



Recent Developments in Inorganic Polymers: A Review with Focus on Si-Al based inorganic polymers

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ABSTRACT

Inorganic polymers are a unique classification of polymers. They contain inorganic atoms in the main chain. Hybrids with organic polymers as well as those chains that contain metals as pendant groups are considered in a special sub-classification as organo-metallic polymers. The networks containing only inorganic elements in main chain are called inorganic polymers. The silicone rubber is the most commercial inorganic polymer. The organo-metallic and inorganic polymers have a different set of applications. The current paper is a review of current applications of polymers with inorganic back-bone networks, especially focusing on Si and Al based inorganic polymeric materials.

Key words: Inorganic polymers, geopolymers, fire resistant polymers, environmental friendly concrete.

INTRODUCTION

Inorganic polymers, by name, stand for many non-organic monomers/repeating units. Distinguishing between inorganic and organometallic polymers depends on one's opinion. Simply put, inorganic polymers contain only inorganic repeating units, while the organometallics have an alternate organic linkage between the inorganic elements. Metal containing polymers can be further classified as per the

position of the metal ion. The metal ions could be in the backbone of the polymer, enmeshed into the chain or as pendant groups to an organic backbone chain. The most common inorganic polymer is polydimethylsiloxane (PDMS), also called silicone rubber. The main interest in this section of polymers arises due to their low temperature elastomeric properties coupled with high temperature stability.

Since the divide between inorganic and organometallics is very confusing, the

polymers can hence be referred to as polymers with non-organic elements. Further, they can be classified as metal in backbone, metal- enmeshed polymers and metal ions in pendent groups¹.

The main reasons for interest in these polymers are their unique property profiles separating them from their organic counterparts. Among them, the main features are²⁻⁴:

- ' Number and variety of elements in these polymers
- ' High abundance of inorganic materials in the earth's crust
- ' Stronger bond formation
- ' High temperature stability
- ' Tailoring new structures with many variations

Thus, inorganic polymers are an opportunity to expand fundamental knowledge, develop new materials and stimulate new thoughts in polymer chemistry⁵. This paper provides an overview of the synthesis; properties and applications of these materials with a special emphasis on the applications of silicate and aluminum based inorganic polymers.

Inorganic polymers

Inorganic polymers of this class are majorly components of soil, mountains and sand. They are used in fire-resistant panels, coatings, flame resistant materials and construction materials. The most widely studied and developed inorganic polymers are silicon based.

Polysiloxanes are the most important inorganic polymers with regard to commercial applications. Their applications range from medical to sealants, water-barriers, cosmetics, etc. PDMS (polydimethylsiloxane) or silicone rubber is the most widely used.

Polysilanes are similar to polysiloxanes in structure. They contain only silicon in the backbone. The applications of polysilanes are based on their property of electron mobility. Their current uses are as photoresists and precursors to other silicon containing materials.

Victor Glukhovskiy^{6,7} is believed to be the first researcher to model the geological formation

of zeolites, in the 1950s. This discovery of a new class of inorganic materials resulted in wide scientific interest and development of a variety of applications. The most comprehensive work in this field is done by Davidovits⁸. He is also responsible for first coining the term "geopolymer" to alkali-activated aluminosilicates. In 1979, Davidovits founded the Geopolymer Institute in France to increase the scientific and commercial interest in geopolymers and their applications.

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material termed "geopolymer" by Davidovits⁸. Instead of referring to them as inorganic polymers, geopolymers can more accurately be sub-classified as mineral polymers. Polysialates (polymers containing silicon, aluminum and oxygen in its backbone) were the first polymers to be synthesized. Silicon, aluminum and oxygen are the major constituents of geopolymers. Geopolymers could be made by dissolving aluminosilicate materials in high alkaline environments like sodium hydroxide or potassium hydroxide solution. The products are amorphous to semi-crystalline with good to high mechanical properties⁹⁻¹⁹.

Sources of aluminum-silicate include natural minerals and industrial wastes like kaolin, fly-ash, slag from blast furnace, etc. The alkali activation is pH sensitive and NaOH or KOH may be used for this purpose. The polymerization process is however not yet fully understood. The effect of various parameters on the polymerization and the micro-structure has been studied extensively. Geopolymers have successfully been used immobilize toxic metals^{16, 19}. Due to its cage structure, geopolymers may even be capable of solidifying radioactive materials.

Synthesis of geopolymers:

Geopolymers can be synthesized at room temperature or at slightly elevated temperature by activating aluminosilicate using silicate and aqueous hydroxide solution. The water content is low and hence, the reaction takes place in colloid form. The activator consists of sodium silicate or potassium silicate and NaOH or KOH solution.

According to Davidovits¹¹, the geopolymer consists of Si, Al and O in the backbone. The reaction can be expressed as¹⁶.

The SiO₂ in reaction 2 is in monomer or polymer form coming from the silicate solution. The final geopolymer backbone is shown in reaction 2. According to the reaction, activator solution consisting of sodium silicate/ potassium silicate and sodium/potassium hydroxide solution will control the dissolving and charge balance of the reaction system.

Kaolinite^{13, 16, 20-23} has been the most widely used material of source for geopolymers. Kaolinite is treated to produce metakaolinite with higher reactivity and activation energy. Potassium polysialate (K-PS) and potassium polysialatedisiloxo (K-PSDS) geopolymer from metakaolinite have shown excellent thermal stability. Sodium silicate and NaOH solution activator system is mainly amorphous and shows layered framework showing that the colloid reaction mainly occurs at flake-like surfaces of metakaolinite particles²⁴.

Metakaolins fly-ash geopolymers

Fly-ash is another source material for aluminosilicate. Fly-ash is a byproduct from thermal power plants. Metakaolin is synthesized from kaolin via various treatment processes. Both the sources

have a very different origin. Metakaolin has lesser impurities and hence, is able to give more manufacturing consistency. The particle size²⁵ may affect the rheology and reaction times but, there is little difference between the reactions.

In contrast to the naturally available kaolin, fly-ash, an industrial waste can also be used as source material for geopolymer synthesis. The chemical composition of fly ash is similar- silicon, aluminum. But, they also contain iron oxides and significant amounts of calcium²⁶. The chemical, elemental and phase composition of particles vary from particle to particle and so does their particle size. This non-homogeneity of particles requires more care when working with fly-ash.

Properties of geopolymers

Since 1950s, studies have been carried out in the field of geopolymers with only one application in mind- as cementitious materials. Hence, the properties of faster setting, better compressive strength and durability of geopolymers over traditional cements have been advantageous.

It has been showed that²⁷ potassium initiated geopolymers show better strength and better setting times than sodium initiated ones. Also, there is a limit to the amounts of NaOH or KOH solution that can be used for polymerization. Excessive amounts are found to have an adverse

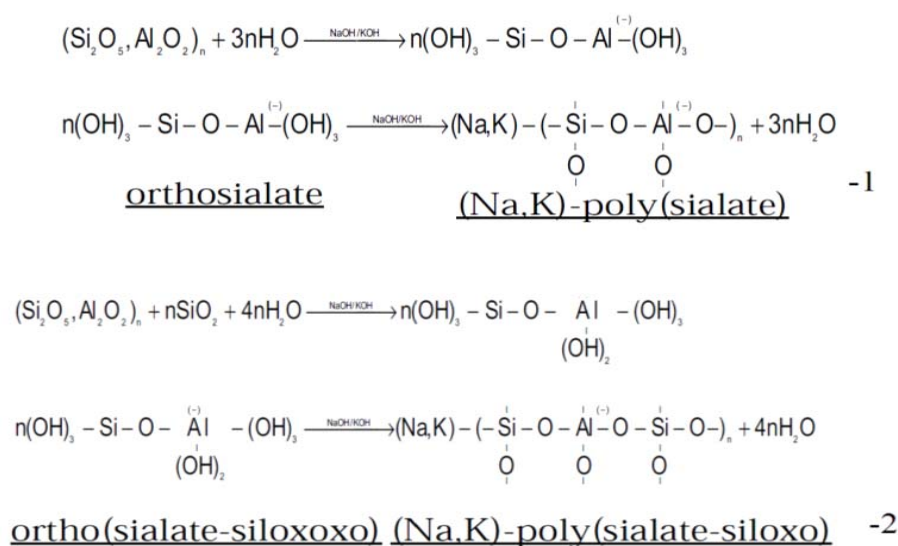


Fig. 1: Reaction 2 involved in the synthesis of Si and Al based geopolymers

effect on compressive strength of the material. Similar effect is shown by silicates. However without silicates, the compressive strength is found to be very much lower than with the presence of them.

Geopolymer composites

In recent years, geopolymers have been used in composites for their fire-resistant and thermal insulation properties. Lyon²⁸ studied carbon fiber reinforced geopolymers. Geopolymer composites performed better than organic matrix composites with carbon fibers and glass fibers in flame resistance tests. Even when the geopolymer composites were exposed to more severe environments, they performed better than their organic counterparts.

The effect of length of the fibers was studied by Lin²⁹ to reinforce a geopolymer matrix. Regardless of the lengths, the filled composites showed pseudo-plastic fracture against the brittle fracture of unfilled geopolymer. In three-point bending tests, a similar pattern was observed where the composites were deformed without full fracture while the geopolymer showed brittle failure. The scanning electron micrographs of the fractured samples showed weak matrix-fiber bonding.

More recently, Bernal³⁰ studied aluminosilicate fibers and particles filled geopolymers. The composites showed increased thermal stability and reduction in volumetric shrinkage. At higher temperatures, densification of the filler-matrix interface takes place increasing the stiffness. The mechanical performances at high temperatures were also found to be remarkable.

The application of geopolymers in reinforced concrete beams³¹ has indicated better performance of geopolymers over organic polymers in adhesion of carbon fibers to reinforced concrete beams.

Polytetrafluoroethylene (PTFE)³² powder addition into the kaolinite based geopolymer matrix changes the tribological behavior. The wear mode changes from severe to mild due to formation of a soft layer during friction.

Geopolymer coatings:

Barbosa³³ studied the thermal behavior of

potassium polysialate (K-PS) and potassium polysialatedisiloxo(K-PSDS) till about 1400°C. The geopolymers show excellent thermal stability at temperatures up to 1000°C. Above 1200°C, the potassium polysialatedisiloxo becomes porous and friable.

The high thermal properties at such high temperatures are associated with the recrystallization of geopolymer at 1000°C. Rickard³⁴⁻³⁵, used these thermal properties of geopolymers to make heat resistant coatings for metal substrates. The coatings show exceptional balance of lightweight, fire retardant and thermal insulation material. The coatings showed thermal expansion of about 3% at 800°C. Another observation was the excellent adhesion to the metal substrates.

Future Research

Geopolymers are gaining huge interest in areas where lightweight thermal insulation is required. The study of these materials due to their growing applications across various fields is becoming increasingly important. The research community hence, needs to develop more into this field to produce sustainable as well as futuristic needs from the material.

Also, the long-term study of these materials properties seems a barrier for its growth. Data of severe environments exposed on these materials will benefit further study.

Study of geopolymers as a sustainable replacement to Portland cement is of great importance. The synthesis of geopolymers and their end properties along with durability should be studied.

CONCLUSION

The history of geopolymers is quite short. Since their birth, they have come a long way in a very short time. The abundance of raw materials in nature and development of commercial applications have secured a large-scale future for them ahead.

The current state of studies coupled with more future work by the research community should help secure a wide acceptance for geopolymers.

However, the fundamental studies need to complete along with large capacity data collection to improve and develop methods for synthesis,

sources for raw materials and end-user applications. This will ensure the future of geopolymers.

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