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Dynamic Mechanical Properties of Geopolymer-Polymer Composites

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Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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February, 2006

Abstract

Dynamic mechanical properties and rheology of the organic polymer modified inorganic polymer systems synthesized from metakaolin were studied and evaluated. These inorganic polymers, popularly known as geopolymers, possess a set of excellent characteristics which includes high compressive strength, high temperature and fire resistance, acid resistance, heavy ion fixation, low temperature curing, good surface finish, low cost raw materials and are environment friendly. Geopolymers are a relatively new class of engineering materials and are in the process of finding their way to industrial products. A few of the problems that are holding back the development of these materials are the control of curing time, enhancement of their workability and knowledge of the dynamic mechanical properties of these systems.

In this project the control of curing time, improvement in the workability and modification of the rheology was achieved by addition of organic polymers including poly (ethylene glycol) and carboxy methyl cellulose, to the geopolymer system. The dynamic mechanical properties of these systems were evaluated using dynamic mechanical analysis for the cured systems in the plaque form and a rheometer for the uncured systems as slurries. The effect of organic polymers on the geopolymer system was quantified using the same techniques.

Poly (ethylene glycol) is commercially used as a plasticizer to increase the lubricity of the ceramic mass and has excellent spreading properties. Carboxy methyl cellulose, a modified polysaccharide, is commercially used as a viscosity modifier and has an excellent water retention capacity. These two organic polymers were added to the geopolymer system with an aim of modification of rheology, processability and dynamic mechanical properties before and after curing. Addition of these polymers to the geopolymer system varies the curing time of these systems in the range of 4 hours to 72 hours. Also the rheology of the uncured slurries is changed. This was quantified using the rheological studies that show increase in the elastic and viscous moduli of the slurries after addition of the organic polymers. The elastic modulus varied between the range of 7 Pa to 54,600 Pa depending on the polymer and water content. Similarly, the viscous modulus also varied between 16 Pa and 25,400 Pa. The increase in the elastic modulus of the uncured slurry is significantly more than that of viscous modulus. The viscosity of these systems with respect to time and shear rate was also observed and showed change after addition of organic polymers. The viscosity varied within the range of 4 Pa.s to 580 Pa.s depending on polymer and water content. The composite slurry exhibited thixotropic behavior. These uncured slurries were cured to form cheesecloth-reinforced plaques. These plaques were used to study their elastic and viscous moduli with respect to temperature using the dynamic mechanical analysis technique. The results are encouraging and showed improvement in the moduli of the systems after addition of organic polymers for a selective loading range. But largely addition of organic polymers had a negative impact on the dynamic mechanical properties of geopolymer system. Addition of organic polymers also imparted flexibility to the cured samples opposing to the brittle nature of the pure geopolymer systems.

Acknowledgements

Any venture requires effort, support and guidance of many people and this is no exception.

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Special thanks to Dr. Hany Ghoneim, who gladly agreed to serve on the project committee. I would like to express my gratitude towards Dr. KSV Santhanam, Program Chair, Center for Materials Science and Engineering, RIT. Also I would like to thank Ms. Natalya Privorotskaya for her cooperation and good time in the lab.

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Chapter 1

Introduction

In recent years a new class of engineering materials has emerged called geopolymers or alkali activated alumino-silicate binders [1]. Geopolymers consist of a three-dimensional polymeric silicon-oxygen-aluminum framework [2]. Materials with similar structure were known and used in B.C. era [3]. As proposed by Prof. Davidovits, the Great Pyramids of Egypt were made using similar materials and that each stone cube was cast from such materials [4,5].

Since the later half of the 20th century there is a renewed interest in these materials from researchers, engineers and technologists associated with various fields of materials. This interest was generated because of the array of properties exhibited by these materials. Geopolymers are fire and high temperature resistant. They are stable and can perform without any loss of properties at the temperatures up to 1300^0C [6,7]. These materials have good acid and sulfates resistance; develop rapid strength up to 70% within four hours of casting. Geopolymers are castable, sprayable, extrudable, stick to many materials including metals, concretes and give glassy finishes. These materials are termed as "Green Materials" because of the low energy consumption and low toxic gas emission for their production. Geopolymers can be synthesized using waste materials like industrial slag, fly ash, volcanic ash and along-with alkali activators. [3] These materials have excellent compressive strength, ranging from 48 MPa to 120 MPa, depending on the starting materials, method of preparation and the added aggregates. Such properties make these materials a very attractive choice for a range of potential applications.

There are a lot of driving factors that are pushing the development of these materials. The factors like rising awareness and stricter laws regarding environmental protection, rising costs of waste disposal and cost cutting efforts made by the construction industry to stay competitive. In contrast to ordinary portland cement concretes, OPC, geopolymers requires only about 3/5 of the energy required to produce OPC. Also the carbon dioxide emissions are 1/5 of as produced with OPC manufacture. Geopolymers can be considered as man made rocks and their disposal should not be a problem. Considering these facts, geopolymers provide a good option for these problems and can be considered as an alternative to materials like portland cements and plastics.

As discussed by Prof. Van Deventer [3], there are some problems that impede the development of the geopolymers industry. According to him the problems are of two kinds: commercial and technical. The geopolymer industry lacks a uniform nomenclature and standards for products. There is a lack of fundamental knowledge and very little cooperation between the players. In addition, there is the fear of unknown as this is a new field. The industry involved with these or a related material is conservative and has vested interests in the already developed, tested and proved materials. Although many of these issues still remained unanswered there is a significant progress made in understanding these materials. The people have much more knowledge and understanding of these materials than a few years back. Inroads have been made in terms of fundamental understanding of these materials.

Currently geopolymers can be considered as the materials still in their embryonic stage, but these materials are developing very fast. Although the geopolymer technology was developed more than 30 years ago, patents and licences closely guarded it. Also, geopolymeric materials were developed as technology rather than science, hence there is a very little fundamental understanding of these materials. Only within the last decade the interest in these materials was revived after the classified information was open to public. Research groups from all over the world showed interest in this field and peer-reviewed research work was initiated. The research groups from all over the world, especially academia, took interest in understanding the fundamentals behind geopolymer technology. The gap between the technology and the science related to geopolymers must be bridged in order to further develop these materials.

A lot of work has been carried out over the last few years and some theories have been proposed and agreed upon. Most of the work was focused on understanding the microstructure of geopolymers, their curing kinetics, elemental analysis before and after curing and their effect on the overall properties and various geopolymeric systems, i.e. different starting materials. Consequently the popular tools employed for these studies were thermal analysis techniques like differential scanning calorimeter and thermogravimetric analysis, microscopes like scanning electron microscope and transmission electron microscope, infrared spectroscopy, X-ray diffraction and nuclear magnetic resonance spectroscopy. Apart from these there are a few important aspects of these materials yet to be understood. Rheology and processing properties of these materials are not yet understood completely and the availability of literature regarding this is very scarce.

To date there is no strong evidence of successful modification of rheology and the setting time of the geopolymers. Solution for this problem will be helpful in the development of geopolymer field and certainly will open up new sets of processing techniques and consequently applications. The work in this project is focused on tackling the problem of control of rheology, workability and curing time of the geopolymers.

This study is a part of the process of bridging the gap between the geopolymer technology and the science behind it. The study of dynamic mechanical properties of geopolymers will help understand the processing of these materials and will be an important step in developing these materials into viable applications. The significance of this study lies in the fact that geopolymers are being talked about to replace cement concretes and there is no active research being done in this area. Another part of this study was evaluating the thermal coating properties of geopolymers as fire retardant coatings. It was successfully demonstrated that geopolymers can be used as high temperature resistant coatings for cement concretes up to 800^0C by Natalya Priorotskaya [8]. For successful utilization of geopolymers as coatings, knowledge of rheological properties of geopolymers is critical.

Geopolymers, being inorganic cementatious materials, can be compared with OPC. Modern day cement concrete systems were developed in the later half of the 19th century [9].

Since then additives were added to these cements to control their properties. Now rheological additives are added to OPC concretes with purposes of improving flowability, decreasing slump loss, and it may provide extra strength upon hardening [10, 11]. Such commercials plasticizers are mainly composed of polymers like substituted polysaccharide sulfates and polysuccinimide [10, 11, 12]. In addition to plasticizers it is a common practice to add retarding agents to the concrete mix to control the curing.

The ultimate aim that can be achieved by geopolymers is to replace cement concrete in all its applications. To achieve this goal the geopolymers need to be developed according to the existing infrastructure used in cement concrete applications like the equipment and the processes.

There is a new class of cement concretes that is being developed. These concretes, called Engineered Cementitious Composites (ECC) [13], behave as regular concretes under normal loading conditions but show flexibility under intense loadings like earthquakes or other natural disasters. Such behavior is attributed to the incorporation of poly (vinyl alcohol) and fly ash in these concrete mixes.

The study by Kecheng Gong et.al. [14] mentions the requirement of organic component for the mineralization process of inorganic materials. It also mentions the function of organic component to bind the micro-crystals of inorganic materials and arrange their orientation to form natural composite materials with superior mechanical properties as compared to ceramics. A similar study by Jui-Ming Yeh et.al. [15] studies a series of polymer-clay nano composite materials prepared using poly (vinyl alcohol) and layered montmorillnite clay suggest enhancement of thermal and mechanical properties with combination of organic and inorganic components.

All these evidences point toward the fact that addition of organic polymers to an inorganic system has an appreciable effect on the final properties of the system. In this project we try to take a similar approach for the geopolymers by adding organic polymers into the geopolymer system.

The aim of this work is to explore the set of organic polymers that can be added to the geopolymer systems that have an effect on the rheology and the processing properties of the overall system. It also aims to study and evaluate the dynamic mechanical properties of these materials in their cured and uncured form, quantify the change in the rheological behavior of these with respect to the organic polymers. The systems were studied and evaluated based on their dynamic mechanical properties using techniques like dynamic mechanical analysis for cured samples and rheometer for uncured slurries.

The geopolymer-polymer composite system, after curing exhibits flexibility without cracking, a fundamental change in the inherent brittle nature of the geopolymers. To understand this phenomemon, dynamic mechanical analysis (DMA) is the most appropriate technique. DMA evaluates a true material property, elastic and loss moduli. These properties are evaluated in a linear region of stress-strain curve as opposed to destructive testing such as compressive and three point bending tests which give the breaking strenght which lies in a nonlinear region. The characterization of material with DMA is on a molecular level as compared to other methods that give a macrosopic properites. DMA is the only techniques that evaluated the material response under oscillating frequency and also gives the amount of energy dissipated in form of viscous modulus. To the best of the author's knowledge, DMA was never used to characterize the geopolymers. To understand and quantify rheology, rheometer is the appropriate technique and hence it was used to understand and quantify the behavior uncured composite slurry.

The initial work in this study included identifying a geopolymer system and identifying the set of organic polymers than might be suitable for this study. These organic polymers must be selected based on criteria with respect to the characteristics of the geopolymer systems. All the pre-selected organic polymers were tried with the same geopolymer system with variable amounts.

Samples were prepared for a range of different characterization techniques that were employed to analyze the effect of these polymers on the geopolmyer system. These characterization techniques include compression test, three point bending test, dynamic mechanical analysis and rheometer.

Based on the initial results and the observations two organic polymers that gave most promising results were selected for further analysis. The next experimental work was carried out to quantify the effect of polymer on the geopolymer system. Samples were prepared using the two selected polymers added individually as well as combined into the system. The variables in the system were the amount of each polymer and the excess water content. The samples were analyzed in two forms, as uncured slurry using a cone and plate rheometer and cured plaques with dynamic mechanical analysis in bending mode.

The parameters like elastic and viscous moduli and viscosity with respect to time and shear rate at room temperature were evaluated for the uncured slurry. While for the cured plaques the elastic and viscous moduli over a temperature range were observed. Recommendations based on the above observations are made for geopolymer – polymer systems that exhibit varying properties.

Chapter 2

Literature Review

2.1 Geopolymers

2.1.1 History

This class of materials was first recognized in the Ukraine, where they were referred to as "soil cements." Glukhovsky [16] hypothesized that the superior durability of ancient concretes resulted from the coexistence of cements containing calcium silicate hydrate (C-S-H) with some form of alkaline aluminosilicate hydrates. The latter are essentially impure forms of current day geopolymers.

It was French Prof. Joseph Davidovits [14] who continued the investigation into these kinds of mineral polymer materials with the structure of three-dimesional cross-linked polysialate chains. These inorganic polymers were initially called as Polysialates [12, 17] (Symposium of Macromolecules, 1976). Nine years later, Prof. Joseph Davidovits [17] coined another term "Geopolymer" in his US Patent for this family of inorganic polymers. Since then the term geopolymer is widely accepted and used.

Prof. Davidovits further developed these materials and demonstrated their use in a wide range of applications. He developed a variety of particulate and fiber reinforced composites for structural applications. Such composites include cements and concrete composites and materials for waste product encapsulation [1]. In addition, Prof. Davidovits and his research group made important progress regarding geopolymers. To date it is the leading research group in the world in the field of geopolymers.

Initially the development of geopolymers was restricted to the research group of Prof. Davidovits because of his patents and licenses. This restricted the knowledge of geopolymers to the other researchers. This trend changed in the last decade, when the classified information was available in the public domain.

Significant contributions have been made by the groups of Comrie, Balaguru and Gauckler [30]. More recently, Deventer et al. and Comrie have focused on composites made from partially reacted geopolymers derived from aluminosilicate containing minerals, such as feldspars, mullite, alusite, muscovite, stilbite, smectites, bentonites, etc [1]. Comrie and Van Deventer et al. also devoted considerable attention to the immobilization of toxic metals using geopolymers. Barbosa and MacKenzie and Singh et al. focused on the more basic science issues by investigating the NMR spectra of amorphous, metakaolinite derived geopolymers, and more recently, on the crystallized phases formed as a result of high temperature heat treatments [18].

Different research groups all over the world have focused their research in various aspects of the geopolymer field. The research group in University of Melbourne, Australia led by Prof. J van Deventer and Dr. Grant Lukey is working simultaneously to gain fundamental understanding of these materials as well as developing new applications based on this knowledge . Other research groups are also active in Australia and New Zealand. A lot of companies and academia are in active pursuit of developing newer applications with geopolymers. The research group led by Prof. Palomo in Madrid, Spain is developing new civil engineering applications while the group in UTAD, Portugal led by Prof. Teixera has been successful in using these materials in restoration work of historical artifacts. WISNUTEC, a German company, has successfully utilized these materials in nuclear waste management. This field is relatively less developed in North America. The group in New Mexico State University is working on a novel field of piezo-electric effects of geopolymers. A research funded by Federal Aviation Administration in Rutgers University focused on development of fire resistant fiber reinforced composites using geopolymers for the aviation industry [19]. There is some growing interest in National Research Council of Canada in this field of geopolymers. But most of the researchers have stumbled because of the lack of the processing knowledge of these materials. A varied range of applications requires a varied range of processing characteristics of geopolymers and currently that is difficult to modify.

Of the all the research carried out, current and past, all over the world there is no evidence of any group focusing on the dynamic mechanical properties of the geopolymers. The research group led by Gong [14] has worked by addition of organic polymers to the inorganic polymer system. Their research paper reports the influence of five kinds of water soluble organic polymers on the polymer/kaolinite composite geopolymers. This research focuses on the change in mechanical properties like compressive strength and cross bending strength of the kaolin system modified with these organic polymers. The study points out the fact that naturally occurring processes like mineralization of inorganic components in bone or shell requires the mediation of organic molecular templates. Organic component binds the micro crystals and arrange their orientation to create naturally occurring composite structural materials with better strength than ceramics. This study assumes that addition of organic polymers with carboxyl groups, amino groups or hydroxyl radicals will improve the properties of composite geopolymer.

The organic polymers used for this study were poly (acrylic acid), poly (ethylene glycol), poly (vinyl alcohol), sodium polyacrylate and polyacrylamide. The geopolymer system used was based on crystalline kaolinite, sodium hydroxide and sodium silicate, very similar to geopolymer system used in this study. The results from this study prove that organic polymers enhance the mechanical properties of the geopolymer system under consideration. There is a noticeable increase in the bending modulus of the system. The organic polymers were added in their powder form and in quantities ranging from 0.2 % to 1.2 % by weight. The most efficient polymers in terms of increasing the mechanical properties of the composites were poly (acrylic acid) and sodium polyacrylate. It was also proposed in the study that poly (acrylic acid) was better than the rest of the polymers as it was more efficient in promoting the polycondensation reaction of silanol groups inside the interfacial layers, resulting in higher binding strength in between kaolinite particles.

Apart from this study there is very limited literature available in the field of geopolymer-organic polymer composites. There is no further research initiated in this field.

2.1.2 Chemistry and Structure

Geopolymers are inorganic polymers formed by a polycondensation reaction between an aluminosilicate source and alkali hydroxide and alkali silicate solutions [14]. The term geopolymer can be applied to a wide range of alkaline- or alkali-silicate-activated aluminosilicate binders having a general composition of $M_2O.mAl_2O_3.nSiO_2$, usually with $m \sim 1$ and $2 \leq n \leq 6$, and where M represents one or more alkali metals [1]. Activation of the polymerization reaction is achieved by mixing solid aluminosilicate materials with metal hydroxide and silicate solutions at near ambient temperatures.

Geopolymers can also be viewed as an amorphous equivalent of certain synthetic zeolites. Prof. Davidovits proposed that geopolymers consist of a polymeric Si-O-Al tetrahedral joined together in three directions by sharing all the oxygen atoms. In the three dimensional geopolymer structure, aluminum is four coordinated with respect to oxygen that creates a negative charge imbalance and therefore the presence of cations is essential to maintain electric neutrality in the matrix.

As of now neither the industry nor the academia is confidant about the geopolymer structure but a lot of work has been put in and various models are proposed. Geopolymers have a structure of three dimensional cross-linked polysialate chains ([-(Si-O) z-Al-O-] n) and are semi-crystalline. The reactants include the natural minerals or industrial aluminosilicate wastes (clay, slag, and fly ash), alkali silicate and alkali hydroxide. Materials that are a good source of aluminum and silicates can be used as a raw material for the geopolymers.

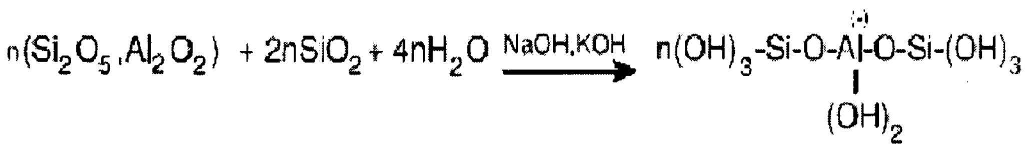
Kaolin, a naturally occurring clay is rich in aluminosilicates called as kaolinite ($Al_2Si_2O_5(OH)_4$) [7, 20]. Before we mix the reactants we convert the clay (kaolinite) into metakaolin. This involves heating of the clay to 750^{0}C for 4-6 hours, dehydroxylating the clay and changing the aluminum structure from octahedral to tetrahedral. The final atomic structure is such that it does not re-hydrate in the presence of water.

$$2Al_2Si_2O_5(OH)_4 \xrightarrow{heat} 2Al_2Si_2O7 + 4H_2O$$

Fig 2.1 Dehydroxylation reaction Kaolin

Unlike kaolin, metalolin is X-ray amorphous and reactive in an alkaline environment [21, 22]. The reactants consist of a aluminosilicate source, aqueous alkali silicate solution and aqueous alkali hydroxide solution. Premixed aqueous solutions of alkali silicate and alkali hydroxide are added to the activated clay.

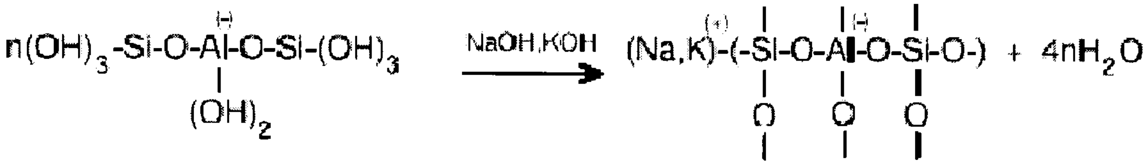
It is proposed that Geopolymerization is a two step reaction [14]. The first step, called as activation step, involves dissolution of the starting materials (metakaolin in this case) into the activator (alkali silicate and alkali hydroxide dissolved in water) and formation of orthosialate ions. Fig 2.2 illustrates the above reaction.



$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O \xrightarrow{NaOH.KOH} n(OH)_3\text{-Si-O-}\overset{(-)}{\underset{(OH)_2}{Al}}\text{-O-Si-}(OH)_3$$

Fig 2.2: Activation step in the geopolymerization reaction

The second step, as illustrated in fig 2.3, is polycondensation between orthosialate ions and surface silanol groups and the formation of three-dimensional cross-linked polysialate structure.



$$n(OH)_3\text{-Si-O-}\underset{(OH)_2}{\overset{(-)}{\text{Al}}}\text{-O-Si-}(OH)_3 \xrightarrow{NaOH,KOH} (Na,K)^{(+)}\text{-(-}\underset{\underset{|}{O}}{\overset{|}{\text{Si}}}\text{-O-}\underset{\underset{|}{O}}{\overset{|\,(-)}{\text{Al}}}\text{-O-}\underset{\underset{|}{O}}{\overset{|}{\text{Si}}}\text{-O-)} + 4nH_2O$$

Fig 2.3: Polycondensation step in geopolymerization reaction

The geopolymerization process starts as soon as the reactants are mixed and it continues until complete curing is achieved [23]. As mentioned earlier, the process of dehydroxylation of the clay changes the aluminum structure from octahedral to tetrahedral with respect to oxygen. This imparts a negative charge on aluminum creating an imbalance. To neutralize this charge presence of cations or positive ions like Na^+ of K^+ are required. Presence of water is of vital importance in the process of geopolymerization. Water acts as a mobile phase transporting the ions and reactive species. The presence of water and the cations can be observed in the following three-dimensional structure of geopolymers.

The three dimensional structure of geopolymers proposed by Barbosa et.al. [18] can be observed in the following figure. It is a three dimensional structure where the tetrahedral bonding of aluminum can be observed. The negative charge on aluminum is balanced out by the positive charge on the alkali metal ions like sodium or potassium. It can be also noted that the structure is porous and water molecules, along with the positive ions, are trapped within the three dimensional cross-linked Si-O-Al structure.

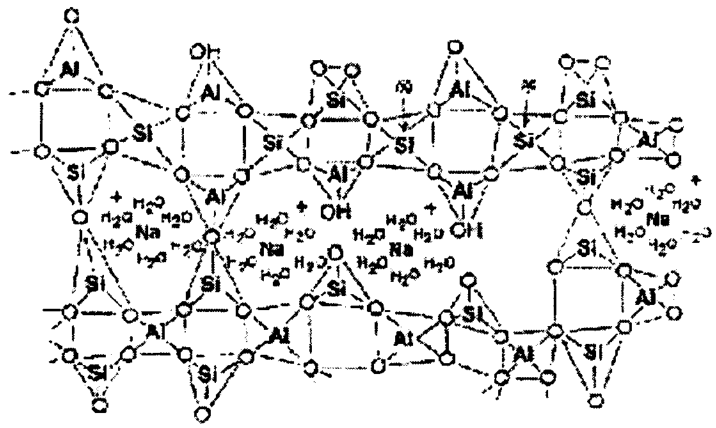


Fig 2.4: The three-dimensional structure of geopolymers proposed by Barbosa et.al.[7]

According to JGS van Jaarsveld and JSJ van Deventer [1] the above mentioned chemistry of geopolymers is an oversimplification and a whole range of related materials can be expected to form in practice. It is also mentioned that any source of silica and alumina that is readily dissolved in alkaline solution will suffice as a source of geopolymer precursor species. Geopolymers follow the same route as that for most zeolites, having three main steps: (1) Dissolution, with formation of mobile precursors through the complexing action of hydroxide ions, (2) Partial orientation of mobile precursors as well as partial internal restructuring of the alkali polysilicates and (3) Reprecipitation where the whole system hardens into an inorganic polymeric structure.

As far as synthesis of geopolymers is concerned, the most important differences between zeolite formation and geopolymerization are the concentration of precursor species as well as the fact that zeolites usually form in close hydrothermal systems unlike geopolymers. Also the setting of geopolymeric reagent mixture occurs very quickly, without enough time for formation of proper crystal structure resulting in a microcrystalline, amorphous or semi-amorphous structure depending on reaction conditions [7, 24].

To obtain optimum mechanical properties, it required that there should be enough alkali ions present for all the constituents to react completely. Another critical factor is the Si : Al ratio. The research conducted by Barbosa et. al. [7, 18] reveals that the geopolymer attains maximum strength when the Si : Al ration is equal to two [18]. Higher water content results in slow curing of the samples and results in poor compressive strength and hardness. The properties of geopolymers also depend on the order in which raw materials are added [25].

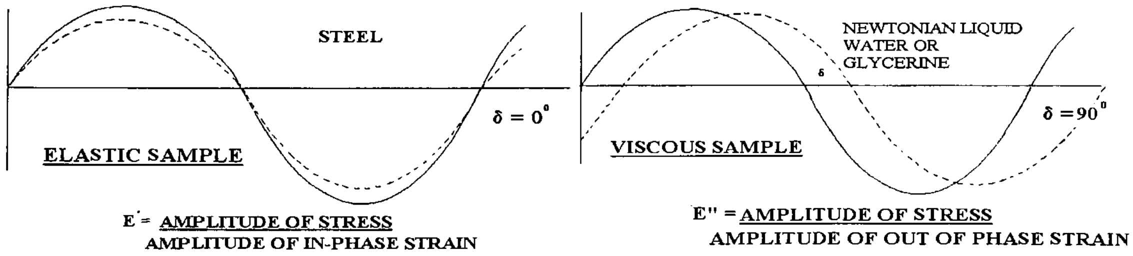
The following sections will focus on understanding the dynamic mechanical properties and rheological properties of viscoelastic materials like organic polymers..

2.2 Dynamic Mechanical Properties of Polymers

One of the major differences between classical materials and the polymers is their viscoelastic behavior. Most classical materials exhibit either elastic or viscous behavior in response to an applied stress. For an elastic system, when stress is applied it deforms proportionally to strain. This response is instantaneous and completely recoverable. The constant that relates stress and strain is called as the modulus of that system. a spring is used as an analogy for these materials.

Fluids, or the materials whose bond energies necessary for long-range translational order have been overcome, are characterized by a property called viscosity. In contrast to the elastic systems, when stress is applied to the system the strain increases proportionally until stress is removed. The strain cannot be recovered (i.e. when stress is removed the deformation is completely restrained). There is a complete loss of energy to the system. These systems that follow the mathematical relationship of applied stress directly proportional to the strain rate are called as Newtonian systems or the behavior is termed as Newtonian behavior after Newton who first defined this mathematical relationship. This behavior is represented by a dashpot in a mathematical model.

The polymers exhibit a behavior that is in between that of an elastic system and a viscous system. Such behavior is called as viscoelastic behavior. This behavior arises because of the very large size of the polymer molecules and its conformational variety that prevents molecules from aligning into a perfectly ordered structure, normally associated with solids. But on the contrary, in the fluid state the chain entanglements inhibit the polymers to behave as Newtonian fluids. Polymers show elastic and viscous responses when placed under stress in its solid as well as fluid state.



(a) (b)

Fig 2.5: Applied stress —; Observed strain: ----; (a) Behavior of elastic system under oscillatory stress, strain is in phase with stress; (b) Behavior of viscous system under oscillatory stress, strain 90^0 out of phase with applied stress

2.2.1 Types of Fluids

Newtonian Fluid

A Newtonian fluid is a fluid in which shear stress is linearly proportional to the velocity gradient in the direction perpendicular to the plane of shear. The constant of proportionality is known as the viscosity. For a Newtonian fluid, the viscosity by definition depends only on temperature and pressure, and also the chemical composition of the fluid if the fluid is not a pure substance. The following figure shows the behavior of the Newtonian fluid. Common examples of these fluids are water and glycerin.

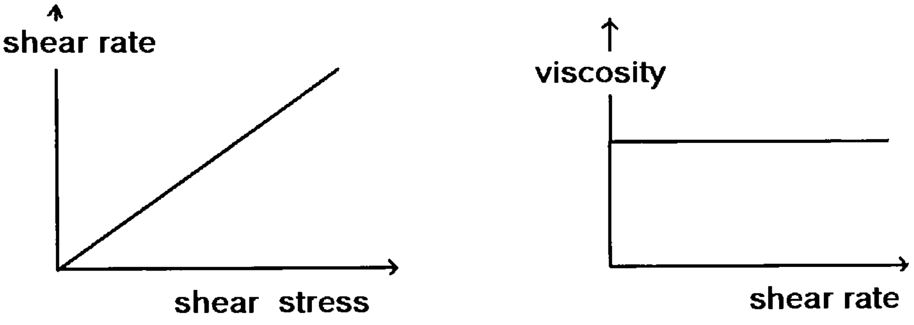


Fig 2.6: Newtonian flow behavior

The fluids that do not have a linear relationship between shear and strain rate are called as non-Newtonian fluids.

Non-Newtonian Fluids – Time Independent

Pseudoplastic

Viscosity decreases with increase in the applied shear. The behavior is called as shear thinning. Common examples include paints and emulsions.

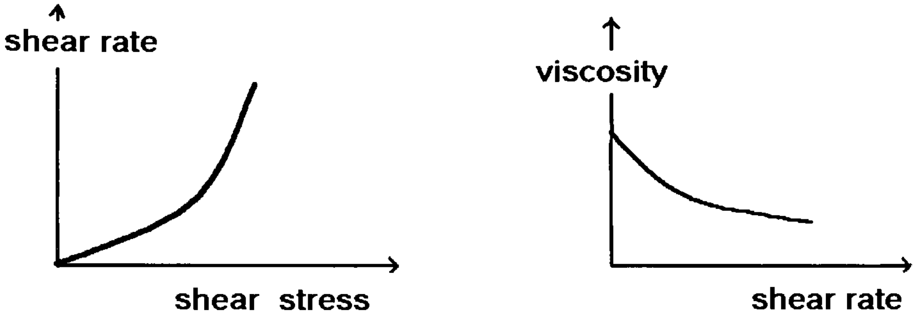


Fig 2.7: Pseudoplastic flow behavior

Dilatant

These fluids are characterized by an increase in the viscosity with an increase in applied shear or shear thickening behavior. Common examples include clay slurries, candy compounds, cornstarch in water and sand/water mixtures.

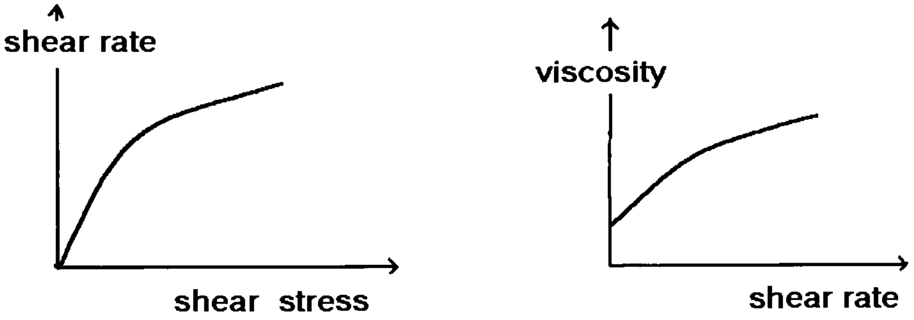


Fig 2.8: Dilatant flow behavior

Bingham fluids

Liquid behaves like solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced. This force is called yield value. Tomato ketchup is an example of such a fluid. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic or dilatant flow characteristics.

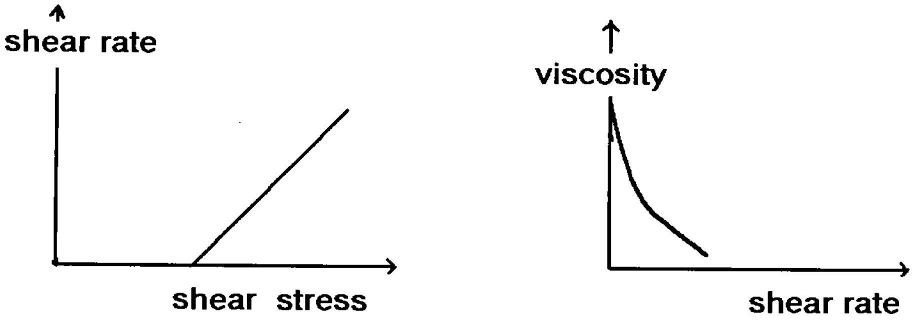


Fig 2.9: Bingham flow behavior

Non-Newtonian Fluids – Time Dependent

Thixotropic

The viscosity decreases with time for a constant shear rate. Greases display this type of behavior.

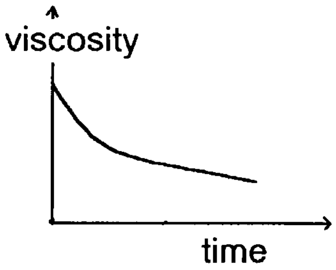


Fig 2.10: Thixotropic flow behavior

Rheopectic

In contrast with the thixotropic behavior, viscosity increases with time for a constant shear.

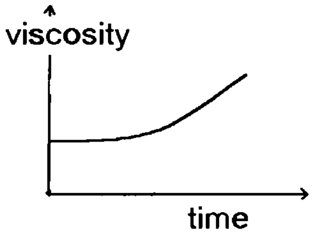


Fig 2.11: Rheopectic flow behavior

2.3 Superplasticizers

Concrete admixtures are materials that are added to the concrete during the mixing process in quantities not larger than five per cent by mass of cement in order to alter its properties in its fresh and hardened state. Superplasticizers are one type of concrete admixtures. The main purpose of using superplasticizers is to produce flowing concrete with very high slump. These materials are eater reducers in the cement concrete systems. The capability of superplasticizers to reduce water requirements 12-25% without affecting the workability leads to production of high-strength concrete and lower permeability. Superplasticizers are linear polymers containing sulfonic acid groups attached to the polymer backbone at regular intervals. Most of the commercial formulations belong to one of three families:

- Sulfonated melamine-formaldehyde condensates (SMF)
- Sulfonated naphthalene-formaldehyde condensates (SNF)
- Polycarboxylate derivatives (PC)

The sulfonic acid groups are responsible for neutralizing the surface charges on the cement particles and causing dispersion, thus releasing the water tied up in the cement particle agglomerations and thereafter reducing the viscosity of the paste and concrete

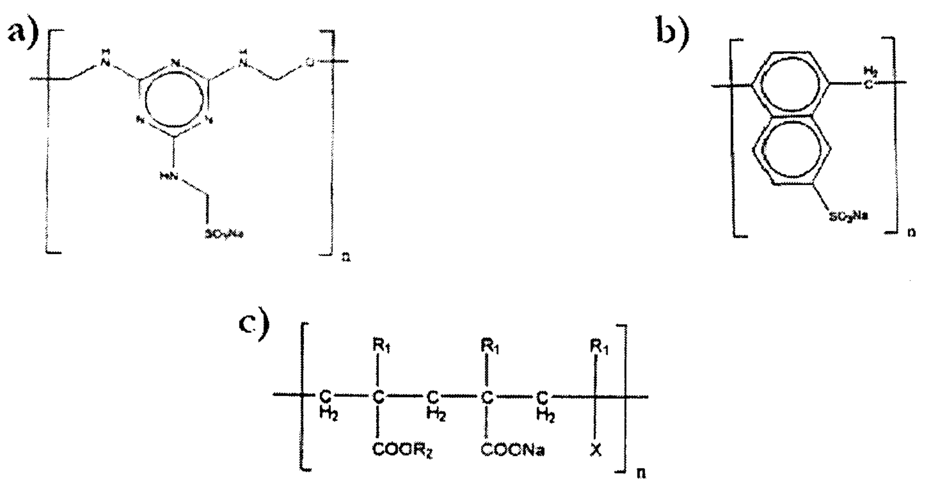


Fig 2.12: Different types of superplasticizers: repetitive molecular unit of (a) Na-PMS; (b) Na-PNS and (c) polycarboxylate. X represents a polar (e.g. CN) or ionic (e.g. SO_3-) group, R_1 represents H or CH_3 and R_2 represents a polyether side chain (e.g. polyethylene oxide) [26]

2.4 Organic Polymers

Poly (Ethylene Glycol)

Polyethylene glycol (PEG) is a condensation polymer of ethylene oxide and water with the general formula $H(OCH_2CH_2)_nOH$, [27] where n is the average number of repeating oxyethylene groups typically from 4 to about 180. The low molecular weight members from n=2 to n=4 are diethylene glycol, triethylene glycol and tetraethylene glycol respectively, which are produced as pure compounds. The low molecular weight compounds up to 700 are colorless, odorless viscous liquids with a freezing point from -10^0C (diethylene gycol), while polymerized compounds with higher molecular weight than 1,000 are wax-like solids with melting point up to 67^0C for n equal to 180.

PEG is one of the most popular water-soluble polymers. It is soluble also in many organic solvents including aromatic hydrocarbons (not aliphatics). They are used to make emulsifying agents and detergents, and as plasticizers, humectants, and water-soluble textile lubricants. PEG is used as a plasticizer to increase lubricity and act as a water retention agent in ceramic mass, adhesives and binders and soldering fluxes with good spreading property. Also because it is non-toxic, odorless, neutral, lubricating, nonvolatile and has nonirritating characteristics, it is used in a variety of pharmaceuticals and in medications as a solvent, dispensing agent, ointment and suppository bases, vehicle, and tablet excipient.

Carboxy Methyl Cellulose

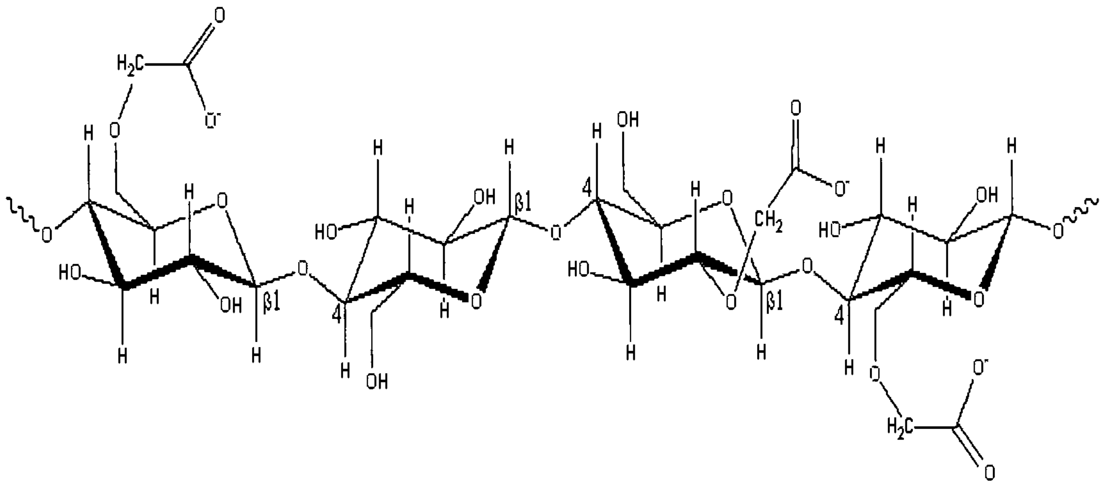


Fig 2.13 Chemical Structure of Carboxy Methyl Cellulose

Carboxy methyl cellulose (CMC) is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid with a general degree of substitution of 0.6 to 0.95 per molecule. It is a semisynthetic water-soluble polymer in which CH_2COOH groups are substituted on the glucose units of the cellulose chain through an ether linkage. It is colorless, odorless, nontoxic, water soluble powder or granules with a pH in the range of 6.5 – 8.0. CMC is stable in pH range 2 – 12. [28]

The applications of CMC range from detergents to soaps to food products where it acts as a water binder, a thickener, a suspending agent, and an emulsion stabilizer. CMC also finds applications in textile manufacturing (sizing), coating paper and paper board to lower porosity, drilling muds, emulsion paints, protective colloid, pharmaceuticals, cosmetics.[29]

The CMC is derived from cellulose, a naturally occurring organic polymer. Cellulose is essentially a polysaccharide [30]. The superplasticizers used in cement concrete systems, mentioned in the previous section, are based on polysaccharides.

2.5 Dynamic Mechanical Analysis (DMA)

DMA is a technique used to study and characterise materials. It is especially useful for observing the viscoelastic nature of polymers. An oscillating force is applied to a sample of material, the resulting displacement of the sample is measured. From this the sample stiffness can be determined and the sample modulus can be calculated. By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. Viscoelastic materials such as polymers typically exist in two distinct states. They exhibit the properties of a glass (high modulus) at low temperatures and those of a rubber (low modulus) at higher temperatures. By scanning the temperature during a DMA experiment the change of state can be observed and the glass transition temperature (Tg) can be determined.

DMA provides valuable data for characterizing the properties of materials, particularly polymers. DMA measures the amplitude and phase of the displacement of a sample in response to an applied oscillating force. The stiffness of the sample is calculated from this data and converted to a modulus to enable sample inter-comparisons. Tan δ, the loss tangent or damping factor, is also calculated. A temperature scan at constant frequency can generate a fingerprint of the material's relaxational processes and its glass transition temperature (Tg). This technique provides valuable data on polymer structure.

The tensile, flexural or the shear moduli are measured by traditional methods, but this test gives the value for a complex modulus. DMA resolves this complex modulus into the storage component and the loss component. The storage component or the elastic modulus is in phase with the strain while the loss modulus or the viscous modulus is 90^0 out of phase with the strain. Generally DMA experiments are conducted to characterize solid polymers.

DMA evaluates a true material property, elastic and loss moduli. These properties are evaluated in a linear region of stress-strain curve as opposed to destructive testing such as compressive and three point bending tests which give the breaking strenght which lies in a nonlinear region. The characterization of material with DMA is on a molecular level as compared to other methods that give a macrosopic properites. DMA is the only techniques that evaluated the material response under oscillating frequency and also gives the amount of energy dissipated in form of viscous modulus. The following table gives the key viscoelastic terms that can be derived from a DMA experiment.

In-phase or Storage (real) properties	**Out-of-Phase or Loss (imaginary) properties**
Youngs' (Pa) $E' = \lvert\sigma/\varepsilon\rvert \cos\delta$	$E'' = \lvert\sigma/\varepsilon\rvert \sin\delta$
Shear (Pa) $G' = \lvert\tau/\gamma\rvert \cos\delta$	$G'' = \lvert\tau/\gamma\rvert \sin\delta$
Compliance $D' = \lvert\varepsilon/\sigma\rvert \cos\delta$	$D'' = \lvert\varepsilon/\sigma\rvert \sin\delta$
(m^2N^{-1}) $D' = E' / (E'^2+E''^2)$	$D'' = E'' / (E'^2+E''^2)$
Viscosity (PaS) $\eta' = G''/\omega$	$\eta'' = G'/\omega$

Table 2.1: Key Viscoealstic Terms

Where,
$\omega = 2\pi$(applied frequency)
σ = Applied stress, in tension compression or bending mode
ε = Strain caused due to applied stress
τ = Shear Stress
γ = Shear Strain
δ = Phase lag between applied stress and corresponding strain

The following table displays the various methods used in a DMA experiment to obtain the required information about the material.

Temperature mode	**Frequency method**	**Typical use & comments**
None	Single or sweep	Modulus and tan δ at RT.
Constant isotherm	Single or sweep	Modulus and tan δ at T
Constant isotherm	Single	Strain sweep at T
Rapid ramp, isotherm	Sweep	cure studies, crystallization kinetics
Thermal scan	Single or multiple	Typical polymer fingerprint, Tg
Stepped Isotherms	Sweep (full range)	Full data set, better T accuracy

Table 2.2: Experimental Methods used in DMA

2.6 Rheology

Rheology can be defined as a study of flow and deformation of matter. In practice, the word "rheology" normally refers to the flow and deformation of "non-classical" materials such as rubber, molten plastics, polymer solutions, slurries and pastes, electro-rheological fluids, blood, muscle, composites, soils, and paints. These materials can exhibit varied and striking rheological properties that classical fluid mechanics and elasticity cannot describe.

The rheological study is carried out for various materials like colloids, emulsions, suspensions, polymer melts and semi-solid materials to understand and quantify their behavior. These materials generally show a viscoelastic behavior that cannot be described by theories used for classical materials.

The system that we dealt with in this project is a semisolid system. The clay particles are dispersed in an aqueous system before the geopolymerization reaction is started. Typically the parameters evaluated for these by the rheological study are the flow behavior (to determine yield stress, shear thinning and/or thixotropic flow behavior), strain sweep (to determine linear viscoelastic range and critical strain) and creep/recovery (to determine relaxation times, zero shear viscosity and viscoelastic properties).

The rheological study is a very critical part of this project since we will be evaluating and comparing the effects of organic polymers on the system. Since one of the aims of this project is to modify the workability of the uncured system, rheological study is very crucial.

Chapter 3

Experimental Work

4.1 Geopolymer System

4.1.1 Raw Materials

The geopolymer system used in this work was synthesized using metakaolin (heat-treated kaolinite or clay obtained from ECC International), sodium hydroxide solution and sodium silicate solution.

The kaolin was heated at 750^{0}C for 12 hours to activate it. The dehydroxylated kaolinite is called as metakaolin (MK). The dehydroxilation process makes the kaolin reactive by changing the geometry of aluminum from octahedral to tetrahedral with respect to oxygen. The chemical composition of kaolin is presented in table 4.1.

Componenets, % mean	Kaolin	Sodium Silicate
SiO_2	49.0	26.5
Al_2O_3	36.0	-
Fe_2O_3	0.75	-
TiO_2	0.02	-
CaO	0.06	-
MgO	0.30	-
K_2O	1.85	-
Na_2O	0.10	10.6
P_2O_5	-	-
H_2O	-	62.9
Loss on ignition	12.0	

Table 3.1: Chemical composition of starting materials

The activator solution is a mixture of aqueous sodium silicate solution and aqueous sodium hydroxide solution. Sodium silicate and sodium hydroxide solutions are mixed together with the ratio of 2:1 by weight, respectively. A 15 molal sodium hydroxide solution is prepared by dissolving sodium hydroxide pellets, obatained from Acros Organics, into distilled water. Commercially available sodium silicates solution supplied by PQ Corporation was used. Its composition is also given in Table 3.1

MK is added gradually to the previously prepared activator solution (mixture of aqueous sodium silicate and aqueous sodium hydroxide). After ensuring complete mixing of the ingredients, the uncured slurry is transferred into the molds to prepare either plaques or cubes. The weight percentages of all the ingredients are given in the following table 3.2.

Table 3.2 gives the composition of the base system that was used in this study. To this system polymer was added in varying proportions.

Reactant, % by weight	Pure Geopolymer system
15 molal aqueous Sodium Hydroxide solution	20
Aqueous Sodium Silicate solution	40
Metakaolin	40

Table 3.2: Pure geopolymer system

A set of organic polymers was selected based on criteria discussed in the next chapter. The list of organic polymers studied included poly (vinyl alcohol), poly (ethylene glycol), poly (acrylic acid), poly (vinyl butyral), poly (styrene-co-maleic anhydride), dextran, gelatin and carboxy methyl cellulose.

3.2 Sample Preparation

Before sample preparation, it is determined if the polymer dissolves in the activator solution or else it is dissolved in distilled water and then added into the geopolymer system. It is preferred that the polymer dissolves in activator so that the total water content in the system remains constant.

Kaolinite was first converted into metakaolin (MK) by the process of dehydroxylation described in the section 3.1. A 15 molal aqueous solution of sodium hydroxide (NaOH) was prepared. Aqueous NaOH was then mixed with aqueous sodium silicate solution with the ratio by weight of 1:2, respectively. Organic polymer was then dissolved either in activator or distilled water. PEG was dissolved in the activator solution while CMC was dissolved in water. These raw materials were then sequentially mixed. This sequence is critical as mixing sequence affects the final properties of the system []. Aqueous sodium hydroxide solution (pellets obtained from ACROS Organics) and aqueous sodium silicate solution (obtained from PQ Corporation) were mixed to form activator solution. The polymer was then dissolved in the activator solution, if soluble. MK is then gradually added to the activator with constant stirring. After complete addition of MK, homogenous slurry was obtained. To this slurry an aqueous organic polymer solution was added, if the polymer dissolved in distilled water. The reactants were mixed to get homogenous slurry. This uncured slurry was used for rheological analysis.

Molds were designed and manufactured to get the consistent samples of dimensions 55mm*8mm*1mm for dynamic mechanical analysis runs. Various designs were tried and modified to achieve the precise dimension control. Also, different materials were used including copper, polyethylene and poly (methyl methacrylate). The polyethylene and poly (methyl methacrylate) molds yielded the better samples as compared to copper. It was evident that the surface finish of the mold material played a dominant role on the surface finish of the samples and accordingly samples prepared using poly (methyl methacrylate) molds had better surface finish than any other. A mold release agent was used to ensure a non-sticky removal of the samples from the mold. The mold release agent used was poly (vinyl alcohol) dissolved in water. This type of mold release agent is used in the fiber reinforced plastics industry.

For the sample preparation mold release agent was first applied to the all the contact surfaces of the molds. After complete drying of the mold release agent, a layer of cheesecloth was spread onto one half of the mold. Gradually the uncured slurry was poured on the spread cheesecloth. Another layer of cheesecloth was put on top of the slurry. The molds were closed. The two halves of the mold were pressed together to squeeze out the excess slurry. The clearance between the two halves of mold was about 1mm. The molds were clamped and transferred into the preheated oven (Quincy Lab Model 20 GC) at 65^0C. Complete curing of the sample was ensured by checking the water / moisture content in the mold. This could be easily checked since the molds were transparent and there was a distinct color difference in the sample with and without moisture. The sample curing time varied with respect to the polymer content and excess water content in the system. Depending on the variables the curing time varied from four hours to 72 hours.

Samples were also prepared for compressive strength measurements and for a three point bending test. For compression testing, the uncured slurry was poured into a 50mm polyethylene cube till it was completely filled and was then covered with parafilm to reduce the water evaporation through the exposed surface. The samples were then cured at 65^0C. After curing the thin walled polyethylene cubes were torn apart to get the samples out of the molds. MTS Systems Corporation tensile/compression testing machine was used for the compression tests.

Another mold was designed and manufactured for a three point bending test. This test was conducted to monitor the change in the bending strength of the system. The samples of dimensions 120mm*10mm*10mm were prepared. An assembly was designed that supported the beam at two points and the beam was loaded at the midpoint. The breaking load was noted and the modulus was calculated.

The above mentioned procedure was followed to prepare samples for rheology study and dynamic mechanical analysis with each of the selected organic polymer with varying quantities. Some of the compositions were tried for compression and three point bending tests. While preparing the samples preliminary observations, qualitative in nature, were noted. Based on these observations the final set of organic polymers was selected for further study. Two polymers, namely, PEG and CMC were selected for further study.

The preliminary observations of the samples prepared using the organic polymers will be discussed in the next chapter.

3.3 Characterization

3.3.1 Thermogravimetric Analysis

Thermogravimetric analysis was performed using TA Instruments TGA 2050 instrument. The thermal behavior of the samples was observed over the temperature range from room temperature to 900^0C with the heating rate of 20^0C/min. The sample used was in pellet form with the amount in the range of 10mg to 15mg. The weight loss peaks and their corresponding temperature were noted. The runs were conducted under air environment.

3.3.2 Dynamic Mechanical Analysis

The cured geopolymer-organic polymer composite samples were characterized using Seiko Instruments' DMS 110 dynamic mechanical analysis in bending mode. The cheesecloth-reinforced composites in the plaque form with the approximate dimensions of 55mm by 8mm by 1mm were used as samples for the characterization. These samples were subjected to the oscillating frequencies of 0.05Hz, 0.5Hz, 5Hz and 50Hz frequencies over a temperature range of 25^0C to 200^0C. Change in the elastic modulus and viscous modulus of the samples with respect to temperature was studied.

3.3.3 Rheology Characterization

The rheology characterization of the uncured resins was performed using TA Instruments' AR 2000 rheometer in cone and plate configuration. The cone and plate were made of steel as the composite slurry did not bond with steel. The diameter of the cone and the plate was 25mm with truncation angle of 4 degrees. The samples used for this characterization were homogenous uncured geopolymer composite slurries. These slurries were characterized in three steps. In the first step the sample was subjected to a constant shear rate of 1.000 s^{-1} for the duration of 600 seconds. This peak hold step quantified the behavior, viscosity in this case, of the sample with respect to time at a constant shear rate. The second step was a frequency sweep step to evaluate the elastic and viscous modulus of the sample. The frequencies of 0.1Hz to 10Hz with increments of 0.1Hz were employed with the controlled variable being % strain of 5.000. The final step of the characterization was the continuous ramp step. In this step the sample was subjected to a continuous increase in the shear rate from 0.1 s^{-1} to 10 s^{-1} over a period of 600 seconds. This evaluated the sample behavior with respect to increasing shear rate. Between each of the three steps the sample was allowed to relax for about five minutes. The film of the partially cured sample along the edges was cleaned.

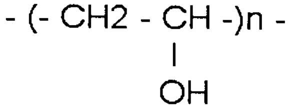
Chapter 4

Results and Discussion

4.1 Selection of Organic Polymers

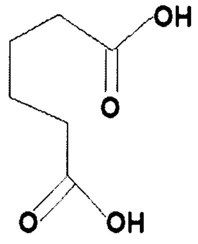
The organic polymers were selected on the basis that the polymer should be water soluble as the geopolymer is a water based system. The hydrophilic nature of polymers will ensure that there is no phase separation within the system. The 15 molal sodium hydroxide solution raised the pH value of the reactants required for the formation of geopolymers. Hence the stability and reactivity of organic polymers in the extreme basic conditions should be considered. These criteria were satisfied by selecting the polymers containing basic O^- or an ether linkage, which under caustic conditions will react with the uncured geopolymer resin. Following is the list of selected organic polymers with their molecular structure:

Poly (vinyl alcohol)
[Enzyme Grade]

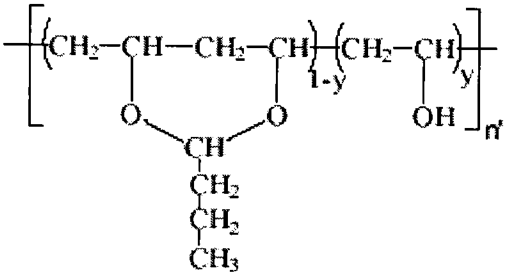


$$-(-\mathrm{CH2}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-)n-$$

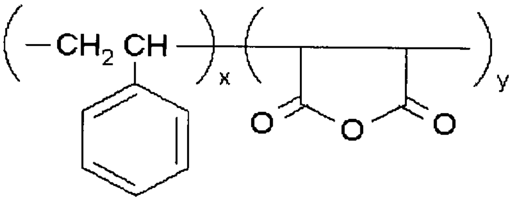
Adipic Acid



Poly (vinyl butyral)



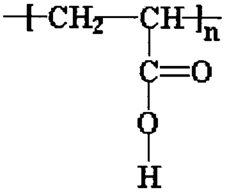
Poly (styrene-co-maleic anhydride)
[Ratio of styrene : maleic anhydride 75 : 25]



Poly (ethylene glycol)
[Molecular weights of 3350 and 35,000]

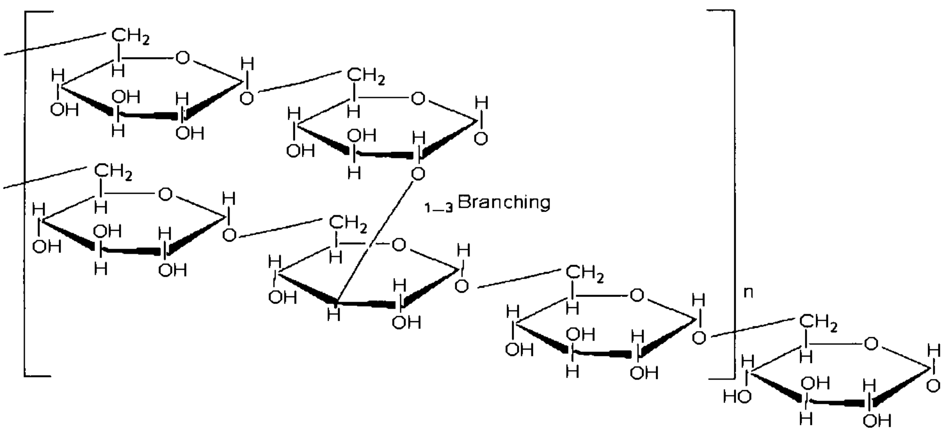
$-(-CH_2 - CH_2 -O-)_n -$

Poly (acrylic acid)

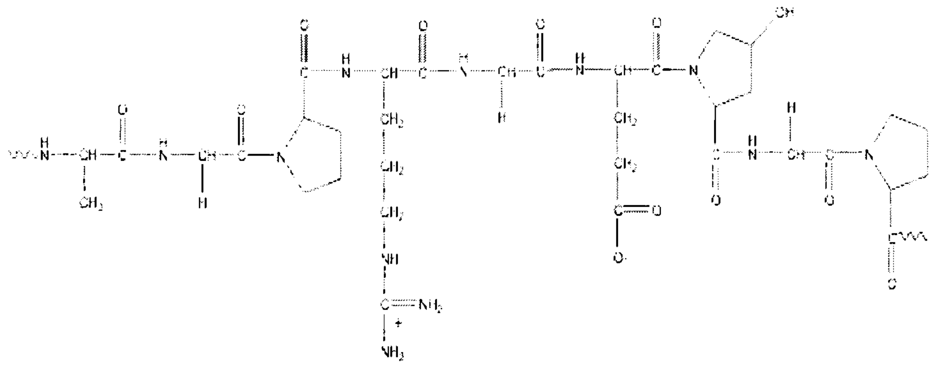


$$-[\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{C=O}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H}}}{\mathrm{CH}}]_n$$

Dextran



Gelatin



Carboxyl Methyl Cellulose

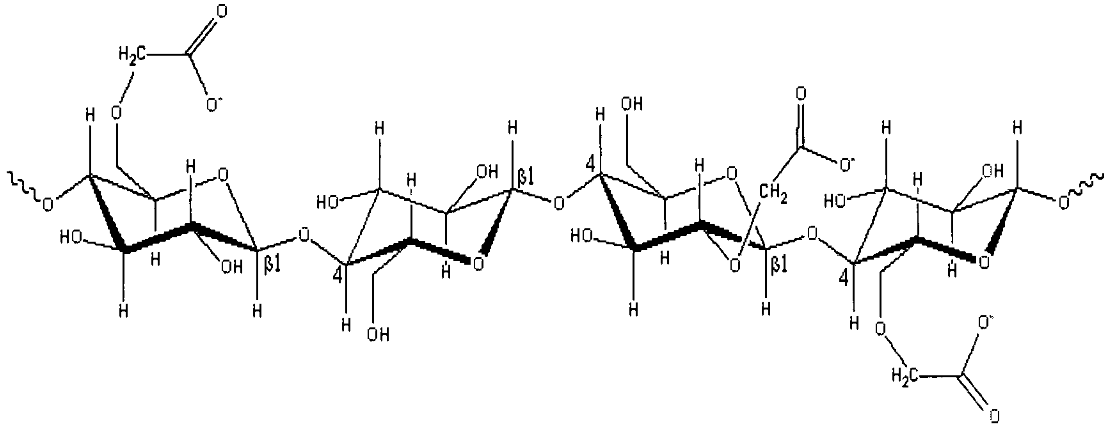


Fig 4.1 List of Organic Polymers and their repetitive structure

Geopolymer samples were prepared using the above mentioned organic polymers. The observations noted during and after the sample preparation are discussed in the following section.

4.2 Preliminary Observations for different Organic Polymers

The initial observations recorded after addition of different organic polymers were vital as they enhanced the existing knowledge about the geopolymer system and its behavior after addition of organic polymers. Based on these observations the two polymers, PEG and CMC were selected for further study.

The geopolymer samples with poly vinyl alcohol prolonged curing time proportional to the amount of polymer present in the sample. The geopolymer system could accept a maximum of 12% by weight of the polymer and it could be dissolved in the activator solution. The curing time was increased roughly 12 times, from six hours for a pure geopolymer sample to about 72 hours for a sample containing 12% by weight of poly vinyl alcohol. The completely cured sample solidifies throughout the sample; keeping this as a criterion the sample curing time was noted. There was no significant difference observed in the uncured slurry of the composite system. The samples obtained were harder than the pure geopolymer samples. The surface exposed to air formed a layer of hard material.

Combination of poly (vinyl alcohol) [PVOH] and adipic acid was tried with the aim of adding another cross-linked matrix along with the existing geopolymer matrix to provide extra rigidity. PVOH and adipic acid react to form a chemical bond and this will induce another set of cross-linked network in the geopolymer system. There was no further study conducted to understand the chemical interaction between the geopolymers and the organic polymers. This combination was successful in terms of making the sample more rigid as compared to the unmodified geopolymer system.

Low molecular weight (M_n~3400) poly (ethylene glycol) [PEG] enhanced workability of the uncured resin. The elasticity of the uncured resin was enhanced. The resin could be spread uniformly onto various substrates and had limited flow under gravity, unlike the unmodified geopolymer resin that had a plastic flow under gravity. There was no appreciable effect on the final properties of the geopolymer system as determined by the compressive strength. The higher molecular weight polymer with Mn~35,000 could not used as it could not be dissolved in either activator solution or the water.

The samples containing poly (acrylic acid) [PAA] and carboxy methyl cellulose had similar effect on the geopolymer system. Both the polymers were dissolved in water as they were not soluble in activator solution. When added to the premixed geopolymer slurry, they changed the viscosity of the system. These polymers when added in their solution form added elasticity to the uncured slurry. CMC is commercially used as a viscosity modifier in various systems including food products. CMC had a similar effect on the geopolymer system.

In addition to the viscosity modification, these polymers prolonged the curing time. The curing was increased 18 fold from 4 hours to 36 hours at the maximum loading of polymer solution of 30% by weight. There was a change in the characteristics of unmodified geopolymer system after addition of the PAA or CMC. These modified systems did not bond to cement concrete systems or steel, unlike the pure geopolymer systems. Geopolymers are known to form a very strong bond with steel. As proved by the research that geopolymer – steel adhesive bond is stronger than the geopolymer – geopolymer cohesive bond.

Another interesting behavior was noted by addition of PAA or CMC to the pure geopolymer systems. These uncured slurries when cured into plaques of thickness of about one millimeter and with cheesecloth reinforcements, they exhibited flexibility without cracking. To the best of our knowledge this kind of behavior was never encountered before with the geopolymer systems. The pure geopolymer system, normally brittle, cracks easily under tension. This phenomenon should open up a wide array of applications for these materials.

Although these polymers satisfy the aim of addition of organic polymers to geopolymers, it comes at a cost of compressive strength and the amount of cross-linking within the geopolymer system. As these polymers prolong the curing time, they act as retarders to the geopolymerization process. Excessive amounts of aqueous polymer solutions in the geopolymer system affect the overall geopolymerization reaction. Such systems did not cure to their fullest extent as could be inferred by drastic reduction in the compressive strengths and easy removal of the clay from its mass.

Another polymer from the selected polymers, dextran, had no effect on the properties of the geopolymer system in its cured as well as uncured form. All the other polymers, namely, poly (styrene-co-maleic anhydride), poly (vinyl butyral) and gelatin had adverse effects on the geopolymer system. Addition of these polymers made the geopolymer more fragile after curing.

A different set of experiments was carried out in terms of addition of amorphous silica to the geopolymer system. Silica has a tendency to hold and retain water and it increases the Si : Al ratio in the geopolymer system. The behavior of these samples is very similar to that of pure geopolymer system. When cured in form of a plaque, these samples remain flexible for a limited period of time.

The above mentioned observations demonstrate that organic polymers affect the properties of geopolymer system. These changes are in the form of viscosity changes, curing time, workability and rheology of the system, consistent with the aim of this study. Although a few polymer geopolymer systems exhibited some interesting properties only two polymers were selected for the in-depth study. The variable space had to be restricted to have a detailed understanding of the geopolymer-organic polymer interaction.

Based on the above observations two organic polymers were selected for further study. The two polymers, namely, carboxy methyl cellulose (CMC) with the degree of substitution of about 30% and poly (ethylene glycol) (PEG) with the molecular weight of about 3350, were used to create one and two polymer-geopolymer systems. These systems were studied using dynamic mechanical analysis for cured systems and rheometer for uncured systems. Another aim for selection of these polymers is that they are very cost effective, just as geopolymeric materials.

4.3 Compression Test and Three Point Bending Test

A compression test was performed with samples with different polymers and varying degree of loadings. These test values did not reveal any significant difference between the pure geopolymer and the composite material with low (0.5% and 1% by weight) loadings. With higher loadings of polymer (2% - 12% by weight, depending on the polymer used) there was a slight decrease (~250psi) in the compressive strength. Also the variation in the values was very high (~40%). This gave little credibility to the results. The inconsistency was observed with multiple samples.

Three point bending test was attempted with an aim to quantify the change in bending modulus of the composite. The samples were difficult to prepare, especially their intact removal from the molds because of their high aspect ratio and the brittle nature of these materials. These tests were unable to give any results.

The organic polymers seem to affect the rheological properties as well as impart some flexibility to the cured samples. Compression test did not seem to be the appropriate characterization technique to quantify the effect of organic polymers on the geopolymer system. Techniques like rheometry are ideally suitable for rheology characterization. For the characterization of samples with flexibility, for this DMA is the most suitable technique since it evaluates the true material property on the molecular level. While the information obtained from compression test or three point bending test will be on macroscopic level and in the nonlinear region of stress strain curve.

Preliminary observations confirm that CMC has some effect on the properties of the geopolymer system. Apart from the changes in moduli of the system, completely cured geopolymer system with CMC show incredible flexibility in sheet form. The samples were cured at 65^0C for 36 hours. All samples discussed henceforth were cured at 65^0C for 36 hours. The following picture exhibits the flexible nature of these materials.

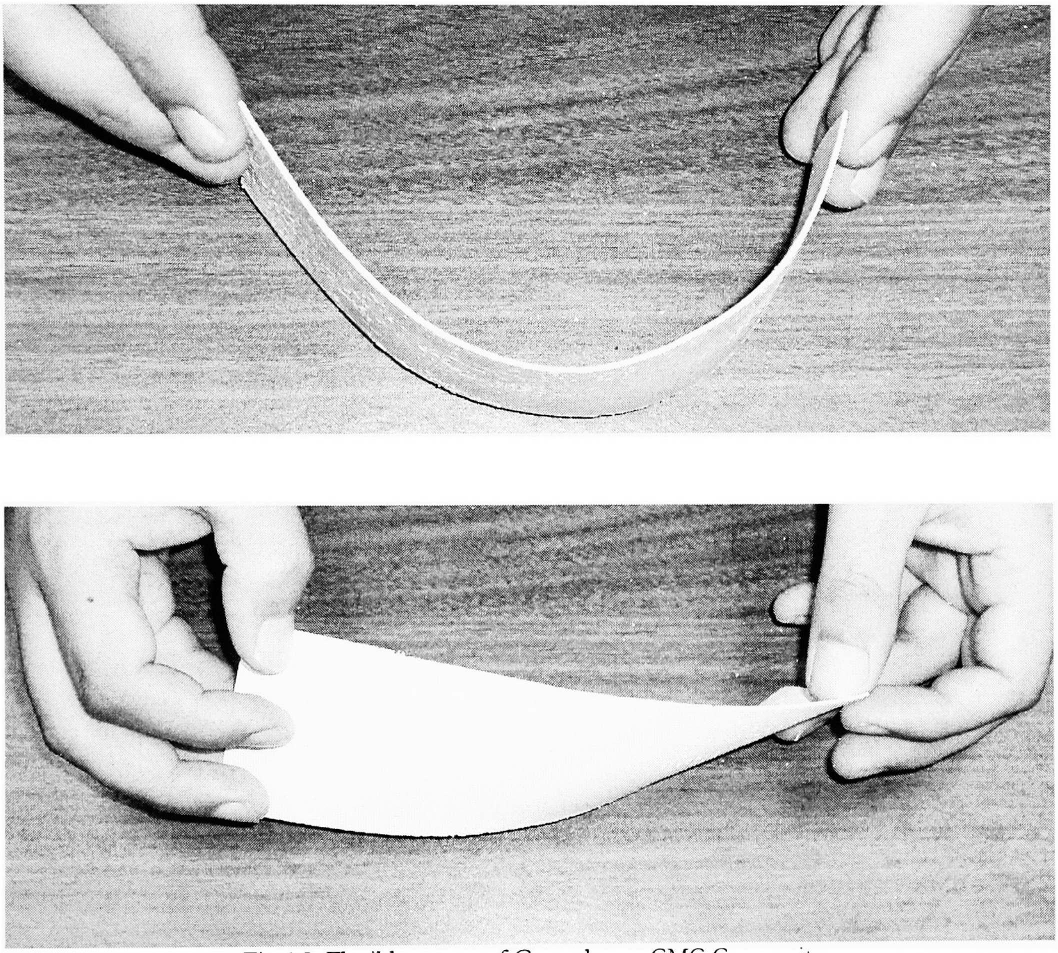


Fig 4.2: Flexible nature of Geopolymer-CMC Composite

The completely cured plaques prepared using the geopolymer-polymer composite showed remarkable flexibility without cracking for at least 18 months. Pure geopolymer plaques do not exhibit any flexibility; rather they are brittle in nature.

Although additional research should be done to understand the cause of this flexibility in a brittle matrix, preliminary observations point towards the reinforcements, the excess water content and the organic polymer geopolymer interaction as the probable cause. The reinforcements used cheesecloth in this case, are extremely flexible and have very low inherent strength. The cheesecloth reinforcements survive the extreme basic conditions of the mixture and hold together the composite matrix. The dimensional changes that take place during the geopolymerization reaction are also compensated by the reinforcements resulting in a uniform stress free material.

Recalling the preliminary experiments the geopolymer sample with amorphous silica, it has a very strong tendency to absorb moisture and retain it. When these samples were prepared into thin plaques, in the same way as any other geopolymer-organic polymer system, they exhibited flexibility. These samples had a feel and flexibility like artificial leather. But these plaques lost their flexibility over a period of about seven to ten days. The probable cause for this being the loss of excess moisture retained by the amorphous silica. This leads us to conclude that excess water content might be essential for the flexibility of these materials. One of the organic polymers added to the geopolymer system was CMC. It has a strong tendency to retain water. During geopolymerization this excess water is trapped in matrix and help in providing flexibility.

Another factor that might aid in achieving and retaining the flexibility of these samples is geopolymer organic polymer interaction. Although the sample with amorphous silica exhibited flexibility, it was for a short time period as compared to the samples with organic polymers that have retained flexibility for more than 18 months. This leads us to believe that there is an interaction between the organic and inorganic polymers that is affecting the characteristics like flexibility of the composites.

As mentioned in chapter 2, water content is very critical in the geopolymerization process. Lower or higher water content results in the samples with poor properties. Since we need higher than normal water content for the samples to be flexible, we reduce the strength of the samples. The excess water content and the presence of organic polymer reduce the amount of geopolymerization. This is evident from the thin layer of clay found on completely cured samples and also the flakiness observed when the sample cubes are cracked. These characteristics are not observed in a pure geopolymer sample.

4.4 Themogravimetric Analysis

The following plots exhibit the behavior of the composite materials, including the one with CMC and one with PEG, over a temperature range from room temperature to 900^0C. The weight loss at the temperature between 130^0C and 140^0C can be noted and can be attributed to the initial loss of excess water content. The second weight loss peak can be identified as a secondary water loss peak. The water trapped in the geopolymer structure would be released. This can be confirmed by the amount of weight loss. This peak is higher incase of PEG, suggesting that addition of PEG enhances the water retention property of overall system. The third peak can be attributed to decomposition of the cheesecloth at around 420^0C. Cheesecloth decomposes at around 350^0C, as confirmed by TGA scan, would require higher temperature to decompose since it is protected by geopolymer matrix. Also, this peak can be associated to the cheesecloth by the amount of weight loss. In case of CMC composite the weight loss peak around 600^{0}C can be attributed to the polymer decomposition; this can be confirmed by comparison of the TGA scan of pure geopolymer against the composite. The polymer decomposition peak incase of PEG composite is at a lower temperature, probably overlapping the secondary water loss peak around 400^{0}C. By comparison of pure geopolymer and composite behavior, it can be observed that the initial water loss peak had shifted to a higher temperature for the composite. This implies that water is better held in by composite as compared to pure geopolymer. Detailed experimentation with TGA may be required to correlate the observed trends with the thermal behavior of the composites.

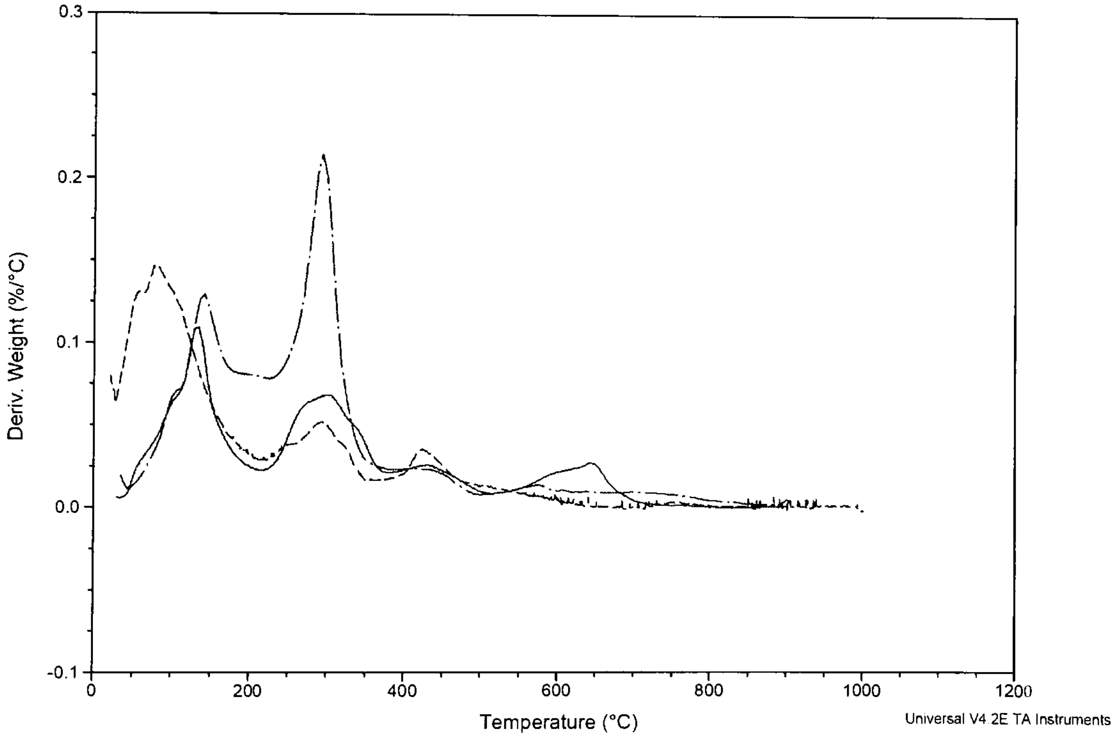


Fig 4.3 TGA scans of pure geopolymer system with cheesecloth (----); geopolymer-CMC composite with cheesecloth (——); geopolymer-PEG composite with cheesecloth (—— –)

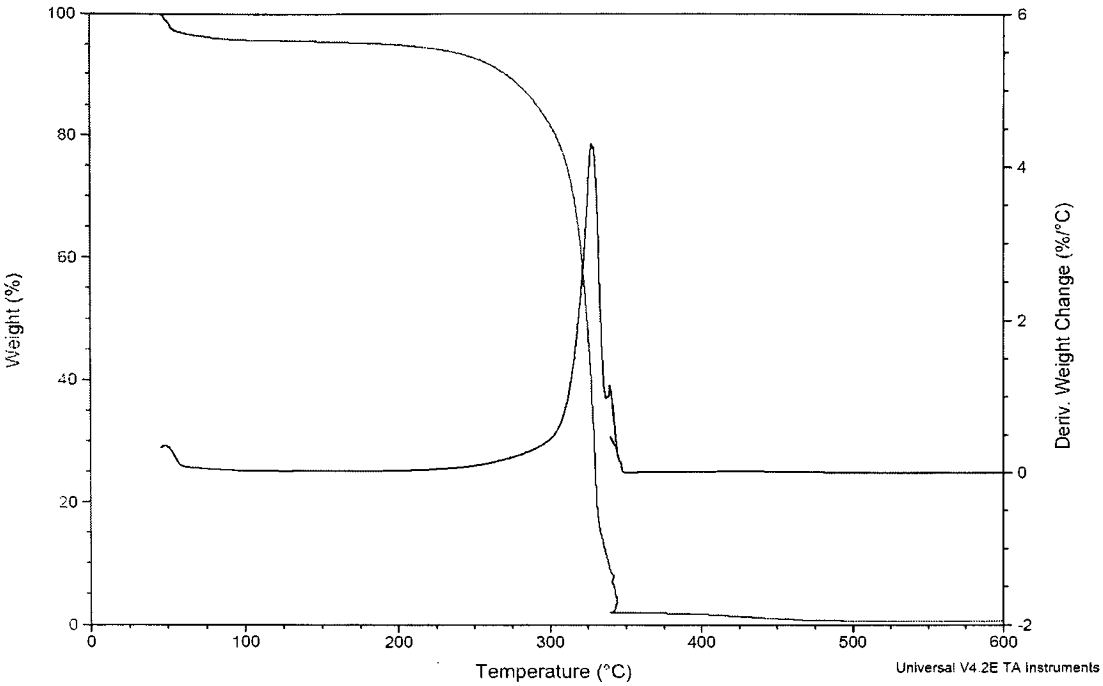


Fig 4.4 TGA scan of only cheesecloth

4.5 Dynamic Mechanical Analysis

The following section summarizes the effect of CMC on the elastic and viscous modulus of the composite. Fig 4.5 and Fig 4.6 show the variation of the elastic modulus and the viscous modulus with respect to the temperature at 5 Hz and 0.05 Hz frequency. Three levels of CMC loadings were tried, 0.45%, 0.90% and 1.35% by weight. Since CMC had to be dissolved in water there was a 22.5% by weight of excess water present in the system. all the samples were cured for the same time, 36 hours at 65^0C.

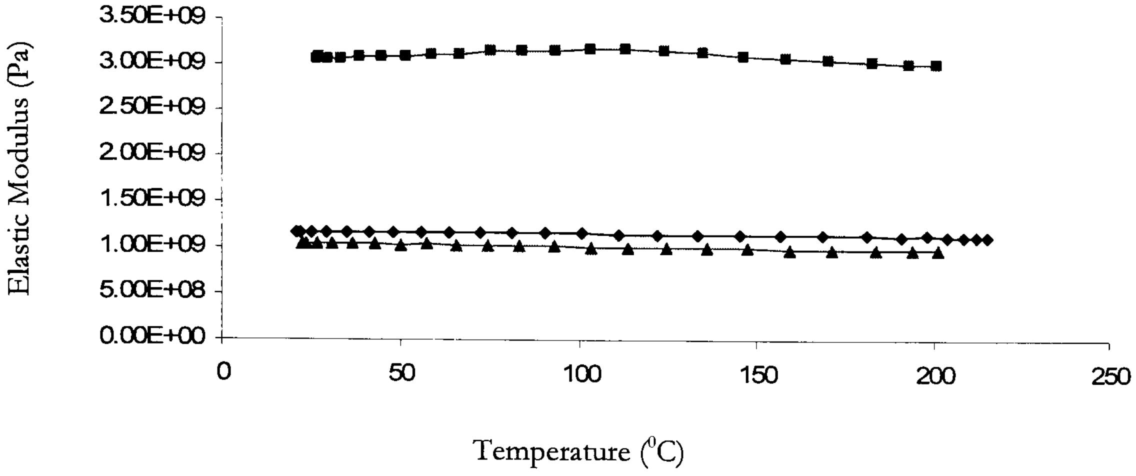


Fig 4.5a: Effect of amount of CMC on the elastic modulus of the system with respect to temperature at 5Hz frequency; -◆- CMC 0.45%, excess water 22.5%; -■- CMC 0.90%, excess water 22.5%, -▲- CMC 1.35%, excess water 22.5%

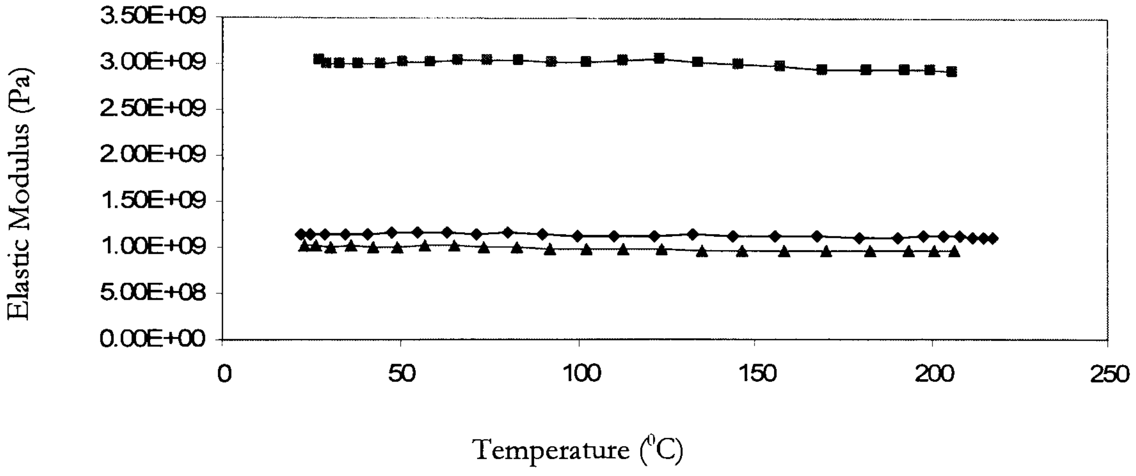


Fig 4.5b: Effect of amount of CMC on the elastic modulus of the system with respect to temperature at 0.05Hz frequency; -◆- CMC 0.45%, excess water 22.5%; -■- CMC 0.90%, excess water 22.5%, -▲- CMC 1.35%, excess water 22.5%

The behavior of the sample in terms of its elastic modulus with respect to temperature at 5 Hz and 0.05 Hz can be observed from the figures 4.3a and 4.3b, respectively. It is evident that an increase in CMC content from 0.45% to 0.90% increases the elastic modulus of the system from about 1150 MPa to about 3050 MPa at room temperature. But a further increase of CMC content decreases the overall elastic modulus of the system to below the value of that with 0.45% CMC. This behavior is consistent irrespective of the frequencies employed. The elastic modulus of the pure geopolymer system is about 3090 MPa. This leads to the conclusion that initial addition of CMC to the geopolymer system adversely affects its elastic modulus. Conversely, further addition of CMC raises the modulus comparable to that of pure geopolymer system. Further addition of polymer decreases it its lowest value in the set of experiments. This decrease in the modulus with an increase in the polymer content can be attributed to the incomplete geopolymerization reaction. This behavior is consistent with other geopolymer-organic polymer systems that were studied. A transition at about 120^{0}C can be noted in the above figures, especially with 0.90% CMC system. This transition can be attributed to the initial water loss from the system. this can be recalled from the TGA scans discussed earlier.

The following figures (4.6a, 4.6b) represent the behavior of the viscous modulus of the geopolymer system with varying quantities of CMC with respect to temperature at 5 Hz and 0.05 Hz frequencies. Although the data contains a large amount of noise, the trend of the system can be observed. The viscous modulus of the system increases with initial increase (0.45% to 0.90%) in the CMC content. But with further increase (0.90% to 1.35%) in the CMC content drops the modulus value comparable to that with 0.45% system.

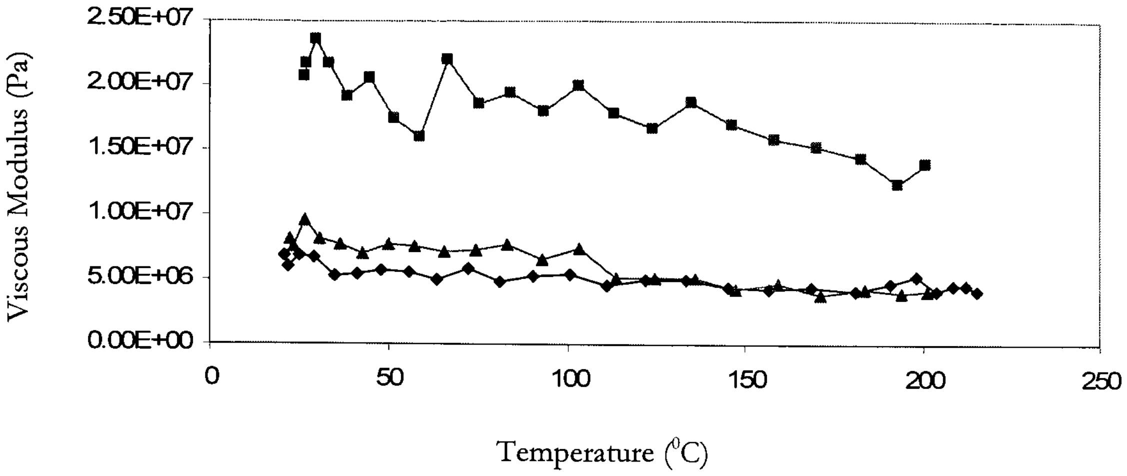


Fig 4.6a: Effect of amount of CMC on the viscous modulus of the system with respect to temperature at 5Hz frequency; -♦- CMC 0.45%, excess water 22.5%; -■- CMC 0.90%, excess water 22.5%, -▲- CMC 1.35%, excess water 22.5%

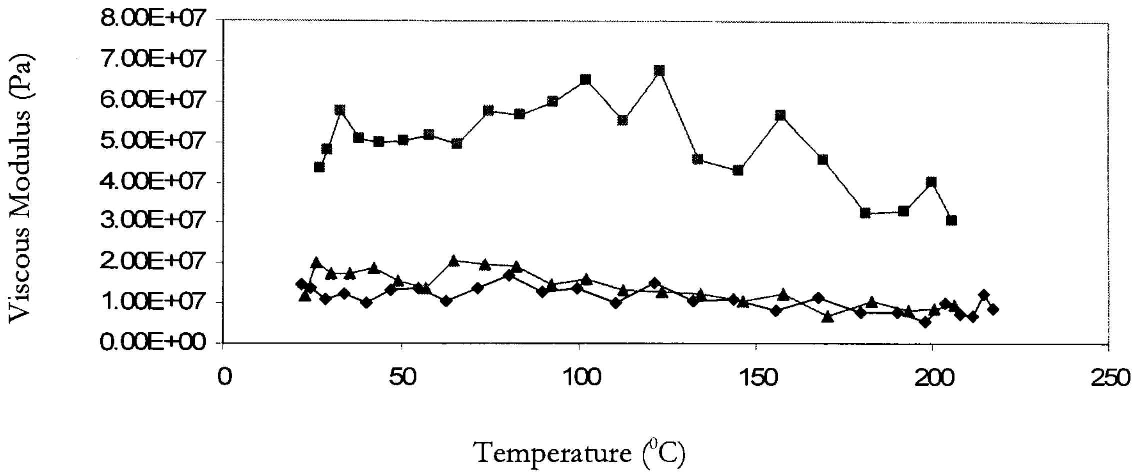


Fig 4.6b: Effect of amount of CMC on the viscous modulus of the system with respect to temperature at 0.05Hz frequency; -♦- CMC 0.45%, excess water 22.5%; -■- CMC 0.90%, excess water 22.5%, -▲- CMC 1.35%, excess water 22.5%

The following section focuses on understanding the effects of PEG on the composite system. The elastic modulus of the sample at 5 Hz frequency initially showed an increase with increase in the PEG content (Fig 4.7). With further increase in the PEG content, the overall elastic modulus drops. The sample containing no PEG shows little variation over the temperature range with its overall elastic modulus in the range of about

1150 MPa. With addition of 3 wt. % of PEG to the system, the elastic modulus increases by about 150 MPa. Also, we observe a transition at about 140^{0}C. With further increase in the PEG content to 6 wt. %, we see a decrease in the overall elastic modulus of the sample. In addition, we notice a sharp transition at 140^{0}C that was not observed in the previous system. This transition can be attributed to the loss of residual water in the system observed in the TGA scans discussed earlier.

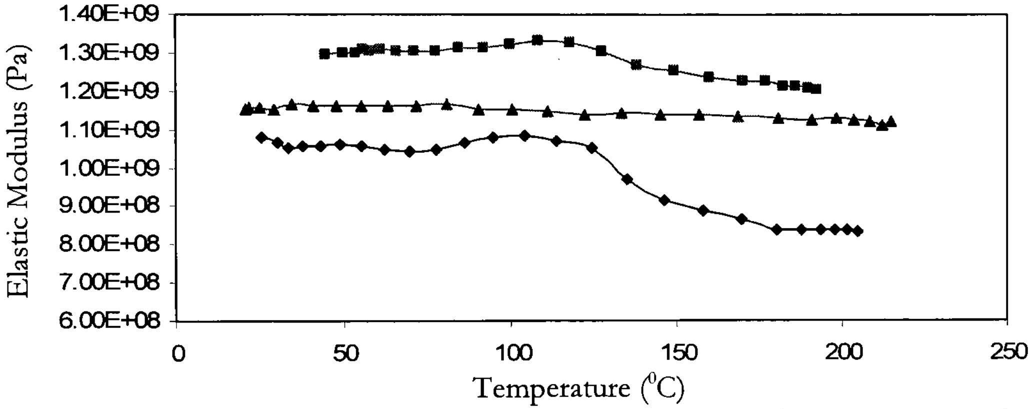


Fig 4.7: Effect of PEG content on elastic modulus of the system at 5 Hz: -▲- : 0.45% CMC, PEG 0%, excess water 22.5%; -■- : 0.45% CMC, PEG 3%, excess water 22.5%; -◆- :0.45% CMC, PEG 6%, excess water 22.5%;

From the above result we can conclude that there is a peak value of the elastic modulus associated with the PEG content between 0% and 6%. When we added 1.5 wt. % of PEG to the system the overall modulus increased from 1150 MPa to 6550 MPa (Fig 4.8).

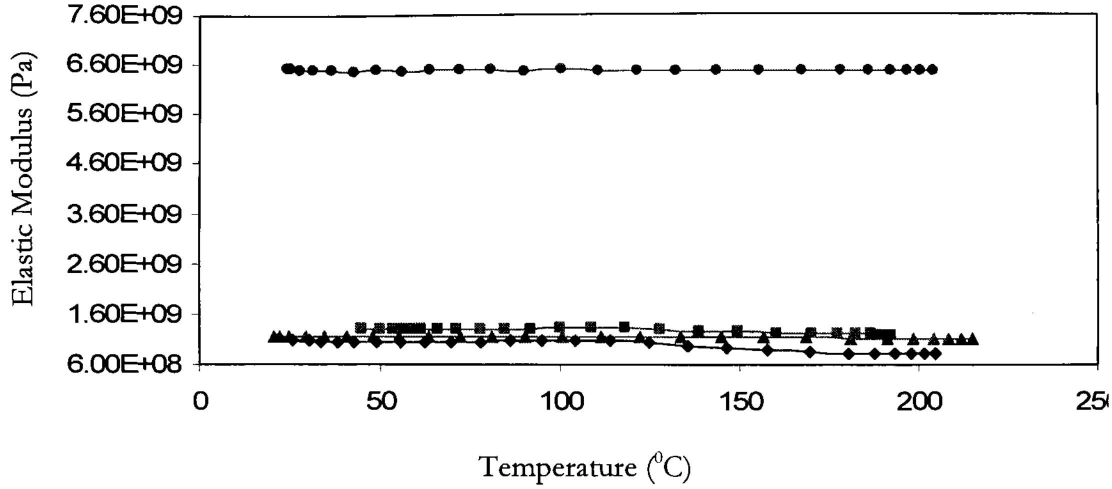


Fig 4.8: Effect of PEG content on elastic modulus of the system at 5 Hz: -▲- : 0.45% CMC, PEG 0%, excess water 22.5%; -●- 0.45% CMC, PEG 1.5%, excess water 22.5%; -■- : 0.45% CMC, PEG 3%, excess water 22.5%; -♦- :0.45% CMC, PEG 6%, excess water 22.5%;

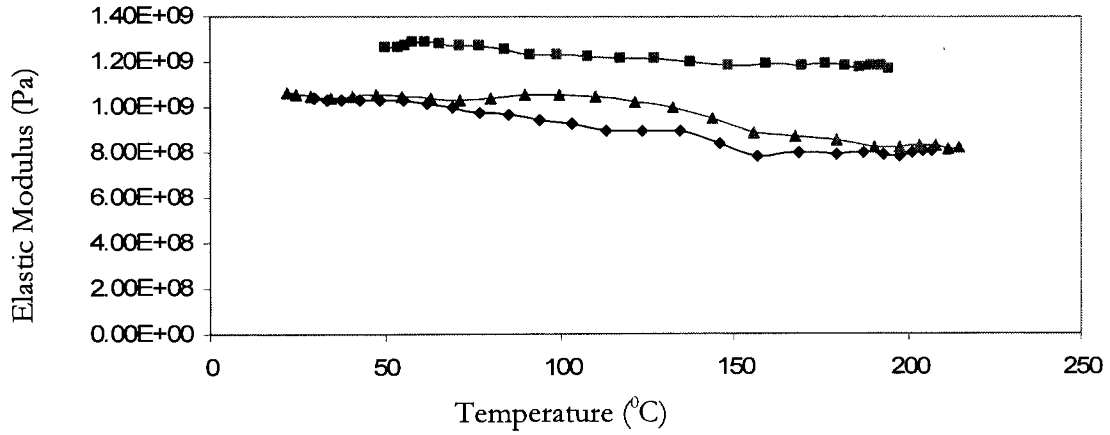


Fig 4.9: Effect of PEG content on elastic modulus of the system at 0.05 Hz: -▲- : 0.45% CMC, PEG 0%, excess water 22.5%; -■- : 0.45% CMC, PEG 3%, excess water 22.5%; -♦- :0.45% CMC, PEG 6%, excess water 22.5%;

We evaluate the same system in terms of elastic modulus, but at a lower frequency of 0.05 Hz and compare it with that at 5 Hz frequency. In Fig 4.9, we observe that the system without any PEG content undergoes a transition at the temperature of about 140^{0}C. This transition was not picked up at a higher frequency of 5 Hz, as given above (refer Fig 4.8). Low frequency measurements are more responsive to macroscopic motions in the sample.

At a higher frequency the sample gets less time to respond to the applied deformation force and only small scale movement can be activated. At a lower frequency, the sample has enough time for a greater portion of its mass to respond to the applied force. For our systems we pick up transitions at lower frequencies for low PEG content and at higher frequencies for high PEG content.

The trends discussed above were not repeated to confirm their reproducibility but these trends were very consistent in the similar systems with minor variations in the contents.

In the second part of DMA studies, we evaluated the systems based on the loss or the viscous modulus of the system. Again, we use the high frequency (5 Hz) and a low frequency (0.05 Hz), as mentioned in the previous section.

Fig 4.10a shows a completely different trend for the effect of PEG on the viscous modulus of the system as compared to that of the elastic modulus of the system. The loss modulus of the sample at 5Hz increases with an increase in the PEG content. We see a major transition around 140^0C for the sample with highest content of PEG. This can be attributed to the loss of water from the system. No such distinct transitions were observed for the other samples. For the low frequency of 0.05 Hz (Fig 4.10b) we have transitions at 80^0C and also at 140^0C. Noise is prominent in this plot indicating that we are approaching the sensitivity limit of the instrument at this low frequency. Unlike the elastic modulus, we did not observe any prominent discrepancy in the trend for the viscous modulus by addition of 1.5 wt. % of PEG.

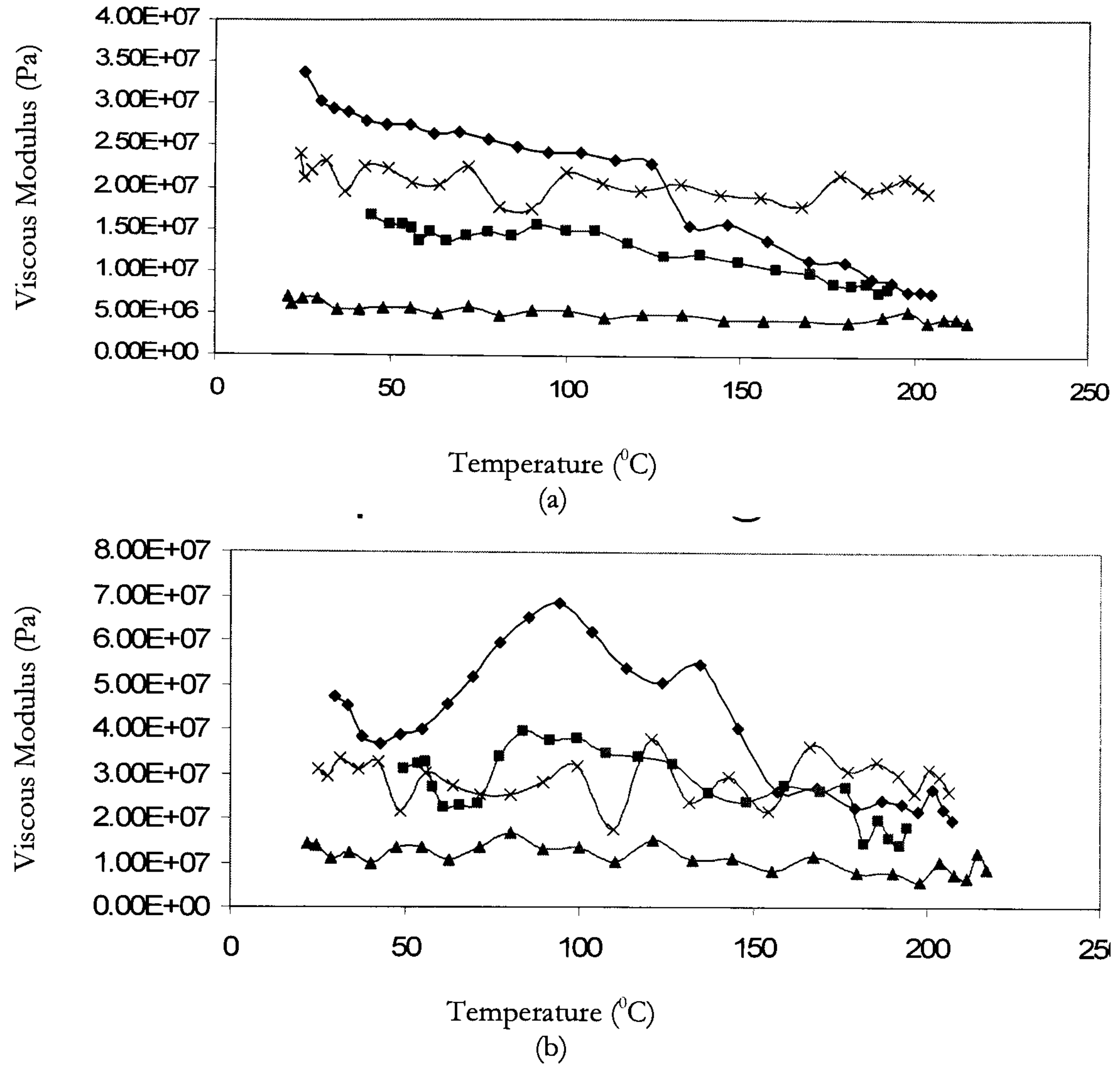


Fig 4.10: Effect of PEG content on viscous modulus of the system at (a) 5Hz and (b) 0.05 Hz: -▲- : 0.45% CMC, PEG 0%, excess water 22.5%; -X- 0.45% CMC, PEG 1.5%, excess water 22.5%; -■- : 0.45% CMC, PEG 3%, excess water 22.5%; -◆- :0.45% CMC, PEG 6%, excess water 22.5%;

Tan δ also known as damping factor increases with increasing polymer content. The damping factor is close to zero with values ranging from a minimum of 0.005 to a maximum of 0.04. PEG has the most dominant effect on tan δ. The tan δ value increases from 0.005 to 0.04 with increase in PEG content of 0% to 6% by weight. With CMC the tan δ value remains largely unchanged. The tan δ value increases from 0.005 to 0.007 with increase in

CMC content from 0.45% to 1.35% by weight. The damping factor for pure geopolymer is around 0.012, suggesting that addition of organic polymers decreases the damping factor of the composite system and it increases only at the higher PEG loadings of 6% by weight. All the tan δ values discussed above were noted at 5Hz frequency and at 24^{0}C.

Table 4.1 gives the data obtained for all the systems at room temperature (24^{0}C) at a frequency of 5Hz. All the systems, except the first one, have a constant amount (0.45%) of CMC. From the values we observe that all the systems with varying quantities of water show similar behavior with respect to PEG content.

System	Elastic Modulus (MPa)	Loss Modulus (MPa)
Pure geopolymer system	3130	30.5
PEG 0%-Excess Water 22.5%	1156	6.3
PEG 1.5%-Excess Water 22.5%	6550	23.9
PEG 3%-Excess Water 22.5%	1730	27
PEG 6%-Excess Water 22.5%	2330	39.3
PEG 0%-Excess Water 7.5%	3320	39.7
PEG 1.5%-Excess Water 7.5%	7040	70.7
PEG 3%-Excess Water 7.5%	822.5	39.6

Table 4.1: DMA data at 24^{0}C and 5Hz frequency

The above table summarizes the trends shown by the organic polymer modified geopolymer system. Two parameters were varied, PEG content and excess water. Increases in PEG have the same effect as that of decreases in the excess water content. The elastic modulus of the system increases over a 100% by addition of 2% CMC, 1.5% PEG and 7.5% excess water, indicating that an increase of water content has an adverse effect on the elastic modulus of the system and PEG increases aids in increasing the elastic modulus of the composite system. A consistent trend can be noted from the above data. The elastic modulus decreases with initial addition of polymer to the geopolymer system and attains the maximum value with 1.5% PEG and then drops below the initial value.

The following figure (4.11) displays the effects of organic polymers on the elastic and the viscous moduli of the geopolymer system. Comparing the trends of change in elastic modulus due to addition of PEG and CMC (fig 4.11(a) and (c)) we can conclude that the optimum amount of polymer that causes an positive change is around 1wt. %. It can be noted that the concentrations of the two polymers added were different, but the optimum concentration of the either of the polymer is in the range of around 1wt. %. System with CMC exhibit consistent trends with elastic modulus and viscous modulus but with PEG the there is a different trend for the two. These trends were not retested for reproducibility. All the values for the elastic and viscous moduli displayed in the trends were recorded at 24^0C and 5Hz frequency.

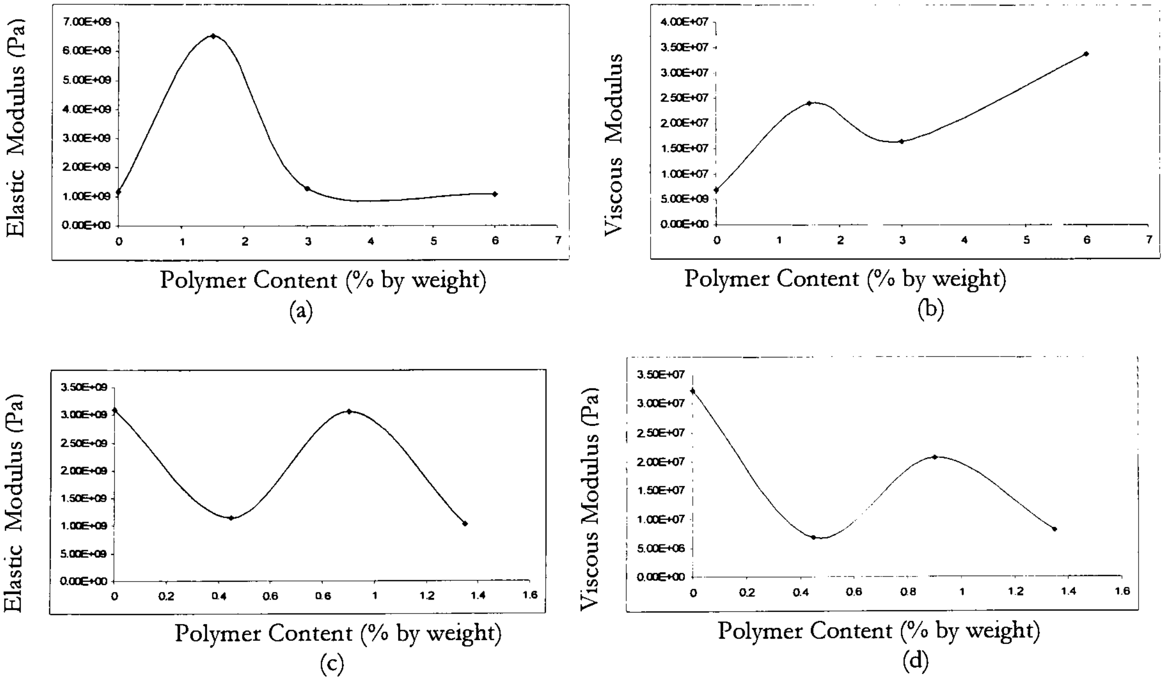


Fig 4.11: Effect of PEG and CMC on elastic and loss modulus of the geopolymer system (a): Effect of PEG concentration on the elastic modulus; (b): Effect of PEG concentration on the viscous modulus; (c): Effect of CMC concentration on the elastic modulus; (d): Effect of CMC concentration on the viscous modulus;

4.6 Rheology

Fig 4.12 evaluates the effect of CMC content on the viscosity of the uncured composite system over the period of 600 seconds. It is clear that increasing the CMC content by 0.45 wt. % increases the viscosity of the system from about 10 Pa.s to about 40 Pa.s. With further 0.45 wt % increases in the system, the viscosity goes up from 40 Pa.s to up to 120 Pa.s. By the end of 600 seconds there is a slight increase in the viscosity. This can be attributed to the curing of the system considering the fact that the geopolymer system is a very fast curing system. Geopolymers completely solidify within a timeframe of about Four hours. There is a consistent rise in the viscosity of the system as the cure progresses. The samples used for rheometer study were used immediately after mixing and homogenizing the reactants.

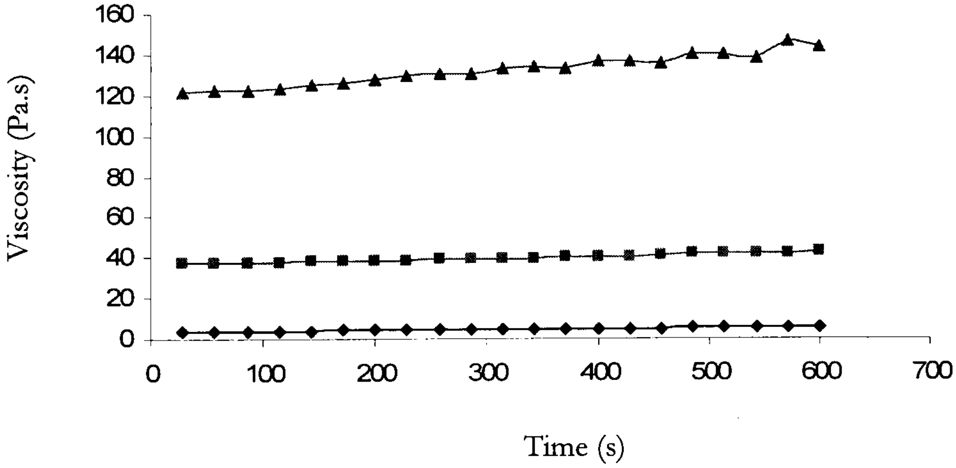


Fig 4.12: Effect of CMC content on the viscosity of the composite system with respect to time; -◆-: 0.45% CMC, PEG 0%, excess water 22.5%; -■-: 0.90% CMC, PEG 0%, excess water 22.5%; -▲-: 1.35% CMC, PEG 0%, excess water 22.5%;

Fig 4.13 evaluates the effect of CMC on the viscosity of the system with respect to shear rate. The shear rate is varied in range of 0.5 s^{-1} to 10 s^{-1}. The initial viscosity is proportional to the CMC content, as discussed in the above diagram. But as the shear rate increases the viscosity decreases. This effect increases with increase in the CMC content in the system. Although the initial viscosity varies, at high shear rate values the viscosities of all the systems collapse into a very narrow range. This result is important since it indicates that geopolymers, unlike concrete, can be delivered using high shear systems like nozzles. This effect is more pronounced in the case of the two polymer system, with PEG and water.

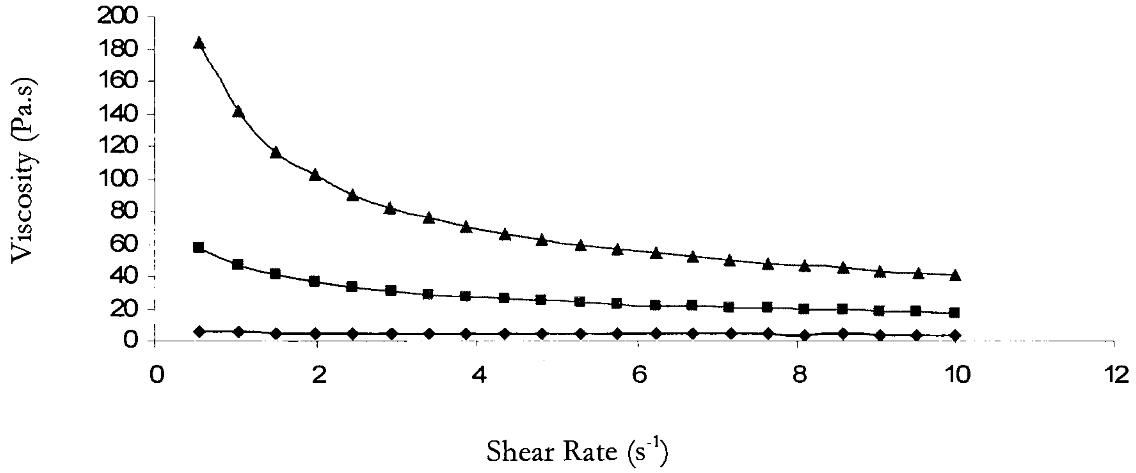


Fig 4.13: Effect of CMC content on the viscosity of the composite system with respect to shear rate; -◆-: 0.45% CMC, PEG 0%, excess water 22.5%; -■-: 0.90% CMC, PEG 0%, excess water 22.5%; -▲-: 1.35% CMC, PEG 0%, excess water 22.5%;

Fig 4.14a and 4.14b give the effect of PEG on the elastic and the viscous modulus of the system, respectively. All the systems display a classic viscoelastic behavior, very typical of organic polymers. This is indicative of the dominant role that the polymer plays in the uncured geopolymer slurry. As we increase the PEG content the overall elastic as well as the viscous modulus increases. It can be noted that the rise in G' is faster as compared to G" after addition of CMC.

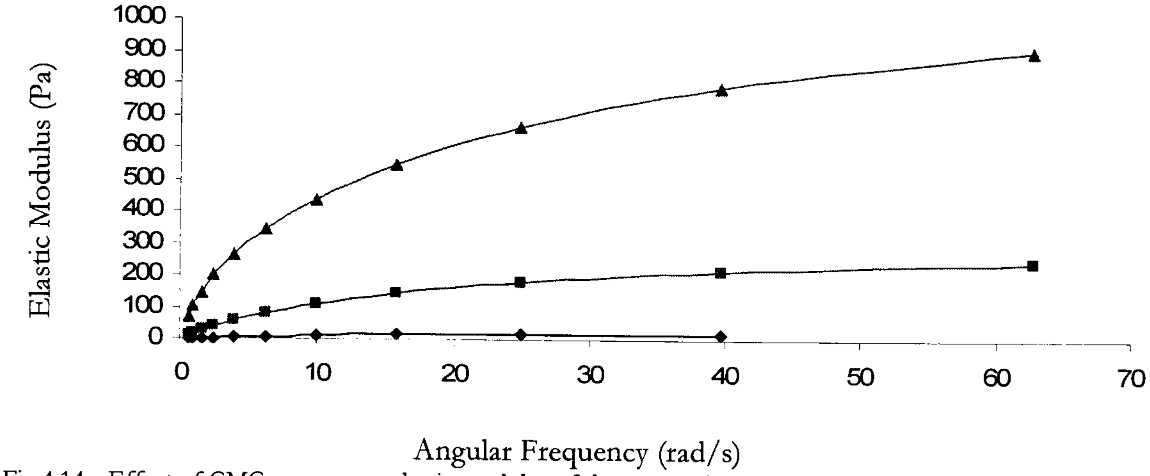


Fig 4.14a: Effect of CMC content on elastic modulus of the composite system; -♦-: 0.45% CMC, PEG 0%, excess water 22.5%; -■-: 0.90% CMC, PEG 0%, excess water 22.5%; -▲-: 1.35% CMC, PEG 0%, excess water 22.5%;

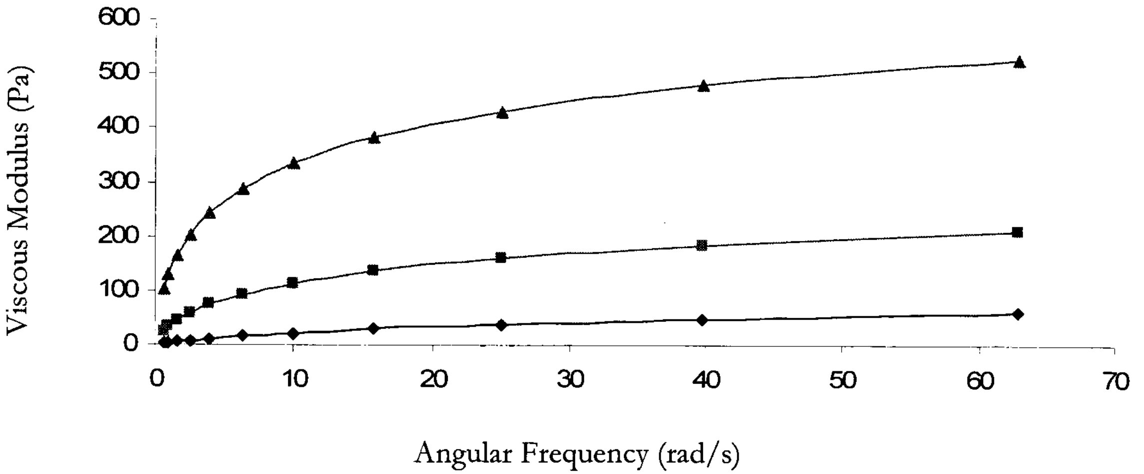


Fig 4.14b: Effect of CMC content on viscous modulus of the composite system; -♦-: 0.45% CMC, PEG 0%, excess water 22.5%; -■-: 0.90% CMC, PEG 0%, excess water 22.5%; -▲-: 1.35% CMC, PEG 0%, excess water 22.5%;

The next section deals with the effect of PEG on the uncured composite system. Fig 4.15 represents the behavior of the system with an increase in the PEG content over the period of 600 seconds. The behavior is similar to that of a system with CMC, but the amount of increase in the viscosity is less as compared. All the samples have fairly constant viscosities over the period.

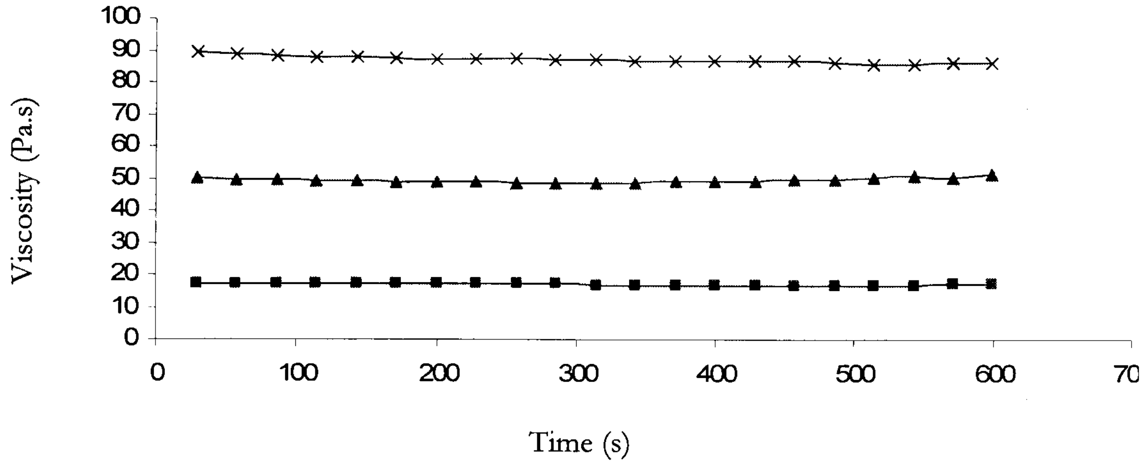


Figure 4.15: Effect of PEG content on the viscosity of the uncured slurry with respect to time; -■-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -▲-: 0.45% CMC, PEG 3%, excess water 22.5%; -x-: 0.45% CMC, PEG 6%, excess water 22.5%;

Fig 4.16 shows similar behavior of the sample viscosities with respect to increasing shear rates. The initial values are comparable to that of CMC, but the final values for PEG system are much lower than that with CMC system.

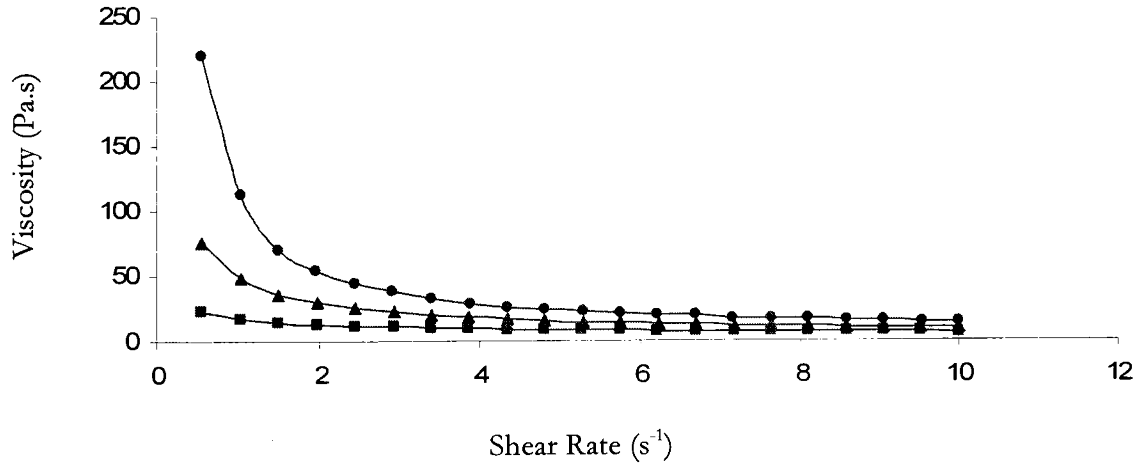


Figure 4.16: Effect of PEG content on the viscosity of the uncured slurry with respect to shear rate; -■-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -▲-: 0.45% CMC, PEG 3%, excess water 22.5%; -●-: 0.45% CMC, PEG 6%, excess water 22.5%;

Fig 4.17a and 4.17b represent the effect of PEG on the elastic and viscous moduli of the composite systems. Although the trends observed are similar to that of CMC, the value for elastic modulus is much lower (by about 600 Pa), but the viscous modulus values are comparable. Hence we see hardly any difference in the elastic and the viscous modulus of the system containing PEG.

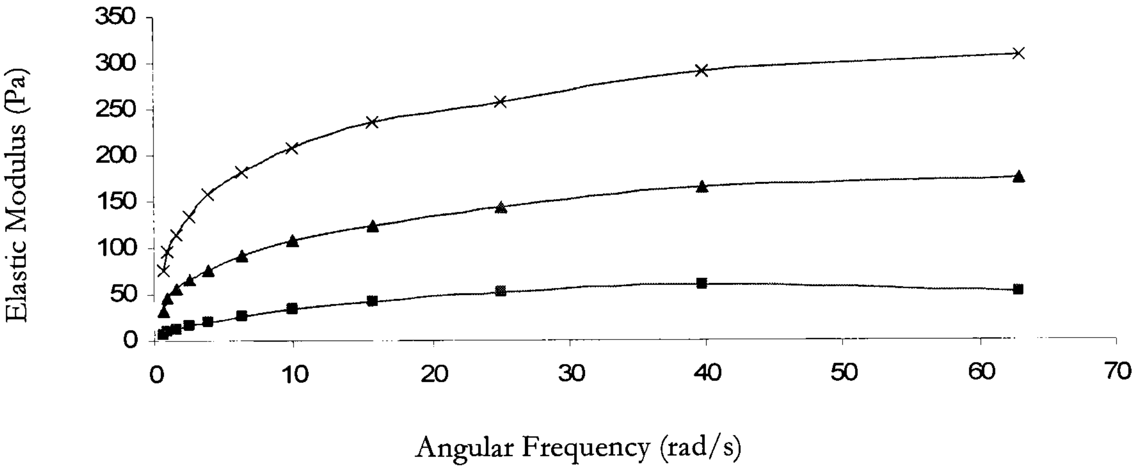


Figure 4.17a: Effect of PEG content on the elastic modulus of the uncured resin; -■-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -▲-: 0.45% CMC, PEG 3%, excess water 22.5%; -x-: 0.45% CMC, PEG 6%, excess water 22.5%;

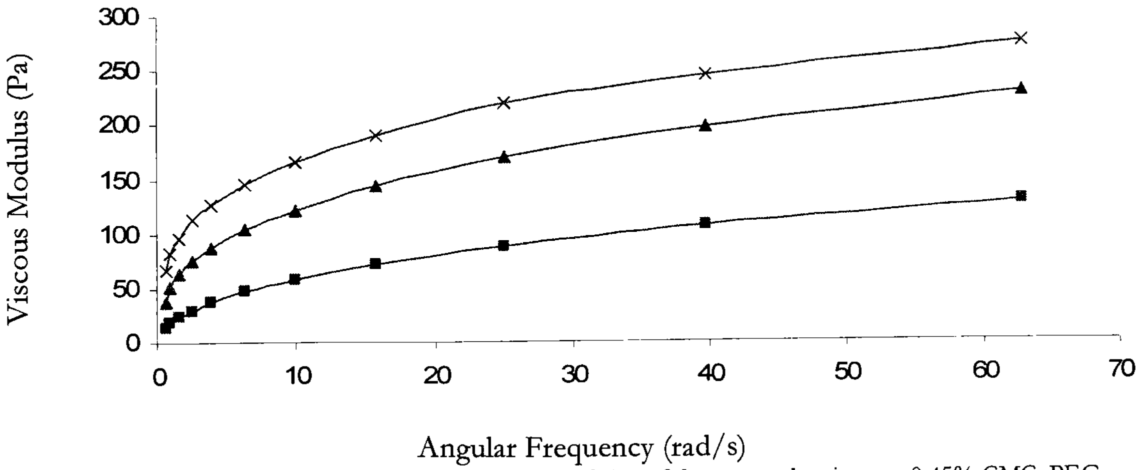


Figure 4.17b: Effect of PEG content on the viscous modulus of the uncured resin; -■-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -▲-: 0.45% CMC, PEG 3%, excess water 22.5%; -x-: 0.45% CMC, PEG 6%, excess water 22.5%;

The following section deals with the effect of water on the viscosity with respect to time, shear rate and on the moduli of the uncured composite system.

Fig 4.18 shows the dependence of the sample viscosities on water content with respect to time. An increase in polymer content has the similar effect to that of a decrease in excess water content. Decreasing the water content by 7.5 wt. % increases the viscosity by 6 times. Further decreasing the water content by 7.5 wt. % the viscosity increases by about 2.5 times. Also we observe the decrease in the viscosity for the system with lowest water content. This figure also confirms that addition of water reduces the cure rate of the geopolymer system.

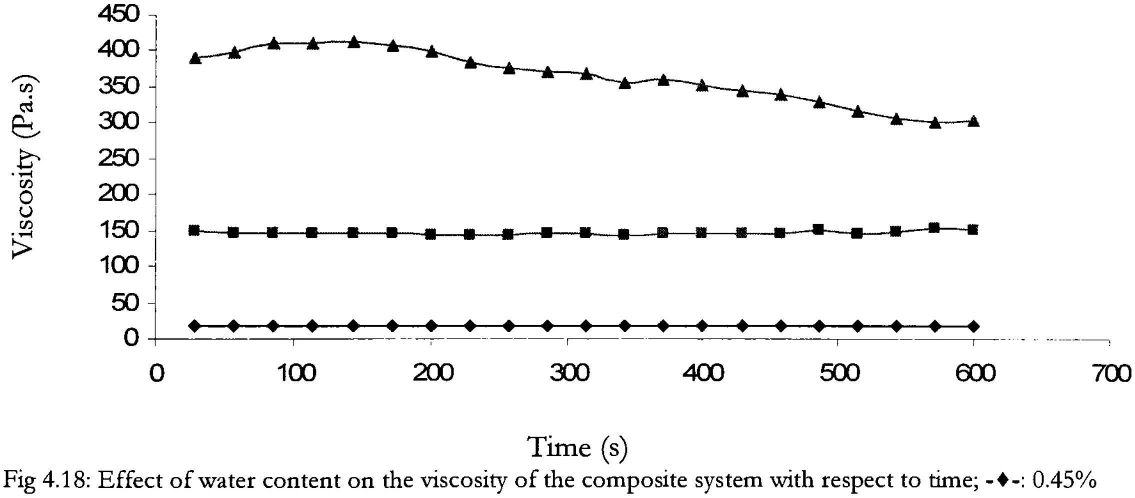


Fig 4.18: Effect of water content on the viscosity of the composite system with respect to time; -♦-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -■-: 0.45% CMC, PEG 1.5%, excess water 15%; -▲-: 0.45% CMC, PEG 1.5%, excess water 7.5%;

Fig 4.19 displays a very similar trend of decreasing viscosity with increase in the shear rate. But in this case the effect is more pronounced. The highest value of viscosity drops by about 10 times as compared to only 3 times in case of CMC.

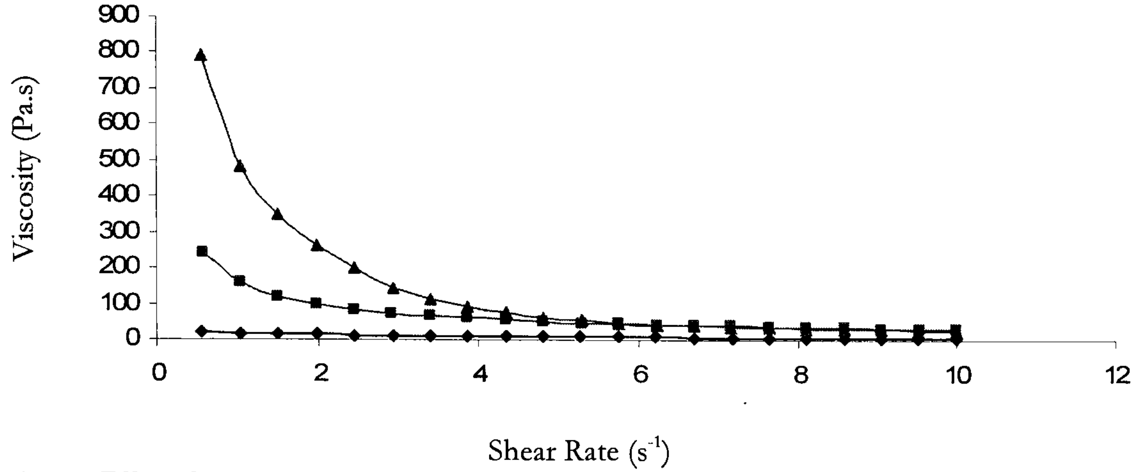


Fig 4.19: Effect of water content on the viscosity of the composite system with respect to shear rate; -♦-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -■-: 0.45% CMC, PEG 1.5%, excess water 15%; -▲-: 0.45% CMC, PEG 1.5%, excess water 7.5%;

The excess water content has a similar effect on the moduli of the composite system as with organic polymers (Fig 4.20a and 4.20b). But the amount of the increase in the moduli from the initial angular frequency to the final is more in case of organic polymers as compared to the water content. Also the initial value of modulus in the case of the organic polymers is lower (~ 250 Pa maximum) than that found with the water content data. The rise in G' and G" is intermediate between that of CMC and PEG.

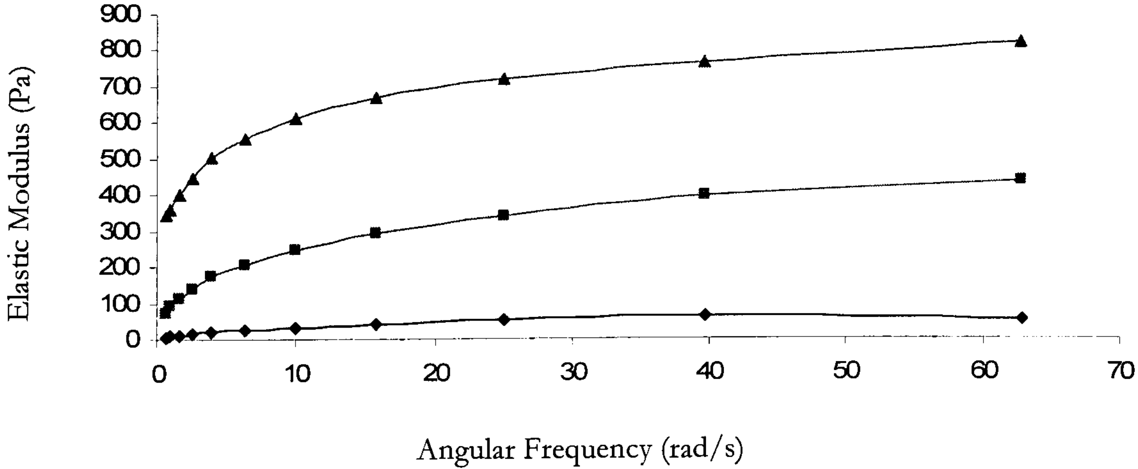


Fig 4.20a: Effect of water content on elastic modulus of the composite system; -♦-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -■-: 0.45% CMC, PEG 1.5%, excess water 15%; -▲-: 0.45% CMC, PEG 1.5%, excess water 7.5%;

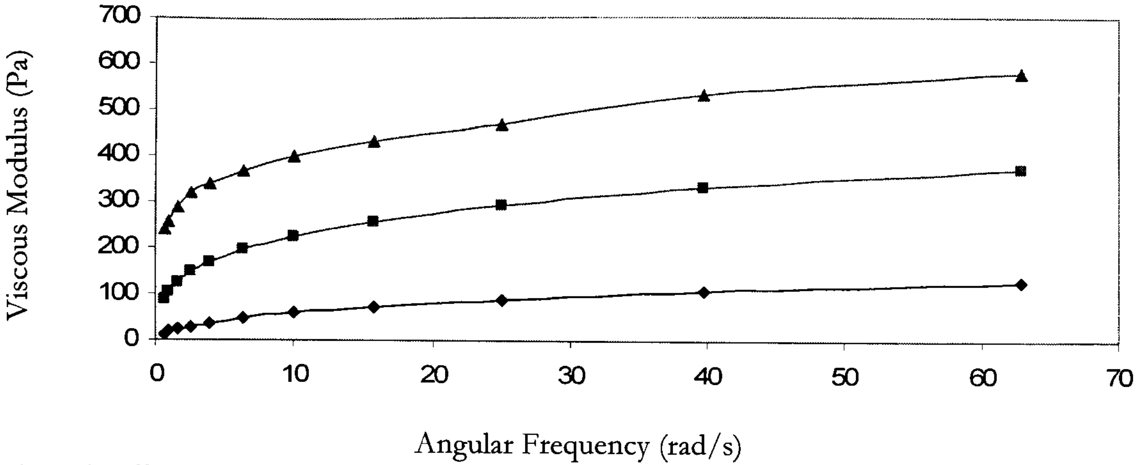


Fig 4.20b: Effect of water content on viscous modulus of the composite system; -♦-: 0.45% CMC, PEG 1.5%, excess water 22.5%; -■-: 0.45% CMC, PEG 1.5%, excess water 15%; -▲-: 0.45% CMC, PEG 1.5%, excess water 7.5%;

The following table presents the viscosity, elastic modulus and viscous modulus values for PEG modified geopolymer systems at room temperature. The viscosity values determined at a constant shear rate of 1 $s^{-1}$and the moduli are determined at the angular frequency of 6.284 rad/s.

Sample	Dynamic Viscosity (Pa.s)	Elastic Mod. (Pa)	Viscous Mod. (Pa)
PEG 0%, Excess Water22.5%	4.3	7.0	16.3
PEG 1.5%, Excess Water22.5%	16.8	26.0	47.32
PEG 3%,Excess Water22.5%	48.2	91.5	104.0
PEG 6%,Excess Water22.5%	86.3	181.6	145.6
PEG 0%,Excess Water15%	42.5	115.3	103.7
PEG 1.5%,Excess Water15%	145.6	208.1	196.3
PEG 3%,Excess Water15%	196.2	278.3	236.5
PEG 6%,Excess Water15%	260.1	667.9	399.4
PEG 0%,Excess Water7.5%	127.9	81.83	77.0
PEG 1.5%,Excess Water7.5%	371.5	555.3	367.4

Table 4.2: Rheological data for the PEG modified geopolymer systems

The data values from the above table give an idea about the behavior trends of geopolymer-polymer composites. The above data gives a clear indication that an increase in

PEG content has the same effect as a decrease in the water content. But PEG has a more dominant effect than the water content, i.e. small quantities (1.5%) of PEG have a comparable effect with that of large quantities (7.5%) of water on the modified geopolymer system. An increase in the polymer content increases the viscosity proportionally. This is true for different sets of samples having different water content. The same trend can be noted for elastic modulus and viscous modulus.

Chapter 5

Conclusions and Recommendations for Future Work

5.1 Conclusions

The aim of this project was to understand and evaluate the dynamic mechanical properties of the geopolymers, modify its rheology, curing time and improve its workability. To achieve these goals, a geopolymer system was modified using organic polymers, namely low molecular weight poly (ethylene glycol) and carboxy methyl cellulose.

From this study it can be concluded that the behavior of geopolymers, in terms of their curing time, workability and rheology, can be modified using organic polymers. The curing time could be increased from 4 hours for an unmodified system to a maximum of 72 hours for a system with organic polymers. The uncured composite slurry exhibited a higher elasticity and better spreadability as compared to the unmodified system. The elastic and the viscous modulus of the slurry were increased with an increase in the organic polymer content.

It can be inferred from this study that the geopolymer systems are shear-thinning systems. The effect of the two organic polymers and water were studied with respect to the change in its viscosity over time period. The effect of these variables on elastic and viscous moduli of the system was also quantified. The results lead to a conclusion that the addition of organic polymers changes the rheology, curing time and workability of these systems.

This study demonstrated that dynamic mechanical analysis in the bending mode could be performed on the geopolymer systems. The dynamic mechanical behavior of the geopolymer systems was evaluated over a temperature range. The effect of organic polymers, namely, PEG and CMC, and water on the cured systems was quantified with respect to the changes in the moduli of the cured geopolymer systems. Overall PEG and CMC have a negative impact on the mechanical properties of geopolymers. PEG and CMC when added in the range of 1% to 2% by weight, the elastic modulus of the composite system was increased.

Addition of organic polymers causes the change in rheological properties of prepared geopolymer slurry. Increases in the amount of polymer content, increases the elastic and the viscous moduli of these systems depending on the amount of polymer and the excess water content. The viscosity can be varied between the range of 4Pa.s to 580Pa.s at a constant shear rate of $1s^{-1}$with varying proportions of polymers and water. Similarly, the elastic and the viscous moduli can be modified within the range of 7Pa to 54.6 KPa and 16Pa to

25.6KPa, respectively at an angular frequency of 6.284 rad/s. Although on the downside, an increase in the polymer and water content decreases the mechanical properties of the cured systems. This is evident from the dynamic mechanical analysis results. The elastic modulus decreases to a third (~800MPa) of its value for unmodified geopolymer system (~3000MPa) for the systems with high polymer loadings like 6% PEG and 0.45% CMC with 5% excess water content. Addition of organic polymers in the selective range like 0.45% to 0.90% CMC and around 1% PEG content had the mechanical properties comparable or better than that of an unmodified geopolymer system.

Organic polymers also change other characteristics of the geopolymer like its bonding with steel and cement concretes. Geopolymers are known for their excellent bond strength with steel and cement concrete, but with the addition of organic polymers these characteristics are diminished. That is the reason poly (vinyl alcohol) could be used as a mold release agent in its aqueous solution.

From the results it can be inferred that water and organic polymers, PEG and CMC, have opposite effect on the system. Small variations in the polymer content has a comparable and opposite effect to large variations in water content suggesting that organic polymers have a dominant effect on the rheological and mechanical properties of the geopolymer – polymer composite systems.

Another interesting result that was achieved from this study was the flexible nature of the cheesecloth-reinforced composite plaques. The brittle nature of geopolymers was diminished dramatically. This increases the possibility of and the range of products that can be achieved using geopolymers.

5.2 Recommendations for Future Work

This project was a novel study of geopolymer – polymer composites. this study could be considered as basis for future work in this novel field of geopolymer – polymer composites. Due to time constraints an in depth understanding of geopolymer and organic polymer interaction could not be obtained. Knowledge of the interaction will explain the results that were observed during this study and open up new avenues for further development in this field.

The other promising systems like the ones with poly (vinyl alcohol) and poly (vinyl alcohol) with adipic acid could be further analyzed. In addition to that, newer organic polymers could be identified based on the interaction between organic and the inorganic component.

It can be concluded that geopolymer – polymer composites show promise in terms of potential applications including coatings, cementatious materials with prolonged curing times, flexible heat resistant materials, composites with variety of reinforcements, insulating materials and many more. In the future work this knowledge could be converted into viable applications. It is the sincere hope of this research team that this study should serve as the basis for the future work in this field as well as overall development of geopolymeric materials.

References

1. Van Jaarsveld, J.G.S and Van Deventer, J.S.J., "The immobilisation and stabilisation of toxic waste using geopolymers", *Oz-Tech '99*. [Taipai, Taiwan, 5-7 April 1999]
2. Davidovits, J., "Geopolymers: Man-Made Rock Geosynthesis and the Resulting Development of Very Early High Strength Cement", J. Materials Education Vol.16 (2 & 3), pp 91-139 (1994)
3. Van Jaarsveld, J., "Geopolymer:Introduction", Geopolymer 2002, Melbourne, Australia
4. Davidovits, J and Morris, M., "The pyramids: An Enigma solved", Hippocrene Books Inc., New York, 1988
5. Campbell, D.H. and Folk, R.L.," The ancient Egyptian pyramids – concrete or rock?", Concrete International, August 1991, pp 29-44
6. Davidovits, J., " Properties of geopolymer cements", Proceedings First International Conference on Alkaline Cements and Concretes, 1994, pp. 131-149
7. Valeria F.F Barbosa, Kenith J.D. MacKenzie, Clelio Thaumaturgo, "Synthesis and characterization of materials based on inorganic polymers of alumina and sodium polysialate polymers", International Journal of Inorganic Materials, 2:309-317, 2000

8. Natalya Privorotskaya; "High temperature effect of geopolymeric coatings on concretes"; Maters Thesis, Rochester Institute of Technology, 2005
9. http://matse1.mse.uiuc.edu/~tw/concrete/hist.html
10. http://cnci.org.za/inf/leaflets_html/admix.html
11. Kemal T. Yücel; The Society of Rheology, Paper SD17 (2002)
12. http://en.wikipedia.org/wiki/Plasticizer
13. http://www.engineeredcomposites.com/publications/Conmat05/Li(ECC).pdf
14. Zhang Shuzheng, Gong Kecheng, Lu Jianwen, "Novel mosification method for inorganic geopolymer by using water soluble organic polymers", Materials Letters 58 (2004) 1292 – 1296
15. Yuan-Hsiang Yu, Chiang-Yi Lin, Jui-Ming Yeh, Wei-Hsiang Lin, "Preparation and properties of poly (vinyl alcohol) – clay nanocomposite materials", Polymer 44 (2003) 3553-3560
16. Kriven Waltraud M, Bell Jonathan, Gordon Matthew; "Microstructure and microchemistry of fully reacted geopolymer and geopolymer matrix composites"; Ceramic Transactions, 153:227-250, 2003
17. US Patent No. 4,509,985, Davidovits, et al., "Early high-strength mineral polymer" April 9, 1985
18. Valeria F.F, Barbosa, Kenith J.D. MacKenzie, "Thermal behavior of inorganic geopolymers and composites derived from sodium polysialate", Materials Research Bulletin, 38(2):319-331, January 2003
19. Lyon Richard, Foden Andrew, Balaguru P, Davodovits J; " Properties of Geopolymer Matrix-Carbon Fiber Composites"; Geopolymer 1999 Proceedings, Pg 123-139

20. Palomo A, Granizo M L, Blanco-Varela M T, Puertas F, Vanquez T, Grutzeck M W, "Chemical stability of cementitious materials based on metakaolin", Cement and Concrete Research, 29-997-1004, 1999

21. Granizo M L, Palomo A, Blanco-Varela M T, "Influence of the starting kaolin on alkali-activated materials based on metakaolin" Journal of Materials Science, 35:6309-6315, 2000

22. Varela Benjamin, " A study of suitability of geopolymers for structural steel fire protection", PhD thesis, New Mexico State University, December, 2002

23. Donaldson Burl, Varela Benjamin, "Evalution of curing kinetics for a geopolymer using differential scanning calorimeter", NATAS Annual Conference, Albuquerque, New Mexico, September 22-24, 2003

24. Davidovits Joseph, "Geopolymers: Inorganic polymeric new materials", Journal of Thermal Analysis, 37:1633-1656, 1991, Reprinted by Geopolymer Institute , 1997

25. Palomo A, Granizo M L, Blanco-Varela M T, Puertas F, "Physical and mechanical characterization of geopolymers", 9th International Congress on Chemistry of Cement, 1992

26. http://psychcentral.com/psypsych/Plasticizer

27. http://www.chemicalland21.com/arokorhi/industrialchem/organic/POLYETHYLENE%20GLYCOL.htm

28. http://www.lsbu.ac.uk/water/hycmc.html

29. http://www.ratson.com/chemicals/carboxy.htm

30. http://en.wikipedia.org/wiki/Cellulose