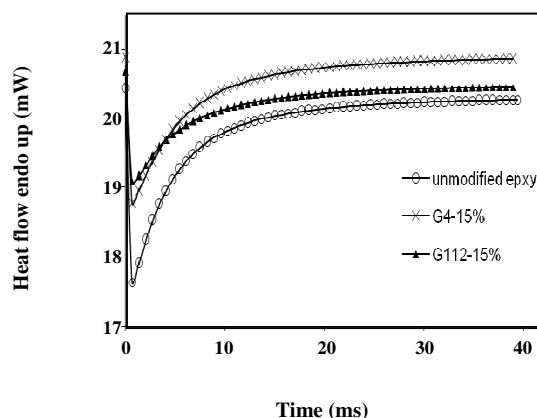

Fig. 8: Iso thermal DSC study for unmodified and modified epoxy with different modifier chain length.
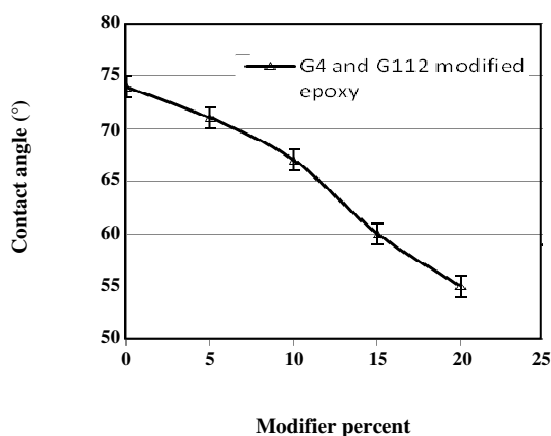

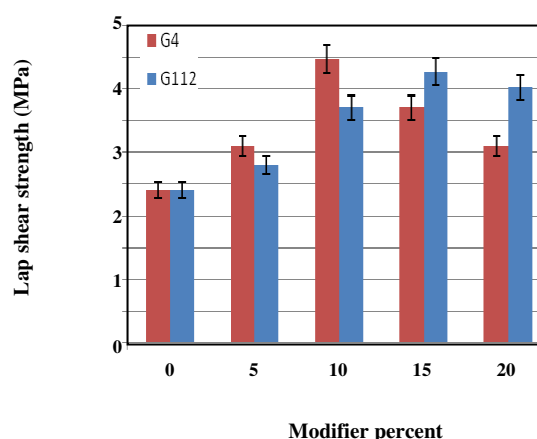**Fig. 9: Static contact angle of modified epoxy resin.**

Fig. 10: Adhesive (lap shear) strength of modified epoxy network Epoxies.

and 15 wt% of G112 because modifiers act as plasticizers after an optimum weight percent. Thus, the higher modifier molecular weight gives low flexibilization.

Dielectric behavior

The dielectric constsnt(ε) of a polymer may increase or decrease depending on variation in its composition. The blends of resins having high ε with those having low ε will increase the ε of the lower ε resin in proportion to the amount and type of resin added. The blends of epoxy resin with both polysulfide modifier(G4 and G112) lead to increase the dielectric constsnt of prepared copolymer. In addition The dielectric constant of prepared epoxy-polysulfide copolymer increases with increasing the polysulfide weight percent in copolymer structure. As shown in Table 2, For the same weight percent of G4 and G112, the G4 modified epoxy showed better insulation properties and lower dielectric constant. it can be attributed to the high crosslinking density of G4 modified epoxy towared that modified witg G112. Crosslink density is an important factor that can be affected the dielectric constsnt of modified epoxies [22].

CONCLUSIONS

The impact strength of epoxy resin was increased by including polysulfide. The slope of elevation of the impact strength is high when high molecular weight of modifier G112 polysulfide resin was used. Thus, the formulations containing 10 wt% G4 and 15 wt% G112 have the highest impact strength. The values of dielectric constsnt of epoxy resin enhanced by increasing the amounts of modifier. G112 modified epoxy samples showed higher dielectric constsnt values than that of modified with G4. The decomposition and curing heat decreased as the amount of both modifiers G4 and G112 resins were increased from 5 wt% to 20 wt%. When the weight percents of G4 and G112 are the same, the decomposition and curing heat of G4 modified epoxy resin is higher than the G112 modified epoxy resin. The adhesive strength is improved by using both polysulfides. The maximum adhesion strength was obtained at 10 wt% of G4 and 15 wt% of G112 polysulfide modifiers. It is observed that the thermal conductivity of epoxy decreasing with incresing polusulfide resin. But thermal conductivity of G112 modified epoxies were lower than those G4 modified.

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