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Effects of epoxy, hardener, and diluent types on the hardened state properties of epoxy mortars

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HIGHLIGHTS

- The highest strength was obtained with TETA hardener, which has six functionalities.
- Monofunctional diluent reduced the compressive strengths of TETA and MXDA mortars.
- The addition of a diluent into epoxy mortars improved their flexural strength.
- The highest adhesion strength was obtained with MXDA hardener and DGEBA resin.
- Moderate to poor chemical resistance against formic and lactic acids were obtained.

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ABSTRACT

Three epoxy resins and three types of glycidylether-based reactive diluents were used together in epoxy mortars. Six different amine-based hardeners, four aliphatic and two cycloaliphatic, were used in the mixtures. Test results showed that a hardener with higher functionality results in mortars with higher strength. The combination of diluent and hardener was found to affect both the compressive and flexural strengths of the mortars. The adhesion strengths of the mortars (to a sand-blasted concrete surface) were obtained by pull-off test. It was found that lactic and acetic acids have different levels of destruction in the epoxy mortars.

1. Introduction

A concrete–polymer composite (C-PC) is the general name given to concrete or mortar in which a polymer is used to partially or fully replace Portland cement in traditional concrete [1]. Polymer concrete (PC) is a type of C-PC containing a polymeric resin as a binder. Thermosetting resins such as epoxy, unsaturated polyester, furan, vinyl ester resin, polyurethane, and phenol are widely used in the production of PCs [2]. Epoxy concrete and mortar have many engineering applications, such as in flooring, pavement, precast products, chemically resistant and anticorrosive linings, and repair owing to their superior durability, abrasion resistance, and adhesion properties. However, because epoxies are hazardous to human health, care should be taken when using these materials.

Difunctional epoxy resins are prepolymers with an epoxy group at each end of a molecule. The diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of bisphenol F (DGEBF) have similar molecular structures: the two methyl groups attached to the carbon between the benzene groups in the former are replaced with H atoms in the latter. F-type epoxies have lower viscosity than A-type epoxies, and for this reason, A and F types are often mixed to lower the viscosity of a mixture, thus preventing the crystallization of the polymers [3].

Hardeners, also known as curing or crosslinking agents, can open the C–O–C ring at the ends of an epoxy molecule and attach themselves to the molecules to convert the resin into a thermoset network structure. A particular hardener should be chosen when considering the processing conditions (pot life, viscosity, mixing ratio, and temperature) and the desired properties of the product (strength, chemical and thermal resistance, toughness, and flexibility) [4]. The most common hardeners for epoxy resins are amine types: aliphatic, aromatic, and cycloaliphatic. The type, amount,

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and functionality of the hardener, as well as the curing conditions (temperature and curing time), affect the properties of hardened epoxy resins.

To investigate the effects of the hardener type on the mechanical properties of DGEBA epoxy networks, Garcia et al. [5,6] analyzed three different hardeners: triethylenetetramine (TETA), which has a linear structure with six functionalities, and two cycloaliphatic amines, isophorone diamine (IPDA) and 1-(2-aminoethyl)piperazine (AEP). An IPDA system has the highest glass transition temperature (T_g) and yield stress among the hardener systems tested. However, the other cyclic amine AEP provides the lowest T_g and yield strength, probably because the latter amine possesses a linear segment. They concluded that the T_g of the network depends on both the crosslink density and chain flexibility; however, the yield strength is better related to the T_g value than to the crosslink density.

Mayr et al. [7] compared two different amines as hardeners with respect to the yielding behavior, one with an aliphatic structure and the other being aromatic, and found that the network formed by the latter amine provides higher yield strength owing to the higher rigidity of the molecular backbone.

In the stoichiometry of an epoxy-hardener system, for each end group of an epoxy molecule, there is a corresponding hydrogen atom attached to the nitrogen for amine-based hardeners. The relative content of the hardener with respect to the stoichiometric composition affects the rigidity, strength, and deformability of an epoxy network [8]. DGEBA/TETA mixtures were prepared with ratios above, below, and equal the stoichiometric ratio; it was found that when a low amount of hardener is used, which corresponds to an epoxy-rich composition, the mixture showed a brittle behavior, and with a greater amount of hardener, a high deformation capacity was reported [8].

The bonding of epoxy resins to different surfaces is another important mechanical property, and Naderi [9] determined the adhesions of different repairing systems to surface-cut concrete based on pull-off tests. The epoxy mortar showed an average adhesion strength of 5.27 MPa at day 350. In the same study, the lowest strength belonged to polyester mortar (1.96 MPa), and a strength level of 2.96 MPa was obtained for Portland cement mortar with a grout surface treatment, showing that epoxy mortar exhibits the highest adherence to the concrete among the mortars tested. In the study on the hardener type mentioned above [6], an inverse relationship was found between T_g and the adhesion strength of epoxy-hardener systems; of the hardeners tested, the mixture with IPDA showed the highest T_g but the lowest adhesion, whereas AEP exhibited a low T_g and the highest adhesion. This highlights the influence of the molecular chain flexibility on the adhesion properties.

In many applications, particularly during the processing of composites, the workability of epoxy mortar or concrete is important. It can be necessary to modify the viscosity of an epoxy mixture using diluents. Diluents are of two main types: reactive and non-reactive. The common solvents, such as xylene, toluene, glycol ethers, ketones, and lower alcohols are used as non-reactive diluents [10]. Reactive diluents participate in the reaction between the epoxy and hardener and join the network structure. Those with epoxy groups play a particularly important role in terms of the properties of the epoxy mixtures and can chemically bind to the resin, and thus may not change the mechanical properties of the resin at low diluent concentrations.

Nunez et al. [11] tested DGEBA and 1,2-diaminecyclohexane (DCH) as hardener systems by introducing the reactive diluent vinylcyclohexane dioxide (VCD) between 5 and 30%; it was concluded that the effects of a diluent on T_g, crosslinking degree, and storage modulus are slight for diluent contents lower than 15%, but not beyond this value. In another study [12], the same diluent (VCD) was used at up to a 25% concentration in an epoxy–amine system; a reduction was reported not only in the apparent viscosity but also in the yield stress. On the other hand, because reactive diluents participate in the reactions between the resin and hardener, they are less volatile and hazardous than non-reactive ones.

The durability of the construction materials is an important issue, particularly under severe exposure conditions, and can be even more important than the mechanical properties for certain applications. Tahri et al. [13] investigated the resistance of different materials (Portland cement concrete, high-performance concrete, epoxy resin, acrylic paint, and a fly ash-based geopolymeric mortar) to a chemical attack using sulfuric, hydrochloric, and nitric acid, and found epoxy resin to have the best resistance. The effects of different aggressive agents, namely, sulfuric, lactic, acetic, citric, and formic acids, as well as seawater, distilled water, and soft drinks, on the flexural and compressive strengths of epoxy mortars were tested [14]. It was reported that formic acid is the most effective agent on both types of strength, whereas acetic acid is more destructive to the flexural strength, and soft drinks are more harmful to the compressive strength. On the other hand, lactic acid was found to be moderately destructive to both types of strength. When the attacked surfaces of epoxy mortars were examined, severe surface damage was observed from formic and acetic acid solutions [15]. Riberio et al. [16] investigated the chemical resistance of epoxy and polyester concrete to sulfuric acid and sodium chloride solutions (10%); it was found that the flexural strength was slightly affected, indicating a good chemical resistance. Furthermore, in a maritime environment, an average loss of 9.6% in flexural strength was reported after a 1-year exposure period [17].

In this study, three different epoxy resins, DGEBA, DGEBF, and a mixture of the two (DGEBAF); six amine type hardeners, four of which are aliphatic and the others are cycloaliphatic; and three glycidyl-ether based reactive diluents were used. In the first part of the study, the workability properties of the epoxy–diluent–hardener systems were investigated [18]. In the part presented herein, we examine the compressive and flexural strengths of epoxy–diluent–hardener systems, adherence to the concrete surfaces, and durability against different chemical solutions.

2. Experimental

2.1. Materials

2.1.1. Epoxy resins

DGEBA (Fig. 1), DGEBF, and a mixture of DGEBA and DGEBF (70 wt% and 30 wt% respectively) (DGEBAF) were used as epoxy resins, the properties of which are given in Table 1.

2.1.2. Hardeners

Six hardeners, four of which are aliphatic and two are cycloaliphatic, were used (Fig. 1), the properties of which are given in Table 2. Benzyl alcohol (BA) (density of 1.04 g/ml and viscosity at 25 °C, 8 cp.) was used as an accelerator for the hardener IPDA.

2.1.3. Reactive diluents

A monofunctional reactive diluent (RDMF) (glycidylether C12-C14 alcohol), difunctional reactive diluent (RDDF) (1,6 hexanediol diglycidylether), and trifunctional reactive diluent (RDTF) (trimethylopropane glycidylether), which are derivatives of glycidyl ether, were employed as the reactive diluents (Table 3).

2.1.4. Aggregate

Silica sand (density of 2.631 g/cm^3 and size of 0.075–4 mm) and silica filler (density of 2.67 g/cm^3 and size of <100 μm) were used in the aggregate mixtures.

2.2. Resin mixtures

Epoxy resin binders were prepared using a hardener, with or without a reactive diluent, and in some mixtures with an accelerator. In mixtures with diluents, an amount of epoxy was replaced with the same amount of diluent. For each batch of mortar mixture, 250 g of binder (resin + hardener + diluent) was mixed with