

# Thermal and chemical resistance behavior of cured epoxy based on diglycidyl ether of bisphenol-A and thiol treated liquid polysulfide blends

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## ABSTRACT

In the present study five blends of Diglycidyl ether of bisphenol-A and thiol terminated liquid polysulfide with varying amount of polysulfide (i.e. 10 to 50 phr) were synthesized by physical mixing at 90°C and synthesized blends were cured with phthalic anhydride. Interaction among epoxide group of DGEBA, -SH group of polysulfide and anhydride group of curing agent discussed through FT-IR analysis. The TGA studies revealed a decrease in thermal stability and activation energy (114.35 - 73.04 kJ/mole) with increase in polysulfide content. Volume resistivity decreases from  $5.34 \times 10^{15}$  to  $3.83 \times 10^{11}$  ohm-cm with increase in polysulfide content in the blends. The study of chemical resistance for various acids, alkalies to distilled water, sea water, xylene, ethanol, methyl ethyl ketone and acetone indicated that chemical resistance of blends decreased with increase in polysulfide content. Scanning electron microscopy (SEM) indicated the presence of two-phase morphology in the blends. Copyright © 2010 VBRI press.

**Keywords:** DGEBA; liquid polysulfide; TGA; limiting oxygen index; volume resistivity.



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## Introduction

Epoxy resins are very important class of thermosetting polymers that often exhibit high tensile strength and modulus, excellent chemical, corrosion resistance and good dimensional stability. Hence they are widely used in structural adhesives, surface coatings, engineering composites, electrical laminates etc. [1]. In the cured state, epoxy resins are brittle materials that have fracture energies some two orders of magnitude lower than modern thermoplastics and other high performance materials [1–2]. As the result they have limited utility in applications requiring high impact and fracture strengths. This inherent brittleness causes poor peeling and shear strength of epoxy based adhesives [3]. Hence toughening of epoxy resin has been the subject of intense investigation throughout the world. Epoxy resins are most successfully toughened by dispersing rubber particles as a distinct phase of microscopic particles in the epoxy matrix [4]. This can be achieved by two ways: 1) by blending with low molecular weight functionalized liquid rubbers, having restricted solubility and limited compatibility with epoxy hardener mixture and undergo phase separation at a certain stage of curing reaction leading to a two phase microstructure, 2) by directly dispersing preformed rubbery particles in the epoxy matrix. Rubber toughened epoxies were reported by McGarry and Willner in using low molecular weight carboxyl terminated copolymer of butadiene and acrylonitrile (CTBN) [5]. They modified different grades of diglycidyl ether of bisphenol-A (DGEBA) epoxies with CTBN and cured with piperidine to get a network having two-phase microstructure and reported a ten-fold increase in fracture toughness. Approximately 5–20% of low molecular weight reactive liquid rubbers like CTBN dispersed in the hot epoxy resin can lead to a multiphase toughened epoxy system on curing [5, 6]. To optimize toughening, parameters such as modifier structure, molecular weight, solubility and rubber concentration must be clearly defined. These parameters are responsible for the dynamics of multiphase morphology [5, 6]. Following this pivotal work extensive research has been done for the past two and a half decades to understand the principle of morphology development, morphology and fracture property relationship and the mechanism of toughening [7, 8].

Nowadays various functionalized synthetic rubbers have been synthesized and investigated as a replacement of CTBN rubber [9–13]. M.J. Abad et al. modified epoxy resin with several amounts of acrylonitrile–butadiene–styrene (ABS) in order to improve the toughness of the resin. Shinn-Gwo Hong and Chau-Kai Chan studied the effects of epoxidized natural rubber (ENR) on the curing behaviors and adhesive strengths of an epoxy (diglycidyl ether of bisphenol-A) and dicyandiamide and 2-methyl imidazole system. They concluded that the lap shear strengths of specimens prepared with etched aluminum substrates increase with increasing the curing temperature because of a better cure at a higher temperature, but decrease with increasing the ENR content resulting from an adverse effect of ENR on the mechanical properties of the cured resins. Dae Su Kim et al. synthesized DGEBA–ATBN (amine terminated butadiene acrylonitrile

copolymer) blends and investigated the real-time phase separation behavior of ATBN-added epoxy system during cure using laser light scattering. D. Ratna and A. K. Banthia used carboxyl-terminated poly(2-ethyl hexyl acrylate) (CTPEHA) liquid rubber to modify epoxy resin. The modified epoxy networks were evaluated with respect to their thermal and impact properties. T.V. T. Velan and I. M. Bilal used hydroxyl-terminated PDMS and DGEBA to synthesize polydimethylsiloxane (PDMS)-diglycerol ether of bisphenol-A (DGEBA) interpenetrating network and found that the synthesized polymer showed better electrical and thermal characteristics with high impact resistance compared to the virgin epoxy system.

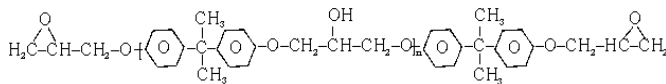
In the present work, DGEBA type epoxy resin has been modified with liquid polysulfide rubber, because polysulfide is compatible with epoxy resin. The polysulfide of low molecular weight of general –SH terminal, (R-SH) reacts with the epoxy groups to cause chain extension but not crosslinking and it becomes an integral part of three-dimensional networks [14] and therefore, do not migrate during subsequent ageing/ storage and also impart flexibility of high order [15, 16]. Optimal performance and properties are obtained by crosslinking the epoxy resin to a three-dimensional insoluble and infusible network by reacting it with curing agents, such as amines, carboxylic acids anhydrides and thermally latent catalysts. Epoxy resins cured by anhydrides usually have better properties than resins cured by amines. Anhydride cured epoxy resins are less poisonous, display a higher glass transition temperature, and absorb less water, lower reaction exothermic, as well as their reaction shrinkage. The anhydride cured resins are preferred for electrical and electronic applications due to their higher thermal stability and transparency [16, 18]. The present work attempts to discuss the role of polysulfide rubber as a modifier for the DGEBA type epoxy resin with reference to the thermal properties, water absorption, volume resistivity, chemical resistance and morphological observations of the cured blends. Furthermore, the effect of thiol terminated liquid polysulfide modifier on the thermal properties and chemical resistance has been analyzed using Thermogravimetric Analyzer, water absorption, volume resistivity and chemical resistance. Morphology of blends was studied by Scanning Electron Microscopy (SEM). Till nowadays, only few reports [19–22] are available regarding the studies of the polysulfide rubber (thiol terminated and epoxy terminated) modified epoxies through mechanical, morphological and thermal studies. In this paper, Thermogravimetric analysis, Water absorption, Volume resistivity and Chemical resistance have been used to understand the thermal properties, volume resistivity and chemical resistance of the cured Epoxy/polysulfide blends.

## Experimental

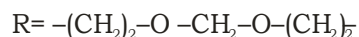
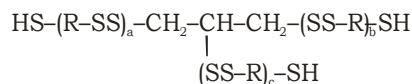
### Materials

The epoxy resins used in this study were diglycidyl ether bisphenol-A (DGEBA), PG-100, (weight per epoxide 185 g) supplied by M/S Parikh Resins and Polymers Ltd, Kanpur, India. Polysulfide (G-4) –SH content 5–7%,

viscosity (1300 mPa·s at 25°C, av. mol. weight g/mol  $\leq 1000$ , crosslinking agent 2% supplied by Thioplast Chemicals, Gmbh, Co. Phthalic anhydride with molecular formula-  $C_8H_4O_3$ , molecular weight- 148.2 and melting point (mp) 130°C of reagent grade from Sigma-Aldrich was used as received. Silicon Grease was used as a mold release agent, which is effective in a temperature range from 46 to 260°C. The structures of raw materials used in this study are given below:

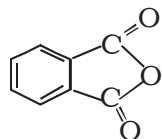


Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin.



$$a+b+c=n < 7$$

Thiol terminated liquid Polysulfide rubber (G4)



Phthalic anhydride

### Blend preparation

Epoxy resin was taken in a three-neck round bottom flask and polysulfide was added in it, the flask was fitted with stirrer and temperature controller. Mixture was stirred continuously for one hour at 90°C after creating vacuum in the flask. After preparation of homogenous transparent blend the stoichiometric amount of curing agent i.e. phthalic anhydride was added in the flask at  $100 \pm 10^\circ\text{C}$  and stirred till complete dissolution of hardener. The mixture was cast immediately in preheated steel-TEFLON mold using high vacuum silicon grease as release agent and was cured at 130°C for 5 h.

A number of blend formulations made by diglycidyl ether of bisphenol-A (epoxy), liquid polysulfide (10-50 Phr.) and curing agent are given in **Table 1**. These blends were characterized by FT-IR, TGA, Water absorption, volume resistivity, SEM and chemical resistance.

**Table 1.** Synthesized polysulfide modified epoxy blends and their ratios.

Sample code	DGEBA: Polysulfide: Phthalic anhydride ratio	Amount of DGEBA (g)	Amount of polysulfide (g)	Amount of Phthalic anhydride (g)
A1	100:10:70	50	5	35
A2	100:20:70	50	10	35
A3	100:30:70	50	15	35
A4	100:40:70	50	20	35
A5	100:50:70	50	25	35

### Characterization

Fourier transform infra red spectroscopy: Pekin-Elmer FT-IR Spectrophotometer was used to scan the IR spectra of epoxy/ liquid polysulfide (A2), by using resolution  $4 \text{ cm}^{-1}$  and the spectra was recorded in wave range  $500 - 4000 \text{ cm}^{-1}$ .

Thermogravimetric analysis: Thermogravimetric analyzer of Perkin Elmer's (Pyris Diamond) was used to study the thermal degradation pattern and thermal stabilities of the cured epoxy specimens at a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen atmosphere. Thermogravimetric analysis is also used as a fast and exact method for determination of the kinetics of thermal degradation of polymers. The activation energy and order of reaction (n) were evaluated by using integral equation of Coats and Redfern [23].

$$\log_{10} \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log_{10} \frac{ZR}{\beta E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.3RT}$$

where, 'T' is the absolute temperature in Kelvin, 'E<sub>a</sub>' is the activation energy, 'R' is gas constant, 'n' is the order of reaction, 'Z' is pre-exponential factor, 'β' is heating rate.

For all values of n except n = 1; for the situation where n = 1, this equation becomes:

$$\log_{10} \left[ \frac{-\log_{10}(1-\alpha)}{T^2} \right] = \log_{10} \frac{ZR}{\beta E_a} \left[ 1 - \frac{2RT}{E_a} \right] - \frac{E_a}{2.3RT}$$

Thus, a plot of either

$$\log_{10} \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] \text{ against } 1/T \text{ (n = 0, 1/2, 2/3, 2.)}$$

or

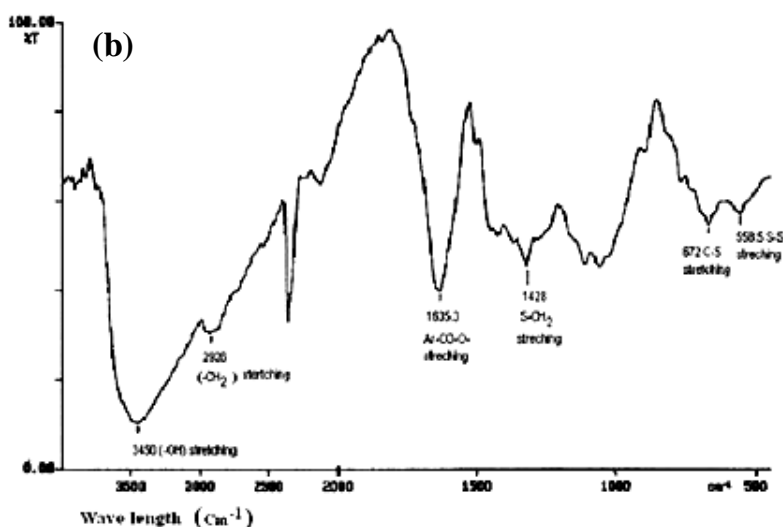
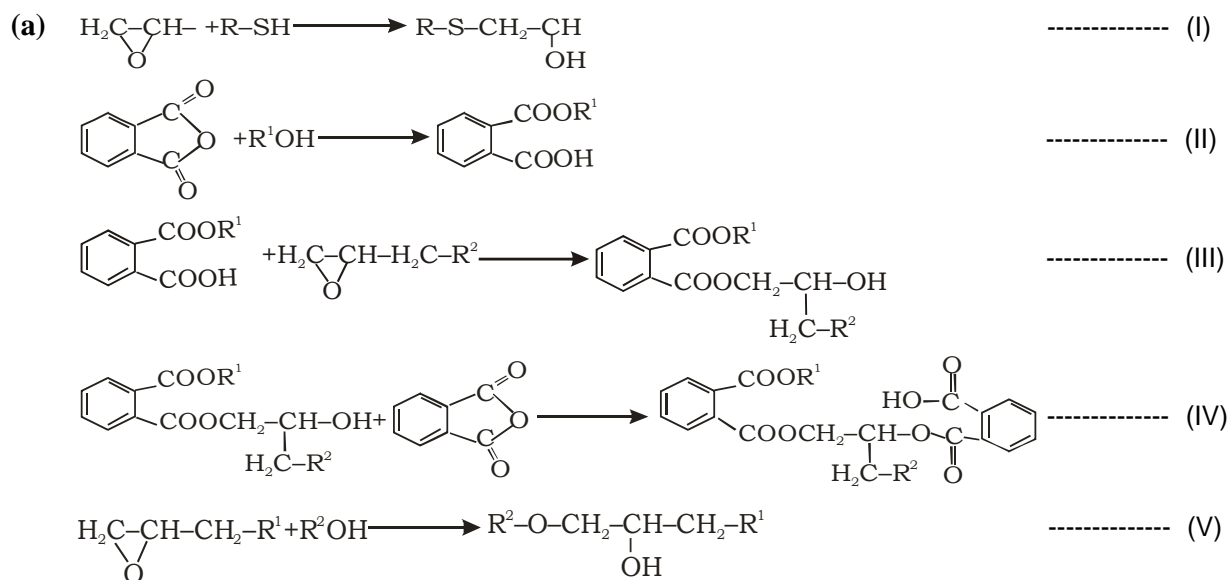
$$\log_{10} \left[ \frac{-\log_{10}(1-\alpha)}{T^2} \right] \text{ against } 1/T \text{ (n = 1)}$$

By using computational technique, the best fit value of "n" for all epoxy/polysulfide blends were calculated in the range of 0-2. Each graph resulted in a straight trend line of slope - (E<sub>a</sub>/2.3R) and the activation energy was calculated from the value of slope of the plot.

### Water absorption

Water absorption was determined by placing the disc samples in distilled water for 8 days at room temperature. The difference between final weight and initial weight was used to calculate the water absorption with the following equation:

$$\text{Water absorption (\%)} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100$$



**Fig. 1.** (a) Proposed mechanism of blend formation and curing and (b) FT-IR spectra of DGEBA/polysulfide/phthalic anhydride blend A2 (100:20:70).

### Volume resistivity

The volume resistivity of blends was measured according to ASTM D-257 on electrometer model SM 8220 (TOA Electronics Ltd. 29-10, Tokyo, Japan) at room temperature of  $25 \pm 2^\circ\text{C}$ .

### Chemical resistance

Acids such as sulphuric acid, hydrochloric acid and acetic acid; bases such as ammonium hydroxide, sodium hydroxide, and potassium hydroxide; and solvents such as distilled water, seawater (synthetic), acetone, methyl ethyl ketone, xylene, and ethanol were taken to determine the chemical resistance of synthesized blends films. The panels were observed for a visible change in the condition of the films at a regular interval, when immersed in these chemicals at room temperature ( $25 \pm 2^\circ\text{C}$ ) for a period of six months.

## Results and discussion

### FT-IR spectroscopy and proposed mechanism

The proposed mechanism of blend formation and FT-IR spectra of blend is given in scheme (**Fig. 1a** and **b**). Thiol group (-SH group) of polysulfide reacts with epoxide group of Diglycidyl ether of bisphenol-A type epoxy resin [24] to give S-CH<sub>2</sub> linkage and -OH groups as given in **reaction-I**. Reaction of epoxy group with mercapton (-SH group) of polysulfide flexibilizer is not as vigorous as with an amine/amide and anhydride group of polyamine/polyamide and aromatic anhydride groups [17, 24, 25].

In contrast to amine curing agents, anhydride reactions with epoxy are usually characterized by a low exothermal reaction, low shrinkage, low internal stresses, reduced water absorption, high glass transition temperatures and



excellent electrical properties. On the other hand most anhydride-epoxy curing reactions are less reactive and relatively high reaction temperature ( $>120^{\circ}\text{C}$ ) are required to initiate and propagate the curing reactions [26].

The epoxy group is characterized by its reactivity towards nucleophilic and electrophilic species and thus it is reactive to a wide range of reagents. The formation of polyester from the unanalyzed reactions of epoxy monomers and cyclic carboxylic acid anhydrides has been intensively studied during the last years.[27] The research resulted in a generally accepted stepwise mechanism that occurs during the non-catalyzed polymerization [28-31] as schematically shown in Fig. 1a. The mechanism involves the presence of hydroxyl groups, which act as an initiator for the reaction. The hydroxyl groups are mostly present as substituents on a fraction of the epoxy resin molecules forms a monoester having a free carboxyl group (**reaction-II**). The monoester then reacts with the epoxide to yield a diester and a new secondary hydroxyl group (**reaction -III**), thus starting the cascade of curing reactions (**reaction-IV**). The evidence that quantities of mono and diester produced are equal to the amount of consumed anhydride confirmed these reaction sequences. Moreover, the fact that no significant difference in the consumption of epoxy and anhydride group [32] has been observed at least up to gelation supports the proposed reaction scheme. The observation that the number of epoxy groups at higher conversions decreases faster than increases in the diester groups can be attributed to the etherification reaction. This reaction occurs between epoxy and hydroxyl groups under the catalytic influence of anhydride or carbonyl groups (**reaction-V**), and constitutes a significant side reaction.

FT-IR spectra of phthalic anhydride cured epoxy/polysulfide blend (A2) is given in Fig. 1b. The absorption bands at  $672\text{ cm}^{-1}$  and  $558.5\text{ cm}^{-1}$  can be ascribed to C-S group and S-S group of polysulfide rubber. The absorption peak at  $1428\text{ cm}^{-1}$  is due to formation of  $-\text{S}-\text{CH}_2$  linkage between  $-\text{SH}$  group of polysulfide and epoxide group of DGEBA (**Scheme 1a, reaction -I**). On the other hand, the broad absorption peak at  $3450\text{ cm}^{-1}$  might indicated the  $-\text{OH}$  group formed due to reaction between (**reaction-V**)  $-\text{SH}$  group of polysulfide and epoxide group of DGEBA (**reaction -I**) and side reaction . Another peak at  $1635.3\text{ cm}^{-1}$  represents the  $\text{Ar}-\text{CO}-\text{O}-$  group as a result of crosslinking between anhydride group of curing agent and epoxide group of DGEBA (**reaction -II to IV**). Thus FT-IR spectra support the proposed mechanism of blend formation and curing.

#### Thermogravimetric analysis

Anderson [33] suggested that TGA provides more reliable and quantitative estimation of relative thermal stabilities of materials. Thermogravimetric analysis (TGA) is a technique to determine the weight loss of a sample, while heating it at programmed heating rate. In the dynamic mode the weight loss or rate of weight loss is measured as a function of programmed rate of increase in temperature.

Thermogram of blends provides the information related to the degradation behaviour of the material. Onset temperature or the temperature of inception or reaction-corresponds to the first detectable temperature at which the degradation of material starts. Maximum decomposition temperature or inflection temperature-corresponds to the temperature at which the maximum weight loss is observed. Final decomposition temperature or temperature of the completion of decomposition reaction or end temperature corresponds to the temperature after which no weight loss or minor weight loss is observed.

The onset temperature generally represents the stability of the material. The initial degradation temperature is to be considered at 1% weight loss of DGEBA/ polysulfide blend.

Thermal stability of epoxy/polysulfide system is of great importance and is dependent in part on chemical structure and bond as well as the crosslink density of the system. Nieman et al., [34] were perhaps the first to attempt to relate the stability of epoxy resins to chemical structure.

On examining the thermograms (**Fig. 2**), it is observed that one step reaction mechanism is operative during the degradation of various DGEBA/polysulfide blends. It is apparent that the shape of thermograms is not linear throughout the degradation reaction in all cases. In initial stage (1-5% wt. loss), the rate of weight loss was comparatively very slow from initial degradation temperature of  $283, 278, 257, 255, 242^{\circ}\text{C}$  to temperature at 5% weight loss  $307, 269, 276, 274$  and  $264^{\circ}\text{C}$  for blends A1, A2, A3, A4 and A5 respectively. Rate of weight loss (5-85%) was significant at higher temperatures, whereas later on after weight loss (85.1%), the rate of weight loss was again very slow up to final degradation temperature of  $450, 440, 435, 428$  and  $425^{\circ}\text{C}$  for blends A1, A2, A3, A4 and A5 respectively. Initial degradation temperature ( $T_i$ ), maximum degradation temperature ( $T_m$ ), final degradation temperature ( $T_f$ ) and char yield at  $500^{\circ}\text{C}$  is shown in **Table 2**. It is clear from the **Table 2** that, in initial stage of polymer decomposition, the extent of crosslinking is greater than the extent of bond rupture. However at middle stage of decomposition, the trend is reversed, and decomposition rate is high and the last stage of decomposition similar trend was found like initial stage. Comparison of data for various blends with increasing 10–50 wt.% polysulfide content showed decrease in thermal stability. This may be due to the increase in the relative amount of dissolved rubber as rubber content increased, because of high susceptibility of the aliphatic chains of the rubber network in the molecular backbone for thermal degradation [35]. The char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the resin in accordance with Van Krevelen and Hoftyzer equation [36].

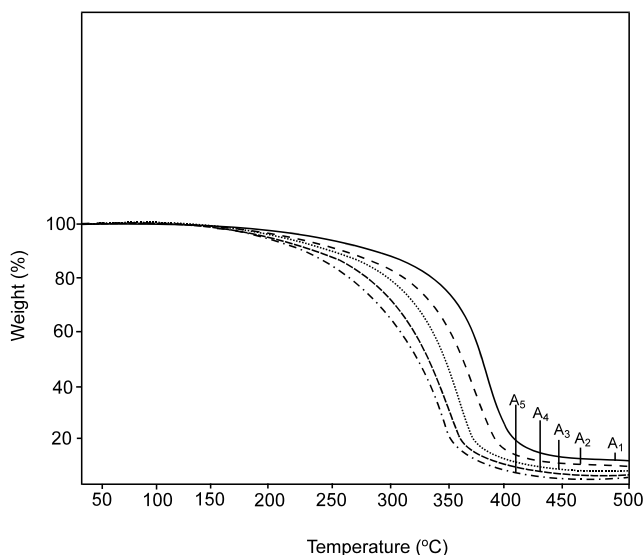
$$\text{LOI} = 17.5 + 0.4Y_c$$

Where  $Y_c$  = char yield

LIO values of different blends calculated on their char yield are shown in **Table 2**.

**Table 2.** Decomposition behavior, LOI and activation energy of various phthalic anhydride cured polysulfide modified blends at a heating rate of  $10^{\circ}\text{C min}^{-1}$ .

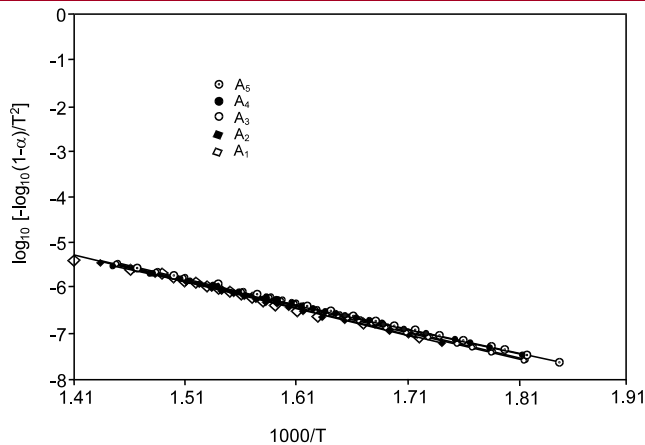
Sample code	Ti	Tm	Tf	Percent char yield at 500°C	LOI (%)	Activation energy, Ea (kJ/mole)
A1	283	380	450	11.12	21.948	114.35
A2	278	375	440	10.54	21.716	108.04
A3	257	369	435	9.37	21.248	89.49
A4	255	366	428	8.54	20.916	80.86
A5	242	361	425	7.23	20.392	73.04



**Fig. 2.** TGA scan of polysulfide modified epoxy blends: A1, A2, A3, A4 and A5.

#### Degradation kinetics of epoxy/polysulfide/phthalic anhydride blends

TGA is also used to study the thermal degradation kinetics of polymers. The statistical analysis of degradation behavior was studied by integral method of Coats and Redfern equation, done by linear regression, provided by the best fit value of  $n$ , where  $n$  was taken as 0, 0.5, 0.67, 1, and 2. The degradation kinetics was analyzed by using the above order of reaction for different blends in the range of 5 to 85 % weight loss of thermograms. The results revealed that degradation follows first order of reaction ( $n = 1$ ) with correlation coefficient values of 0.9887, 0.9877, 0.9895, 0.9929 and 0.9912, for the blends A1, A2, A3, A4 and A5. From the value of correlation coefficients, close to unity indicate the best fit. The graphs are plotted between the  $\log_{10} [1-(1-\alpha) / T^2 (1-n)]$  and  $1000/T$  obtained from the data have been shown in **Fig. 3**. From the slope of plots and its intercept value, the activation energy ( $E_a$ ) were calculated and summarized in **Table 2**. When the polysulfide content increases from 10 to 50 phr in DGEBA/polysulfide blends (A1, A2, A3, A4 and A5), the activation energy decreases from 114.35 to 73.04 kJ/mole due to the increase in the relative amount of dissolved rubber as rubber content increased.



**Fig. 3.** Plot for calculation of activation energy of polysulfide modified blends: A1, A2, A3, A4 and A5 by Coats and Redfern method.

#### Water absorption

The data for percentage water absorption for samples (A1 to A5) are listed in **Table 3**. The result indicated that as the percentage of polysulfide increased in, the water absorption tendency increased. The water absorption was increased from 0.071 to 1.14% as the polysulfide content increased from 10 to 50 wt%. This could have been due to formation of H-bonding by  $-\text{OH}$  groups produced as a result of interaction between epoxide groups of DGEBA and  $-\text{SH}$  groups of polysulfide. Presence of broad peak of  $-\text{OH}$  group is also observed in FTIR spectra (**Fig. 1b**) of blend.

**Table 3.** Water absorption study of polysulfide modified epoxy blends.

Sample Code	Initial weight (g)	Final weight (g)	% Water absorption (after one week)
A1	1.408	1.409	0.071
A2	0.685	0.0686	0.145
A3	1.731	1.735	0.231
A4	1.329	1.341	0.902
A5	0.435	0.440	1.149

#### Volume resistivity

The volume resistivity of blends (A1 to A5) is shown in **Table 4**. It is clear from the table-4 that volume resistivity of blends decrease from  $5.34 \times 10^{15}$  to  $3.83 \times 10^{11}$  with increase in polysulfide content from 10 to 50 wt.% in synthesized blends. This decrease in volume resistivity is due to decrease in crosslink density of blends with increase in polysulfide content, because polysulfide causes chain extension of epoxy.

#### Chemical resistance

The chemical resistance of a polymeric material is its ability to withstand chemical attack with minimal change in appearance, dimensions, mechanical properties, and weight over a period of time. Test conditions include the length of exposure, concentration, temperature and internal stress. Polymer can absorb, react chemically, become plasticized,

dissolve, or be stress cracked by chemical environments. Epoxy resins have good chemical resistance that partially depends on the curing technique; they are used in coatings in the chemical process industry. The good resistance to chemical attack is derived mainly from the aromatic nature of bisphenol-A portion of the molecule and phenolic ether linkage.

**Table 4.** Volume resistivity of polysulfide modified epoxy blends.

Sample code	wt.% Polysulfide content	Volume resistivity (Ohm-cm)
A1	10	$5.34 \times 10^{15}$
A2	20	$8.79 \times 10^{14}$
A3	30	$1.89 \times 10^{12}$
A4	40	$6.21 \times 10^{11}$
A5	50	$3.83 \times 10^{11}$

**Table 5.** Comparative study of acids, alkali and solvent resistance of polysulfide modified epoxy blend films cured at 130°C showing the period of six months.

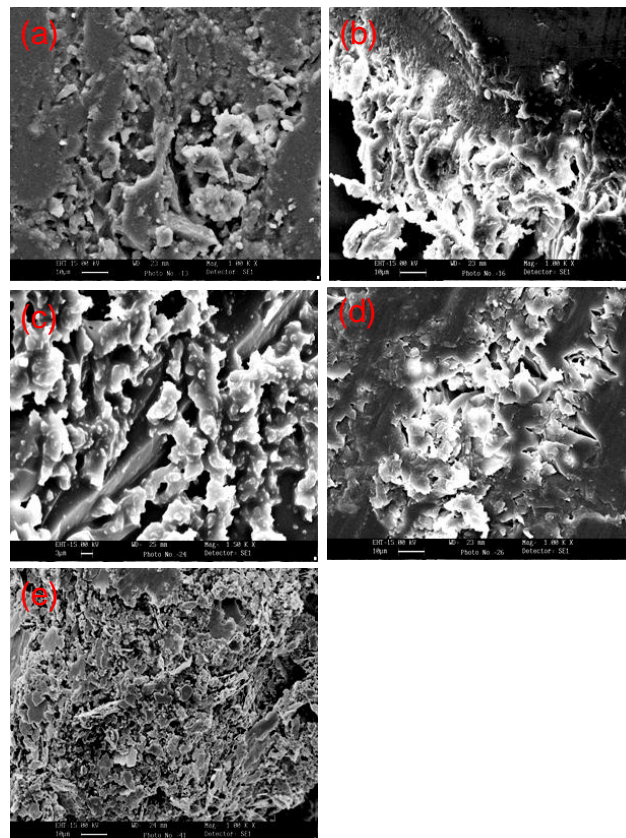
Sl. No.	Reagents	Effect <sup>a</sup> on film in the Period of six months				
		A1	A2	A3	A4	A5
1	Sulphuric acid (10%)	5	5	5	4	4
2	Hydrochloric acid (10%)	5	5	5	4	4
3	Acetic acid (10%)	5	5	5	4	4
4	Sodium hydroxide (10%)	5	5	4	3	3
5	Ammonium hydroxide (10%)	5	5	4	3	3
6	Potassium hydroxide (10%)	5	5	4	3	3
7	Distilled water	5	5	5	4	4
8	Sea water	5	5	5	4	4
9	Xylene	4	3	2	1	1
10	Ethanol	3	3	2	1	0
11	MEK	4	3	2	1	0
12	Acetone	4	3	3	2	1

a: 5 = Film unaffected; 4 = Change in colour and loss in glass; 3 = Blistering of film; 2 = Softening of film; 1 = Partial removal of film from the panel; 0 = complete removal of film from the panel.

**Table 5** shows the comparative acids and alkalis resistance of cured films of DGEBA/polysulfide blends with different weight ratio of polysulfide. A quick perusal of **Table 5** clearly illustrated that the films prepared from A1 and A2 blend ratios have offered maximum resistance

towards different concentrations of acids and alkalis as compared to the films of other blends.

This behaviour might be attributed due to greater reactivity resulting in a more complex structure to provide these resistances as compared to other compositions. The cured films of all blend samples were completely unaffected by 10% sulphuric acid solution for the entire period of exposure of 6 months. The films when exposed to 30% sulphuric acid and hydrochloric acid solutions were found to be resistant for 5 months, whereas in other solutions, they were resistant for less than 4 months. The films of blend samples containing 10 and 20 wt % polysulfide showed better resistance towards all acid solutions as compared to the blend samples containing 30, 40 and 50 wt% polysulfide were found to be resistance. The lower concentration of alkali solution less affected the film surface than higher alkali solutions. This behaviour might be attributed to the fact that the formation of more crosslink structure [40] by the addition of epoxy resin.



**Fig. 4.** Scanning Electron Micrographs of polysulfide modified blends: (a) A1, (b) A2, (c) A3, (d) A4 and (e) A5.

#### Scanning electron microscopy

SEM of the fractured surface of the liquid polysulfide modified epoxy matrix containing polysulfide ranging between 10 to 50 phr with interval of 10 phr are shown in **Fig. 4 (a-e)**. SEM of blends A1 to A5 showed that at higher rubber content, however, the matrix might be less restricted by the presence of rubber globules with sizes increased by rubber particles coalescence, cavitations and homogeneity of the system [37]. This could be very well seen in SEM



micrographs (Fig. 4). The SEM micrograph of polysulfide modified blends (A1 to A5) showed the presence of precipitated, discrete rubber particles which were dispersed throughout the epoxy matrix, i.e., they revealed the presence of two-phase morphology feature. The soft elastomeric phase was phase separated from the hard epoxy matrix during early stage of cure. The size of the precipitated rubber particles increased with increasing rubber content in the formulation. The size of rubber particles, in the epoxy matrix, was larger in sample A3, A4 and A5 than that observed in the blend sample A1 and A2. This increase in the size of the dispersed rubber phase might be associated with the reagglomeration or coalescence of the dispersed rubber particles [38, 39]. It can be seen that with rubber levels higher than optimum (A3 to A5), the second rubbery phase got more and more aggregated leading to that phase being less distinguishable from the epoxy matrix. This situation led to flexibilization of the matrix resulting in the reduction of thermal properties, chemical resistance and water absorption behaviour.

## Conclusion

In the present investigation, DGEBA was modified with -SH terminated liquid polysulfide using phthalic anhydride curing. TGA studied of cured system showed decrease in thermal stability with increase in polysulfide content. Chemical resistance study showed decrease in chemical resistance of blends with increase in polysulfide content. Morphology study of system revealed a two-phase region where the liquid rubber particles are distributed in epoxy matrix. On the basis of present investigation we conclude that incorporation of elastomer of about 10-20 phr polysulfide rubber into the epoxy resin showed better thermal properties and chemical resistance. A further increase in the concentration of elastomer led to phase inversion. Thermal stability, activation energy, limiting oxygen index, and chemical resistance showed reduction, where as water absorption increased with higher concentration of polysulfide.

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