REVIEW ARTICLE

INFLUENCE OF CASHEW NUTSHELL LIQUID (CNSL)-BASED PHENALKAMINE ON THE CURE KINETICS AND MECHANICAL PROPERTIES OF EPOXY RESIN

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ABSTRACT

The curing reaction of Diglycidyl Ether of Bisphenol A (DGEBA) resin with phenalkamine and tetraethylene tetramine was compared using differential scanning calorimetry (DSC) at various heating rates. Kinetic parameters of the curing process were determined through isoconversional and Kissinger methods. The two-parameter (m, n) Sestak-Berggren autocatalytic model was identified as the most suitable for describing the kinetics of the curing agents studied. The average activation energy for the phenalkamine curing agent was 60.27 kJ/mol, compared to the minimum activation energy of 55.48 kJ/mol for tetraethylene tetramine. Additionally, the phenalkamine curing agent enhanced both the flexural and impact properties relative to tetraethylenetetramine. Keywords: Phenalkamine, Non-isothermal kinetics, Bio-based curing agent

INTRODUCTION

The use of renewable resources in polymer production has gained increasing attention due to concerns over the depletion of petroleum reserves, rising carbon footprints, and stringent environmental regulations promoting sustainability in industrial processes (1). Epoxy resins, specifically diglycidyl ether of bisphenol A (DGEBA), have been widely used as thermosetting materials due to their excellent chemical resistance and adhesive properties. They are utilized in a variety of applications, including adhesives, coatings, and paints. However, their inherent poor impact resistance and susceptibility to stress cracking limit their practical use in many applications (2). Various methods have been explored to improve the flexibility of epoxy resins, such as introducing flexible structures like rubbers, thermoplastics, silica, and glass beads into the rigid epoxy backbone, or by lowering the functionality of the curing agents (3). In response to the growing concern over reducing CO2 and other greenhouse gas emissions, researchers have turned to modifying epoxy materials by incorporating vegetable oil-based prepolymers (4). Cashew nutshell liquid (CNSL), derived from *Anacardium occidentale*, is a renewable biomaterial and an abundant natural source of phenols from non-food-chain resources.

CNSL contains four major components with unsaturated C15 chains: cardanol, cardol, anacardic acid, and 2-methylcardol. Phenalkamine, a curing agent synthesized from cardanol, is produced via a condensation reaction with formaldehyde and polyamines (5,6). The aromatic backbone of phenalkamine enhances the rigidity of the epoxy network, while its aliphatic side chains improve flexibility and extend pot life when used as a hardener. Additionally, the phenolic-OH groups make phenalkamine highly reactive even at low temperatures, and the amine side chains contribute to the high cross-linked density (6,7,8). The structure of the phenalkamine material is shown in Figure 1.
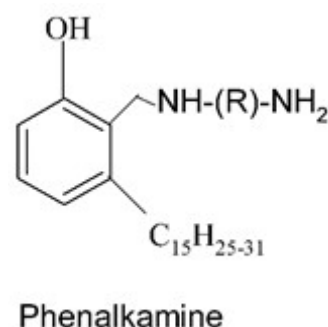

Figure 1. Chemical structure of phenalkamine

The study of curing kinetics provides crucial insights into the structure-property-processing relationships of epoxy systems. Numerous researchers have investigated and modeled the curing kinetics of epoxy resins using non-isothermal differential scanning calorimetry (DSC) scans (9). Zvetkov (2001) modeled the non-isothermal reaction kinetics of diglycidyl ether of bisphenol A (DGEBA) with m-phenylene diamine (mPDA) using isoconversional methods (10). Similarly, Yao et al. studied the curing behavior of DGEBA with hyperbranched poly(3-hydroxyphenyl) phosphate (HHPP) as the curing agent and found that the flexible groups present in HHPP enhanced the reaction rate and lowered the activation energy (11). The two-parameter autocatalytic model, represented by the Sestak-Berggren equation, was found to best describe the cure kinetics of the system across different heating rates. Sultania et al. also explored the cure kinetics of a vinyl ester-styrene system, concluding that the two-parameter (m, n) autocatalytic model was most suitable for describing the curing behavior through the isoconversional method (12). The cure kinetics of epoxy/phenalkamine systems has not been extensively documented in the literature, despite its increasing use in low-temperature epoxy curing across various applications. This paper presents an analysis of the kinetic parameters of the epoxy/phenalkamine system, including reaction order, activation energy, and kinetic rate constants. Additionally, the effects on mechanical properties are evaluated and compared with those of the epoxy/polyamine network.

Experimental

Materials: Phenalkamine (PKA) with an amine value of 490-550 mg KOH/g and a density of 0.99 g/cm³ was sourced from Cardolite Specialty Chemicals India Pvt. Ltd., Mangalore, India. The epoxy resin, supplied by Huntsman Advanced Materials, had an epoxy equivalent weight of 183-189 g/eq and a density of 1.17 g/cm³. Triethylenetetramine (TETA), also obtained from Huntsman Advanced Materials (India) Pvt. Ltd., had an amine value of 1443 mg KOH/g.

DSC Measurements: A NETZSCH DSC 200F3 instrument was employed to investigate the comparative curing characteristics of thermoset material systems. The Epoxy+PKA and Epoxy+TETA mixtures were prepared in stoichiometric ratios of 10:3 and 10:1, respectively, at room temperature and stored at −20°C. Weighed samples (15 mg) were placed in the DSC cell and analyzed using three different constant heating rates. Pure indium was used as a standard for calibration, and an identical empty aluminum hermetic pan served as the reference.

Physical and Mechanical Properties: The densities of all samples were measured using a precision balance and determined by Archimedes' principle of buoyancy. The density data for all materials prepared in this study are presented in Table 4. Tensile tests were performed in accordance with ASTM D 638 using an Instron Universal Testing Machine. The tests were conducted at a crosshead speed of 5 mm/min in a room temperature environment. The specimens had dimensions of 162 mm × 12 mm × 3.5 mm. Notched impact strengths were measured using an impact pendulum tester, following ASTM D 256 standards. The dimensions of the samples were 64 mm × 13 mm × 3 mm. The impact strength (kJ/m²) was calculated by dividing the absorbed impact energy by the cross-sectional area of the

samples. Flexural tests were conducted as per ASTM D 790 using the Instron Universal Testing Machine. The tests were performed at a crosshead speed of 5 mm/min in a room temperature environment, with specimens measuring 60 mm × 10 mm × 4 mm.Three measurements were taken for each specimen, and the average values are reported in Table 4.

Theoretical Background of Cure Kinetics Studies Using DSC: Non-isothermal measurements involve applying a thermal gradient to the sample at various constant heating rates across a specified temperature range. In Differential Scanning Calorimetry (DSC), the difference in heat required to raise the temperature of the sample compared to the reference is measured as a function of temperature. The temperatures of the sample and reference are maintained equally throughout the experiment. As the thermoset material cures, it generates exothermic heat, and the differences in heat flow rates between the sample and reference are recorded over time and temperature. The rate of reaction ($d\alpha/dt$) was assumed to be proportional to the rate of heat generation and mathematically expressed as follows (13).

$$\frac{d\alpha}{dt} \alpha \frac{dH(t)}{dt} \quad \text{Eq-1}$$

The degree of cure (α) ranges from 0 (completely uncured) to 1 (fully cured) and is defined as (17, 18, 19, and 20) follows:

$$\alpha(t) = H(t)/H(T) \quad \text{Eq-2}$$

Where $\alpha(t)$ = degree of cure at time t.
H(t) = Heat generated up to time t.
H (T) = Total heat of reaction.

It was also assumed that the rate of reaction ($d\alpha/dt$) can be defined by two separable functions K (T) and f (α) and mathematically expressed as follows.

$$\frac{d\alpha}{dt} = K(T).f(\alpha) \quad \text{Eq-3}$$

Where $d\alpha/dt$ is the rate of reaction, K (T) is the temperature dependent rate constant,and f (α) corresponds to the reaction model. The temperature dependence of thereaction rate is generally defined through an Arrhenius expression and represents mathematically as follows. (21, 22)

$$K(T) = A \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Eq-4})$$

Where E_a is the activation energy, A is the pre-exponential factor, R refers to the universal gas constant, and T corresponds to the absolute temperature.

The Eq -3 and Eq-4 combined and expressed mathematically in logarithmic form as follows.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A.f(\alpha)) - \frac{E_a}{RT} \quad (\text{Eq-5})$$

The E_a was determined from the slope of linear dependency between $\ln\left(\frac{d\alpha}{dt}\right)$ and $\frac{1}{T}$ using similar values of conversion at different heating rate using the equation-Eq-5 (12). The selection of f(α)were determined with the introducing of special functiony (α) and z (α) as suggested by Malek (14).

$$y\,(\alpha) = \frac{d\alpha}{dt}\,e^{x} \qquad\qquad\qquad\qquad \text{(Eq-6)}$$

$$z\,(\alpha) = \pi\,(x)\,\frac{d\alpha}{dt}\,\frac{T}{\beta} \qquad\qquad\qquad \text{(Eq-7)}$$

Where x, β T and $\pi(x)$ is the reduced activation energy (E_a/RT),heating rate (K min^{-1}), absolute temperature (K), and the expressionfor temperature integral, respectively. The temperature $\pi(x)$ was calculated using fourth rational expression given by Senumand Yang. (13, 15)

$$\pi\,(x) = \frac{x3 + 18x2 + 88x + 96}{x4 + 20x3 + 120x2 + 240x + 120} \qquad \text{(Eq-8)}$$

The y (α) and z (α) functions were normalizedwithin 0to 1 range and the maximum of y (α) function and z (α) function was used to choose most suitable kinetic model. The Kinetic parameters was calculated using the Kissinger method in which the activation energy and pre-exponential factor are assumed to be constant irrespective of different heating rate. It assumes the curing reaction is in first order by considering one data point for each heating rate that is the maximum temperature in DSC curve. (16) Kissinger equation mathematically represents as follows

$$\ln\frac{\beta}{Tm2} = \ln\frac{AR}{Ea} - \frac{Ea}{RTm} \qquad\qquad \text{(Eq-9)}$$

Where Tm is maximum temperature in DSC curve.By plotting ln (β/T_{m2}) verses $1/T_m$ the activation energy (E_a) and pre-exponential factor (A) was estimated from the slope of the linear fit and the y-intercept respectively(17).
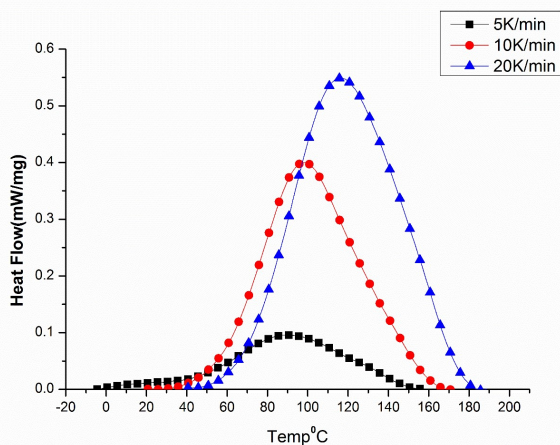
RESULTS AND DISCUSSION

Fig. 2. Heat flow vs temperature for Epoxy/PKA system

Fig 3 shows the DSC curve of Epoxy/PKA system at three different heating rates of 5, 10, and 20 ◦K min^{-1}.The cure reaction took place in one stage regardless of the heating rate in the studied temperature range.The maximum temperature(T_m) shifts to a higher temperature range with the increasing heating rate. Both initiation temperature (T_i) and final temperature (T_f) also increased with the increase of scan rates. A comparison of the values has been summarized in Table 1. It was observed from table1that the onset (T_i) temperature decreases with the addition of alkyl phenol due to may bephenolic hydroxyl groups weremore reactive compared amino hydrogen groups at lower temperature in opening

epoxide rings. The final temperature (T_f) of the curing reaction shifts to higher side due to may beincreases of viscosity of the mixture restricting mobility of active hydrogens in epoxide ring opening.It was observed thattotal heat of reaction ΔH increases with higher heating rates. This reason for this could be attributed to a more complete curing at higher heating rate and measurement uncertainty in lower heating rate due to diffusion of small molecules.The total heat of reaction was found to be lower for Epoxy/PKA system compared to Epoxy/TETA system.The activation energy (E_a) and preexponential (ln A) was calculated according to Kissinger computational method and was found to be 52.85kJ/mol and 3.34 s^{-1} respectively.
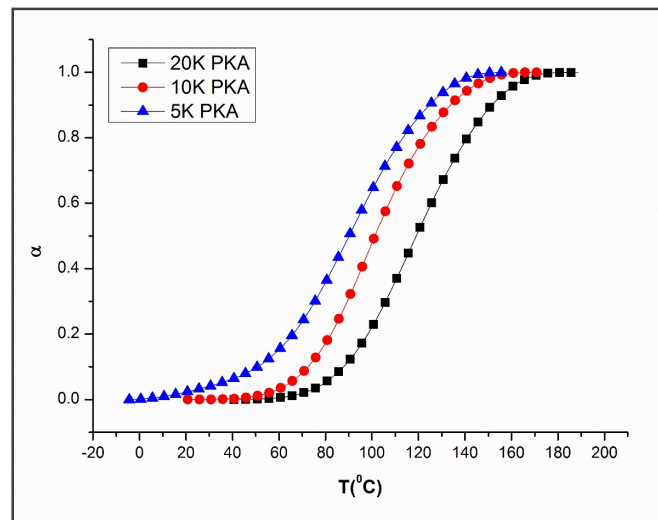
Fig. 3. Fractional conversion as a function of temperature for Epoxy/PKA system

Fig. 3 shows the variation of fractional conversion as a function of temperature at three different heating rates.The curves shows that the conversion increased very slowly in the initial stage and rose abruptly in the range of 65–140^{0}C and it was almost constant in the final stage. The shape of the was observed S-shape and shifted to right hand side due to may be in non-isothermal conditions K (T) and f (α) vary simultaneously with heating rate. Table 2 lists the values of maxima α_M and α^{∞}_P corresponding to the y (α) and z(α) for the Epoxy/PKA and Epoxy/TETA system together with α_P taken as the maximum of DSC peak of each thermoset system.The values of α_P found less than $\alpha\infty_P$for both the systems while $\alpha\infty_P$shows less than 0.632. These values shows that the both systems could be represented by two-parameter autocatalytic kinetic equation of sestak-Berggren. (13,19,21)

The sestak-Berggren equation was represented mathematically as follows

$$f\,(\alpha) = \alpha^{m}(1-\alpha)^{n} \qquad\qquad\qquad \text{(Eq-10)}$$

Where m and n are the kinetic exponents (18) The kinetic exponent n was calculated by linear fitting of ln (($d\alpha/dt$) e^{x}) verses ln ($\alpha^{p}\,(1-\alpha)$).

The kinetic exponent m was calculated according to Eq-11. $m = pn$, where $p = \alpha_M/(1-\alpha_M)$(Eq-11)

The pre-exponential factor A was calculated according to Eq-12

Table 1. Curing characteristics of Epoxy/PKA and Epoxy/TETA system at different heating rates.

Composition	Heating rate(β) in $\circ C\ min^{-1}$	Onset Temperature (T_i) in ^0C	Peak Temperature $T_m(^0C)$	Final Temperature T_f ($\circ C$)	Heat of Reaction, ΔH (J g−1)
EP+PKA	5	49.3	92.5	148.564	79.48
	10	60.7	98.7	151.791	138.59
	20	77.6	118.6	173.661	104.17
Epoxy+ TETA	5	56.7	107.5	113.4	214.40
	10	69.5	93.8	115.2	496.76
	15	70.2	101.9	138.7	494.24

Table 2. The calculated values of α_p, α_M and $\alpha_{\infty p}$ of Epoxy/PKA and Epoxy/TETA systems

Composition	Heating rate, ($\circ$C min−1)	α_p	α_M	$\alpha_{\infty p}$
Epoxy+PKA	5	0.50677	0.0045	0.5642
	10	0.43746	0.08	0.4745
	20	0.44737	0.085	0.5101
Epoxy+TETA	5	0.4968	0.1010	0.5154
	10	0.5596	0.3405	0.5897
	15	0.4459	0.2008	0.5065

Composition	Heating rate, ($\circ$C min−1)	Ea(KJ mol^{-1})	ln A	Mean	m	mean	n	mean	Overall m+n
Epoxy +Phenalkamine	5		14.5		0.0059		1.3045		
	10		15	**14.71**	0.0873		1.0041	**1.0958**	**1.1572**
	20	**60.27**	14.65		0.0910	**0.0614**	0.9788		
Epoxy +TETA	5		12.18		0.1085		0.9661		
	10	**55.48**	14.2		0.4642		0.89892	**1.009**	**1.2972**
	15		13.92	**13.43**	0.2920	**0.2882**	1.162		

Table 4. Mechanical Properties of Epoxy/TETA and Epoxy/PKA Systems

Composition	Density in(gm/cm^3)	Tensile modulus in (MPa)	Elongation in (%)	Impact strength in (kJ/m^2)	Flexural modulus
Epoxy+TETA	1.50	975.73±78.17	5.39±1.99	13.68±0.01	2369.72±154
Epoxy+PKA	1.45	938.77±50.87	8.88±2.57	13.92±0.01	3739.43±351

$$A= -\frac{\beta x p}{Tf'(\alpha p)} e^{xp} \qquad \text{(Eq-12)}$$

Where $f'(\alpha p)$ the differential form of the kinetic model, α_p is the conversion corresponding to maximum at DSC curve and p is the maximum of DSC curve. The kinetic exponents andpre exponentialfactor for both the systems was reported in Table 3.The predicted reaction rate $(d\alpha/dt)$ was calculated according Eq-13 using previously calculated activation energy (E_a) and kinetic exponents (m,n)

$$\frac{d\alpha}{dT}=A \exp\left(\frac{-Ea}{RT}\right)\alpha^m (1-\alpha)^n \qquad \text{(Eq-13)}$$

It was observed from table no 3 by comparing activation energy, pre exponential factor and reaction order for both the systems found similar. **Fig 4** showsvariation of activation energy (Ea) vs conversion (α) for both the systems. It was observed the activation energy in case of Epoxy/PKA was increasing with the extent of curing contrary to Epoxy/TETA system.

The reason for this behavior may be related tosteric hindrance created by longer side polymer chains present in molecular structure of phenalkamine(20).

Mechanical behavior: Table 4 presents the elongation at break, flexural modulus, and impact strength for the Epoxy/PKA system, which are higher compared to the Epoxy/TETA system. These improvements are likely due to the long aliphatic carbon chains present in the phenalkamine molecular structure, which provide enhanced flexibility to the epoxy resin. Additionally, the improved mechanical properties may be attributed to better particle-to-particle adhesion, as the long side chains of phenalkamine create steric hindrance that reduces moisture absorption by hydroxyl and oxygen-containing groups during curing. This enhanced adhesion may limit crosslinking, which is associated with a reduction in tensile strength. The proposed kinetic model was confirmed by plotting dα/dt (experimental) vs dα/dt (predicted) as explained in Eq 13 and shown in fig 5.The predicted curves shows higher deviation compared to experimental curves because of may be phenomenological models are unable to adequately define the complex cure behavior in the dynamic DSC measurements.

The activation energy estimated from Kissinger method and through sestak-Berggren kinetic model was found similar, so both the model was capable for describe the studied thermoset system.
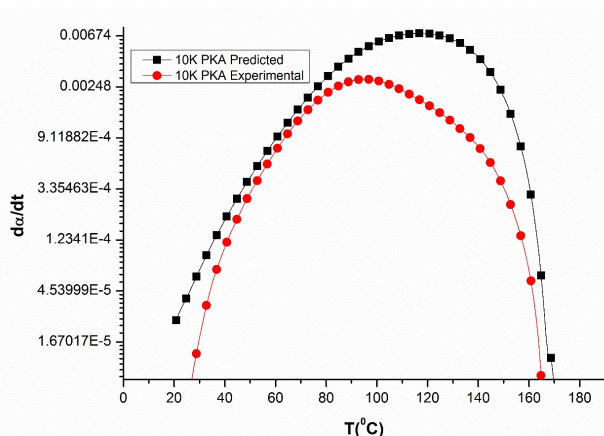

Fig-5 Comparison of experimental and calculated DSC curves for epoxy/phenalkamine system

CONCLUSION

Cashew nut oil (CSNL) based phenalkamine can be utilized as a curing agentfor improving flexibility of epoxy resin. The kinetic exponents, pre exponential factor and activation energy obtained for both the curing agent was found similar. The values of E_a in theconversion interval between 0.2 and 0.8 were increasing for Epoxy/PKA system. The curing reaction of the epoxy/phenalkaminesystem could be defined by a sestak–Berggren equation. The impact, flexural and elongation property were improved with the addition of phenalkamine in epoxy resin.

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