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# Development of physical and mechanical properties of a cold-curing structural adhesive in a wet bridge environment

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## HIGHLIGHTS

- Effect of humidity on physical and mechanical properties of a cold-curing adhesive.
- Properties driven by simultaneous (reversible) plasticization and curing.
- Plasticization changed stress-strain behavior from linear to highly nonlinear.
- No detrimental effects of immersion in alkaline/water environments measured.
- Prediction of 70% strength and E-modulus retention at 10 °C after 100 years.

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## ABSTRACT

The physical and mechanical properties of a cold-curing structural epoxy adhesive, exposed to a wet bridge environment, were investigated. A significant decrease of the glass transition temperature, tensile E-modulus and tensile strength was observed which could be attributed to plasticization. The retention of 70% of the E-modulus and strength at an average 10 °C reference temperature was predicted using the Arrhenius law after a 100-year bridge service life. Full recovery of the properties was obtained after drying the immersed and fully saturated material. The immersion in alkaline water had no detrimental effect in the case of concrete-adhesive joints. In an immersed not yet fully cured material, the continuation of curing and plasticization concurred. The former was dominant in the early age and led to an increase of the glass transition temperature, E-modulus and strength. The latter decelerated the increase of the glass transition temperature and led to a decrease of the E-modulus and strength in the later age. Both approached the values of those of the fully cured material; the E-modulus after one month and strength after 20 months.

## 1. Introduction

Structural adhesives have been used in bridge construction since the 1960s [1]. Today, state-of-the-art applications consist of bonding steel or carbon fiber-reinforced polymer (CFRP) strips or plates onto existing reinforced concrete, steel or timber structures or bonding steel rebars into holes drilled into existing concrete structures for strengthening or upgrading purposes [2]. More recent applications are bonding of reinforced concrete or glass fiber-reinforced polymer (GFRP) bridge decks onto steel or concrete main girders [3]. In contrast to mechanical connections, in these applications adhesives allow the easy joining of different materials and adherends of different geometries.

Due to the often large bonding surfaces and usually outdoor applications, cold-curing adhesives are required for such joints. Thermosetting bisphenol epoxy resins are used in most cases since they cure at ambient temperatures if appropriate curing agents, i.e. aliphatic amines, are used. However, depending on the ambient temperature, curing and full development of the physical and mechanical properties may take up to one year for mechanical and even much longer for physical properties, such as the glass transition temperature [4].

Cold-curing epoxy bonded joints used in bridge construction are normally sealed to prevent exposure to humidity and UV radiation. The corresponding aging behavior of cold-curing structural epoxy adhesives under dry bridge conditions has already been investigated [4]. It has been shown that the material is exposed to concurring mechanisms, i.e. continuation of curing and physical aging, which both influence the physical and mechanical proper-

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ties. In view of the long service life of bridges, up to 100 years, it cannot however be excluded that, sooner or later, an initially sealed joint may start leaking and the adhesive may thus be exposed to moisture or even stagnant water during several decades. If sealing is not correctly carried out this can already occur before the adhesive is fully cured. Furthermore, the adhesive may also be exposed to humidity if the adherends have a certain porosity (e.g. in the case of concrete) or diffusivity (e.g. the matrix of CFRP materials) [5]. In the former case, the concrete pore water solution is, in addition, alkaline and has a high pH value of approximately 12.5 [6]. A similar case occurs if wet concrete is poured onto a fresh and still wet epoxy adhesive, as in the installation of a lightweight concrete-GFRP sandwich bridge deck in order to improve the adherence of the lightweight concrete to a GFRP T-web face sheet [7].

The effect of humidity or water on the physical and mechanical properties of epoxy resins has already been investigated. Plasticization of the resin occurred, resulting in a significant reduction of the glass transition temperature, stiffness and strength [8–10]. These effects were found to be reversible however when the material was dried again [11,12] and plasticization was thus considered as a physical degradation [9]. In contrast, irreversible chemical degradation has been observed in some cases and morphological effects such as cracking or material leaching were involved [11,13–15]. In most of these studies, fully cured or almost fully cured materials were investigated, i.e. the effect of the curing degree on these degradation mechanisms and their related decreases of physical and mechanical properties have not yet been specifically addressed.

The effect of alkalinity, i.e. alkaline water exposure, on physical and mechanical epoxy resin properties has also already been investigated, although with contradictory results. Exposure to pure water and alkaline solutions during 5 [13], 18 [14] and 24 [16] months at different temperatures resulted in a higher decrease of tensile strength in the case of alkaline exposure (15% at 60 °C [13], 86% at 40 °C [14] and 5% at 23 °C [16]) than in pure water (4% at 60 °C [13], 37% at 40 °C [14] and 43% at 23 °C [16]). Another study however [17] did not find any effect of alkalinity, with water uptake in pure and alkaline water and resistances being the same.

Current knowledge concerning the long-term performance of cold-curing epoxies exposed to different environments is mainly based on laboratory investigations of a very limited duration of one to two years. Accelerated methods were thus developed whereby the physical and chemical processes are accelerated by higher temperatures or increased concentrations of solutions [18–20] in order to predict the long-term properties of polymers. The Arrhenius law, which is based on acceleration by increased temperature, is frequently used in this respect, and ASTM D3045 [21] provides corresponding guidance for polymers. With regard to bulk epoxies, the Arrhenius law has been applied in viscosity models [22], modeling of gelation and curing reactions [23], and diffusivity development during aqueous exposure [24].

In this work, based on the above-described scenario of adhesives not yet fully cured and exposed to a wet bridge environment, the effects of curing degree and exposure to humidity and alkalinity on the long-term physical and mechanical properties of a structural epoxy adhesive were investigated, as well as the potential recovery of properties after drying in order to consider the effect of a dry period following a wet period of weather. Since the previous study on a dry bridge environment [4] showed that the same cold-curing epoxy adhesive as used in this study was almost fully cured after only one year of exposure in a dry environment, this study of the wet environment also investigated materials fully cured before exposure, in addition to partially cured materials. The long-term behavior was predicted based on the Arrhenius law. However, this method was only applicable for the fully cured materials since the elevated temperatures would have led to the rapid curing of partially cured materials.

## 2. Experimental program

### 2.1. Materials and conditioning

The commercial cold-curing epoxy adhesive Sikadur-330, supplied by SIKA Schweiz AG, was selected for this study as it is frequently used in structural civil engineering applications, e.g. for the bonding of carbon fiber-reinforced polymer (CFRP) plates or as impregnation resin for fabrics to strengthen existing structures. The thixotropic bi-component resin/adhesive comprises a bisphenol-A-based epoxy resin and a hardener consisting of aliphatic amines, and a small quantity, less than 20% per weight, of silica-based fillers [25]. Its viscosity is approximately 6000 mPa·s at 23 °C, according to the product data sheet.

The adhesive specimens were produced under laboratory conditions ($T = 21 \pm 3$ °C and $RH = 40 \pm 10\%$) with 4:1 resin to hardener mixing ratio, as suggested by the supplier. The adhesive was then poured into aluminum molds of specimen dimensions as described in the next section. To represent adhesive applications under on-site bridge conditions, no vacuum was applied to remove entrapped air. As explained above, post-cured (i.e. fully cured) and cold-curing (i.e. partially cured) specimens were manufactured. The post-cured specimens were left, after pouring, for seven days' curing under laboratory conditions, followed by three-day post-curing at 60 ± 0.5 °C in an oven. Directly after pouring, the cold-curing specimens were conditioned at a low temperature of 13 °C for two days, i.e. the time necessary for demolding. The post-curing also dried the post-cured specimens, whereas for the cold-curing specimens drying before immersion was not possible.

After this first phase of conditioning, the specimens were immersed in different baths. Six baths were prepared for the post-cured specimens, i.e. three baths containing demineralized water at 13, 30 and 50 °C (specimens PD13, PD30, PD50) and three baths with alkaline water at the same temperatures (specimens PA13, PA30, PA50), see Table 1. Three temperatures were thus selected in order to subsequently apply the Arrhenius law as mentioned above. The maximum temperature was limited to 50 °C to clearly remain below the onset of glass transition (approximately 65 °C, obtained from reference P21) and thus not activate additional degradation mechanisms. The three alkaline baths had a pH value slightly fluctuating around 13.0, obtained from dissolving 0.25 mol/L KOH, 0.14 mol/L NaOH and 0.02 mol/L $Ca(OH)_2$ in demineralized water. The cold-curing specimens (CD13) were immersed in demineralized water at low temperature, 13 °C, in order to delay the curing progression. The temperatures of the seven baths in total were maintained with a precision of ±1.5 °C. A total of 595 specimens were subjected to this second conditioning phase for a period of up to 24 months.

**Table 1**
Specimen designation, conditioning (C = cold-curing, P = post-cured) and immersion conditions.

| Conditioning | Immersion medium | Temperature [°C] | Max. immersion time [days] |
|---|---|---|---|
| C13, P21 reference | None | 13, 21 | 0 (dry) |
| CD13 | Demineralizedwater, pH ≈ 7.0 | 13 | 754 |
| PD13 | | 13 | 740 |
| PD30 | | 30 | 737 |
| PD50 | | 50 | 557 |
| PA13 | Alkaline water, pH ≈ 13.0 | 13 | 726 |
| PA30 | | 30 | 730 |
| PA50 | | 50 | 684 |