Some aspects of composite inorganic polysialates

Jaroslav Šesták · Bronislav Foller

Abstract The state-of-art of polyaluminosialates is reviewed in terms of inorganic ⟨mers⟩ showing the composition, degree of netting, function of modifying atoms and the role of non-bridging oxygen as well as hydroxyl groups (biocompatibility). The polymeric condensation is compared with the vitrification of glasses upon cooling. The replacement of Si by P is discussed as well as the analogous precipitation process of amorphous hydrous silica (opal). Progress of geopolymers and biopolymers usefulness is shown within the framework of generalized world of macromolecules screening hundred contemporary citations. Pultrusion technology is presented, capable to produce composite geopolymers reinforced by basalt fibers staying suitable for mechanical applications.

Keywords Geopolymers · Biopolymer · Polysialate · Polyphosphate · Opal · Non-bridging oxygen · Hydroxyl group · Pultrusion technology

Reviewing geopolymers and their links with the classical state of quenched glasses

As a matter of curiosity the novel so-called geopolymeric materials were introduced about 10 years ago on the pages of this journal [1, 2] by Davidovits (cf. Fig. 1).

Geopolymers—X-ray-amorphous inorganic polysialates [1–5] are cementitious composites, which are commonly produced by idiosyncratic wet copolymerization (i.e.,

synthesis via solution) of the individual alumina and silica components [1–14]. Such a room-temperature synthesis process takes place when aluminosilicate source materials are dissolved in aqueous solution at very high pH yielding thus mostly non-crystalline zeolitic-like precursor, which is also termed as *copolymer*. The reactive Si–OH-based easy-soluble monomers in water-glass rather easily penetrate into the structure of inserted solid Al-compounds. This can be compared with the case of a high-temperature melting process of precursor glass batch, where conversely the rigid structure of quartz sand is diffusion-disintegrated by the penetration of Ca, Na, Al atoms from their more easily melted compounds thus braking up the original –Si–O–Si– structure. Both routes factually represent a mutually comparable type of vitrification reactions equally facilitating ionic interactions by either the movable hydrated ions or the diffusible atoms in the melted viscous state.

Aluminosilicate gels (zeolite precursors) are mostly synthesized [14–23] with the composition characterized by general formula $M_m[-(Si-O)_z-Al-O]_n \cdot wH_2O$, where M_m are modifying cations (mostly Na, K, Ca, Mg), n is the degree of polycondensation and z is structural ranking (1, 2, 3,…). Configurationally tetrahedrons SiO_4 and AlO_4 are mutually bonded by oxygen bridges forming thus Si–O–Al-based chains and rings. The positively charged M_m ions ought to be compensated by the negative charge of four coordinated Al. Generated gel-like structure is partially amorphous or nanocrystalline depending on both the amount of initial solid matter and its nature (character of raw materials) as well as on the condition of the reaction conditions (pH). The amorphous state is primarily favored for a higher concentration of solid precursor in the preparatory suspension.

The gel subsequently hardens into rigid geopolymers (resembling the glass formation upon the melt solidification), which may be characterized in a number of ways,

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Fig. 1 Animated discussion between two pioneers of geopolymeric materials, French professor Joseph Davidovits and Czech professor Jiří Brandštetr (VUT Brno, 2007)

correspondingly applicable to classical glasses. For example, the description in terms of principal constituents (alumina and silica) [22–26], their structure (tetrahedral Al–O and Si–O units in random three-dimensional framework), charge-balancing role of the tuning metallic (often alkali) ions, thermal glass-formation characteristics [27, 28] and their macroscopic properties (moderately strong and hard, stable up to 1000 °C, etc.). The specific circumstances of the low temperature synthesis [14–28] such as the condensation temperature of alumina and silica resources at high pH and distinctiveness of various sorts of water-glasses [29] are worth of a further clarification. XRD patterns of commercial melted glass and wet synthesized inorganic polymer were compared [29] showing broad peaks between 17° and 34° 2θ (typical for amorphous phases) which for inorganic polymer is slightly shifted to the higher 2θ revealing questioningly its relatively more "dense" structure than that for analogous commercial glass. Further deconvolution of such broad peaks in XRD patterns can enable a more quantitative estimation of the degree of amorphicity.

Certain formalism was developed in order to investigate structural units involved, mostly in the terms of fragments such as [–Si–O–Al–O–] called *sialate* units [1–14] (or *polysialate* when condensed concurrently). Further suggested units contain different Si:Al ratios, such as [–Si–O–Al–O–Si–O–] (*sialate-siloxo* [1–4, 8, 14–16]) and [–Si–O–Al–O–Si–O–Si–O–] (*sialate-disiloxo*). The Si:Al atomic ratio implies 1, 2, and 3, however, non-integer ratios intermediate between 1:1 and 1:3 may be anticipated as changeable combinations of basic units, provided that the content of charge-balancing cations is appropriate (often water content controlled). The units with Si:Al > 3 are designated as *sialate* and *polysialate* geopolymers. In the sense of majority of the Earth's crust, which is composed of siloxo-sialates and sialates, the common feldspar series are albite–anorthite ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$)

describable as poly(sialate-disiloxo) for albite to poly(disialate) for anorthite.

Hypocrystalline materials and their 'mers' framework

So far not enough attention has been paid to the basic structural disposition though detailed studies on reaction mechanism are available [30–39]. The inherent stoichiometry can be understood analogously to organic and/or inorganic –*mers* (known in classical polymeric chains) [39–47]. Such generalized spheres of the so-called hypocrystalline materials (an newly coined term more appropriate for an approved terminology) are specific of possessing the regular polyhedrons AO_n (such as SiO_4, AlO_3, AlO_4, BO_4, BO_3, PO_4, etc.) [33, 47]. Important is the linking function of *bridges* formed by all n atoms of oxygen. If oxygen is bridged with two central cations, A- (e.g., $\{SiO_{4/2}\}$ as $AO_{n/2}$) then i atoms of oxygen become bridged with A by a double bond (the so called *terminal bonds*, known from a single component glass composed, for example, of phosphorus oxides containing –*mers* of $\{O=P(-O-)_3\}$. The adequate coordination formula ensues as $\{AO_{i/1}O_{(n-i)/2}\}$, where $\{PO_{1/1}O_{3/2}\}$ may serve as an illustrative example of coinciding multifaceted stoichiometry. In the analogy with organic polymers, the group $\{AO_{i/1}O_{(n-i)/2}\}$ can be considered as $(n-i)$-functional—*mer*. Similar attitude can be applied to geopolymers based on aluminosilicates composed of tetrahedral alumina and silica units. When condensed at ambient temperature the *mer*—units of $AO_{n/2}$ become repositionable because of their concoction long lifetime this is comparable with the degree of immovability at the high temperature state of melts. Similarly to oxide glasses of a randomly interconnected web (*continuous random network* [40–47]) a relatively more complex copolymer system (containing supplements of moderating electropositive elements typically alkaline oxides, M_2O, or other metallic oxides) persevere the function of *modifying oxides*. In oxide systems (melts/glasses/macromolecules) such additions to a single-component (tetragonally netted) solution result in the breakdown of bridging bonds A–O–A and formation of the so-called non-bridging oxygen. They can be described by set of equations: $M_2O \Rightarrow 2 M^+ + O^{2-}$ and $M'O \Rightarrow M'^{2+} + O^{2-}$ and $A-O-A + O^{2-} \Rightarrow 2A-O^-$, which are factually responsible for the dissociation concerning a single molecule of modifying oxide and the subsequent breakdown of bridging bonds (A–O–A). In the case of typical modifying oxides the equilibrium [42, 46] shifts toward the products and the arrangement can be easily derivable from melt/glass/polymer initial stoichiometry.

The cation distribution affects the species in the silicate solution, i.e., the amount of monomers, dimers, etc. [19, 29, 32, 33, 48–50]. Water-glass enforced by few percent of

Al-ions [50] or partly substituted by P_2O_5 increases its penetrating reactivity. The study of vitrification of silicate solution indicates that the reaction commencement becomes associated with a concentration decrement as a result of separate phase growth [29, 30]. Comparing the molecular structure of reactants (metakaolinite and silicate solution) with the geopolymers, a complete rearrangement of molecular environment (short-range order of Al and Si) is evident [33]. Alumina is likely altered from their distorted crystal order via certain intermediate species (associated with valences IV, V, and VI) and linked to one SiO_4 unit in metakaolinite forming the regular $Al^{IV}\{Q^4(4Si)\}$ [33, 44–46] where Q's are the standard representation of Si-based configurationally motives [44–46], see below. However, the Al atoms seem to attain a more symmetrical environment in final geopolymers than in the original metakaolinite. The most reactive species in silicate solution is likely the hydroxyl anion OH^- (or $H_3SiO_4^-$), which can draw parallel thoughts toward the basis of bioactivity of inorganic materials [51–56] and the coupled effect of non-bridging oxygen [47, 54]. It may even catch the attention of an innovative conception toward life creation on the Earth [51, 52] providing geopolymers as a new target biomaterial [57].

Accounting for the specificity of geopolymers, the charge-balancing metal ions factually make feasible the crucial polymerization in (–Si–O–Al–O–Si–O–) sialate-silixo chains where the atomic ratio remains Si:Al = 1:1 (however, capable to increase up to 3:1). When reaching the value above 3, generalized polysilicates became comparable to melted (counter-partner) glass. This approach, however, has not been applied to a geopolymeric state due to yet unacquainted methodology. The difference between melted glass and condensed sialate-silixo polymers endures in the subsistence of a certain coordination of (–Si–O–Al–O–Si–O–) with both Si^{4+} and Al^{3+} cations in the fourfold coordination, which is unavoidably balanced by the presence of modifying cations. It is ranging from fully amorphous up to partly organized (modulated) compositions of hyper-crystalline states thus exhibiting definite nano-crystalline regions. Single and multiple Al–O–Al bridging cannot carry on to subsist, nevertheless, alternatively can survive in minerals such as above-mentioned albite ($NaAlSi_3O_8$) and anortite ($CaAl_2Si_2O_8$).

Worth another attention is still an apparent analogy with generalized (even organic) polymers mentioning the so-called mean degree of netting. Structural motives, Q, which appear throughout the melt–glass–polymers [33, 44, 45, 47] can be characterized by a coordination formula $\{AO_{(i+j)/1}O_{(n-i-j)/2}\}$, where j is the number of bridging oxygen atoms associated with a single central atom being ripped away by the action of oxygen produced through the dissociation of modifying oxides ($j \leq n-i$). In the case of

silica glasses ($i = 0$, $n = 4$) there is a direct link between the concept of the so called Q-notation (i.e., Q^k, $k = 0, 1, 2, 3, 4$) and a coordination formula, $Q^k \equiv \{SiO_{(4-k)/1}O_{k/2}\}$. Similar approach may become welcome for its alternative implementation to the circumstances of geopolymers, which fashion is still under prospect. Nonetheless, it was shown from NMR data [58, 59] that $Q^4Si(2Al)$ and $Q^4Si(3Al)$ components can exist in alkaline geopolymers, the latter being the highest for the Si/Al ratio of 1.5. For higher concentration of Na and consequently lower Si/Na ratio in the activating water-glass (and with Si/Al ratio measured in the polymer support) a feasible scheme points up that the hydrated sodium aluminosilicates bears a three-dimensional structure in which $Q^4Si(3Al)$ predominates.

Some prospective studies

An alternative attitude to geopolymers can be anticipated when assuming a wider stoichiometry range by, e.g., the incorporating phosphates in addition or even instead silicates (where Si is totally or partially replaced by P) and/or borates as an alternative to aluminates. On the contrary to the needed alkaline environment for polyaluminosialates the phosphates are formed by an acid–base reaction between a metal oxide and an acid phosphate. Virtually any divalent or trivalent oxide that is sparingly soluble may be used to form these phosphate geopolymers. Berlinite ($AlPO_4$) may serve as a good example, which is formed by the reaction between alumina and phosphoric acid ($Al_2O_3 + 2H_3PO_4 \Rightarrow 2AlPO_4 + 3H_2O$). It was also demonstrated that phosphate geopolymers of trivalent oxides such as Fe_2O_3 and Mn_2O_3 may possibly be produced by the oxide reduction and then acid–base reaction of the reduced oxide with phosphoric acid. Such wide-ranging phosphate materials represent another variety of mineral geopolymers [60–63] possibly promoting the incorporation of Fe cations for magnetic applications [48, 63, 82].

Relevance of bridging and non-bridging oxygen [45–47] to polysialate–polyphosphate geopolymers overlapping tetrahedral alumina/silicate/phosphate units has not been so far studied nor analysed so that this would become a target of future investigations. Notwithstanding the addition of acids, which occasionally accelerates the formation of gels, may support an idea that the gelling mechanism involves a cross-linking of preexisting (often linear) polymers someway analogous to organic polymeric systems. A range of other activation processes were also investigated [63, 64], however, any indistinct integration of theory of organic polymers, occasionally applied even to soluble silicates, may not assist a better interpretation of such aqueous inorganic systems.

Strategy for geopolymers applicability as a matrix for reinforced composites (fibers, foam, and/or ceramic) is

different from the practice in similarly activated cements [25, 65] producing, however, analogous materials that possesses 'cementitious' property. It is foreseeable that the structures of these alkali-activated cement, alkali-activated slag, fly ash, etc., are different resulting from different chemical-mechanistic paths. The calcium silicate hydrate is a major binding phase in Portland cements holding also somewhat unstable ettringite. In dissimilarity the binding property of geopolymers results from the formation of a three-dimensional (mostly amorphous) aluminosilicate network containing tetrahedral unit with diminishing transport properties (causing thus a low mobility of particles). Therefore, the viscosity of such dispersal heterogeneous system tolerates systematical formation of a required shape by slow rearrangement. The rates of partial polymerization reactions are in agreement with the rate of structure ordering processes. Depolymerization requires the formation of zeolite nuclei within a geopolymer micelle in the hydrous aluminosilicate gel. The time needed for such crystallization varies from a few hours to several days; aging time at room temperature is about one day and crystallization time at 100 °C up to 100 h (for the relevant glassy $Na_2O/K_2O–Al_2O_3–SiO_2$ system the crystallization temperature is in the range from 150 to 230 °C). The structure of amorphous silica is of a more open arrangement than that of closely related cristobalite. Spaces/sites on the reaction surface are worth of extra attention being capable to accommodate hydroxyl ions. Such a reactive surface bears an ionic charge and particularly silica is under continual switching process of equilibration between solution and interfaces, which thus enables better physical–chemical interaction even with the enforced fillers.

Some practical aspects of geopolymeric composites can be seen from the matrix primary properties exhibiting the compressive strength of 100 MPa, which is about twice that of cement but having only one-half its density. Filling with all-length polypropylene fibers increases its strength up to

about 200 MPa. For a plausible technological application we brought in a special so-called pultrusion technology [66] in which the enforcing material is a yarn bundle, better a rowing of basalt fibers [67, 68] (2520 TEX, $\phi = 13$ μm), which is enforced through an extrusion nozzle to harden, see Fig. 2. For a weight ratio of rowing of about 80%, with commercial matrix (Baucis FG), the resulting banding strength reaches 360 MPa, which becomes reliable for mechanical applications (when expensive classical epoxy analogous composite is not more than twice stronger) [67–69]. The advantage of this geopolymeric composite is its excellent fire resistance (so-called fire–smoke-toxicity).

There are some unclear points as the determinability of glass transition temperature of polysialates. It is often accomplished from the position of loss modulus apex (resolved by DMA) [39] but for many amorphous materials the glass transition temperature becomes overlapped by crystallization upshots [70]. Better solid phase identification is needed [70–74]. So far there were no attempts to look for a glass-formation coefficient, common in other types of glassy materials [75], which may provide a better insight to the structure of geopolymers (and their modeling challenge [76–79]) as well as for some new applicability [80, 81].

Further interrelation aspects of far-reaching polymeric materials

Another extension of a generalized understanding of inorganic polymeric materials can be located in the sphere of amorphous hydrous silica—*opals* [82–88], which is a remarkable material with the general formula $SiO_2 \cdot nH_2O$, but is precipitated as mono-dispersed colloidal particles (from 150 to 400 nm in diameter). In the most common weathering model [83–85, 87, 88] it is formed analogously to the gel process [67, 68] via geopolymers-like formation
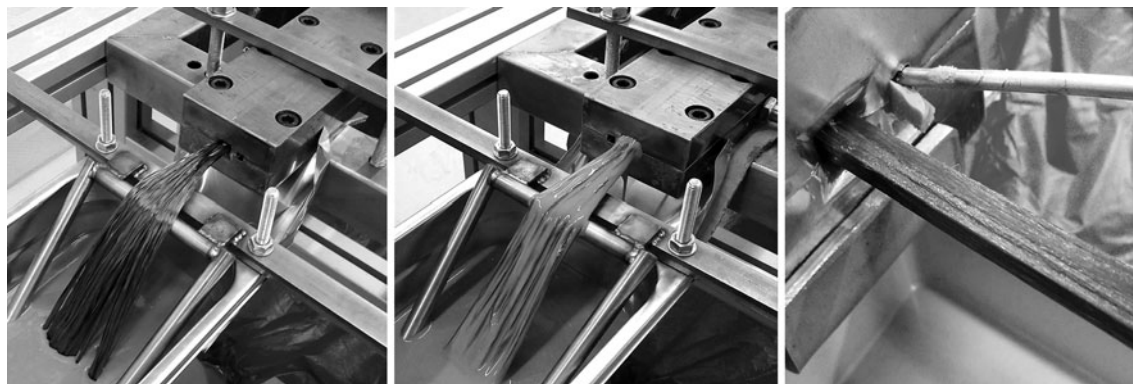

Fig. 2 Newly employed pultrusion technology showing from the left yet dry rowing of basalt fibers, in the middle the rowing which is already dipped to the suspension matrix (kaolin Baucis FC; water

glass Bindzil) finally hardened in the furnace under tension to form final oblong chips about 20 × 20 mm

through gelatinous state of approximate stoichiometry $(M_m(SiO_2)_Z\ (AlO_2)_Y\ n MOH \cdot w H_2 O)$. Sandstones are a common source of silica where the process of chemical weathering (of relatively soluble silicates such as the feldspars contained in these sediments) results in the formation of an alkaline silica solution. An example of such a mineral is potassium feldspar which weathers through the idealized stoichiometry (e.g., $2KAlSi_3O_8 + 3H_2O \Rightarrow Al_2Si_2O_5(OH)_4 + 2KOH + 4SiO_2$) by the permeation of ground water through the sediments resulting in kaolin, dissolved silica, and an increase in pH through the release of potassium hydroxide.

The process of cross-linking via sol–gel processes is characteristic of possible incorporating a substantial amount of organic compounds as additives [88]. Thus, the characteristic property of a more broadly viewed naturally occurring geopolymers can involve a substantial amount of organic/humid materials. The term geopolymers can thus be understood by geochemical communities as macromolecular organic-containing polymers (or biopolymers) indicating the geological transformation of various geo-molecules through geochemical processes [89–93] during diagenesis. Consequently, such a mineralization path provides a stable material as the final (alternating) products in the Earth, such as kerogen, asphalt, etc. Such an attitude is also cross-boundary to an assortment of geo- and bio-polymers along with a generalized comprehension of existence of various biomaterials (for example biological glasses [94–97]) representing innumerable organic macromolecules accountable for life, their nucleation and transformation records, where an important role plays common states of low ordering, either forming glasses, amorphous matter, modulated, and nano-crystalline structures [98]. It incorporates basic questions of the determinability of such glassy and amorphous states [70–75, 98], adequate structure analysis [76–78, 99], search for a wide-ranging material applicability [11, 61, 99], etc. It involves a huge sphere of biological life, its diverseness, and also its curiosity to ever appear [51, 52].

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