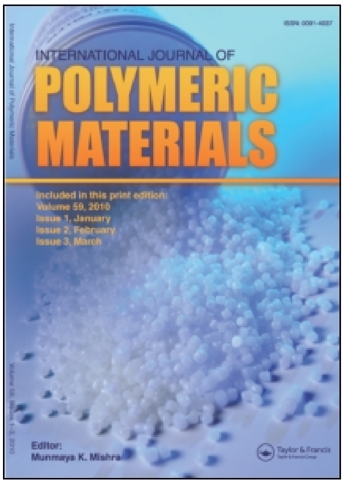

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Composites of Poly(Keto-Sulfide)-Epoxy Resin Systems and Their Thermal and Mechanical Properties

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Composites of Poly(Keto-Sulfide)–Epoxy Resin Systems and Their Thermal and Mechanical Properties

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A novel matrix resin system, poly(keto-sulfide)–epoxy resin, has been developed. The poly(keto-sulfide)s (PKS), based on various ketones, formaldehyde, and sodium hydrogen sulfide (NaSH), were prepared by the reported process. These (PKS) having terminal thiol (–SH) groups were used for curing commercial epoxy resin (i.e., diglycidyl ether of bisphenol A – DGEBA), to fabricate crosslinked epoxy-poly(keto-sulfide) resin glass fiber-reinforced composites (GRC). Various epoxy/hardener (PKS) mixing ratios were used, and the curing of epoxy-PKS has been monitored using differential scanning calorimetry (DSC) in dynamic mode. Based on DSC parameters the GRC of epoxy-PKS were prepared and characterized by thermal and mechanical methods. The variation in resin/hardener ratio led to variations in thermal and mechanical properties.

Keywords differential scanning calorimetry, epoxy resin, glass fiber-reinforced composites, mechanical properties, poly(keto-sulfide)s, thermogravimetric analysis, thiol

INTRODUCTION

Only one instant has been reported for poly(keto-sulfide)s (PKS) by Russian scientists [1]. In extension of that work [1], one of the present authors (HSP) have studied the (PKS) resins systematically [2–4]. Having resinous properties and active hydrogen in mercaptan group (–SH), it may interact with epoxy resins diglycidyl ether of bisphenol A (DGEBA). Hence, it was thought

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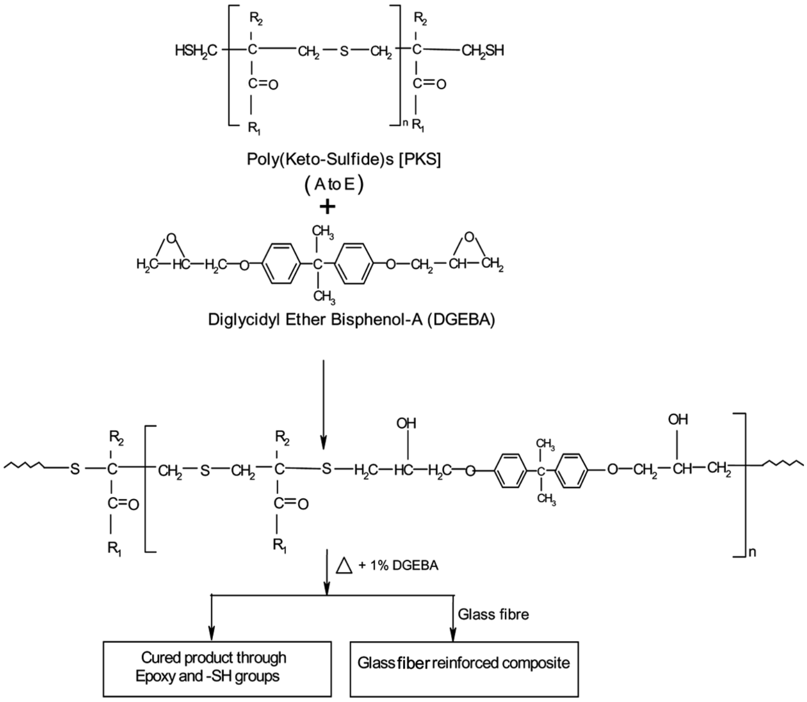
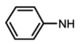
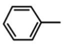
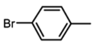
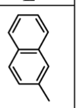
interesting to study a DGEBA-PKS curing system. The large spectrum of properties available with epoxy thermosets coupled with their formulating and processing versatility have made epoxy resins useful in several applications, such as adhesives and coating [5,6], corrosion protectants [7,8], electronic encapsulants, [9,10], fiber optic-sheathing [11], building construction, aerospace industries, sport applications, laminates and composites [12–14].

In order to fulfill a demand for high – performance epoxy resin, novel curing agents are still being sought. Various curing agents can be used to cure epoxy resins. The curing reaction of the thermosetting polymers originate infusible, three-dimensional networks after chemical reaction of the epoxy resin and the chosen hardener, which lead to coupling as well as crosslinking. The active hydrogen catalysts are polyamins [15], polyamides [16], polyureas [17], polyurethanes [18], polyisocyanates [19], imadozole [20], aminoamides [21], polyphenoles [22],

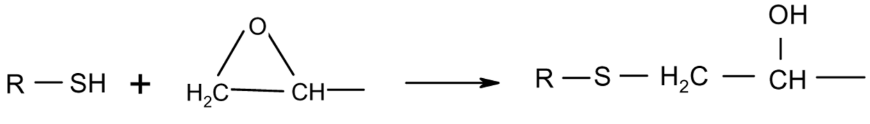


where:

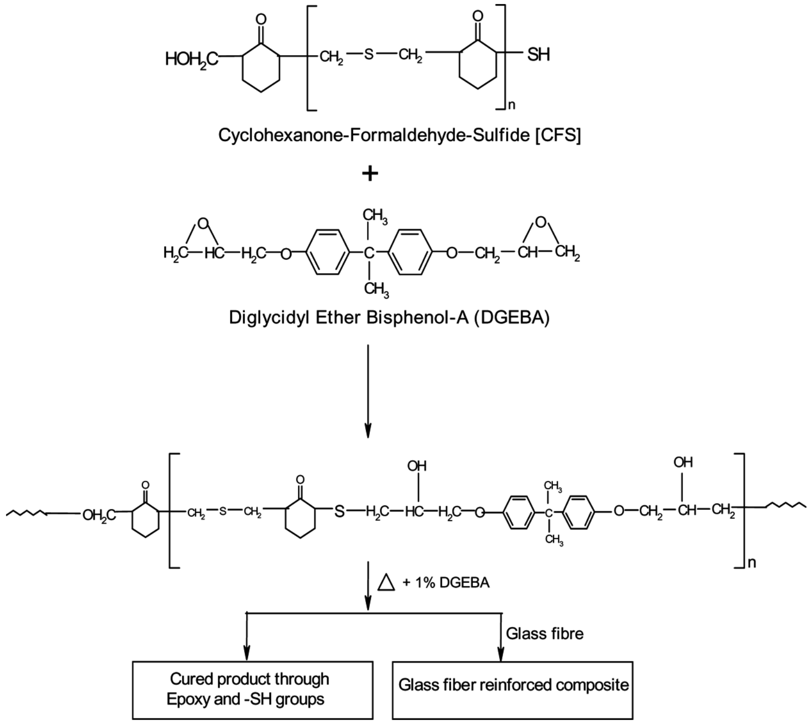
Group	A	B	C	D	E
R_1			$-CH_3$		
R_2	$-CH_3$	$-H$	$-H$	$-H$	$-H$

Scheme 1: Poly(keto-sulfide)-epoxy thermosets.

polycarboxylic acids [23], acid anhydrides [24], silanes [25], and esters [22], thiols and polymercaptans [26–30]. Excellent reviews of curing epoxide system with mercaptans have been published by Lee et al. [31], and Zaheer [32], Newey [33] has established that mercaptans react faster than amines and that the addition of mercaptide ion to epoxy group is the rate determining step:



To achieve the desired end properties of this thermosetting material it is essential to control the degree of the cure. The curing behavior and kinetics of epoxy systems can be studied by many different analytical methods such as gel permeation chromatography (GPC) [34], nuclear magnetic resonance (NMR) [35,36] vibrational spectroscopy [36,37]. However, because of the highly exothermic character of the polymerization process of epoxy resins, in which the librated heat can self-accelerate the reaction, the techniques used in the characterization of the curing stage are fundamentally calorimetric.



Scheme 2: Poly (cyclohexanone-formaldehyde-sulfide)-epoxy thermosets.

Differential scanning calorimetry (DSC) has been widely recognized as a useful method to determine cure kinetics of thermoset resins [23,38–42].

In this work we investigated cure kinetics of DGEBA with PKS, and the effect of various loading on the mechanical and thermal behavior is studied. The network forms by polyaddition reaction during which resin and hardener molecules are connected via thiol group and oxirane rings as depicted in Schemes 1 and 2.

EXPERIMENTAL

Materials

All poly(keto-sulfide)s were prepared by the method reported in the literature [1]. Commercial diglycidyl ether bisphenol A (DGEBA) epoxy resin was obtained from Synpole Product Pvt. Ltd., Ahmedabad, India. The specification of the epoxy resin is as follows: epoxy equivalent weight 190–210, viscosity 4–10 p at 25°C, density at 25°C 1.16–1.17 g/cm^3. E-type fiberglass woven fabric of 0.25 mm thickness (Unnati Chemicals, Ahmedabad, India) of areal weight 270 g/m^2 was used for laminate preparation. All other chemicals used were of laboratory grades.

Composite Fabrication

A typical method of composite fabrication is given below:

A suspension mixture of poly(keto-sulfide) – DGEBA epoxy resin in tetrahydrofuran was prepared and stirred well for 10 to 15 min. The suspension mixture was applied with a brush onto a 250 mm × 250 mm fiberglass cloth and the solvent was allowed to evaporate. The 10 dried prepregs prepared by this way were stacked one on top of another and pressed between steel plates coated with a Teflon release sheet and compressed in a flat platen press under about 70 psi pressure. The prepreg stack was cured by heating in the press at 240–250°C for 2 h. The composite so obtained was cooled to 45°C before the pressure was released. Test specimens were made by cutting the composite and machining them to final dimensions. All the chemical, mechanical and electrical tests were conducted according to ASTM or IS methods (as listed below) using three test specimens for each test.

MEASUREMENTS

Differential Scanning Calorimetry

The prepared poly(keto-sulfides)s were used as a hardener to cure DGEBA epoxy resin. The resin and the hardener were mixed using weight ratio of

DGEBA: PKS 40:60, 30:70, 20:80, 10:90. T. A. Instrument DSC 2920 differential scanning calorimeter was used to measure the heat flow under dynamic conditions, at a heating rate of 10°C/min. The calorimeter was previously calibrated according to ASTM D 3417 for temperature calibration and Joule effect for power calibration. The reference used was a sealed empty pan. The mass of the sample was about 3.0–4.6 mg.

Chemical Resistance

The chemical resistance of the composite was measured according to ASTM D543. The sample size was approximately 20 mm × 20 mm.

Thermogravimetric Analysis

The thermogravimetric (TG) analysis of DGEBA: PKS systems I-VI were carried out on Perkin – Elmer Pyres 1 TGA. For this, the samples were prepared by mixing the DGEBA: PKS of given ratio in a glass crucible and heated at the DSC cure temperature for 15–20 min. The material was then crushed by pestel pressure and 4–8 mg of the cured resin were used. The samples were heated at a rate of 10°C/min in air atmosphere.

Mechanical Properties

All the mechanical properties were measured on three individual specimens and average results have been recorded.

Compression Strength Test

The compression strength was measured according to ASTM D 3410. The sample size was 12.5 mm × 12.5 mm × 12.5 mm and the cross head speed was 0.5 – 1.0 mm/min.

Impact Strength Test

Izod impact strength of notched samples was measured on a pendulum impact testing machine at room temperature following the method of ASTM D 256 with a notch angle of 45°.

Hardness Test

The Rockwell hardness strength was measured according to ASTM D785. The sample size was 25 mm × 25 mm. A hardness TSE machine was used.

RESULTS AND DISCUSSION

Commercial DGEBA epoxy resin was cured by using aromatic, aliphatic and cyclic poly(keto-sulfide)s (PKS). The curing process of epoxy-PKS systems has been studied by differential scanning calorimetry. The structure of the cured epoxy resin depends on cure specifics, the kinetics of the reaction, the steric and diffusive restrictions of the reactants during cure, and the functionality of epoxide curing agent [33,43,44].

The kinetic data were obtained from DSC thermograms Figures 1–2 of the I-VI epoxy: poly(keto-sulfide)s systems at 10°C/min heating rate. The curing reactions for various ratios of epoxy: poly(keto-sulfide)s systems were found to be different in respect of total heat of reaction and the temperature at which the reactions were initiated, peaked and terminated. From the characteristic DSC scans, the temperature at which the curing reaction started (T_i), attained a maximum (T_p) and completed (T_f), values of total exothermic heat of curing ΔH and the activation energy (kj/mol) are shown in Table 1.

Arrhenius plots Figures 3–8 for all the systems are linear, hence it is reasonable to assume that any change in the curing mechanism with curing temperature does not affect the overall reaction rate. It was observed that the curing temperature of the different epoxy: PKS systems increases with increasing PKS ratios.

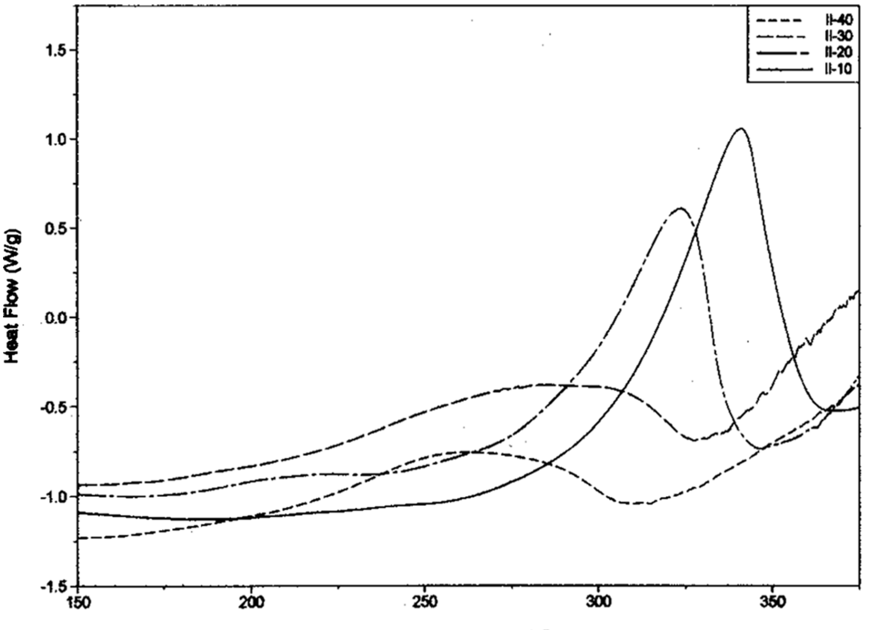


Figure 1: DSC curves for system-II.

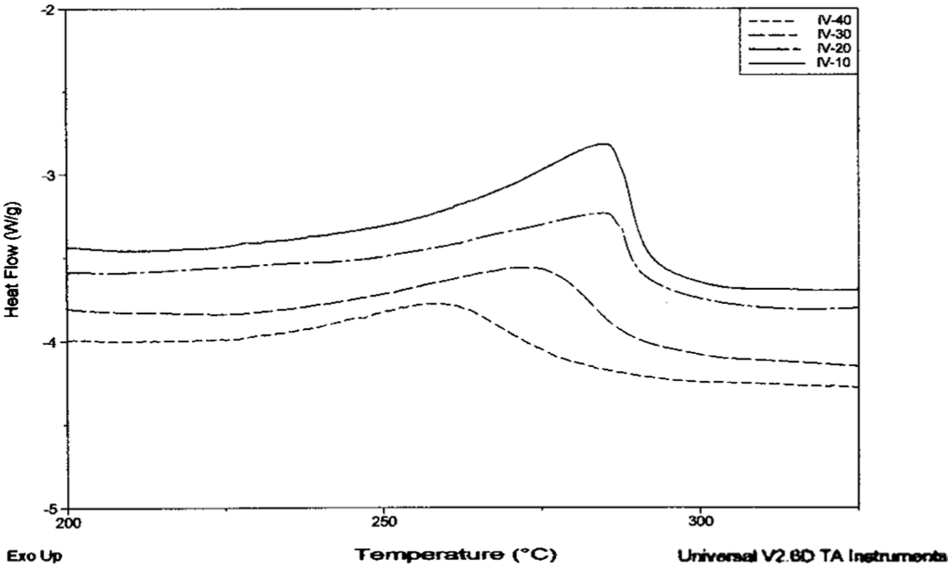


Figure 2: DSC curves for system-IV.

Table 1: Curing characteristics of epoxy-PKS systems I-VI at 10°C/minutes scan rate.

System no.	PHR	T_i °C	T_p °C	T_f °C	ΔH j/g^{-1}	Activation energy kj/mol
I	40:60	214.42	273.03	310.81	44.39	115.8
	30:70	215.07	307.54	320.77	52.72	120.4
	20:80	216.60	321.46	342.98	73.81	150.1
	10:90	223.28	332.18	352.18	105.1	274.3
II	40:60	160.80	258.11	302.66	143.1	88.3
	30:70	170.60	276.52	320.67	174.9	89.8
	20:80	180.1	323.08	345.08	306.8	140.5
	10:90	210.63	340.42	380.7	336.7	191.7
III	40:60	227.33	281.55	324.6	53.22	158.4
	30:70	244.18	304.33	326.13	81.76	159.4
	20:80	244.94	309.58	335.32	85.02	251.1
	10:90	258.73	325.73	351.41	122.4	258.0
IV	40:60	213.54	259.49	293.96	59.5	112.4
	30:70	220.43	274.18	302.39	84.37	139.1
	20:80	224.26	284.84	306.45	105.7	254.8
	10:90	228.86	285.20	313.11	145.4	342.7
V	40:60	260.1	309.47	321.54	49.08	216.8
	30:70	261.03	312.27	323.84	63.68	227.0
	20:80	270.98	323.16	337.62	73.05	271.3
	10:90	282.47	328.76	352.94	75.55	345.7
VI	40:60	280.18	317.45	350.41	76.43	364.4
	30:70	283.77	320.91	355.07	88.92	368.8
	20:80	286.3	326.14	360.88	94.12	372.0
	10:90	289.71	331.31	370.01	99.21	391.4

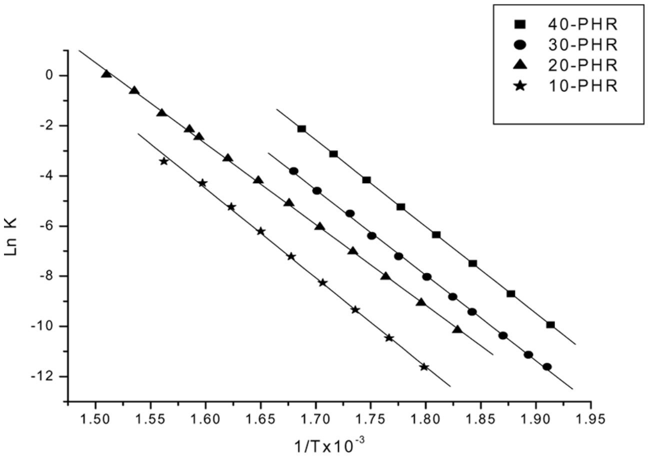


Figure 3: Arrhenius plot for epoxy-cyclohexanone-formaldehyde-sulfide (system-I).

Typical TGA traces are shown in Figures 9–10. The TGA data of all (epoxy-PKS) systems are given in Table 2. The thermal parameters estimated from TGA curves showed that all systems of 10:90 polymer hardener ratio (phr) are more thermally stable than the system of 40:60 phr. This may be attributed to the high degree of crosslinking. This is further confirmed by the DSC data which shows that all the 10:90 phr systems have higher total exothermic heat of curing than those of 40:60 phr. Examination of thermogravemetric data reveals that all the resin samples undergo stepwise degradation. In the first stage, below 200°C, the polymer remains virtually intact. During this stage mainly residual solvent and unreacted monomers which

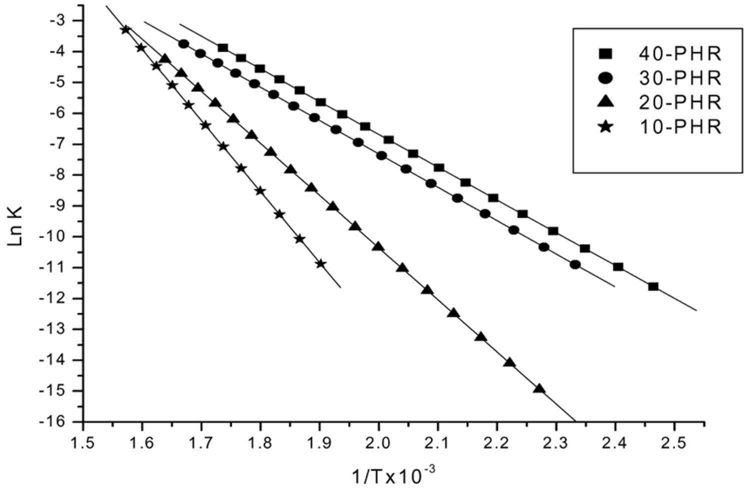


Figure 4: Arrhenius plot for epoxy-acetoacetanalide-formaldehyde-sulfide (system-II).

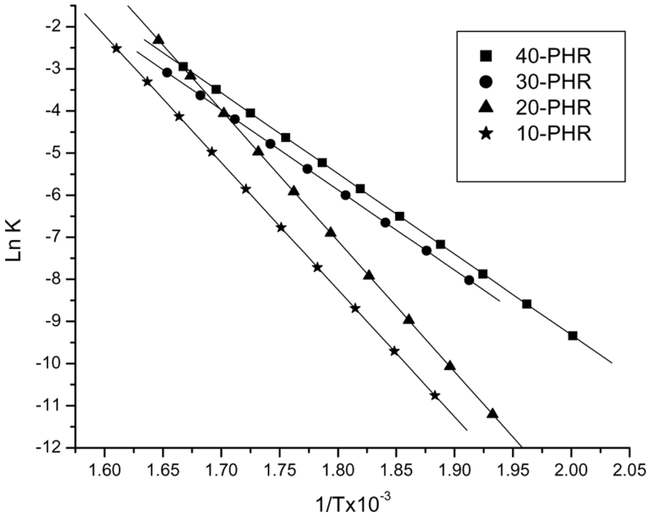


Figure 5: Arrhenius plot for epoxy-acetophenone-formaldehyde-sulfide (system-III).

were trapped during curing are released. All the samples exhibited less than 2.5% and 4% weight loss at 200°C for 10:90 and 40:60 phr, respectively. Decomposition commences at approximately 300°C, and samples degraded completely in the range 300–600°C. A very rapid rate of weight loss was observed around 350–550°C for almost all systems. The polymer samples showed 50% weight loss in the ranges of 547–401°C and 475–356°C for 10:90 and 40:60 phr, respectively. The systems based on aromatic PKS are more stable than those based on cyclic and aliphatic PKS. Comparison of

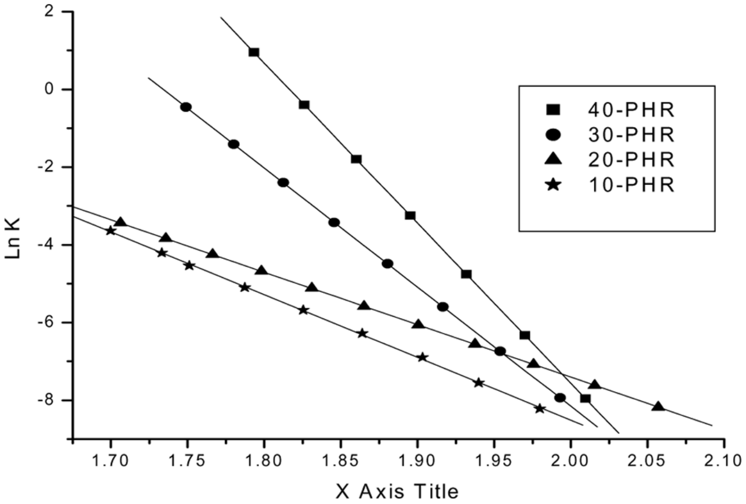


Figure 6: Arrhenius plot for epoxy-acetone-formaldehyde-sulfide (system-IV).

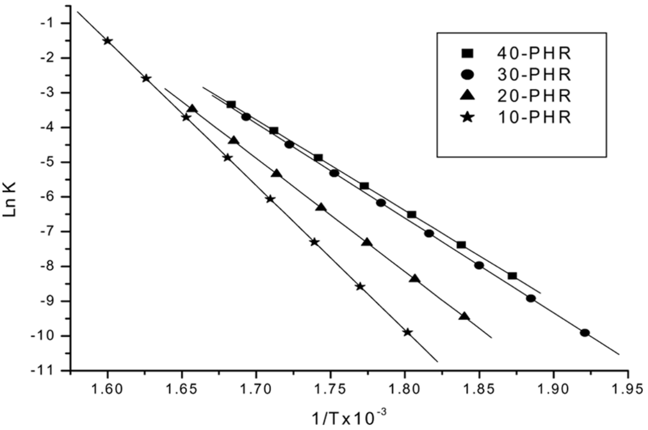


Figure 7: Arrhenius plot for epoxy-p-br-acetophenone-formaldehyde-sulfide (system-V).

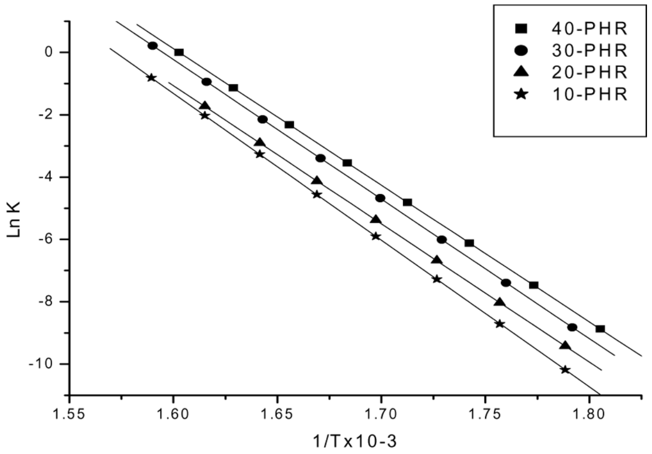


Figure 8: Arrhenius plot for epoxy-(2-acetyl napthone)-formaldehyde-sulfide (system-VI).

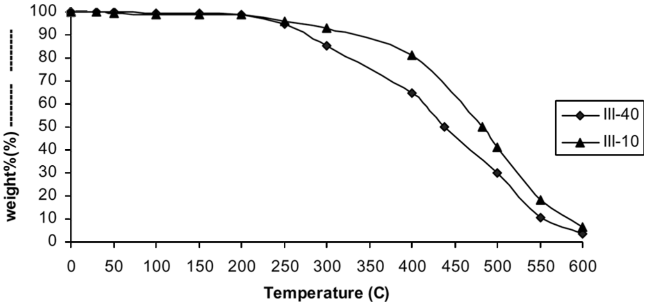


Figure 9: TGA thermogram of system-III.

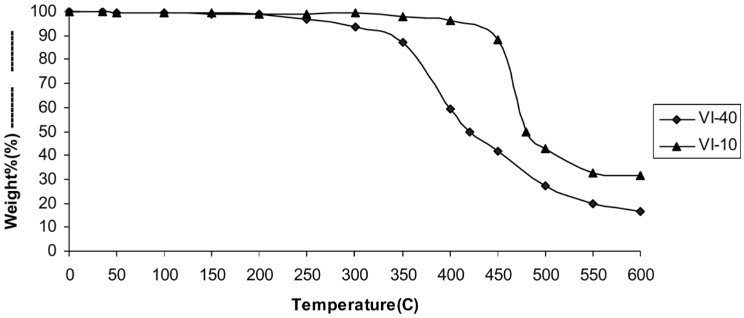


Figure 10: TGA thermogram of system-VI.

the thermal stability of all systems based on 50% weight loss temperature, reveals the following order of stability

$$\mathrm{II} > \mathrm{III} > \mathrm{V} > \mathrm{VI} > \mathrm{I} > \mathrm{IV}$$

All composites were prepared at 240–250°C for 2 hours and were in the form of light to dark brown sheets. The specific gravity of these composites is in the range of 1.60–1.180, Table 3. It looks that there is no appreciable change in the specific gravity with respect of nature of system. The results of chemical resistance of all composites (Table 3) to organic solvents, acids and alkali reveal that the organic solvents and concentrated (15% v\v) acid did not affect the composites which have remarkable resistance to acids. However, the concentrated alkali, causes changes of about (0.8–1.2) % in their thickness and weight (Table 3).

The mechanical properties of all composites are shown in Table 3, and the results reveal that all composites have good mechanical properties. It can be

TABLE 2: Thermogravimetric analysis of epoxy-PKS systems I-VI.

System no.	PHR	% wt. loss at 200°C	% wt. loss at 300°C	% wt. loss at 400°C	% wt. loss at 500°C	50% wt. loss temp. °C
I	40–60	3.1	24.5	69.5	88.5	402
I	10–90	2.1	13.8	39.3	62.4	453
II	40–60	1.6	3.2	10.2	62.2	475
II	10–90	0.5	1.2	3.2	31.4	547
III	40–60	1.2	14.5	35.2	70.0	438
III	10–90	1.0	7.1	18.7	59.1	483
IV	40–60	3.6	25.1	69.5	89.9	356
IV	10–90	2.2	15.6	44.6	77.7	401
V	40–60	1.0	21.6	41.5	66.1	431
V	10–90	0.6	2.4	3.6	55.3	482
VI	40–60	1.3	6.4	32.7	72.4	421
VI	10–90	1.0	1.6	3.5	57.4	480

Table 3: Mechanical and chemical properties of glass-reinforced composites based on epoxy-PKS systems I-VI.

Resin system	Poly(keto-sulfide): epoxy resin ratio	Percentage change on exposure to 25%(W/V) NaOH		Specific gravity	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness
		thickness	weight				
I	40:60	1.1	1.0	1.81	164	170	84
I	10:90	1.0	0.9	1.76	193	189	88
II	40:60	0.9	0.8	1.62	193	203	110
II	10:90	0.8	0.8	1.59	211	205	120
III	40:60	1.1	1.2	1.65	180	191	105
III	10:90	1.1	1.1	1.59	208	200	118
IV	40:60	1.1	1.3	1.89	157	166	73
IV	10:90	1.0	1.1	1.79	192	186	85
V	40:60	1.0	1.2	1.66	172	184	97
V	10:90	0.9	1.1	1.60	200	199	113
VI	40:60	1.1	1.0	1.67	171	183	90
VI	10:90	1.0	0.9	1.62	199	194	101

PKS: Poly(keto-sulfide), Epoxy Resin (DGEBA).
Conditions for reinforcement:
E-Glass cloth, Plane weaves 10 mm, 10 layers.
Resin: Fiber Ratio = 40:60, Curing Temperature 240–250°C.
Time: 3 Hours, Pressure 60–70 psi.
Composite Size: 150 mm × 150 mm, 3.0–3.2 mm thick.

observed that as the hardener loading increases in the epoxy resin, the mechanical properties decrease, and system based on 10:90 phr shows better mechanical properties than that based on 40:60 phr. This is traced to the fact that in most epoxy resin systems the chemical reaction between the epoxy functional group and the hardener are diffusion controlled and don't proceed to completion [45]. Therefore, due to steric and diffusional restriction, not all the poly(keto-sulfide)s would fully react with the epoxy resin. The applied stress, therefore, would be unevenly distributed on the network chains [46,47]. Thus, the highly stressed chains break first and their loads are distributed to other network chains, forcing them to break or slip to relieve the stress on them. Furthermore, the unreacted PKS molecules in the epoxy resin would lead to failure in the epoxy resin. Consequently the mechanical strength reduces.

CONCLUSION

1. PKS can be used as a curing agent for epoxy DGEBA resin.
2. Void-free composites could be prepared with good mechanical properties.
3. At high levels of hardener, a heterogeneous crosslink network is formed and it is unable to hold the molecular chains tightly together, leading to a reduced stiffness of the resin.
4. The curing behavior of epoxy resin can be altered by changing the molar ratio of the curing agent. Thermal and mechanical stability of the cured material was found to be dependent on the structure of the network.

REFERENCES

[1] Dronov, V. L., Nigmatullina, R. F., Kalilove, L. M., and Niktin, Yu. E. *Zh. Org. Khim* **16**, 1392 (1980).

[2] Majmudar, G. H., and Patel, H. S. *Phosphorus, Sulphur and Silicon* **48**, 181–188 (1990).

[3] Majmudar, G. H., and Patel, H. S. *Journal of India Council of Chemists* (**IV**) (3), 99 (1988).

[4] Patel, Ku. S. R., Patel, H. S., and Patel, S. R. *European Polymer Journal* **23**, 389 (1987).

[5] Possart, G., Presser, M., Passlack, S., Geiss, P. L., Kopnarski, M., Brodyanski, A., and Steinman, P. *International Journal of Adhesion and Adhesives*, **29**, 478 (2009).

[6] Mallik, B. P. *Paintindia, Exhibition Special Issue*, 21–23 February (2002).

[7] Kondekar, R. N. *Paintindia Exhibition Special Issue*, 21–23 February (2002).

[8] Gummenson, J. J. *Paintindia, P. 75* November (2006).

[9] Wang, C.-S., and Ho, T.-H. U.S. Patent, 5,686,541 November 11, (1997).

[10] Ho, T.-H., and Wang, C. S. *Journal of Applied Polymer Science* **54** (1), 13–33 (1994).

[11] Montena, N. U.S. Patent 6,979,133 December (2005).

[12] Muskopf, J. W., and McCollister, S. B. (2003). *Epoxy Resins, in Ulllmanns Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, Vol. 12.

[13] Gannon, J. (1996), *Epoxy Resins in Encyclopedia of Chemical Technology*, Wiley – Interscience Publications, John Wiley & Sons, New York, Fourth Edition, Vol. 9, p. 730.

[14] Chenghong, H., Zuoguang, Z., Yubin, Li, and Zhijie, S. *Journal of Reinforced Plastics and Composites* **28**, 133 (2009).

[15] Macan, J., Brnardic, I., Ivankovic, M., and Mencer, H. J. *Journal of Thermal Analysis and Calorimetry* **81**, 369 (2005).

[16] Atta, A. M., Mansour, R., Abdon, M. I., and El-Sayed, A. M. *Journal of Polymer Research* **12**, 127 (2005).

[17] Yuan, Li, Aijuan, Gu, and Liang, G. *Material Chemistry and Physics* **110** (2–3), 417–425, 15 August (2008).

[18] Wang, H. H., and Chen, J. C. *Polymer Plastics Technology and Engineering* **33** (5), 637–651 (1994).

[19] Almeida, E. *Industrial and Engineering Chemistry Research* **40** (1), 3–14 (2001).

[20] Tianle, Z. Mingyuan, Gu Yanping, J., and Junxiang, W. *Polymer Journal* **37** (11), 833–840 (2005).

[21] Sharma, P., Choudhary, V., and Narula, A. K. *Journal of Thermal Analysis and Calorimetry* **91** (1), 231–336 (2008).

[22] Nishimoto, Y., Ueoka, K., and Nakamura, S. *Journal of Thermal Analysis and Calorimetry* **70**, 741–746 (2002).

[23] Barton, J. M. (1985). In *Advances in Polymer Science*. Vol. 72, Springer Verlag, Berlin, 111–154.

[24] Firouzmanesh, M. R. *Journal of Reinforced Plastics and Composites* **24** (4), 345–353 (2005).

[25] Wang, P., and Schaefer, D. W. *Langmuir* **24**, 13496–13501 (2008).

[26] Carioscia, J. A., Stansbury, J. W., and Bowman, C. N. *Polymer* **48** (6), 1526–1532, March (2007).

[27] Nishikubo, T., Kameyama, A., Kashiwagi, K., and Oyama, N. *Polymer Journal* **28** (9), 795–800 (1996).

[28] Sakata, H., Yokota, T., Mori, K., Hirai, K., Takenchi, K., and Hatajima, T. U.S. Patent 5, 430,112, July 4 (1995).

[29] Paul, K. U.S. Patent 6,265,519 July 249 (2001).

[30] Abbey, Kirk, J., and Pressley, Mark, W. U.S. Patent 6. 153, 719 November 28, (2000).

[31] Lee, H., and Neville, K. (1967). *Handbook of Epoxy Resins.* McGraw Hill, New-York.

[32] Zaheer, S. A. (1982). *Advanced Organic Coating*, Technomic Publ., Lancaster, PA.

[33] Bhatnagar, M. S. *Polymer Plastic Technology and Engineering* **32** (1), 53–113 (1993).

[34] Rogers, R. N., and Smith, L. C. *Analytical Chemistry* **39**, 1024 (1967).

[35] Fyee, C. A., Niu, J., Retting, S. J., Wang, D. W., and Poliks, M. D. *Journal of Polymer Science Part A: Polymer Chemistry* **32** (12), 2203–2221 (1994).

[36] Martzel, E., and Koeing, J. L. (1986). In *Advances in Polymer Science*. Vol. 75, Springer–Verlag, Berlin, 73–112.

[37] Conavate, J. Colom, X. Pages, P., and Carraseo, F. *Polymer Plastics Technology and Engineering* **39** (5), 937–943 (2000).

[38] Shim, J. S., Lee, W., and Jang, J. *Polymer Journal* **23** (7), 911–916 (1991).

[39] Vyazovkin, S., and Sbirrazzuoli, N. *Marcromolecules* **29** (6), (1996).

[40] Fraga, F., Soto, V. H., Rodriguez- Nunez, E., Martinez- Ageitos, J. M., and Rodriguez, V. *Journal of Thermal Analysis and Calorimetry* **87**, 97 (2007).

[41] Jain, R., Choudhary, V., and Narula, A. K. *Journal of Thermal Analysis and Calorimetry* **90** (2), 495–501 (2007).

[42] Nunez, L., Fraga, F., Fraga, L., Salgado, T., and Rodriguez, A. J. *Pure and Applied Chemistry* **67** (7), 1091–1094 (1995).

[43] Kollek, H. Adhesion, (London) 12, 166 (1988).

[44] Dusek, K. (1986). In *Advances in Polymer Science*. Vol. 78, Springer Verlag, Berline, 1–59.

[45] Morgan, R. J., and O'Neal, J. E. *Polymer Plastic Technology and Engineering* **10** (49), (1978).

[46] Fanke, W., Beer, W., and Seitz, U. *Progress in Colloid and Polymer Science* **57** (48), (1975).

[47] Nielsen, L. E. (1974). *Mechanical Properties of Polymer and Composites*, Marcel Dekker, Inc, New York.