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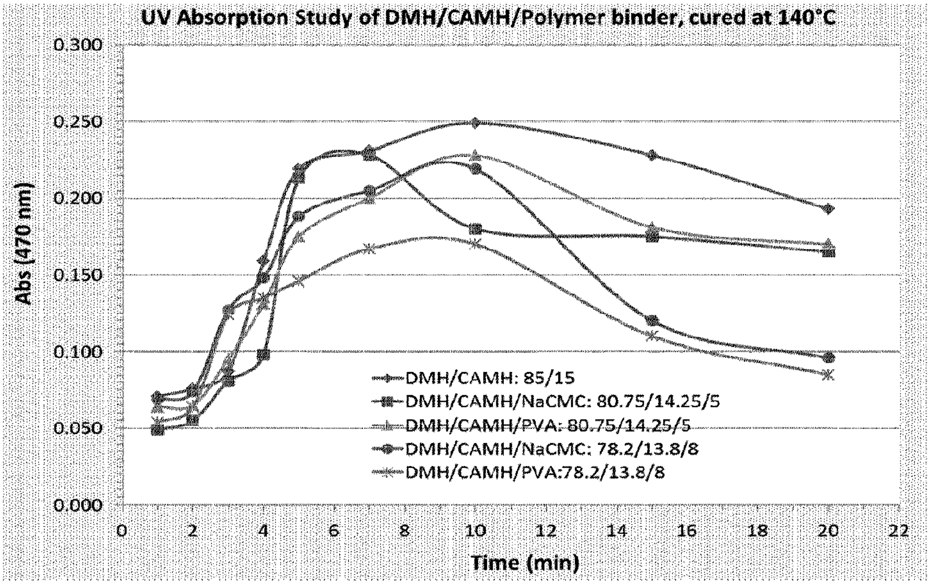

(57) **Abrégé/Abstract:**

The present invention relates to new aqueous binder compositions comprising an aqueous curable binder composition comprising starting materials required for forming a thermoset resin upon curing and a matrix polymer, wherein the starting materials required for forming a thermoset resin upon curing comprise (i) a polyhydroxy component and a polycarboxylic acid component, or an anhydride, ester or salt derivative thereof and/or reaction product thereof, or (ii) a carbohydrate component and a nitrogen containing component and/or a reaction product thereof.

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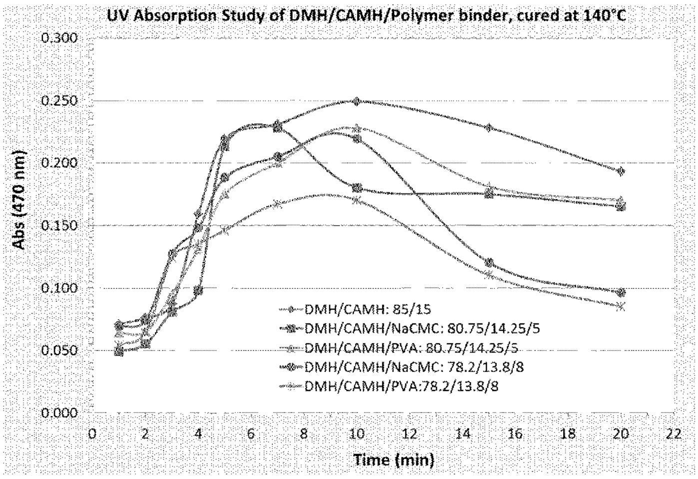
Fig. 2



(57) **Abstract**: The present invention relates to new aqueous binder compositions comprising an aqueous curable binder composition comprising starting materials required for forming a thermoset resin upon curing and a matrix polymer, wherein the starting materials required for forming a thermoset resin upon curing comprise (i) a polyhydroxy component and a polycarboxylic acid component, or an anhydride, ester or salt derivative thereof and/or reaction product thereof, or (ii) a carbohydrate component and a nitrogen containing component and/or a reaction product thereof.

Improved Binder Compositions and Uses Thereof

The present invention relates to new improved binder compositions, more specifically curable binder compositions for use in manufacturing products from a collection of non or loosely assembled matter. For example, these binder compositions may be employed to fabricate fiber products which may be made from woven or nonwoven fibers. In one illustrative embodiment, the binder compositions are used to bind glass fibers to make fiberglass. In another illustrative embodiment, the binder compositions are used to bind mineral wool fibers, such as glass wool or stone wool in a matted layer, such as an insulating product. In a further embodiment, the binders are used to make cellulosic compositions. With respect to cellulosic compositions, the binders may be used to bind cellulosic matter to fabricate, for example, wood fiber board or particle board which has desirable physical properties (e.g., mechanical strength). The invention further extends to a product made from loosely assembled matter bound by a binder of the invention.

Several formaldehyde-free binder compositions have been developed in recent times. One such curable binder composition involves sustainable materials and is based on polyester chemistry, more particularly curable aqueous binder compositions comprising a polyacid component or anhydride or salt derivatives thereof, and a polyhydroxy component, possibly together with a silicon containing compound. Another such composition involves the condensation of ammonium salt of inorganic acids or of polycarboxylic acids or an amine, preferably a polyamine, with reducing sugars as thermosets. These chemistries show advantages as compared to prior formaldehyde based technology, but also show certain weaknesses, and there still is a need for improved binder chemistry. Some of the known binder chemistries show a relatively high binder weight loss upon exposure to heat. Some also show undesirable degradation in humid environments which may negatively affect the bond strength properties of the products containing same. There further is an ongoing interest in improving the bond strength of the employed binder compositions, hence providing improved final products, showing improved properties, and/or final products with reduced binder content, at more advantageous costs.

The present invention seeks to provide binders which generate or promote cohesion and are capable of holding a collection of matter together such that the matter adheres in a manner to resist separation. An objective of the present invention is to provide binders showing improved bond strength, as compared to close prior art binder compositions, more particularly such binder compositions based on polyester chemistry or the condensation of ammonium salt of inorganic acid or ammonium salt of polycarboxylic acids or amine with reducing sugars as thermosets.

Another objective of the present invention is to provide cost-effective binder compositions for large volume applications.

Another objective is to provide a binder composition based on renewable and/or sustainable resources.

Further, the invention seeks to provide binder compositions that rapidly cure into strong binders.

Yet another purpose of the invention is to provide an assembly of matter bonded with the invention binder.

The present invention now provides an aqueous curable binder composition comprising the starting materials required for forming a thermoset resin upon curing and a matrix polymer.

The matrix polymer may be of natural and/or synthetic origin. These polymers may act as an active filling agent in the binder formulation, and may form intra- and inter- molecular chain interactions. Naturally derived polymers may advantageously be selected from polysaccharides, such as chitosan, cellulose and its derivatives, such as cellulose ether and ester derivatives. The cellulose ether derivatives can be prepared by carboxymethylation, carboxyethylation and carboxypropylation. Examples of preferred cellulose ether derivatives are: nanocellulose, carboxymethyl cellulose (CMC), sodium carboxymethyl cellulose (NaCMC), hydroxypropyl cellulose (HPC), hydroxyethyl cellulose (HEC), hydroxypropylmethyl cellulose (HPMC), methyl cellulose (MC), ethyl cellulose (EC), trityl cellulose, and so on. The preferred cellulose ester derivatives include acetates, butyrates, benzoates, phthalates and anthranilic acid esters of cellulose, preferably, cellulose acetate phthalate (CAP), cellulose acetate butyrate (CAB), cellulose acetate trimelitate (CAT), hydroxylpropylmethyl cellulose phthalate (HPMCP), succinoyl cellulose, cellulose fuoroate, cellulose carbanilate, and mixtures thereof. In some binder compositions cationic cellulose derivatives may be used. Some binder compositions may comprise other polysaccharides such as alginates, starch, chitin and chitosan, agarose, hyaluronic acid, and their derivatives or copolymers (e.g., graft-copolymer, block copolymer, random copolymers), or mixtures thereof.

Chitosan is a polysaccharide derived from crustacean shells, like shrimp shells. Chitosan may have different molecular weights and deacetylation degrees. Preferred are molecular weights between 500 Daltons and $2 . 10^6$ Daltons, more preferably between 60×10^3 and 2×10^5Da.

Synthetically derived polymers may include polyacrylates, polymethacrylates, polyacrylamides, polymethacrylamides, polyurethanes, polyesters, polyvinyls and/or their copolymers, aliphatic isocyanate oligomers, azetidinium groups containing polymer (azetidinium polymer) or mixtures thereof.

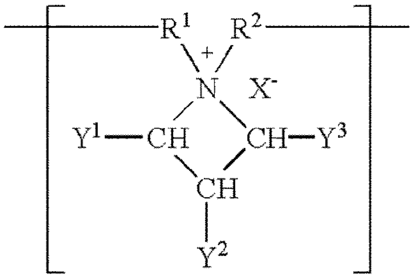
In one embodiment the binder formulation may comprise polyacrylate, polymethacrylate or polyacrylamide or mixtures thereof, which may be formed from polymerisation of one or more, typically two or three, monomers, which may be present in differing amounts. Preferably the one of the monomers is a substituted alkyl methacrylate or acrylate monomer. The alkyl group of the substituted alkyl function may have from 1 to 10, preferably 1 to 4 carbon atoms and the substituent group may be an alkoxy group with 1 to 4 carbon atoms, such as a methoxy group, or a dialkylamino group, such as dimethylamino. Particularly preferred acrylate monomers are: 2-methoxyacrylate (MEA), 3,5,5-trimethylhexyl acrylate (TMHA), ethylene glycol acrylate (EGA), 2-ethoxyethyl acrylate (EOEA), ethylene glycol diacrylate (EGDA), ethyl 2-ethylacrylate (EEA), (ethyl-cyano)acrylate (ECA), ethyl 2-propyl acrylate (EPA), ethyl 2-(trimethylsilylmethyl)acrylate (ETMSMA), butyl acrylate (BA), butylcyclohexyl acrylate (BCHA), benzyl 2-propyl acrylate (BPA), carboxyethyl acrylate (CEA), 2-(diethylamino)ethyl acrylate (DEAEA), 2-(diethylamino)propyl acrylate (DEAPA). The examples of preferred metharcylate monomers are: methylmethacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2-methoxymethacrylate (MEMA), 2-(diethylamino) ethyl methacrylate (DEAEMA), 2-aminoethyl methacrylate (AEMA), benzyl methacrylate (BMA), 2-butoxyethyl methacrylate (BEMA), 2-(tert-butylamino)ethyl methacrylate (TBAEMA), cyclohexyl methacrylate (CHMA), ethylene glycol methacrylate (EGMA), 2-(diisopropylamino)ethyl methacrylate (DIPAEMA). Preferred acrylamide/methacrylamide monomers are: alkylacrylamide (AAAm), butylacrylamide (BAAm), diethylacrylamide(DEAAm), N,N-dimethyl acrylamide (DMAAm), ethylacrylamide (EAAm), hydroxyethyl acrylamide (HEAAm), hydroxymethyl acrylamide (HMAAm), N-isopropyl acrylamide (NIPAAm), N,N-diethylmethacrylamide (DEMAAm), N-diphenyl methacrylamide (DPMAAm). Preferred polymers comprise two or more monomers and typically a mixture of MEMA or MEA, and DEAEMA or vise versa, in the range between 5:95 and 95:5 percent by weight, advantageously from 10:90 to 90:10, preferably from 20:80 to 80:20, more preferably from 30:70 to 70:30. Optionally further monomers may be present, such as acrylic acid (AA) or methacrylic acid (MAA) in a weight ratio of 1 to 10 percent, preferably about 5 percent by weight. A suitable polymer includes MEMA, DEAEMA and AA in a ratio of 55:40:5 to 75:20:5. Such polymers may comprise one or more monomers which include an aryl group, such as styrene (St) and optionally a dialkylacrylamide group (alkyl representing 1 to 4 carbon atoms), such as dimethylacrylamide (DMAA); and diethylacrylamide (DEAA). Preferably the polymers comprise two monomers selected from styrene and a dialkylacrylamide. Preferred polymers comprise, or consist of the following monomers: St:DMAA and St:DEAA and which may be present in the range of ratios between 40:60 and 95:5. Additional polymers which may be used in binder formulations of the invention may comprise MEA (2-methoxyacrylate) and a dialkylacrylamide group (alkyl representing 1 to 4 carbon atoms), such as dimethylacrylamide (DMAA); and diethylacrylamide (DEAA). Preferred polymers comprise or consist of MEA:DMAA and MEA:DEAA, which may be present in the ratios between 30-80:70-20 respectively.

According to another embodiment of the invention, the binder composition may comprise a polyurethane matrix polymer which provides bond strength and faster curing. Polyurethane polymers may be formed by polymerising a polydiol with a diisocyanate and optionally with an extender molecule, such as a diol. The extender molecules have the effect of modifying the physical character of the polymers, for example, polymer shape, viscosity and polymer state. The polydiol may be selected from the group consisting of but not limited to, poly(polypropylene glycol)-poly(ethylene glycol) (PPG-PEG), polyethylene glycol (PEG), poly(caprolactone)-diol (PCL-diol), poly(lactic acid)-diol (PLA-diol), poly(glycolic acid)-diol (PGA-diol), poly(tetramethylene glycol) (PTMG) also known as poly(butylene glycol), poly[1,6-hexanediol/neopentyl glycol-alt-(adipic acid)]diol (PHNAD), poly[1,6-hexanediol/neopentyl glycol/diethylene glycol-alt-(adipic acid)]diol (PHNDGAD), poly(dimethyl siloxane)-diol (PDMS). The molecular weight of the polydiol may range from M_n=200 to M_n=7000 and it may be present in an amount of 15-55% by weight, such as 20-50% by weight of the polymer. The diisocyanate may be selected from the group consisting of but not limited to methylene diphenyl diisocyanate (MDI), 1,4-phenylene diisocyanate (PDI), 1,1'-methylenebis(4-isocyanatocyclohexane) (HMDI), 2,4-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), 1,3-bis(isocynanatomethyl) cyclohexane (BICH). Typically the diisocyanate is present in an amount of 45-55% by weight of the polymer. Suitable extenders include 1,4-butanediol (BD), ethylene glycol (EG), 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (OFHD); and 3-dimethylamino-1,2-propanediol (DMAPD). When present, the extender may be present in an amount of 10-30 mol% of the polymer, typically 10-25%.

In yet another embodiment, the binder composition may comprise polyesters, copolymers or mixtures (blends) thereof. Non limiting examples of preferred polyesters are: polyglycolide or polyglycolic acid (PGA), polylactic acid (PLA), polycaprolactone (PCL), polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), polyethylene adipate (PEA), polybutylene succinate (PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene naphthalate (PEN), vectran, and /or their copolymers such as PCL-PLA, PCL-PGA, PLA-PGA, PCL-PLA-PCL, PIBVE-b-PCL, and others.

Furthermore, the binder composition of the invention may comprise vinyl polymers and amic acid based polymers, such as poly(pyromellitic dianhydride-co-4,4'oxodianiline) amic acid. Preferably, these may include polyethylene, polypropylene, polybutadiene, polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), partially hydrolized polyvinyl acetate, polyacrylonitrile (PAN), polyvinyl butyral (PVB), and polyvinyl toluene (PVT) and/or their copolymers such as PVA-b-PS, PS-b-PMMA, PS-b-PAN, PVA-PGMA, or mixtures thereof. The above said polymers may be incorporated into the binder formulation in homogeneous (aqueous solution) or heterogeneous (emulsion) systems. The solution or emulsion polymers may be present in the composition in an amount ranging from 0.5% up to 50% by weight based on total solids.

In another preferred embodiment, the binder composition may comprise an azetidinium polymer. Such material is known per se and may be obtained by the reaction of a polyamidoamine and a halohydrin. An azetidinium polymer is made up of at least two monomeric units containing a substituted or unsubstituted four membered nitrogen containing heterocycle. The azetidinium polymer may be a homopolymer or a copolymer comprising one or more non-azetidinium monomer units incorporated into the polymer structure. A preferred polyazetidinium suitable for use in accordance with the invention shows the formula



wherein R_1 may be $C_1 - C_{25}$ alkanediyl, preferably $C_1 - C_{10}$ alkanediyl or $C_1 - C_5$ alkanediyl, possibly substituted with a hydroxyl group, carboxyl functional group or an amine,

R_2 may be independently R1 or $-R_3$-NH-C(O)-R4-, with R_3 and R_4 being independently $C_1 - C_{25}$ alkanediyl, preferably $C_1 - C_{10}$ alkanediyl or $C_1 - C_5$ alkanediyl,

Y_1 and Y_3 being H or a C1-C5 alkyl group, possibly substituted with a hydroxyl group, an amine or a carboxyl group,

Y2 being OH or independently Y1,

X^- being a halogen counter ion.

An example of such an azetidinium polymer is the product coded CA1025.

Carbohydrate based binders or binder compositions may comprise polymer micro- and/or nano-particles. Preferred micro- and/or nano-particles derived from natural polymers are selected from polysaccharides, such as chitin and chitosan, cellulose and its derivatives, such as cellulose ether and ester derivatives, alginates, starch, agarose, hyaluronic acid, and their derivatives or copolymers, and mixtures thereof. Preferable nano materials are nanocelluloses such as cellulose nanocrystals or cellulose nanowhiskers or nanofibres and / or mixtures thereof.

Synthetically derived polymer micro- and/or nano-particles particularly suitable for carbohydrate based binders are advantageously selected from polyacrylates, polymethacrylates, polyacrylamides, polymethacrylamides, polyurethanes, polyesters, and aliphatic isocyanate oligomers, or copolymers and/or mixtures thereof.

The weight ratio of the matrix polymer may make up from about 1 to 20 % dry weight of the binder composition, preferably from about 2 to 18 % dry weight, more preferably from 5 to 15 % dry weight of the composition.

The said matrix polymers, more specifically the polymers exemplified above, may show a molecular weight ranging from 500 Daltons (Da) to $2x10^6$ Da, preferably from $1 \times 10^3 - 5 \times 10^5$ Da, more preferably 5×10^4 Da – 3×10^5 Da.

One or more pre-formed polymers, or monomers, possibly together with initiator, may be emulsion dispersed or solubilised in the binder composition.

It has been found that by adding additional matrix polymer into the binder composition comprising the starting materials for forming the desired binder resin upon curing, higher bonding strength may be obtained. The addition of such matrix polymer may further reduce the binder loss upon curing of the binder resin. Also, the addition of a matrix polymer reduces the water absorption of the binder, as compared to the same binder which includes no additional matrix polymer.

When a polyester resin type binder is desired, the starting materials are selected from compounds bearing hydroxide functional groups and compounds bearing carboxylic acid functional groups, or anhydride or salt derivatives thereof, such that upon curing under appropriate curing conditions the desired polyester resin is obtained. Such polyester based resins are well known in the technical field. As mentioned above, the hydroxide functional compound may be selected from carbohydrates, such as dextrose, and the compound bearing carboxylic acid functional groups, or anhydride or salt derivatives thereof, may be selected from polycarboxylic acid, anhydride or salt thereof.

The polycarboxylic acid may advantageously be selected from monomeric and polymeric polycarboxylic acids. Illustratively, a monomeric polycarboxylic acid may be a dicarboxylic acid, including, but not limited to, unsaturated aliphatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids, unsaturated cyclic dicarboxylic acids, saturated cyclic dicarboxylic acids, hydroxy-substituted derivatives thereof, and the like. Or, illustratively, the polycarboxylic acid(s) itself may be a tricarboxylic acid, including, but not limited to, unsaturated aliphatic tricarboxylic acids, saturated aliphatic tricarboxylic acids, aromatic tricarboxylic acids, unsaturated cyclic tricarboxylic acids, saturated cyclic tricarboxylic acids, hydroxy-substituted derivatives thereof, and the like. It is appreciated that any such polycarboxylic acids may be optionally substituted, such as with hydroxy, halo, alkyl, alkoxy, and the like. In one variation, the polycarboxylic acid is the saturated aliphatic tricarboxylic acid, citric acid. Other suitable polycarboxylic acids are contemplated to include, but are not limited to, aconitic acid, adipic acid, azelaic acid, butane tetracarboxylic acid dihydride, butane tricarboxylic acid, chlorendic acid, citraconic acid, dicyclopentadiene-maleic acid adducts, diethylenetriamine pentaacetic acid, adducts of dipentene and maleic acid, ethylenediamine tetraacetic acid (EDTA), fully maleated rosin, maleated tall-oil fatty acids, fumaric acid, glutaric acid, isophthalic acid, itaconic acid, maleated rosin oxidized with potassium peroxide to alcohol then carboxylic acid, maleic acid, malic acid, mesaconic acid, bisphenol A or bisphenol F reacted via the KOLBE-Schmidt reaction with carbon dioxide to introduce 3-4 carboxyl groups, oxalic acid, phthalic acid, sebacic acid, succinic acid, tartaric acid, terephthalic acid, tetrabromophthalic acid, tetrachlorophthalic acid, tetrahydrophthalic acid, trimellitic acid, trimesic acid, and the like, and anhydrides, and combinations thereof. Illustratively, a polymeric polycarboxylic acid may be an acid, for example, polyacrylic acid, polymethacrylic acid, polymaleic acid, and like polymeric polycarboxylic acids, copolymers thereof, anhydrides thereof, and mixtures thereof. Examples of commercially available polyacrylic acids include AQUASET-529 (Rohm & Haas, Philadelphia, PA, USA), CRITERION 2000 (Kemira, Helsinki, Finland, Europe), NF1 (H.B. Fuller, St. Paul, MN, USA), and SOKALAN (BASF, Ludwigshafen, Germany, Europe). With respect to SOKALAN, this is a water-soluble polyacrylic copolymer of acrylic acid and maleic acid, having a molecular weight of approximately 4000. AQUASET- 529 is a composition containing polyacrylic acid cross-linked with glycerol, also containing sodium hypophosphite as a catalyst. CRITERION 2000 is an acidic solution of a partial salt of polyacrylic acid, having a molecular weight of approximately 2000. With respect to NF1, this is a copolymer containing carboxylic acid functionality and hydroxy functionality, as well as units with neither functionality; NF1 also contains chain transfer agents, such as sodium hypophosphite or organophosphate catalysts.

As described in U.S. Patents Nos. 5,318,990 and 6,331,350, the polymeric polycarboxylic acid comprises an organic polymer or oligomer containing more than one pendant carboxy group. The polymeric polycarboxylic acid may be a homopolymer or copolymer prepared from unsaturated carboxylic acids including, but not necessarily limited to, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, cinnamic acid, 2-methylmaleic acid, itaconic acid, 2-methylitaconic acid, α,β-methyleneglutaric acid, and the like. Alternatively, the polymeric polycarboxylic acid may be prepared from unsaturated anhydrides including, but not necessarily limited to, maleic anhydride, itaconic anhydride, acrylic anhydride, methacrylic anhydride, and the like, as well as mixtures thereof. Methods for polymerizing these acids and anhydrides are well-known in the chemical art. The polymeric polycarboxylic acid may additionally comprise a copolymer of one or more of the aforementioned unsaturated carboxylic acids or anhydrides and one or more vinyl compounds including, but not necessarily limited to, styrene, α-methylstyrene, acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, glycidyl methacrylate, vinyl methyl ether, vinyl acetate, and the like. Methods for preparing these copolymers are well-known in the art. The polymeric polycarboxylic acids may comprise homopolymers and copolymers of polyacrylic acid. The molecular weight of the polymeric polycarboxylic acid, and in particular polyacrylic acid polymer, may be is less than 10000 Da, less than 5000 Da, or about 3000 Da or less. For example, the molecular weight may be 2000 Da.

The carbohydrate may include one or more reactants having one or more reducing sugars. In one aspect, any carbohydrate reactant should be sufficiently nonvolatile to maximize its ability to remain available for reaction with the amine reactant. The carbohydrate reactant may be a monosaccharide in its aldose or ketose form, including a triose, a tetrose, a pentose, a hexose, or a heptose; or a polysaccharide; or combinations thereof. A carbohydrate reactant may be a reducing sugar, or one that yields one or more reducing sugars *in situ* under thermal curing conditions. For example, when a triose serves as the carbohydrate reactant, or is used in combination with other reducing sugars and/or a polysaccharide, an aldotriose sugar or a ketotriose sugar may be utilized, such as glyceraldehyde and dihydroxyacetone, respectively. When a tetrose serves as the carbohydrate reactant, or is used in combination with other reducing sugars and/or a polysaccharide, aldotetrose sugars, such as erythrose and threose; and ketotetrose sugars, such as erythrulose, may be utilized. When a pentose serves as the carbohydrate reactant, or is used in combination with other reducing sugars and/or a polysaccharide, aldopentose sugars, such as ribose, arabinose, xylose, and lyxose; and ketopentose sugars, such as ribulose, arabulose, xylulose, and lyxulose, may be utilized. When a hexose serves as the carbohydrate reactant, or is used in combination with other reducing sugars and/or a polysaccharide, aldohexose sugars, such as glucose (i.e., dextrose), mannose, galactose, allose, altrose, talose, gulose, and idose; and ketohexose sugars, such as fructose, psicose, sorbose and tagatose, may be utilized. When a heptose serves as the carbohydrate reactant, or is used in combination with other reducing sugars and/or a polysaccharide, a ketoheptose sugar such as sedoheptulose may be utilized. Other stereoisomers of such carbohydrate reactants not known to occur naturally are also contemplated to be useful in preparing the binder compositions as described herein. When a polysaccharide serves as the carbohydrate, or is used in combination with monosaccharides, sucrose, lactose, maltose, starch, and cellulose may be utilized. The carbohydrate component may advantageously comprise oligomers or polymers that result from the hydrolysis of a polysaccharide, such as starch, cellulose or molasses. Such hydrolysates are capable of generating reducing sugars in situ and/or already comprise reducing sugars and further may contribute to the effect of the matrix polymer. Preferred are hydrolysates that show a DE (dextrose equivalent) of 25 to 90, preferably 35 to 85, or 45 to 85, most preferably 55 to 80.

When Maillard compounds based binders are desired, that means binders based on the reaction between a reducing sugar and a nitrogen containing compound, the carbohydrate compound may advantageously be selected from the carbohydrates mentioned here above. Among these dextrose is the most preferred. The nitrogen containing compound may advantageously be selected from ammonium salt of inorganic acids or organic acids and amine compounds.

The inorganic acid part of ammonium salt may advantageously be selected from phosphoric, sulphuric, nitric and carbonic acid. Ammonium sulphate and ammonium phosphate are preferred. The organic acid may be selected from the polycarboxylic acids mentioned here above.

The amine compound may advantageously be selected from polyamine functional compounds comprising primary and/or secondary amine functional groups. In illustrative embodiments, the polyamine is a primary polyamine. In one embodiment, the polyamine may be a molecule having the formula of $H_2N\text{-}Q\text{-}NH_2$, wherein Q is an alkyl, cycloalkyl, heteroalkyl, or cycloheteroalkyl, each of which may be optionally substituted. In one embodiment, Q is an alkyl selected from a group consisting of C_2-C_{24}. In another embodiment, Q is an alkyl selected from a group consisting of C_2-C_8. In another embodiment, Q is an alkyl selected from a group consisting of C_3-C_7. In yet another embodiment, Q is a C_6 alkyl. In one embodiment, Q is selected from the group consisting of a cyclohexyl, cyclopentyl or cyclobutyl. In another embodiment, Q is a benzyl. In illustrative embodiments, the polyamine is selected from a group consisting of a di-amine, tri-amine, tetra-amine, and penta-amine. In one embodiment, the polyamine is a diamine selected from a group consisting of 1,6-diaminohexane and 1,5-diamino-2-methylpentane. In a preferred embodiment, the di-amine is 1,6-diaminohexane. In one embodiment, the polyamine is a tri-amine selected from a group consisting of diethylenetriamine, 1-piperazineethaneamine, and bis(hexamethylene)triamine. In another embodiment, the polyamine is a tetra-amine such as triethylenetetramine. In another embodiment, the polyamine is a penta-amine, such as tetraethylenepentamine. In another embodiment, the polyamine is selected from polyethyleneimine (PEI), polyninyl amine, polyether amine, polylysine. As is known to the skilled person, several different types of polyethylenimines are available, such as linear polyethylenimines, branched polyethylenimines and dendrimer type polyethylenimine; all are suitable in the binder compositions of the invention. Similarly, polyetheramines may show a linear form and branched forms, and all are believed to be suitable for the generation of binder compositions and, hence, binders of the invention.

The dry weight ratio of carbohydrate to ammonium salt of inorganic or polycarboxylic acid ranges from about 2 to about 15, preferably from about 2.5 to about 13. The matrix polymer may make up from about 1 to 20 % dry weight of the binder composition, preferably from about 2 to 18 % dry weight, more preferably from 5 to 15 % dry weight of the composition.

The binder compositions of the invention and binders produced therefrom are essentially formaldehyde-free (that is comprising less than about 1 ppm formaldehyde based on the weight of the composition) and do not liberate substantial formaldehyde. They furthermore are based on natural, hence renewable, resources.

The invention compositions may obviously further comprise coupling agents, dyes, antifungal agents, antibacterial agents, hydrophobes and other additives known in the art for such binder applications, as may be appropriate. Silicon-containing coupling agents are typically present in such binders, generally in the range from about 0.1 to about 1 % by weight based on the weight of the solids in the binder composition. These additives are obviously selected such as not to antagonise the adhesive properties of the binder nor the mechanical and other desired properties of the final product comprising such binder composition or binder produced therefrom, and advantageously comply with stringent environmental and health related requirements.

Without being bound by theory, it is believed that curing generates highly crosslinked high molecular weight polymers. These may be analysed by techniques generally known in the art, including determination of molecular weight, and other known techniques.

According to the present invention, the term “binder composition” is not particularly restricted and generally includes any composition which is capable of binding loosely assembled matter, either as such or upon curing.

As used herein, the term “aqueous” is not particularly limited and generally relates to a solution and/or dispersion which is based on water as a solvent. Said term further includes compositions or mixtures which contain water and one or more additional solvents. An "aqueous binder composition" of the invention may be a solution or partial solution of one or more of said binder components or may be a dispersion, such as an emulsion or suspension.

The solid content of the invention aqueous binder composition may range from 5 to 95 w%, advantageously from 8 to 90 w%, preferably from 10 to 85 w%, based on the weight of the total aqueous binder composition. More specifically, when used as a binder for mineral wool insulation, the solid content of the aqueous binder composition may be in the range from 5 to 25 w%, preferably from 8 to 20 w%, more preferably from 10 to 20 w% or even 12 to 18 w%, based on the weight of the total aqueous binder composition. When used as a binder in wood boards, the solid content of the aqueous binder composition may range from 50 to 95 w%, preferably 50 to 90 w%, more preferably 55 to 85 w% or even 60 to 80 w%, based upon the weight of the total aqueous binder composition.

Binder compositions of the invention may further comprise nano-particles derived from inorganic materials such as metal-oxides, preferably MgO, CaO, Al_2O_3 and $CaCO_4$. Furthermore, nanoclays may be incorporated in the binder formulations. Such nanoclays include, without being limited to, montmorillonite, bentonite, kaolinite, hectorite, and halloysite and other organically-modified nanoclays, and/or mixtures thereof. Such inorganic materials may be present in an amount ranging from 0.1 to 10 w%, preferably 0.1 to 5 w%, of solid content of the total composition.

The components of the invention binder compositions may be transported separately and combined shortly before use in the relevant manufacturing plant. It is also possible to transport the binder composition as such.

The binders of the invention may be used to bond a collection of non or loosely assembled matter. The collection of matter includes any collection of matter which comprises fibers selected from mineral fibers, including but not limited to slag wool fibers, stone wool fibers, glass fibers, aramid fibers, ceramic fibers, metal fibers, carbon fibers, polyimide fibers, polyester fibers, rayon fibers, and cellulosic fibers. Further examples of collection of matter include particulates such as coal, sand, cellulosic fibers, wood shavings, saw dust, wood pulp, ground wood, wood chips, wood strands, wood layers, other natural fibers, such as jute, flax, hemp, straw, wood veneers, facings and other particles, woven or non-woven materials. According to a specific embodiment of the invention, the collection of matter is selected from wood particles and mineral fibers.

In one illustrative embodiment, the binder composition of the invention may be used to make insulation products, comprising mineral fibers. In such an application, the fibers are bonded together such that they become organized in a fiberglass mat which may then be processed into an insulation product. In such an application, the fibers are generally present in an amount ranging from 70 to 99%.

According to another embodiment of the invention, the binder may be used to bond cellulosic particles, such as cellulosic fibers, wood shavings, wood pulp and other materials commonly used to manufacture composite wood boards, including fiber boards, particle boards, oriented strand boards etc. Such wood boards show nominal thicknesses ranging from 6 to 30 mm and a modulus of Elasticity of at least about 1000 N/mm^2, bending strength of at least about 5 N/mm^2 and/or an internal bond strength of at least 0.10 N/mm^2. In such applications, the binder content in the final wood board may range from about 5 to 30 % wt with respect to the total weight of the wood board notably from 9 to 20%.

According to the invention, the aqueous binder composition may be applied in a manner known per se onto the fiber or particular material. The binder composition may preferably be applied by spray application. Other techniques include roll application or mixing and/or tumbling the collection of matter with the binder composition. As water evaporates the binder composition forms a gel that bonds the particulate material together when arranged into a desirable assembly as detailed further herein below. When curing, the reactive binder components are caused to react to form essentially water insoluble macromolecular binder intermingled with matrix polymer. Curing thus imparts increased adhesion, durability and water resistance as compared to uncured binder. Curing may be effected at temperatures between ambient (from about 10 to 25 °C) and up to 280 °C.

According to another aspect, the invention covers a process for the preparation of a bonded assembly of fibrous materials or particulate materials by application of binder, curing and water evaporation. The obtained product may then be further processed in suitable process steps to make intermediate or final products, including but not limited to insulation products. More specifically, a process for the manufacturing of an assembly of fibers or cellulosic particles may comprise the successive or concomitant application of the relevant components of the binder composition described here above or the application of an aqueous binder composition as previously described onto a collection of fibers or particles; the gathering of the coated fibers or particles in an assembly; and curing whereby the carbohydrate and ammonium salt components are caused to react to form a macromolecular binder, and evaporating water.

Curing may be effected at a temperature ranging from 90 – 200 °C, preferably higher than 140 °C, more preferably lower than 190 °C, typically between 160 and 180 °C. In the manufacture of wood boards, curing is performed while the material is subjected to pressing.

The invention will be explained in more details in the examples below with reference to the attached Figures, in which:

- Figures 1 – 3 show the cure rate of several binder compositions;
- Figures 4a, 4b and 4c show bond strength before and after weathering for dextrose/ammonium sulphate/chitosan, dextrose/ammonium sulphate/PVA and dextrose/ammonium sulphate/CMC based binder compositions, respectively;
- Figure 5 shows the bond strength before and after weathering for dextrose/citric acid/polymer based binder compositions;
- Figures 6a and 6b show bond strength before and after weathering for dextrose/diammonium phosphate/CMC and dextrose/diammonium phosphate/chitosan based binder compositions, respectively; and
- Figures 7a, 7b and 7c show bond strength before and after weathering for dextrose/diammonium phosphate/CMC, dextrose/diammonium phosphate/PVA and dextrose/diammonium phosphate/chitosan based binder compositions, respectively.

In the following, examples, the following matrix polymers have been used:

Carboxymethyl cellulose (Na CMC) – M_W of approx. 250 kDa

Hydroxypropyl cellulose (HPC) – M_W of approx. 100 kDa

Hydroxyethyl cellulose (HEC) – M_W of approx. 250 kDa

Chitosan (CS) – Mw in the range 60 kDa – 220 kDa

Partially hydrolysed PVA - M_W in the range of 30 kDa – 70 kDa.

Preparation of binder compositions

The required amount of matrix polymer was dissolved in water. Similarly, the required amount of dextrose monohydrate (DMH) was dissolved in water separately, followed by addition of ammonium sulphate (AmSO4), diammonium phosphate (DAP) or citric acid monohydrate (CAMH) with constant stirring, as the case may be. Then the desired amount of polymer solution was added to the mixture of DMH solution or vice versa. The mixture was vigorously stirred in order to obtain a homogenous solution, followed by addition of other additives into the solution if applicable and vigorous stirring.

Determination of cure rate

A 50 µL sample of binder solution was dispensed onto a spot of a Whatman™ glass microfiber filter surface. Samples were kept on the top shelf in an oven, avoiding high moisture content inside the oven during curing. For each binder solution, samples were cured for different time periods ranging from 1 minute up to 20 minutes, at different temperatures. After curing, each glass filter sample was cut and fully immersed in 50 mL cold water in a 150 mL glass beaker, and then sonicated for 15 minutes at room temperature. The extract solution was filtered and the absorbance of the extract was determined with a spectrophotometer at 470 nm. The absorbance was plotted as a function of cure time. The results of various binder compositions are presented in Figures 1 – 3. As shown in Fig. 1, the matrix polymer addition to DMH/AmSO4 binder compositions shows no significant effect on the cure rate. The addition of matrix polymer to CAMH based binder compositions (Fig. 2) and DAP based binder compositions (Fig. 3) accelerated curing as demonstrated in Figures 2 and 3.

Determination of bond strength before and after weathering

Commercial PF (phenol formaldehyde) impregnated (A4 size) glass fiber veils were placed into a muffle furnace oven for 30 minutes at 600°C in order to burnout the PF binder, and were then allowed to cool for 30 minutes. The obtained veil samples were weighted.

Approx. 400 g binder solution samples were poured into dip trays, and the obtained veil samples carefully fully immersed into the relevant binder solutions. The impregnated veils were cured at desired temperature for desired periods of time. Binder content was then measured and bond strength determined as follows.

The bond strength of the relevant cured binder impregnated veils was determined by means of a testometric machine (M350-10CT). For each test a cured binder impregnated A4 veil was cut into 8 equal strips. Each strip was tested separately using a 50 Kg load cell (DBBMTCL-50 kg) at an automated test speed of 10 mm/min controlled by winTest Analysis software. Glass veil tensile plates were attached to the testometric machine in order to ensure a 100 mm gap between plates. Samples were placed vertically in the grippers; and the force was tarred to zero. Various parameters such as maximum load at peak, stress at peak and modulus (stiffness) were evaluated by the software, and data presented as an average of 8 samples with standard deviation. The average maximum load at peak or stress at peak defined as the bond strength.

Cured binder impregnated veils were placed in an autoclave (J8341, Vessel: PVO2626 with associated safety valve, door interlock and integrated pipework) system. Samples were treated at 90% humidity and at a temperature ranging from 40°C to 110°C (full cycle), at a pressure of up to 2.62 bar, for 3 hours. The samples were dried completely in order to ensure no moisture remains onto the veils. The autoclave treated samples were tested for bond strength by means of testometric machine (M350-10CT) described here above, and the results were compared with those of untreated samples.

The evaluation of bond strength was investigated for the veils impregnated with various binder compositions – see Figures 4 - 7. These impregnated veils were cured at 190 °C for 20 minutes and mechanical tests were performed at dry conditions.

In Fig. 4, the results for the following binder compositions are shown: DMH/AmSO4/CS, DMH/AmSO4/NaCMC and DMH/AmSO4/PVA. The bond strength was found to be ~ 66N for DMH/AmSO4 (85/15), when CS was added into the binder composition, the bond strength increased significantly. More specifically, the bond strength increased to 96N for DMH/AmSO4/CS (74/13/13) which is 45% higher bond strength as compared to that of DMH/AmSO4(85/15) binder (Figure 4a). Similarly the bond strength of DMH/AmSO4/NaCMC (particularly for the ratios of 74/13/13, 85/15/10 and 85/15/5) was higher than for DMH/AmSO4 (85/15) (Figure 4c). In the figures, the values presented in each graph are average values for the corresponding formulations. The dotted lines represent bond strength of binder composition containing no additional matrix polymer.

Bond strength after weathering was not significantly increased by addition of matrix polymer.

Figure 5 shows the bond strength results of various DMH/CAMH/NaCMC binder compositions impregnated into glass fiber veils. When NaCMC (5%) was added into the citric acid based composition, the bond strength increased by ~23% (Fig 5). Increase of the NaCMC concentration in the binder composition (DMH/CAMH/NaCMC) does not significantly affect the bond strength.

Figure 6 shows the bond strength before and after extreme weather treatment. The study was performed with 7% DAP, and the ratio of DMH/polymer was varied. Results (Fig 6) indicate the bond strength of DMH/DAP (93/7) is increased by addition of CMC or CS matrix polymer. When adding more matrix polymer into the binder composition (93/7), the bond strength remains essentially steady within the range.

The weather stability bond strength of all these DMH/DAP/NaCMC and DMH/DAP/CS compositions was also investigated, and the results are plotted in Figure 6 too. Results indicate that CS significantly increases the weather stability (compare DMH/DAP/CS to DMH/DAP (93/7)).

Figure 7 shows the bond strength of DMH/DAP/Polymer compositions before and after full cycle autoclaving: (a) DMH/DAP/NaCMC, (b) DMH/DAP/PVA and (c) DMH/DAP/CS. The values presented in each graph are the average values of the corresponding compositions. The DAP concentration was kept constant (12 - 13%). Results indicate that both NaCMC and CS significantly increase the bond strength as well as improved the weather stability as compared to that of DMH/DAP (87/13).

Binder weight loss upon curing

Binder solutions were prepared as described above and weighted samples showing a solids content of 2-5% were poured into aluminium petri dishes and kept in an oven for 2 hours at 140 °C. The theoretical and experimental values were determined and the weight loss was calculated. The results obtained for various compositions are shown in **Table 1** below. As can be seen, the binder weight loss is significantly reduced with addition of matrix polymer in the compositions.

Table 1. Binder weight loss upon curing at 140°C for 2 hours.

Formulations (wt. %)	**Binder Weight Loss (%)**
85% DMH + 15% AmSO4	31.52
80% DMH + 15% AmSO4 + 5% NaCMC	22.76
75% DMH + 15% AmSO4 + 10% NaCMC	16.67
70% DMH + 15% AmSO4 + 15% NaCMC	8.46
80% DMH + 15% AmSO4 + 5% CS	26.76
80% DMH + 15% AmSO4 + 5% PVA	21.65
85% DMH + 15% CAMH	32.75
80.75% DMH + 14.25% CAMH + 5% NaCMC	23.98
80.75% DMH + 14.25% CAMH + 5% PVA	24.72
78.2% DMH + 13.8% CAMH + 8% NaCMC	23.59
78.2% DMH + 13.8% CAMH + 8% PVA	24.68
85% DMH + 15% CAMH	32.75
87% DMH + 13% DAP	32.44
80% DMH + 12% DAP + 8% NaCMC	27.27
80% DMH + 12% DAP + 8% PVA	29.37
82.65% DMH + 12.35% DAP + 5% CS	27.97

Water absorption

100 g of binder solutions were prepared with desired solid content. Glass microfiber filter GFA were completely immerged and kept for 10 seconds in the relevant binder solutions, and then removed. The binder impregnated GFA samples were cured at desired temperatures, e.g. at 180 – 190 °C for 10 minutes, and the weight was measured (4 decimal point). Thereafter, the cured GFA samples were fully immerged into a beaker filled with 200 mL water. The samples were maintained for 1 hour under water by means of a glass rod. After 1 hour, the GFA samples were withdrawn and the surface water was absorbed by absorbent paper. The weight of the wet GFA sample was measured. The percentage of water absorption was determined for each sample in three replicates according to the following relationship.

% Water absorption = [(Mass of GFA wet – Mass of GFA dry)/Mass of GFA dry] x 100

Table 2 represents water absorption (%) for various compositions of DMH/AmSO4/Polymer, DMH/CAMH/Polymer and DMH/DAP/Polymer, with and without additive (silicone). It can be seen that water absorption is about 247% for standard known DMH/AmSO4 (85/15) binder. With the addition of matrix polymer such as NaCMC and CS the water absorption is significantly reduced, depending on the type and ratio of the matrix polymer used in the formulation. The addition of silicone (1% or 1.5%) in the composition further reduces water absorption significantly.

Table 2. Water absorption (%) of DMH/AmSO4/Polymer, DAP/CAMH/Polymer and DMH/DAP/Polymer binders.

DMH/AmSO4/Polymer Formulation	**Water Absorption**	**STDEV**
	(%)	**(+/-)**
DMH/AmSO4: 85/15	246.64	6.37
DMH/AmSO4/NaCMC: 85/15/5	210.32	0.47
DMH/AmSO4/NaCMC/Silicone: 85/15/5/1	144.85	10.49
DMH/AmSO4/NaCMC/Silicone: 85/15/5/1.5	115.36	5.71
DMH/AmSO4/NaCMC/Silicone: 85/15/5/3.0	109.47	1.36
DMH/AmSO4/NaCMC: 85/15/10	153.05	7.36
DMH/AmSO4/NaCMC/Silicone: 85/15/10/1	134.75	3.52
DMH/AmSO4/NaCMC/Silicone: 85/15/10/1.5	112.97	8.42
DMH/AmSO4/NaCMC/Silicone: 85/15/10/3.0	119.52	10.96
DMH/AmSO4/NaCMC 74/13/13	112.67	7.77
DMH/AmSO4/NaCMC/Silicone: 74/13/13/1	130.45	6.55
DMH/AmSO4/NaCMC/Silicone: 74/13/13/1.5	116.80	9.78
DMH/AmSO4/NaCMC/Silicone: 74/13/13/3.0	143.62	1.66
DMH/AmSO4/CS: 85/15/5	198.62	8.98
DMH/AmSO4/CS/Silicone: 85/15/5/1	76.92	0.97
DMH/AmSO4/CS: 85/15/10	145.25	5.78
DMH/AmSO4/CS/Silicone: 85/15/10/1	82.65	4.73
DMH/AmSO4/CS/Silicone: 85/15/10/1.5	79.76	0.56
DMH/CAMH/Polymer Formulation		
DMH/CAMH: 85/15	273.55	5.39
DMH/CAMH/NaCMC: 80.75/14.25/5	224.65	8.30
DMH/CAMH/NaCMC/Silicone: 80.75/14.25/5/1	76.33	4.43
DMH/CAMH/NaCMC: 78.2/13.8/8	190.18	12.62
DMH/CAMH/NaCMC/Silicone: 78.2/13.8/8/1	83.97	6.38
DMH/CAMH/NaCMC: 74/13/13	143.25	17.68
DMH/CAMH/NaCMC/Silicone: 74/13/13/1	125.34	3.57
DMH/CAMH/HEC: 74/13/13	198.23	7.78
DMH/CAMH/HEC/Silicone: 74/13/13/1	77.25	6.39
DMH/CAMH/HEC/Silicone: 74/13/13/3	76.35	7.56
DMH/DAP/Polymer Formulation		
DMH/DAP: 87/13	261.61	4.62
DMH/DAP/NaCMC: 80/12/8	203.96	7.37
DMH/DAP/PVA: 80/12/8	231.99	10.75

Binder solutions comprising 2 % solids were prepared according to the method disclosed above and showed the compositions indicated in the tables below. Bond strength of weathered and unweathered veils impregnated with the relevant binder compositions and cured for 8 minutes at

200 °C were measured as disclosed above. The results are summarized in the tables below, averaged over 8 replicates.

Table 3:

Binder Formulations	Bond strength of veils, unweathered		Bond strength after weather treatment	
	Average Bond Strength (N)	STDEV (+/-)	Average Bond Strength (N)	STDEV (+/-)
85%DMH+15%AmSO4 (control)	63.347	10.896	36.847	7.001
84%DMH+15%AmSO4+1%CS	63.930	4.880	36.278	4.683
83%DMH+15%AmSO4+2%CS	71.741	9.679	40.750	11.168
82%DMH+15%AmSO4+3%CS	73.794	7.956	41.389	6.299
81%DMH+15%AmSO4+4%CS	74.638	3.456	42.615	4.071
80%DMH+15%AmSO4+5%CS	78.263	7.636	45.519	7.849

Table 4:

Binder Formulations	Bond strength of veils, unweathered		Bond strength after weather treatment	
	Average Bond Strength (N)	STDEV (+/-)	Average Bond Strength (N)	STDEV (+/-)
49.73% DMH+35.28% Fructose +15%AmSO4 (control)	65.56	8.86	49.13	12.91
49.14% DMH+34.16% Fructose+15%AmSO4+1%CS	77.22	8.04	56.87	10.69
48.56% DMH+34.44% Fructose + 15%AmSO4+2%CS	80.63	5.39	53.80	9.84
47.97% DMH+34.03% Fructose + 5%AmSO4+3%CS	89.95	8.92	55.39	7.74
47.39% DMH+33.61% Fructose +15%AmSO4+4%CS	90.35	10.59	55.46	5.87
46.8% DMH+33.2%Fructose +15%AmSO4+5%CS	93.36	10.44	55.45	4.20

Table 5:

Binder Formulations	**Bond strength of veils unweathered**		**Bond strength after weather treatment**	
	Average Bond Strength (N)	**STDEV (+/-)**	**Average Bond Strength (N)**	**STDEV(+/-)**
93%DMH+7%DAP (control)	61.879	5.623	47.517	7.113
92%DMH+7%DAP+1%CS	76.365	11.618	62.671	7.041
91%DMH+7%DAP+2%CS	77.228	19.285	71.698	9.090
90%DMH+7%DAP+3%CS	80.586	7.494	65.023	6.975
89%DMH+7%DAP+4%CS	83.593	3.745	63.070	6.317
88%DMH+7%DAP+5%CS	85.106	8.047	68.655	5.123
87%DMH+13%DAP	63.593	3.692	56.608	7.624
86%DMH+13%DAP+1%CS	83.311	4.994	56.714	9.745
85%DMH+13%DAP+2%CS	82.974	7.375	68.743	9.176
84%DMH+13%DAP+3%CS	91.810	13.908	74.988	6.892

The data clearly shows the beneficial effect of chitosan polymer matrix (CS) addition to the hydrocarbon based binder compositions.

The experiments were repeated with binder compositions comprising 2 % solids. The compositions are shown in the tables below and comprise a polyazetidinium (CA1025) as polymer matrix. Bond strength of weathered and unweathered veils impregnated with the relevant binder compositions and cured for 8 minutes at 200 °C were measured as disclosed above. The results are summarized in Table 6 below, averaged over 8 replicates.

Table 6:

Binder Formulations	Bond strength of veils unweathered		Bond strength after weather treatment	
	Average Bond Strength (N)	**STDEV (+/-)**	**Average Bond Strength (N)**	**STDEV (+/-)**
85%DMH+15%AmSO4	66.812	4.145	52.123	4.542
84%DMH+15%AmSO4+1%CA1025	76.345	11.167	63.410	5.393
83%DMH+15%AmSO4+2%CA1025	91.245	6.388	60.231	10.250
82%DMH+15%AmSO4+3%CA1025	86.144	8.922	61.076	13.230
81%DMH+15%AmSO4+4%CA1025	85.144	11.654	59.530	6.549
80%DMH+15%AmSO4+5%CA1025	90.640	15.134	59.614	4.720
85%DMH+15%CAMH	84.766	6.047	59.569	10.650
84%DMH+15%CAMH+1%CA1025	116.151	8.766	103.040	15.460
83%DMH+15%CAMH+2%CA1025	113.480	12.390	99.004	19.273
82%DMH+15%CAMH+3%CA1025	108.101	9.386	93.758	14.468
81%DMH+15%CAMH+4%CA1025	113.229	11.863	96.023	11.444
93%DMH+7%DAP	73.499	6.763	61.000	10.738
92%DMH+7%DAP+1%CA1025	76.266	9.219	65.361	12.090
91%DMH+7%DAP+2%CA1025	86.489	5.461	68.984	10.122
90%DMH+7%DAP+3%CA1025	87.264	10.278	69.571	9.345
89%DMH+7%DAP+4%CA1025	87.280	6.899	66.944	8.225
87%DMH+13%DAP	67.843	7.629	59.438	6.947
86%DMH+13%DAP+1%CA1025	73.781	15.805	82.893	7.693
85%DMH+13%DAP+2%CA1025	87.873	6.696	83.829	8.665
84%DMH+13%DAP+3%CA1025	88.965	13.690	85.755	14.067
83%DMH+13%DAP+4%CA1025	88.611	7.886	85.308	8.783

Again, the effect on bond strength of the addition of CA1025 is clearly evidenced.

DMH: dextrose monohydrate
AmSO4: ammonium sulphate
DAP: Diammonium phosphate
CS: High molecular weight chitosan from Sigma Aldrich, CAS n° 9012-76-4 (419419)
CaMH: citric acid monohydrate
CA1025: trade name of a commercially available azetidinium polymer

The experiments were repeated with binder compositions as shown in Table 7 below. Bond strength of weathered and unweathered veils impregnated with the relevant binder compositions and cured for 8 minutes at 200 °C were determined as disclosed above. The results averaged over 8 replicates are shown in Table 7 below.

Table 7:

Binder Formulations	Bond Strength of Veils Unweathered		Bond Strength of Veils after weather treatment	
	Average Bond Strength (N)	**STDEV (+/-)**	**Average Bond Strength (N)**	**STDEV (+/-)**
85%DMH+15%HMDA	72.843	7.760	59.972	10.264
80%DMH+15%HMDA+5%HPC	67.175	6.859	53.989	5.306
80%DMH+15%HMDA+5%NaCMC	93.310	7.224	77.060	6.285
80%DMH+15%HMDA+5%CA1025	85.703	9.744	88.180	7.190
75%DMH+15%HMDA+10%CA1025	85.419	12.881	93.776	7.381

DMH: dextrose monohydrate
HMDA: hexamethylene diamine
HPC: hydroxypropyl cellulose
CA1025: trade name of a commercially available azetidinium polymer

Clearly, bond strength of weathered and unweathered veils is essentially maintained or even increased despite reduced dextrose available for reaction with HMDA cross-linker.

Accorder to further aspects, the present invention provides an aqueous curable binder composition, an assembly of fibers or particles and a process as set out in the following aspects:

Aspect 1. An aqueous curable binder composition comprising starting materials required for forming a thermoset resin upon curing and a matrix polymer.

Aspect 2. The aqueous curable binder composition of aspect 1 comprising a polyhydroxy component, a polycarboxylic acid component, or an anhydride, ester or salt derivative thereof for forming a thermoset resin upon curing, and a matrix polymer.

Aspect 3. The aqueous curable binder composition of aspect 2 wherein the polycarboxylic acid component is selected from monomeric and polymeric polycarboxylic acids.

Aspect 4. The aqueous curable binder composition of aspect 4 wherein the polycarboxylic acid component is a monomeric polycarboxylic acid, such as dicarboxylic acid, including, but not limited to, unsaturated aliphatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids, unsaturated cyclic dicarboxylic acids, saturated cyclic dicarboxylic acids, hydroxy-substituted derivatives thereof, or, tricarboxylic acid, including, but not limited to, unsaturated aliphatic tricarboxylic acids, saturated aliphatic tricarboxylic acids, aromatic tricarboxylic acids, unsaturated cyclic tricarboxylic acids, saturated cyclic tricarboxylic acids, hydroxy-substituted derivatives thereof, preferably citric acid, and mixtures thereof.

Aspect 5. The aqueous curable binder composition of aspect 2 wherein the salt derivative of the polycarboxylic acid component is an ammonium salt.

Aspect 6. The aqueous curable binder composition of any of the preceding aspects wherein the polyhydroxy component is a carbohydrate component selected from monosaccharide in its aldose or ketose form, including a triose, a tetrose, a pentose, a hexose, or a heptose; or a polysaccharide or an oligosaccharide; or a component that yields one or more reducing sugars *in situ*, or combinations thereof.

Aspect 7. The aqueous curable binder composition of aspect 1 comprising a carbohydrate component and a nitrogen containing component for forming a thermoset resin upon curing, and a matrix polymer.

Aspect 8. The aqueous curable binder composition of aspect 7 wherein the carbohydrate component is selected from monosaccharide in its aldose or ketose form, including a triose, a tetrose, a pentose, a hexose, or a heptose; or an oligosaccharide or a polysaccharide; or a component that yields one or more reducing sugars *in situ*, or combinations thereof.

Aspect 9. The aqueous curable binder composition of any of aspects 7 or 8 wherein the nitrogen containing component is an ammonium salt of an inorganic acid, selected from phosphoric, sulphuric, nitric and carbonic acid, preferably ammonium sulphate or ammonium phosphate.

Aspect 10. The aqueous curable binder composition of any of aspects 7 or 8 wherein the nitrogen containing component is selected from polyamine functional compounds comprising primary and/or secondary and /or tertialy and /or quaternary amine functional groups.

Aspect 11. The aqueous curable binder composition of any of aspect 10 wherein the polyamine functional compound has the formula of H_2N-Q-NH_2, wherein Q is an alkyl, cycloalkyl, heteroalkyl, or cycloheteroalkyl, each of which optionally substituted.

Aspect 12. The aqueous curable binder composition of aspect 11 wherein the polyamine functional compound is selected from di-amine, tri-amine, tetra-amine, and penta-amine, more specifically 1,6-diaminohexane and 1,5-diamino-2-methylpentane, diethylenetriamine, 1-piperazine-ethaneamine, and bis(hexamethylene)triamine, triethylenetetramine, tetraethylenepentamine, polyethyleneimine (PEI), polyninyl amine, polyether amine, polylysine.

Aspect 13. The aqueous curable binder composition of any of the preceding aspects wherein the matrix polymer is selected from naturally derived polymers, such as polysaccharides, such as cellulose, starch, alginate, hyaluronic acid, and their derivatives, carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), 2-hydroxyethyl cellulose (HEC), synthetically derived polymers, such as polyvinyls (PVA, PVAc, PAN), polyacrylics, polyacrylate, polymethacrylate, polyacrylamide, polymethacrylamides, polyurethanes, polyesters, aliphatic isocyanate oligomers, polyazetidinium, copolymers thereof and mixtures thereof.

Aspect 14. The aqueous curable binder composition of aspect 13 wherein the matrix polymer is selected from cellulose derivatives, such as carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), 2-hydroxyethyl cellulose (HEC); polyvinyl acetate (PVAc), aliphatic isocyanate oligomers, or mixtures thereof .

Aspect 15. The aqueous curable binder composition of any of the preceding aspects wherein the matrix polymer shows a molecular weight ranging from 500 Daltons (Da) to $2x10^6$ Da, preferably from $1 \times 10^3 - 5 \times 10^5$ Da, more preferably from 5×10^4 Da – 3×10^5 Da.

Aspect 16. The aqueous curable binder composition of any of aspects 7 – 15 wherein the dry weight ratio of carbohydrate to ammonium salt of inorganic or polycarboxylic acid or polyamine functional compound ranges from about 2 to about 35, preferably from about 2.5 to about 13.

Aspect 17. The aqueous curable binder composition of aspect 16 wherein the matrix polymer makes up from about 1 to 20 % of the dry weight of the binder composition, preferably from about 2 to 18 % dry weight, more preferably from 5 to 15 % dry weight of the composition.

Aspect 18. The aqueous curable binder composition of any of the preceding aspects further comprising dyes, antifungal agents, antibacterial agents, hydrophobes, silicone containing coupling agents and/or other additives known in the art for such binder compositions.

Aspect 19. The aqueous binder composition of any of the preceding aspects wherein a component is selected micro-/or nano-particles derived from natural or synthetic polymers of their combination such as nanocelluloses, or from inorganic materials such as MgO, CaO, Al_2O_3 and $CaCO_4$, or nanoclays such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite and other organically-modified nanoclays, and /or mixtures thereof.

Aspect 20. An assembly of fibers or particles bonded with an aqueous curable binder composition according to any of the preceding aspects or with a binder resulting from the curing of any of the curable binder compositions of the preceding aspects.

Aspect 21. The assembly of fibers according to aspect 20 being an insulation product, such as a mineral wool mat or other.

Aspect 22. The assembly of particles according to aspect 20 being a composite wood board, such as wood fiber board, wood particle board, plywood or similar board.

Aspect 23. A process for the manufacturing of an assembly of fibers or particles according to any of aspects 20 – 22 characterized in that it comprises the successive or concomitant application of the relevant components of the aqueous curable binder composition of any of aspects 1 – 19, or the application of an aqueous binder composition according to any of aspects 1 to 19 onto a collection of fibers or particles; the gathering of the coated fibers or particles in an assembly; and curing, whereby the components of the aqueous curable binder composition are caused to react to form a macromolecular binder, and evaporating water.

Aspect 24. The process according to aspect 23 characterized in that curing is performed at a temperature ranging from 120 °C - 200 °C, preferably higher than 140 °C, more preferably lower than 190 °C, typically between 160 and 180 °C.

Aspect 25. The process according to any of aspects 23 - 24 characterized in that the aqueous binder composition is applied by spraying onto the collection of fibers or particles.

Aspect 26. The process of any of aspects 23 to 25 wherein the assembly is a wood fiber board or wood particle board or similar wood board, subjected to pressing during curing.

CLAIMS

1. An aqueous curable binder composition comprising starting materials required for forming a thermoset resin upon curing and a matrix polymer, wherein the starting materials required for forming a thermoset resin upon curing comprise (i) a polyhydroxy component selected from carbohydrate components, said carbohydrate components selected from monosaccharide in its aldose form, monosaccharide in its ketose form, a triose, a tetrose, a pentose, a hexose, and a heptose; an oligosaccharide; a polysaccharide; a component that yields one or more reducing sugars *in situ*; and combinations thereof, and a polycarboxylic acid component, or an anhydride, ester or salt derivative thereof, or reaction product thereof, or (ii) a carbohydrate component, said carbohydrate component being reducing sugars, or that yield one or more reducing sugars in situ under thermal curing conditions; a nitrogen containing component; and a reaction product thereof, wherein the matrix polymer makes up from about 2 to 20 % of the dry weight of the binder composition and wherein the matrix polymer is selected from cellulose, starch, alginate, hyaluronic acid, their derivatives, starch derivatives, starch copolymers, carboxymethyl cellulose (CMC), sodium carboxymethyl cellulose (NaCMC), hydroxypropyl cellulose (HPC), 2-hydroxyethyl cellulose (HEC), chitosan, polyurethanes, polyesters, aliphatic isocyanate oligomers, azetidinium polymer, copolymers thereof and mixtures thereof.

2. The aqueous curable binder composition of claim 1 wherein the polycarboxylic acid component is selected from monomeric and polymeric polycarboxylic acids.

3. The aqueous curable binder composition of claim 2 wherein the polycarboxylic acid component is a monomeric polycarboxylic acid, dicarboxylic acid, unsaturated aliphatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, aromatic dicarboxylic acids, unsaturated cyclic dicarboxylic acids, saturated cyclic dicarboxylic acids, hydroxy-substituted derivatives thereof, tricarboxylic acid, including, unsaturated aliphatic tricarboxylic acids, saturated aliphatic tricarboxylic acids, aromatic tricarboxylic acids, unsaturated cyclic tricarboxylic acids, saturated cyclic tricarboxylic acids, hydroxy-substituted derivatives thereof, or mixtures thereof.

4. The aqueous curable binder composition of claim 3, wherein the polycarboxylic acid component is citric acid.

5. The aqueous curable binder composition of claim 1, wherein the salt derivative of the polycarboxylic acid component is an ammonium salt.

6. The aqueous curable binder composition of any one of claims 1 and 5, wherein the nitrogen containing component is an ammonium salt of an inorganic acid, selected from phosphoric, sulphuric, nitric and carbonic acid.

7. The aqueous curable binder composition of claim 6, wherein the nitrogen containing component is ammonium sulphate or ammonium phosphate.

8. The aqueous curable binder composition of any one of claims 1 and 7, wherein the nitrogen containing component is a polyamine functional compound comprising primary, secondary, tertiary, or quaternary amine functional groups.

9. The aqueous curable binder composition of claim 8, wherein the polyamine functional compound has the formula of $H_2N\text{-}Q\text{-}NH_2$, wherein Q is an alkylene, cycloalkylene, heteroalkylene, cycloheteroalkylene, or each of which substituted.

10. The aqueous curable binder composition of claim 8, wherein the polyamine functional compound is selected from di-amine, tri-amine, tetra-amine, penta-amine, 1,6-diaminohexane, 1,5-diamino-2-methylpentane, diethylenetriamine, 1-piperazineethaneamine, bis(hexamethylene)triamine, triethylenetetramine, tetraethylenepentamine, polyethyleneimine (PEI), polyvinyl amine, polyether amine, and polylysine.

11. The aqueous curable binder composition of claim 1, wherein the matrix polymer is carboxymethyl cellulose (CMC), sodium carboxymethyl cellulose (NaCMC), hydroxypropyl cellulose (HPC), 2-hydroxyethyl cellulose (HEC); nanocellulose, , aliphatic isocyanate oligomers, chitosan, azetidinium polymer or mixtures thereof .

12. The aqueous curable binder composition of any one of claims 1 to 11, wherein the matrix polymer shows a molecular weight ranging from 500 Daltons (Da) to $2x10^6$ Da.

13. The aqueous curable binder composition of any one of claims 1 to 12, wherein the matrix polymer shows a molecular weight ranging from $1 \times 10^3 – 5 \times 10^5$ Da.

14. The aqueous curable binder composition of any one of claims 1 to 13, wherein the matrix polymer shows a molecular weight ranging from 5×10^4 Da – 3×10^5 Da.

15. The aqueous curable binder composition of any one of claims 1 to 14, wherein the dry weight ratio of carbohydrate to ammonium salt of inorganic or polycarboxylic acid or polyamine functional compound ranges from about 2 to about 35.

16. The aqueous curable binder composition of any one of claims 1 to 15, wherein the dry weight ratio of carbohydrate to ammonium salt of inorganic or polycarboxylic acid or polyamine functional compound ranges from about 2.5 to about 13.

17. The aqueous curable binder composition of claim 12, wherein the matrix polymer makes up from about 1 to 20 % of the dry weight of the binder composition.

18. The aqueous curable binder composition of claim 12 or 17, wherein the matrix polymer makes up, from about 2 to 18 % dry weight.

19. The aqueous curable binder composition of any one of claims 12, 17 and 18, wherein the matrix polymer makes up from 5 to 15 % dry weight of the composition.

20. The aqueous curable binder composition of any one of claims 1 to 19, further comprising dyes, antifungal agents, antibacterial agents, hydrophobes, or silicone containing coupling agents..

21. The aqueous binder composition of any of one of claims 1 to 20, wherein a component is selected micro-/or nano-particles derived from natural or synthetic polymers, from inorganic materials, nanoclays, and mixtures thereof.

22. The aqueous binder composition of claim 21, wherein the natural polymers are nanocelluloses.

23. The aqueous binder composition of claim 21, wherein the inorganic materials are MgO, CaO, Al_2O_3 or $CaCO_4$.

24. The aqueous binder composition of claim 21, wherein the nanoclays are montmorillonite, bentonite, kaolinite, hectorite, or halloysite.

25. An assembly of fibers or particles bonded with an aqueous curable binder composition according to any one of claims 1 to 24 or with a binder resulting from the curing of the curable binder compositions of any one of claims 1 to 24.

26. The assembly of fibers according to claim 25, being an insulation product.

27. The assembly of fibers according to claim 26, wherein the insulation product is a mineral wool mat.

28. The assembly of particles according to claim 25, being a composite wood board.

29. The assembly of particles according to claim 28, wherein the composite wood board is a wood fiber board, a wood particle board, or a plywood.

30. A process for the manufacturing of an assembly of fibers or particles according to any one of claims 25 to 29, characterized in that it comprises the successive or concomitant application of the relevant components of the aqueous curable binder composition of any one of claims 1 to 24, or the application of an aqueous binder composition according to any one of claims 1 to 24 onto a collection of fibers or particles; the gathering of the coated fibers or particles in an assembly; and curing, whereby the components of the aqueous curable binder composition are caused to react to form a macromolecular binder, and evaporating water.

31. The process according to claim 30, characterized in that curing is performed at a temperature ranging from 90 °C - 200 °C.

32. The process according to claim 30, characterized in that curing is performed at a temperature higher than 140 °C.

33. The process according to claim 30, characterized in that curing is performed at a temperature lower than 190 °C.

34. The process according to claim 30, characterized in that curing is performed at a temperature between 160 and 180 °C.

35. The process according to any one of claims 30 to 34, characterized in that the aqueous binder composition is applied by spraying onto the collection of fibers or particles.

36. The process of any one of claims 30 to 35, wherein the assembly is a wood fiber board or wood particle board or similar wood board, subjected to pressing during curing.

Fig. 1

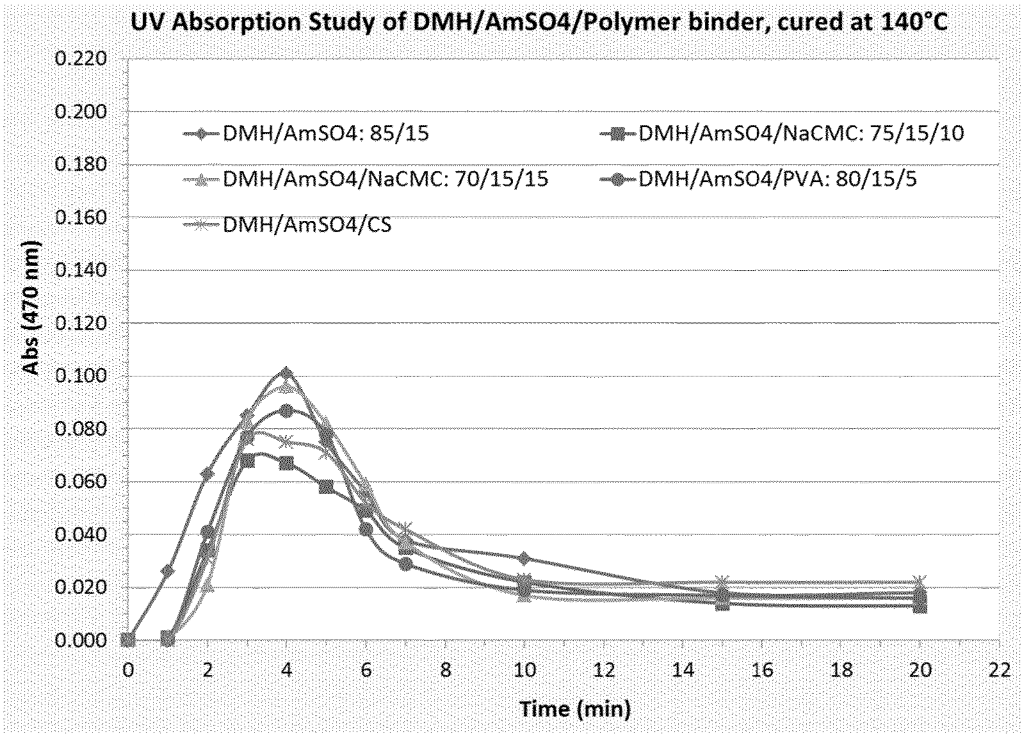

UV Absorption Study of DMH/AmSO4/Polymer binder, cured at 140°C
Abs (470 nm)
0.220
0.200
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0
2
4
6
8
10
12
14
16
18
20
22
Time (min)
DMH/AmSO4: 85/15
DMH/AmSO4/NaCMC: 75/15/10
DMH/AmSO4/NaCMC: 70/15/15
DMH/AmSO4/PVA: 80/15/5
DMH/AmSO4/CS

Fig. 2

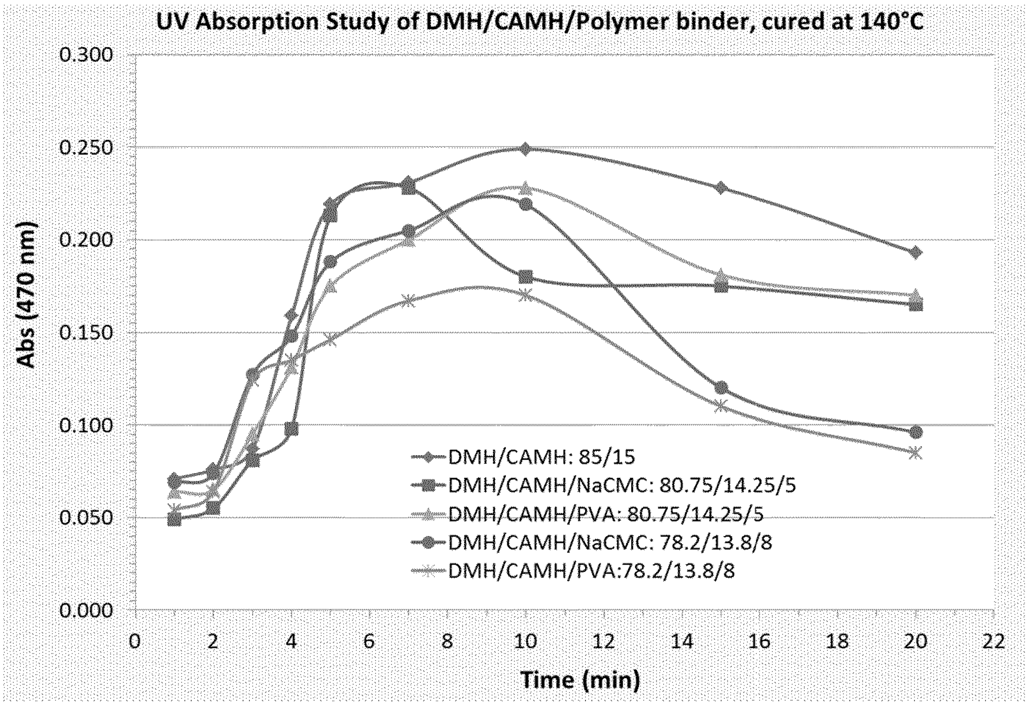

UV Absorption Study of DMH/CAMH/Polymer binder, cured at 140°C
Abs (470 nm)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
2
4
6
8
10
12
14
16
18
20
22
Time (min)
DMH/CAMH: 85/15
DMH/CAMH/NaCMC: 80.75/14.25/5
DMH/CAMH/PVA: 80.75/14.25/5
DMH/CAMH/NaCMC: 78.2/13.8/8
DMH/CAMH/PVA:78.2/13.8/8

Fig. 3

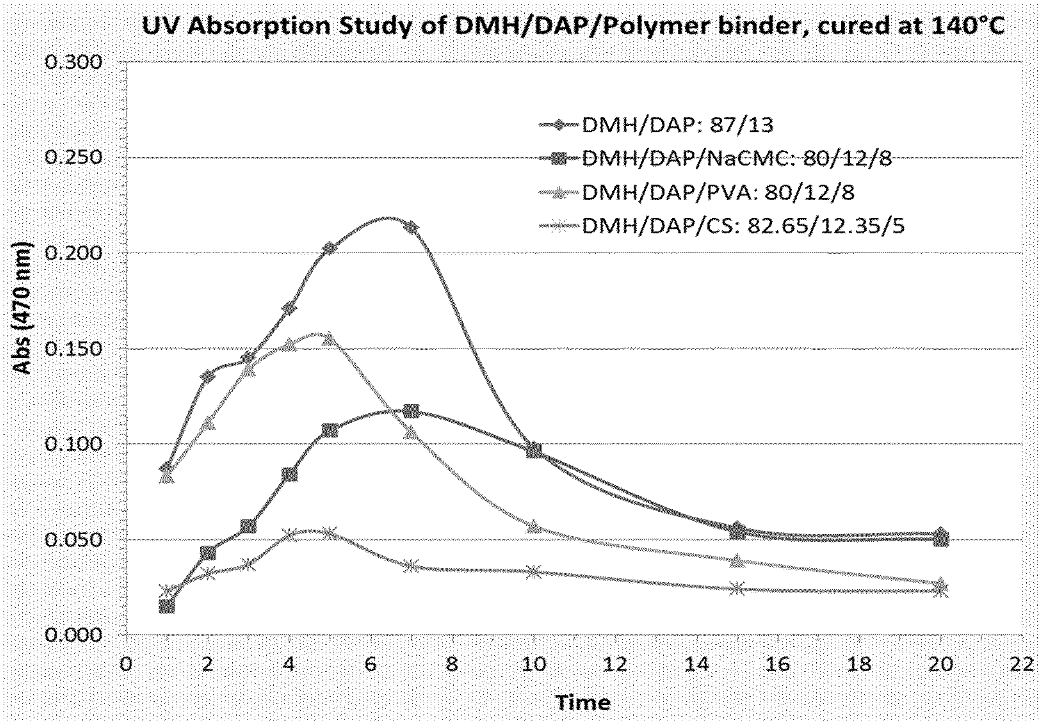

UV Absorption Study of DMH/DAP/Polymer binder, cured at 140°C
DMH/DAP: 87/13
DMH/DAP/NaCMC: 80/12/8
DMH/DAP/PVA: 80/12/8
DMH/DAP/CS: 82.65/12.35/5
Abs (470 nm)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
2
4
6
8
10
12
14
16
18
20
22
Time

Fig. 4a

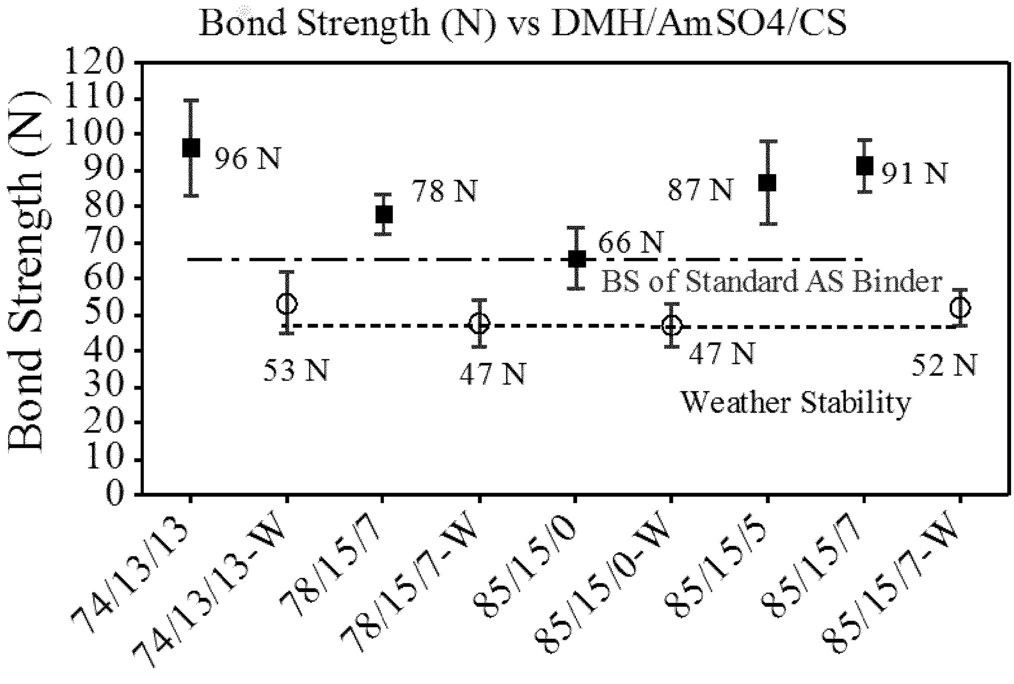

Bond Strength (N) vs DMH/AmSO4/CS
Bond Strength (N)
120
110
100
90
80
70
60
50
40
30
20
10
0
96 N
78 N
66 N
87 N
91 N
53 N
47 N
47 N
52 N
BS of Standard AS Binder
Weather Stability
74/13/13
74/13/13-W
78/15/7
78/15/7-W
85/15/0
85/15/0-W
85/15/5
85/15/7
85/15/7-W

Fig. 4b

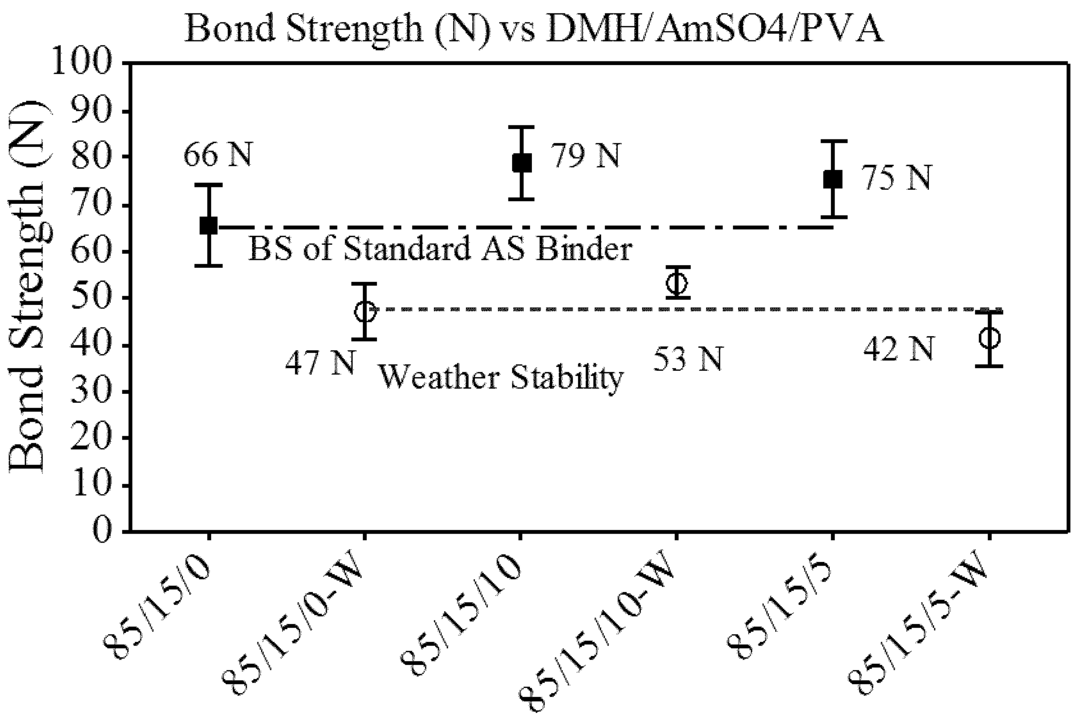

Bond Strength (N) vs DMH/AmSO4/PVA
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
66 N
79 N
75 N
BS of Standard AS Binder
47 N
Weather Stability
53 N
42 N
85/15/0
85/15/0-W
85/15/10
85/15/10-W
85/15/5
85/15/5-W

Fig. 4c

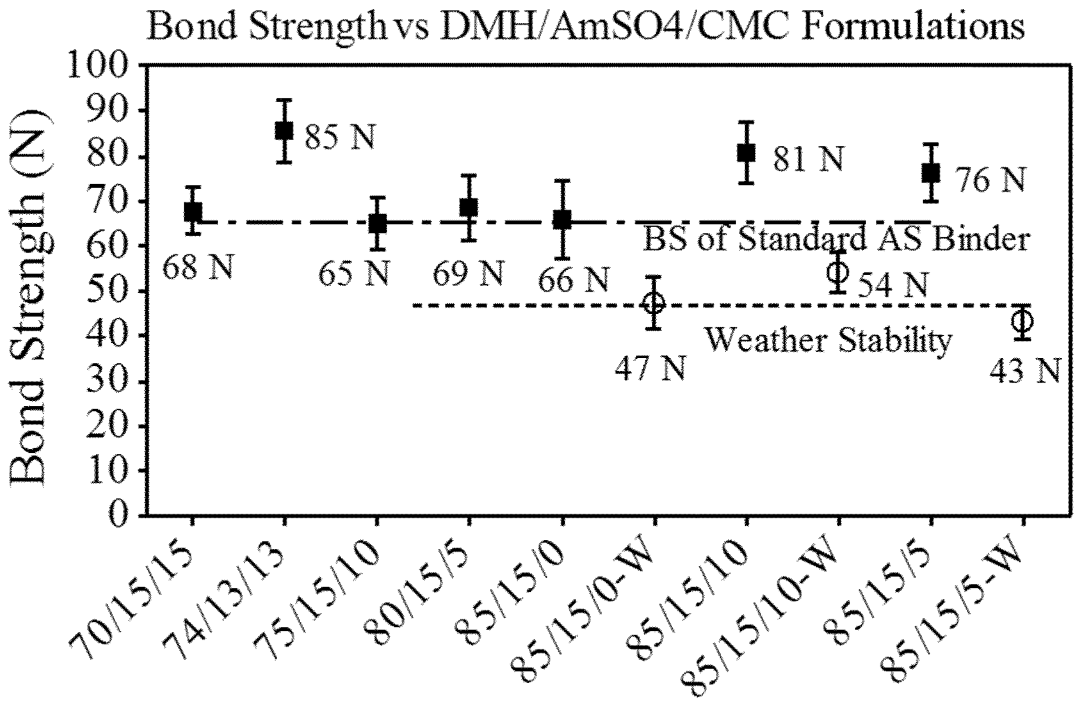

Bond Strength vs DMH/AmSO4/CMC Formulations
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
85 N
81 N
76 N
68 N
65 N
69 N
66 N
BS of Standard AS Binder
54 N
47 N
Weather Stability
43 N
70/15/15
74/13/13
75/15/10
80/15/5
85/15/0
85/15/0-W
85/15/10
85/15/10-W
85/15/5
85/15/5-W

Fig. 5

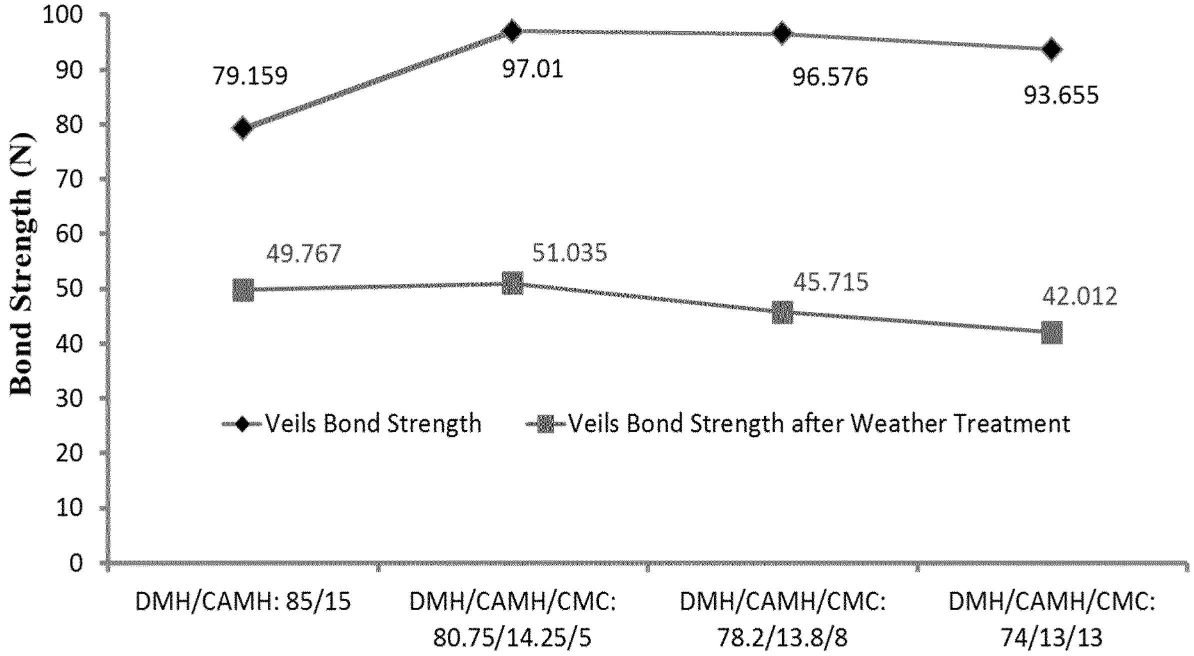

Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
79.159
97.01
96.576
93.655
49.767
51.035
45.715
42.012
Veils Bond Strength
Veils Bond Strength after Weather Treatment
DMH/CAMH: 85/15
DMH/CAMH/CMC: 80.75/14.25/5
DMH/CAMH/CMC: 78.2/13.8/8
DMH/CAMH/CMC: 74/13/13

Fig. 6a

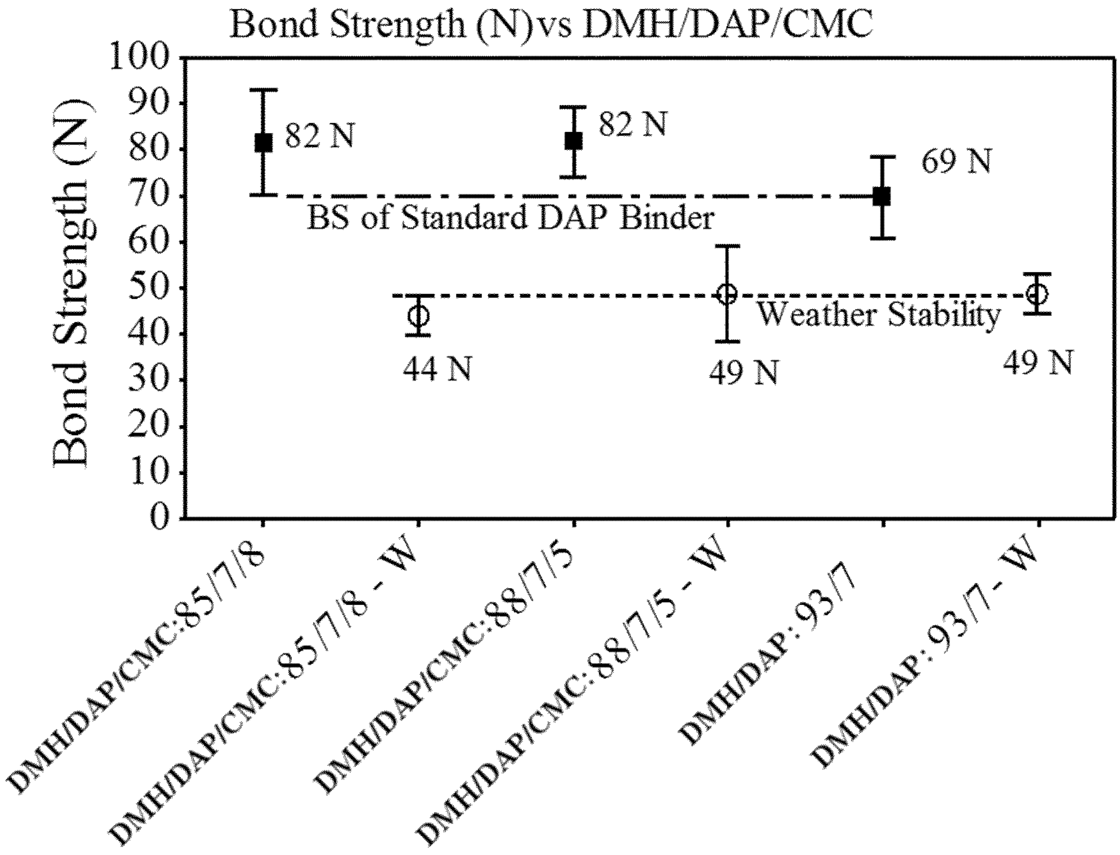

Bond Strength (N)vs DMH/DAP/CMC
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
82 N
82 N
69 N
BS of Standard DAP Binder
Weather Stability
44 N
49 N
49 N
DMH/DAP/CMC:85/7/8
DMH/DAP/CMC:85/7/8 - W
DMH/DAP/CMC:88/7/5
DMH/DAP/CMC:88/7/5 - W
DMH/DAP: 93/7
DMH/DAP: 93/7 - W

Fig. 6b

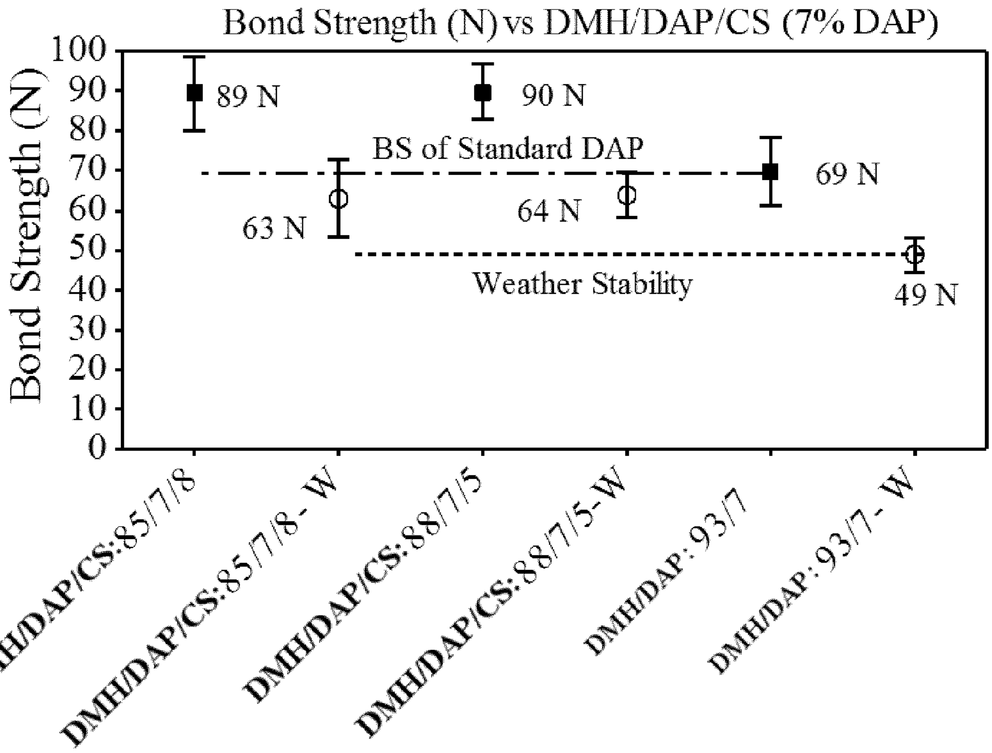

Bond Strength (N) vs DMH/DAP/CS (7% DAP)
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
89 N
90 N
BS of Standard DAP
69 N
63 N
64 N
Weather Stability
49 N
DMH/DAP/CS:85/7/8
DMH/DAP/CS:85/7/8 - W
DMH/DAP/CS:88/7/5
DMH/DAP/CS:88/7/5-W
DMH/DAP: 93/7
DMH/DAP: 93/7 - W

Fig.7a

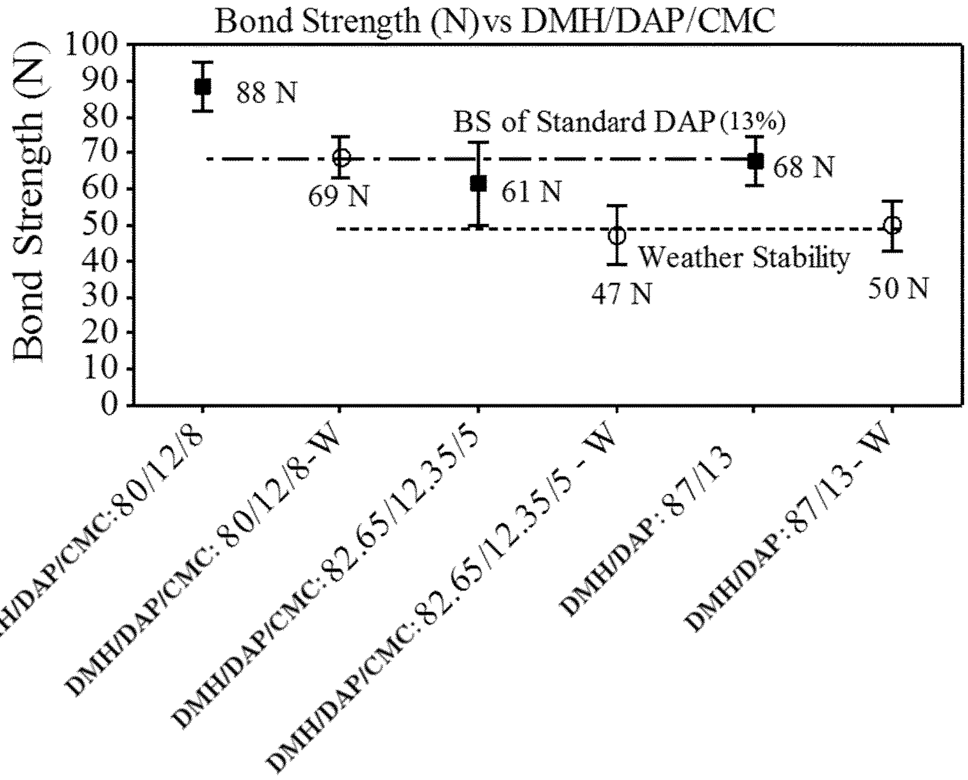

Bond Strength (N) vs DMH/DAP/CMC
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
88 N
BS of Standard DAP (13%)
69 N
61 N
68 N
Weather Stability
47 N
50 N
DMH/DAP/CMC:80/12/8
DMH/DAP/CMC: 80/12/8-W
DMH/DAP/CMC:82.65/12.35/5
DMH/DAP/CMC:82.65/12.35/5 - W
DMH/DAP: 87/13
DMH/DAP: 87/13 - W

Fig.7b

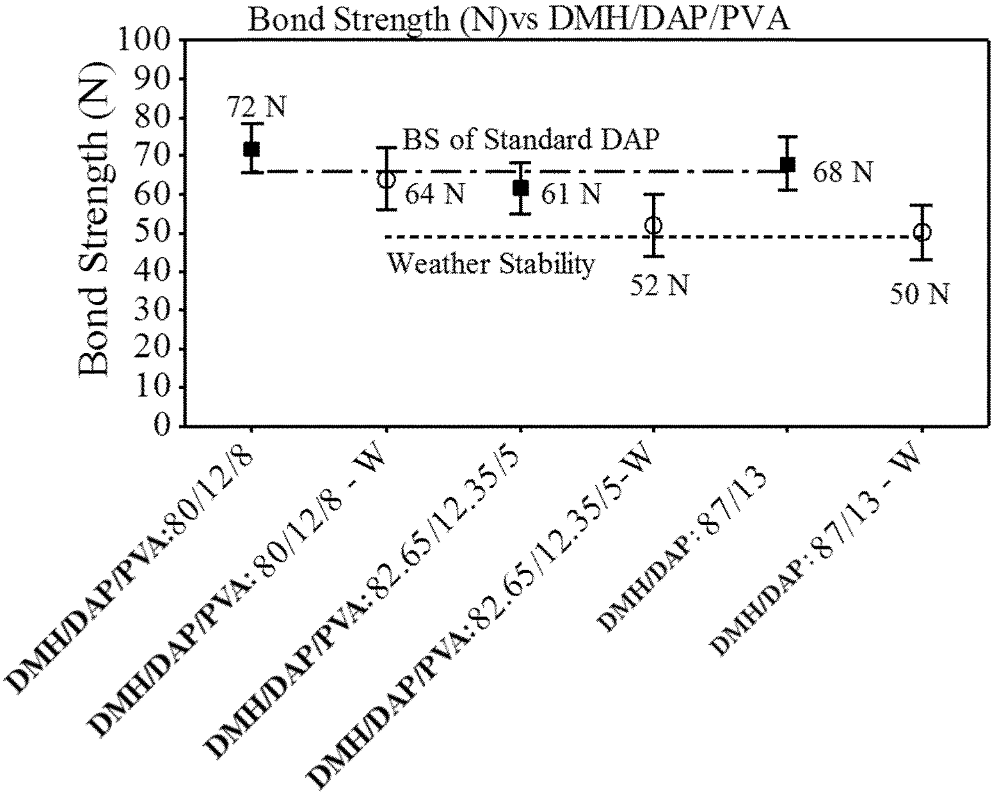
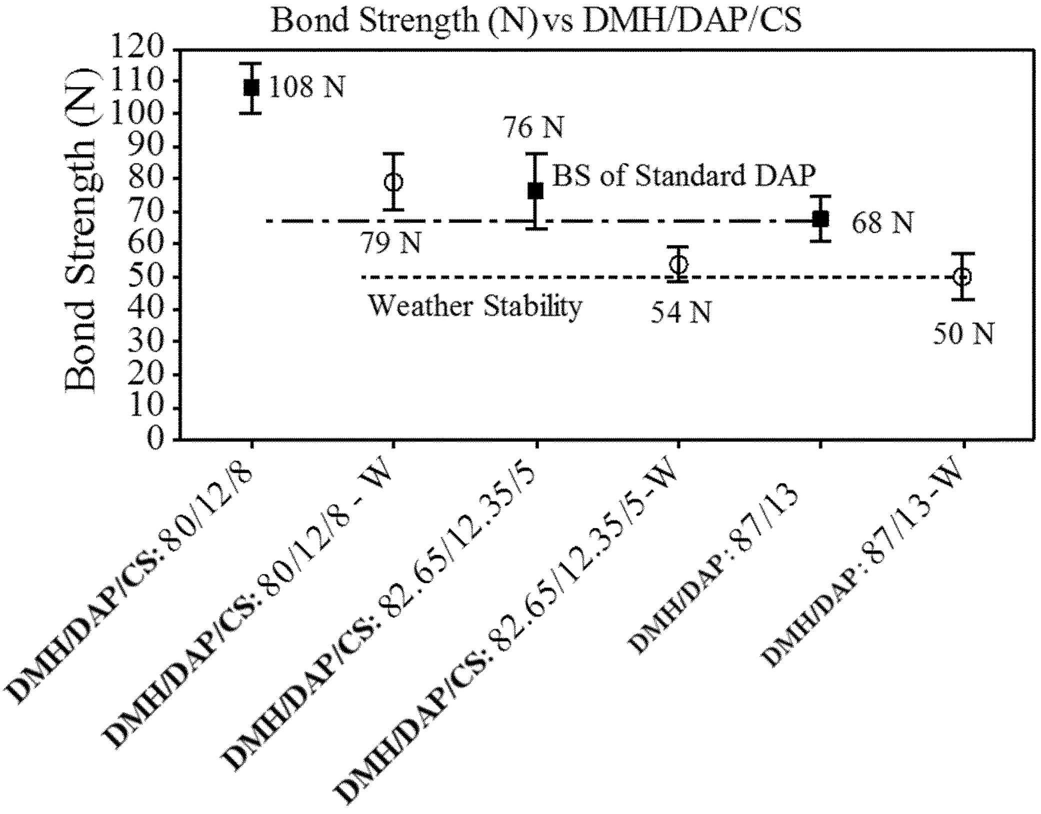
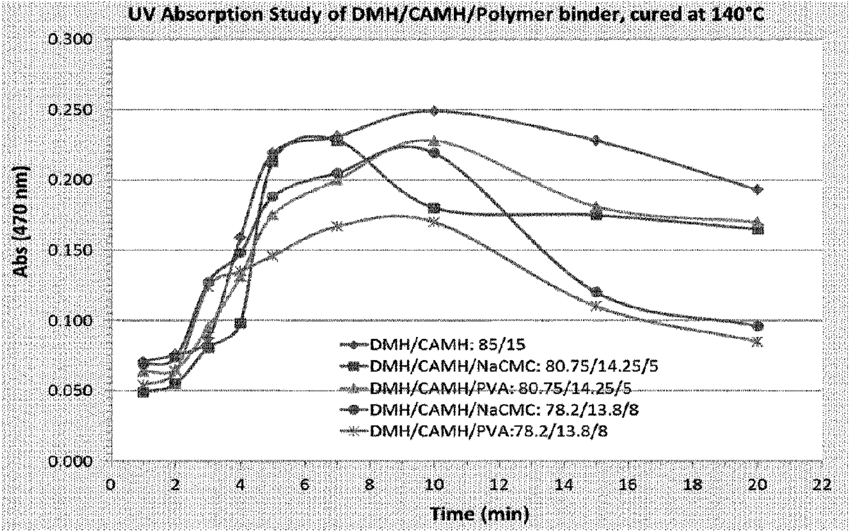

Bond Strength (N)vs DMH/DAP/PVA
Bond Strength (N)
100
90
80
70
60
50
40
30
20
10
0
72 N
BS of Standard DAP
64 N
61 N
68 N
52 N
50 N
Weather Stability
DMH/DAP/PVA:80/12/8
DMH/DAP/PVA: 80/12/8 - W
DMH/DAP/PVA:82.65/12.35/5
DMH/DAP/PVA:82.65/12.35/5-W
DMH/DAP: 87/13
DMH/DAP: 87/13 - W

Fig.7c


Bond Strength (N)vs DMH/DAP/CS
Bond Strength (N)
120
110
100
90
80
70
60
50
40
30
20
10
0
108 N
76 N
BS of Standard DAP
79 N
68 N
54 N
50 N
Weather Stability
DMH/DAP/CS: 80/12/8
DMH/DAP/CS: 80/12/8 - W
DMH/DAP/CS: 82.65/12.35/5
DMH/DAP/CS: 82.65/12.35/5-W
DMH/DAP: 87/13
DMH/DAP: 87/13-W


UV Absorption Study of DMH/CAMH/Polymer binder, cured at 140°C
Abs (470 nm)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
2
4
6
8
10
12
14
16
18
20
22
Time (min)
DMH/CAMH: 85/15
DMH/CAMH/NaCMC: 80.75/14.25/5
DMH/CAMH/PVA: 80.75/14.25/5
DMH/CAMH/NaCMC: 78.2/13.8/8
DMH/CAMH/PVA:78.2/13.8/8