

**MODIFIED POLYACRYLIC GLUES OF INCREASED HEAT RESISTANCE
FOR INDUSTRIAL CONSTRUCTION****S.Voliuvach***Kharkov National Academy of Municipal Economy***L.Shutenko****M.Zolotov****S.Zolotov***Kharkov National Academy of Municipal Economy***Abstract**

The results of investigating heat resistance, physical and mechanic properties and adhesion of modified polyacrylic glues of cold hardening for industrial construction, in particular for joining anchor bolts and concrete as well as construction elements and structures are presented.

The necessity of working out construction polyacrylic glues with increased chemical and heat resistance designed for application in thermal and chemical corrosive conditions at high dynamic and static load has been substantiated.

Chemical structure of self hardened two-component acrylic compositions based on polymethylmetacrylate and methylmetacrylate has been analyzed and the methods of modifying their thermal and physical strength properties using active fillers and strengthening intermolecule interaction, forming lateral chemical bonds between macromolecules of polymer as well as maximum exhausting of residual monomer have been proposed.

Keywords: poly-acrylic glue, anchor bolt, compound, polymethylmetacrylate, methylmetacrylate, heat resistance, modification, macromolecule, copolymerization, filler, adhesion, strength.

INTRODUCTION

Poly-acrylic glues of cold hardening are efficiently used in industrial construction for fastening anchor bolts in concrete, for joining construction elements and structures due to their good adhesion to different materials and high strength characteristics.

However, self-hardened compositions belong to the group of glues with moderate heat resistance and it makes their use in thermal strained media impossible.

That is why modification of construction poly-acrylic glues for improving their heat resistance and reduction of their creeping under the influence of great static and dynamic loads and increasing resistance to heat aging of glue compositions exposed to long-term heating is considered to be very urgent.

EXPOSITION

Technological equipment is in operation at high temperatures at the enterprises of ferrous and non-ferrous metal industries, heat power engineering, coke chemistry and other branches of chemical industry.

Metal rolling is known to be one of three main stages of a production cycle at metallurgical works. A great number of anchor bolts are used for fastening equipment of rolling-mills and foundry and rolling assemblies combining the processes of foundry and rolling in one unbroken production line.

Anchors used for fastening foundation steel slabs, carrying massive plates (60-120 tons) of working cages [1] to concrete and reinforced concrete foundations are known to be applied in thermal and chemical corrosive media.

Field testing showed that because of high initial temperatures of steel (1000-1300 °C), titanium and its alloys (950-1100 °C), copper (750-850 °C) the temperature may be 130 °C in concrete foundations [2]. Chemical corrosion of medium is caused by the lubricant penetrating into anchor junctions due to its uninterrupted feed to all working mechanisms of rolling assemblies.

In such cases modified construction poly-acrylic glues with high heat and chemical resistance and good strength characteristics are to be applied for fastening anchor bolts.

Low heat resistance of compounds on the basis of polymethylmetacrylate (PMMA), being a powder polymer ingredient and methylmetacrylate (MMA) being a monomer liquid ingredient is conditioned both by PMMA structure and by peculiarities of cold polymerization of MMA.

Small-dispersive PMMA (fraction passes through a sieve with 6400 mesh/sm² fully) with average molecular mass equal to 80000-120000, used in compounds is an amorphous atactical polymer. About 80% of monomer links are included into macromolecules of PMMA in syndiotactical sequence (the temperature of glassening is 115 °C) as its formation requires less activation energy than isotactical ($t_{gl} = 45^{\circ}\text{C}$) – the difference in activation enthalpy is about 4,19 kJ/mol. Also isotactical fraction content is not large, it decreases the temperature of glassening considerably as a result.

On the other hand full exhausting of MMA is impossible at cold polymerization (20-25°C), that is why residuum monomer making polymer plastic reduces the temperature of glassening. The presence of 1% of MMA in PMMA is known to reduce the temperature of glassening by 50 °C.

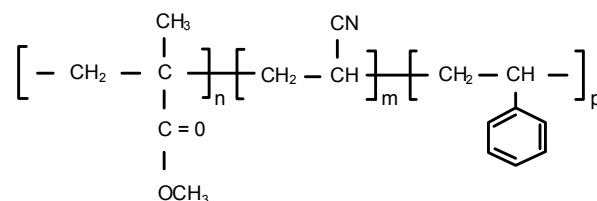
As a result hardened compound has rather low heat resistance – 45 °C by Martens and 60°C by Wick. It should be taken into account that polymer heat resistance gives an insight into upper limit temperatures of its use at short-term heating. In conditions of industrial use heat resistance of glue anchor junctions depends on applied mechanic load and on the duration of heat influence. That is why real heat resistance of polymers under long-term influence of high temperature at rolling assemblies is some dozens degrees lower.

Therefore, maximum exhausting of residuum monomer possible at polymerization acceleration is considered to be one of the ways of heat resistance increase achieved by choosing optimal concentration of polymerization initiators in oxidation and rehabilitation system consisting of benzoyl and dimethylaniline. The minimum hardening time (20 minutes at 20 °C) corresponds to the content of 2% of benzoyl peroxide in powder PMMA and 3% of dimethylaniline in liquid MMA.

Another way of increasing heat resistance of self-hardened acrylic compositions is intro-

ducing active fillers, intensifying interaction inside and between molecules with the help of copolymerization, as well as the formation of cross chemical bonds between macromolecules.

The use of acryl nitrile and sterol for copolymerization with MMA allows to increase heat resistance up to 94-102 °C by Wick copolymer containing mineral filler [3]:



It is conditioned by chemical structure of acryl nitril link containing strongly polar cyanic group and is confirmed by values of dipole moments of polymer model compositions which can be considered as hydrate monomers – for ethyl cyanide $\text{CH}_3\text{--CH}_2\text{--CN}$ $\mu=4,04\text{D}$, and for ethyl benzene $\text{CH}_3\text{--CH}_2\text{--C}_6\text{H}_5$ $\mu=0,58\text{D}$.

Saturation of copolymer macromolecule with polar groups (–CN) and aromatic nuclei (–C₆H₅) causes strengthening the interaction inside and between molecules.

Interaction inside molecules of side substitutes causes changes in trans-configuration of poly-methylene polymer chain from planar zigzag into spiral form due to rotation around C-C bonds, and it increases hardness of macromolecule and heat resistance. So, conformations of coagulated macromolecules are determined in general by intra-molecular forces repulsing polar substitutes –CN, by sterical difficulties of placing volumetrical phenyl substitutes and by bonds orientation of neighboring chain links.

Interaction between molecules of polymer chains is conditioned by forces Van der Waals characterizing cohesion energy and being the forces of secondary valencies (energy 2,1-41,9 kJ/mol, distance 3-10Å).

80-90% of forces between molecules in polymers are usually conditioned by dispersive forces caused by interaction of momentary dipoles of moving electrons in outer layers of atoms. A great amount of outer electrons in macromolecules results in considerable attractive force under the influence of dispersive forces:

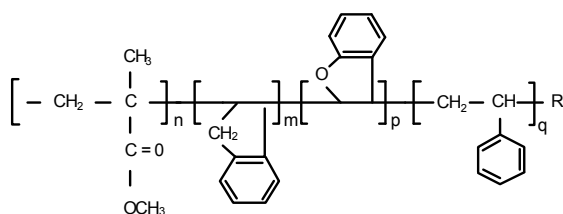
$$P = \frac{9}{2} \frac{\alpha^2}{r^7} \sqrt{\frac{n}{\alpha}}$$

where α – being polarized; r – distance; n – the number of electrons.

The main merit of this polymer-mineral composition is in 2,4 to 3,5 times increase of its chemical resistance, namely, resistance to oils. Strength losses of bended samples treated with waste engine oil ($\tau = 60$ days) was 0,48-0,68%. Bending strength limit is 39,2-40,9 MPa, tensile strength limit is 35,6-37,7 MPa. Adhesion to concrete is 14,1-14,8 MPa.

Modification of poly-acrylic glue with polyvinylchloride chlorinated resin and indene (sterol-indene) resin increases its heat resistance up to 106-111 °C by Wick [4]. Polyvinylchloride chlorinated resin is used as an active polymer filler and does not enter into reaction with MMA. Indene resin copolymerizes with MMA in presence of benzoyl peroxide due to reaction ability of double bonds of cyclopentadiene rings of indene $\text{C}_6\text{H}_4\text{CH}_2\text{-CH=CH}$

and coumarone $\text{C}_6\text{H}_4\text{O-CH=CH}$ at the ends of resin macromolecules:



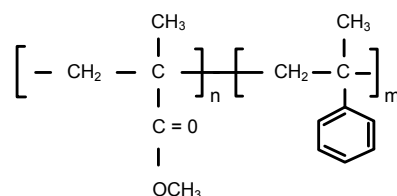
R – residuum of indene resin macromolecule in which indene links (~55%), coumarone (~23%) and sterol (~22%) are placed irregularly.

Mentioned above circumstance can explain relatively small increase of heat resistance of copolymer as compared with the possible increase at stereo-regular structure (syndiotactical and isotactical) of macromolecule chain. Mention should be made that carbo-cyclic (indene) and heterocyclic (coumarone) links included into the main chain cause hardness increase of linear chains of macromolecules and the increase of heat resistance, since conformation of chains changes and transfers from step trans-configuration to gosh-configuration.

As indene and coumarone chains are able to enter substitution reactions the appearance of side chains in copolymer linear macromolecules is quite possible. For the more, monomethyl- and dimethylderivatives of indene and coumarone, α -methyl-sterol, dicyclopentadiene and other monomers able to copolymerization with MMA present in indene resin.

Polymer-mineral composition on the basis of this copolymer has good strength characteristics. Bending strength limit is equal to 45,2-50,6 MPa and tensile strength limit is 43,5-46,8 MPa. Adhesion to concrete is 8,9-9,7 MPa.

It is possible to increase heat resistance to 107-112 °C by Wick copolymer having stereo-regular structure using copolymerization of MMA with α -methyl-sterol:

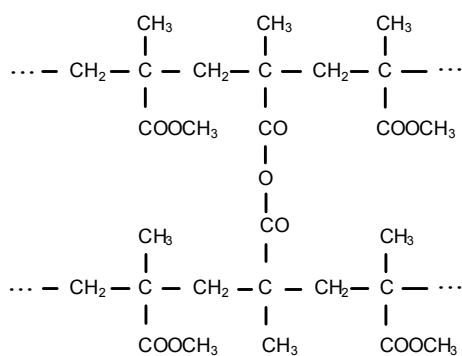


It can be also explained by the presence of two substitutes, one of which is phenyl $\text{-C}_6\text{H}_5$, in one atom of carbon in a chain α -methyl-sterol of poly-methylene chain $(\text{-CH}_2\text{-CX}_2\text{-})_n$, strengthening interaction inside molecules and increasing hardness of coagulated macromolecule. And poly- α -methyl-sterol has high temperature of glassening ($t_{gl} = 147^\circ\text{C}$) as compared with syndiotactic PMMA ($t_{gl} = 115^\circ\text{C}$) and isotactic PMMA ($t_{gl} = 45^\circ\text{C}$), it causes copolymer heat resistance increase.

This copolymer composition filled with quartz sand has bending strength limit 40,4-41,6 MPa, tensile strength limit 37,3-38,6 MPa. Adhesion to concrete is 15,3-16,2 MPa.

As forces strength by Van der Waals decreases at temperature elevation, the increase of heat resistance achieved by interaction between molecules is limited. Chemical bonds between macromolecules caused by polymers fastening and resulting in heat resistance increase are more stable.

In the process of copolymerization of MMA with metacrylic anhydride being four functional composition heat resistance of poly-acrylic composition by Wick increases to 124-129 °C [6] due to formation of spatial and structuralized copolymer:

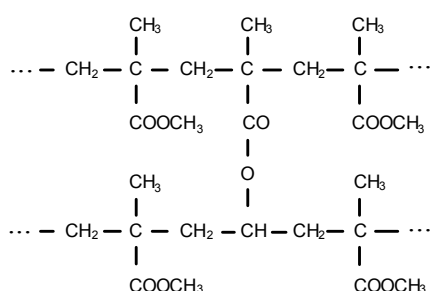


Cross chemical bonds between macromolecules interlaced in a chaotic way create spatially fastened three-dimensional copolymer product with high heat resistance.

Spatial “bridges” allow to redistribute load between neighboring parcels of coagulated polymer chains and to prevent macromolecules from free mutual transference in the process of heat movement.

Composition for fastening anchor bolts in concrete on the basis of this polymer containing quartz sand and mica as fillers possess the following physical and mechanic indices: bending strength limit – 37,5-38,7 MPa, tensile strength limit – 34,9-36,4 MPa. Adhesion to concrete is 13,4-14,6 MPa.

Vinyl-metacrylate being a four functional composition is able to increase heat resistance of poly-acrylic composition by Wick [7] to 128-134 °C at copolymerization with MMA due to spatial fastening of macromolecules on the scheme:



When using vinyl-metacrylate as a fastening agent a spatial “bridge” has smaller length than when metacrylic anhydride is used and it causes higher increase of heat resistance, as short cross chemical bonds are less flexible and limit mutual transference of macromolecules resulting in their fastening in a hard three-dimensional product.

The degree of spatial fastening is determined by the share of molecules of four func-

tional compositions reacting by two unsaturated groups. In general, it depends both on chemical structure of a fastening agent and on its concentration and polymerization conditions.

The type and dispersion level of poly-acrylic compositions filler are also very important due to its possible high surface activity which may result in adsorption interaction with polymer.

Self-hardened composition based on this polymer and containing polyvinylchloride chlorinated resin as polymer active filler and sand from electric furnace slag as inorganic filler has good physical and mechanic characteristics. Bending strength limit is equal to 47,8-48,5 MPa, tensile strength limit is equal to 44,9-46,3 MPa. Adhesion to concrete is 10,1-10,6 MPa.

As can be seen from described above, modification of properties of poly-acrylic compositions is considered to be a compromise task as when increasing heat resistance playing a decisive role for the use in thermal corrosive medium one has to put up with some deterioration of other characteristics, such as strength, adhesion, chemical resistance and others. That is why, practical purpose determines the trend of modification of poly-acrylic glues by changing the composition, chemical structure of polymers and fillers.

CONCLUSION

Modification of poly-acrylic construction glues of cold hardening by introducing active fillers and by means of copolymerization of methyl-metacrylate with different monomers allowing either to strengthen interaction inside and between polymer macromolecules or to create spatial and structuralized polymers due to fastening macromolecules using cross chemical bonds is expedient for increasing their heat resistance.

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