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Effects of epoxy, hardener, and diluent types on the workability of epoxy mixtures

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HIGHLIGHTS

- The addition of 5% diluent caused a decrease in viscosities between 52 and 72%.
- Glycidylether C12-C14 alcohol is the most effective diluent in reducing the viscosities of epoxy-diluent mixtures.
- There is a correlation between the flow of the mortars and the viscosities of the epoxy-diluent mixtures.
- Altering the type of the hardener used in epoxy mortars may increase the flow rate up to 2.8-fold.
- The higher the functionality of a hardener the shorter is the pot life of epoxy-hardener-diluent mixtures.

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ABSTRACT

Three types of epoxy resins, namely, diglycidyl ether of bisphenol A and F, and a third obtained by mixing the two resins, and three types of reactive diluents, based on glycidylether, were used to form epoxy mixtures. The effect of diluent content up to 15 wt% on the viscosities of the three epoxies was investigated. The flow properties of mortars prepared with epoxy, hardener, and diluent, as a binder, were compared with respect to the viscosity and molecular weight of the epoxies and diluents, as well as the viscosity and shape of the hardeners used. Six types of hardeners, including four aliphatic and two based on cycloaliphatic amine, were used in the production of mortars. Furthermore, the effects of the type of epoxy, content, type and functionality of diluents, and the functionality and molecular structure of hardeners, on the pot lives of the mixtures were examined. In this study, it is found that not only the viscosities of resin and diluents but also viscosities and molecular structures of hardener and accelerator are effective on the workability properties of epoxy mortars.

1. Introduction

The term "Concrete-Polymer Composite" (C-PC) is commonly used to define concretes containing a polymer as a binder, or as part of a binder [1]. The former type of concrete, known as a "polymer concrete" (PC), contains a low viscosity resin as the polymer and does not include any cement. The latter type, named as "polymer cement concrete" (PCC), includes a polymer, usually in the form of latex or emulsion, which serves as a modifier and also as a part of the Portland cement binding system. A third type of C-PC, namely, "polymer impregnated concrete" (PIC), can be added to this list. Epoxy resins are widely used in civil engineering applications. In view of their high resistance to abrasion, epoxy mortars and concretes can be used as surface coatings in bridges, pavements, and in industrial floors. Due to their outstanding durability, epoxy resins can be used in industrial buildings, underground applications, and in constructions on seashores. Another important area of application of epoxy resins is in repairing reinforced concrete structures for either filling concrete cracks or patching damaged concrete, due to the excellent adhesion of epoxy to concrete surfaces. In addition, epoxy resins also find applications in corrosion repairing. However, epoxies can pose certain health hazards and care should be taken while using them.

Diglycidyl ether of bisphenol A (DGEBA), based on epichlorohydrin, is the most widely used epoxy (Fig. 1), whose viscosity depends on the number of repeating units (n) and the molecular weight. The diglycidyl ether of bisphenol F (DGEBF) has a similar molecular structure to DGEBA, but with the difference that the two methyl groups attached to the carbon located between the benzene groups are replaced by H atoms. F-type epoxies have lower molecular weight than A-type and show lower viscosities.

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For this reason, A and F types are mixed to lower the viscosity of the mixture and also to prevent the crystallization of DGEBA.

In the pre-polymerized state, epoxy resins are in the liquid state and a crosslinking process is necessary to convert them into a thermoset polymer. A and F type epoxy resins contain epoxy groups at the end of the molecule (two functionalities) consisting of an oxygen atom bonded to two carbon atoms so as to form a three-membered ring. The strained character of the C—O bond and the high electron affinity of O make the epoxy group highly unstable [2], which means that a number of systems can open the ring to attach to the epoxy resin molecules. Molecules which can react with epoxy groups are known both as hardeners and curing or crosslinking agents. Hardener molecules enable the resin molecules to connect to each other to form a three-dimensional network. There are many types of hardeners, but the most important ones are classified into aliphatic and aromatic amines, anhydrides, and polyamides.

Usually, hardener molecules are much smaller than resin molecules and therefore, have low viscosities. The addition of a hardener into a resin lowers the viscosity of the mixture to different extents depending on the viscosity and shape of the hardener and its stoichiometric amount used in the mixture. In some cases, it may be necessary to modify the viscosity of an epoxy resin by using diluents to improve its processability [3]. Diluents reduce the viscosity of epoxy mixtures by weakening the interaction between the resin molecules [4]. There are two main types of diluents, namely, non-reactive and reactive. Non-reactive diluents, which include aromatic hydrocarbons such as toluene or xylene, dibutyl phthalate, styrene and various phenolic compounds [5], do not participate in the reaction between the epoxy and the hardener. Reactive diluents can be classified into epoxy-based and those which are not based on epoxides. Among the reactive diluents, those with epoxy groups significantly influence the properties of epoxy resins. They can chemically bind to the resin and form a part of the network following crosslinking. For this reason, they are less volatile and therefore, more environmentally friendly than non-reactive diluents.

Nonvolatile reactive diluents have been used to increase the workability of epoxy mortars, where a fivefold increase in fluidity was reported when 15% of a diluent was added [6]. Epoxidized soybean oil (20% ratio), was added as a reactive diluent to modify DGEBA, and the rheological properties were measured using a rheometer [7]. Test results showed that when the concentration of the oil in the mixture increased, the consistency index (zero shear viscosity) decreased, indicating improved flow properties. In another study, the reactive diluent vinyl cyclohexane dioxide at concentrations up to 25% was used in epoxy-amine systems and a reduction in both apparent viscosity and yield stress was reported [8].

To improve the impact strength of epoxy resins, polyol based reactive diluents were added [9], which, besides increasing the toughness, decreased viscosity, extended pot life and improved wetting properties. Ethanol was used as a diluent in an epoxy system, which allowed the maximum silica filler content to be increased from 40% to 60% [10]. Loos et al. [11] performed rheological measurements on DGEBA resin, using acetone as a diluent and showed that the addition of 10% acetone reduced the viscosity by ~50%, which resulted in a better dispersion of nanofillers.

In this study, three types of epoxy resins, six amine type hardeners (four aliphatic and two cycloaliphatic), and three reactive diluents (glycidyl ether-based) were used [12]. In the first part of the study, the viscosity of epoxy-diluent mixtures and workability properties of epoxy-diluent-hardener-sand mortars were investigated and the results were presented in this paper. In the second part of the study, the hardened state properties (compressive and flexural strengths, adherence strength to the concrete surface and chemical resistance) of the same mortars have been explored and the results will be presented in a forthcoming paper.

2. Experimental

2.1. Materials

2.1.1. Epoxy resins

The epoxy resins used in this study are diglycidyl ether of bisphenol A (DGEBA) (Fig. 1) and diglycidyl ether of bisphenol F (DGEBF), both of which are commercial products. As a third type of epoxy resin, the mixture of DGEBA and DGEBF (70% from the former and 30% from the latter) (DGEBAF), which is sold commercially, was used. Since DGEBF has lower viscosity relative to DGEBA, the two resins are blended to lower the viscosity; in this way each resin prevents the crystallization of the other one at the room temperature [13]. General information on the epoxy resins is given in Table 1.

2.1.2. Hardeners

Six hardeners are used in this study and their properties are given in Table 2. For the hardeners trimethylhexamethylene diamine, cyanoethylated mixture of isomers (trimethylhexane -1,6-diamine) (CTMDA) and isophorone diamine (IPDA), the long pot-life times necessitated the use of benzyl alcohol (density 1.04 g/ml and viscosity@25 °C 8 cp.) as an accelerator (Fig. 1).

2.1.3. Reactive diluents

The derivatives of glycidyl ether are the most widely used reactive diluents. Three types of glycidyl ether-based reactive diluents are employed, namely, a monofunctional reactive diluent (RDMF) (glycidylether C12-C14 alcohol), a difunctional reactive diluent (RDDF) (1,6 Hexanediol diglycidylether), and a trifunctional reactive diluent (RDTF) (trimethylopropane glycidylether) (Table 3 and Fig. 1).

2.1.4. Aggregate

The aggregate mixture used in the study consists of 82% silica sand (density: 2.631 g/cm^3) in size in the range 0.075–4 mm and 18% of fine silica (density: 2.67 g/cm^3) with size <100 μm.

2.1.5. Resin mixtures

In the mortar formulations, silica sand, fine silica and epoxy resin binders were used. Epoxy resin binder consists of an epoxy, a reactive diluent (if exists), stoichiometric amount hardener for both epoxy and diluent, and an accelerator (if exists). When a diluent is used, the amount of epoxy is reduced with the same amount of diluent. The quantities of hardeners were determined from stoichiometry calculations and the amounts of each hardener calculated for DGEBA are listed in Table 2; adjustments from these values were made for the other epoxies and diluents. For hardeners CTMDA or IPDA, pot–life times were very long, and hence, benzyl alcohol was used in 30 and 10% with respect to epoxy (and diluent if exists) as the accelerator. The resin binder/aggregate ratio was determined to have at least a flow rate of 100 ± 10%. In all mortar mixtures, epoxy resin binder, sand and fine silica contents were 15.1%, 69.6% and 15.3% by mass, respectively.

2.2. Testing procedures

The tests were carried out at a temperature and R.H of 23 ± 2 °C and 60 ± 5%, respectively and all the materials used were conditioned for 24 h before testing.

2.2.1. Viscosity measurement

Viscosity measurements were carried out using a Brookfield viscometer on mixtures of resin and diluent.

2.2.2. Flow measurement

The flow of fresh mortar was determined using a cone of height 60 mm, a bottom surface diameter of 100 mm, and a top surface diameter of 70 mm.

2.2.3. Pot life

Pot life is the time required for the epoxy resin-hardener-diluent mixtures to become rigid. For the mixtures containing CTMDA or IPDA, an accelerator (benzyl alcohol) was used as an additive. Pot life tests were carried out on 100 g of resin (with or without diluent) mixed with a stoichiometric amount of the hardener at room temperature in accordance with ISO 10364: 2007(E) [16]. The pot life of the mixture was measured from the amount of time between when it was first mixed, up to the point when the mixture could not be spread by hand.