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ADVANCE IN NANOCOMPOSITES BASED ON HYBRID ORGANO-SILICATE MATRIX

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Abstract: This paper presents some features and applications of sol-gel technology for production of organic mineral hybrid nanocomposites which might be affected. It defines some principles of synthesis and application of hybrid nanomaterials in various fields of technology, using specific examples.

Keywords: nanocomposites, nanotechnology, sol-gel, hybrid composites, silicate matrix.

1. Introduction

In our previous study on organic-mineral hybrid nanocomposite materials we focused, in general, on the sol-gel technology for production of composite materials, including those of hybrid nature. We gave a detailed review of alkoxy, non-hydrolytic and colloidal methods of sol-gel synthesis, and, in particular, highlighted the role of soluble silicates as their precursors in the sol-gel technology for production of nanocomposites. It also addressed the possibility of nanocomposites production through aerogel and other techniques, as well as the influence of various factors on the structure and properties of the hybrid materials, including the geometry of packing of spherical, fibrous and layered filler particles [1].

Synthesis and study of the properties of new organic-mineral hybrid nanocomposites are of great importance. Based on the study the specialists have found solutions of many specific technological problems. In the field of organic-mineral hybrid nanocomposite materials, the methods of synthesis of multicomponent materials, such as "net in net" and "host-guest" are promising, as well as methods of using alkoxides of various metals, including complex, polynuclear and multi-functional in the sol-gel processes. The fundamental problem with the chemistry and physics of nanocomposites remains the "structure-property" relationship. Solution to this problem will allow us to move forward from conducting study of materials to targeted designing.

In this paper we try to analyze such an important area of nanocomposite materials as organic silicate-based hybrid materials in more details.

2. Modification of Aqueous Dispersion Compositions of Chlorosulfonated Polyethylene and other Polymers

Introduction of polymeric modifying addition into silicate nanocomposite materials can solve the following problems:

– Increase in tack and curing of the adhesive layer when mounting the insulating material on the metal surfaces;

– Possibility of adjusting the activities while mounting structures;

– Dealkalization of the composition to prevent the reactivity of adhesive with respect to the primer compositions;

– Decrease in the average density of the composition;

– Preservation of mounting properties of compositions at temperatures up to 263 K;

– Preservation of adhesion of the adhesive bonding in a high impact;

– Giving elasticity and water resistance to the adhesive line (glue line).

It is known that aqueous dispersions of polymer (PVD) are thermodynamically unstable systems. The polymer is in the form of particles-globules with the size of 0.1–0.3 μm stabilized with surfactants. Under the action of electrolytes, stabilizers can be desorbed from the surface of dispersed particles, and the formation of large clumps of polymer coagulates. Such electrolytes are sols obtained from water glass and an aqueous solution of sodium or potassium silicates.

Coagulation was prevented only after directional, preliminary modification waterglass, by introducing the colloidal agent in the amount from 0.5 to 1 %. The resulting effect is due to the influence of additive on the structure of the colloidal particles in a hydrogel formed from the sodium silicate, and the possibility of condensation of the hydroxyl groups of orthosilicic acid when changing their degree of ionization. At the same time, pH decreases slightly, by approximately 0.2–0.4 units. Modified liquid glass is combined with all studied polymeric aqueous dispersions in ratios of 99:1 to 75:25. This range is suitable for use in adhesive compositions to create a fire protection [2].

Liquid glass is capable of forming stable emulsions with solutions of a number of polymers. This phenomenon was observed for the compositions of liquid glass solutions with chlorosulfonated polyethylene [3]. Composite materials of this type are of great interest, as they have a reduced flammability, and are essentially cheaper than starting polymers. The durability of such materials and the stability of aqueous emulsions depend on the properties of the starting silicate. These compositions can be used as waterproofing and fire retardant materials, due to the fact that the silicate contained in them, passes into a water resistant form during the drying of the emulsion.

Elastic coatings based on chlorosulfonated polyethylene (CSPE) are characterized by a complex of the valuable properties. They are resistant to ozone, acid and alkaline environments, fire resistant, resistant to oils and fuels. It allows using products from CSPE in almost all fields of engineering. When mixing, CSPE solutions with the conventional liquid glass form emulsions which are stratified faster than drying of the system occurs. Films of such materials which are dried at the substrates are not capable to soak silicate, which is formed by dissolving and, therefore, peeled off when wetted. With solutions of CSPE, liquid glass solution forms stable emulsions. These emulsions are almost of transparent appearance. If they were dried, plastic films could be prepared with a high content of sodium silicate uniformly distributed. When mixing of approximately equal amounts by weight of modified liquid glass with a solution of CSPE in toluene a stable emulsion was obtained. After drying of the emulsion films that contained 65 % of water-insoluble silicate were formed. CSPE concentration was 15 % and the mixing ratio by volume equaled 1:1.7. Such films are not peeled off from the metal, when immersed in water or under the influence of atmospheric precipitations.

Silicates of chemical elements with multiply charged cations are insoluble in water. For example, when a liquid glass aqueous solution of copper sulfate is added, the mixture becomes turbid and after some time, light blue gelatinous precipitate appears on the bottom of a vessel. However, cuprammonium complex sulphate solution is mixed with liquid glass to form water soluble silicates. Spectral data show that ammoniate of copper when in contact with the liquid glass does not change its structure and homogeneity even when heated, but changes its color from deep blue to pale blue or aquamarine. This fact alone points to the restructuring of the cuprammonium complex. The dried films of liquid glass that contain copper ammoniates have less shrinkage and do not crack when drying. Introduction of copper complex improves the stability of liquid glass emulsions when in contact with the solution of CSPE. When films obtained from these emulsions through the loss of ammonia are used, the liquid glass passes into insoluble copper silicate.

Hydrolysis of dimethyldichlorosilane with diethyl ether results in oligodimethylsiloxanes containing 98 % of cyclic oligomers [1]. Addition of oligodimethylsiloxanes or hexamethyldisilazane into the liquid glass and CSPE facilitates their emulsification by plasticizing the dried product and gives additional water repellency to the film. After one year of outdoor use, the film containing 3.9 % oligodimethylsiloxane retains its strength and elasticity.

Combination of aqueous sodium silicate with a toluene solution of CSPE results in the formation of water-in-oil emulsion. The polymer solution constitutes the continuous phase, and silicate is distributed fairly uniformly in it. Such emulsions can be easily diluted with solvent for polymers. Addition of water does not affect the viscosity. After drying the film components remain uniform in a fairly wide range of compositions. Mixing and formation of emulsions occur very easy, and often result in almost transparent compositions.

Stable emulsions and liquid glass form not only CSPE toluene solutions, but other polymer solutions in non-polar organic liquids. The smaller the difference between the surface tension and viscosity of the mixed solutions, the more successful homogenization is. At present this trend is observed in solutions of chlorinated polyvinyl chloride, copolymer VHVD-40, polystyrene and nitrocellulose.

NTI & Polymate has created a series of new materials based on liquid glasses, including those containing organic cations, as nano structuring additives use tetrafurfuryloxysilane (TFS) and CSPE aqueous dispersion.

To reduce the fire hazard of wooden constructions and structures, special fire-protection methods and means, active and passive, are developed and successfully used. So-called passive means of fire protection of construction elements are used to prevent fires, that is, for preventive purposes. The passive means, in turn, are divided into two groups: chemical and structural. Fire protection of construction elements is most often provided by the treatment with various fire retardants – fire-protecting chemicals for wood. There are many types of these compounds: paints and varnishes, enamels and coatings, plastering and soaking compounds. Fire retardants (fire retarding compounds) should possess certain characteristics to provide the proper level of fire protection of wood and wooden structures. When exposed to high temperature the paints and varnishes swell up which prevents the heat from penetrating to the material and impede the propagation of flame on a wooden surface. Although the choice of fire-retarding paints and varnishes is rich, they all have one common drawback: they cover (conceal) the wood grain which adversely affects the exterior, and therefore they are mainly used for fire protection of internal wooden structures (woodwork).

On the background of fire-retardant coatings available on the market, Silaguard compound developed by NTI & Polymate is unique. It includes a number of modifications for wood, metals and plastic products, including highly transparent options. This allows using of the above-mentioned compound not only as a coating of concealed wooden structures, but as a decorative coating as well.

The components of Silaguard are available on the world market. As the plasticizer for the given compound SEPOLEX CSM latex produced by SUMITOMO SEIKA CHEMICALS Co., Ltd, Japan, is used. It has the following average parameters: particle size 1.09 ± 0.09 μm; viscosity 30 ± 7 mPa·s; and solid content 40.1 ± 0.2 wt %.

A distinctive feature of Silaguard is the presence of fire-retardants that do not reduce the transparency of the coating, if its thickness is adequate to ensure the fire protection. It also uses a plasticizer which increases its resistance to weathering. The advantage of the proposed compound is that it does not contain organic solvents. It assures a high fire-resistance at a lower consumption rate. When exposed to fire, it does not emit any harmful substances, which makes the coating environmentally friendly. Silaguard fire-retardant coating for wood is produced in a stirred mixer designed for making suspensions containing up to 30 % of solid particles. Its cost is 40–50 % lower than the cost of epoxy fire-retardant coatings.

This technology is developed to obtain a special binder based on liquid glass containing organic cations and nano-structuring TFS additive for "cold" technology for production of glass and carbon composites and honeycomb structures for aerospace industry. With the same cost, heat distortion temperature of heat-treated materials is up to 1323 K, compared with 413–453 K of traditional epoxy composites. Compared with polyphosphazene-based materials with a higher heat resistance, their cost is 8–10 times lower. Thus, their heat resistance is at least two times higher.

This invention relates to novel chemical compounds that contain water-soluble organic polymer and alkali-stabilized colloidal silica, and, in particular, compounds in which the water-soluble organic polymer is a mixture of adhesive or film-former and alkali-stabilized colloidal silica, that is, the material with finite-size particles up to 0.03 μm that is preferably obtained in a manner which implies passage of alkali silicate solution through an acid-regenerated ion exchange resin. An aqueous medium having an alkali-stabilized colloidal silica sol with finite-size particles in the range between 0.01 and 0.03 μm dispersed therein and a water-soluble organic polymer dissolved therein, the polymer being selected from the group consisting of polyvinyl alcohol and methyl cellulose and the silica having a molecular weight of from 0.6 to 50 million as determined by light scattering in aqueous solution [2].

Manufacture of polymeric materials with specified properties is a very acute problem, which is closely related to the structure of hardened materials; and it is the structure that determines the final properties of the polymer. The process of space-network structure formation with the use of CSPE is slow. The degree of cure in the presence of γ-aminopropyltriethoxysilane (AGM-9) is not more than 70 % at 313 K. For material with stable properties, it is essential to provide conditions to ensure the most complete curing reaction.

In order to control the formation of space-network structure, CSPE and low molecular weight organosilicon compound – alkylalkoxysilanes, octamethylcyclotetrasiloxane (MCTS) – are used. The process has been studied by changing the viscosity of the CSPE solution with time. It should be noted that systems that do not contain AGM-9 cured slowly, and that their viscosity remained practically unchanged for two months. The curing occurred only in the presence of AGM-9. Addition of silane derivatives (methyltriethoxysilane (MTS), vinyltriethoxysilane (VTS) ethyltriethoxysilane (ETS), a partial hydrolysis product of tetraalkoxysilane (ETS-40) in the amount of 1–5 wt %) resulted in reduction of the system lifetime from 90 to 60 min, and in increase in its viscosity. The enhanced adhesive strength was observed in the compounds which had been modified by ETS-40. Methods have been developed that make it possible to regulate the strength and technological properties of CSPE using elementorganic and organosilicon compounds of different nature. These modifiers improved the strength and technological properties of materials based on CSPE [4].

3. Modification of Sol-Gel Synthesis Products by Polyurethanes

New high-strength organic mineral products were obtained by joint gelation of polyisocyanates, aqueous alkali silicate solutions and cement. These products compared with the conventional polyurethane compounds, and alkali silicate masses are characterized by more rapid curing, increased hardness and incombustibility [5, 6]. They are suitable for use as putties, bonding agents, thermal insulation and sound-proof materials, as well as for waterproofing. They differ from previously known products by high mechanical strength.

For these organic and mineral products, the interaction of polyisocyanate and alkali silicate solution occurs in the presence of a polyisocyanate crosslinking catalyst. This leads to the formation of inorganic and organic three-dimensional bodies of enhanced mechanical strength, closely linked.

Ref. [7] describes method for hardening and sealing coal mining, ground or brick structures in mining, tunnel construction and construction industry. This method is the reaction of the polyisocyanate and the alkali silicate solution, leading to the formation of organic mineral products. Under this method, the mixture of the starter compounds is introduced into the reinforcing stratum or injection tubes. In some cases, to achieve the purpose, use high pressure. The starter compounds can be placed in separate vessels of multi-chamber cartridges and, after introduction into the compound, be mixed due to the destruction of the cartridge.

The method described in [7] results in significant strengthening of treated rock compared to uncontrolled transformation of components. The interaction of polyisocyanate and the alkali silicate solution is controlled, which results in three-dimensional network of inorganic and organic polymer frame, linked together. However, since the organic components are not completely inflammable, flammability of the resulting organic mineral products is significantly reduced compared to polyurethane systems used for the same purpose.

Ref. [8] discloses organic mineral synthetic material of higher strength, elasticity, resistance to deformation at higher temperatures and incombustibility. This material is suitable for use as putty for repairing cracks and hollow spaces, and also for the manufacture of building materials. Material is obtained by mixing the organic compound which contains two or more reactive hydrogen atoms and one or more non-ionic hydrophilic group with an aqueous silicate solution and organic polyisocyanate. The resulting mixture is used for the manufacture of colloidal dispersion. For these synthetic materials, in order to promote the reaction of isocyanates with reactive hydrogen atoms, catalysts such as tertiary amines, silaminy, nitrogen bases and organometallic compounds may be used. These synthetic materials can be administered by various auxiliary and additional substances. For such additives the following substances may be used: surfactants, additives, foam stabilizers, reaction inhibitors, enhancers, organic or inorganic fillers or diluents of various types.

In some examples, cement additive is used in the process of manufacturing synthetic materials [8]. Such examples describe direct interaction of three components: polyisocyanate, silicate and organic compound with reactive hydrogen atoms. The first component is introduced into the prepared mixture of the second and third components. Triethylamine is used as a catalyst in this reaction.

These studies indicate that the resulting composite material may be used with fillers, in fairly large quantities, without losing their valuable properties. However, in the case of cement additives, even at low volume fraction of filling an increased compressive strength is achieved. Furthermore, the duration of the setting, i.e. the time between start of mixing and curing is significantly increased by the addition of cement.

When certain catalysts are in use, the presence of cement in the compositions gives an interesting synergic effect – namely that the reaction of polyisocyanates and aqueous alkali silicate solutions, and cement setting reaction with the available water lead to hardening of the material, which occurs in a very short time. As a result, there are products of high mechanical strength. Furthermore, due to the high portion of inorganic substances, these products are non-combustible.

Ref. [5] indicates that polyisocyanates in aqueous alkaline solution containing SiO_2 can tend towards cross-linking. Moreover, they significantly inhibit the NCO/water reaction and form controlled amount of gaseous CO_2, which is used to interact with liquid glass. The reaction simultaneously produces two intertwined polymeric frames.

In the first stage of reaction a part of polyisocyanate reacts with water to form a polyuria and cleavage of gaseous CO_2. CO_2 formed *in situ* reacts with the alkali component of liquid glass solution to form $Me_2CO_3 \cdot H_2O$ (where: Me – alkali metal, especially sodium or potassium). It increases the silicate module water glass solution and forms polysilicon acid. During this reaction, a significant amount of heat is released.

As a result, there are high-strength organic mineral products. An optimal technique to produce these products is the reaction of polyisocyanate, an aqueous solution of alkali metal silicate, and cement: molar ratios of $NCO/SiO_2 = 0.8–1.4$, $SiO_2/Me_2O = 2.09–3.44$ (where: Me – alkali metal) and the ratio of NCO/cement = 10–0.5.

The process is carried out with a dispersed catalyst, stable in polyisocyanate, – hetero-cyclosubstituted ether having the formula: B-A-O-A-B, where A – C_1-C_4 alkylene, B – 5-8-membered N- and/or O-, and/or S-containing mono- or bicyclic heterocyclic radical, whereas the preference is given to simple dimorpholinoethyl ester. Moreover, dispersed cement and catalyst must be added to the mixture of polyisocyanate and aqueous alkali metal silicate solution.

According to the invention [6], the reaction of polyisocyanate and water glass in the presence of cement, as well as in the presence of catalyst which is stable in polyisocyanate and dispersed therein, ensures almost immediate gelling and instantaneous hardening of the mass (body).

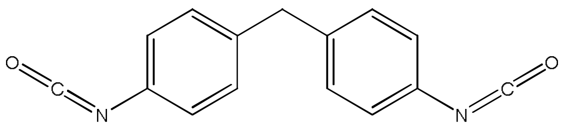
For most of alkaline liquid glasses, in which silicate modulus is significantly lower than the standard range of conventional liquid glass in the formula, it is necessary to provide a higher portion of components which reactions give CO_2.

For optimal product hardness, determination of the amount of other components of the reaction and, under certain conditions, the amount of the catalyst needs to account for composition and amount of used liquid glass. According to the invention [6], organic mineral products with high bending strength are obtained, if the molar ratio of NCO/SiO_2 in polyisocyanate and liquid glass solution used is 0.8–1.4. The preferred molar ratio of NCO/SiO_2 is 1.0.

The use of concentrated solutions of liquid glass is preferable as it reduces the total water content in the products, which negatively affects their strength properties. As to the cement used, the portion of water should be 20–80 %, preferably 40–60 %. This value represents the water-cement ratio, *i.e.* the weight ratio of water and cement. The required water fraction comes mainly from the liquid glass. A minimum amount of liquid glass is determined by the fact that it should be sufficient for the construction of inorganic framework. The required ratio of liquid glass and polyisocyanate is at least 0.2:1 parts by weight, preferably 0.5:1 parts by weight. A maximum allowable amount of liquid glass in this compound is provided if the amount of CO_2 emitted is not sufficient to bind all of Me_2O, contained in the liquid glass. Exactly the same is true at too high water content, so it is impossible to achieve complete curing. When using liquid glass with the molar ratio of SiO_2/Me_2O equal to 2.85, a maximum content liquid glass is, for example, 1.6–1.7 parts by weight of liquid glass to 1 part by weight of polyisocyanate. These limit values for liquid glasses of different compositions may shift slightly.

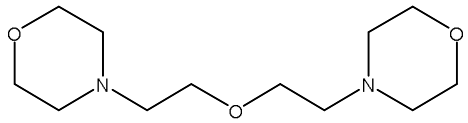
According to the invention, for organic mineral products polyisocyanates commonly used in this field, such as those described in [9], can be used. In addition, other products of the prior attachment of NCO are also suitable for the preparation of polyurethanes.

To obtain organic mineral products, as provided in the invention [6], polyisocyanates that can react readily with other elements are preferable for cross-linking when creating an organic, three-dimensional framework. These are compounds which have no steric hindrance to groups of NCO involved in the interaction. A specific example of such sterically unhindered polyisocyanate is 4,4'-diphenylmethanediisocyanate (1):



bis(4-isocyanatophenyl)methane (1)

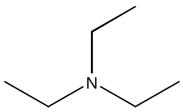
At present the most preferred catalyst is a simple 2,2-di-morpholinodiethyl ester (4,4'-(oxybis(ethane-2,1-diyl))dimorpholine) (2) having the following formula:



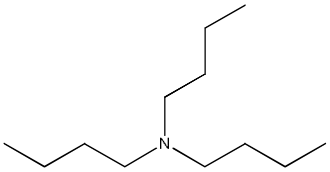
4,4'-(oxybis(ethane-2,1-diyl))dimorpholine (2)

The catalyst of this type has a number of technological advantages, namely a stable, resistant dispersion. In addition to the catalyst, to accelerate the interaction the catalysts known from polyurethane chemistry can be used.

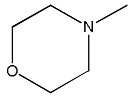
Examples of such catalysts are: tertiary amines (triethylamine (3), tributylamine (4), *N*-methylmorpholine (5), *N*-ethylmorpholine (6), *N*1,*N*1,*N*2,*N*2-tetramethylethane-1,2-diamine (7), 1,4-diazabicyclo(2,2,2)octane (8), *N*,*N*-dimethyl-2-(4-methylpiperazin-1-yl)ethanamine (9), *N*,*N*-dimethyl-benzyl-amine (10), bis(2-(diethylamino)ethyl) adipate (11), *N*-benzyl-*N*-ethylethanamine (12), *N*,*N*-dimethyl-cyclo-hexyl-amine (13), *N*1-(2-(dimethylamino)ethyl)-*N*1,*N*2,*N*2-trimethylethane-1,2-diamine (14), *N*1,*N*1,*N*3,*N*3-tetramethylbutane-1,3-diamine (15), *N*,*N*-dimethyl-2-phenylethanamine (16), 1,2-dimethyl-1*H*-imidazole (17), 2-methyl-1*H*-imidazole (18) and derivatives of 1,3,5-triazinane (19)); silamins with carbon-silicon bonds, as described in [6], (2,2,4-trimethyl-2-silamorfolin (20) and 2,2'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diethanamine (21)); nitrogen bases (tetraalkylammonium hydroxides (22), alkali metal hydroxides, alkali metal phenolates, or alkali metal alkoxides); organic metal compounds, in particular, organic tin compounds, tin(II) salts of carboxylic acids, (tin(II) acetate, tin(II) octoate, tin(II) 2-ethyl-hexanoate and tin(II) laurate), dialkyltin salts of carboxylic acids (dibutyltin diacetate, dibutyltin laurate, dibutyltin maleate or dibutyltin diacetate); ε-caprolactam, aza-norbornane of the formula (24).


triethylamine

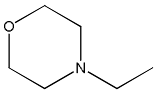
(3)


tributylamine

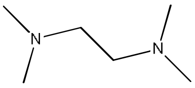
(4)


4-methylmorpholine

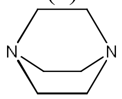
(5)


4-ethylmorpholine

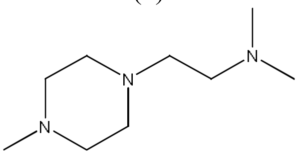
(6)


N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine

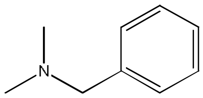
(7)


1,4-diazabicyclo[2.2.2]octane

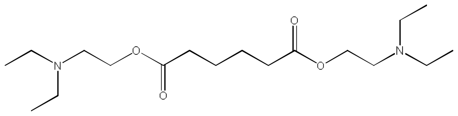
(8)


N,*N*-dimethyl-2-(4-methylpiperazin-1-yl)ethanamine

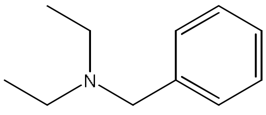
(9)


N,*N*-dimethyl-1-phenylmethanamine

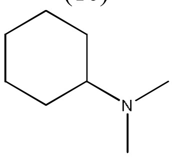
(10)


bis(2-(diethylamino)ethyl) adipate

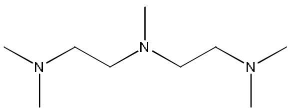
(11)


N-benzyl-*N*-ethylethanamine

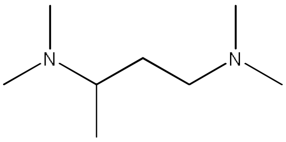
(12)


N,*N*-dimethylcyclohexanamine

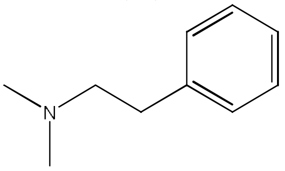
(13)


N^1-(2-(dimethylamino)ethyl)-N^1,N^2,N^2-trimethylethane-1,2-diamine

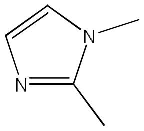
(14)


N^1,N^1,N^3,N^3-tetramethylbutane-1,3-diamine

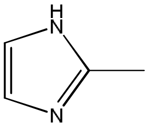
(15)


N,*N*-dimethyl-2-phenylethanamine

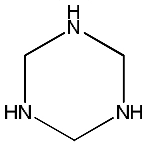
(16)


1,2-dimethyl-1*H*-imidazole

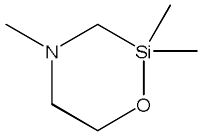
(17)


2-methyl-1*H*-imidazole

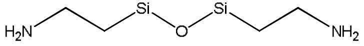
(18)

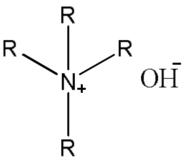

1,3,5-triazinane

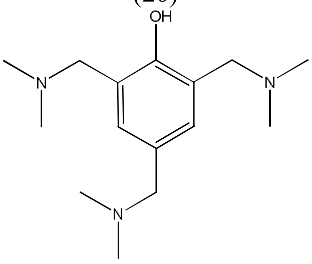
(19)


2,2,4-trimethyl-1,4,2-oxazasilinane

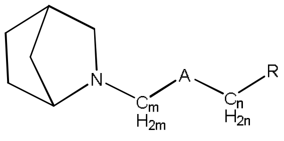
(20)


2,2'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)diethanamine




2,4,6-tris((dimethylamino)methyl)phenol

(21) (22) (23)



(24)

where A = O or CH_2, R = H or OH, **m** and **n** – whole numbers; catalysts, which catalyze the addition reaction, polymerization and crosslinking of isocyanates, such as 2,4,6-tris-(dimethyl-aminomethyl)-phenol (23).

To produce high quality organic mineral products by means of the reaction of polyisocyanate and liquid glass solution, uniform distribution of the catalyst in the reaction mixture is preferred. When adding the catalyst to the liquid glass solution, it is impossible to achieve a uniform dispersion as the resulting mixture tends to spontaneous delamination. Therefore, according to the invention [6], the catalyst is added to isocyanate, and, as mentioned above, heterocyclic substituted ethers are particularly suitable.

For foaming the product, volatile substances which are liquid at room temperatures and evaporate during interaction of liquid glass with a polyisocyanate, are suitable; as a result, the reaction heat is emitted. Examples of suitable volatile substances are alkanes and halogen alkanes.

4. Synthesis and Application of Hybrid Materials Based on Silica with Grafted Polymers

Organic polymer/inorganic hybrid nanocomposites are subjects of this study because of their improved mechanical, electrical and optical properties [10]. Among the inorganic nanoparticles, silica is extensively used as a filler or reinforcement agent in polymeric matrixes. The chemical modification of the silica particles by a polymer improves the solubility, the stability and the dispersion in various solvents. Processing techniques are based on either physicochemical routes or polymerization methods. Chemical grafting techniques include "grafting onto" and "grafting from" methods [11, 12]. "Grafting from" method begins by the fixation of initiating groups on the surface of the particles followed by in situ polymerization.

Organofunctional silanes such as 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) are widely used for "grafting from" processes since it contains simultaneously a silicon–alcoxy function and a double-bond end-group. So, free double bonds can be fixed at the surfaces of particles using a condensation step of $–Si(OMe)_3$ with ≡Si–OH groups. A variety of polymerization techniques, including conventional free radical, cationic, anionic, ringopening and controlled radical polymerizations (CRPs) have been used for the growth of polymer chains from the solid surface of different inorganic particles. "Grafting onto" route is another effective method. It involves the reaction of functional end groups of polymers onto the silica nanoparticles bearing reactives groups [18]. In this paper, we propose a new method to obtain fluorinated silica nanoparticles bearing free double bond making them reactive in a polymerization process. Most often, fluorinated silica nanoparticles are obtained either by a sol-gel process using a perfluoroalkyl di- or trialkoxysilane [13] or by condensation of perfluoroalkyl di- or tri-alkoxysilane onto preformed silica nanoparticles [14]. In [15] processes, cotelomers bearing one unsaturation were condensed onto silica nanoparticles. So, new poly[(3-(trimethoxysilyl)propylmethacrylate)-*stat*-(perfluorodecylacrylate)] P(TMSPMA-*stat*-PFDA) were synthesized by cotelomerization leading to oligomers with α-functional end-group. As already said in the previous paper [16], only perfluoroacrylate polymers with short chains can be obtained due to the insolubility of longer ones in most organic solvents. The telomerization of perfluorodecylacrylate with 2-mercaptoethanol has been explored and the efficiency of this transfer agent has been outlined in several investigations [15].

The free-radical cotelomerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) with perfluorodecylacrylate (PFDA) in the presence of 2-mercaptoethanol was performed at 353 K in acetonitrile. Hydroxy end-groups of the cotelomers were reacted with 2-isocyanatoethyl methacrylate (IME) to give macromonomers. The P(TMSPMA-*stat*-PFDA) cotelomers, containing fluoro- and silanes-groups, were then grafted onto silica nanoparticles. Optimal grafting conditions were found with TMSPMA monomer alone in toluene at 383 K. The structure of the modified silica was analyzed by FTIR and ^{29}Si solid-state NMR. The amount of grafted TMSPMA or P(TMSPMA-*stat*-PFDA) was calculated by thermogravimetric and elemental analyses. The grafting yield increased with the copolymer/silica weight ratio until the maximum value of $2.26\ \mu mol \cdot m^{-2}$. Moreover grafting density in cotelomers was quantified by thermogravimetric and elemental analyses with similar values. A maximum grafting density value has been observed while increasing the silane/silica weight ratio. As to the potential uses, such hydride nanocomposites can be considered as building blocks to fabricate more complex nanomaterials using the reactive polymer end-chains [15].

Nowadays, a variety of nanomaterials with different structures have been applied in biomedicine because of their unique characteristics inherent to the nanoscale [17-20]. For example, mesoporous materials have been widely investigated and effectively used in drug delivery systems; different metallic nanoclusters based on gold, iron, silver nanodots, and its hybrids have found potential application in sensing and magnetic resonance imagining [18].

Preparation of nanoscale systems with new functional properties is a major challenge; however, silica nanoparticles remain widely used due to their unique features such as a high surface area, thermal and chemical stabilities [21]. The unique compatibility and possible size control in synthesis are allowed to realize different comounds of silica particles with other available materials. One of such approaches based on using silica as a scaffold for templating another material such as dyes, quantum, or magnetic dots [22]. Here, silica is used as a shell for the protection of encapsulated materials. In another way, silica nanoparticles can be considered as seeds or cores around which other materials can be grafted (Figure 1 b). In this field, different functional polymers are being involved for surface modification of silica core [23]. Functional groups in polymeric chain provide excellent binding properties of modified silica surface for effective captures of different small objects: magnetite or fluorescent nanoparticles, drugs, *etc*. A number of polymers has been already synthesized and applied for silica functionalization. The most common studies include poly(acrylamide), polyethilenglycol, and polyacrilic acid [24-26]. For this reason, a new kind of polymers should be examined for developing the new surface properties of polymer-coated silica particles. Taking into account the published results about polymer science and biotechnology, we suggest considering a new guanidine-containing polymer based on polydiallyl and polymethacryloyl guanidine (Fig. 1a) as one of the most promising candidates for silica modification due to their low hemotoxicity and high ionic properties [27-29]. There are only few studies concerning investigation and application of guanidine-containing polymers excepting polythexamethylen guanidine and its analogues [30]. Besides, It was reported that guanidine fragment in a polymeric chain is more promising than their amine equivalents due to capability of guanidine groups bind stronger with negative molecules compared to amine groups [31].

Polymer-coated silica particles have received tremendous attention as adsorbents for many organic compounds [32]. At present, synthesis of highly effective adsorbents has become a promising technique for blood detoxification, especially for bilirubin removal [33]. Bilirubin (Fig. 1c) is a dicarboxylic acid and circulates in human blood plasma where it is bound to serum albumin to form a water-soluble complex [34]. It is transported to the liver as a complex with albumin, where it is normally conjugated with glucuronic acid and excreted into bile [35]. However, bilirubin can be accumulated in blood at high concentration once patients suffer from a liver disease (hyperbilirubinemia) [36]. Several techniques have been employed for removal of the high concentration of free bilirubin from plasma in order to prevent hepatic and brain damage [37]. However, hemoperfusion treatment based on application of hemoadsorbents is one of the most effective techniques. Many kinds of adsorbents (carbon nanotubes, mesoporous silica, and graphene oxide) have been exploited. All of them have some drawbacks related to the low adsorption capacity, biocompatibility, or high toxicity [36]. Therefore, the search and synthesis of new adsorbents for efficient bilirubin removal is very demanding.

In Ref. [27], polymer-coated silica particles were synthesized *via* sol-gel method in the presence of guanidinecontaining polymer. A subsequent treatment of silica particles with positively charged guanidine-containing polymers leads to the great increase in adsorption capacity for bilirubin compared to unmodified silica. Authors demonstrated successful modification of silica core by guanidine-containing polymers using an electron microscope, Fourier transform infrared (FTIR) spectroscopy, and thermal analysis.

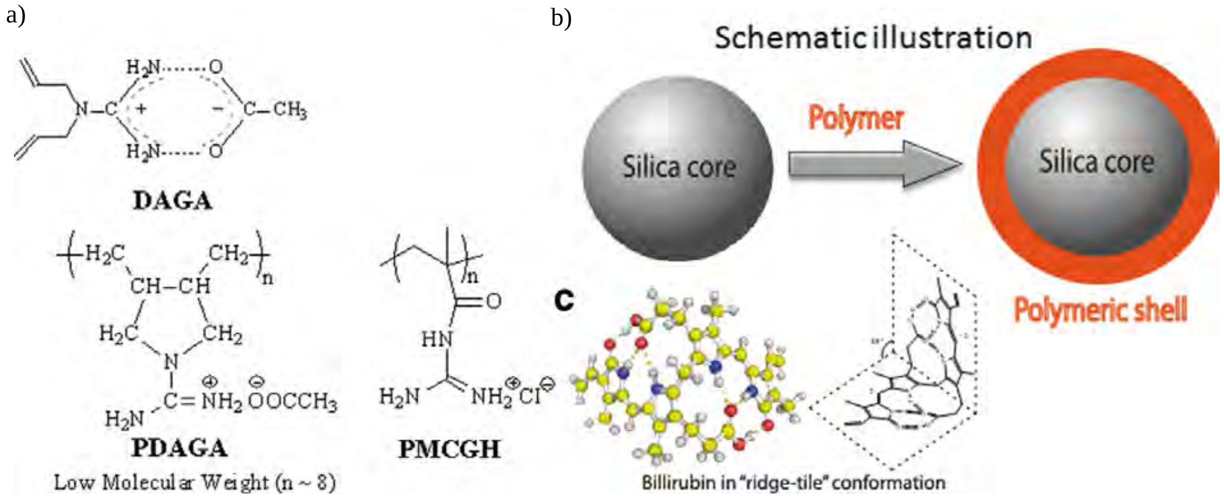


Fig. 1. Structures of diallyl guanidine acetate (DAGA), polydiallyl guanidine acetate (PDAGA) and polymethacryloyl guanidine hydrochloride (PMCGH) (a); schematic illustration of modification of silica core (b) and structure formula of bilirubin in "ridge-tile" 5Z, 15Z conformation stabilized by six intramolecular hydrogen bonds [27] (c)

The development and design of adsorbents with high adsorption performance is the actual aim for successful toxin removal. In this work, we report the performance of new guanidine-containing polymers as a shell orientated around silica particles with the following application for effective bilirubin removal. To evaluate polymer-shell modification, Fourier transform infrared spectroscopy and high-resolution electron microscopy were performed. Changes in surface morphology of polymer-coated silica were detected. It was shown that polymeric shell completely covers silica surface. The grafting amount was evaluated by thermogravimetric and was in 18–34 % range. Incorporation of guanidine containing polymers into silica matrix leads to the great increase in adsorption capacity According to the Langmuir model, the maximum adsorption capacity for bilirubin was 43.47 mg/g. We also demonstrated that prepared polymer-coated silica could well adsorb bilirubin from the bilirubin-albumin solution at low concentration of albumin.

Therefore, this study has revealed that guanidine-containing polymers have great potential to serve as effective agents for improving the adsorbent to remove bilirubin [27].

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ПОСТУП В НАНОКОМПОЗИТАХ НА ОСНОВІ ГІБРИДНОЇ ОРГАНО-СИЛІКАТНОЇ МАТРИЦІ

Анотація. *Наведено функції і можливості золь-гель технології для виробництва органічних мінеральних гібридних нанокомпозитів, на які можна впливати. На конкретних прикладах показано вплив на деякі принципи синтезу і застосування гібридних наноматеріалів у різних областях техніки.*

Ключові слова: *нанокомпозит, нанотехнологія, золь-гель, гібридні композити, силікатна матриця.*