





Research Article

Investigation of Curing Mechanism and Mechanical Properties of Polypropylene/Aliphatic Epoxy Composites

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Temperature-sensitive cure kinetics based on bisphenol A oligomeric diglycidyl ether and branching diphenylmethane di-isocyanate, polymer aliphatic or lower molecular weight aromatic amines, and polypropylene and epoxy composites were examined. Polypropylene networks are formed initially, followed by amine hardeners interfering with epoxy oxirane rings to form linear oligomers. Finally, the system is formed by a reaction between amines obtained in the second phase and epoxy oxirane rings during the curing step. This three-stage treatment was illustrated. The activation energy was calculated using the Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose isoconversional approaches to cure degree. The E_a -to- α correlation was determined using these approaches, revealing that the research curing systems exhibited autocatalytic effects. Among the materials studied, compounds with low molecular weight aromatic amines had the strongest and longest-lasting tensile characteristics. There are numerous advantages to slow curing and discrete stages of composite creation, including better mechanical properties.

1. Introduction

Epoxy resins are both fast-setting thermosets and composite matrices [1]. The aircraft and maritime industries, electronics, coatings, and glues all use them. Thermal, mechanical, and dielectric qualities, as well as a confrontation with erosion

and less contraction upon cure, are critical in the applications mentioned above [2, 3]. However, despite their improved hardness, they are still considered rigid and brittle materials, which presents a challenge. The fracture toughness of epoxies can be improved by adding a second phase to remedy this problem [4–6]. Curing is vital for developing strength and

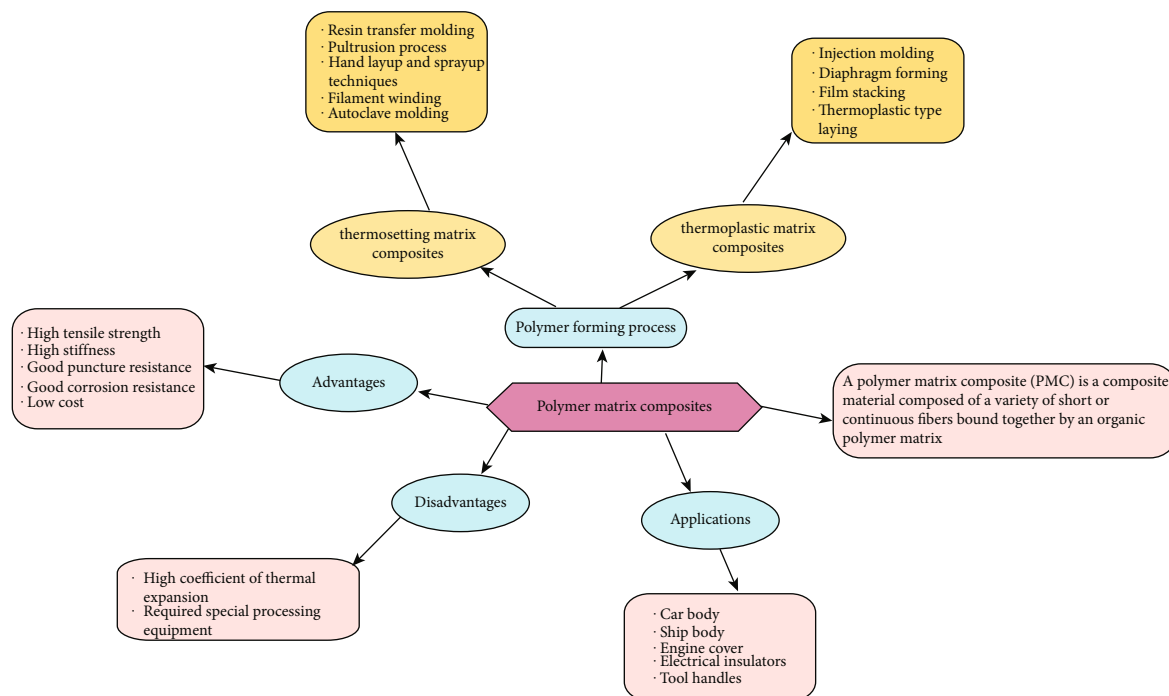


FIGURE 1: Schematic diagram of polymer matrix composite advantages and applications.

durability, as well as controlling the reaction rate and determining performance parameters. According to research, a secondary phase may include utilizing various polymers [7]. With polypropylene's excellent material qualities (good thermostability, high mechanical and adhesive strength, and strong corrosion and weather and chemical resistance), we considered it to be an exciting alternative in our quest to produce a toughening epoxy [8, 9]. Linear polypropylene has also been successfully used for curing epoxy [10]. Customized thermoset cure kinetics are crucial to both process development and quality assurance. As part of our research, we hope to confirm the relationship between temperature, time, and conversion while also developing a function to describe reaction rates [11, 12].

Consequently, epoxy and polypropylene are the primary focus of this investigation. The cross-linker's efficiency was tested using differential scanning calorimetry (DSC). As amine hardeners, various nucleophilicity and molecular weight and branching architecture were considered while formulating the compounds [13, 14]. Due to the many competing reactions during polypropylene's cross-linking kinetics, we tested a variety of kinetic models. Such a kinetic investigation is ideally suited for differential scanning calorimetry [15, 16]. Such a time and temperature-based optimization of reaction conversion would greatly assist in designing the epoxy's toughness. Figure 1 reveals the schematic diagram of polymer matrix composite advantages and applications.

2. Experimental Part

2.1. Differential Scanning Calorimetry Analysis. Specified amounts of epoxy polyethylene glycol-400, PIC-200, and polyamine hardener were combined at room temperature

according to Table 1 requirements. Polyethylene glycol-400 was first dissolved into an equal amount of epoxy and then blended evenly. As a final step, PIC-200 and hardener were mixed together until the resin was utterly homogeneous before being added in order. To determine the kinetics of the drug, we took 20–25 mg samples. Over a temperature range of 25–200°C, a Q600 thermal instrument was used to conduct dynamic differential scanning calorimetry measurements. Onset, peak, and endset temperatures of the exothermic curing reaction, as well as its total heat, were all measured. The responses' precision was utilized in a similar quantity (20–25 mg) for each experiment.

2.2. Preparation of Sample for a Performance Analysis. One-pot approaches were used to make epoxy-polypropylene composites. It was necessary to conduct this polymerization reaction in an apparatus containing a nitrogen intake pipe, thermometer, and mechanical stirrer measuring 500 mL. It was stirred for 30 minutes at room temperature in the mandatory epoxy and polyethylene glycol-400. It took 12 hours of gradual injection at room temperature to add the correct amount of PIC-200 needed. Prepolymer was created by raising the response temperature to 60°C and stirring the reaction for one hour. The amine hardener was added after allowing the reaction mixture to settle to room temperature. A homogeneous mixture was drawn into specific forms to obtain mechanical testing samples. The Universal Testing Machine, as in Figure 2, was utilized to assess the tensile strength and elongation at the break of specimens with proportions of $0.1 \times 0.01 \times 0.00035$ m. Each composition features at least five simple harmonies.

TABLE 1: Masses of different compositions of polyethylene polyamine.

Samples	Diglycidyl ether of bisphenol A	Polyethylene glycol-400	PIC-200	Polyethylene polyamine
100-0 polyethylene polyamine	100	0	0	13
95-5 polyethylene polyamine	95	5	3.34	12.3
90-10 polyethylene polyamine	90	10	6.68	11.7
85-15 polyethylene polyamine	85	15	10.02	11.1
80-20 polyethylene polyamine	80	20	13.36	10.4

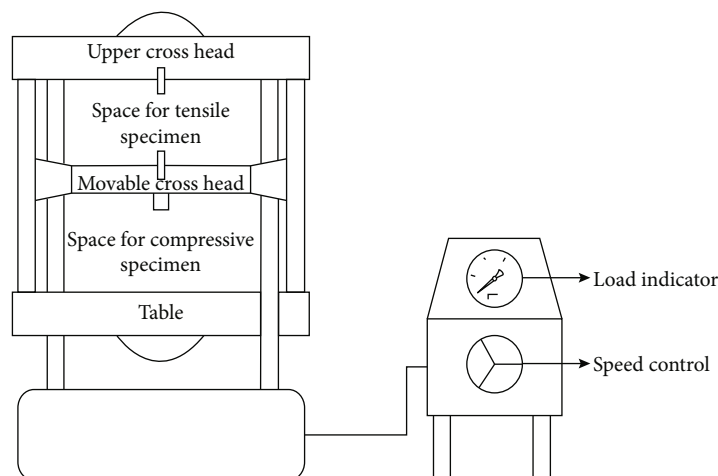


FIGURE 2: Schematic view of Universal Testing Machine.

3. Results and Discussion

3.1. The Cure Kinetics. At varying heating speeds, a dynamic differential scanning calorimetry curve is indicated in Figure 3. The differential scanning calorimetry readings show that the cross-linking processes are exothermic from start to finish. Table 2 contains the values for these variables. The polypropylene/epoxy mixture's cross-linking approach is multifaceted and involves several conflicting reactions. Because of this, we opted to define the curing response as single kinetic progress as the first calculation, even though differential scanning calorimetry curves show just one shared exothermic peak.

The reactivity of the precursors determines the reaction's starting temperature, whereas the reaction's length determines the process' end temperature [17]. Branching agents are particularly effective in curing epoxy-polypropylene systems [18]. Aromatic amines have a lower nucleophilicity than aliphatic amines, influencing their interactions with the epoxy and isocyanate groups.

A variety of kinetic equations govern the polyurethane/epoxy mixture's healing procedure, which is complex in and of itself. The precise concentration of the reactants can be challenging to determine in many cases. The validity of phenomenological models has been demonstrated in such circumstances [19, 20]. To accurately quantify the quantity of heat emitted, differential scanning calorimetry measurements are necessary. To link the produced heat with the reaction rate, the area beneath each curve is considered directly proportional

to the degree of conversion [21]. Heat transfer can be expressed as a percentage of total heat transfer at complete transformation at the given time. The following is the formula for calculating the degree of conversion:

$$\alpha = \frac{1}{\Delta H_0} \int_0^t \left(\frac{dH}{dt} \right) dt, \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{dH}{dt \cdot \Delta H_0}.$$

Figure 4 depicts the relationship between heating rate and degree of conversion. As you can see, there is a clear correlation. At whatever rate of heating, the entire conversion occurs. Figure 5 depicts the relationships between the rate of curing response and the degree of cure. The heating rate accelerates the curing reaction. At an extreme response rate, the cure degree essentially remains the same, but the cure degree for systems treated with PPA is shifted to smaller. Researchers employed oligomeric epoxy resins with secondary hydroxyl groups in our investigation. When polyethylene glycol-400 and isocyanate are combined with epoxy, hydroxyl groups' reactivity to isocyanate groups is significantly more potent than the amines' reaction with oxirane rings. In this case, PIC200 has shallow molecular weight differences from polyethylene glycol-400. Linear polymers are formed by epoxy hardener and amine hardener, as depicted in the picture

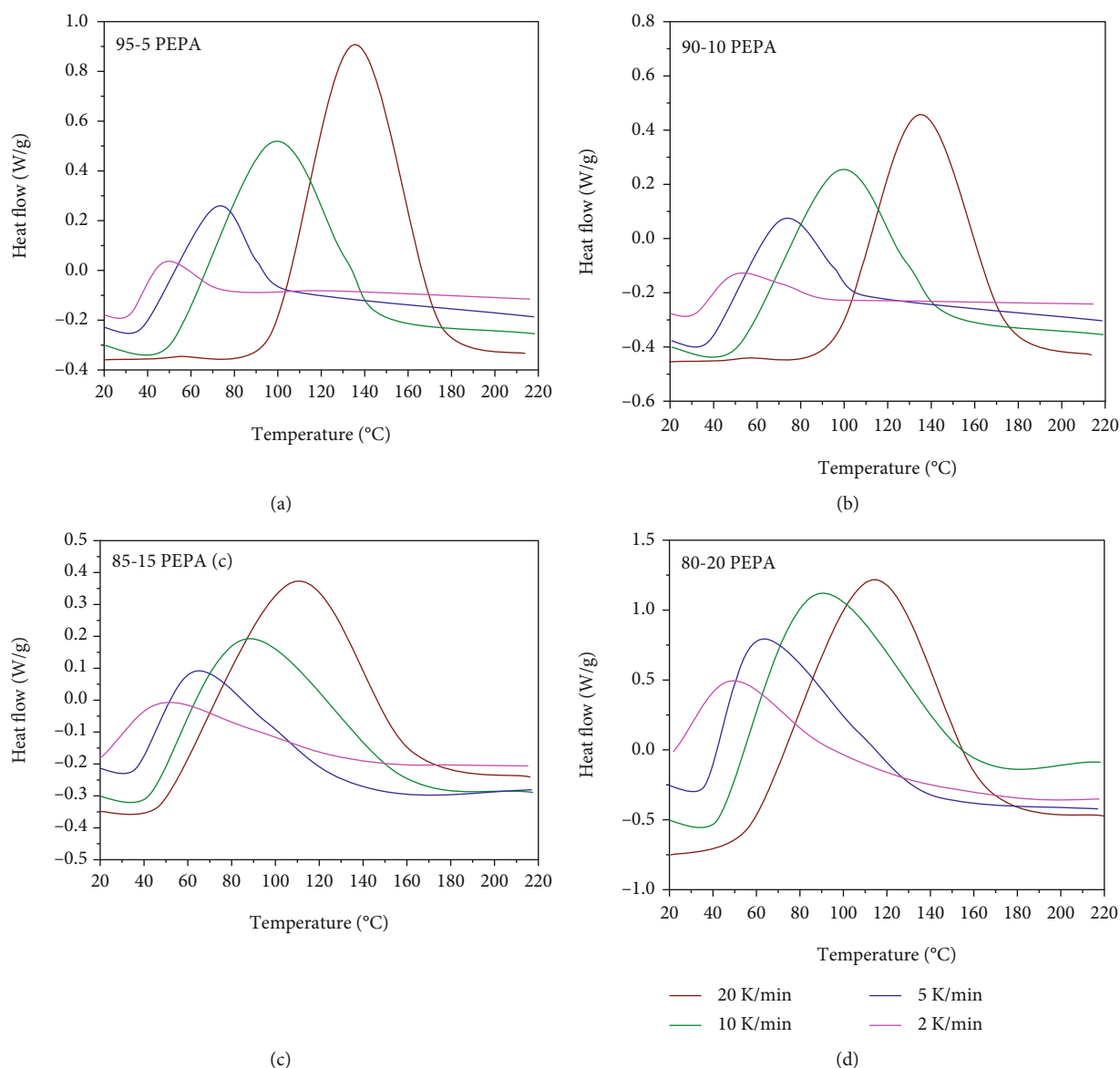


FIGURE 3: Differential scanning calorimetry curves of polyethylene polyamine: (a) 95-5; (b) 90-10; (c) 85-15; (d) 80-20.

above. The network is created by the reaction between oxirane rings and secondary amines.

We selected Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose from various kinetic methods to analyze kinetic parameters. They give data on the link between activation energy and degree of curing (α) during the process. It is possible to obtain an activation energy value using either integral isoconversational approaches without deciding the reaction form. Both approaches' activation energy fit graphs are displayed in Figure 6, and their consequences are listed in Table 3 for convenience.

E_a is displayed in Figure 7 about the degree of cure (α). Even though the Flynn-Wall-Ozawa approach results in E_a values 3 to 6 kJ/mol greater than the Kissinger-Akahira-Sunose method, overall trends in E_a are similar. Polyethylene polyamine toughened compositions did not experience any significant activation energy decrease upon conversion, as seen by

these dependencies. On the other hand, these graphs allow us to identify three stages of reaction. Because the final curing condition occurs at a higher temperature in a nonisothermal experiment, thermal energy overcomes the diffusion limitation, and only chemical parameters influence reaction activation energy. Non- or pure catalytic interaction of hydroxyl groups with isocyanate groups in this composition can be attributed to the rise in activation energy at the early stage. However, aromatic amines' catalytic activity is significantly lower than their aliphatic counterpart, making this process more challenging to catalyze. Amines and oxirane rings react during the second stage of curing. Curing is self-catalytic, which lowers the activation energy of the process. In this tendency, polyethylene polyamine's high activity as a hardener and catalyst is leveled.

Analysis of epoxy resin curing kinetics plays a critical role in establishing precise formulations and improving curing procedures (Table 4). To determine the most important

TABLE 2: Differential scanning calorimetry curing parameters of polyethylene polyamine and systems.

Specimen	β	T_{onset} ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	T_{endset} ($^{\circ}\text{C}$)
95-5 polyethylene polyamine	2	35.24	73.14	110.62
	5	46.12	88.62	142.12
	10	54.36	105.42	154.45
	20	67.11	124.32	189.63
90-10 polyethylene polyamine	2	35.62	72.84	113.62
	5	46.66	90.42	146.48
	10	57.82	106.62	168.32
	20	77.06	124.52	195.44
85-15 polyethylene polyamine	2	36.42	66.10	126.08
	5	48.13	87.24	149.81
	10	55.88	100.04	172.12
	20	64.14	116.62	184.62
80-20 polyethylene polyamine	2	32.22	60.62	112.42
	5	44.42	83.64	131.12
	10	55.24	94.12	165.88
	20	69.87	106.11	199.82

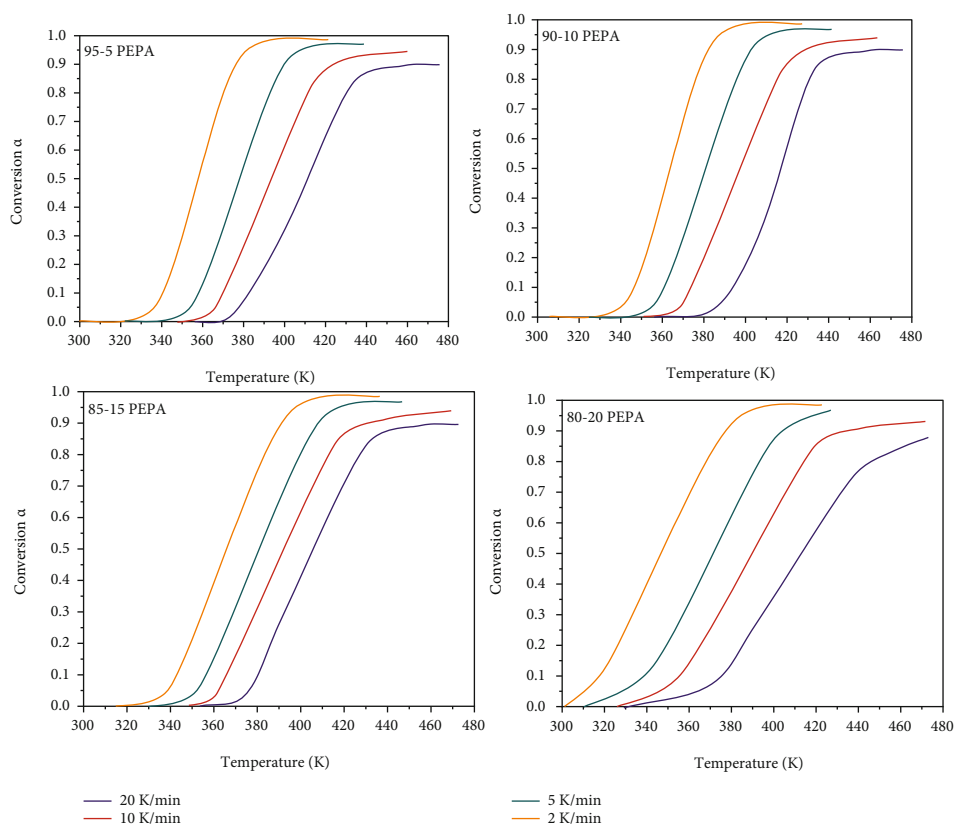


FIGURE 4: Polyethylene polyamine temperature vs. conversion curves at various heating rates: (a) 95-5; (b) 90-10; (c) 85-15; (d) 80-20.

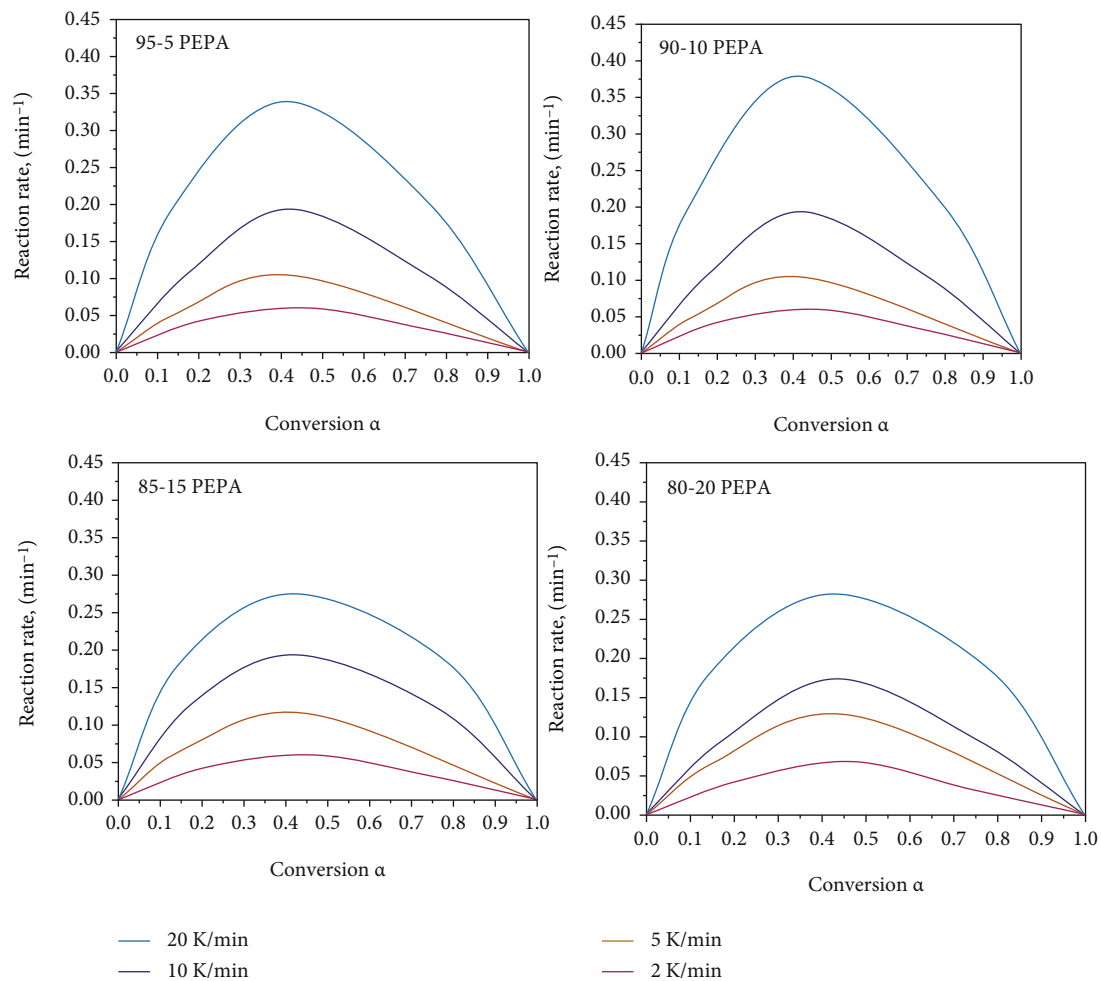


FIGURE 5: Nonisothermal reaction rate da/dt as a function of cure degree α for the curing reaction at the indicated heating rates.

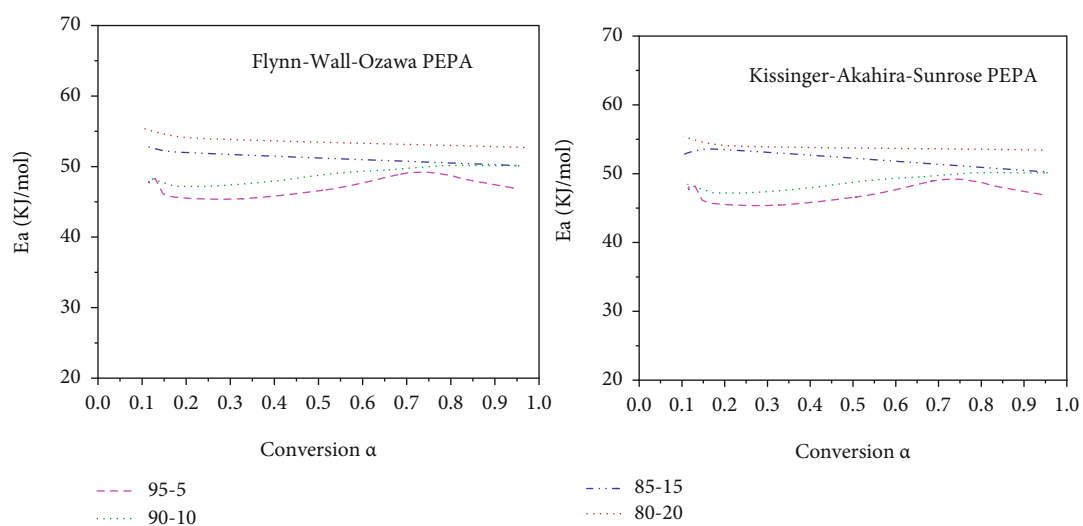
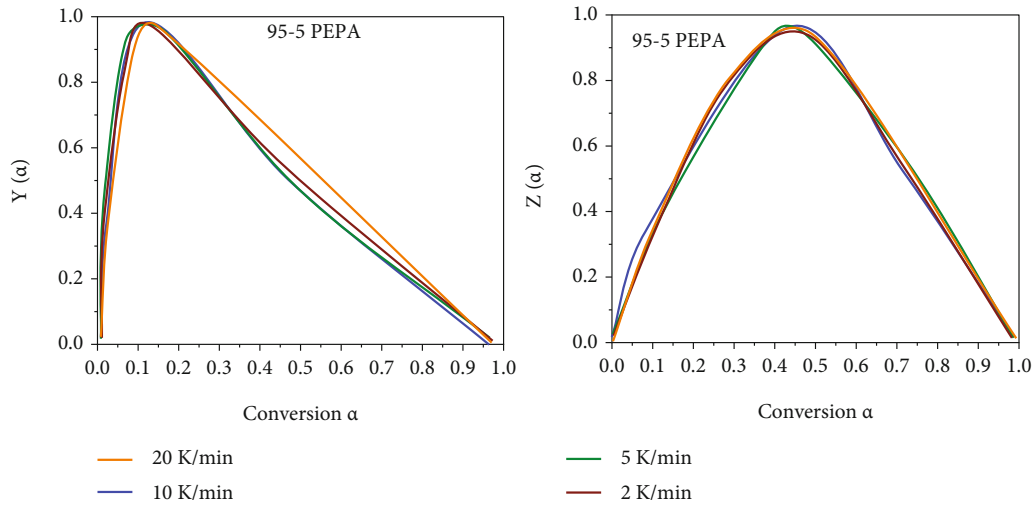


FIGURE 6: Flynn-Wall-Ozawa and Kissinger-Akahira-Sunrose techniques were used to determine the activation energy vs. conversion degree of the PU/epoxy systems studied.

TABLE 3: Overall activation energies for all compositions.

Sample	β (k/min)	Polyethylene polyamine			
		Ea (KAS)	Ea (FWO)	α_m	α_p^-
95-5	20	37.6-42.5	42.8-46.4	0.18	0.47
	10			0.19	0.51
	5			0.21	0.52
	2			0.23	0.56
90-10	20	40.05-42.8	45.5-48.2	0.18	0.50
	10			0.19	0.51
	5			0.20	0.55
	2			0.21	0.54
85-15	20	42.8-48.1	45.7-51.1	0.16	0.51
	10			0.17	0.50
	5			0.18	0.50
	2			0.20	0.51
80-20	20	43.7-50.1	48.1-53.5	0.18	0.53
	10			0.19	0.52
	5			0.20	0.53
	2			0.19	0.53

FIGURE 7: Functions of $y(\alpha)$ and $z(\alpha)$ vs. conversion degree.

curing kinetic parameters, we turned to [22]. $y(\alpha)$ and $z(\alpha)$ are two model functions used in this method to estimate kinetic parameters:

$$y(\alpha) = \frac{d\alpha}{dt} \cdot e^x, \quad (2)$$

$$z(\alpha) = \pi(x) \cdot \frac{d\alpha}{dt} \cdot \frac{\beta}{T}, \quad (3)$$

$$\pi(x) = \frac{x^3 + 16x^2 + 86x + 98}{x^4 + 18x^3 + 124x^2 + 246x + 124}, \quad (4)$$

where $x = E_u/RT$, $\pi(x)$, is the integral temperature, accu-

rately evaluated by Senum-Yang Equation (3). We utilized the activation energy acquired by the KAS technique to compute the $y(\alpha)$ and $z(\alpha)$ functions since it was more appropriate. According to the graphs in Figure 6, the conversion of $y(\alpha)$ and $z(\alpha)$ parameters is depicted. It lets us regulate constraints α_m and α_p^{∞} as extreme spots in Table 3.

As shown, for all experimental settings, the values of am and α_{oop} did not rely on the heating rate suggesting the exact curing mechanism, according to Malek's methodology ($\alpha_{oop} \neq 0.632$ and $0 < am < \alpha_{oop}$); these findings support the autocatalytic character of cure. To calculate kinetic parameters, we can utilize Equation (2). Table 3 lists these values. Increased use of active hardener (polyethylene

TABLE 4: Kinetic parameters.

Sample	β ($^{\circ}\text{C}/\text{min}$)	$\ln A$	PEPA m	n
95-5	20	7.815	0.241	1.206
	10	7.902	0.254	1.212
	5	8.012	0.302	2.232
	2	8.116	0.273	1.196
	Average	7.9612	0.265	1.461
Reaction rate constant			$k(T) = 0.28 \cdot 10^4 e^{(-37751/RT)}$	
90-10	20	8.562	0.248	1.282
	10	8.491	0.271	1.304
	5	8.423	0.294	1.332
	2	8.451	0.315	1.328
	Average	8.481	0.282	1.311
Reaction rate constant			$k(T) = 0.51 \cdot 10^4 e^{(-48262/RT)}$	
85-15	20	9.416	0.212	1.270
	10	9.318	0.206	1.178
	5	9.381	0.232	1.190
	2	9.452	0.278	1.240
	Average	9.392	0.232	1.219
Reaction rate constant			$k(T) = 1.43 \cdot 10^4 e^{(-52561/RT)}$	
80-20	20	10.118	0.286	1.494
	10	10.168	0.266	2.280
	5	10.352	0.248	1.116
	2	10.389	0.250	1.206
	Average	10.256	0.262	1.524
Reaction rate constant			$k(T) = 3.26 \cdot 10^4 e^{(-47463/RT)}$	

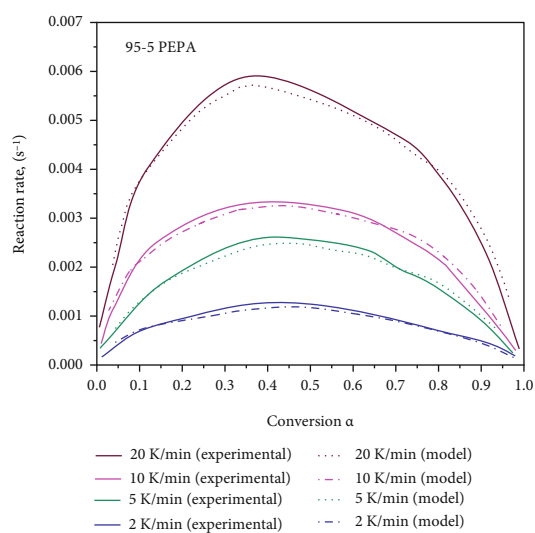


FIGURE 8: The autocatalytic model is compared to the experimental data.

TABLE 5: Mechanical properties of polyethylene polyamine.

Specimen	TS (MPa)	ϵ (%)	CS (MPa)	Hardness
100-0 polyethylene polyamine	51.6	1.1	112	84
95-5 polyethylene polyamine	46.8	1.3	107	81
90-10 polyethylene polyamine	40.2	1.2	99	79
85-15 polyethylene polyamine	36.7	1.6	96	78
80-20 polyethylene polyamine	32.8	1.8	92	76

polyamine) reduces n values, as can be shown. The autocatalytic curing of both hardeners occurs at almost the exact grade, as evidenced by the identical values of m . According to the autocatalytic model, Figure 8 compares the experimental data and the graph depicted using the model parameters calculated above. The experimental results and the cure kinetic model are in good accord in dynamic scans.

3.2. Epoxy Resins with Cured Mechanical Properties. Tensile test results for curing formulations are summarised in Table 5. The structural changes in composites have a substantial influence on their mechanical characteristics. Because the microphase zones have the elasticity of polypropylene, they weaken the overall tensile strength of composites. As the percentage of polyurethane in the composition and the elongation increase, the tensile strength decreases. Because of the lengthy curing process, composites with a more uniform structure are formed, which improves their mechanical properties.

4. Conclusion

This study has examined the curing dynamics and mechanical characteristics of bisphenol A diglycidyl ether-based epoxy resin with the polymer of aliphatic polyamine or a combination of less molecular aromatic amines. Networks are created by amine hardeners that respond with epoxy to form linear oligomers, followed by secondary amines that react with epoxy oxirane rings obtained in the second phase. A three-stage cure procedure is employed: Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose isoconversional methods are used to evaluate the activation energy as a function of cure degree. E_a and α were shown to be correlated using these approaches, indicating that the curing systems under investigation had autocatalytic effects. Interestingly, among all materials tested, combinations of low molecular weight aromatically substituted alkylamines showed the most significant increase in strength and lengthening when the compositions were dried. Essentially, this means that composites with a more regular structure are better able to withstand mechanical stress because of a more gradual curing process.

Data Availability

The data used to support the findings of this study are included within the article. Further data or information is available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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