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Kinetic Analysis of Structural Acrylic Curing by DSC: Polymerization and Phase Transition Optimization

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Abstract

Differential Scanning Calorimetry (DSC) was used to analyse the thermal properties and curing behaviour of a structural acrylic adhesive at heating rates of 5, 10, and 15 °C/min. The study focused on the curing kinetics, glass transition temperature (T_g), specific rate (k), and activation energy (E_a) of the polymerization reaction. The material is tested according to ASTM 3418 standards. Results showed that increasing the heating rate shifted the endothermic curing occurred at lower temperatures, consistent with kinetic control of the reaction. It was interpreted that higher heating rates delay the curing reaction to higher temperatures due to kinetic control resulting less time for molecular rearrangement. The heat flow in the sample is negative. The T_g exhibited a heating rate dependence, increasing at higher rates due to thermal lag. The transition temperature is clustered between 82 °C to 89 °C . The activation energy, determined using Ozawa-Flynn method, was found to be 57.81 KJ/mol, indicating the energy barrier for the curing process. These findings highlighted the trade-off between heating rate and curing quality: slower rates ensure thorough crosslinking but prolong processing, while faster rates save time but risk residual stresses or incomplete curing. The outcome provides critical insights into the thermal behaviour of structural acrylics, aiding in the optimization of curing conditions for industrial applications

Keywords: DSC, structural acrylic, heating rate, curing kinetics, activation energy, specific heat capacity, glass transition temperature

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INTRODUCTION

Structural adhesives are designed to form permanent, load-bearing joints between rigid, high-strength adherends [1]. They have been used commercially for over 50 years [2]. Structural adhesives offer numerous benefits, such as being cost-efficient, fast, allowing for homogeneous stress distribution, providing high specific strength, and offering design flexibility [3,4]. Historically, some of the first structural adhesives were developed for the aircraft industry [5].

Briggs, P. C et al, [2] examined the historical development of methacrylate adhesive systems, covering both first- and second-generation products, as well as advanced technology products. The term ‘second generation acrylic’ or SGA was introduced to distinguish these products from the earlier versions that utilised benzoyl peroxide and tertiary amines, which were referred to as ‘first generation’ products. The main advantages of SGAs are

enhanced toughness and impact strength of metal-to-metal connections, along with the capability to bond metal surfaces, including those that are oily, with minimal or no surface preparation required. They proved to be efficient as alternatives to solvent cements, with a composition of '100% solids.' Advanced reactive acrylics have developed to match or surpass epoxies and polyurethanes in demanding bonding applications, particularly those involving thermoplastics, composites, and metal combinations [2].

Acrylic adhesives, are formulated from acrylate and methacrylate monomers [2]. The leading and commercially viable structural acrylic adhesives consist of polymerizable blends of polymers that are either dispersed or dissolved in methyl methacrylate (MMA) monomer. [4]. These products are generally provided in two distinct parts. One component comprises a peroxide compound, serving as an oxidising agent, while the second consists of an amine or metal salt, acting as a reducing agent [2]. When these components are combined, they undergo a reaction that triggers the free-radical polymerisation of the MMA monomer [2]. The essential elements in acrylic adhesive formulations consist of monomers, tougheners, and catalyst systems. Monofunctional methacrylates are commonly utilised in structural acrylics to attain a reduced crosslink density, which is essential for enhancing the toughness of the acrylic matrix [6].

The process of toughening incorporates agents like chlorosulfonated polyethylene. Grafting techniques facilitate the formation of chemical connections between the acrylic matrix and the rubbery toughener phase, thereby improving toughening [6]. The combination of acrylic polyol resins with epoxy polyol resin (DGEBA), along with the application of a polyisocyanate hardener, can markedly enhance toughness in comparison to solely using acrylic resins [7]. Ramsi Rau et al. [7] demonstrated that a composition consisting of 90 wt% acrylic resin and 10 wt% DGEBA exhibited favourable adhesion and impact resistance properties [7].

- Bonding low energy surfaces, especially polyolefins, without extensive surface preparation presents a notable challenge. However, developments in organoborane chemistry have addressed this [2]. Methacrylate is preferred over acrylates due to its ease of synthesis, performance, speed of cure, and lower oxygen sensitivity . Methacrylic acid is used in some formulations to improve adhesion to metal and raise temperature resistance, although it has an objectionable odour [6].
- Commercial acrylics have been evaluated for bonding metals, fiberglass, plastics, and oily/unprepared metals and are considered comparable to flexible two-part epoxy adhesives [6].
- Pressure sensitive adhesives create a bond when pressure is applied and can be removed without leaving any residue. The mechanical properties, including tack, shear resistance, and peel strength, are significantly influenced by the bulk viscoelastic properties [8]. S. Sun et al. [8] reviewed that a good adhesive needs appropriate rheological properties, surface energies, roughness, and cavitation. Surface roughness plays a critical role in adhesion properties. The interaction between tackifier and base polymer plays a crucial role in determining the ultimate characteristics of pressure-sensitive adhesives [8].
- Structural acrylic adhesives demonstrate adequate strength and toughness when subjected to static conditions at room temperature. Nonetheless, given that the Tg of many materials typically falls below 100°C, their fracture behaviour can exhibit significant dependence on both time and temperature. Below the glass transition temperature, the fracture energy of methacrylate adhesives was observed to rise with increasing temperature, while above the glass transition temperature, the fracture energy typically declines [9]. The rate of fatigue crack growth (FCG) may diminish as joint thickness increases, while fracture toughness tends to rise. This phenomenon is linked to the constraint effect on the size of the plastic zone within the adhesive layer. Increasing thickness can eliminate constraints, resulting in enhanced plasticity and improved crack resistance [1].

Thermal Behaviour of Structural Acrylic

The incorporation of elastomer toughening additives can have a notable impact on the Tg of the cured adhesive. When there is good compatibility between the poly (MMA) and the elastomer, the Tg is

reduced. Conversely, if there is incompatibility, the elastomer tends to form discrete particles, leaving the T_g unaffected [2]. Briggs P. C et al [2] demonstrated that phase separation of the rubber phase may take place during curing, resulting in two separate Tg values. An increase in elastomer content may result in a minor reduction of the glass transition temperature of the main phase. The glass transition temperature of the cured adhesive constrains its performance at elevated temperatures. This constraint can be somewhat mitigated by enhancing the cross-link density through the use of difunctional and polyfunctional methacrylates, although this method does have its own limitations [2].

Structural acrylic adhesives undergo curing through a free radical polymerisation mechanism that is initiated by a redox system, usually consisting of a two-part system that is mixed immediately before application [2,6]. Control of the exotherm is important, especially for thick bond cross-sections, to reduce outgassing. The cure profile, including a rapid cure after a delay time, is a significant advantage [2]. Curing temperature and post-curing can significantly affect the thermal and mechanical properties and the extent of cross-linking [5]. A desirable cross-linking density is essential for achieving optimal properties [7]. Cross-linking monomers generally improve heat and solvent resistance [2]. Polyacrylic acid decomposes thermally in steps, involving water evolution (anhydride formation) and carbon dioxide evolution (anhydride decomposition) [11,12]. Grafting acrylic monomers onto cellulose can increase its thermal stability [12]. Thermal analysis techniques like DSC and TGA are used to characterize thermal stability and decomposition [11-13].

Temperature significantly affects mechanical properties and fracture behaviour. Lower temperatures and higher loading rates increase maximum stress but decrease elongation, making the adhesive more brittle. Higher temperatures and loading rates can increase fracture toughness, potentially doubling energy compared to room temperature and slower rates, while stick-slip crack propagation occurs at lower temperatures [9]. Higher temperatures generally lead to shorter fatigue life in adhesive joints, particularly when the temperature is near or above the adhesive's glass transition temperature [1].

Experimental Procedure

DSC is extensively used to characterize the curing or hardening process of adhesives [17-21]. This includes determining the heat of cure [18-21], reaction rate [16-17, 20-21], kinetics [16-17, 20-21], and degree of cure [20,21]. Kinetic model Flynn-Wall-Ozawa, is applied to DSC data to analyze cure kinetics [18, 20]. The experimental procedure for DSC analysis of the structural acrylic adhesive began with sample preparation, where approximately 5 mg of the uncured clear structural acrylic adhesive was precisely weighed using a microbalance and loaded into a standard aluminum DSC crucible with a non-hermetic lid to allow gas exchange. A reference was established using an empty aluminum pan. The DSC instrument was calibrated using high-purity indium (In) and zinc (Zn) standards to ensure temperature and heat flow accuracy. Prior to testing, the system underwent purging with nitrogen (N_2) at a flow rate of 50 mL/min to avert oxidative degradation. Additionally, a baseline correction was executed using an empty pan scan to remove any instrumental artefacts.

Dynamic DSC scans were conducted at heating rates of 5, 10, and 15 Kcal/min, at temperatures ranging between 30°C to 300°C to ensure complete curing. Each run included an optional isothermal hold segment to study curing kinetics and, in some cases, a controlled cooling cycle to analyze post-cure behaviour. The specific heat capacity (Cp) was calculated using a sapphire standard as a reference, while the activation energy (Ea) of the curing reaction was estimated using the Ozawa-Flynn method based on multi-heating-rate data. To ensure reproducibility, each heating rate condition was tested in triplicate. The final results, including curing temperatures, T_g, C_p, and E_a were compiled for comparative analysis across different heating rates.

RESULTS AND DISCUSSION

DSC Analysis

DSC analysis has been performed to the structural acrylic sample at the heating rates of 5, 10 and 15 Kcal/min. The DSC thermograms of the structural acrylic adhesive revealed critical insights into its

curing behavior and thermal properties. The negative sign indicates the reaction to be purely exothermic representing the heat released during the polymerization and cross-linking, confirming its exothermic nature. From Figure 1 it was noted that at 5 °C/min, the curing reaction exhibited a broad exothermic peak initiating around 81.96 °C , indicating a gradual and uniform polymerization process. In contrast, at 15 °C/min, the reaction shifted to higher temperatures, starting near 88.89°C, reflecting kinetic limitations due to reduced time for molecular rearrangement. The 10 °C/min scan displayed an intermediate trend, with curing onset at 89.19°C , striking a balance between reaction control and processing speed. The observed peak broadening at slower heating rates suggests better heat distribution and more complete crosslinking, while the sharper peaks at faster rates imply rapid but potentially incomplete curing. The summarized reaction temperatures are mentioned in Table 1 for the respective heating rates.

Kinetic Modelling

The DSC thermograms enable comprehensive kinetic analysis of the structural acrylic's curing process through several complementary approaches. Since there is no significant peak temperature in the graph according to Figure 2, Kissinger equation cannot be applied. The peak shift analysis is done using Flynn-Wall-Ozawa method an integral approach to determine the kinetic parameters of the acrylic sample. The shift in exothermic peak temperatures (T_p) with heating rate (β) follows characteristic kinetic behaviour described by the Flynn-Wall-Ozawa method as mentioned in Eq-1. The activation energy (E_a) of the sample is calculated from the slope (m) of the Ozawa plot as shown in Figure 3. The equation for pre-exponential factor is mentioned in Eq-3.

$$\log(\beta) = A - 0.4567\frac{E_a}{RT_p} \qquad Eq - \tag{1}$$

$$E_a = R\,x\,(-m) \qquad Eq - \tag{2}$$

$$A = \frac{\beta E e^{\left(\frac{E}{RT}\right)}}{\frac{1}{RT_p^2}} \qquad Eq - \tag{3}$$

$$k = A\,e^{-\frac{E}{RT_p}} \qquad Eq - \tag{4}$$

Figure 1. Clear structural acrylic.

Table 1. Temperature ranges in DSC analysis.

Heating rate (°C/min)	Glass transition temperature (T_g) (°C)
5	81.96
10	89.19
15	88.89

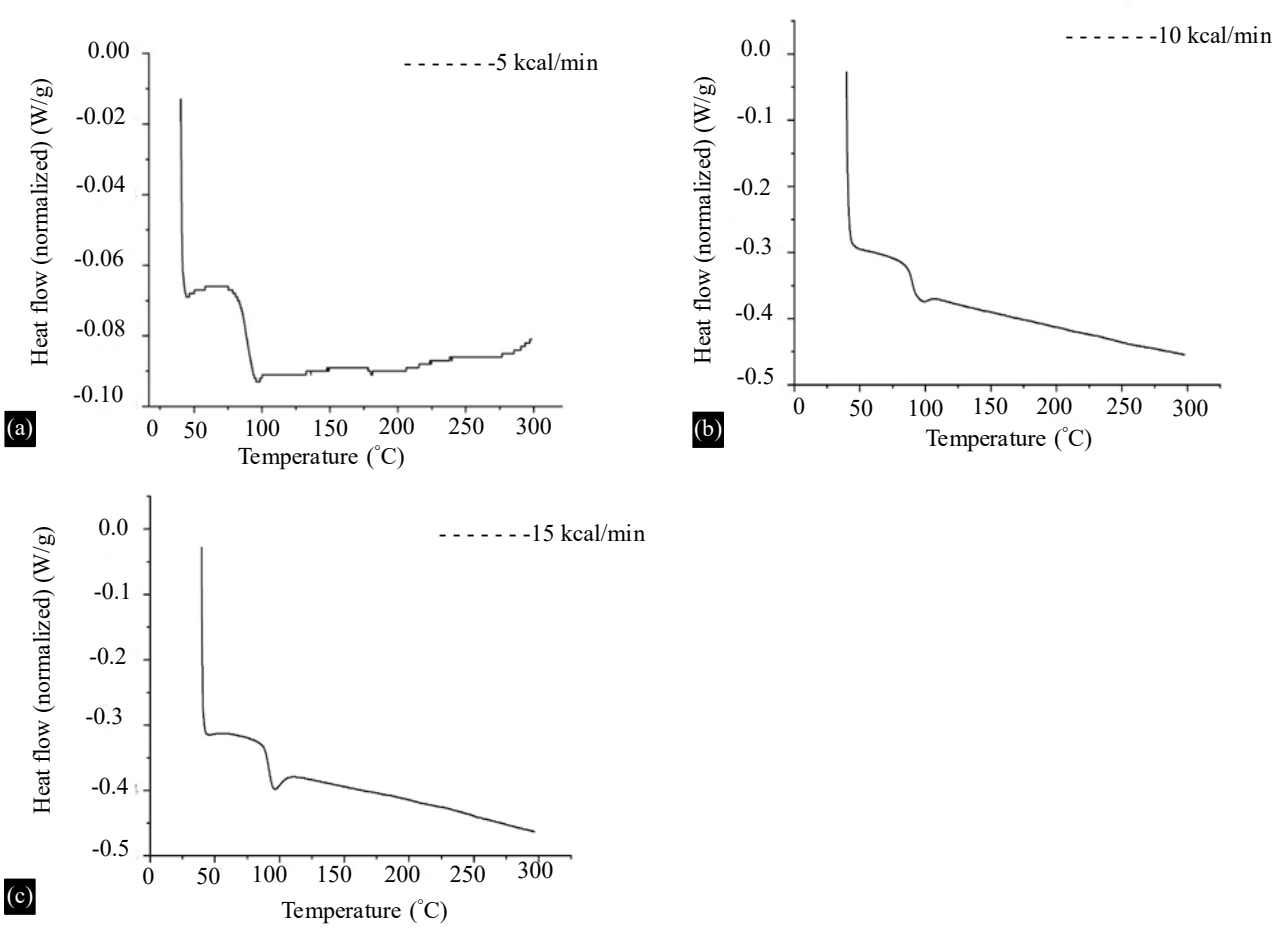

Figure2. Heat flow (Q) vs. Temperature (^{0}C) at different heating rate.(a) 5 Kcal/min (b) 10 Kcal/min (c) 15 Kcal/min

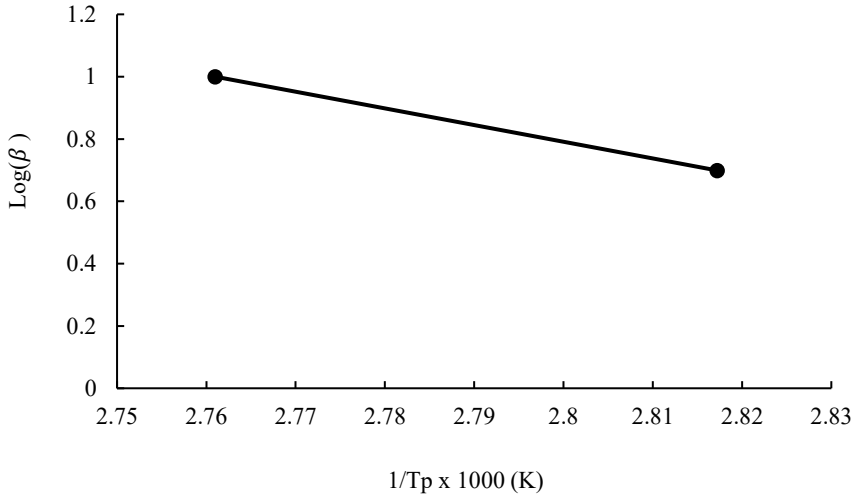

Figure 3. log (β) vs. ($1/T_P$ x 1000) temperature (K^{-1}).

The equation for specific heat rate (k) is given in eq-4. The observed peak temperatures from Table 1 as 81.96 ºC, 89.19 ºC, 88.89 ºC. Graph is plotted between logarithm of heating rate and inverse of peak temperature ($1/T_p$) ref Figure 3. 5 ºC /min, 10 ºC /min are considered, since there is no significant difference in 10 C/min and 15 C/min heating rates.

The activation energy (E_a) was found as 57.14 kJ/mol, this is 15.22% less than acrylic acid, as its activation energy was found out as 67.4 kJ/mol by L. Qiu et al, [13]. Low activation energy leads to rapid, self-sustaining curing process, consistent with the free-radical polymerization mechanism which defines amorphous nature of structural acrylic adhesives.

Post-Cure Glass Transition (T_g) Analysis

The glass transition temperature values can shift to higher temperatures with aging, potentially due to increased molecular interaction like hydrogen bonding [14]. Drying temperature can influence the T_g of poly acrylic acid and lead to anhydride formation [10]. Tg is considered a critical property when selecting an adhesive, and aiming for a cured resin Tg approximately 30°C above the operational temperature is suggested. The limited temperature range of 82−89 ^{0}C indicates that this adhesive is suitable for applications at or below this threshold, allowing designers to anticipate their performance without the need to consider a broad spectrum of Tg values. The consistency of this predictability is crucial for applications such as bonding automotive components or electronics, where precise thermal conditions are anticipated. Water absorption can cause the T_g to shift to lower temperatures and may result in the appearance of two peaks [5]. The sample is initially heated till the curing temperature and cooled down to room temperature rapidly. T_g is typically a change in the sample state from glassy to ruby, often characterized by step change in heat capacity [15]. In case of amorphous material, the glass transition temperature (T_g) is considered as peak temperature (T_p). This peak in DSC is latent heat event, which is a change in heat flow associated with melting or crystallization [16]. As curing advances, the molecular network of the adhesive forms and develops, leading to decreased molecular mobility [8]. The glass transition temperature of amorphous material is indicated by the shift in baseline of the graph from Figure 1. The transition of structural acrylic is depicted in Figure 4. T_g is also critical for predicting material transitions from rigid to flexible states [17]. Briggs, P. C et al, [2] reviewed the glass transition temperature ranges of several structural acrylic materials. However, the T_g ranges between 80-120 ^{0}C. A typical poly methyl methacrylate exhibited the glass transition state at 100 ^{0}C [2].

Specific Heat Capacity (C_p) and Arrhenius Plot

From the obtained results depicted in Figure 2, there are no detectable exothermic curing peaks in the experimented temperature range of 0 ºC - 300 ºC. However, the specific heat rate of the sample is found through the exothermic transitions that are obtained as glass transitions T_g. The analyzed thermal behavior for the observed glass transitions are mentioned in Table 2. The decrease in the specific heat rate is due to the reduced molecular mobility. However, the heating rate affects the apparent C_p due to thermal lag. The Arrhenius plot depicted in Figure 5, is drawn between the specific heat rate (k) and ($1/T_P$) as shown in Figure 4.

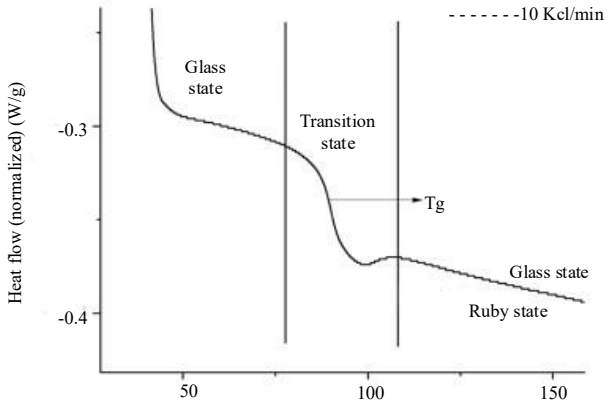

Figure 4. Glass transition of structural acrylic at 10 Kcal/min

Table 2. Specific heat capacity (C_p).

Heating rate (°C/min)	Midpoint temperature (T_g)	Apparent C_p jump (J/g°C)
5	81.96	~0.15
10	89.19	~0.12
15	88.89	~0.10

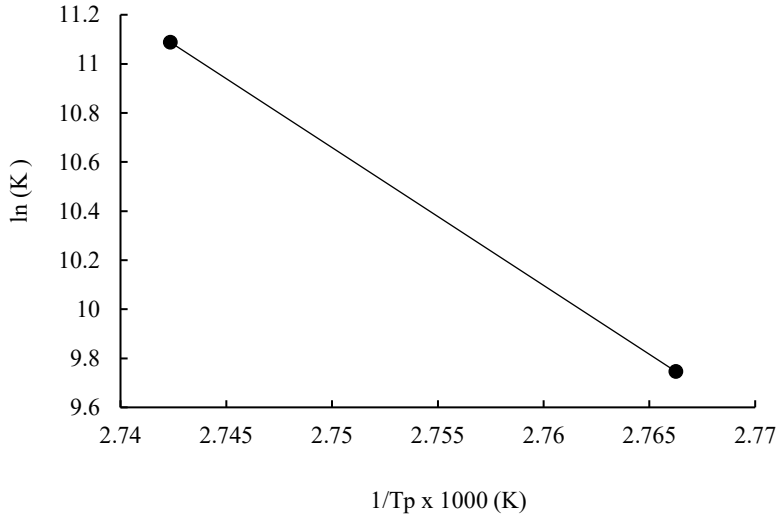

Figure 5. Arrhenius plot for specific heat rate.

CONCLUSION

The following observations are made upon performing the thermal analysis to structural acrylic adhesive:

- There is significant exothermic curve in the graph as it is purely endothermic.
- The obtained glass transition temperatures concluded the material structural acrylic as uncured adhesive.
- The broader peak at 5 °C/min suggests more uniform heat distribution and gradual curing.
- The sharper peak at 10 °C/min indicates rapid polymerization, which may lead to incomplete curing if not held at high temperatures long enough.
- 10 °C/min was considered the optimum heating rate for transparent structural acrylic . It indicated gradual polymerization.
- The obtained activation energy is $E_a < 60$ KJ/mol enabling fast and speed curing, thus saving energy.
- The specific heat capacity varied with temperature and heating rate, reflecting changes in molecular mobility during curing.
- The material is concluded to be pure amorphous.

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