MECHANICAL PROPERTIES OF EPOXY STRUCTURAL ADHESIVES AS A FUNCTION OF CURING TIME

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Abstract: The present study aims to evaluate the influence of curing time on the tensile and shear mechanical properties of epoxy structural adhesives. From the results, it was observed that, depending on the adhesive used, the curing time may influence the shear strength properties of bonded metal joints (steel SAE 1020) and tensile strength. For Betamate™ 2096, an increase in mechanical properties was observed when a curing time of 7 days was used at room temperature, while for Scotch-Weld™ DP420NS Black, the results remained unchanged, regardless of the curing time. This influence is associated with the curing conditions, which depend on the catalyst and additives used in the formulation when comparing materials with the same chemical base.

Keywords: Structural adhesives; epoxy; shear test; tensile strength.

PROPRIEDADES MECÂNICAS DE ADESIVOS ESTRUTURAIS EPÓXI EM FUNÇÃO DO TEMPO DE CURA

Resumo: O presente estudo tem como objetivo avaliar a influência do tempo de cura nas propriedades mecânicas de tração e cisalhamento de adesivos estruturais epóxi. Pelos resultados, foi observado que, dependendo do adesivo utilizado, o tempo de cura pode apresentar influência sobre as propriedades de resistência ao cisalhamento de juntas metálicas adesivadas (aço SAE 1020) e de resistência à tração. Para o Betamate™ 2096, foi observado aumento nas propriedades mecânicas quando utilizado tempo de cura de 7 dias a temperatura ambiente, enquanto para o Scotch-Weld™ DP420NS Black, os resultados se mantiveram inalterados, mesmo variando o tempo de cura. Essa influência está associada as condições de cura, que dependem do catalisador e aditivos utilizados na formulação, mesmo mantendo a base química.

Palavras-chave: Adesivos estruturais; epóxi; teste de cisalhamento; resistência à tração.

1. INTRODUCTION

Adhesives are materials used to bond two surfaces or substrates, creating a strong and lasting connection. The most used adhesives in hybrid joining processes are the structural ones which are selected with the aim of fastening together elements in order to produce high modulus, high strength and permanent bonds [1]. Structural adhesives are replacing traditional joining methods like welding, riveting, and screwing. Adhesive bonding allows flexibility in materials selection and offers improved production efficiency from product design and manufacture to final assembly, enabling cost reduction [2]. Using adhesives for connection technology has many benefits, such as cost-efficient, fast, and allows homogeneous stress distribution between the bonded surfaces[3].

Most structural adhesives are based on six main types of chemical composition: epoxy (or epoxide), polyurethane, reactive acrylic, toughened acrylic, anaerobic acrylic, cyanoacrylate, and silicone [4]. Epoxy adhesives can be formulated to provide strong bond in different types of substrates over a vast range of conditions [5]. Are used due to their hardness and excellent weatherability characteristics despite their slow cure speed and high brittleness [6]These adhesives offer the advantages of relatively low cure temperatures, relatively low cost, a variety of formulating and application possibilities, and have the advantage that no volatiles are released during the curing process[1].

Two-part epoxy adhesives start to react under ambient conditions once the two components have been mixed and such are often called room-temperature (RT) curing adhesives[4]. During the curing of this material, crosslinking occurs between the epoxy monomer and reactive groups on each end of the curing agent [7]. The cure kinetics and Tg of epoxy resins are dependent on the molecular structure of the curing agents, which can be divided into amine-type, alkali, anhydrides, and catalytic curing agents according to their chemical compositions [8,9]. Therefore, the formulation influences the curing conditions of these adhesives, emphasizing that although various types of epoxy adhesives from different brands are available in the market, their properties are not solely associated with the chemical base of these materials, but also with the types of curing agents and other additives added to the formulation.

Thus, the objective of this study is to assess the influence of curing time on the shear and tensile strength properties of epoxy-based structural adhesives. Specifically, both adhesives were cured at room temperature using curing times of 24 and 168 hours. In addition to characterizing the shear strength of bonded metallic substrates (SAE 1020 steel) and the tensile properties of the adhesive specimens, a skin time test was conducted to evaluate the initiation of curing, which corresponds to the time at which the adhesive begins to form a skin. This allowed for an evaluation of the curing process of the two adhesives studied and a comparison with the obtained mechanical properties.

2. METHODOLOGY

For the tests, two epoxy adhesives were used: Betamate™ 2096 from DuPont and Scotch-Weld™ DP420 NS Black supplied by 3M. The methodology involved several steps including adhesive preparation and mixing, substrate preparation, adhesive application, and test development, with analysis of adhesive tensile strength and shear strength of adhesive joints, varying the curing time between 24 hours and 168 hours (7 days) at room temperature.

Lap shear tests were conducted on an EMIC universal testing machine, Model DL 2000, with Tesc 2000 software for data processing. A 20 kN load cell was used with a crosshead speed of 1.3 mm/min, following ASTM D1002-10[10] standards. Three repetitions were performed for each adhesive using cold rolled steel substrates measuring 100x25 mm with a thickness of 1.2 mm. The substrates were prepared by immersing them in an HCl solution and then sanding to remove rust, using a sequence of sandpaper with grit sizes of 220, 360, 400, and 800.

Prior to adhesive application, the specimens were cleaned with acetone, heptane, and isopropyl alcohol to remove dirt and grease. A PTFE strip with an approximate thickness of 0.25 mm was attached to both ends of the specimens to secure the adhesives thickness, and the adhesive was applied to the bonding area. The adhesives were manually mixed for 1 minute and applied onto the 1.2 mm thick metal sheets.

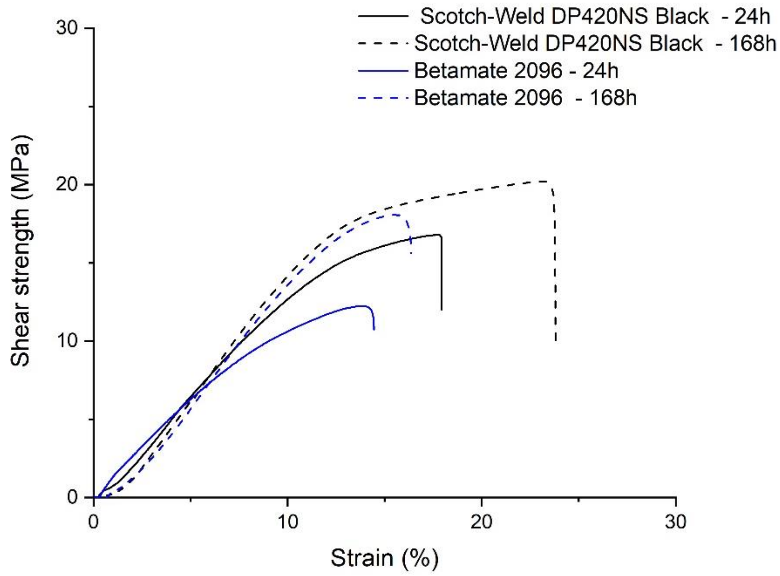
Tensile strength tests were performed according to ASTM D638[11]. The adhesive components were manually mixed and deposited into the poly (tetrafluoroethylene) (PTFE) mold on an aluminum base. To minimize the presence of bubbles, a vibrating system (sieve shaker with a vibration amplitude of 3.5) was used during adhesive injection. After 24 or 168 hours, the molded specimens were tested on an EMIC universal testing machine, Model DL 2000, with Tesc 2000 software and a 10 kN load cell, using a speed of 5 mm/min. The tests were carried out with five specimens of Type IV of the reference standard. This allowed obtaining stress-strain curves for the adhesives, as well as the maximum stress and strain, stress and strain at rupture.

In order to better understand the tensile and shear results obtained, tests were conducted to evaluate the curing time of the structural adhesives under study. Skin time tests were performed after manual mixing of the adhesive components. The sample and substrate were conditioned at a temperature of 23 ± 2 °C and a relative humidity of 50 ± 5% for 24 hours, which were maintained during the test. Approximately 10 g of adhesive was used, mixed with a spatula for 1 minute. The adhesives were applied as a continuous line of approximately 20 cm in length on the plate. A stopwatch was used to record the time, and a glass rod was used to touch the sample at different points of the adhesive every 1 minute until no transfer of adhesive to the glass rod was observed. The time recorded on the stopwatch at that moment was considered the skin time.

3. RESULTS AND DISCUSSION

An evaluation of the influence of curing time on the lap shear of the adhesives was performed. Figure 1 show the strain (%) *versus* shear strength (MPa) curves of the studied adhesives.

Figure 1. Shear strength versus strain of the adhesives with 24h and 168h of curing time



Based on the results, it was possible to observe higher shear strength and a higher percentage of strain in the adhesives that underwent a curing process for 168 hours. Therefore, the 24-hour curing time was insufficient for the complete cure of the studied epoxy adhesives. The results of shear strength, shear strain, and fracture surface are shown in Table 1.

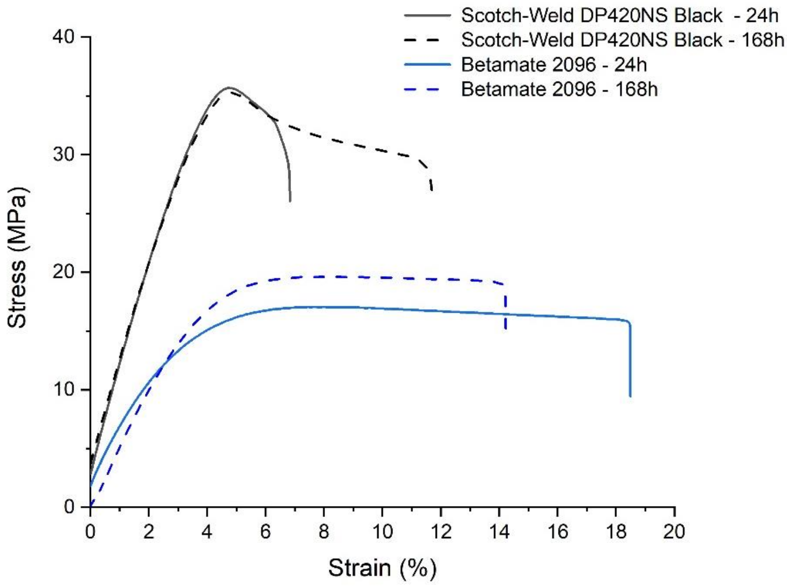
Table 1. Results obtained in lap shear tests for adhesives after 24h and 168h of curing time

Adhesive	**Betamate™ 2096 (24h)**	**Betamate™ 2096 (168h)**	**Scotch-Weld™ DP 420NS Black (24h)**	**Scotch-Weld™ DP 420NS Black (168h)**
Shear strength (MPa)	12.2 ± 0.1	18.3 ± 0.5	16.7 ± 0.4	19.5 ± 1.4
Shear strain (%)	14.0 ± 1.8	15.0 ± 1.4	21.0 ± 2.8	22.8 ± 1.7
Failure	100% Cohesive Failure	100% Cohesive Failure	100% Adhesive Failure	100% Adhesive Failure

Analyzing the average shear strength values of the two adhesives studied, an increase in the maximum strength of the Betamate™ 2096 adhesive is observed, but the strain remains unchanged with the change in curing time (considering the standard deviation), as well as the maximum shear strength and shear strain of Scotch-Weld™ DP 420NS Black adhesive. In addition, it was observed that the Betamate™ 2096 adhesive exhibited cohesive failure regardless of the curing time, meaning the failure is not due to an improper adhesion process [12]. On the other hand, the Scotch-Weld™ DP 420NS Black adhesive exhibited adhesive failure, characterized by failure at the adhesive adherend joint interface, which can occur due to improper surface preparation, wrong adhesive selection, and high peel stress [13]. Therefore, considering the two adhesives studied, no influence of curing time on the type of failure after shear testing was observed.

The effect of curing time on the tensile strength was also evaluated. The results obtained after 24h and 168h of curing can be seen in Figure 2.

Figure 2. Stress vs. strain plots for adhesives after 24h and 168h cure time.



From the results, it was possible to observe that the curing time does not change the maximum tensile strength the adhesive Scotch-Weld™ DP 420NS Black, with values of 34.5±1.2 MPa for the adhesive after 24 h of curing and 35±1.0 MPa for 168 h of curing, as can be seen in the Table 2. Considering the standard deviation, there is no difference between the values, that is, there is no influence of the curing time on the tensile strength of this adhesive. Similar results were observed for the mean values of deformation at maximum strength and deformation at the break, reiterating that, in this case, the curing time did not interfere with the properties of the Scotch-Weld™ DP 420NS Black adhesive.

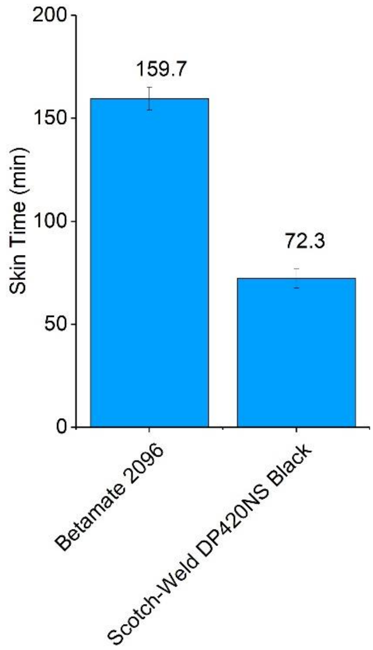
Table 2. Tensile strength results for DP420 adhesive after 24h and 168h cure time

Adhesive	**Betamate™ 2096 (24h)**	**Betamate™ 2096 (168h)**	**Scotch-Weld™ DP 420NS Black (24h)**	**Scotch-Weld™ DP 420NS Black (168h)**
Ultimate Tensile strength (MPa)	16.7 ± 0.4	19.4 ± 0.3	34.5 ± 1.2	35.0 ± 1.0
Strain (Ultimate Tensile strength) (%)	7.9 ± 0.4	8.4 ± 0.5	5.0 ± 0.3	4.8 ± 0.1
Fracture strength (MPa)	15.1 ± 0.6	18.8 ± 0.1	27.6 ± 0.6	28.8 ± 2.1
Fracture Strain (%)	19.4 ± 11.2	14.5 ± 1.2	8.0 ± 1.5	9.0 ± 2.4

On the other hand, for Betamate™ 2096, an increase in tensile strength was observed. The ultimate tensile strength went from 16.7±0.4 MPa after a 24-hour cure to 19.4±0.3 MPa after 168 hours of cure at room temperature. Similarly, the fracture strength increased from 15.1±0.6 to 18.8±0.1 for curing times of 24 hours and 168 hours, respectively. However, it is worth noting that there was an increase in the standard deviation of strain for the 24-hour cure, indicating a greater variability of results when using a shorter curing time.

In order to evaluate the difference between the mechanical strength results of the studied epoxy adhesives, skin time tests were performed to evaluate the time available between the mixing/application of the adhesive and the deposition of the adhesive on the substrate. Figure 3 shows the skin time results.

Figure 3. Skin time of the studied adhesives.



From the results, was possible to observe that the epoxy chemical-based adhesives studied had a high skin time when compared to adhesives of other chemical base such as the acrylyc-based adhesives that curing faster [6], with times varying between about 160 minutes for the Betamate™ 2096 adhesive and 72 minutes for the Scotch-Weld™ DP 420NS Black. Therefore, when applied at room temperature, these materials have a long time for skin formation. From an application point of view, knowing the skin time of the adhesives is essential, since it is necessary that the bonding before the skin formation time, to ensure wettability and good adhesion.

Evaluating the results obtained in this study, it is evident that the curing time has a significant impact on the mechanical properties of Betamate™ 2096. This finding aligns with the adhesive's longer skin time, indicating lower curing reactivity and necessitating longer times to achieve complete curing of this material. In addition, it was observed that DP420NS Black presents greater reactivity, with less influence of curing time on the properties of this adhesive. This variation in curing time in structural adhesives is associated with variation in the use of catalysts and additives in their formulation, although the chemical base is the same.

4. CONCLUSION

From the present study, it was possible to evaluate the influence of curing time on the mechanical properties of epoxy structural adhesives, noting that, depending on the adhesive used, a greater influence of curing conditions on shear and tensile strength can be observed. In addition, the skin formation time was also evaluated, and the results obtained corroborated the mechanical properties, and it was observed that the adhesive with the shortest time for skin formation had less influence on the curing time, with similar properties being observed at 24h and 168h of cure.

Therefore, the selection of a structural adhesive for practical applications involves not only the choice of the best chemical base according to needs, but also the concern with the time available for adhesive bonding and the total curing time of the same. It is also worth noting that high temperatures can be used to accelerate curing. Therefore, in addition to evaluating the curing time at room temperature, studies can be carried out evaluating the combination of time and temperature on the properties of epoxy structural adhesives. The results provided insights into the mechanical properties and curing characteristics of the adhesives, important parameters for application and the beginning of exposure of these materials to mechanical efforts.

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