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Synthesis and Properties of a Flexible Curing Agent

X. WANG, S.R. ZHENG and R.M. WANG*

Department of Applied of Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, P.R. China

*Corresponding author: E-mail: npu18101@163.com; wangxi0215@hotmail.com

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This paper presents the synthesis of a new type of flexible epoxy curing agent and an approach to improve the toughness of epoxy resin by curing without reducing the strength and modulus of the resin-cured material. The results show that the degree of toughness reaches maximum values when the flexible curing agent is applied at weight percentages (wt. %) between 10 and 15 %. When the amount of flexible curing agent added to epoxy resin weight is 10 wt. %, the impact toughness and fracture toughness increases by 33.3 % and 96.3 %, respectively, compared with the pure epoxy resin. When the amount of flexible curing agent added to epoxy is 10 wt. %, the resulting impact thoughness of the material is 19.5 kJ m^{-2} at -50 ºC, the impact toughness of pure epoxy resin is only 7.96 kJ m^{-2}.

Key Words: Epoxy resin, Flexible curing agent, Fracture toughness, Toughening mechanism.

INTRODUCTION

Epoxy resin contains two or more epoxy polymers composed mainly of aliphatic, alicyclic or aromatic chain segment. Epoxy resin is a useful thermosetting product for polymer oligomer formation by the reaction of epoxy groups with liquid and exclusion of thick and solid-state varieties, among other forms. Although most of types of epoxy resins are utilized at room temperature, the liquid itself is a thermoplastic linear polymer. It almost did not separate the use of value at room temperature or heated conditions, the epoxy oligomers and curing agent reactions cross-linked into three-dimensional network structure of insoluble and infusible polymer. its inherent excellent performance. Epoxy resin is most commonly used in the aerospace, aviation and defense sectors as a thermosetting polymer due to its strong bonding ability, excellent electrical insulating, processing and chemical properties and good stability. It is widely used in coatings, adhesives, electrical and electronic devices, wood construction, composite materials and many other fields[1-3]. Cured pure epoxy resin has high crosslinking density thus, it is brittle, fatigue-resistant, heat-resistant and has impact toughness. However, it also presents several disadvantages, including failure to meet requirements and the fact that epoxy application is subject to certain restrictions. As such, many studies hava sought to determin methods by which modification of the toughness epoxy resin could be achieved[4-7].

EXPERIMENTAL

The materials used in the experiment are presented in Table-1.

TABLE-1
MATERIALS AND REAGENTS OF EXPERIMENTAL

Name	Formula
3,3-Dimethyl-1-bromobutane	$C_6H_{13}Br$
Lithium	Li
Tetrahydrofuran	C_4H_8O
MeTHPA	$C_9H_{10}O_3$
Phosphorus	P

For nuclear magnetic resonance (NMR) analysis, a Bruker Avance 300 MHz NMR spectrometer was used to analysis ^{13}C and hydrogen side nitrile flexible epoxy resin curing agent of ^{13}C NMR spectra of ^1H. For transform infrared spectroscopy (FTIR), a Nicolet Avatar360 FT-IR E.S.P spectrometer to analyze the chemical structure of the end of nitrile flexible epoxy curing agent. For differential thermal analysis, a TA Q200 differential scanning calorimeter was used to determine the curing reaction between the epoxy resin and the flexible curing agent in the nitrogen environment.

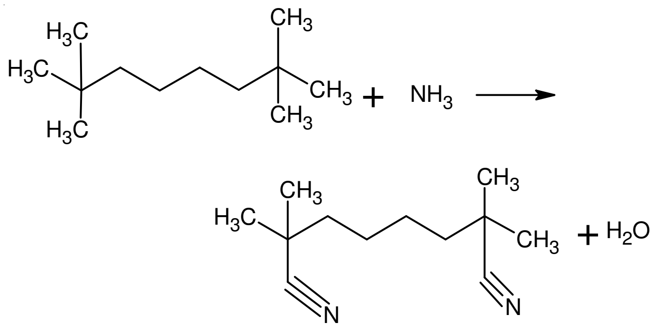
For the mechanical tests, bending performance was determined using a universal material testing machines (Shenzhen SanSen Electronic). An XJJ 50 impact testing machine (Chengde Testing Machine Co. Ltd.) was used for the impact toughness test.

Synthesis of the flexible epoxy curing agent: Gilman reagent was prepared by the following reactions:

$$R\text{-}X + 2Li \rightarrow RLi + LiX \ (X = Cl, Br, \text{ or } I)$$
$$2RLi + CuX \rightarrow R_2CuLi + LiX$$

In this experiment, 4,4-dimethyl-1-bromopentane with lithium metal was used as the starting material.

The flexible epoxy resin curing agent was synthesized the following steps: 1) Preparation of the Gilman reagent and 2) Reaction of Gilman reagent with 2,2,9,9-tetramethyldecane as follows:



NMR analysis: ^{13}C NMR results show a peak at 118 ppm which is the characteristic peak, of C=N bond. Peaks at 49 ppm and 44 ppm correspond to the quaternary carbon of the flexible curing agent, which at 30 ppm and 28 ppm indicate secondary carbons from the test compound containing. Finally, at a peak at 18 ppm, corresponds to the primary carbon of the compounds. Further it confirms that the compound contains three kinds of hydrogen *i.e.*, CH, CH_2 and CH_3. From the integrated NMR analysis results, we can confirm formation of the final synthesis product.

Fig. 1, shows the characteristic absorption peak of CH_3 at 2960 cm^{-1}, the characteristic absorption peak of C=N at 2240 cm^{-1} and the characteristic absorption peak of CH_2 at 2850 cm^{-1}.

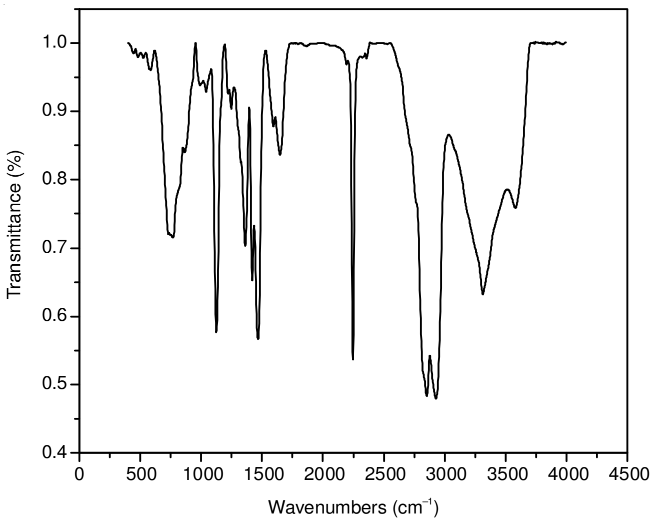


Fig. 1. FTIR spectrum of the flexible curing agent

RESULTS AND DISCUSSION

Curing of the epoxy resin was carried out using a ladder temperature program; here, the curing peak starting temperature was designated as to, the peak temperature T_P and the termination temperature was designated as Te. The initial temperature of the curing peak is usually approximated as the temperature of gel. The differential thermal analysis curve peak showed different heating rates at different curing temperatures, determination of the actual curing temperature of the thermosetting material difficult. The curing process temperature usually refers to the occurrence of a minimum temperature during the curing reaction in the polymer material, that is, when the heating rate is 0 ºC/min, corresponding to the curing reaction temperature, the reaction in which constant temperature equals curing temperature. Many studies have shown that the curing reaction temperature T and the curing process have a linear relationship with the heating rate β. Therefore, the linear relationship between T and β, which is $T = A + B\beta$ in epitaxy, can be used to find the initial curing process temperature.

For the same sample and using different heating rates, the differential thermal analysis scanning curve of Ti and T_P values increased as the heating rate increased. Extrapolation was obtained at $\beta = 0$ ºC/min. The point T_{0i} and T_{0P} approximate the gel temperature and the curing temperature, respectively, in the curing reaction system, which can be used as the basis for determining resin system curing reaction process parameters. Fig. 2 illustrates a flexible curing agent for the pure epoxy 0 wt % T-β curve indicates a linear relationship. During β-extrapolation to zero, the isothermal curing temperature and the minimum temperature for the curing reaction to occur can be obtained. The gel temperatures of the different components of a modified system, including the flexible curing agent during the curing reaction, specifically, the starting temperature (T_o), the curing temperature, the peak temperature (T_P) and the after curing treatment temperature [termination of temperature (T_i)], as shown in Table-2.

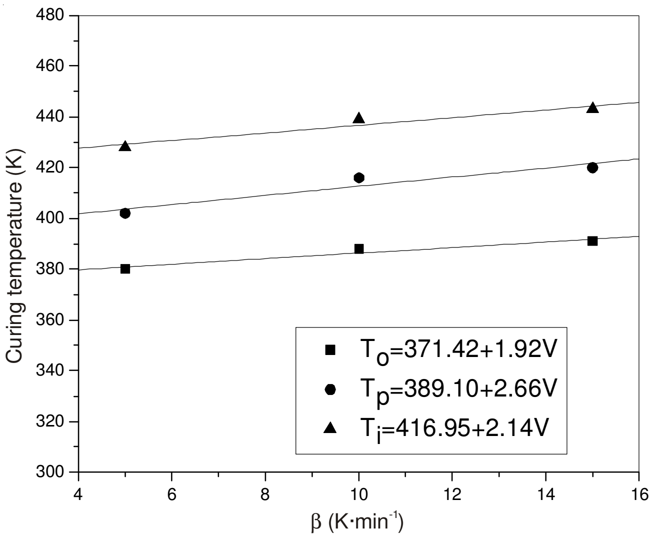


Fig. 2. Extrapolated curves of T and β

TABLE-2
CURING TEMPERATURE OF DIFFERENT FLEXIBLE CURING AGENT

Percentage of flexible curing agent (%)	Gel temperature (ºC)	Curing temperature (ºC)	After curing treatment temperature (ºC)
0	99.06	116.35	144.98
10	100.62	128.68	147.69
20	114.65	132.59	150.58

The initial curing temperature was about 100 ºC. The optimal curing process of epoxy resin/flexible curing agent/MeTHPA system was as follows: The resin gel is heated to

100 °C, after which thermostat curing is performed at to 120 °C. Finally, heating up to 160 °C is performed and maintained to ensure that the epoxy is fully cured. The curing temperature obtained by extrapolation continued to increase without considering its proliferation. Therefore, in the actual curing process, when the the kinetics of the curing reaction becomes diffusion-controlled, the mobility of the molecular chain greatly decreases and the curing reaction becomes extremely slow such that the system will requires further post-processing at high temperatures to cure fully. Differential thermal analysis was used to obtained the initial curing temperature, constant curing temperature and post-processing temperature of the curing reaction. While these parameters are directly equivalent to the curing process, they provide a reliable basis determining optimum curing conditions.

Figs. 3 and 4 show that the application of the flexible curing agent results in improvements in the impact toughness and bending properties of the cured epoxy resin. With increasing in the amount of flexible curing agent added to the resin, the impact toughness exhibited a slow increase. When the amount of flexible curing agent added was 10 wt. %, the impact toughness of the cured epoxy resin achieved a maximum, improvements of 33.3 % for 24.01 KJ·m^{-2}. Modification of the toughness of epoxy resin at the same time often reduces its strength and modulus.

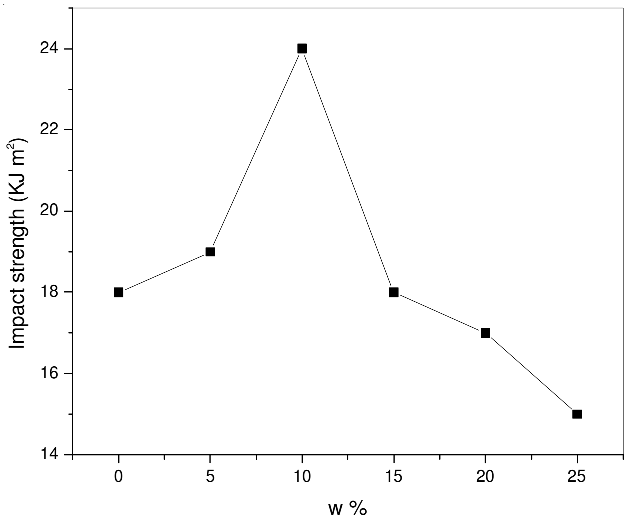


Fig. 3. Impact toughness as. a function of flexible curing agent content

Fig. 4 shows that the strength and modulus of the flexible epoxy resin curing system increased slightly with increasing flexible curing agent content. When the amount of curing agent added was 10 wt. %, the flexural strength of the cured epoxy resin reached a maximum of 130.1 MPa, 12.6 % higher than that of pure epoxy resin. The flexible curing agent toughened the epoxy resin but did not change the backbone structure of the epoxy resin itself. Thus, compared with pure cured epoxy resin, curing of the cross-linked network yielded minimal changes to the cross-linking density of the resin to which the curing agent had been added and no decreases in the strength and modulus of the cured epoxy resin were observe. Figs. 3 and 4 also show that when the amount of flexible curing agent added is excessive (>10 wt. %), the performance of the cured resin quickly declines.

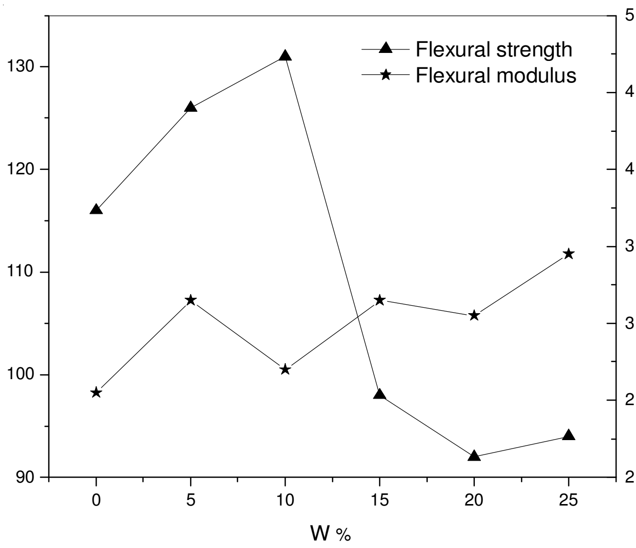


Fig. 4. Flexural properties as a function of flexible curing agent content

The fracture toughness (K_{IC}) of epoxy resin systems modified with the flexible curing agent is shown in Fig. 5. K_{IC} increased with increasing amount of flexible curing agent added, reaching a maximum value of the 4.515 MN· m$^{-3/2}$ at 15 wt. % curing agent. Compared with pure epoxy resin, K_{IC} exhibited an increase of 96.3 %. The reaction of hydroxyl groups in the flexible curing agent with the epoxy resin, allows carbon chain in the flexible curing agent to bond with the main chain of the epoxy resin, effectively increasing the critical stress required for crack unstable growth.

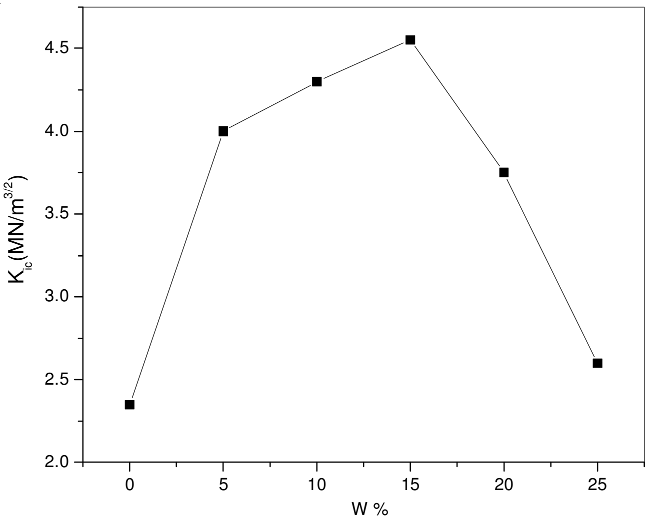


Fig. 5. Flexural toughness K_{IC} as a function of flexible curing agent content

In Fig. 6, (a) 200 × and (b)1000 × magnifications of the impact of pure cured epoxy resin are shown. Based on the magnified images, pure cured epoxy resin is very smooth impact, which then causes fractures. After fracturing, several stress stripes are observed; these indicate significant stress dispersion and typical brittle fracture characteristics of the cured resin. Sweep surface photographs in Fig. 6 show (c) 5,000 × and (d) 10,000 × magnifications of pure cured epoxy resin as a single-phase structure; no holes were observed in the pure resin after curing.

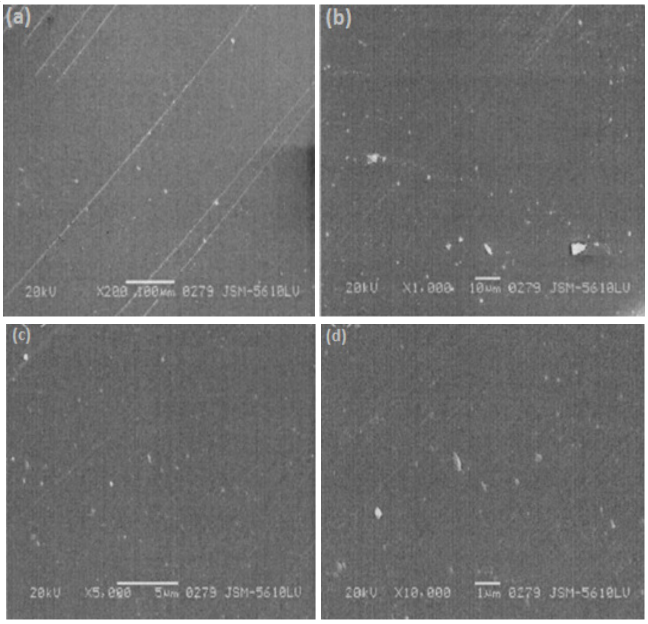


Fig. 6. Scanning electron micrographs of impact strength surfaces of cured pure epoxy blends

The amount of flexible curing agent added to the epoxy resin was 10 wt. %, the maximum impact toughness of the cured epoxy resin was achieved, as proven by the cross-sectional morphology of the impact surface shown in Fig. 7. The figure shows SEM photographs (a) 100 × and (b) 1000 × morphology of the impact surface of the cured resin, illustrating the typical texture of shells. Root like branches are also visible due to specimen impact fracture, leading to the occurrence of shear yielding. The fracture stripes tend to disperse, showing obvious ductile fracture characteristics. Magnification (c) 5,000 × and (d) 10,000 × in Fig. 7 no obvious epoxy curing phase, indicating that results obtained are the overall feature of a single phase.

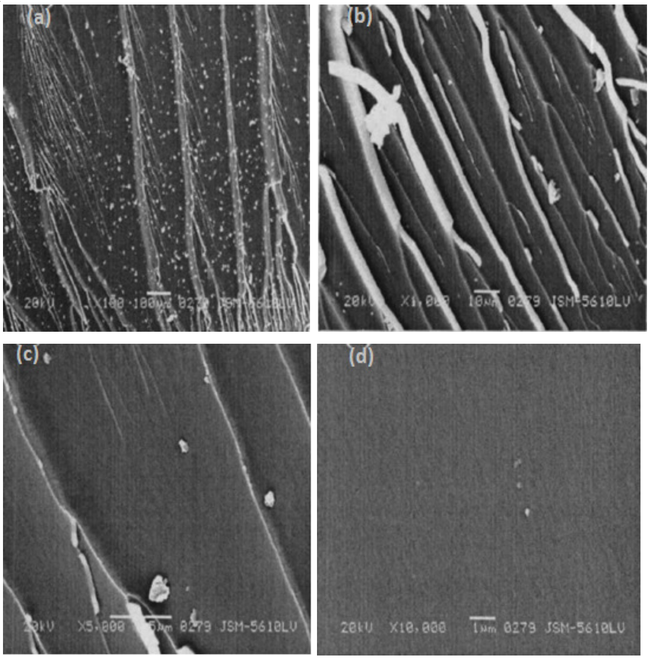


Fig. 7. Scanning electron micrographs of impact used 10 wt. % flexible curing agent

Addition of over 10 wt. % flexible curing agent cause a decline in the impact toughness of the cured epoxy resin. Addition of 15 wt. % and 25 wt. % flexible curing agent was performed to determin the impact fracture surface of the cured epoxy resin, as shown in Fig. 8. Fig. 8 (a) shows that when the flexible curing agent added is 15 wt. %, obvious conchoidal textures and root-like branches are formed in the cured resin. Fig. 8 (b) shows that the curing material had a homogeneous structure holes were not observed on the surfaceof the resin. Fig. 8 (c) and (d) illustrate that when the 25 wt. % flexible curing agent, the cross-section of the resulting cured resin showed a conchoidal texture but the root-like branches remain very small.

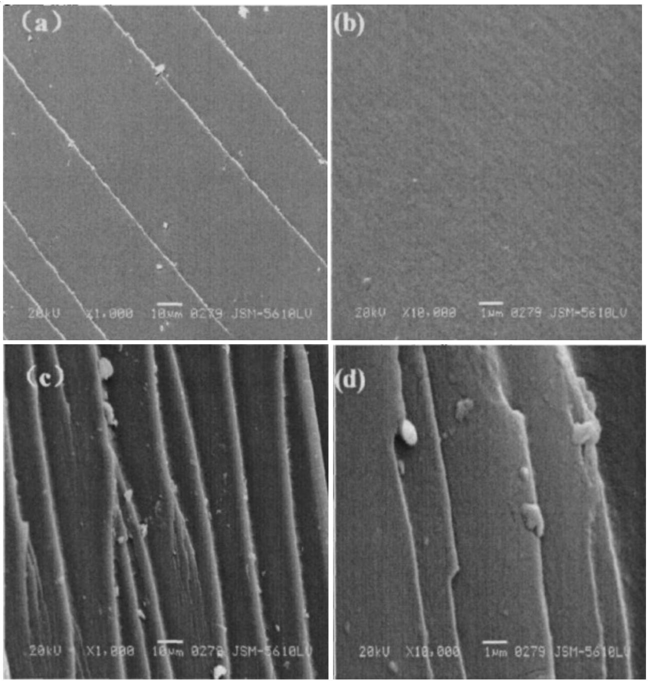


Fig. 8. Scanning electron micrographs of impact strength surfaces of cured pure epoxy blends; (a and b: 15 wt. % curing agent, c and d: 25 wt. % flexible curing agent)

From the different amounts of flexible epoxy curing agent added, the cured G_{IC} values were calculated and are shown in Fig. 9. The G_{IC} of pure cured epoxy resin was 2.16 KJ/m^{-2}. The G_{IC} of cured modified increased with increasing curing agent content. About 15 wt. % flexible curing agent must be added the resin system to achieve a maximum G_{IC} of 7.01 KJ/m^{-2}. As the amount of curing agent continuously increased, the G_{IC} began to decrease. Two reasons may be cited for this phenomenon: (1) introduction of the flexible curing agent improved the G_{IC} of the cured epoxy resin and (2) small, hard molecules in the cured product were not reflected, thus resulting in lower toughness of the cured epoxy resin.

Conclusion

This paper studied the network structure of flexible curing agent modified epoxy resin to explore the curing mechanism of the epoxy resin/flexible curing agent/ MeTHPA system. The following conclusions are drawn:

1) When the flexible curing agent is introduced into the epoxy resin heterogeneity is observed in the molecular chain

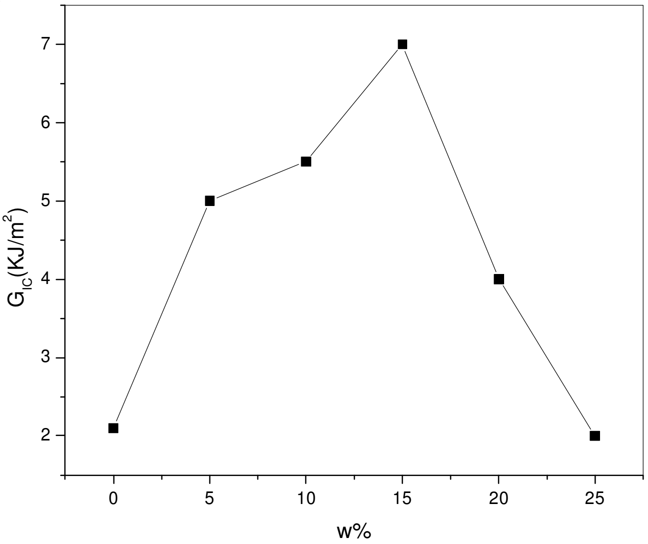


Fig. 9. Fracture energy G_{IC} as a function of flexible curing agent content

cross-linked network due to differences in molecular weight. A submicroscopic two-phase structure is then formed. The toughening mechanism of the curing agent is attributed to its flexible side chains interspersed with the cross-linked network of the epoxy resin. Stress can play a decentralized role in the impact energy of the material.

2) A mathematical model G_{IC} yield a linear relationship between the increase in toughness and weight percentage of the curing agent. Analysis showed a relationship between the curing agent and toughness of the curing agent and the impact toughness of the epoxy resin and curing agent.

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