Influence of Chemical Structure on the Thermal and Mechanical Properties of Structural Adhesives

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This study aims to evaluate the influence of the chemical structure of acrylic and epoxy structural adhesives on their thermal and mechanical properties. Differential scanning calorimetry (DSC) and uniaxial tensile strength tests were conducted to assess the characteristic transition temperatures and mechanical properties. The DSC results indicated that the acrylic adhesives have higher glass transition temperatures than the epoxy-based adhesives. Regarding mechanical properties, the epoxy adhesives exhibited greater maximum resistance and lower deformation at break than the acrylic adhesives. The findings revealed that the chemical structure of adhesives significantly influences their thermal and mechanical properties, necessitating careful selection based on the specific application requirements across a wide range of products being developed and commercialized.

Keywords: Structural Adhesive. Chemical Structure. Thermal Properties. Mechanical Properties.

Adhesives are materials applied to surfaces to join items through adhesive bonding [1] permanently. They are responsible for wetting surfaces by spreading at a contact angle close to zero and must harden into a solid, cohesive, and strong material [2] through the curing process. To join high-strength adherents, structural adhesives are increasingly used as an alternative to traditional mechanical joining methods such as rivets, screws, and welding.

Structural adhesives offer several advantages, including application at room temperature, combining bonding and sealing in a single operation, and providing thermal and electrical insulation. They also ensure even stress distribution, a smooth surface appearance, and enhanced resistance to fatigue, vibration, and acoustic damping [3]. Additionally, it is cost-efficient process that allows for a homogeneous distribution of stresses between bonded surfaces under load [4].

A structural adhesive is a substance that joins elements to produce high-modulus, high-strength permanent bonds capable of transmitting structural stresses without losing integrity within design limits [5]. Structural adhesives are widely used in various fields such as aerospace, automotive, electronics, semiconductors, construction, footwear, clothing, and emerging areas like biology and medicine [6].

The main classes of adhesives, categorized by their chemical nature, include epoxy, polyurethane, acrylic, cyanoacrylate (superglue), anaerobic, and high-temperature adhesives [3,4]. Epoxies are the most versatile family of adhesives, known for their excellent adhesion to many substrates and varied properties such as high-temperature resistance, durability, resistance to extreme environments, relatively low curing temperatures (for two-component formulations), ease of use, and low-cost [4,7].

Acrylic adhesives are characterized by their polymerization with acrylate and methacrylate monomers. These adhesives are classified as single component (including anaerobic adhesives, cyanoacrylates, and UV-cured adhesives) or two-component (reactive acrylics). Some notable properties of acrylic adhesives include design flexibility, high strength, fast curing, and tolerating less prepared surfaces [3,4]. They

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exhibit excellent adhesion to various substrates, including aluminum, brass, copper, stainless steel, carbon steel, most plastics, wood, glass, asbestos-cement boards, and hardboard [1].

Studies are being conducted to evaluate structural adhesives' thermal and mechanical properties, including acrylic and epoxy-based adhesives. These studies have observed that the adhesive formulation, including its chemical base and hardener, can significantly influence its properties [8-10]. Considering the differences in adhesive properties according to the chemical structure and the presence of additives in the formulation, as noted in the literature, the present study aims to evaluate the influence of the chemical structure of acrylic and epoxy structural adhesives on their thermal and mechanical properties.

Materials and Methods

In this study, the following adhesives were used: Methacrylate: 1 - Adekit A310 from Sika (A1), and 2 - Araldite® F362 from Huntsman (A2); Epoxy: 1 - Betamate™ 2096 from DuPont (E1), and 2 - Scotch-Weld™ DP420 from 3M (E2).

Tensile strength tests were carried out by ASTM D638, using five Type IV test specimens for each adhesive, produced using a poly(tetrafluoroethylene) (PTFE) mold on an aluminum base. The adhesive components were mixed manually and then placed inside the mold. A vibrating system (shaker sieve with a vibration amplitude of 3.5) was used to reduce the number of bubbles when applying the adhesive to the mold. After 24 hours (for acrylics) and 168 hours (for epoxy), the molded specimens were tested on an Emic universal testing machine, Model DL 2000, with Tesc 2000 data processing software and a 10 kN load cell, at a speed of 5 mm/min. DSC analysis was performed using a TA Q10 V9.9 Build 303 device. For all compositions, samples of approximately 7 mg were heated at 10 °C/min from 20 to 150 °C and then cooled to 20 °C to eliminate the initial thermal history.

After that, the samples were heated again from 20 to 150 °C at the same heating rate to determine the glass transition temperature. The analysis was conducted under a 50 mL/min nitrogen gas flow, used as purge and protection gas.

Results and Discussion

Figure 1a shows the curves of the second heating of the adhesives at 10 °C/min, revealing a deviation from the linear baseline corresponding to the glass transition temperature range (Tg). The DSC curves indicate a slight deviation at average temperatures of approximately 99 °C, 108.1 °C, 47 °C, and 76 °C for adhesives A1, A2, E1, and E2, respectively, indicating the glass transition.

Figure 1b shows that, among the adhesives studied, those with an epoxy chemical base exhibited a lower Tg than the acrylic ones. This may be associated with bulky functional groups in the chemical structure of epoxy adhesives. Functional groups that may be present in the structure of epoxy adhesives cured with the reaction of an epoxy resin composed of bisphenol A diglycidyl ether (DGEBA) and 4,4'-diaminodiphenyl sulfone (DDS) include hydroxy, benzene-ether, alkyl, epoxy rings, benzene-NH2, and benzene-amine groups [11]. Bulky side groups limit the proximity of the polymer chains, and the greater the distance between them, the more quickly they can move, increasing the free volume and consequently decreasing the Tg [12].

The two acrylic adhesives studied have similar Tg values. This similarity can be attributed to both adhesives containing a methyl group on the same carbon as the methacrylate group, which increases the rigidity of the polymer chain, thereby increasing Tg [13,14]. Epoxy adhesives, on the other hand, exhibited different Tg values, suggesting that factors beyond chemical composition, such as the use of different hardeners or the presence of additives, can alter the properties of the adhesives. Additionally, Azúa and colleagues noted that an excess of epoxy groups can undergo a homopolymerization reaction initiated by tertiary

Figure 1. a. DSC curves related to the second heating of the adhesives at 10 °C/min; b. Glass transition temperature of the studied adhesives.

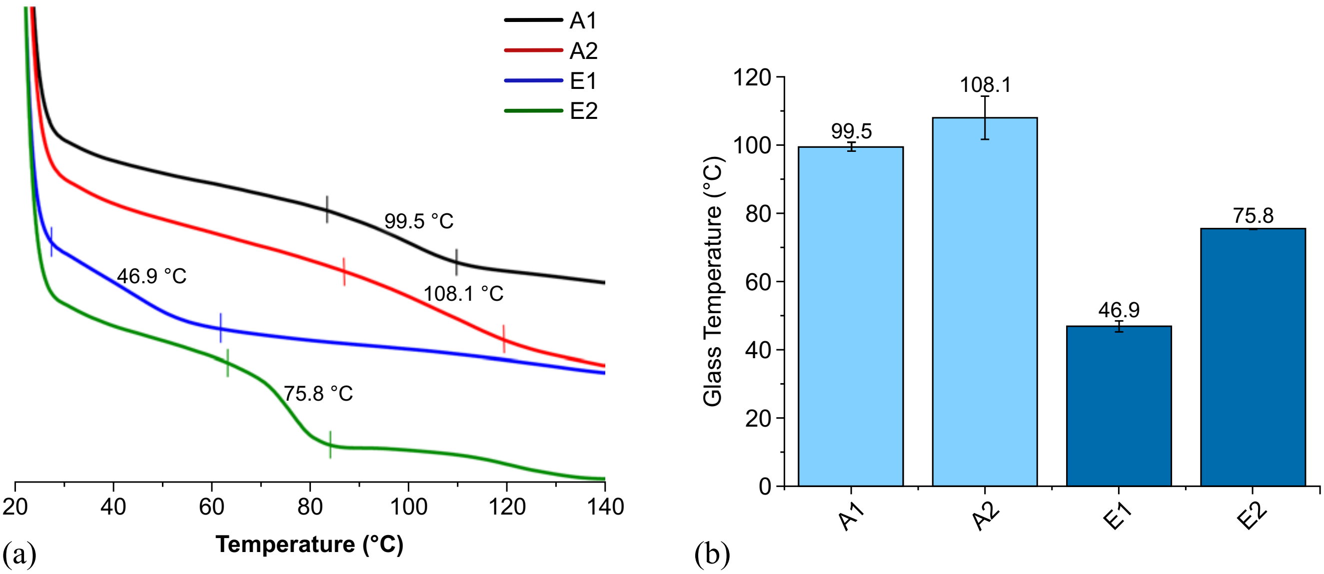
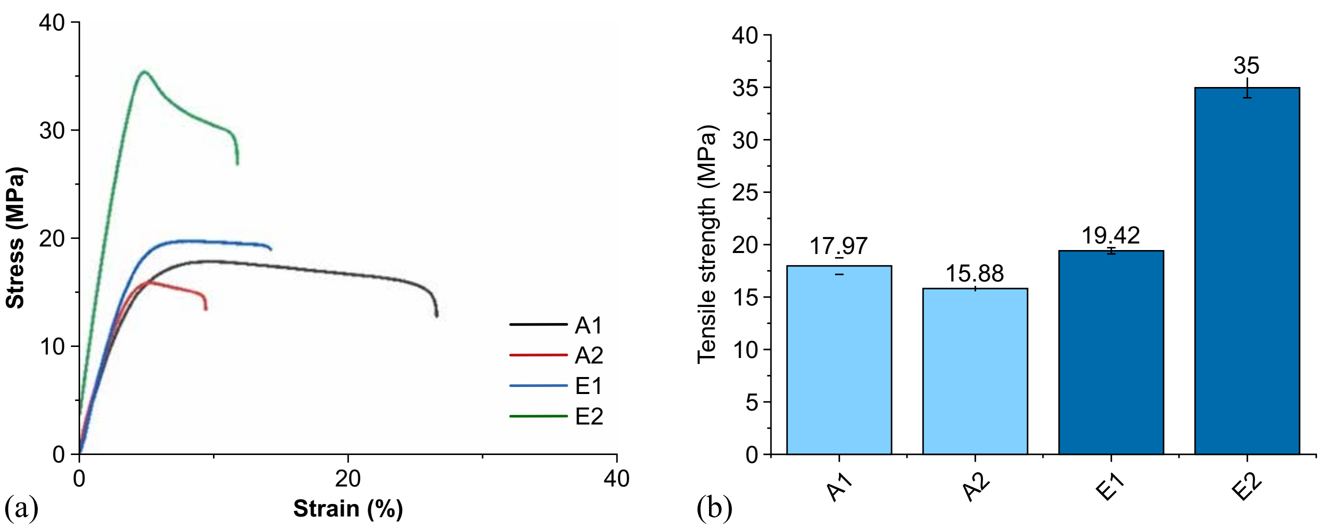


Figure 2. a. Stress x strain curves of the studied adhesives; b. Maximum tensile strength of the studied adhesives.



amines at high temperatures, leading to an increase in Tg [14].

Figure 2 shows the curves of (a) stress *versus* strain and (b) the maximum tensile strength of structural adhesives. The maximum tensile strength values of epoxy adhesives were higher than those observed for acrylic adhesives. As noted with the glass transition temperature, the two acrylic adhesives exhibited similar maximum tensile strength values, around 18 MPa and 16 MPa for adhesives A1 and A2, respectively. Since both acrylic adhesives are based on methacrylate, similar thermal and mechanical behavior is expected. If one of the adhesives were an acrylic with an acrylate group, the results would likely be more significant variation. According to Betz [12], the restricted movement of the methyl group provides methacrylate polymers with higher tensile strength and lower elongation percentages compared to acrylate polymers.

Epoxy adhesives, in turn, presented different maximum resistance values, highlighting that the presence of additives and different compositions in the adhesive formulation can also interfere with the properties, with different thermal and mechanical behavior being observed, even for adhesives with the same chemical base.

Conclusion

This study evaluated the influence of the chemical structure on the thermal (glass transition temperature) and mechanical properties (maximum tensile strength and deformation until rupture) of epoxy and acrylic structural adhesives. The results demonstrate that, in addition to the chemical structure, the presence of different additives and hardeners significantly affects the properties of structural adhesives.

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