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(54) **Title**: EPOXY-BASED ADHESIVE COMPOSITION FOR CEMENTITIOUS JOINTS AND CEMENTITIOUS STRUCTURES

(57) **Abstract**: An adhesive composition adapted for cementitious segmental joint structures including a Part (A) formulation including at least one epoxy resin and at least one filler; and a Part (B) formulation including at least one hardening agent and at least one filler; wherein a rheology modifying, fiber filler is incorporated into at least one of Part (A) or Part (B), or is added to a mixture of Part (A) and Part (B), wherein the adhesive composition exhibits a compressive strength of at least about 55,000 kPa (8000 psi) upon cure.

EPOXY-BASED ADHESIVE COMPOSITION FOR CEMENTITIOUS JOINTS AND CEMENTITIOUS STRUCTURES

An adhesive composition for bonding and sealing joints between the sections of a segmental bridge is provided.

Segmental bridges are bridges constructed out of individual and separate sections or units which are pieced together and joined to each other at the construction site in order to form the bridge. The individual sections which comprise segmental bridges are made from concrete that is either cast-in-place (formed at the construction site) or precast at a separate location and transported to the construction site for assembly with other bridge sections.

Between each segment or section of a segmental bridge are joints which connect two segmental sections of the bridge together. Typical joints used in precast segmental structures include multiple shear joints in webs and shear key joints. These joints are designed to accommodate both pre- and post- stressing forces in order to prevent cracking as they are often the source of concrete and rebar degradation within bridges. Pre-stressing forces occur during the construction of the bridge and result from losses from anchor set, elastic shortening, creep and shrinkage of the concrete, and relaxation of the pre-stressed steel. Post-stressing forces include cyclic service loads, changes in temperature and weather conditions such as wind, and seismic forces which may cause displacement of the segmental sections. These forces may cause strain or shear between the segmental sections of the bridge causing the sections to be displaced upwardly, downwardly, or transversely over time. In severe cases of stress, the concrete deck or the steel reinforcement (rebar) within the segmental sections may buckle.

These joints must also be shielded from the environment to prevent water, bacteria, chemicals and debris from entering the joint and penetrating the concrete and metal structural supports which hold the bridge together. Such materials can enter through exposed joints, causing the natural degradation of the concrete to accelerate. They can also cause the metal structural supports (rebar) to oxidize and deteriorate which can weaken the integrity of the bridge.

Various adhesive compositions have been used in filling the gap between the joints of segmental bridges. These adhesives are capable of bonding the sections of the segmental bridge together and sealing the sections of the segmental bridge from the environment. These adhesives are also capable of enduring a high yield stress in order to accommodate the various loads typically encountered in the day-to-day use of segmental bridges. Adhesives capable of providing these properties include epoxy-based adhesives. Epoxy-based adhesives have two states – a workable state and a hardened state. In its workable state, epoxy-based adhesives function as a lubricant for joining the segments of the bridge together. They are capable of completely filling all interstitial space between adjoining segmental sections of the bridge. In its hardened state, epoxy based adhesives provide a sufficient connection for stress transfer and form a watertight seal between the segments of the bridge.

Epoxy-based adhesives generally comprise a resin and a hardener. For example, a common epoxy resin is produced from the reaction of epichlorohydrin and bisphenol-A. Hardeners used in epoxy-based adhesives typically comprise amine structures which may be used to form polyamine monomers such as triethylenetetramine.

Epoxy-based adhesives have many applications. Examples of epoxy-based adhesives in the building and construction industry include Concresive® 1440 SBA by BASF Construction Chemicals, LLC of Shakopee MN. Other examples of epoxy-based adhesives used in the building and construction industry include Unitex Segmental Bridge Adhesive and Pro-Poxy Segmental Bridge Adhesive by Unitex Concrete Construction Chemicals of Kansas City, MO and Dural 100 Precast Segmental Epoxy Adhesive by The Euclid Chemical Company (Cleveland, OH). Further examples of epoxy-based adhesives used in the building and construction industry include Sikadur® -31; Sikadur® 31, SBA Slow Set; Sikadur® 31, SBA Normal Set; Sikadur® -31 SBA S-02; and, Sika® CarboDur® Composite Strengthening Systems by Sika Corporation of Lyndhust, NJ. In addition to filling the joints within segmental bridges, these epoxy-based adhesives have also been used for repairing cracks and defects within concrete structures as well as for filling joints within other cementitious structures in addition to segmental bridges.

Epoxy-based adhesives must be within a certain range of viscosity so that application of the adhesive within the cementitious system is both feasible and economical.

Various types of hardeners may be used such that when they are combined and mixed with certain resins, the set time of the epoxy-based adhesive is sufficient to allow the adhesive to be applied to the desired location.

Rheology modifiers are often incorporated into the epoxy-based adhesive depending on the chemical make-up of the adhesive and on the particular application. These rheology modifiers alter the thixotropy of the resin-hardener mixture, enabling the end-user to apply the epoxy-based adhesive to the desired location with minimal sag.

FIG. 1 is a force (mN or g) vs. distance (mm) curve for a normal set medium temperature range epoxy-based adhesive formulation as disclosed herein.

FIG. 2 is a force (mN or g) vs. distance (mm) curve of a commercially available, normal set medium temperature range segmental bridge adhesive.

FIG. 3 is a force (mN or g) vs. distance (mm) curve for a normal set high temperature range epoxy-based adhesive formulation as disclosed herein.

FIG. 4 is a force (mN or g) vs. distance (mm) curve of a commercially available, normal set high temperature range segmental bridge adhesive.

An epoxy-based adhesive is provided for bonding and sealing cementitious structures such as concrete segments used in segmental bridges.

Epoxy-based adhesives generally comprise two parts – a Part (A) formulation and a Part (B) formulation. Part (A) of the epoxy-based adhesive generally comprises at least one epoxy resin; optionally, at least one filler; and optionally, at least one thixotropic or rheology modifying agent. Part (B) of the epoxy-based adhesive generally comprises at least one hardening agent; optionally, at least one filler; optionally, at least one thixotropic or rheology modifying agent; and optionally, at least one pigment. Epoxy-based adhesives are formed by mixing the epoxy resin of Part (A) with the hardening agent of Part (B) and allowing the mixture to cure.

The epoxy resin of Part (A) typically comprises monomers and short-chain polymers comprising an epoxide group. The hardening agent typically comprises monomers and short-chain polymers comprising polyamine groups. The curing rate and other properties of the epoxy-based adhesive such as the strength, flexibility, elasticity, and hardness can be controlled by the selection of specific resin(s) to be used for Part (A) and specific hardening agent(s) to be used for Part (B) of the mixture and by the selection of the appropriate curing temperature. Curing rates may vary ranging from minutes to hours depending on the desired application of the epoxy-based adhesive. By altering the curing process through these methods, the desired curing rate of the epoxy-based adhesive can be obtained.

Examples of epoxy resins which may be used in Part (A) of the present epoxy-based adhesive composition include bisphenol A-epichlorohydrin resins, bisphenol F-epichlorohydrinl epoxy resins, brominated epoxy resins, multifunctional resins, flame resistant epoxy resins such as glycidyl ether of tetrabromobisphenol A, novolac-type epoxy resins, hydrogenated bisphenol A-type epoxy resins, glycidyl ether of bisphenol A propyleneoxide adduct type epoxy resins, m-aminophenol epoxy resins, diaminodiphenylmethane epoxy resins, urethane modified epoxy resins, alicyclic epoxy resins, N,N-diglycidylaniline, N,N-diglycidyl-o-toluidine, triglycidylisocyanurate, polyalkylene glycol diglycidyl ether, glycidyl ethers of polyhydric alcohols such as glycerin, hydantoin-type epoxy resins and epoxidized substances of unsaturated polymers such as petroleum resins, or mixtures thereof.

In certain embodiments, the epoxy resin is a bisphenol A-epichlorohydrin resin. Suitable examples of bisphenol A-type liquid epoxy resins which may be used as a component of Part (A) of the epoxy-based resin include the Araldite series resins, commercially available from Huntsman International LLC (Dusseldorf, Germany), D.E.R. series resins, commercially available from The Dow Chemical Company (Midland, Michigan), and the EPON series resins commercially available from Momentive Specialty Chemicals (Columbus, Ohio).

Part (A) of the epoxy-based adhesive may also include at least one filler. An example of a filler that may be incorporated into Part (A) of the epoxy-based adhesive is fumed silica. In certain embodiments, the filler may also function as a thixotropic or

rheology modifying agent. An example of a filler which also functions as a thixotropic agent is calcium carbonate. Other examples of rheology modifying agent(s)/filler(s) include an alkyl quaternary ammonium clay which may be used as a substitute to fumed silica.

Examples of hardening agents which may be used in Part (B) of the present epoxy-based adhesive composition include aliphatic primary, secondary and tertiary amines, aromatic amines, cycloaliphatic amines, heterocyclic amines, amido amines, polyether amines and mixtures thereof. Examples of primary and secondary amines include triethylenetetramine, tetraethylenepentamine, diethylaminopropylamine, N-aminoethylpiperidine, m-xylenediamine, m-phenylediamine, diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, and polyethers with amine terminal groups. Examples of tertiary amines include 2,4,6-tris(dimethylaminomethyl)phenol and tripropylamine, salts of tertiary amines or mixtures thereof. Suitable examples of hardening agents which may be used as a component of Part B of the epoxy-based resin include compositions comprising a cycloaliphatic amine and an alkylphenol and compositions comprising a tertiary amine. In certain embodiments, the hardening agent comprises at least one of a cycloaliphatic amine and a tertiary amine.

Other examples of hardening agents which may be used in Part (B) of the present epoxy-based adhesive composition include polyamide resins, imidazoles, dicyandiamides, borontrifluoride complexes, carboxylic acid anhydrides such as phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, dodecynylsuccinic anhydride, pyromellitic anhydride and chlorendic anhydride, alcohols, phenols, carboxylic acids, diketone complexes of aluminum or zirconium and mixtures thereof.

Other components which may be included in Part (B) of the epoxy-based adhesive include various types of pigments and fillers. In certain embodiments, the pigment utilized in Part (B) may also comprise a filler. One example of a pigment/filler which may be used in Part (B) is carbon black. Carbon black comprises a folded graphite network having oxygen complexes (such as carboxylic, quinonic, lactonic, and phenolic groups) chemisorbed on the surface. At least one pigment may also be incorporated into the resin (Part (A) of the epoxy-based adhesive). The mixing of the resin and the hardening agent may further result in the pigments producing a third color similar to the color of the

concrete in the bridge segments. Alternatively, at least one pigment may be incorporated into the resin (Part (A) of the epoxy-based adhesive) alone. In other embodiments, the pigment may comprise titanium dioxide.

Part (B) of the epoxy-based adhesive may also include at least one filler. In certain embodiments, the filler may also function as a thixotropic or rheology modifying agent. Examples of fillers which function as a thixotropic agent include calcium-carbonate which may be in the form of a precipitate or ground and fumed silica, including hydrophilic and hydrophobic fumed silica. Other examples of fillers which may be used include natural based fillers such as juut and hemp.

Part (B) may also comprise one or more accelerants to increase the rate of cure of the epoxy-based adhesive composition. An example of one type of accelerant which may be used is an amine accelerant (a compound which contains both tertiary amine and hydroxyl functionalities). In certain embodiments, a suitable amine-accelerant is a tertiary amine, 2,4,6-tri(dimethylaminomethyl)phenol. Other types of accelerants which may be used within Part (B) of the epoxy-based adhesive include nonyl phenols.

The rate of cure of the epoxy-based adhesive composition may also be adjusted by altering the temperature and/or the volume or amount of Part (B) formulation which is combined with the Part (A) formulation. For example, an increase in temperature of the adhesive mixture acts as a catalyst in that it increases the rate of cure of the epoxy-based adhesive composition. Likewise, an increase in the concentration of Part (B) formulation also results in an increase in the rate of cure of the epoxy-based adhesive composition.

Epoxy-based adhesive formulations may be highly viscous which can make application of the adhesive between joints such as those present in segmental bridges rather difficult. Therefore, it may be desirable to alter the viscosity of the epoxy-based adhesive so that the adhesive composition can more easily flow or spread and penetrate through cementitious joints. One way to alter the viscosity and spreadability of the epoxy-based adhesive composition is by altering the rheology of the composition. Rheology of a liquid mixture is defined as the deformation and flow of the liquid with applied stress and strain over a period of time. If the rheology of the epoxy-based adhesive mixture can be modified to deform and flow more easily into the desired joint, the adhesive may be able to

more thoroughly penetrate the joint within the cementitious structure. This can result in a more effective bond between the joints of cementitious segments or within the area of the cementitious structure to be repaired. Accordingly, the present epoxy-based adhesive composition also includes a rheology modifying filler.

The rheology modifying filler is capable of thixing the epoxy-based adhesive mixture of Part (A) and Part (B) to obtain the desired viscosity during agitation of the mixture. Thixing refers to the process of incorporating a component into the epoxy adhesive mixture to obtain a more flowable liquid mixture upon agitation and which allows the mixture to retain its ability to form a high strength solid adhesive upon curing. In certain embodiments, the high strength bond formed by the epoxy-based adhesive upon curing is at least as strong as the bond exhibited by the adhesive without the addition of a rheology modifying filler.

Accordingly, at least one of Part (A) or Part (B) of the present epoxy-based adhesive also includes a rheology modifying fiber filler comprising at least one fiber filler which not only functions as a thixotropic or rheology modifier but is also capable of increasing or retaining the compressive strength of the epoxy-based adhesive when cured. This fiber filler is also capable of being applied smoothly and cleanly to the cementitious substrate allowing for ease of application. This rheology modifying, fiber filler comprises a network of fibers incorporated into the epoxy-based adhesive mixture. The rheology modifying, fiber filler incorporated into the epoxy-based adhesive mixture of resin (Part A) and hardening agent (Part B) may thus comprise at least one of organic or inorganic fibers. Organic and inorganic fibers which may employed as a rheology filler include polymer fibers such as acrylic polyester fibers, nylon fibers, polyamide fibers, polyester fibers, polyvinyl alcohol fibers, polyvinyl chloride fibers, polyolefin fibers, aromatic polyamids, elastomers, and polyurethane fibers. In certain embodiments, inorganic fibers may be treated with an organic coating.

In certain embodiments, the rheology modifying, fiber filler may comprise polyolefin fibers. The polyolefin fibers may vary in length from about 0.1 mm to about 2.3 mm, in diameter from about 5 microns/micrometers to about 20 microns/micrometers and have a melting point ranging from about 250°F (121°C) to about 275°F (135°C). The polyolefin fibers may be fluffed and/or dry fibrillated. Examples of polyolefin fibers which

may be incorporated in the epoxy-based adhesive include polyethylene fibers. A suitable example of a polyolefin fiber which may utilized within at least one of Part (A) or Part (B) of the epoxy-based adhesive is Grade E385F polyethylene fibers commercially available from Minifibers, Inc. (Johnson City, TN). Other grades of polyethylene fibers available from Minifibers, Inc. may be incorporated into Part (A) of the epoxy-based adhesive. A summary of the various grades of polyethylene fibers available from Minifibers, Inc. which may be used are set forth below in Table I. In general, the smaller the fibers which are incorporated into the epoxy-based adhesive composition, the higher the compressive strength demonstrated by the epoxy-based adhesive when cured.

Table I

Grade	Length (millimeters)	Diameter (microns or micrometers)	Melt Point (°F/°C)	Standard Compaction
ESS2F	0.6	5	~275/135	Full
ESS5F	0.1	5	~275/135	Reduced
ESS50F*	0.1	5	~275/135	Reduced
E380F	0.55-0.80	15	~275/135	Full
E385F*	0.55-0.80	15	~275/135	Full
E400F	0.75-1.05	15	~275/135	Full
E505F*	0.8-1.1	15	~275/135	Full
E780F	1.3-2.0	25	~275/135	Reduced
E990F	1.8-2.3	20	~275/135	Reduced
UL410F	1.0	15	~275/135	Reduced

* water-dispersible grades for improved dispersion in aqueous systems

Fillers added to the epoxy system act as a heat sink, effectively absorbing heat from the system. This reduction of thermal energy present within the epoxy system can slow down the rate of cure of the Part (A) and Part (B) formulations. In order to counteract this effect, various accelerants such as amine accelerants and nonyl phenols may be added to the Part (A) and Part (B) formulations and/or the temperature of the adhesive composition and/or concentration of the Part (B) formulation may be increased in order to increase the rate of cure.

Other components may also be added to the epoxy-based adhesive, for example, diluents such as aliphatic glycidyl ethers or aromatic glycidyl ethers.

The amounts of resin in Part (A) and hardening agent in Part (B) are typically combined to form a mixture having a certain stoichiometric ratio. According to certain embodiments, the volume ratio of Part (A) to Part (B) within the mixture may be about 2:1. According to other embodiments the volume ratio of Part A to Part B within the mixture may be about 3:1. In other embodiments, the volume ratio of Part A to Part B within the mixture may be about 1:1.

In certain embodiments, the epoxy-based adhesive composition comprises from about 25 to about 55 percent by weight of epoxy resin, from about 50 to about 80 percent by weight of hardening agent, and from about 1 to about 5 percent by weight of rheology modifying, fiber filler. In other embodiments, the epoxy-based adhesive comprises from about 35 to about 45 percent by weight of epoxy resin, from about 60 to about 70 percent by weight of hardening agent, and from about 1 to about 2 percent by weight of rheology modifying, fiber filler.

A number of preparation steps may be performed before the epoxy-based adhesive composition is to be applied to the cementitious substrate. Generally, the surface of the substrate being sealed and bonded is cleaned. The cementitious substrate bonding surface can be cleaned by using an industrial-grade detergent or a degreasing compound followed by mechanical cleaning to remove grease, wax, and oil contaminants. Weak or deteriorated concrete may be removed by bushhammering, gritblasting, scarifying, waterblasting, or other suitable mechanical means. Dirt, dust, laitance, and curing compounds may be removed by gritblasting, sanding, light sandblasting or wire brushing. Acid etching may also be used in certain situations. After cleaning, the cementitious substrate surface can be flushed with water and scrubbed. The surface of the substrate may then be tested for removal of acid with a moist pH paper. It is desired that the pH not be more than about 10. After flushing with water, the surface may be cleaned with a vacuum. If applying the epoxy-based adhesive to a steel surface, the surface may be cleaned with a suitable industrial-grade detergent and degreasing compound to remove dirt, grease, and oil. Rust and mill scale may be removed by gritblasting the steel to white metal, followed by gritblasting with vacuum or oil-free dry-air blast.

It is possible to bond the epoxy-based adhesive to a damp surface, however, in most cases the epoxy-based adhesive will be applied to a dry surface. In general, a surface is

considered to be damp if a dry rag becomes damp after being wiped over the surface. If the epoxy-based adhesive is to be applied to a damp surface, it may be required to remove free-standing water by air blasting the area.

Modifying the viscosity of the epoxy-based adhesive mixture prior to cure may assist in application of the epoxy-based adhesive. There are several ways to modify the viscosity of the epoxy-based adhesive mixture. One way, mentioned above, is by incorporating the subject rheology modifying fiber filler into the mixture. The fibrous rheology modifying filler is capable of lowering the viscosity of the mixture without compromising other properties of the cured resin such as abrasion resistance, compressive strength, flexural strength, flexural modulus, tensile strength, tensile elongation, shear strength, and linear shrinkage. In fact, incorporation of a rheology modifying filler into the epoxy-based mixture may significantly increase certain properties of the cured adhesive composition such as compressive strength. The subject epoxy-based adhesive may be provided by compounding the rheology modifying fiber filler initially into Part (A) or Part (B), or may be added to the mixture of Parts (A) and (B) of the epoxy-based adhesive.

The resin containing component (Part (A)) and the hardening agent containing component (Part (B)) of the epoxy-based adhesive may be thoroughly mixed before they are combined. After Part (A) and Part (B) of the epoxy-based adhesive are combined, the resulting combination may be thoroughly mixed. In certain embodiments, Part (A) and Part (B) are thoroughly mixed until a uniform color is achieved. Mixing may be performed in an appropriate mechanical mixer, which in certain embodiments operates at no more than 600 rpm.

Application of the epoxy-based adhesive may occur immediately after a batch of the epoxy-based adhesive is mixed. In certain situations, application of the epoxy-based adhesive should occur within a maximum of 20 minutes after combining the components. The epoxy-based adhesive may be applied to the contact surface by methods known in the art for bridge segments. The epoxy-based adhesive has properties which allow the user to smoothly apply the adhesive with ease and with minimal mess as the epoxy-based adhesive is capable of cleanly coming off an application tool when applied to the desired surface. Initially, application of the epoxy-based adhesive may be at a nominal thickness such as 0.16 cm (1/16 of an inch) with additional adhesive composition being subsequently applied

to achieve a final thickness of about 0.64 cm (1/4 of an inch). The epoxy-based adhesive may be applied by hand to one or both contact surfaces to be joined, and may be included in holes formed by ducts. Additional epoxy-based adhesive may be applied to equal the shim thickness when shims are placed in a joint and to extrude a bead line of epoxy-based adhesive from the joint after application of the compressive contact pressure to the joint.

The epoxy-based adhesive composition may also be applied by gravity feed or by pressure injection. The process of applying the epoxy-based adhesive composition by gravity feed comprises pouring the adhesive directly into the segmental joint and spreading the adhesive out if necessary. The adhesive may be spread by hand or by various devices. Devices which may be used to spread the epoxy-based adhesive include a roller, a broom, a squeegee or other applicable device. The amount of epoxy-based adhesive used should be sufficient to fill the joint to the desired level to create an effective seal. Sand or other types of filler may be used to fill large joints prior to applying the epoxy-based adhesive.

Alternatively, the epoxy-based adhesive may be applied by pressure injection. The process of applying the epoxy-based adhesive by pressure injection typically involves a low pressure injection of epoxy-based adhesive into the segmental joint. Low pressure injection is generally performed at a pressure of up to about 140 kPa (20 psi). In certain applications, a low pressure injection of 70-83 kPa (10-12 psi) is used.

After the epoxy-based adhesive is applied to the segments comprising a segmental joint, a certain amount of contact pressure may be applied to each joint in order to facilitate the bonding of the adhesive to the segments which are to be connected. Contact pressure may be applied through combinations of weight and temporary and/or permanent post-tensioning of the segmental structures. Contact pressure may be applied uniformly to each joint and may comprise approximately 280 kPa (40 psi). Contact pressure may be increased at any time after the epoxy-based adhesive has taken an initial set but may not be reduced until the epoxy-based adhesive has hardened and cured. When reducing contact pressure, in certain embodiments, the joint is not subjected to tensile stress. In certain applications of the epoxy-based adhesive, the time elapsing between the mixing of the components of the epoxy-based adhesive, the application of the epoxy-based adhesive to the to-be-joined cementitious segments and the application of a compressive contact

pressure across the joint, does not exceed 70% of the open time for the particular formulation of the epoxy bonding agent used.

In certain embodiments, the epoxy-based adhesive applied to a cementitious segmental joint is to be allowed to cure for at least 20 hours after mixing of the last batch of epoxy-based adhesive before the erection truss or support system is removed in a span-by-span erection. In a cantilever erection of cementitious segments, the independent support to a newly erected cantilever segment may be removed when the epoxy-based adhesive in the third previous segmental mating joint has set. It is not necessary for the epoxy-based adhesive in the new segmental joint or the immediately previous segmental joint to set prior to removing the independent support for the new segmental joint provided that temporary and/or permanent post-tensioning has been installed to carry the load of the new and previous cementitious segments.

The epoxy-based adhesive also exhibits an excellent working life or open time. Working life of an epoxy-based adhesive is the amount of time after the resin in Part (A) and the hardening agent in Part (B) are mixed, during which the adhesive can be applied to the segmental cementitious joint before the adhesive mixture gels and hardens to where it is no longer workable. This is in contrast to gel time, which is the amount of time it takes for the adhesive composition to completely harden.

The working life of epoxy-based adhesives are generally classified as "normal set epoxy" and "slow set epoxy". Normal set epoxy has a short open time, meaning that it remains workable for a short period of time, typically about one to two hours. Normal set epoxies are typically used in segmental bridges constructed from a cantilever erection process. Slow set epoxy has an extended open time, meaning that it remains workable over a much longer period of time, typically about 6 to about 8 hours. Slow set epoxies are typically used in segmental bridges constructed in a span-by-span erection process, which typically require more open time. In certain embodiments, the epoxy-based adhesive is a normal set epoxy, meaning that it has a working life of about one to about two hours once the adhesive is mixed before it cures. In certain embodiments, the working life of the epoxy-based adhesive is about one hour. In other embodiments, the epoxy-based adhesive is a slow set epoxy meaning it has a working life of about 8 hours.

Both normal and slow set epoxies may be formulated to be applied to substrates within specified substrate temperature ranges. Typically, epoxy-based adhesives are capable of bonding cast segments to substrates at temperatures between about 40°F (4°C) to about 115°F (46°C). The temperatures that the adhesive must endure during the application process have an effect on the working life of the epoxy-based adhesive. Therefore, epoxy-based adhesives may comprise several formulations in order to obtain an appropriate working life at various temperature ranges.

The epoxy-based adhesive may comprise at least two, in some cases three or more, formulations which are capable of being applied in different temperature sub-ranges within the range of about 40°F (4°C) to about 115°F (46°C). The different formulations of the epoxy-based adhesive may be adapted to be applied in particular temperature sub-ranges of equally sized ranges and which overlap by at least about 5°F (2.8°C). Epoxy-based adhesives are typically designated as "H" (hot), "M" (medium temperature), "C" (cold) or "VC" (very cold) to designate the preferred temperature range of the particular formulation. Epoxy-based adhesives designated as "H" are typically applied within a substrate temperature range of about 90°F (32°C) to about 115°F (46°C). Epoxy-based adhesives designated as "M" are typically applied within a substrate temperature range of about 55°F (13°C) to about 95°F (35°C). Epoxy-based adhesives designated as "C" are typically applied within a substrate temperature range of about 40°F (4°C) to about 60°F (16°C). Epoxy-based adhesives designated as "VC" are typically applied within a substrate temperature range of about 20°F (-7°C) to about 40°F (4°C).

The present epoxy-based adhesive may be formulated to be applied to substrates having a temperature ranging from about 20°F (-7°C) to 40°F (4°C) to about 115°F (46°C). In certain embodiments, the epoxy-based adhesive may comprise at least four formulations, wherein a first formulation is capable of being applied between about 20°F (-7°C) to about 40°F (4°C), wherein a second formulation is capable of being applied between about 40°F (4°C) to about 60°F (16°C), wherein a third formulation is capable of being applied between about 55°F (13°C) to about 95°F (35°C), and wherein a fourth formulation is capable of being applied between about 90°F (32°C) to about 115°F (46°C). In other embodiments, the epoxy-based adhesive may comprise at least three formulations, wherein a first formulation is capable of being applied between about 40°F (4°C) to about 60°F (16°C), wherein a second formulation is capable of being applied between about 55°F

(13°C) to about 95°F (35°C), and wherein a third formulation is capable of being applied between about 90°F (32°C) to about 115°F (46°C).

In certain cases where the segmental joint substrate temperature exceeds about 115°F (46°C), shading and/or wetting of the substrate may be performed to keep the substrate cool and within the application temperature. However, it may be necessary to dry the substrate before application of the epoxy-based adhesive at the application temperature. In cases where the segmental joint substrate is below about 40°F (4°C), an artificial environment may be created around the cementitious segmental joint substrates wherein warm air is circulated around the cementitious segmental joint substrate in order to increase the cementitious segmental joint substrate temperature.

The present epoxy-based adhesive is also capable of sealing segmental cementitious joints to a strength at least as great as that of the cementitious substrate and exhibits high bonding strength to cured concrete as well as a high compressive strength.

One method for testing the bond strength and compressive strength of the present epoxy-based adhesive to concrete is by conducting a slant shear test (a.k.a. a slant cylinder test) according to ASTM C 882/C and ASTM C39. This test is conducted by bonding together two equal sections of a Portland-cement mortar cylinder with an epoxy system. The two sections of the cylinder are of equal volume and form an angle of 30° from the vertical at the cylinder bonding area. The cement mortar/concrete material of the cylinder utilized in the slant-cylinder test has a compressive strength of at least 31,000 kPa (4,500 psi) at 28 days when tested to ASTM C39. In general, an epoxy system is applied to the gap present between the two slanted sections of the cylinder. Joining of the slanted surfaces of the two cylinder sections, however, is delayed from the time the epoxy-based adhesive is mixed for 60 minutes for normal-set epoxy and for 6 hours for slow set epoxy. Also, from the time of mixing the epoxy-based adhesive to the time of joining the slanted sections of the cylinder, the slanted sections of the cylinder are uncovered and maintained at the maximum temperature of the application range for the formulation tested.

After the epoxy-based adhesive is applied to the gap between the two slanted sections of the cylinder, the cylinder is allowed to cure at the maximum temperature for the

epoxy-based adhesive formulation temperature range (48 hours for normal set and 14 days for slow set epoxies) prior to testing.

The cylinder is then placed onto a testing machine comprising two steel bearing blocks with hardened faces. One of the bearing blocks of the testing machine is a spherically seated block that will bear a load on the upper surface of the specimen. The other steel bearing block serves as the area upon which the specimen will rest. The specimen is placed on the testing machine and compressive load is applied onto the specimen continuously and without shock. The compressive load is applied until the load indicator shows that the load is decreasing and the specimen displays a fracture pattern. Maximum load carried by the specimen during the test is then recorded.

Bond strength may be calculated by dividing the load carried by the specimen at failure by the area of the bonded surface. Measurements of bond strength are taken when the test cylinder achieves a compressive strength of at least 41,300 kPa (6,000 psi) at seven days after cure. Compressive strength of the specimen is calculated by dividing the maximum load carried by the specimen during the test by the average cross-sectional area of the specimen.

The present epoxy-based adhesive composition comprising a fibrous rheology modifying filler is capable of sustaining a stress or contact strength (calculated as the axial or vertical load divided by the area of the slant ellipse) of 6,900 kPa (1,000 psi) at 48 hours after joining for normal-set epoxy and 6,900 kPa (1,000 psi) at 14 days after joining for slow-set epoxy. For slow set epoxy-based adhesives, an additional test specimen is made and tested for failure at 24 hours. The formulation of the slow set epoxy-based adhesive is considered acceptable if this additional test specimen exhibits a brittle break at 24 hours.

EXAMPLES

The following examples are set forth merely to further illustrate the advantages of the epoxy-based adhesive disclosed herein. The illustrative examples should not be construed as limiting the elements comprising epoxy-based adhesive, the methods of making the epoxy-based adhesive, or the methods of applying the epoxy-based adhesive in any manner.

The following components were used to prepare two illustrative epoxy-based adhesives.

Example 1

Part A	Weight %	Amount (g)
Bisphenol A-Type Epoxy Resin	39.525	108.696
Filler (Calcium Carbonate)	58.495	160.869
Rheology Modifying Filler (alkyl quaternary ammonium clay)	1.980	5.435
Total	100.000	275.000

Part B	Weight %	Amount (g)
Hardening Agent A (cycloaliphatic amine)	65.724	180.741
Hardening Agent B (tertiary amine)	2.629	7.230
Pigment (Carbon Black)	0.100	0.275
Filler (Fumed Silica)	3.953	10.870
Filler (Calcium Carbonate)	27.594	75.884
Total	100.000	275.000

Example 2

Part A	Weight %	Amount (g)
Bisphenol A-Type Epoxy Resin	39.525	108.696
Filler (Calcium Carbonate)	58.495	160.869
Rheology Modifying Filler (Polyethylene Fibers – E385F)	1.980	5.435
Total	100.000	275.000

Hardening Agent A (cycloaliphatic amine)	65.724	180.741
Hardening Agent B (tertiary amine)	2.629	7.230
Pigment (Carbon Black)	0.100	0.275
Filler (Fumed Silica)	3.953	10.870
Filler (Calcium Carbonate)	27.594	75.884
Total	100.000	275.000

The two illustrative epoxy-based adhesives were then tested for compressive strength. The results of those tests are provided below.

Testing for Compressive Strength

Example 1

	Maximum Load (kPa)/(lb/ft.^{2})	Compressive Strength (kPa)/(psi)
Sample 1	2309.25 / 48229.69	47044 / 6823.11
Sample 2	1968.37 / 41110.40	40099 / 5815.93
Mean	2138.82 / 44670.05	43572 / 6319.52
Std. Dev.	241.03 / 5034.09	4910 / 712.17

Example 2

	Maximum Load (kPa)/(lb/ft.^{2})	Compressive Strength (kPa)/(psi)
Sample 1	2999.64 / 62648.76	61102 / 8862.14
Sample 2	3178.15 / 66376.89	64745 / 9390.41
Mean	3088.75 / 64509.83	62923 / 9126.27
Std. Dev.	126.42 / 2640.43	2576 / 373.54

As shown in the above Examples 1 and 2, substituting polyethylene fibers for a typical rheology modifying agent, such as an alkyl quaternary ammonium clay, resulted in a significant increase in the compressive strength of the epoxy-based adhesive after cure. The compressive strength of the epoxy-based adhesive containing polyethylene fibers was greater than 55,000 kPa (8000 psi) upon cure [at least about 58,000 kPa (8400 psi) upon cure]. In general, samples of the epoxy-based adhesive composition which included polyethylene fibers yielded an average compressive strength which was about 30% greater than the compressive strength of samples of the epoxy-based adhesive composition which did not contain polyethylene fibers.

Several illustrative formulations have been developed for normal set and slow set epoxy systems at various temperature ranges. These formulations are summarized in Tables II-VIII set forth below. All weight percents are based on the total weight percent of the relative Part (A) or Part (B) components of the epoxy-based adhesive formulation.

Table II

Normal Set Epoxy at 20°F (-7°C) to 40°F (4°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Filler	Calcium Carbonate	~48 to ~72.5
Part (B)			
	Hardening Agent A	MXDA Mannich Base Amine	~20 to ~30
	Hardening Agent B	Mecaptan Terminated Amine Blend	~20 to~30
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2.25
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table III

Normal Set Epoxy at 40°F (4°C) to 60°F (16°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Filler	Calcium Carbonate	~48 to ~72.5
Part (B)			
	Hardening Agent A	MXDA Mannich Base Amine	~40 to ~60
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2.25
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table IV

Normal Set Epoxy at 55°F (13°C) to 95°F (35°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Accelerant	Nonyl Phenol	~2.25 to ~3.75
	Filler	Calcium Carbonate	~45 to ~70
Part (B)			
	Hardening Agent A	Cycloaliphatic Amine	~20 to ~30
	Hardening Agent B	Phenol Free Mannich Base Amine	~20 to ~30
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2.25
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table V

Normal Set Epoxy at 80°F (27°C) to 115°F (46°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Accelerant	Nonyl Phenol	~2.25 to ~3.75
	Filler	Calcium Carbonate	~45 to ~70
Part (B)			
	Hardening Agent A	Cycloaliphatic Amine	~40 to ~60
	Hardening Agent B	Phenol Free Mannich Base Amine	~20 to ~30
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2.25
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table VI

Slow Set Epoxy at 40°F (4°C) to 60°F (16°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Filler	Calcium Carbonate	~47.5 to ~72.5
Part (B)			
	Hardening Agent A	Modified Polyamido Amine	~30 to ~47.5
	Hardening Agent B	Phenol Free Mannich Base Amine	~10 to ~15
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2.25
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table VII

Slow Set Epoxy at 55°F (13°C) to 95°F (35°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~30 to ~47.5
	Accelerant	Nonyl Phenol	~2.25 to ~3.75
	Filler	Calcium Carbonate	~45 to ~70
Part (B)			
	Hardening Agent A	Modified Polyamido Amine	~35 to ~55
	Hardening Agent B	Phenol Free Mannich Base Amine	~4.25 to ~6.75
	Pigment	Black dispersion	~0.05 to ~0.15
	Filler	Fumed Silica	~1.25 to ~2
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

Table VIII

Slow Set Epoxy at 80°F (27°C) to 115°F (46°C)

	Component	Chemical Name	Weight Percent
Part (A)			
	Epoxy Resin	Bisphenol A-Type	~31.6 to ~47.4
	Filler	Calcium Carbonate	~48.4 to ~72.6
Part (B)			
	Hardening Agent A	Modified Polyamido Amine	~40.6 to ~60.9
	Pigment	Black dispersion	~0.08 to ~0.12
	Filler	Fumed Silica	~1.25 to ~2
	Rheology Modifying Filler	Polyethylene Fibers (E380F)	~1 to ~1.75
	Filler	Calcium Carbonate	~35 to ~55

The present epoxy-based adhesive composition has also been shown in application to exhibit improved spreadability compared to other known adhesive compositions. Improvements in spreadability have been quantified using a TA.XT.Plus Texture Analyzer available from Stable Micro Systems (Goldaming, UK).

Representative samples of normal set epoxy-based adhesives were prepared and tested for spreadability. The samples tested included a medium temperature range formulation (Fig. 1) and a high temperature range formulation (Fig. 3). These were compared to spreadability values obtained for normal set samples of commercially available Sikadur® 31 SBA (Figs. 2 and 4). Spreadability was quantified using a TA.XT.Plus Texture Analyzer. The TA.XT.Plus Texture Analyzer was calibrated to the following settings and parameters:

Sequence Title: Return to Start (Set Dist)
Test Mode: Compression
Pre-Test Speed: 1.0 mm/sec
Test Speed: 10.0 mm/sec
Post-Test Speed: 10 mm/sec
Target Mode: Distance
Force: 980.7 mN (100.0 g)
Distance: 32.0 mm
Strain: 10.0 %
Trigger Type: Auto (Force)
Trigger Force: 49 mN (5.0 g)
Probe: P/100; 100 mm
Compression Platen
Points Per Second: 200
Test Run By: user

The TA.XT.Plus Texture Analyzer output a graph of force (mN)/(g) versus distance (mm) for each sample tested (See Figs. 1 through 4). These graphs quantify the amount of force required for each tested adhesive composition to spread a distance of 32.0 mm. For example, according to Fig. 1, a force greater than 2150 mN (220 g) was required to compress a medium temperature range normal set adhesive having a formulation in accordance with the present disclosure, a total distance of 32.0 mm. According to Fig. 2, however, a force greater than 3430 mN (350 g) was required to compress a commercially available medium temperature range normal set adhesive known as Sikadur® 31 SBA, a total distance of 32.0 mm.

Fig. 3 shows that a force greater than 2450 mN (250 g) was required to compress a high temperature range normal set adhesive having a formulation in accordance with the present disclosure, a total distance of 32.0 mm. According to Fig. 4, however, a force greater than 5390 mN (550 g) was required to compress a commercially available high temperature range normal set adhesive known as Sikadur® 31 SBA, a total distance of 32.0 mm. Thus, the present epoxy-based adhesive formulation generally requires less force to compress and spread than other segmental bridge adhesives known in the art.

Spreadability values for each of the samples set forth in Table IX were determined by computer calculation of the area underneath each curve set forth in Figs. 1 through 4. The results of these tests are provided in Table IX below.

Table IX

Spreadability of the Epoxy-Based Adhesive Composition Compared to Sikadur® 31 SBA

Adhesive Composition Sample	Spreadability (mN/mm) / (g/mm)
Normal Set – Med. Temp. Formula	75 / 7.6
Sikadur®31 Normal Set–Med. Temp. Formula	135 / 13.8
Normal Set – High Temp. Formula	86 / 8.8
Sikadur®31 Normal Set–High Temp. Formula	180 / 18.4

In general, samples which exhibit a lower spreadability value (mN/mm) / (g/mm) in Table IX are less concentrated within a given area and are more spreadable than samples which exhibit a higher spreadability value. According to Table IX, the normal set medium

temperature range formula of the present adhesive composition had a greater spreadability than the Sikadur® 31 normal set medium temperature range formula and the normal set high temperature range formula of the present adhesive composition had a greater spreadability than the Sikadur® 31 normal set high temperature range formula [i.e., lower spreadability mN/mm (g/mm) values].

A first embodiment of the present subject matter includes an adhesive composition adapted for cementitious segmental joint structures comprising a Part (A) formulation comprising at least one epoxy resin and at least one filler; and a Part (B) formulation comprising at least one hardening agent and at least one filler; wherein a rheology modifying, fiber filler is incorporated into at least one of Part (A) or Part (B), or is added to a mixture of Part (A) and Part (B), wherein the adhesive composition exhibits a compressive strength of at least about 55,000 kPa (8000 psi) upon cure.

The composition of the first embodiment may further include that the epoxy resin comprises at least one of bisphenol A-epichlorohydrin resins, bisphenol F-epichlorohydrinl epoxy resins, brominated epoxy resins, multifunctional resins, flame resistant epoxy resins such as glycidyl ether of tetrabromobisphenol A, novolac-type epoxy resins, hydrogenated bisphenol A-type epoxy resins, glycidyl ether of bisphenol A propyleneoxide adduct type epoxy resins, m-aminophenol epoxy resins, diaminodiphenylmethane epoxy resins, urethane modified epoxy resins, alicyclic epoxy resins, N,N-diglycidylaniline, N,N-diglycidyl-o-toluidine, triglycidylisocyanurate, polyalkylene glycol diglycidyl ether, glycidyl ethers of polyhydric alcohols, glycerin, hydantoin-type epoxy resins, epoxidized substances of unsaturated polymers, petroleum resin, or mixtures thereof. The epoxy resin may comprise a bisphenol A-epichlorohydrin resin.

The composition of either or both of the first or subsequent embodiments may further include that the at least one filler of Part (A) comprises a rheology modifying filler. The at least one filler of Part (A) may comprise calcium carbonate.

The composition of any of the first or subsequent embodiments may further include that the rheology modifying fiber filler is incorporated into the Part (A) formulation.

The composition of any of the first or subsequent embodiments may include that the rheology modifying fiber filler comprises at least one of organic or inorganic fibers. The rheology modifying fiber filler may comprise an organic fiber. The organic fiber may be a polymer fiber comprising at least one of acrylic polyester fibers, nylon fibers, polyamide fibers, polyester fibers, polyvinyl alcohol fibers, polyvinyl chloride fibers, polyolefins, aromatic polyamides, elastomers, polyurethane fibers, or mixtures thereof. The polymer fiber may comprise polyolefin fibers. The polyolefin fibers may comprise polyethylene fibers.

The composition of any of the first or subsequent embodiments may further include a hardening agent that comprises at least one of aliphatic primary amines, aliphatic secondary amines, aliphatic tertiary amines, aromatic amines, cycloaliphatic amines, heterocyclic amines, amido amines, polyether amines polyamide resins, imidazoles, dicyandiamides, borontrifluoride complexes, carboxylic acid anhydrides, alcohols, phenols, carboxylic acids, diketone complexes of aluminum or zirconium, or mixtures thereof. The hardening agent may comprise at least one of triethylenetetramine, tetraethylenepentamine, diethylaminopropylamine, N-aminoethylpiperidine, m-xylenediamine, m-phenylediamine, diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, polyethers with amine terminal groups, 2,4,6-tris(dimethylaminomethyl)phenol, tripropylamine, salts of tertiary amines, phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride, dodecynylsuccinic anhydride, pyromellitic anhydride, chlorendic anhydride, or mixtures thereof. The hardening agent may comprise at least one of a cycloaliphatic amine and a tertiary amine.

The composition of any of the first or subsequent embodiments may include that the Part (B) formulation further comprises a second hardening agent, a pigment, wherein the at least one filler of Part (B) comprises a rheology modifying filler. The second hardening agent may be a cycloaliphatic amine, the pigment may be carbon black, and the fillers may be fumed silica and calcium carbonate.

In the composition of any of the first or subsequent embodiments, the hardening agent may comprise an amine which also functions as an accelerant.

The composition of any of the first or subsequent embodiments may comprise from about 25 to about 55 percent by weight of epoxy resin, from about 50 to about 80 percent by weight of hardening agent, and from about 1 to about 5 percent by weight of rheology modifying fiber filler.

In the composition of any of the first or subsequent embodiments, the volume ratio of the Part (A) formulation to the Part (B) formulation is about 2 to 1. In certain embodiments, the ratio of the Part (A) formulation to the Part (B) formulation may range from about 3 to 1 to about 1 to 1.

The composition of any of the first or subsequent embodiments may have a post-cure compressive strength of at least 55,000 kPa (8000 psi). In certain embodiments, the adhesive composition has a post-cure compressive strength from about 58,000 kPa (8400 psi) to about 107,000 kPa (15,500 psi). In certain embodiments, the adhesive composition has a post-cure compressive strength from about 62,000 kPa (9000 psi) to about 107,000 kPa (15,500 psi).

The composition of any of the first or subsequent embodiments may have a spreadability value of less than 135 mN/mm (13.8 g/mm). In other embodiments, the composition may have a spreadability value of less than about 128 mN/mm (13 g/mm), less than about 118 mN/mm (12 g/mm), less than about 108 mN/mm (11 g/mm), less than about 98 mN/mm (10 g/mm), less than about 88 mN/mm (9 g/mm), or less than about 79 mN/mm (8 g/mm).

A second embodiment of the present subject matter includes a method of adhering cementitious structure bridge segments by applying an adhesive composition comprising cleaning the area on the cementitious structure where the adhesive composition is to be applied; providing the adhesive composition of any of the above embodiments by mixing the Part (A) formulation with the Part (B) formulation to form a fluid epoxy mixture comprising the rheology modifying fiber filler; applying the fluid epoxy mixture to the cementitious structure or product; and, curing the fluid epoxy mixture to form a seal and bond having a compressive strength of at least 55,000 kPa (8000 psi).

The method of the second embodiment may further comprise that the epoxy resin comprises a bisphenol A-epichlorohydrin resin, the hardening agent comprises a cycloaliphatic amine and the rheology modifying fiber filler comprises polyethylene fibers.

The embodiments described above are not necessarily in the alternative, as various embodiments may be combined to provide the desired characteristics.

CLAIMS

1. An adhesive composition adapted for cementitious segmental joint structures comprising

a Part (A) formulation comprising at least one epoxy resin and at least one filler; and

a Part (B) formulation comprising at least one hardening agent and at least one filler;

wherein a rheology modifying, fiber filler is incorporated into at least one of Part (A) or Part (B), or is added to a mixture of Part (A) and Part (B), wherein the adhesive composition exhibits a compressive strength of at least about 55,000 kPa (8000 psi) upon cure.

2. The adhesive composition of claim 1, wherein the epoxy resin comprises at least one of bisphenol A-epichlorohydrin resins, bisphenol F-epichlorohydrinl epoxy resins, brominated epoxy resins, multifunctional resins, flame resistant epoxy resins such as glycidyl ether of tetrabromobisphenol A, novolac-type epoxy resins, hydrogenated bisphenol A-type epoxy resins, glycidyl ether of bisphenol A propyleneoxide adduct type epoxy resins, m-aminophenol epoxy resins, diaminodiphenylmethane epoxy resins, urethane modified epoxy resins, alicyclic epoxy resins, N,N-diglycidylaniline, N,N-diglycidyl-o-toluidine, triglycidylisocyanurate, polyalkylene glycol diglycidyl ether, glycidyl ethers of polyhydric alcohols, glycerin, hydantoin-type epoxy resins, epoxidized substances of unsaturated polymers, petroleum resin, or mixtures thereof.

3. The adhesive composition of claim 2, wherein the epoxy resin comprises a bisphenol A-epichlorohydrin resin.

4. The adhesive composition of claim 1, wherein the at least one filler of Part (A) comprises a rheology modifying filler.

5. The adhesive composition of claim 4, wherein the at least one filler of Part (A) comprises calcium carbonate.

6. The adhesive composition of claim 1, wherein the rheology modifying fiber filler is incorporated into the Part (A) formulation.

7. The adhesive composition of claim 1, wherein the rheology modifying fiber filler comprises at least one of organic or inorganic fibers.

8. The adhesive composition of claim 7, wherein the rheology modifying fiber filler comprises a polymer fiber comprising at least one of acrylic polyester fibers, nylon fibers, polyamide fibers, polyester fibers, polyvinyl alcohol fibers, polyvinyl chloride fibers, polyolefins, aromatic polyamids, elastomers, polyurethane fibers, or mixtures thereof.

9. The adhesive composition of claim 8, wherein the polymer fiber comprises polyolefin fibers.

10. The adhesive composition of claim 9, wherein the polyolefin fibers comprise polyethylene fibers.

11. The adhesive composition of claim 1, wherein the hardening agent comprises at least one of aliphatic primary amines, aliphatic secondary amines, aliphatic tertiary amines, aromatic amines, cycloaliphatic amines, heterocyclic amines, amido amines, polyether amines, polyamide resins, imidazoles, dicyandiamides, borontrifluoride complexes, carboxylic acid anhydrides, alcohols, phenols, carboxylic acids, diketone complexes of aluminum or zirconium, or mixtures thereof.

12. The adhesive composition of claim 11, wherein the hardening agent comprises at least one of triethylenetetramine, tetraethylenepentamine, diethylaminopropylamine, N-aminoethylpiperidine, m-xylenediamine, m-phenylediamine, diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, polyethers with amine terminal groups, 2,4,6-tris(dimethylaminomethyl)phenol, tripropylamine, salts of tertiary amines, phthalic anhydride, hexahydrophthalic anhydride, tetrahydrophthalic anhydride,

dodecynylsuccinic anhydride, pyromellitic anhydride, chlorendic anhydride, or mixtures thereof.

13. The adhesive composition of claim 11, wherein the hardening agent comprises at least one of a cycloaliphatic amine and a tertiary amine.

14. The adhesive composition of claim 1, wherein the Part (B) formulation further comprises a second hardening agent, a pigment and wherein the at least one filler of Part (B) comprises a rheology modifying filler.

15. The adhesive composition of claim 14, wherein the second hardening agent is a cycloaliphatic amine, the pigment is carbon black, and the fillers are fumed silica and calcium carbonate.

16. The adhesive composition of claim 1, wherein the hardening agent comprises an amine which also functions as an accelerant.

17. The adhesive composition of claim 1 comprising from about 25 to about 55 percent by weight of epoxy resin, from about 50 to about 80 percent by weight of hardening agent, and from about 1 to about 5 percent by weight of rheology modifying fiber filler.

18. The adhesive composition of claim 1, wherein the volume ratio of the Part (A) formulation to the Part (B) formulation is 2 to 1.

19. The adhesive composition of claim 1, having a post-cure compressive strength of at least 58,000 kPa (8400 psi).

20. The adhesive composition of claim 1, having a spreadability value of less than 135 mN/mm (13.8 g/mm).

21. A method of adhering cementitious structure bridge segments by applying an adhesive composition thereon comprising:

cleaning the area on the cementitious structure where the adhesive composition is to be applied;

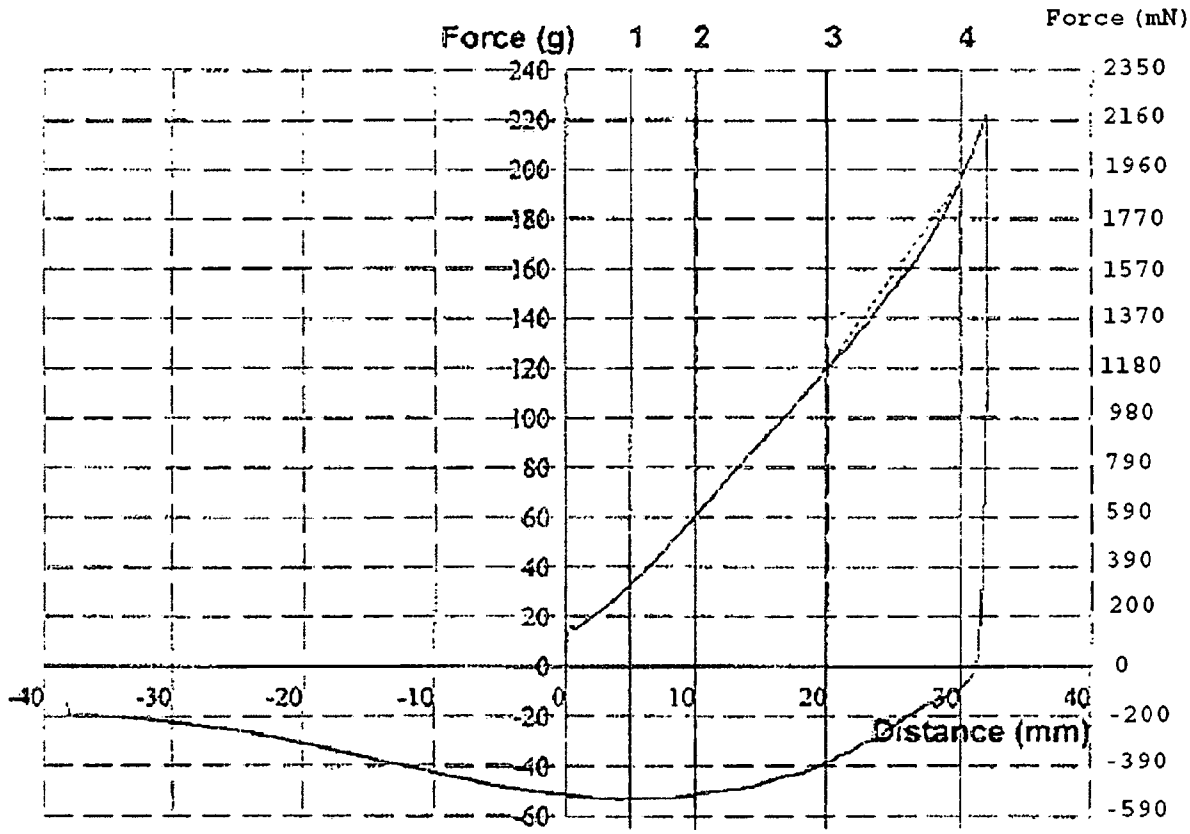
providing the adhesive composition of any one of claims 1-20 by mixing the Part (A) formulation with the Part (B) formulation to form a fluid epoxy mixture comprising the rheology modifying fiber filler;

applying the fluid epoxy mixture to the cementitious structure; and,

curing the fluid epoxy mixture to form a seal and bond having a compressive strength of at least 55,000 kPa (8000 psi).

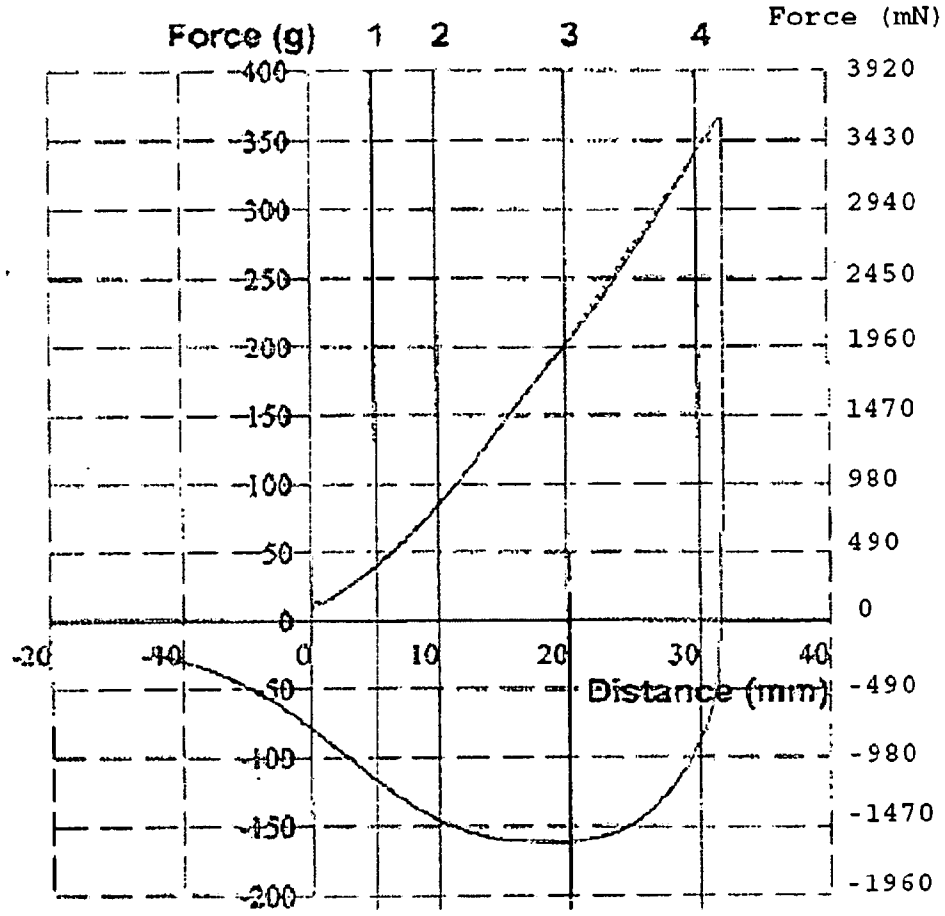
22. The method of claim 21, wherein the epoxy resin comprises a bisphenol A-epichlorohydrin resin, the hardening agent comprises at least one of a cycloaliphatic amine and a tertiary amine and the rheology modifying fiber filler comprises polyethylene fibers.

Figure 1



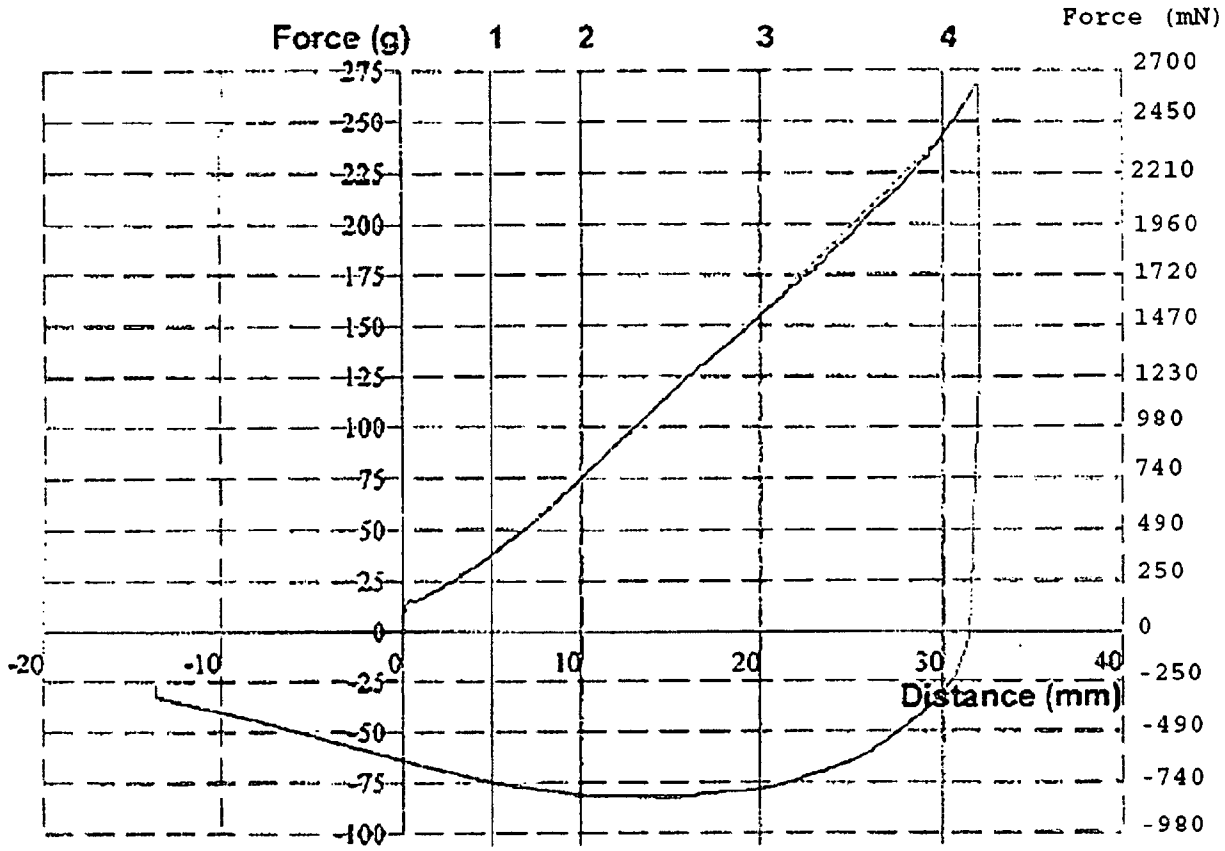
Normal Set Adhesive – Medium Temperature Range

Figure 2



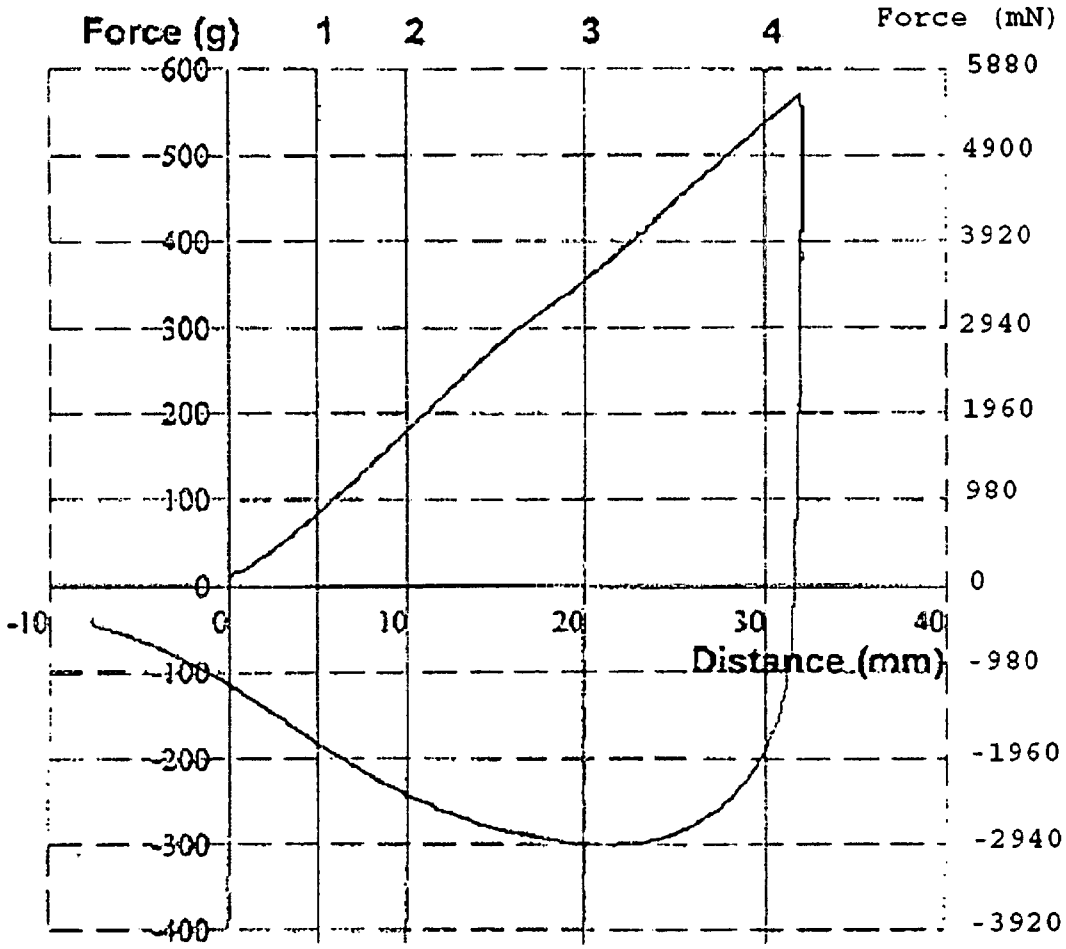
Normal Set Adhesive – Medium Temperature Range (Prior Art)

Figure 3



Normal Set Adhesive – High Temperature Range

Figure 4



Normal Set Adhesive - High Temperature Range (Prior Art)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/057469

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J183/00 C08J5/04 C08G59/06 C08G59/50 E01D19/06
C08K7/02
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J C08J C08G E01D C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 248 204 B1 (SCHUFT CHARLES F [US]) 19 June 2001 (2001-06-19)	1-4,6-8, 11-14, 16-19
Y	tables 1-4 abstract columns 3-8	1-22

X	WO 2010/011710 A2 (3M INNOVATIVE PROPERTIES CO [US]; CAMPBELL CHRISTOPHER J [US]; POCIUS) 28 January 2010 (2010-01-28)	1-20
Y	pages 3-8; table 17 pages 17-23	1-22

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 July 2012	18/07/2012

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/057469

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200529 Thomson Scientific, London, GB; AN 2005-273561 XP002679549, -& CN 1 546 589 A (LIAONING DATONG ROAD ENG CO LTD) 17 November 2004 (2004-11-17)	1,21
Y	abstract examples 1-8; table 1	1-22
Y	PHAM ET AL: "Epoxy Resins", 1 January 2004 (2004-01-01), ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY,, PAGE(S) 1 - 127, XP007920796, pages 786,784; tables 21-22,14	1-22
A	US 2007/264506 A1 (WIGGER THOMAS [CH]) 15 November 2007 (2007-11-15) paragraphs [0053] - [0055]; example 1	1-22

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/057469

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6248204 B1	19-06-2001	NONE	
WO 2010011710 A2	28-01-2010	CN 102159615 A	17-08-2011
		EP 2310436 A2	20-04-2011
		JP 2011529118 A	01-12-2011
		KR 20110034673 A	05-04-2011
		US 2011126980 A1	02-06-2011
		WO 2010011710 A2	28-01-2010
CN 1546589 A	17-11-2004	NONE	
US 2007264506 A1	15-11-2007	CN 1764692 A	26-04-2006
		EP 1475412 A1	10-11-2004
		EP 1622977 A1	08-02-2006
		JP 4308248 B2	05-08-2009
		JP 2006524716 A	02-11-2006
		US 2007264506 A1	15-11-2007
		WO 2004099312 A1	18-11-2004