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Comparative Thermal Stability of Structural Acrylic and Polyurethane Adhesives under High Heating Rate Conditions

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Abstract

This study examines the thermal stability and degradation characteristics of structural acrylic and polyurethane adhesives through Differential Scanning Calorimetry (DSC) at an elevated heating rate of 15 °C/min. The purpose of this study is to assess the impact of rapid thermal excitation on the volatile loss of adhesives, their curing behaviour, and thermal decomposition profiles elements that are essential in high-speed manufacturing and thermally challenging settings. The findings indicated that both materials displayed initial endothermic behaviour attributed to the evaporation of volatile components, with polyurethane demonstrating a more significant reaction, probably due to the release of plasticisers and moisture. Structural acrylic exhibits a clearly defined glass transition occurring at 88.9°C, succeeded by a broad exothermic region 120–250°C, which suggests post-curing or further crosslinking processes. In contrast, polyurethane exhibits a wider transition zone from 100–200°C, attributed to microphase segmental rearrangements, with limited indications of additional curing and glass transitions being formed at 125°C and 225°C. The onset of thermal degradation for both materials occurs at approximately 250°C. The results provide valuable insights for choosing materials in thermally demanding bonding processes and advocate for the application of acrylics in scenarios that necessitate enhanced thermal stability and durability during rapid processing conditions.

Keywords: DSC, structural acrylic, high heating rate, polyurethane, initial volatile loss, glass transition, crosslinking, thermal stability

INTRODUCTION

PUR adhesives are valued for their excellent adhesion, flexibility, good low-temperature performance, and controllable cure speeds [1,8]. Polyurethane (PUR) elastomers are a versatile class of organic polymers extensively used in various industries, including building and construction, transportation, medicine, and furniture production [1,3]. Synthesis usually occurs via a polyaddition reaction involving a polyol and either a diisocyanate or a polyisocyanate [1,3,5]. The basic formation of polyurethanes involves the polyaddition of polyols and isocyanates, often with chain extenders and catalysts, leading to a segmented structure of hard and soft domains. The precise composition and structure of these segments, influenced by the choice of raw materials and their ratios, dictate the degree of microphase separation, hydrogen bonding, and cross-linking, which in turn defines the final polyurethane elastomer [1,9]. The varied and

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beneficial characteristics of PURs encompass significant impact strength, commendable elasticity, substantial elongation, resistance to abrasion, exceptional durability against oils and solvents, and notable tear resistance [1]. This broad spectrum of applications is intricately linked to their characteristic chemical group, the urethane group, formed by the reaction of a hydroxyl and an isocyanate group [1,2].

The fundamental aspect of PUR structure is their two-phase system, consisting of chemically distinct hard segments (HSs) and soft segments (SSs). The elastomeric behaviour of PUR systems is primarily attributed to the microphase separation of these hard and soft segments [1]. Due to their inherent thermodynamic incompatibility, HSs and SSs tend to segregate, forming rigid hard domains within an elastomeric soft matrix [1,3,9]. These rigid domains effectively reinforce the elastomeric matrix, functioning like covalent linkages in chemically cross-linked elastomers [2]. The degree of microphase separation and the effectiveness of these physical cross-links are crucial for the mechanical stability and properties of the final polymer [1,3,9].

Similarly, on the other hand structural acrylic adhesives are considered structural adhesives due to their ability to form permanent, load-bearing joints [11]. These adhesives are closely related to anaerobic adhesives, sharing many aspects of their chemistry, compositions, and terminology. Both are free radical cure systems that achieve high performance from a room temperature cure and are initiated by surface reactions. They are often compared to two-part room temperature-curing epoxies, with their properties, such as high peel strength, shear strength, and chemical resistance, comparing favourably [10].

Anaerobics cure well in oxygen-free environments, such as closely mated assemblies, since oxygen slows free radical polymerisation. They can be one-part systems that initiate redox on active metal substrates. The second component curative is applied as a primer and reacts with the adhesive to induce polymerisation, making structural adhesives "no mix" two-part systems [10].

The thermal stability of a polymer, which can also be referred to as thermal durability or heat resistance, is inherently connected to its chemical structure, specifically the bond energy between individual atoms. The energy required for bond dissociation into radicals dictates a material's resistance to change under thermal stress. Strong bonds for example multiple bonds like C=N, C=C, or bonds containing elements like boron, nitrogen, or silicon such as C-F, B-O, B-N, Si-O) contribute to higher thermostability. In polyurethanes, thermal resistance is primarily linked to the thermal dissociation temperature of the weakest bonds present in their structure [1,7]. Specific dissociation temperatures for various bonds found in PURs include: Allofanian bonds: 106 °C, Biuret bonds: 130–145 °C, Urethane bonds: 200 °C, Carbodiimide bonds: 240 °C, Urea bonds: 250 °C, Ester bonds: 260 °C, Isocyanurate bonds: 300 °C, Ether bonds: 350 °C [1,7]. Acrylic polyols decompose due to polyol backbone breakage or random scission from weak spots like bulky and ester groups. Initially, highly stressed crosslinks and other weak links in heavily crosslinked polymers can break, followed by random scission of the linear chains generated. The thermal stability of acrylic polyols decreases with an increase in hydroxyl value, which is reflected in a decrease in the activation energy of decomposition [12].

DSC revealed the glass transition temperature of the soft segment, typically around -64 °C for polypropylene glycol-based PURs, which remains relatively constant with increasing chain extender content due to consistent polyol content [1]. For polytetrahydrofuran (PTHF)-based elastomers, T_g values were observed around -69 °C [3]. In contrast, the glass transition temperature of the hard segment (T_g, HS) is difficult to evaluate clearly by DSC [6]. The cold crystallisation and subsequent melting phenomena during heating, particularly in polyurethane elastomers containing long-chained polyetherol components like PTHF2000 and PTHF2900. This effect is usually prohibited when the polytetrahydrofuran is integrated into an elastomeric network [3]. The enthalpy of melting (ΔH_m) tends to increase with increasing chain extender content, indicating an increase in the crystalline phase and improved hard segment phase separation within the PUR structure [1]. The addition of 1,4-butanediol (which forms physical cross-links) reduces the cold crystallisation effect, while the addition of glycerol

which forms chemical cross-links can prevent it entirely [3].

Increasing the hard segment length within the PU structure enhances hard segment motion, making it more difficult to move at low temperatures [1]. Increasing the overall crystallinity level enhances thermal stability [1,7]. A high level of crystalline ordering, achieved by increasing chain extender content, also improves thermal conductivity. The soft segment glass transition temperature (T_g, SS) was consistently observed to be approximately -64°C through DSC, and ranged from -57°C to -52°C when measured by DMA. The glass transition temperature of the hard segment (T_g, HS), as determined by DMA, showed an increasing trend from 10°C to 93°C with higher monoethylene glycol (mEG) content [1]. A synthesised castor oil-based PU adhesive demonstrated stability up to 250°C. Its degradation occurred in two stages: the first starting at 270°C, attributed to the breaking of urethane bonds, and the second at approximately 470°C, due to the breaking of high-energy double and single bonds [8]. The degradation of formed polyurethane chains can contribute to the overall heat flow near 460 K [5]. The thermal dissociation temperatures of various bonds in PUR-PIR foams are as follows: urethane bonds at 200°C, ester bonds at 260°C, ether bonds at 350°C, allophanate bonds at 106°C, urea bonds at 250°C, biuret bonds ranging from 130-145°C, isocyanurate bonds near 300°C, and carbodiimide bonds at about 240°C [7].

The thermal decomposition of hydroxyl terminated polyether (HTPE) based polyurethane in mixed systems was observed at approximately 378°C, 385°C, and 387°C. The distinctive two-step decomposition of HTPE-based polyurethane, which is initiated by endothermic melting and involves exothermic depolymerisation and significant decomposition, plays a crucial role in enhancing the thermal safety of HTPE-based composites [4]. The modification of foams with a new polyol (E16) resulted in a slight reduction in the temperature of the initial weight loss (T1), decreasing from 77°C to 75°C. Additionally, there was a significant drop in the onset of decomposition (T2), which decreased from 293°C to 219°C. This can be linked to the inferior thermal stability of E16 in comparison to the industrial polyol, Rokopol RF-551. The E16 polyol exhibited a 5% mass reduction at 170°C and a 10% reduction at 212°C. The T_{max} recorded was 366°C at 55% mass loss, in contrast to Rokopol RF-551, which exhibited a T_{max} of 411°C at 70% mass loss [7].

METHODOLOGY

This study connected the selection of two commercially available adhesive systems: a structural acrylic adhesive (3M Clear Acrylic Sheet) and a polyurethane adhesive (3M Polyurethane PU 540 series) shown in Fig. 1, both of which are frequently utilised in engineering bonding applications. The structural acrylic offers good material bonding and shear strength. This materials is light weight yet durable solution for structural support with 99% transparency. Polyurethane adhesive offers moisture curing that forms permanent elastic bond. These adhesives were acquired in their cured or semi-cured state according to supplier specifications, guaranteeing uniformity in formulation and sample preparation.

Sample Preparation

Using a precise microtome blade, small samples of each adhesive, ranging from approximately 5 to 10 milligrams, were meticulously sectioned from the bulk material. This was done to guarantee that the mass and thermal contact were uniform. In order to reduce the amount of ambient moisture interference and oxidation that occurred during the heating process, the samples were hermetically sealed in conventional aluminium DSC pans.

The thermal analysis was performed using a Differential Scanning Calorimetry setup equipped with a high-sensitivity sensor and nitrogen purge environment to maintain inert conditions. Each sample was subjected to a dynamic heating cycle from room temperature approximately 25°C to 400°C at a constant heating rate of 15 ºC/min. This elevated rate was chosen to simulate rapid thermal events, such as those occurring in industrial processing or fire exposure scenarios. The baseline was corrected using an empty pan reference, and heat flow (mW) versus temperature (°C) data were recorded. The thermograms were analysed to identify key thermal transitions, including glass transition temperature (T_g), curing exotherms, and thermal degradation onset. Particular attention was given to the onset, peak, and endset

of each thermal event to compare the adhesives' thermal stability profiles.

Figure 1. Structural acrylic and polyurethane.

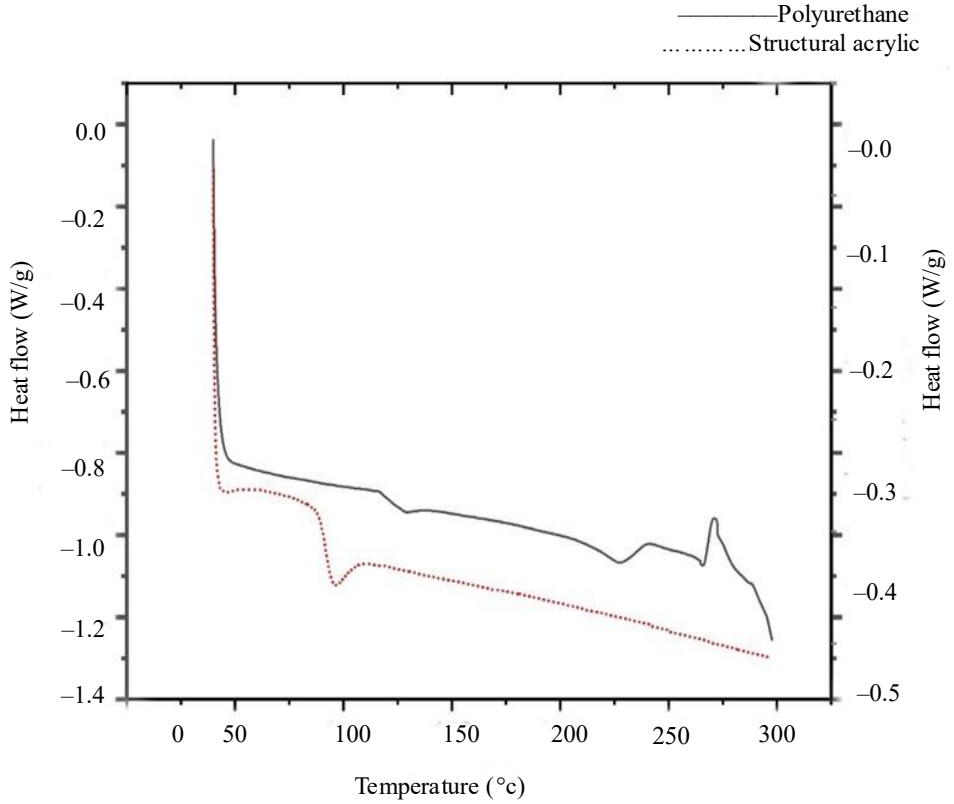

Figure 2. DSC thermograms of structural acrylic and polyurethane at higher heating rates.

Table 1. Comparative summary: effect of high heating rate.

Parameter	Structural Acrylic	Polyurethane
Initial Volatile Loss	40–60°C	30–60°C
Softening	90–120°C	100–230°C, soft segments
Glass Transition Temperature (T_g)	88.89 °C	125 °C and 225
Curing	120–250°C	150 Structural Acrylic 200°C
Crosslinking	Major	Possible Minor
Degradation Onset	>250°C	250°C
Thermal Stability	Higher up to 300°C	Lower, major breakdown starts at 250°C

Effect of High Heating Rate	Suppressed transitions, stable profile	Broad, pronounced degradation peaks

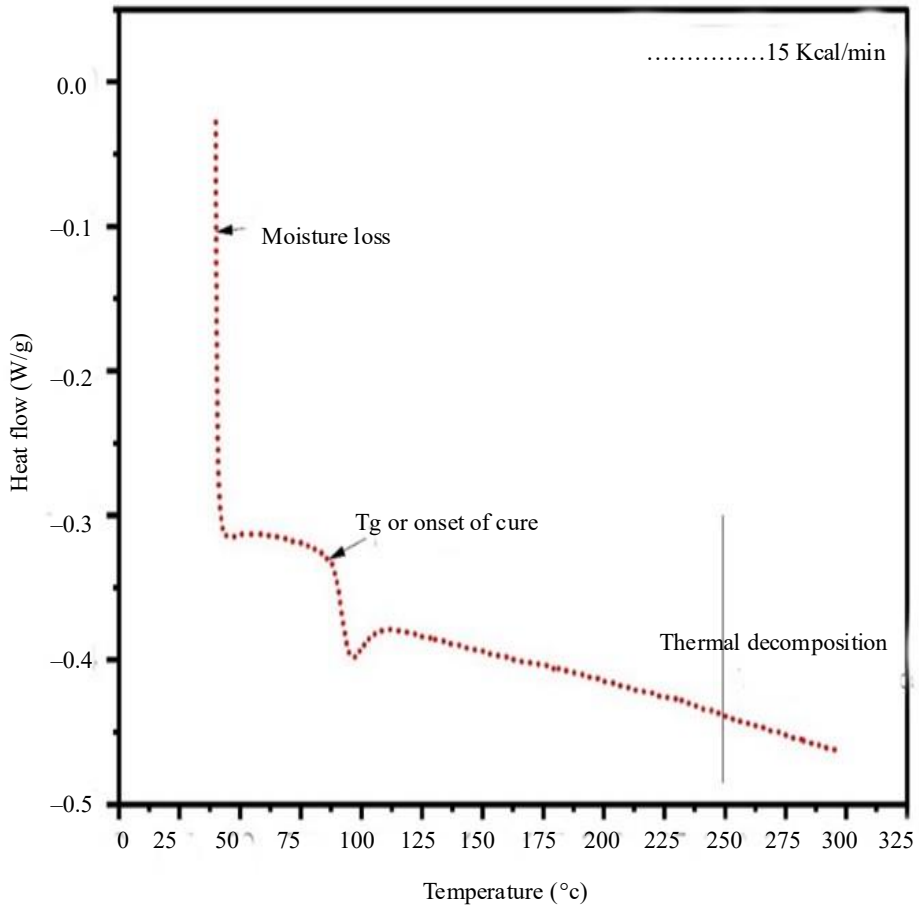

Figure 3. Phase Transitions of structural acrylic at 15^0C/min.

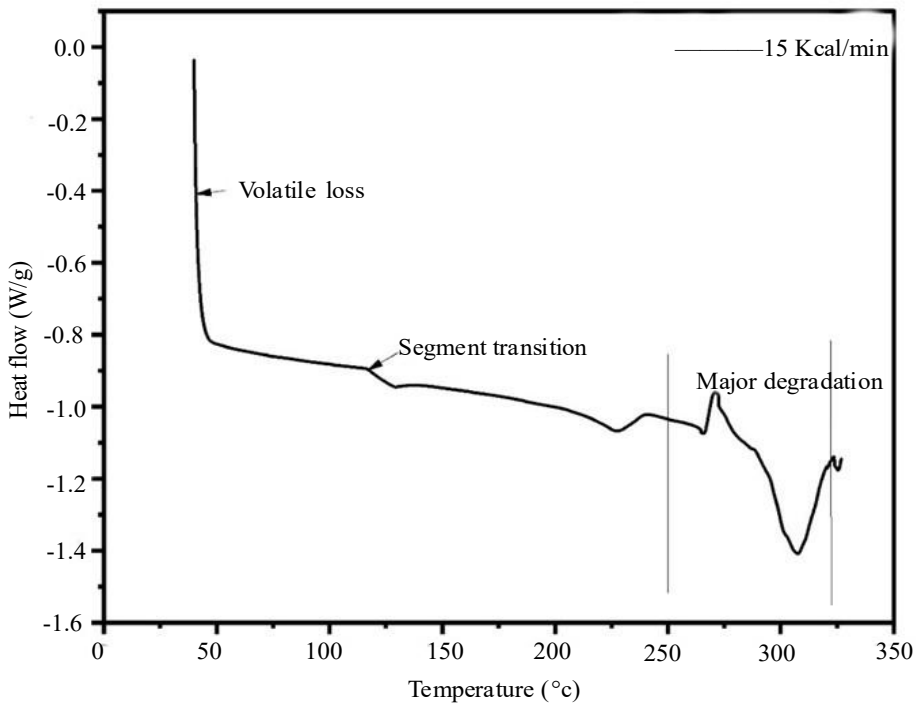

Figure 4. Phase Transitions of polyurethane at 15^0C/min.

RESULTS AND DISCUSSIONS

Figure 2 illustrates the comparison between Structural Acrylic and Polyurethane thermal behaviour at higher heating rates by DSC Thermograms analysis. Both materials exhibit a sharp exothermic drop near room temperature, indicating initial thermal transitions. Polyurethane shows greater thermal stability at high temperatures with distinct thermal transitions. Whereas Structural Acylic gives a more gradual transition and degradation, with a likely lower T_g and Stability. The effect of high heating rate in terms of comparative summary are shown in Table 1.

Initial Volatile Loss

From Figure 3 and Figure4, in the initial phases of heating, both structural acrylic and polyurethane adhesives exhibit notable endothermic behaviour, mainly as a result of volatile loss. In the case of structural acrylic, this phenomnon takes place within a temperature range of roughly 40–60°C, during which moisture and potentially leftover monomeric solvents are eliminated through evaporation. Acrylics have a tendency to absorb moisture from the environment and frequently hold onto unreacted monomers following their synthesis or application, which accounts for this initial thermal reaction. Polyurethanes exhibit a similar initial decline in the 30–60°C range, although this effect is frequently more significant. The presence of plasticisers or low molecular weight additives in polyurethane formulations is a significant factor, as these components tend to volatilise easily. Due to volatilisation, glycerol triacetate (TA), an inert plasticiser, has a gravimetric peak at 121.9 °C for HTPE-based polyurethanes. Due to the polymeric matrix inhibiting evaporation, polyurethane material does not lose mass before disintegration. N-butyl-N-(2-nitroxyethyl)nitramine (NENA), an energetic plasticiser, volatilises before decomposing and loses bulk near 130 °C [4].

Glass Transition (Tg)/Softening Behaviour

The initial volatile loss typically does not have a direct correlation with the glass transition. Glass transition refers to a change in the physical state of the polymer, heavily influenced by its composition. Key factors include the content of hard segments, the type and quantity of chain extenders, the molecular weight of the polyol, and the resulting degree of cross-linking and phase separation [1]. From the above analysis structural acrylic exhibited a relatively distinct glass transition temperature (Tg) or cure initiation point in the 90–120°C range forming Tg at 88.89°C. This is where the polymer matrix transitions from a rigid, glassy state to a more rubbery, flexible state, allowing further chain mobility and crosslinking if unreacted groups are present. In contrast, polyurethane displayed a broader transition zone between 100–230°C, attributed to the segmental mobility of its soft and hard domains resulting in two glass transition temperatures one at 125°C (soft domain) and the other at 225°C (hard domain). Polyurethanes are typically phase-separated materials, with soft polyol-based and hard diisocyanate-derived segments that respond differently to heat. These transitions are not as sharp as in acrylics due to the internal complexity of the polymer architecture.

The broad nature of these thermal events in polyurethane makes it harder to pinpoint a precise Tg, but they still indicate increasing molecular motion as temperature rises.

Crosslinking/Curing

The strength of physical cross-linking is crucial for the mechanical strength of the polymer [9]. Cross-linking directly enhances tensile strength and increases urethane domain rigidity [1].

Trifunctional alcohols, such as glycerol, are specifically mentioned as being responsible for creating covalent three-dimensional linkages or chemical cross-links in PURs [3]. Unlike physical cross-links, conventional rubber-like elastomers achieve their strength primarily through chemical cross-linking [9]. A notable thermal process occurs for structural acrylic within the temperature range of 120°C to 250°C, suggesting the presence of thermal curing or post-curing reactions. The reactions in question entail residual acrylate groups that participate in polymerization or crosslinking, thereby improving the

structural integrity and performance of the adhesive. This behavior is characteristic of structural adhesives designed to cure quickly at higher temperatures. Polyurethane, nonetheless, exhibits minimal or no significant curing activity in this area. At temperatures ranging from 150–200°C, it is possible for some soft segment rearrangements or minor reactions to take place; however, polyurethane adhesives are typically fully reacted or pre-cured during the manufacturing process. The degree of cure of polyurethane at high heating rate is depicted in Fig. 5. Consequently, they do not depend on post-curing during application and exhibit reduced thermal reactivity in this range under elevated heating rates. Above room temperature, 1,4-butanediol increases physical cross-links hard phases and storage modulus. 1,4-butanediol improves hard phase physical cross-links and storage modulus above room temperature. Glycerol cross-links prevent cold crystallisation. Chemical cross-links hinder polymer chains from organizing during heating [3]. Due to hard segment chain length, chain extender presence increases hard segment glass transition temperature (Tg, HS). At large chain extender concentrations, hard segments cross-linking the polyol segment's motion obscures DSC measurements of soft segment Tg, resulting in less ordered soft segments [1].

Thermal Decomposition

The presence or absence of a catalyst can also influence kinetic parameters like apparent activation energy and reaction order, potentially observable through DSC [2]. Raminder Kaur et al., [8] incorporated titanium dioxide (TiO2) into castor oil-based PU adhesives increased the glass transition temperature (Tg), which indicates an enhancement of thermal stability and a favoring of phase separation between hard and soft segments [8]. Thermal degradation for both materials begins near 250°C, but the nature and severity differ significantly. In structural acrylic, this degradation is relatively gradual and typically involves main-chain scission of the polymethacrylate backbone. Because of prior crosslinking, the breakdown is restrained and does not immediately lead to catastrophic loss of material properties. On the contrary, polyurethane degradation is more complex and violent, involving bond cleavage of urethane groups, isocyanurate ring opening, and evolution of gaseous byproducts. Energetic plasticizers like NENA and A3 were observed to decompose before the HTPE based PU polymer matrix itself, whereas an inert plasticizer (TA) showed only a moderate exothermic effect in DSC without a distinguishable boundary [4]. This process is usually exothermic and results in a noticeable drop in mechanical integrity and potential smoke or char formation. The degradation pathway in PU is not only chemical but also structural, leading to broader peaks and significant heat release compared to acrylics. Higher hard segment content can result in narrower and more intense endotherm peaks in DSC [1]. Using a new polyol (E16) in PUR-PIR foams, for example, caused a slight decrease in the temperature of the beginning of decomposition (T2) compared to foams made with an industrial polyol, indicating poorer thermal stability for the new polyol [7].

Maximum Thermal Stability

A polymer's thermal stability is intrinsically linked to its chemical structure and the energy of the bonds between its atoms [1,7]. The presence of multiple bonds like C=N, C=C or bonds containing elements like boron, nitrogen, or silicon such as C-F, B-O, B-N, Si-O that have high energy values contributes to higher thermostability [7]. Polyurethane elastomers based on polypropylene glycol and 4,4′-diphenylmethane diisocyanate showed thermal conductivity increasing from 0.255 to 0.329 W/m.K with higher chain extender content [1].

Structural acrylic maintains thermal stability up to approximately 300°C, with a smooth and slow decline in heat flow after its post-curing reactions. This behavior implies that acrylic adhesives are more suitable for high-temperature applications, especially those that involve brief but intense thermal exposures such as spot curing or heated bonding in assembly lines. On the other hand, polyurethane undergoes progressive thermal degradation starting from around 250°C, with major breakdown occurring before 320°C. This earlier failure under high thermal stress limits polyurethane's application in environments with extreme or rapid heating, even though it remains an excellent material for medium-temperature and flexible bonding solutions.

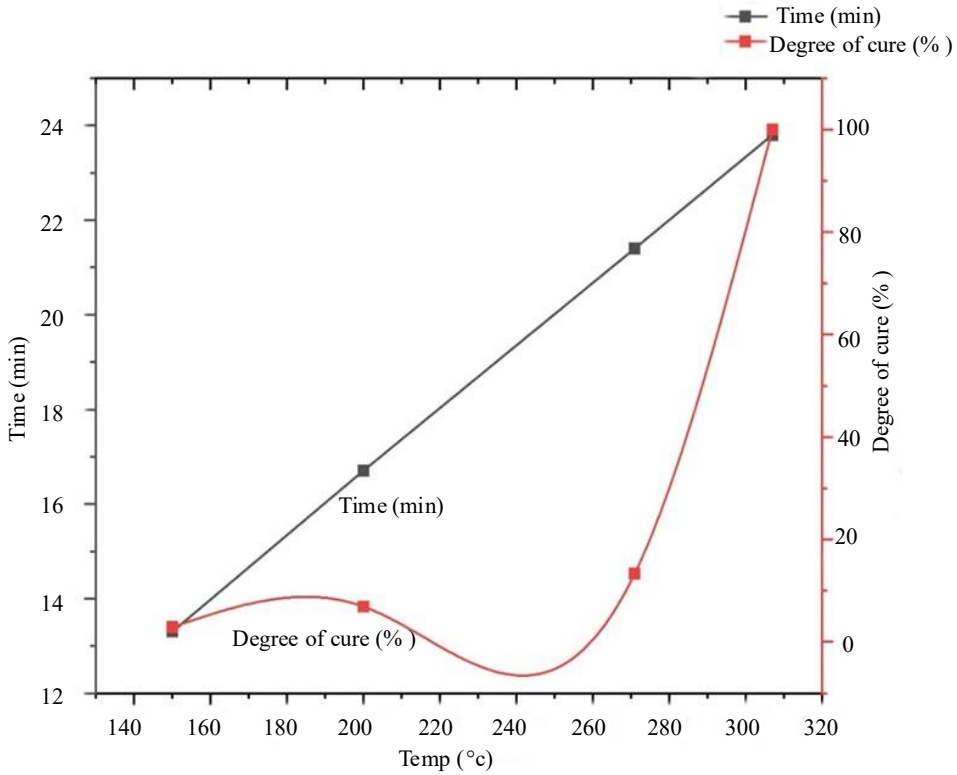

Figure 5. Degree of cure of polyurethane at higher heating rate.

CONCLUSION

The elevated heating rate of 15°C/min compresses thermal transitions and frequently obscures the clarity of phase changes and reactions. In structural acrylic, this leads to altered thermal events, obscuring some of the more subtle transition details while still distinctly illustrating the overall stability and sequential degradation. This observation indicates that structural acrylic adhesives can endure rapid thermal shocks or high-temperature processes without experiencing early degradation. In contrast, polyurethane exhibits extensive and significant degradation phenomena, with distinct indications of multi-phase thermal decomposition. This renders PU less appropriate for high-rate thermal environments; however, its segmented structure facilitates more controlled and elastic behavior in less extreme thermal cycles.

- Structural acrylic adhesives demonstrated exceptional thermal stability when subjected to high heating rates, exhibiting distinct yet subtle transitions along with a postponed degradation process. The capacity to undergo post-curing and maintain integrity at high temperatures renders them suitable for structural and industrial applications that demand durability under thermal stress.
- Structural acrylic experiences a gradual deterioration, remaining stable up to around 300°C, whereas polyurethane demonstrates intricate, multi-phase degradation that concludes below 320°C
- Polyurethane adhesives are known for their versatility and widespread application. However, it demonstrated a multi-step degradation and show reduced thermal stability when subjected to rapid heating conditions.
- The pronounced exothermic peaks observed in polyurethane indicate a swift breakdown of urethane linkages and hard segment structures. The elevated heating rate condenses thermal transitions and may mask subtle thermal occurrences. However, the data distinctly indicate that structural acrylic adhesives exhibit enhanced thermal resilience during rapid heating in comparison to polyurethane.

These materials excel in moderate-temperature applications, particularly for flexible bonding tasks, where their segmented structure and durability can be effectively leveraged without surpassing thermal thresholds.

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