DEVELOPMENT OF COMPOSITE MATERIALS BASED ON DISPERSION OF INORGANIC FILLERS WITHIN POLYMER MATRIX BY THE SOL-GEL METHOD

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By

TAPASI KOTOKY, M.Sc.

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School of Science and Technology
Department of Chemical Sciences
Tezpur University

To

Tsunesaburo Makiguchi

(1871-1944)

pioneer in value creating education

TEZPUR UNIVERSITY
(A Central University established by an Act of Parliament)
NAPAAM, TEZPUR -784028
DISTRICT:SONITPUR::ASSAM::INDIA

Ph: 03712-267004
03712-267005
Fax: 03712-267006
03712-267005
email:adm@agnigarh.tezu.ernet.in
dolui

CERTIFICATE

Date: 25.7.05

This is to certify that the thesis titled " Development of composite materials based on dispersion of inorganic fillers within polymer matrix by the sol-gel method " submitted to the Tezpur University in the Department of Chemical Sciences under the School of Science and Technology, in partial fulfillment of the award of the Degree of Doctor of Philosophy in Science, is a record of research work carried out by Ms. Tapasi Kotoky under my supervision and guidance.

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No part of this thesis has been submitted elsewhere for award of any other degree.

Prof.S.K Dolui (Supervisor)
Designation: Dean, School of Science and Technology
Department: Chemical Sciences

Preface

Hybrid organic-inorganic composite materials is an emerging area of research. In these materials one of the phases is finely dispersed into the other and this leads to the introduction of new and improved properties in the composite materials.

The sol-gel method has become immensely popular in recent years because of its wide scope of application, flexibility in the choice of reagents and easy processing parameters. Most importantly, it allows the synthesis of optically transparent materials. Fundamentally, the sol-gel synthesis method involves the generation of a colloidal dispersion, known as 'sol', which undergoes gelation to form a crosslinked network, known as 'gel'.

Traditional applications of sol-gel products have been in the field of abrasion resistant coatings, catalysis, etc. The scope offered by the sol-gel synthesis method is extending day by day to incorporate newer applications such as sensors, luminescent materials, hybrid optical switching and data storage devices and biomedical and tissue engineering.

The major problem encountered in hybrid synthesis with polymers and inorganic compounds by the sol-gel method is maintaining the homogeneity of the sol-gel mixture. Homogeneity of the reaction mixture is affected by various factors such as pH, solvent, and water to alkoxide ratio, concentration, catalyst and temperature. Each of these factors plays an important role in the gelation process and the structure of the final products.

The present work deals with the study and optimization of reaction parameters for getting homogeneous sol-gel mixtures. The effect of the various reaction parameters in influencing the nature of dispersion of the inorganic phase within the polymer phase has been studied and bulk properties were characterized.
Polyvinyl alcohol (PVA)/silica, Polyacrylamide (PAA)/silica, Polystyrene/silica and Polystyrene-butyl acrylate/silica hybrid systems were selected for the study.

In spite of lack of immediate access to analytical equipments, we have made a sincere attempt to delve into the subject as closely as possible. We hope that this study contributes a little to the rapidly advancing field of hybrid synthesis and also opens up the possibilities of further research on the subject.

This research was carried out in the Department of Chemical Sciences, Tezpur University with financial assistance from the Indian Space Research Organization (ISRO), and the Council of Scientific and Industrial Research (CSIR), Govt. of India.

Tapasi Kotoky.

Ms. Tapasi Kotoky
Tezpur University
Tezpur, Assam, India

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Development of composite materials based on dispersion of inorganic filler within polymer matrix by the sol-gel method

ABSTRACT

Hybrid organic- inorganic composite materials are produced by a synergistic combination of both organic and inorganic compounds. Polymer-ceramic synthetic chemists seek to combine, retain and enhance the best properties of both ceramic and polymeric materials. For example, high temperature resistance and hardness is a characteristic of ceramic materials. However, their use is limited in many applications because of their brittle nature. Polymers are characterized by elasticity and high impact strength. However, they have low heat resistance, low wear and scratch resistance and in some cases low dimensional stability. The sol-gel method is a versatile and homogeneous solution method which allows the two phases, organic and inorganic, to be combined in such a manner as to retain and enhance the properties of both, giving rise to a hybrid material. The properties of composite materials are dependent on the nature of interfacial cohesion between the two phases. The sol-gel method helps to establish better interfacial force between the two phases as compared to other methods. As a result, phase separation can be controlled or minimized by controlling the reaction parameters. This results in the formation of composites that are optically transparent. The sol-gel process has been utilized to incorporate highly crosslinked networks of

inorganic compounds into polymeric matrices. The flexibility of the sol-gel method has allowed the incorporation of inorganic phase into almost every kind of polymeric system.

In the present work, synthesis of polymer-inorganic composites has been carried out by the sol-gel method with the objective of attaining improvement in the mechanical, thermal and other physical properties of the polymers by incorporation of silica. The extent of improvement in these properties depends on the degree of compatibility between the two phases. This can be measured by observing the dispersion characteristics of the inorganic phase within the polymeric matrix. We have therefore carried out the synthesis work to get good dispersion of the inorganic phase within the polymer matrix. Finally, the composite properties were characterized.

Poly (vinyl alcohol), polyacrylamide, polystyrene and copolymers of polystyrene and butyl acrylate were used for the purpose.

Chapter 1: This chapter covers a general description of hybrid organic-inorganic composites and their applications, methods of synthesis of hybrid organic-inorganic composites, classification and nomenclature of hybrid organic-inorganic composites synthesized by the sol-gel method, history of the sol-gel method and its synthetic aspects, discussion on polymer-inorganic hybrid composites synthesized by the sol-gel method and objective and relevance of the present study.

Chapter 2: This chapter describes the synthesis of polyvinyl alcohol (PVA)/silica hybrid materials. Polyvinyl alcohol/silica hybrid materials were synthesized in aqueous medium using sodium silicate as a source of silica and dil HCl as a catalyst. The amount of acid catalyst (0.5NHCl) required to form the sol decreased with an increase in the concentration of sodium silicate. Transparent and flexible hybrid films were obtained after gelation at 45 ^{0} C for 24 hours and extended drying for another 48 hours. The hybrid composites were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), tensile strength, elongation at break and water uptake measurements. SEM micrographs revealed that silica was dispersed in the PVA matrix without the large aggregation of particles for a molar composition of 0.004 PVA: 0.048 Sodium silicate: 0.004 HCl:0.13 H_20.

The synthesis of polyacrylamide/silica hybrid composites is also described in Chapter 2. The polyacrylamide/silica hybrid composites showed a difference in morphology from the PVA/silica hybrid composites under SEM.

Chapter 3: In this chapter we have reported the use of modified polystyrene as a matrix for getting homogenous dispersion with silica by the in-situ sol-gel method. The polymer matrix was prepared by the copolymerization of styrene and methyl vinyl dichloro silane. This was done in order to enhance the compatibilization of polystyrene with the

silica phase. In the preparation of these hybrid composites, the source of the inorganic component silica is tetraethyl orthosilicate (TEOS). The SEM micrograph for the hybrid composite derived from polystyrene showed non-uniform dispersion of silica particles in the polymer matrix. However, the dispersion was much improved with the silane functionalized copolymers showing that they had better compatibility between the two phases.

Chapter 4: This chapter describes the synthesis and characterization of hybrid composites where copolymer of styrene and butylacrylate was used as the matrix. The styrene-butyl acrylate copolymer was then functionalized with methyl vinyl dichlorosilane to enhance compatibilization with silica. The objective was to study the effect of incorporation of flexibility in the polymeric backbone on the dispersion characteristics of silica within the copolymer matrix. The SEM results also showed that the styrene-butylacrylate copolymers loaded with silica were crack free, whereas composites produced with polystyrene and silica were not crackfree.

Chapter 5: In this chapter the results of the previous chapters have been summarized and compared.

It is concluded that the formation of colloidally stable sol helped to attain better dispersion of the inorganic filler within the polymer matrix in all cases. Silane functionalisation enhances the compatibility of polystyrene backbone with the silica matrix. Incorporation of butylacrylate also improves compatibility between the polymer and inorganic phases.

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CHAPTER 4. Synthesis and characterization of Polystyrene-butylacrylate/silica hybrid composites by the sol-gel method

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List of abbreviations

1	PAA	Polyacrylamide
2	PVA	Polyvinyl alcohol
3	PS	Polystyrene
4	PSMVS	Styrene-methyl vinyl dichlorosilane copolymer
5	PSBUA	Styrene-butyl acrylate copolymer
6	PSBUAMVS	Styrene-butyl acrylate methyl vinyl dichlorosilanecopolymer
7	TEOS	Tetraethyl orthosilicate
8	THF	Tetrahydrofuran
9	DSC	Differential Scanning Calorimetry
10	TGA	Thermogravimetric Analysis
11	FTIR	Fourier Transform Infrared Spectroscopy
12	NMR	Nuclear Magnetic Resonance Spectroscopy
13	SEM	Scanning Electron Microscopy
14	TEM	Transmission Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1. Definition of hybrid organic-inorganic composites

Hybrid organic- inorganic composite materials have emerged in response to the newer demands of the industry for a synergistic combination of both organic and inorganic compounds. The enormous number of research publications and patents depicts the growing importance of this field [1-15].

By definition, a composite material consists of two or more physically distinct components, showing better properties than its constituents [2]. A composite material consists of filler (or reinforcing agent) usually as particles or fibers, and a matrix material. The role of the filler or reinforcing agent is to provide intrinsic strength and stiffness and the role of the matrix is to adhere to and bind the fillers. In addition, the matrix protects the surfaces of the filler so that forces applied to the composite are transmitted evenly to the filler [3]. The matrix also keeps the particles apart to hinder crack propagation. While keeping intact the intrinsic physical properties of the components, composite materials can often display special properties as a result of the interfacial interaction between the matrix and filler particles [15].

In Nature, organic-inorganic composite materials play important roles as structural materials and represent some of the finest examples of optimized interfacial interaction between the matrix and filler particles through small scale design [16-18]. For example, biological structural composites such as bone, tendon and dentin consist of nanometer scale inorganic hydroxyapatite crystals grown within an anisotropic organic matrix of aligned collagen fibrils. Evolution has optimized the interfaces and nanometer scale architecture of these biogenic composites to afford unique materials that are lightweight yet strong and flexible [16].

Versatile synthetic routes are now available for the synthesis of hybrid organic –inorganic composites [19-23]. It is possible to either modify the two components independently or to bring about the introduction, entrapment, and dispersion or in-situ formation of suitable low molecular weight compounds, functional groups or large aggregations [24-25]. Precursors for structured single phase materials such as hollow particles and templated mesoporous inorganic oxides can also be produced, where one of the components in the hybrid is selectively removed in the last fabrication step [26-27].

The mechanical [28-29], adhesive [30-31], electrical [32-33], optical [34], photochemical [35], catalytic [36] or magnetic properties [37] of these new hybrid materials are often a synergistic combination or utterly new ones with respect to those of their constituents. For example, organic substances or polymers while retaining their inherent properties such as flexibility can also be imparted with higher heat resistance, toughness, or other desired functional properties such as catalytic, photochemical, electrical or magnetic behaviour through incorporation of the suitable inorganic component. Such hybrid composites can be obtained by interpenetration, inclusion or dispersion of an inorganic component. The necessary compatibility between the organic and inorganic phases is provided by hydrophilic interaction or coordinative/covalent bonding with a concurrent control of the shape, morphology and topology of phase separated domains or pore structure in sizes varying from the macroscopic to the nanometer range [12]. The term hybrid therefore encompasses a wide variety of molecular and macromolecular systems. It is also loosely employed to describe systems that are actually simple multicomponent heterogeneous mixtures.

Polymer-inorganic hybrid composites are one of the most important classes of synthetic materials. They can combine the properties of ceramic materials, eg. hardness and modulus with the lightweight, yet flexible nature of polymers [16]. Some of these materials are classified as biomimetic materials because they attempt to attain the properties of many structural materials such as bone, tendon and dentin.

Polymer-inorganic composites are widely used in the tissue engineering field for artificial bone substitutes [38-40].

1.2. Synthesis of hybrid organic- inorganic composites

Synthetic methods for hybrid organic-inorganic compounds may be classified under the broad categories of ex-situ and in-situ methods.

Ex situ method: The ex-situ method commonly involves blending inorganic fillers by melt processing or mixing with reactive resins and monomers. The advantage of this method is that composites can be fabricated by common industrial processing equipment such as low and high shear mixers and extruders. A common example is the synthesis of polymer/silicate layered compounds [41-49]. Pioneering work on polymer/layered silicate nano composites was carried out by researchers at Toyota [41]. Two idealized polymer/clay nanocomposites are possible, intercalated and exfoliated. Intercalation results from penetration of the polymer chains into the interlayer region and interlayer expansion. Usually the ordered layer structure is preserved and can be detected by x-ray diffraction spectroscopy (XRD). By contrast, exfoliation involves extensive polymer penetration and silicate crystallites delamination, and the individual nanometer thick silicate platelets are randomly dispersed in the polymer matrix. Exfoliated nanocomposites usually provide better property enhancement due to the large aspect ratio and surface area of the clay [43].

Limitations of the ex-situ approach: The incompatibility of many inorganic fillers with organic polymers requires the use of plasticizers, dispersion aids or filler surface treatment in order to obtain complete dispersion. In addition, highly oriented microstructures are obtainable in only a limited number of systems [16].

In-situ method: The in-situ method involves generation of inorganic particles from precursor materials within the polymer matrix. The in-situ method has been used to prepare highly oriented microstructures with uniform pore sizes and volumes [16.]

Common in-situ methods are:

i. The sol-gel method

ii. Precipitation of inorganic nanoparticles from soluble precursors

iii. Metal deposition in nanoporous polymer membranes

Precipitation of inorganic nanoparticles from soluble precursors: In this method, dissolved metal ion solutions are made to react with a variety of mild precipitating agents to afford in soluble metal salts, such as metal chalcogenide semiconductors, magnetic particles, metal phosphates and metal carbonates [16]. Similarly, exposure of dissolved metal salts to mild reducing agents can generate metal particles in-situ. When these reactions are performed on polymeric or monomeric matrices incorporating inorganic particles formed in situ to generate polymer inorganic nanocomposites [15]. The development of synthetic analogs to biological nanocomposites also uses this approach [50-57].

Metal deposition in nanoporous polymer membranes: This method involves electrodepositing metals in the pores of nanoporous polymer membranes. Generally termed "template synthesis" this approach utilizes commercial microporous and nanoporous polymeric membranes [58-59]. These membranes are typically polycarbonate /polysulfone films containing cylindrical pores of uniform diameter (down to 10nm) randomly distributed across the membrane surface. Nanocomposites are made by either electrochemical or chemical reduction process [60].

Cation exchange intercalation: Cation exchange intercalation into layered compounds allows the synthesis of many air stable intercalates [61]. These intercalates exhibit a variety of unusual physical properties. Guest host complexes are created by cation transfer intercalation chemistry. These nanocomposites exhibit unusual magnetic, electrical and non-linear optical properties.

The sol-gel method: The sol-gel method has emerged as one of the most popular methods for the synthesis of hybrid organic-inorganic composite materials. The process has been developed in the last two decades leading to new materials in various areas [62-83]. The term sol-gel science was coined in the 1950s to refer to the art of manufacturing materials by preparation of a sol, gelation of the sol and removal of the solvent [84].

The sol-gel technology has in fact been practiced since the first encounter with colloidal materials. The sol-gel technology was originally developed by mineralogists for the preparation of homogeneous powders for use in phase equilibria, by chemists for manufacture of nuclear fuel pellets and by ceramists for the preparation of advanced ceramic materials [84]. According to pioneering sol-gel scientist, Jeffrey Brinker, " *a sol is defined as a colloidal dispersion of particles in a liquid. A gel is a substance that encloses a continuous solid skeleton enclosing a continuous liquid phase. The liquid prevents the solid from collapsing; the solid prevents the liquid from escaping. Thus the formal definition of sol-gel processing is the growth of colloidal particles and their linking together to form a gel* " [85]. The sol-gel reaction is a method for synthesizing pure metal oxides at relatively low temperatures in alcoholic or aqueous media. The most obvious precursors for oxides are molecules already having metal-oxygen bonds, namely metal alkoxides $M(OR)_n$ or oxoalkoxides $MO(OR)_n$ (R=saturated or unsaturated organic group, alkyl or aryl), βdiketonates, $M(\beta\text{-dik})_n$, β-diketonate =RCOCHCOR and metal carboxylates $M(O_2CR)_n$. The reaction employs an alcohol or organic solution of a semimetal alkoxide precursor M (OR)n and water. M is an element that has a valency greater than 2 so that crosslinking can occur (eg.Si, Ti, Al, Zr, V) [15]. The most commonly used precursors of oxides are alkoxides due to their commercial availability, convenient rates of hydrolysis and the high lability of the M-OR bond. The first step in the sol-gel process is the hydrolysis of the metal or semimetal alkoxide to produce M-OH groups. For M=Si, the initial hydrolysis step is acid or base catalyzed. However, for nonsilicate metal alkoxides, no catalyst is required due to their higher intrinsic hydrolytic activity. The second step in the process is thermal condensation of the hydroxy groups with either alkoxy groups (alcoxolation) or hydroxy groups (oxolation) on other M centers to afford a crosslinked amorphous network or gel.

The molecular precursors used in the sol-gel process are essentially alkoxide M(OR)n, where M is metal with a valency higher than 2, R is a alkyl group and n is the oxidation number of M [86].The reaction occurs in two steps, the first one is a hydrolysis reaction, which creates the reactive group M-OH:

$$\text{M-OR} + H_2O = \text{M-OH} + \text{R-OH}$$

The second one is a condensation reaction leading to the formation of oxo bridges with water or alcohol as by product.

$$\text{M-OH} + \text{M-OH} = \text{M-O-M} + H_2O$$

$$\text{M-OH} + \text{M-OR} = \text{M-O-M} + \text{R-OH}$$

A typical sol-gel process may be illustrated process may be illustrated with a precursor silicon alkoxides Si $(OR)_4$ as follows:

$$\text{Si}\,(OR)_4 + H_2O \longrightarrow \text{Si}\,(OH)_4 + 4ROH$$

$$\equiv\text{Si-OH} + \equiv\text{Si-OH} \longrightarrow \equiv\text{Si-O-Si}\equiv + H_2O$$

As shown above for silicon, the addition of an acid or base catalyst to a solution of an alkoxysilane reagant such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS), in water and methanol leads to hydrolysis of the Si-OEt or SiOMe bonds to form Si-OH functional groups. Subsequent elimination of water from two such Si-OH groups gives eventually an extended silica gel matrix (known as xerogel when dry). As hydrolysis and condensation reactions occur concurrently, monomeric silanols proceed to xerogel through oligomeric and polymeric intermediates. As these reactions progress, the viscosity of sol-gel solution increases and can reach a spinnable stage at which point thin fibres or films can be produced. Otherwise, xerogel (dry gel) products are obtained as porous powders or monoliths that assume the shape of the container. If desired, residual Si-OH groups remaining in the xerogel product can be removed at elevated temperature to give fully densified SiO_2 [84]. On the other hand, solvent evaporation of the wet gel in an autoclave below the critical temperature of the liquid can give a highly porous material known as xerogel [84]. Drying the sol-gel mixture under supercritical conditions forms aerogels. Such composites have large surface area [84].

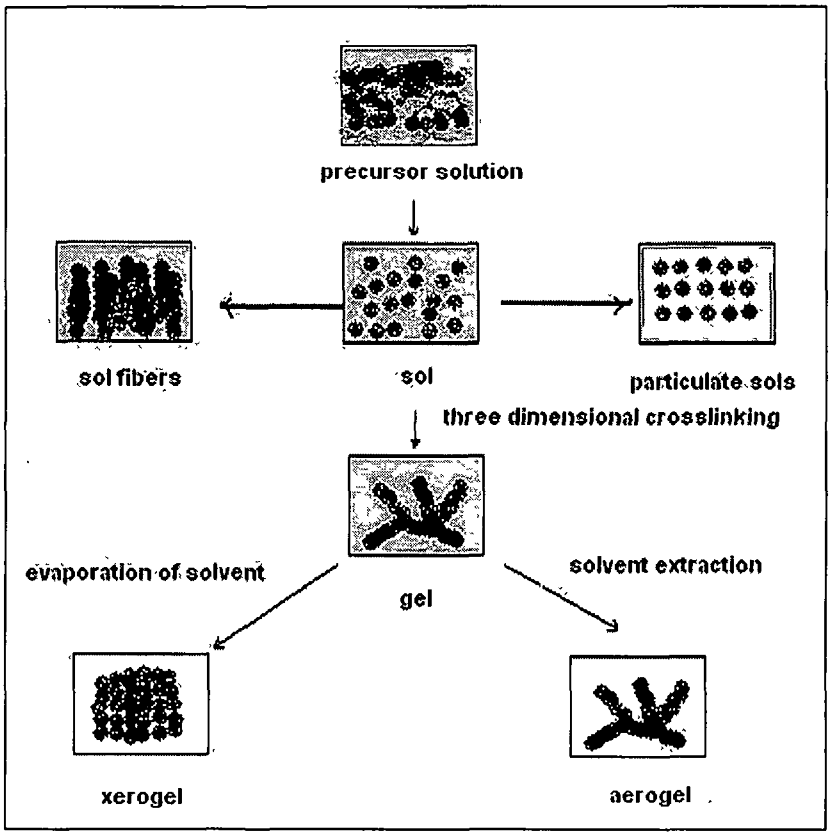

Fig.1.1. Schematic diagram of the sol-gel process.

Mixtures of precursor compounds for two or more elements can also undergo heterocondensation to form mixed element gels.

1.3. Special features and advantages of the sol-gel method

The sol-gel route to the synthesis of ceramics and complex hybrid compounds has got several special features [11].

i. Low temperature synthesis (at or near room temperature) for complex hybrid organic compounds and below 900°C for inorganic ceramics can be carried out.

ii. The solution method leads to the formation of homogeneous materials and high chemical purity can be maintained because of the absence of grinding and pressing steps.

iii. A wide variety of host matrices can be formed under veryild conditions with relatively inexpensive reagents using sol- gel chemistry. This flexibility enables the tuning of pore size, surface area, density, dielectric constant, refractive index and chemical composition of the host matrix .

iv. Sol-gel nanocomposites can be obtained as optically transparent materials because the phase separated organic and inorganic domains in the matrix are well below the wavelength of visible light.

The interest in sol-gel materials is not only related to their physical and chemical properties, but also to the wide possibilities in materials processing offered by the colloidal state [34]. The viscosity of sols easily allows the preparation of films by dip coating, spraying or spin coating. Compared to other thin film forming processes such as sputtering, evaporation and chemical vapor deposition, (CVD), sol-gel film formation has the advantage that both the composition and the microstructure can be controlled in the molecular level [62]. Thus the films can be tailored for specific applications, for example, dense films for protective or optical applications and porous films for sensors and membranes [62].

1.4. Recent nano - structured hybrid materials

A wide range of starting materials and production processes has been studied in recent years for the controlled synthesis and characterization of hybrid materials. In particular, aqueous systems and water borne dispersions are being studied. These are more environmentally acceptable and might even become a mandatory choice for any future development of large output applications (e.g. in paint, ink and coating industry). These systems are being used for self-assembling of ampiphilics, adsorption onto colloidal particles or partitioning of the hybrid's precursors between the dispersed nanosized reaction loci. Recent developments in this direction include the synthesis of hybrid nanoparticle by encapsulation of inorganic pigments, lamellae or mesospheres through graft or dispersed phase polymerization, synthesis of core shell particles in dispersed phase etc. Both polymer coated inorganic particles and polymer spheres with an inorganic outer layer have been produced. These may be used as film formers or precursors for hollow nanospheres. Common procedures are in-situ synthesis of bulk and templated mesoporous materials [87-90], mesoporous silica and hollow silica particles [91-94],Self assembling hybrid precursors [95-96], Hierarchically self-organized structures and bio-doped nanocomposites [97-98], and ampiphilic polymer based functional polymer-inorganic hybrid materials [99-105].

1.5. Nomenclature and classification of hybrid materials synthesized by the sol-gel method

The sol-gel hybrid materials can be classified in many ways depending on the relative composition of the constituent components, the nature of chemical interactions between them or the chemical bonds involved. However, the more widely used classification is based on the type of interaction or the nature of interaction between the organic and inorganic species. Following this criterion, the different organic inorganic hybrids can be classified into two broad families [106].

Class I hybrids: In these hybrid systems one of the components (organic, biological or inorganic) which can be molecules, oligomers or polymers is entrapped within a network of the other component. Weak type interactions such as van der wall, hydrogen bonding or electrostatic interactions exist between the host network and entrapped species.

ClassII hybrids: In these hybrids the inorganic and organic parts are chemically bonded by a covalent or ionocovalent bond. The frontier between ClassI and ClassII hybrids is not always distinct and we often see hybrid systems with both ClassI and ClassII characteristics. A typical example of such cases are hybrid materials for optical applications made by encapsulation of organic chromophores within a hybrid matrix which belongs to Class I. Although the dye interacts with the hybrid host via Vanderwaals or hydrogen bonding forces, the strong chemical bonds between the organic and inorganic parts which make up the host material has a significant impact on the overall properties of the system and therefore may also be classified as Class II hybrids.

Nomenclature: According to a recent system of nomenclature, sol-gel hybrid organic- inorganic composites have been classified according to their mode of synthesis as follows [108-110].

i. Ormosils and ormocers: They contain a silane coupling agent which is initially polymerized with a metal alkoxide by the sol-gel process. The resultant system is subsequently blended with reactive monomers and appropriate catalysts for a secondary polymerization reaction, which produces a monolithic network. These materials were previously known as ormosils but have been recently referred to as ormocers to reflect their more ceramic like properties following thermal post cures.

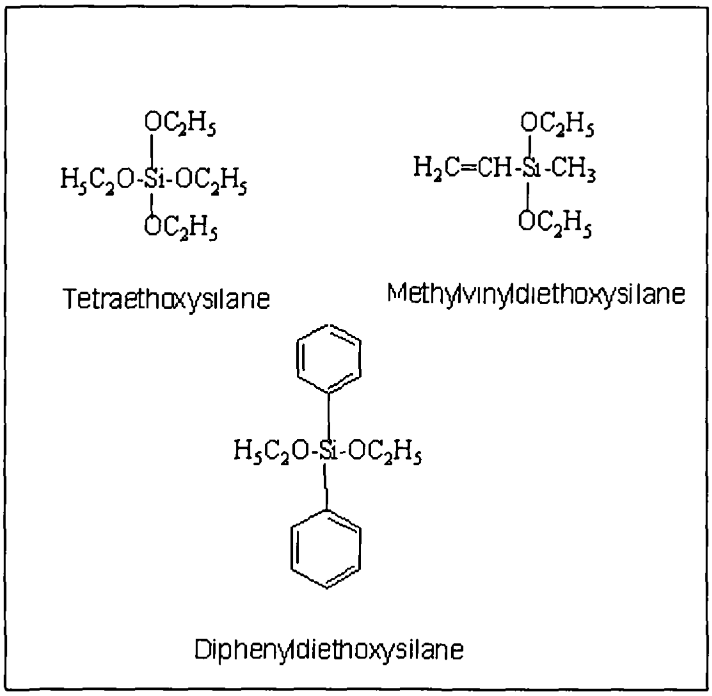

Fig. 1.2. A few ormocer monomers

ii. Ceramers: These are monolithic networks prepared exclusively by a sol-gel process. The reactive components are soluble metal alkoxides and an oligomer or polymer with an alkoxysilane functionality. The oligomers can be functionalized through a reaction of end groups, such as hydroxyls or amines, with the reactive organic group of a silane coupling agent such as (3-isocyanatopropyl) triethoxysilane.

1.6. Applications of hybrid organic-inorganic composites synthesized by the sol-gel method

Sol-gel hybrid materials have found applications as adhesives, laminating resins, coating texture finishes, corrosion resistant materials, etc. [111-115] They have also been used as dielectric layers in micro electric applications due to their high insulating behavior [116-119]. There are many attractive prospects for the applications of sol-gel hybrids as non-linear optically active (NLO) materials, hybrid optical storage devices and luminescent materials [120-125]. Sol-gel hybrids have been used as chemical sensors and catalysts by the entrapment of various substances within the sol-gel matrices [126-130]. The sol-gel technology has been used to synthesize metalloprotein–silica nanocomposites [131-133]. Sol-gel biosensors have been synthesized based on flavoproteinglucose oxidase (Gox)[134-137]. Sol-gel hybrid organic–inorganic composites synthesized have been envisaged for applications as bioactive glasses and glass ceramics [138-142]. These materials have potential for bone repairing [143].

1.7. Review of sol-gel chemistry of silica

Among all other elements silica has been most extensively used for incorporation into an organic or polymer matrix. This is because there are many available modes for the synthesis of an Si-C bond and the Si-C bond, once formed is very stable to air, bases, acids, etc [107]. Moreover, the sol-gel processes are well adapted to the preparation of oxide networks under reaction conditions, which do not cleave Si-C bonds [107]. There are also many available silica precursors with controllable rates of hydrolysis. Most importantly, the synthesis and applications of colloidal silica is well documented with a large number of patents and research papers [144]. It is therefore pertinent to discuss about the sol-gel chemistry of silica.

Silica- occurrence and structural variations: The term silica is used broadly to cover a variety of chemical forms having the stoichiometric composition of SiO_2. Silicon dioxide is the main component of the crust of the earth. The content of SiO_2 in the lithosphere is thought to be 58.3% and the percentage of SiO_2 in independent rocks (quartz, opal and chalcedony) is approximately 12% [145]. Combined with the oxides of Mg, Al, Ca and Fe it forms the silicates minerals in our rocks and soils [145].

Silica can be natural or synthetic, crystalline or amorphous. The building block of silica and the silicate structure is the SiO_4 tetrahedron, which has four oxygen atoms at the corners of a regular tetrahedron with silicon at the center cavity or centroid. Natural silicas can be crystalline as in quartz, cristobalite, tridymite, coesite, and stishovite and amorphous as in opal [145]. The bulk structures of silicas are classified as crystalline and amorphous polymorphs. More than 35 well-defined crystalline silicas are known, which are well characterized by the Si-O bond length, the Si-O-Si bond angle, and the Si-O bond topology and coordination [10]. All forms of silica contain the Si-O bond, which is the most stable of Si-X element bonds. The Si-O bond length is about 0.162 nm, which is considerably smaller than the sum of the covalent radii of silicon and oxygen atoms [145].

In amorphous silica the bulk structure is determined, as opposed to crystalline silica, by a random packing of SiO_4^{-4} units, which results in a non-periodic structure.

1.8. History of silica sol-gel research

The pioneering work in the field of silica sol-gel chemistry is often attributed to three scientists, Thomas Graham, Walter A. Patrick and Ralph K. Iler [144]. The first published work on dilute silica sol and their properties is credited to Graham (1830) [146]. About fifty years later, Walter A Patrick, Professor of Chemistry at the Johns Hopkins University developed a laboratory method and ultimately an industrial process for the manufacture of silica, which was patented in 1919. The process was commercialized by the Silica Gel Corporation. However the credit for providing the theoretical basis for silica sol-gel research goes to Ralph

K.Iler whose first published book, *Colloidal chemistry of silica and silicates* gave a new spurt to research in this area [144]. As technical manager of Dupont, Iler also developed a large number of applications for colloidal silica. Starting from the flint weapons of the prehistoric caves to today's sophisticated microcircuit parts, silica has continued to play an important part in the development of world civilization [147].

1.9. Colloidal silica

Definition: According to the IUPAC, a colloidal dispersion is a system in which particles of colloid size (1-1000nm) of any nature (solid, liquid or gas are dispersed in a continuous phase of a different composition or state. In a restricted sense, the term colloidal silica is often used to refer to concentrated stable dispersions or sols and of discrete, dense particles of amorphous silicas of uniform particle size from about 5 to about 1500nm [148].

Stability and aggregation of colloidal silica: Colloidal systems have three types of stability [144].

i. Phase stability, analogous to the phase stability of ordinary solutions.
ii. Stability of disperse composition, that is stability with respect to change in dispersity.
iii. Aggregative stability, which is the most characteristic feature of colloidal systems.

In general, the term colloidally stable means that the particles do not aggregate at a significant rate [144].

1.10. Traditional modes of preparation of silica sol

Numerous methods such as dialysis, electrodialysis, peptization, acid neutralization and ion exchange have been proposed for manufacturing silica sol. Among these, the acid neutralization, ion exchange and peptization methods are considered to be the most important [149].

Acid neutralization method: An acid, such as sulfuric or hydrochloric acid, is added to a dilute aqueous solution of water glass while heating and stirring. The addition results in silica sol nucleation and particle growth to obtain a dilute silica sol containing salt. The salt is removed by either dialysis or electrodialysis, and the solution is concentrated to obtain a silica sol. In recent years, as the removal of salt has been made easier through the use of ultrafiltration membranes, this method is considered as having potential for the future [149].

Ion exchange method: Sophisticated ion-exchange resins have been developed to efficiently remove sodium ions at the industrial application level. This method is currently primary means of manufacturing silica sols [149].

Peptization method: An acid such as sulfuric or hydrochloric acid is added to a dilute aqueous solution of water glass while stirring, or while heating as necessary, to neutralize and obtain a silica gel containing salt.

Next, the crude silica gel is washed with water to remove the salt and obtain a wet silica gel. Then, water and an aqueous sodium hydroxide solution are added to the gel so that the pH of the resulting solution is 8.5-10 and silica gel slurry is formed. The slurry is then heated for several hours in an autoclave at 120C to 150C to allow the gel to peptize and form a sol [149]. The silica precursor is usually an aqueous water glass solution.

1.11. Sol-gel processing of silica

The sol-gel reaction, which involves the hydrolysis and condensation of metal oxides or alkoxide precursors, was discussed in Section 1.2. The structure of the polymers produced in the sol ultimately dictate both gel and glass properties. A number of variables such as pH, solvent, water to silicon ratio (W), and monomer influence this structural evolution [150]. These are discussed below.

Effect of pH on the hydrolysis and condensation reaction: Each of the steps, hydrolysis and condensation, in the sol-gel process are reversible. The hydrolysis reaction replaces alkoxide groups with hydroxyl groups, the reverse of which is esterification. The condensation reaction produces siloxane bond, the reverse of which is siloxane bond hydrolysis. The pH affects the reaction mechanism. In the hydrolysis reaction, acid catalysts protonate the alkoxide group and base catalysts dissociate water. In the condensation reaction, acidic silanols are deprotonated above pH 2. Below pH 2, weakly acidic silanols or ethoxides are protonated. The rate of siloxane bond hydrolysis increases above pH 4 and at very low pH. Several mechanisms have been put forward for the hydrolysis of $Si(OR)_4$ [151-154]. Computational chemistry simulation results by Elany and co-workers for the hydrolysis reaction of TEOS showed that a flank side attack mechanism involving a pentacoordinate silicon intermediate is favored under acidic, basic and neutral conditions [154].

Effect of pH and catalyst on gel times: The most widely studied and important reaction variables are pH and catalyst [150-155]. Studies on the catalytic effects on both hydrolysis and condensation have shown that gel times depend on the catalytic mechanism of the catalyst as well as the pH [155]. For example, sols catalyzed by HF and acetic acid have surprisingly short gel times, The gel times for the following catalysts are in the following order: HF< HOAc< HCl< HNO_3< H_2SO_4<NH_4OH< No catalyst [155].

Effect of precursor monomer on hydrolysis and condensation: The precursor monomer chosen affects hydrolysis rates and gel times [156-158]. By contrast to silicon alkoxides whose hydrolysis requires catalysts for effective gelation rates, hydrolysis of most metal alkoxides is rapid and can lead to uncontrolled precipitation. The electronegative alkoxide groups make the metal highly prone to nucleophilic attack by water. The more electrophilic metal centres as compared to Si as well as larger and more stereolabile coordination sphere result in a higher hydrolytic susceptibility. The following sequence of reactivity is usually found: Si << Sn ~ Ti < Zr ~

Ce. This order is dependent on the R group and a slightly different order of hydrolytic susceptibility, namely Al< Zr< Ti was reported for n-butoxides. Number, type and substitution of alkyl groups attached to the Si atom also affects its hydrolysis rates. Increasing the steric bulk of the alkoxy ligands decreases hydrolysis rates by about a factor of six on going from ethoxy to hexyloxy [157]. However, some additional factors may also come into play. For example, TMOS sols gel faster relative to TEOS (160 vs. 321 hr). This property is not entirely due to hydrolysis rates but also due to structural evolution of the sol [158]. 29 Si NMR spectroscopy show that TEOS derived sols grow through intermediates containing more compact, cyclic structures than TMOS sols. Thus TMOS polymers are more extended chain like structures that result in larger overlap of the polymers in solution and thus shorter gelation times [158].

Modification of the silicon monomer in the following ways helps to adjust the hydrolysis ratio, which enables one to control the extent of hydrolysis.

i. Changing the nature of the organic group R: Alkoxide with primary organic groups such as n-butoxides are less sensitive to hydrolysis than secondary one such as isopropoxides.

ii. Increase of the metal coordination: This hinders attack of water and formation of the metal hydroxyl bond, M-OH necessary for the development of the network).

iii. Decreasing the functionality of the precursor by partial substitution of the OR ligands such as carboxylates or β-diketonates: This produces M-Z bonds less susceptible to hydrolysis.

Differences in volume shrinkage, bulk density and surface area have been reported for gels derived from different monomers [158].

Effect of monomer concentration: One important parameter influencing the structural evolution of silicate polymers is the molecular separation of the reactive species [159-160]. For example, TEOS concentration strongly influences the size of the silicate polymers. The effect is modified by the amount of water present. Concentrating the reacting solutions results in significant polymer growth if silanols are present.

Effect of solvents: Solvent polarity plays an important role in sol-gel reactions [161]. The solvent's ability to solvate or hydrogen bond with available cations or anions greatly alters rates of reaction and particle size. It has been reported that increased viscosity and strong hydrogen bonding under both acidic and basic conditions reduces the hydrolysis rate [161].

Polymerization modes and structural evolution of silica sols: The possibility of producing uniform and reproducible ceramic microstructures through sol-gel techniques requires a better understanding of the processes of silica nucleation, growth and polymerization [162]. Classic silica aquasols 5-100 nm in particle size are prepared by nucleation, polymerization and growth in aqueous systems [162]. Monodisperse silica sols of particle size up to about 2-3 µm in size were first obtained by

Stober in an alcohol-ammonia system [163]. In an aqueous medium, three stages are recognized for the polymerization process.

Polymerization of monomers to form particles, growth of particles, and linking of particles into branched chains, networks and finally gels [162]. The polymerization process has been divided into three approximate pH domains- pH <2, 2-7 and >7 [162]. Gel times decrease steadily between pH 2 and 6. Polymerization is believed to occur through a bimolecular nucleophilic condensation mechanism involving the attack of hydrolyzed, anionic species on neutral species.

$$\equiv\mathrm{SiO^-} + \equiv\mathrm{Si\text{-}OH} \longrightarrow \equiv\mathrm{Si\text{-}O\text{-}Si}\equiv + \mathrm{H_2O}$$

The most acidic silanols are the most highly condensed species. A typical condensation pathway is therefore monomer, dimer, trimer, tetramer. Tetramers tend to cyclize because of proximity of chain ends. Further growth occurs by the aggregation of particles to form chains and networks. Above pH 7 particle growth occurs by a process known as ostwald ripening, a process by which smaller, more small particles dissolve and reprecipitate on larger, less soluble particles [162]. Below pH 2, condensation is believed to occur through a bimolecular nucleophilic mechanism involving a protonated silanol [162].

$$\equiv\mathrm{Si\text{-}OH_2^+} + \equiv\mathrm{Si\text{-}OH} \longrightarrow \equiv\mathrm{Si\text{-}O\text{-}Si}\equiv + \mathrm{H^+}$$

Si NMR spectra for aqueous silicate sols show an abundance of Q4 species. This suggests the presence of greater number of cyclic structures through internal condensation. For silicon alkoxide precursors, above the isoelectric point, condensation proceeds by nucleophilic attack of silanols followed by electrophilic attack. These reactions favor less highly condensed sites, because these are the most electron rich, and lead to more extended ramified structures. Thus one can see spherical particles in aqueous sols and ramified structures from TEOS or TMOS based species in alcoholic solution. It has also been shown that hydrolysis is enhanced under acidic conditions, but retarded under basic conditions, by methyl substitution of ethoxysilane derivatives. This result is important for the generation of organic-inorganic hybrid materials [164].

Gelation and aging: The gel point is defined as the time when an aggregate first appears [164]. For aqueous systems the formation of three dimensional gel networks below pH 7 or 7-10 are observed with salts present. Gelation is attributed to what is known as ballistic cluster-cluster aggregation [164]. Gelation in both aqueous and alkoxide derived sols is consistent with a percolative process involving cluster –cluster aggregates [164].

Aging: Aging is done in order to incorporate more of the reactants in the gel network and thus impart strength and stiffness [164]. Gels are often aged prior to drying in either the mother liquor or other liquid. The aging process comprises the following steps in order. Continued polymerization, syneresis, coarsening, phase separation, and in some cases, hydrolysis and esterification. Polymerization continues both between monomers or polymers and the spanning network, resulting in expulsion of liquid from the pores.

Drying: Drying is generally accomplished by evaporation to form a xerogel.

Factors leading to fracture of the gel surface: At the initial stages of drying, the gel is quite compliant and the network shrinks in response to this tension. However, shrinkage is accompanied by continued polymerization reactions within the network. As the network stiffens the capillary pressure increases. This results in a pressure gradient between the gel surface and its interior. As the pressure gradient increases, so does the variation in the free strain rate, with the surface tending to contract faster than the interior. The spatial variation in stress causes the stress that leads to fracture [164].

Strategies to slow down cracking: Several strategies reduce the tendencies of gels to crack during drying [165]. Very slow drying reduces the gradient in strain by allowing the surface and interior to shrink at comparable rates. Aging strengthens the network and in some cases increases the pore radius and so reduces the capillary pressure. The use of surfactants or so-called drying control chemical additives (DCCA) or, for example, replacement of water with alcohol reduces the pore fluid surface tension (or increases the contact angle), which also reduces the capillary pressure. Another process, called supercritical drying involves the extraction of solvent above its critical point and was first used by Prassas and Hench to produce large silica monoliths without cracking [166].

Characterization :The structures of dried gels are determined on the molecular, mesoscopic and macroscopic length scales by using a combination of solid state magic angle spinning (MAS), NMR, small angle x-ray diffraction spectroscopy (SAXS) and nitrogen adsorption-condensation [162]

1.11. Polymer-inorganic hybrid composites

Synthesis approaches used by the polymer chemist: The polymer chemist's objective is to improve or modulate mechanical, thermal or adhesion properties by incorporating an inorganic phase while still preserving a number of advantages due to the organic polymeric nature of the system (high flexibility, low density, etc.) [167].

Polymer-Inorganic or Polymer-ceramic synthetic chemists seek to combine, retain and enhance the best properties of both ceramic and polymeric materials. For example, high temperature resistance and hardness is a characteristic of ceramic materials. However, their use is limited in many applications because of their brittle nature. Polymers are characterized by elasticity and high impact strength. However, they have low heat resistance, low wear and scratch resistance and in some cases low dimensional stability. The sol-gel method allows the two phases to be combined in such a manner as to retain and enhance the properties of both, giving rise to a truly hybrid material. This is because composite properties are dependent on the nature of interfacial cohesion between the two phases. The sol-gel method helps to establish better interfacial force between the two components as compared to other methods [168]. As a result, phase separation can be controlled or minimized by controlling the reaction parameters. This results in the formation of composites that are optically transparent. The sol-gel process has been utilized to incorporate highly crosslinked networks into polymeric matrices [169-181]. The flexibility of the sol-gel method has allowed the incorporation of inorganic phase into almost every kind of polymeric system. A large number of polymeric matrices such as polyacrylates, polystyrene, polyoxazoline, polyimides, polyamides, polyetherketone, polyethyleneoxide, polybutadiene, epoxy resin, polyvinylalcohol, polyacrylonitrile, cellulose acetate, etc. have been used for the incorporation of an inorganic phase such as silica [182-210]. These composites have been classified as Class I or Class II hybrids depending on the presence or absence of a covalent bond between the polymer and inorganic phases [211]. Silica filled polymers are used in many commercial applications. The silica acts as a reinforcing agent, imparting increased hardness, compressive strength, heat distortion temperature, plateau modulus and lower thermal expansion coefficient to the polymer. Important factors in determining to what extent these properties are enhanced are filler concentration, shape and the adhesion between the silica and the organic polymer [181].

1.12. Reaction parameters affecting the bulk properties of polymer-in organic hybrid composites

The pH, solvent, water to alkoxide ratio, concentration, catalyst and temperature play an important role in the gelation process and in the structure of the final products [168-181]. A number of authors have discussed the effect of variation of such reaction parameters on the bulk properties of the composites. Huang and co-workers synthesized a hybrid material incorporating polydimethylsiloxane (PDMS) with TEOS [212]. They studied the effect of acid content, content of TEOS and the molecular weight of PDMS on the structure of such materials with the help of wide angle x-ray diffraction (WAXD), small angle x-ray scattering (SAXS), scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). The relative length of three periods, self-condensation of PDMS, co-condensation and self-condensation of TEOS, was found to determine the final structure of the hybrid material. The points of transition were found to be influenced by either the rate of TEOS hydrolysis and its self-condensation or the relative amount of the reactants. While the former was done by using different acid contents, the latter was varied by changing the composition ratio of TEOS to that of PDMS [212]. As the TEOS glass content increased, the network structure became more highly crosslinked. The tighter structure imposed restrictions on the chain mobilities. As a result, the Tg values shifted further to the right on the high temperature scale. The samples were found to exhibit higher brittleness with the increase of TEOS content. The authors found that an increase in acid content shortens the period of self-condensation of PDMS and results in a material with more dispersed oligomers. Consequently, the homogeneity and flexibility of the sample can be improved [212].

Landry and co-workers showed that the morphology and physical properties of a hybrid composite synthesized by the in-situ polymerization of TEOS in a PMMA binder were governed by the mode of sample preparation and the catalyst used to polymerize the TEOS [213]. Major differences were obtained when the polymerization of TEOS was carried out in different pH regimes. Dynamic mechanical analysis(DMA) and transmission electron microscopy (TEM) were used to investigate the properties of the composites. When TEOS was reacted under acidic conditions at elevated temperatures, small SiO_2 domains that are well dispersed in the PMMA matrix result, producing a composite material with a high plateau modulus above the Tg of the PMMA, which extends to at least 250C.

In another example, Sharp used formic acid as solvent, water source and catalyst for both hydrolytic and condensation reactions in the synthesis of hybrid materials from polyvinyl alcohol (PVA) and TEOS [214]. The polymer converted to flexible, amorphous, polyvinylformate. The hybrids were characterized by small angle x-ray spectroscopy (SAXS), NMR spectroscopy, transmission electron microscopy (TEM) and dynamic mechanical analysis (DMA). Formic acid was found to assist in the formation of continuous, load bearing networks [214].

1.13. Common characterization methods employed for analyzing Polymer-Inorganic hybrid composites

For Polymer-Inorganic hybrid composites, mechanical properties are commonly analysed with tensile tests, stress-strain behaviour, modulus of elasticity, Tg values and elongation at break. These may be carried out with the help of a tensile testing machine or dynamic mechanical analysis(DMA). Thermal properties are generally analysed with help of a thermogravimetric analysis (TGA) or differential Scanning calorimetry (DSC) [16].

Other techniques include solid state CPMAS (crossed polarized magic angle spectroscopy), ^{13}C and ^{29}SiNMR, light scattering, x-ray scattering and thermal mechanical analysis. ^{29}SiNMR is particularly useful for determining the average shape of the inorganic phase. It can be used to distinguish between ramified, elongated structure and dense particles. The degree of condensation within these particles is best evaluated by measuring percent Q4 species in their structure.

Thermal analysis can be used to help evaluate the degree of mixing between the two phases. Another thermal technique that can be used to probe structure at an even finer length scale is dynamic mechanical analysis (DMA) [215].

1.14. A few non-conventional sol-gel routes

Many modifications has been carried out to the conventional sol-gel method for getting better composite properties or for the synthesis of tailor made compounds. Some of these approaches seek to overcome some inherent drawbacks associated with the traditional route such as volume shrinkage during drying. Some of these are as follows.

Organic-inorganic hybrids through simultaneous processes

Non-shrinking sol-gel composites: Novak and co-workers developed non-shrinking sol-gel composites to circumvent the solubility limitations of preformed polymers and provide better homogeneity between the two phases [216]. In this approach the methoxide or ethoxide on the silicon orthoester precursors are replaced with polymerizable alkoxides. By employing in-situ organic polymerization catalysts, the alcohol liberated during the formation of the inorganic network is polymerized rather than being left to evaporate during the dying process [216].

ROMP (Ring opening polymerization) method: In another example, Novak and co-workers developed a method for the simultaneous formation of sol-gel nanocomposites by employing aqueous metathesis ring opening polymerization (ROMP) [216-217]. In aqueous ROMP, Ru++ and Ru+++ salts catalyse the ring opening addition polymerization of strained cyclic olefin monomers. The mild conditions required for aqueous ROMP and the reaction's tolerance for water and other functional groups make this polymerization reaction ideal for use with sol-gel technology.

Sol-gel synthesis in a reactive organic monomer medium: In this approach sol-gel condensation occurs in a reactive organic monomer rather than a polymer. The monomer is polymerized subsequently to, or concurrently with, the sol-gel reaction. Early work in this area was pioneered by Schmidt and co-workers, who synthesized TiO_2/SiO_2 nanocomposites containing polymethylmethacryalte (PMMA) by condensing TiO_2 from Ti $(OR)_4$ in a mixture containing a trialkoxysilyl epoxide compound [219]. Methyl methacrylate, a trialkoxysilyl functionalized methacrylate and a thermally activated radical initiator. In this approach the application of heat initiates the step growth condensation of the $Ti(OR)_4$ and simultaneously initiates radical chain polymerization of the acrylates to form PMMA [219]. During the sol-gel condensation, the epoxide compound is hydrolyzed to afford pendant hydroxyl groups, and the trialkoxy silyl groups of the methacrylate monomer become integrated into the TiO_2 framework. Thus the trialkxysilyl functionalized methacrylate serves as the crosslinking agent between the organic and inorganic domains. Incorporation of PMMA in the TiO_2 matrix yields materials that are stronger than materials without PMMA [219].

Synthesis of sol-gel composites in a crystalline polymer matrix: The sol-gel hybrid materials in conventional organic polymers and monomers produce amorphous materials. Gin and co-workers have recently demonstrated that highly ordered polymer-inorganic nanocomposites with hexagonal symmetry can be synthesized by performing sol-gel chemistry within a crosslinkable lyotropic crystal (LLC monomer assembly) [220]. In this assembly, the sol-gel precursor solution resides in close packed channels with uniform diameters of ~2 nm with surrounding matrix comprising of the polymerizable organic tails of the ampiphiles. Irradiation with UV light initiates radical crosslinking of the organic regions to lock in the nanoarchitecture. Simultaneously, the UV light generates free protons in the hydrophilic channels through the photoacid, catalyzing the condensation of the encapsulated $Si(OEt)_4$ into silica clusters [220].

The non-hydrolytic sol-gel route (NHSG): The first relevant report of NHSG modification by a silica network were reported by Andrianov et al in 1956 [221]. The non-hydrolytic sol-gel route has potential advantages for the synthesis of hydrophobic hybrids [222]. The non-hydrolytic route involves the reaction of a metal halide with an oxygen donor such as an alkoxide, an ether, an alcohol and so forth under nonaqueous conditions to form an inorganic oxide .The byproduct of this reaction is commonly an alkylhalide whose structure depends on the precise nature of the oxygen donor molecule. The electronic factors, which control the course of the non-hydrolytic sol-gel route, are different from the hydrolytic sol-gel process [222].

1.15. Objective of the present study

In the present work, synthesis of polymer-inorganic composites has been carried out by the sol-gel method with the objective of attaining improvement in the mechanical, thermal and other physical properties of the polymers by incorporation of a silica phase. The extent of improvement in these properties depends on the degree of compatibility between the two phases. This can be measured by observing the dispersion characteristics of the inorganic phase within the polymeric matrix. We have therefore carried out the synthesis work with the objective of getting good dispersivity of the inorganic phase within the polymer matrix. This was done by studying the effect of reaction parameters on the dispersivity and optimizing the synthesis conditions. Finally, the improvement in the polymer's properties was characterized.

The choice of silica as the inorganic phase has been made because many silica precursors are readily available. They also have a more controllable rate of hydrolysis which is advantageous for use with polymeric systems. The covalent Si-C bond is also very stable to hydrolysis. In addition literature on silica sol-gel chemistry is abundant.

In the synthesis of polymer-inorganic hybrid composites, the flexibility of the polymer matrix plays an important role in deciding the properties of the composite. A higher degree of interfacial cohesion between the polymer and inorganic phase is important as it brings about better compatibility between the two phases. Keeping the above aspects in view the following work plan has been made:

i. Optimization of reaction parameters such as pH, temperature, concentration and viscosity for the preparation of stable silica sol.

ii. Synthesis of Poly(vinylalcohol)/silica and Polyacrylamide/silica hybrid composites.

iii. Synthesis of silane functionalized Polystyrene/silica composites.

iv. Synthesis of polystyrene- butylacrylate/silica hybrid composites and silane functionalized polystyrene-butylacrylate /silica hybrid composites

v. Characterization of polymers by FTIR, NMR and GPC and composites by SEM, TEM, TGA, DSC etc.

vi. Comparison of results.

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CHAPTER 2

Synthesis of polyvinylalcohol (PVA)/ silica and polyacrylamide (PAA) /silica hybrid composites by the sol-gel method

2.1. Introduction

This chapter describes the synthesis of polymer-inorganic hybrid composites in which polyvinylalcohol (PAA) and polyacrylamide (PAA) were used as the polymer matrices and silica was used as the inorganic filler.

The major applications of polyvinylalcohol and polyacrylamide have mainly been due to their hydrogel behaviour, that is, the ability to adopt water insoluble, three dimensional, crosslinked structures possessing tissue like elasticity [1-7]. As these gels exhibit dramatic change in their structure by responding to environmental changes, they have been increasingly studied as vehicles for applications such as drug delivery, separation media, and the construction of sensors [8].

Poly(vinyl alcohol) (PVA) is recognized as one of the very few vinyl polymers soluble in water which is also susceptible to ultimate biodegradation in the presence of suitably acclimated microorganisms [9-15]. Accordingly, increasing attention is devoted to the preparation of environmentally compatible PVA based materials for a wide range of applications [16-25]. However, the applicability of hydrogels in many areas is limited by their poor strength and the high water content, which acts as a plasticizer. Therefore there have been attempts to improve the performance of hydrogels by physical or chemical crosslinking [26-27]. One such chemical method is the incorporation of inorganic fillers by the sol-gel method. The sol-gel method has been used to synthesize and combine bioactive glasses, compounds which bind spontaneously to living tissue, with polymers having hydrogel behavior such as PVA and polyacrylamide. For example polyacrylic acid and PMMA have been combined with hydroxyapatite to form bone cement [28-30]. The combination of such polymers with bioactive glasses improve their performance for load bearing applications. Pereira et al have reported the synthesis and reactivity of PVA/silica hybrids obtained via the sol-gel method [31]. The composites were prepared from PVA and tetraethyl orthosilicate (TEOS) with further modification of the inorganic phase with bioactive soda-lime phosphate silicate glasses [31]. The structure property relationships of a PVA/silica hybrid has been reported by Nakane et al which may have possible applications as water perm-selective membranes or immobilization carriers for a biocatalyst [32]. Hsu et al. [33] used PVA (average Mw 1.5×10^5), TEOS and a mixture of dimethyl sulfoxide (DMSO), water and alcohol to form the sol-gel mixture and Sharp et al. [34] used formic acid as a catalyst and solvent to form the sol-gel mixture from PVA and TEOS.

Of late, the choice of reagents and synthetic strategies have been based on those which are biocompatible and environment friendly (benign methods of synthesis) [35-45]. Synthesis in aqueous medium and the use of reactants which are potentially less harmful are being favored. For example, in the synthesis of PVA/silica composite materials for biological applications the use of sodium silicate is to be preferred over TEOS or TMOS because sodium silicate completely avoids the generation of alcohols [38]. Use of TEOS or TMOS as starting materials leads to the generation of methanol or ethanol, the presence of which in large quantities can be detrimental to the use of proteins and cells [41].

Keeping in view all the above aspects, the objective of the present study is to incorporate silica, inorganic filler, into polyvinylalcohol (PVA) and polyacrylamide (PAA) matrices to get composite materials with improved tensile strength and less water absorbance. Sodium silicate has been used as the silica precursor in view of the fact that it does not generate alcohol and can be used with water, a non-toxic and environment friendly solvent medium. The polymers PVA and polyacrylamide are also water-soluble.

The final bulk properties of the hybrid polymer-inorganic composites synthesized by the sol-gel method depend on the ability to generate homogeneous sol-gel mixtures [46]. The formation of homogeneous mixtures depends on the ability of the evolving silica structure to form a crosslinked network with the polymer matrix. This cannot be achieved if the hydrolysis and condensation (gelation) of the precursor inorganic monomer is very fast. Sodium silicate is not commonly used for the synthesis of hybrid composites with polymers because of its high rate of gelation. By an optimization of reaction parameters such as pH, temperature, concentration and viscosity we have tried to achieve convenient rates of gelation for sodium silicate, which enables the production of homogeneous sol-gel mixtures with the polymers.

The morphology of these polymer-inorganic hybrid composites have been observed under scanning electron microscopy (SEM) and the thermal, mechanical and other physical properties have been determined.

2.2. Experimental

Raw materials: Polyvinyl alcohol (PVA) $\overline{Mn}$: (14,000); degree of hydrolysis (98%); and HCl (S.d fine chem) were used without further purification. Sodium silicate (CDH chem) was purified by recrystallisation from water. Acrylamide (C.D.H fine Chem) was recrystallised from ethyl acetate.

Synthesis of Polyacrylamide (PAA): 35 g of acrylamide dissolved in 280 ml of distilled water was taken in a 500 ml three necked round bottomed flask fitted with a condenser, a nitrogen inlet and a stirrer. The reaction mixture was heated to 70C and 5 ml of Isopropyl alcohol was added along with 0.95 g of initiator, potassium persulfate. The reaction was continued for 5 hours and the product was precipitated in ethanol.

Yield 95 %, Inherent viscosity:0.35 dl/g.

Preparation of colloidally stable sol from sodium silicate solution: Sol-gel mixtures were prepared using sodium silicate, HCl (0.5N) and H_2O. Mole ratios of components are listed in Table 2.1. 0.5N HCl was added to the sodium silicate at 60C with constant stirring. The pH of the solutions was maintained between 1-2. The amount of catalyst (0.5 N HCl) was adjusted by noting the excess amount, which caused instantaneous gelation. The sol was then passed through a cation exchange resin amberlite for removal of Na^+ ions .

Preparation of sol-gel mixtures from polymers and sodium silicate: The mole ratios of PVA, sodium silicate, H_2O and HCl used for preparing the sol-gel mixtures are listed in Table 2.1. The mole ratios of PAA, sodium silicate, H_2O and HCl used for preparing the sol-gel mixtures are listed in Table 2.3. Sodium silicate solution was added with stirring to the polymer solution to form a homogenous mixture. Then the acid catalyst (0.5N HCl) was added slowly with stirring at a temperature of 60C. The solution was stirred at 60C for 30 minutes to carry out the in-situ acid hydrolysis of sodium silicate within the polymer solution. The pH of the mixtures was maintained between 1-2. The sol-gel mixture was then passed through the cation exchange resin amberlite for the removal of Na^+ ions.

Preparation of composite films from polymer/silica sol-gel mixtures: The sol-gel mixtures were poured into a glass tray and covered with a perforated polyethylene film to allow the system to gel. A perforated e film was used in order to reduce the rate of evaporation and hence avoid shrinkage of the gel. After 24 hours at ambient temperature, all the samples gelled and the film was removed to continue the drying process for another 48 hours at 47C.

2.3. Characterization

FTIR: IR spectra of the polymer, silica and composite films were taken with a FTIR spectrophotometer. (Model Impact 400, Nicolet, USA).

SEM analysis: Scanning electron micrographs were obtained using a scanning electron microscope (Jeol, Japan). The samples were coated with gold in a vacuum evaporator so as to provide an electrically conductive layer, minimize radiation damage and increase electron emission.

TEM analysis: TEM analysis was carried out in a JEM-100CXII (Jeol, Tokyo, Japan) instrument at an accelerating voltage of 80 kV. For TEM analysis equal volumes of the sample suspension and 0.2% uranyl acetate aqueous solution were mixed thoroughly. A drop of the mixture was placed on a formvar coated copper grid and the excess left to be dried.

TGA analysis: Thermogravimetric analysis was performed in a Mettler Toledo Star System in N_2 atmosphere at a heating rate of 10C per minute.

Tensile strength and elongation at break: The tensile strength and elongation at break of hybrid films were measured using a Universal Testing Instrument (Zwick, Model Z010), at room temperature (27C), using a crosshead speed of 4mm per minute. The sample dimension was approximately 60x20x 0.6mm (lxbxh) and the length between the clamps was 25mm. The measurements were carried out following the test specification ASTM- D 638-77.

Water uptake measurement: The relative rate of water absorption under saturated conditions was measured by immersing the dry films in distilled water, and then measuring the weight change until it became constant. Water absorption by the films under saturated conditions was measured by the method described in ASTM –D570 –81.

2.4. Results and Discussion

Preparation of sodium silicate sol by the acid hydrolysis method:

In the sol-gel condensation process, it has been shown that there are three modes of condensation, which affect the final structure of the sol-gel composites. The relative length of the three periods, self-condensation of the silica precursor, co-condensation of the silica precursor with the polymer and self-condensation among polymer end groups, can determine the final structure of the hybrid material [46].

In the present case also there are three possibilities of condensation—self-condensation of sodium silicate, co-condensation of silanol groups with the hydroxyl groups from PVA, and self condensation among the hydroxyl groups of PVA. Colloidally stable sols were prepared with the objective of lengthening the gelation time by decreasing the rate of self-condensation of silica. This in turn is expected to lead to an increase of the rate of co-condensation of silica within PVA matrix. If co-condensation is the dominant reaction and the entire system maintains homogenous during the process, it should lead to a more uniform structure [46]. On the other hand, domination of the self-condensation will most likely produce a system displaying either macro or micro phase separation of the polymer from the sodium silicate based species [46].

The acid hydrolysis method was used for sol preparation. Although there are many known routes towards the production of silica sols [47-49], we chose the acid hydrolysis method [47] because the acid has been reported to play a catalytic role in enhancing sol-gel condensation of silicon alkoxides within PVA matrix [45].

For getting homogeneous sol-gel mixtures from the inorganic precursor and the polymeric components our approach was to first control the gelation of sodium silicate sol. This was done by optimizing reaction parameters for the formation of colloidally stable sol from sodium silicate solution. The term colloidally stable implies that the sol particles do not aggregate at a significant rate [50].

Different concentrations of sodium silicate solution were taken (Table2.1). The acid catalyst (0.5N) was added at a temperature of 60C with continuous stirring of the solution. The point of instantaneous gelation was noted. The amount of acid catalyst added just prior to reaching this point was taken for the preparation of colloidally stable sol. Table 2.1 shows the mole ratios of sodium silicate, HCl and H_2O used for preparing colloidally stable sol. The table shows that the amount of acid catalyst (0.5NHCl) required to form the sol decreased with an increase in the concentration of sodium silicate. The reason may be attributed to the fact that aggregation of silica particles to form sol increases with an increase in the concentration. These colloidally stable sols were then allowed to undergo slow gelation. The onset of gelation was detected by observing a thickening in the reaction mixture.

Table 2.1. Concentration and mole ratio of reagants used for preparation of colloidally stable sol from sodium silicate solution

Sl	Conc. of 10 ml Sodium silicate (w/v %)	* Volume of 0.5N HCl (ml)	Mole ratio of sodium silicate :HCl :H_2O
1	3.5	30	0.016 : 0.014: 0.408
2	6	16	0.029: 0.008 : 0.237
3	10	10	0.048:0.004: 0.13

- The amount of HCl required to form colloidally stable sol

Preparation of sol-gel mixtures by the in-situ acid hydrolysis of silica solution within Polymers and composite films thereof: effect of acid content, polymer viscosity and silica content on morphological characteristics of Polymer/ silica hybrid composites

i. PVA/silica hybrids:

The reaction scheme in Fig.2.1 shows the sol-gel condensation for sodium silicate alone and in presence of PVA, and the possible nature of interphase bonding between the PVA and silica phase.

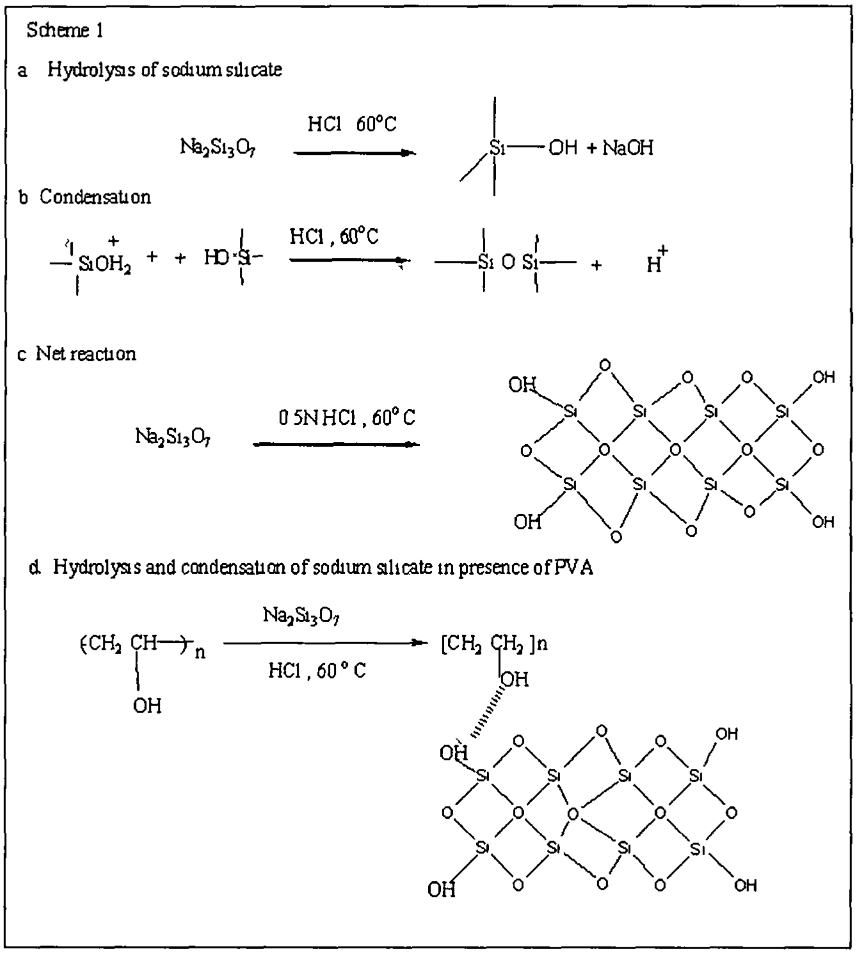


Fig 2 1 Hydrolysis and condensation of sodium silicate alone and in presence of PVA

Table 2 2 shows the mole ratios of PVA, sodium silicate, HCl and H_2O used for in-situ acid hydrolysis of sodium silicate within PVA

Table 2.2 : Mole ratio of reagants used for preparation of Polyvinyl alcohol /silica hybrid composites and their physical properties (silica content, tensile strength and elongation at break)

sn	sample code	Mole ratio PVA:Na silicate: HCl: H_2O	% silica calc	% silica obs	Tensile strength MPa	Elongation %
1	1	3x10^{3}0	0	0	3 75 ± 0 03	200
2	1a	3x10^{3}0 016 0 014 0 048	9 75	8	15 5 ± 0 15	225
3	1b	3x10^{3}0 029 0 008 0 237	16	15 5	20 ± 0 12	216
4	1c	3x10^{3}0 048 0 004 0 013	24	23	22 ± 0 15	210
5	2	4x10^{3}0	0	0	5 15 ± 0 05	205
6	2a	4x10^{3}0 016 0 014 0 048	6 6	6 6	25 2 ± 0 21	225
7	2b	4x10^{3}0 029 0 008 0 237	11 7	11	26 8 ± 0 51	220
8	2c	4x10^{3}0 048 0 004 0 013	18	18	28 8 ± 0 17	314
9	3	6x10^{3}0	0	0	7 0 0 ± 25	210
10	3a	6x10^{3}0 016 0 014 0 048	5 6	6	26 ± 0 2 4	215
11	3b	6x10^{3}0 029 0 008 0 237	9 9	10	28 ± 0 18	268
12	3c	6x10^{3}0 048 0 004 0 013	16 5	16	37 75 ±0 60	226

Series 1* -- Samples 1 , 1a, 1b, 1c prepared from 75 ml of 6% PVA (w/v)
Series 2*-- Samples 2, 2a, 2b, 2c prepared from 75 ml of 8.56 % PVA (w/v)
Series 3 *-- Samples 3, 3a, 3b, 3c prepared from 75 ml of 11.5% PVA.

Samples 1a, 1b, 1c are made from 6% PVA solution (w/v) (Series1), Samples 2a, 2b, 2c are made from 8 56% PVA solution (w/v) (Series 2) and samples 3a, 3b and 3c are made from 11.5% PVA solution (w/v) (Series 3). Comparison of Table2.1 and Table 2.2 shows that the mole ratio of the components sodium silicate, HCl and water in the sol-gel reaction for a particular silicate concentration remained unaltered in presence of PVA.

Evidently, the presence of PVA in the mixture does not create any drastic change in reaction conditions for the hydrolysis and condensation of sodium silicate. However, the polymer concentration and viscosity was found to significantly affect the tendency of co-condensation of silica within PVA. It appears that when the PVA concentration (and hence viscosity) is lower, the silica has a higher tendency to undergo self-condensation reaction. At intermediate PVA concentration, co-condensation is favored while at higher concentration self-condensation again becomes the dominant reaction. This was concluded from a study of the SEM micrographs of the composites, shown for three compositions (Fig. 2.2a, 2.2b and 2.2c). Fig.2.1a shows SEM micrograph of composite prepared from sample 1c (mole ratio 0.0003 PVA: 0.048 sodium silicate: 0.004 HCl: 0.13 H_2O). Large scale aggregation of silica particles is visible from this photograph. Fig. 2.2b shows the SEM micrograph of composite prepared from sample 2c (mole ratio 0.0004 PVA: 0.048 sodium silicate: 0.004 HCl: 0.13 H_2O). In this case there is no large scale aggregation of silica particles and the pattern of dispersion is more uniform. The SEM micrograph in Fig.2.2b shows spherical or disc shaped silica. This may be due to the effect of the catalyst, which not only has a kinetic effect on the hydrolysis and condensation reactions but also modifies the network structure. In acidic conditions, low branched species are formed leading to opened structures. These reactions favor less highly condensed sites, because these are the most highly electron rich, and lead to more highly extended ramified structures. The explanation for spherical or disc shaped silica may be that the extended ramified structure of silicic acid adopts a spherical configuration in acidic media. Such a mechanism has been reported by Christine J.T Landry et al [51]. In acidic media, the individual spheres are small and not densely crosslinked. The observed disc shaped morphologies of the SiO_2 domains might be due to collapse of the silicic acid polymer chains during shrinkage [52]. In such a case, high temperature curing should further densify the SiO_2 network. Such an effect was observed in practice when conducting experiments for water uptake and thermal analysis. Fig. 2.2c shows the SEM micrograph of the composite prepared from sample 3c (0.0006 PVA: 0.048 sodium silicate: 0.004 HCl: 0.13 H_2O), which again shows a clustering of silica particles in the PVA matrix. It is believed that the co-condensation mechanism involves interaction between the hydroxy groups of PVA and the hydroxy groups of silanol from hydrolyzed silica. At low PVA concentration, the number of hydroxy groups from PVA is low and therefore the condensation mechanism primarily involves linkages between the hydroxy groups from silanol. At intermediate concentrations of PVA, the number of hydroxy groups is sufficiently large to allow for a co-condensation mechanism and therefore we get homogenous sol-gel dispersions and uniformly dispersed silica. At higher concentrations of PVA (higher than 10%) self- condensation and co-condensation seem to proceed at equal rates because hydroxy groups from PVA might show an increasing tendency to form linkages among themselves. It is also an indirect observation from the above that the formation of colloidally stable sol enhances co-condensation. The amount of acid catalyst used plays a significant role in this. Homogeneous sol-gel mixtures could not be formed beyond 11.5% PVA concentration (w/v) because the higher viscosity of PVA resisted mixing with the inorganic component and resulted in lump formation. The concentration of PVA and sodium silicate used in the sol-gel mixtures was crucial in determining the maximum amount of silica that could be incorporated to give flexible and transparent composites. The silica content in the hybrids was obtained from thermogravimetric analysis. It was observed that with 6% PVA (w/v) the maximum value of incorporated silica giving transparent and flexible composites was 23% w/w (Table2.2, Sample1c) but with 11.5% PVA (w/v) the maximum value of silica incorporated was 16%(w/w) (Table 2.2, sample 3c). Transparent and flexible hybrid materials of homogenous thickness were obtained for all the samples listed in Table 2.2. The maximum value of incorporated silica was, however found to be lower than that reported for PVA/silica composites synthesized from TEOS as silica source [32].

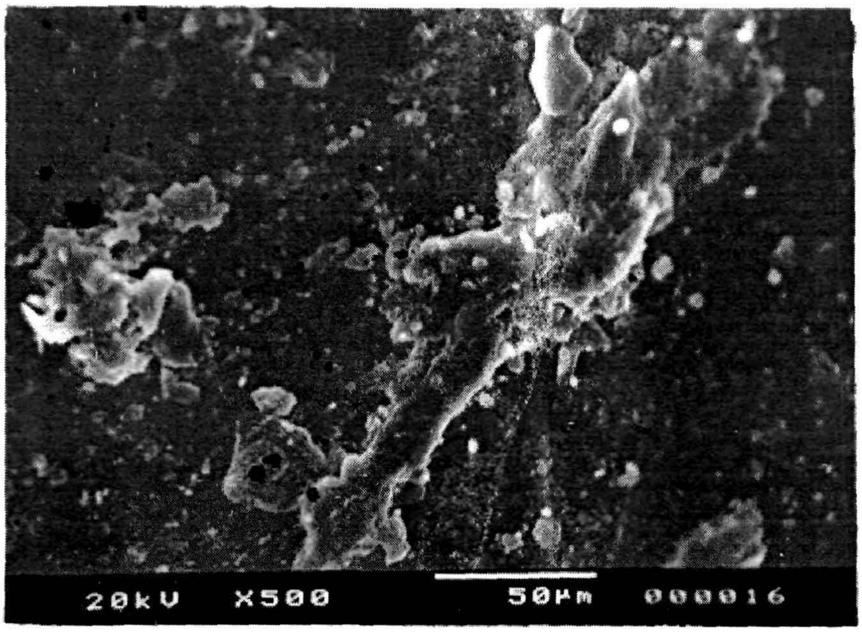


Fig.2.2a .SEM micrograph of the composite derived from sample 1c (0.0003 PVA: 0.048 Sodium silicate: 0.004 HCl: $0.13H_2O$)

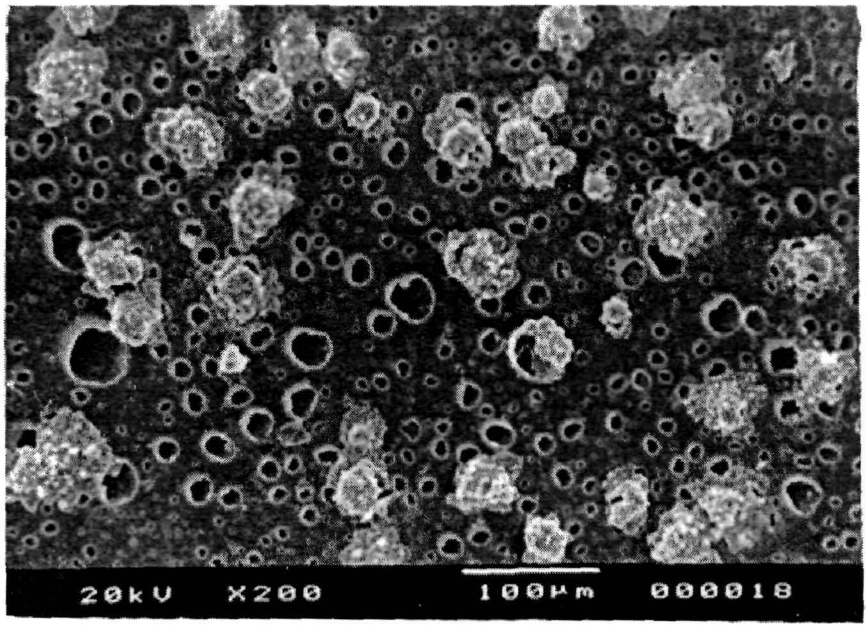


Fig.2.2b. SEM micrograph of the composite derived from sample 2c (0.0004 PVA: 0.048 Sodium silicate: 0.004 HCl: 0.13 H_2O)

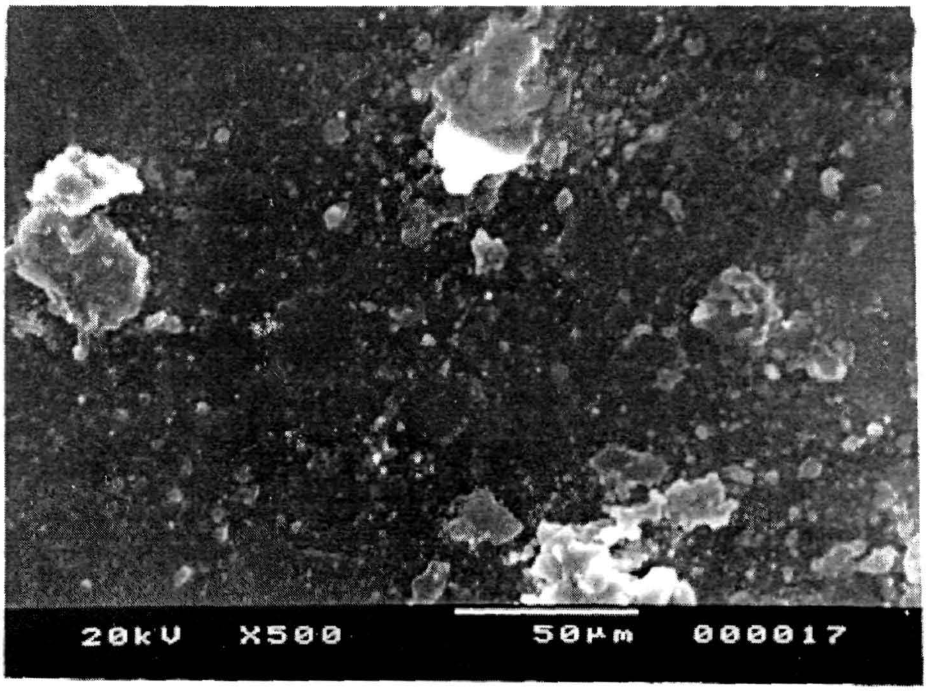
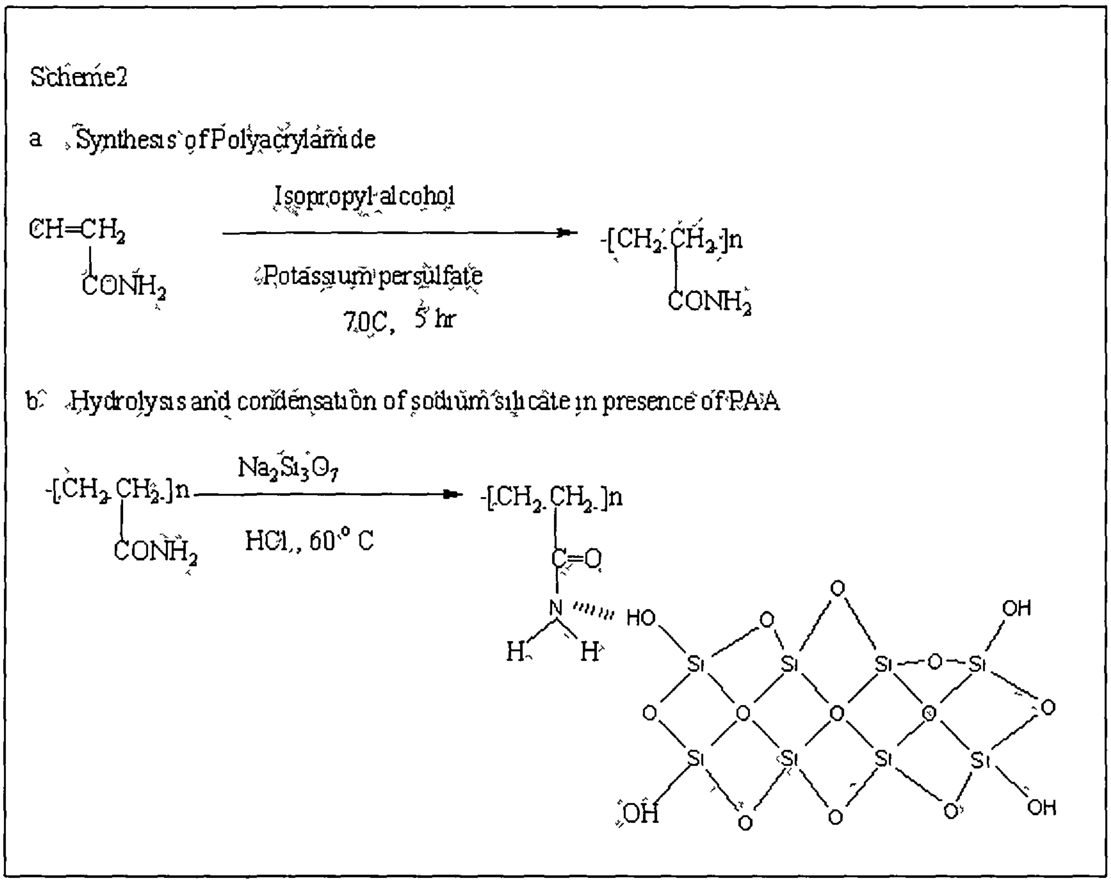


Fig. 2.2c. SEM micrograph of the composite derived from sample 3c (0.0006 PVA: 0.048 Sodium silicate: 0.004 HCl: 0.13 H_2O)

b. **Polyacrylamide (PAA) /silica hybrid composites:** The reaction scheme in Fig.2.3 shows possible nature of interphase bonding between silica network and PAA. Table 2.3 shows the mole ratio of reagents for the in-situ hydrolysis of sodium silicate within PAA.

Table 2.3. Composition of the sol-gel mixtures for composite synthesis from PAA and sodium silicate

SL	Mole ratio PAA: Na silicate: HCl: H_2O	% silica calc.	% silica obs
1	0.0104: 1.55×10^{-3}:0.408:0.972	3.5	3.3
2	0.0104: 2.29×10^{-3}:0.347:0.972	5	5.3
3	0.0104: 2.75×10^{-3}:0. 223:0.972	6	5.8
4	0.0104: 3.66×10^{-3}:0.166:0.972	8	8.1
5	0.0104: 4.58×10^{-3}:0.138:0.972	10	10


Scheme2

a. Synthesis of Polyacrylamide

b. Hydrolysis and condensation of sodium silicate in presence of PAA

Fig. 2.3. Synthesis of PAA and sol-gel condensation of sodium silicate in presence of PAA

The SEM micrographs for the PAA/silica composites are shown in Fig 2.4a, 2.4b and 2.4c The SEM micrographs for the composite 3.4% silica in 10% PAA [Fig.2.4a] shows a densely crosslinked silica phase, which is evenly distributed in the polymer matrix. At higher concentrations of silica, [Fig. 2.4b (6% silica in 10% (w/v) PAA) and Fig. 2.4c (10% silica in 10% PAA (w/v))], the silica particles grow in size but the mode of distribution remains even. Such dense structures are obtained when the rate of condensation of silanol groups is faster than the rate of hydrolysis of the precursor solution[52]

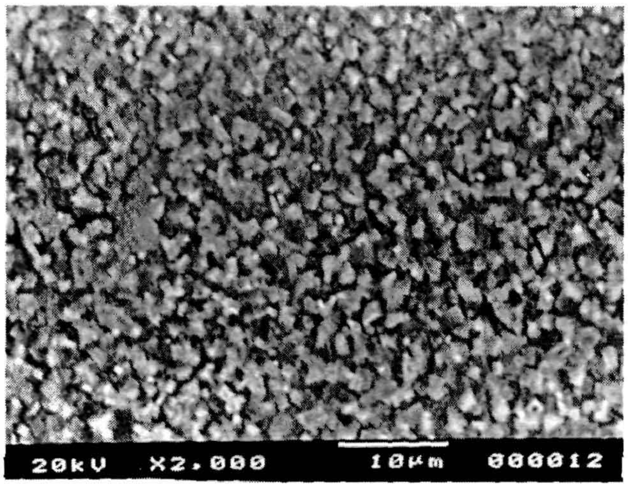


Fig. 2.4a SEM micrograph for the composition 0.0104 PAA: 2.75x10-3Na silicate: 0.223 HCl:0.972 H2O

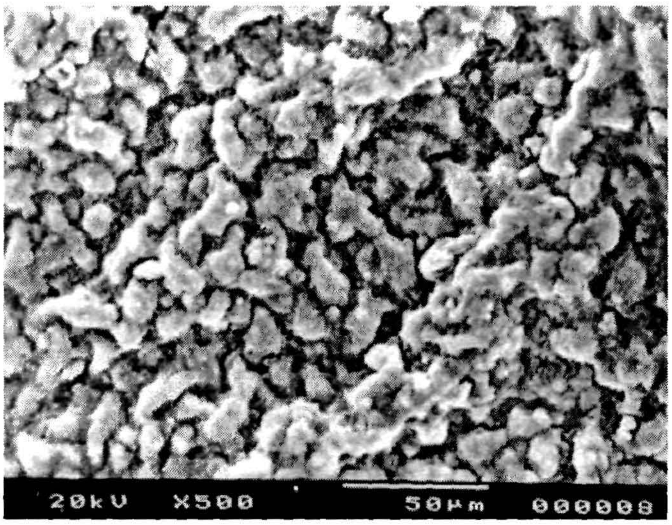


Fig. 2.4b SEM micrograph for the composition 0.014PAA: 3.66x10-3 Na silicate:0.166 HCl: 0.972 H20

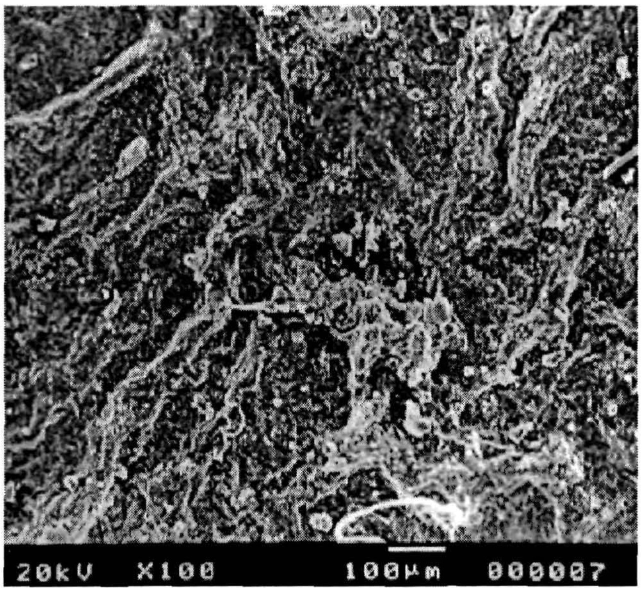


Fig.. 2.4c .0.0104PAA:4.58x10-3Na silicate:0.138 HCl:0.0972H2O

Fig. 2.4d .0.0104PAA:4.58x10-3Na silicate:0.138 HCl:0.0972H2O

Acrylamide groups from PAA in aqueous solution increases the pH of the PAA/silica system. An increase in the pH of the medium favors the condensation reaction relative to the hydrolysis reaction [52-55].

Strong hydrogen bonding of the growing silica phase with the solvent also favors a higher rate of condensation [56]. The TEM micrograph of the PAA/silica sol-gel mixture shows the silica particle to be spherical in shape [Fig.2.4d].

It is possible to study the mode of distribution of silica particles using small angle x-ray spectroscopy (SAXS). The degree of condensation of the silica particle (percent Q4 species) can be studied by SiNMR. We were unable to report these data because of lack of access to these facilities.

The nature of interphase bonding

FTIR analysis: Fig. 2.5 shows the IR spectra for PVA (curve a), silica (curve b) and PVA/silica composites (curve c). The stretching frequency range of the Si-O-Si group is~1063 cm^{-1} [57]. The hybrid composite shows a broadened band in the region 1052-1100 cm^{-1} which might be ascribed to Si-O-Si linkages in the network (curve c). The hydroxy stretching frequency of pure PVA appears in the range 3440-3500 cm^{-1} [58]. The hydroxy stretching frequency in the PVA/silica hybrid shows a broadening (curve c) in comparison to the hydroxy stretching frequency of pure PVA (curve a). The broadening might be due to hydrogen bonding between the pendant hydroxy groups from the PVA chains and hydroxy groups from silanol ends of the silica network (Scheme2d). It has been reported that hydrogen bonded silanols show a broad absorption around 3530 cm^{-1}. It may be possible that the silicate network is linked with the polymer chain by hydrogen bonds [32]. The terminal vinyl groups of the PVA which appear at 1955 cm^{-1} (curve a) disappear in the PVA/silica composite (curve c), which suggests that these bonds might be involved in crosslinking with silica.

The polyacrylamide/silica composite shows a band at 1095 cm^{-1} due to Si-O-Si stretching and another at 3440 cm-1 due to NH_2 stretching.

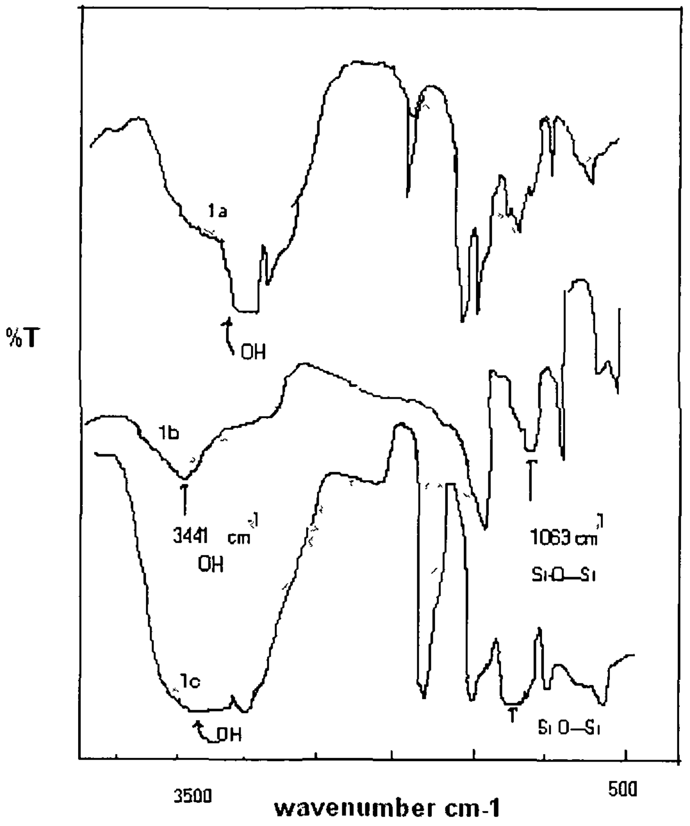


Fig.2.5. FTIR spectra of PVA(1a), silica(1b) and PVA/silica composite(1c)

Measurement of tensile strength and elongation at break: Table 2.2 lists the values of tensile strength and percent elongation at break for the various samples. The tensile strength increased with silica content for samples 1a, 1b, 1c (Series1), 2a, 2b, 2c (Series 2) and 3a, 3b, 3c (Series 3). But the percent elongation at break generally decreased at higher silica content. This is a typical mechanical behavior of polymer/ silica hybrid composites, which possess microsize fillers in the polymer matrix [59]. Nakane et al [32] have also reported this trend for PVA/silica hybrid materials synthesized using TEOS as silica source. Sample 2c records the highest value of percent elongation at break in Series 2 although it has a higher value of silica content than 2a and 2b. This may be due to strong interaction between polymer and silica, which arises from the higher rate of co-condensation in this composition and results in a higher uniformity in microlevel dispersion of silica particles.

Measurement of Water uptake: Water uptake percentage is a measure of the hydrophilicity of the PVA composites. The hydrophilic nature of PVA is due to the large number of hydroxyl groups available for hydrogen bonding with water molecules. Fig. 2.6 shows the extent of water absorption in the hybrid films as a function of silica percentage. The graphs show that there is a considerable decrease in the water absorption in the films, which contain silica. The decrease in water uptake is proportional to the increase in silica content. The decrease in water uptake suggests that the number of hydroxyl groups available for hydrogen bonding with water molecules decreased because of their involvement with the silanol groups from the hydrolyzed silica precursor. Water uptake experiments were repeated after heating the hybrid samples at 60^0C for another 24 hours. It was observed that swelling in water further decreased after heat treatment It has been suggested that samples heat treated at higher temperatures have a denser inorganic network due to condensation reactions between residual Si-OH groups. These more rigid structures restrict dilation of the hybrid network [31]. Pereira et al [31] and Nakane et al [32] who investigated the rate of hydrolysis for PVA/silica hybrid materials have also reported that the solubility and degree of swelling in water decreased linearly with silica content in the composites. This implied that materials with controllable hydrolysis could be synthesized by controlling the silica content in the composites. Possible applications of this behaviour could be as water perm selective membranes or as immobilization carriers for biocatalyst [32].

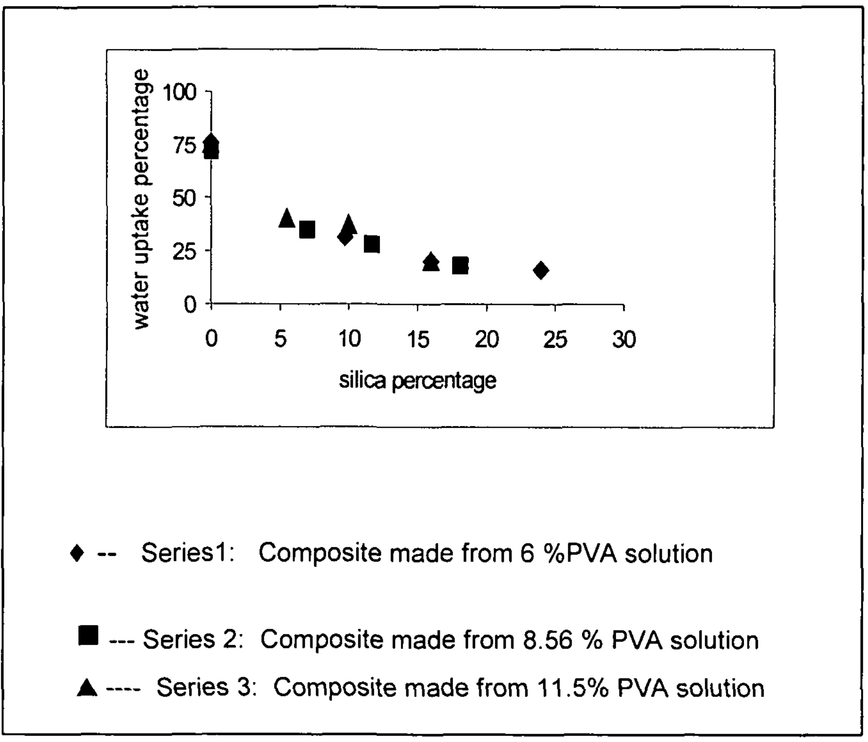


Fig.2.6 Water uptake percentage as a function of silica percentage for PVA/silica hybrid

The water uptake experiments for Polyacrylamide/silica composites also showed a similar decrease in water uptake with an increase in the silica content in the composites.

TGA analysis: TGA curves are shown for PVA and PVA/silica composite in Fig.2.5 The TGA curves show that show that there is an increase in the thermal stability of the PVA/silica composites in comparison to the virgin polymer. The initial decomposition temperature for PVA is at 235°C but for the composites degradation starts at around 310°C. The enhancement in thermal stability for the composites suggests that thermal motion of PVA chain was prevented due to crosslinking with the silica network.

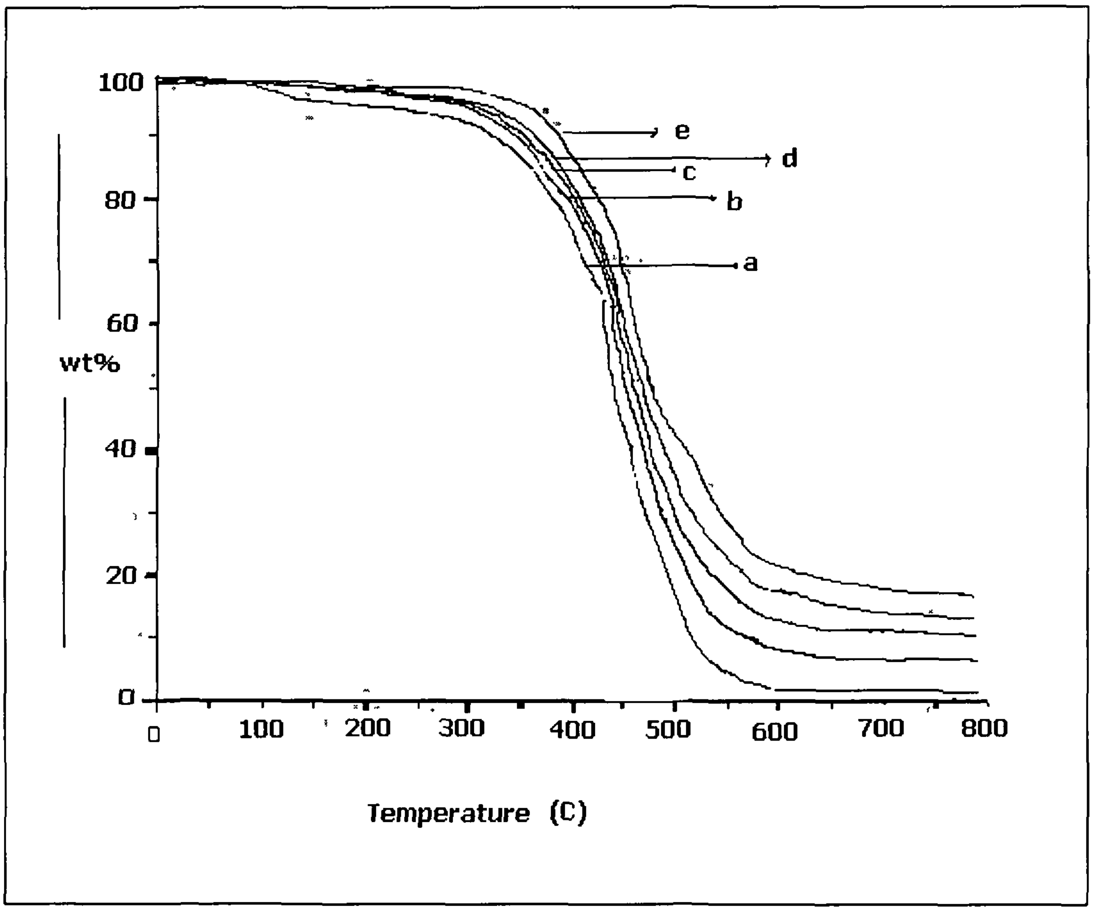


Fig.2.7. TGA curves for PVA (curve a) and for the PVA/silica composites (b, c, d and e)

The TGA curves for the polyacrylamide/silica composite materials also showed a similar enhancement in thermal stability with increase in silica content in the composite materials [Fig.2.8]

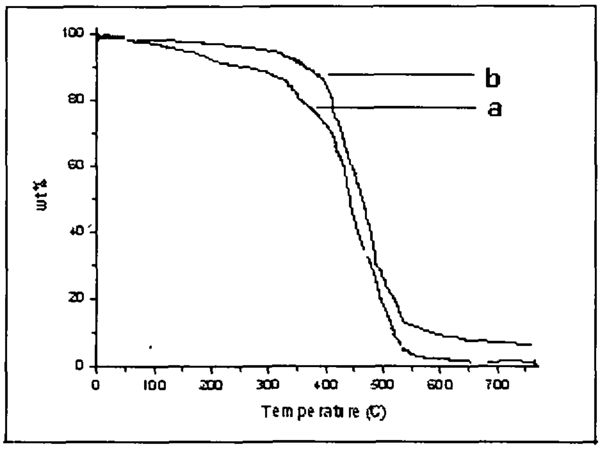


Fig.2.8. TGA curves forPAA(a) and PAA/silica composite(b)

2.5. Conclusion

The results of this chapter show that in the synthesis of PVA/silica hybrid composites, the concentration of PVA and sodium silicate used in the sol-gel mixtures were crucial in determining the maximum amount of silica that could be incorporated in the PVA matrices while retaining the flexibility and transparency in the composites. With 6% PVA (w/v), a maximum of 23% silica could be incorporated but with 11.5% PVA (w/v), a maximum of 16% silica could be incorporated.

Scanning electron microscopy (SEM) showed that for the PVA/silica composites, the dispersion characteristics are affected by viscosity of the sol-gel mixture and concentration of silica in mixture. The dispersion characteristics affect the bulk properties. For example, the elongation at break is maximum for the PVA/silica composition in which there was no large scale aggregation of silica particles (18% silica dispersed in 8.5% PVA (w/v). The tensile strength was found to increase with an increase in the silica content. The maximum value of tensile strength (37.75Mpa) was obtained for the composition 16% silica in 11.5% (w/v) PVA.

For the PAA/silica composites, the SEM micrographs showed the silica to be distributed in an even manner throughout the PAA matrix. With an increase in the silica content in the composites, there is a growth and densification of silica particles within the matrix. This is in contrast to the dispersion of silica within the PVA matrix where a random distribution of lumps or aggregates is observed. This is due to a difference in the mode of structural evolution of the silica sol within the PAA and PVA matrices.

The thermal stability of the hybrid composites PVA/silica and PAA/silica are found to increase with an increase in the silica content in the hybrids and the water uptake is found to decrease with an increase in the silica content.

The formation of colloidally stable sol through optimization of reaction parameters helped attain better properties in the composites.

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CHAPTER 3

Synthesis of Polystyrene/ silica hybrid composites by the sol-gel method

3.1 Introduction

This chapter describes the synthesis of sol-gel hybrid composites where polystyrene and copolymers of styrene with methylvinyldichlorosilane (MVS) were used as the matrix for the synthesis of hybrid organic - inorganic composites through the in-situ acid hydrolysis of tetraethylorthosilicate (TEOS) in toluene.

In the synthesis of hybrid organic-inorganic composites using the sol-gel method, the interfacial force between the organic and inorganic phases plays a major role in controlling the microstructure and properties of the composite materials [1]. Two approaches are normally utilized to establish the interfacial force. The first approach is the formation of hydrogen-bond between the basic group of the H-acceptor in polymer and the silanol group (Si-OH) of the intermediate species from $Si(OR)_4$. Such bonding is most common with polymers having groups capable of forming hydrogen bonds such as the polyamides and the polyurethanes [2-5]. The second approach is the formation of a covalent bond between polymer and silica [6-7] .Huang et al have reported the synthesis and properties of hybrid organic inorganic composite materials obtained from the in-situ sol-gel method by taking trialkoxysilyl functionalised acrylic polymers as the polymer matrix [8] .The use of glycidyl-propyl trimethoxysilane as a coupling agent to compatibilize tetraethoxysilane with polyamic acids has also been reported [9]. In vinyl polymers such as polystyrene, the formation of hydrogen bond to assist interfacial cohesion is ruled out. The modification of vinyl monomers such as methylmethacrylate, acrylonitrile and styrene by copolymerisation with 3-trialkoxysilyl propyl methacrylate has been reported by Wang et al [10]. Polystyrene based resins have been used as solid phase catalysts, polymer supports for organic synthesis, absorption and separation of chemicals [11-12]. Polystyrene/silica hollow spheres, synthesized by performing sol-gel polycondensation within a surfactant stabilized emulsion of a solution of polystyrene in tetraethyl orthosilicate were found to be good carriers for entrapped dye molecules[11]. Non-porous hybrid styrene-divinylbenzene silica composites were recently developed as an encapsulated silica stationary phase for chromatographic application [12].

In this chapter we have reported the use of a copolymer of styrene with methyl vinyldichlorosilane(MVS) for getting homogenous dispersions with silica by the in-situ sol-gel method.Tetraethyl orthosilicate (TEOS) was used as the source of the inorganic silica used for the synthesis of the hybrid organic-inorganic composites. The polystyrene/silica hybrid composites were prepared by in-situ hydrolysis of TEOS within the silane functionalized polystyrene matrices. It is expected that the condensation of the Si-OH of TEOS and the Si-OH of silane functionalised polystyrene would help in uniformly dispersing silica within the polymer matrix. The ratio of the silylating monomer, methylvinyldichlorosilane (MVS), and the comonomer styrene, was varied. The effect of this variation in enhancing the uniformity of dispersion of silica within polymer matrix, morphology and thermal behavior of the composites have been studied.

3.2 Experimental

Raw materials:

Tetraethylorthosilicate(TEOS)(Merck-Schuchardt.), methylvinyldichlorosilane (Fluka), benzoyl peroxide(S.d fine chem) were used as received. Styrene (Merck-Schuchardt) was purified by removing inhibitor with sodium hydroxide solution followed by drying over molecular sieves.

Synthesis of polystyrene:

15 ml of styrene was polymerized in bulk in a three necked round bottomed flask fitted with a condenser, a nitrogen inlet, and a guard tube. 0.15g of initiator benzoyl peroxide was added at 60C and then the temperature was raised to 75C. Reaction was completed by stirring the mixture at 75C for a period of three hours. The polymer was precipitated in

cold ethanol. It was then purified by dissolving in tetrahydrofuran and then reprecipitating in ethanol. Yield: 95%

Synthesis of silane functionalised copolymers of styrene and methyl vinyl dichlorosilane (PSMVS):

The copolymers (PSMVS) were prepared by changing the proportion of monomers. One typical reaction is given below: 15ml of styrene and 40ml of benzene were taken together in a three necked flask fitted with a condenser, a guard tube, a mechanical stirrer and a nitrogen inlet. Then 0.5 ml of methylvinyldichlorosilane (MVS) was added dropwise with constant stirring. The temperature was raised to 70C and 0.15 g of the initiator benzoyl peroxide was added. The polymerization was continued at a temperature of 70C over a period of three hours. The copolymer (PSMVS) was precipitated in cold ethanol and purified by dissolving in tetrahydrofuran and reprecipitation in ethanol. The composition of the reaction mixture was varied by changing the ratio of styrene to methylvinyldichlorosilane.

Yield: 95%

Preparation of the stable silica sol from tetraethylorthosilicate (TEOS) solution in toluene:

2.5%, 5%, 7% and 8% of TEOS solution in toluene were prepared separately. 1ml of each concentration of TEOS was taken in the stoppered conical flask separately and the catalyst, 0.5 N HCl was added at 60 C with constant stirring over a period of thirty minutes. The amount of HCl was adjusted by noting the excess amount which caused instantaneous gelation. Molar proportions of the mixtures are listed in Table3.2.

Preparation of sol-gel mixture from polystyrene (PS) / copolymer of styrene(PS MVS) and TEOS

TEOS solution in toluene was added to the solutions of polymer/copolymer and 0.5N acid catalyst was added to bring about the in-situ hydrolysis of TEOS within the polymer/copolymer matrices.The molar proportions of the sol-gel mixtures are listed in Table3.3. .

Composite films from the sol-gel mixtures :

The sol-gel mixtures were cast onto glass plates and allowed to dry at 30°C for 72 hours. The composition, appearance and morphological characteristics of the composite materials are listed in Table 3.2. The optical transparency can be used as an initial criterion for the formation of a homogeneous phase of both inorganic and organic constituents. When macroscopic phase separation occurs, products look opaque because the large domain size in the inorganic oxide causes light scattering in the system [3].These composite films were analysed by FTIR, SEM, TGA and DSC .

3.3. Characterization

FTIR: The dried composite films cast over glass plate were used for spectroscopic analysis. The IR spectra were recorded in a FTIR spectrophotometer (Nicolet USA, Impact 401)

SEM analysis:The samples for scanning electron microscopy were prepared in the form of thin film on glass plates. The samples were kept in a dessicator for two hours and then coated with gold. The tests were conducted by using a scanning electron microscope (Jeol, Japan). The magnification and acceleration voltages varied from 20 kV × 150 to 20 kV× 1000.

NMR analysis: 1HNMR analysis was carried out in a 400 MHz Brucker NMR spectrometer using $CDCl_3$ as solvent.

GPC analysis: GPC analysis for the copolymers were carried out using GPC (Water, USA, Model 515) solvent delivery system at a flow rate of 1 ml/min through a set of three ultrastyregel columns. Analysis was done at controlled temperature at 45°C using HPLC grade tetrahydrofuran (THF) as eluent.

Viscosity: The viscosity of a 0.5% solution in THF was measured using Ubbelohde viscometer at 30^0 C and reported in terms of inherent viscosity η = (ln $t/t_0)/$ c dl g^{-1}. where 't_o' is the time taken by the solvent THF and ' t 'is the time taken by the solution and c is the concentration of the polymer solution.

TGA analysis: TGA analysis for the copolymer and composites were carried out in a PYRIS1 thermogravimetric analyzer (Shelton, USA) in nitrogen atmosphere at a heating rate of 10C per minute within a temperature range of 50C to 700C.

DSC analysis: DSC analysis for the copolymers and composite samples were carried out using a Diamond DSC instrument (Perkin Elmer, USA). The samples were preheated at 40C and the analysis was carried out in nitrogen atmosphere at a heating rate of 10C per minute within a temperature range of 70C to 300C.

Water uptake experiment: The relative rate of water absorption under saturated conditions was measured by initially drying the films in a vaccum oven at 50 C for 12 hours, immersing the films in distilled water, and then measuring the weight change until it became constant. Water absorption by the films under saturated conditions was measured following procedure in ASTM-D570-81.

3.4. RESULTS AND DISCUSSION

Synthesis of polystyrene (PS) and copolymers (PSMVS) of styrene with methylvinyldichloro silane (MVS):

Copolymers were synthesised from styrene and methylvinyldichlorosilane (MVS) using the molar ratios listed in Table3.1. The Molecular weight and inherent viscosities are listed in Table 3.1.

Table 3.1. Synthesis of polystyrene(PS) and copolymers of styrene with MVS(PSMVS)

SL	polymer/ copolymer	styrene: mvs molar ratio	$\overline{Mn}$ g/mole	inherent viscosity of 0.5% soln in CHCl3 dl/g
1	PS	15	~70, 000	0.38
2	PSMVSA	0.129:0.0025	~50, 000	0.58
3	PSMVSB	0.129:0.005	~63, 000	1.11
4	PSMVSC	0.129:0.100	~35,000	0.5

Initiator (Benzoyl peroxide) for samples 1-3 was 0.15g and for sample 4 was 0.05g
Temperature: 75-80C, Time: 3-5 hrs

The molecular weight($\overline{Mn}$) values for PSMVSA and PSMVSB are around 50,000 and 63,000. PSMVSC was synthesised by lowering the initiator concentration and has a Mn value around 35,000. This was done in order to study the effect of molecular weight on the composites. The films obtained by casting the copolymers PSMVSA and PSMVSB were found to be less brittle than polystyrene. The structure of the copolymers is shown in Fig.3.1. Polystyrene (PS) and its copolymers PSMVSA and PSMVSB were characterized by FTIR and NMR. The FTIR spectrum of polystyrene, shown in Fig.3.2,(curve a) is characterized by an intense peak at 1490cm^{-1} (alkene CH_2 bending), 765 cm^{-1} (aromatic C-H bending), 2929

cm^{-1}(aromatic C-H stretching) [13].The copolymer PSMVS A shows a sharp band at 1267 cm^{-1}[Fig 3.2, curve b], while PSMVS B shows this band at 1265cm^{-1}[Fig. 3.2, curve c]. This band is due to the CH_3 symmetric deformation of Si-CH_3 group [14]. There is an intense band at 540cm^{-1} for the copolymers and this is due to $SiCl_2$ group vibration . Therefore FTIR reveals the incorporation of the silane functionality into the polystyrene backbone. ^1H NMR [Fig.3.3] (δ , ppm,$CDCl_3$) for PSMVSA shows δ values at 7.48 , 7.41 , 7.34 , 7.25 and 7.1 due to the five aromatic protons and δ values at 6.59, 1.45, 1.86 and 1.27 due to four different proton environments which may be ascribed to the copolymer structure shown in the Fig.3.1. The 1HNMR therefore provides evidence for incorporation of silane functionality.

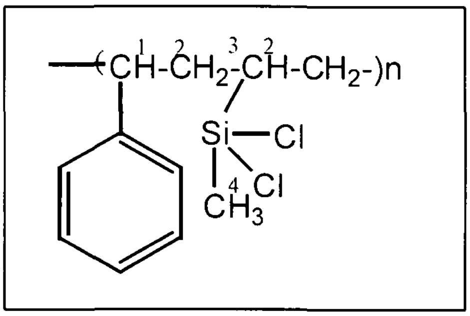


Fig.3.1. Copolymer of styrene and methyl vinyl dichloro silane

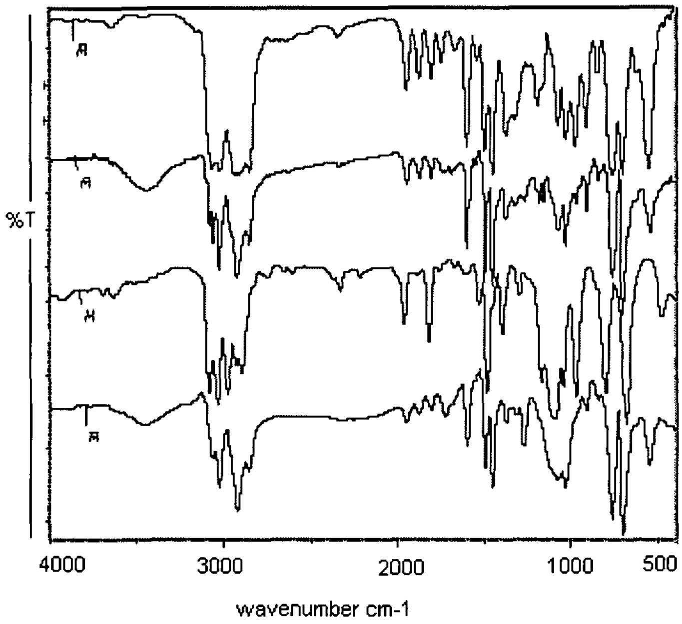


Fig. 3.2. FTIR for PS (a), PSMVS(b), silica (c) and PSMVSB/silica composite

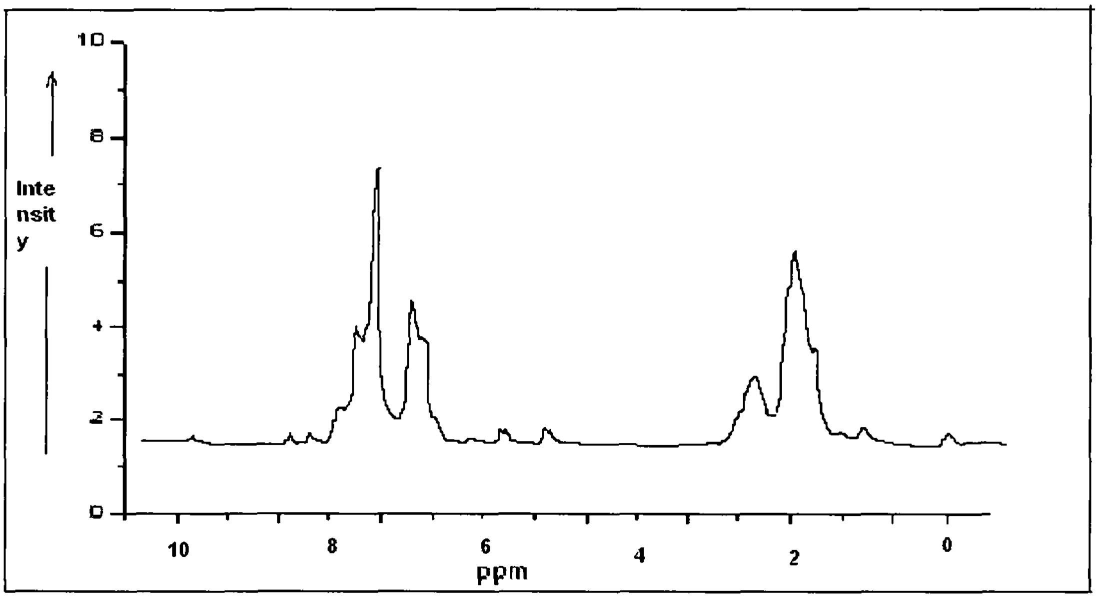


Fig. 3.3. 1H NMR for copolymer derived from styrene and MVS (PSMVS).

Preparation of colloidally stable silica sol from Tetraethyl orthosilicate (TEOS):

The acid catalysed method was chosen for the hydrolysis of TEOS in toluene. This method has several advantages over the base catalysed one. It was reported that a low pH helps in the formation of uniform composites from TEOS within a PMMA matrix and retards the phase separation of SiO_2 into large, isolated regions [13]. The base catalysed sample contained several wt% residual TEOS, whereas the acid catalysed sample contained less than 50ppm [13]. The optimum volume of acid catalyst required to form stable sol in TEOS solution was adjusted by noting the excess amount of the acid catalyst (0.5N HCl), which caused instantaneous gelation. Table 3.2 shows that the amount of acid catalyst (.5NHCl) required to form the sol decreased with an increase in the concentration of TEOS.The reason may be attributed to the fact that aggregation of silica particles to form sol increases with an increase in the silica concentration.

Table 3. 2 . Optimisation of amount of HCl for stable sol preparation from tetraethyl orthosilicate (TEOS) solution in toluene

Serial number	Concentration of of TEOS solution in toluene	Volume of 0.5N HCl required (ml)*
1	2.5%	4
2	5%	2
3	7%	1.4
4	8%	1.3

* above this volume, instantaneous gelation will occur

Preparation of silica sol from TEOS in the presence of Polystyrene and its copolymers:

The proportion of HCl to TEOS solution required for sol formation from TEOS was determined in the previous experiment [Table 3.2]. The volumes of acid catalyst used to bring about acid hydrolysis of TEOS in presence of polymer and copolymer [Table 3.3] were close to the above values (as determined in Table 3.2). The conditions required for the formation of colloidally stable sol from TEOS remained essentially same in the presence of the polymer matrix. Similar observations have also been made by Landry et al [13].

Although the MVS content in the copolymers PSMVSA and PSMVSB are different, there is very little difference in the volume of catalyst required to form the sol-gel mixtures from the two copolymers. This may probably be due to the small difference in MVS content in the polymers

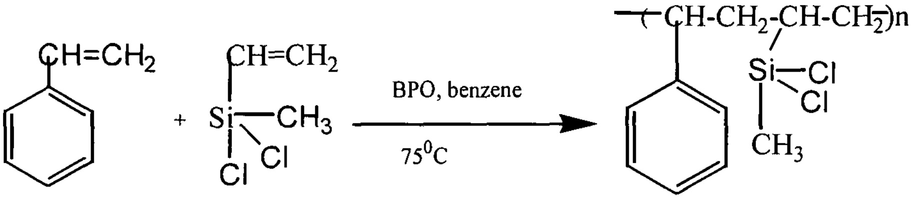
PSMVSA and PSMVSB. The hydrolysis and condensation of TEOS in presence of the silylated copolymer are shown in scheme 3 [Fig. 3.4.]

Composite films from the sol-gel mixtures derived from Polystyrene (PS)/ copolymers of Polystyrene (PSMVS) with silica from TEOS:

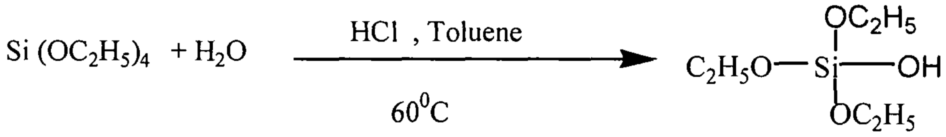
The composite films obtained after the gelation and subsequent drying of the sol-gel mixture on glass slides were analysed by FTIR, SEM and TGA. The FTIR spectrum of the composite shows the presence of bands in the region around 1068 -1100cm^{-1} [Fig. 3.2, (curve d)] which may be taken as evidence for formation of Si-O-Si linkages[14] . However due to the presence of other vibrations in the same region in the copolymer as well, the IR evidence is not conclusive.

Scheme 3.

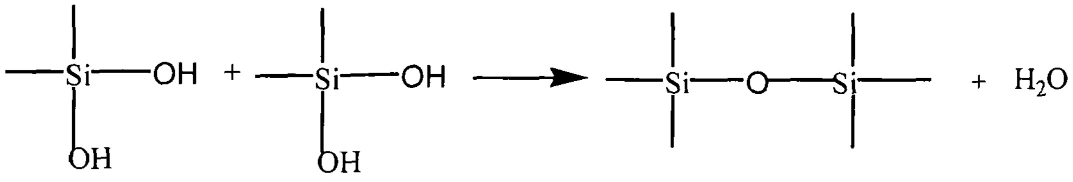
a) Synthesis of copolymers



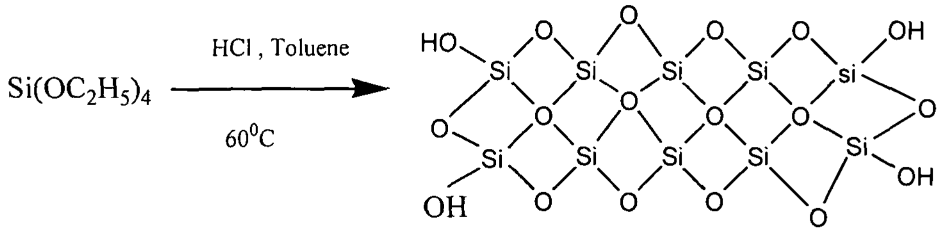
b) Hydrolysis of TEOS



c) Condensation



d) Net Reaction



e) Hydrolysis and condensation of TEOS in presence of silylated polymer

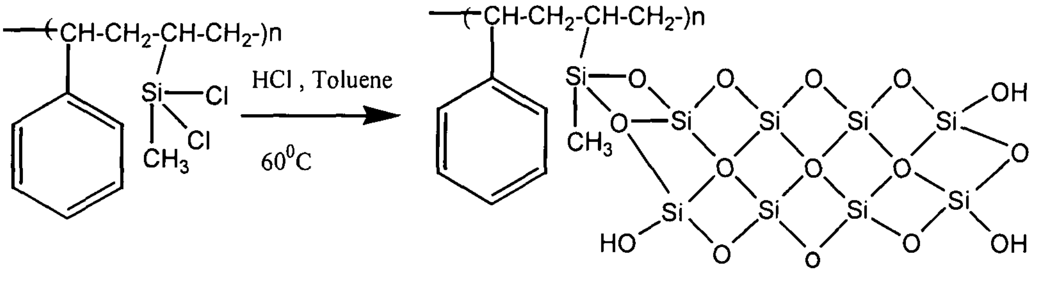


Fig.3.4. Synthesis of copolymers, sol-gel condensation for TEOS alone and in presence of silylated polymer

SEM analysis: Scanning electron micrographs are shown for polystyrene/silica [Fig. 3.5a], PSMVSA/silica [Fig. 3.5b], PSMVSB/silica [Fig. 3.5c], and PSMVSC/silica [Fig.3.5d].

0.1ml of TEOS was added externally to polystyrene, 0.5 ml to PSMVSA and PSMVSB, and 0.8 ml TEOS was added to PSMVSC. The SEM micrograph for the hybrid composite derived with polystyrene and silica shows phase separation [Fig. 3.5a]. However, the dispersion was much improved with copolymers PSMVSA [Fig.3.5b], PSMVSB [Fig. 3.5c] and PSMVSC [Fig.3.5d]. It appears that the silane functionalized polymers had better compatibility between the two phases. Comparison of the SEM micrographs for PSMVSA/silica [Fig. 3.5b], PSMVSB/silica [Fig.3.5c] and PSMVSC/silica [Fig.3.5d] shows better interfacial properties for the PSMVSA/silica and PSMVSC/silica composites. The surfaces of PSMVSA/silica [Fig. 3.5b] and PSMVSC/ silica [Fig. 3.5d] are smooth while pores appear on the surface of PSMVSB/silica [Fig.3.5c]. Although the silane content in the copolymer PSMVSB was higher, the viscosity was also higher in this case, which might have prevented the formation of a homogenous mixture with silica (Mole ratio of styrene: MVS in case of PSMVSA was 0.129:0.0025 while that in PSMVSB was 0.129: 0.005). The higher silane content in PSMVSB/silica is not reflected in the TGA analysis which shows ~ 6.6% incorporated silica in composites derived from both PSMVSA and PSMVSB. This may be due to the small difference in incorporated MVS in PSMVSA and PSMVSB. Other concentrations show similar differences in dispersion pattern with polystyrene, PSMVSA and PSMVSB.

As the molecular weight of PSMVSC was lower, it was possible to load higher proportion of TEOS in the sol-gel mixtures [Table 3.3] producing transparent composites, which showed smooth morphologies under SEM [Fig.3.5d]. PSMVSC also contains higher proportion of MVS (mole ratio of styrene: MVS is 0.129:0.01), which helps in incorporation of more TEOS without phase separation.

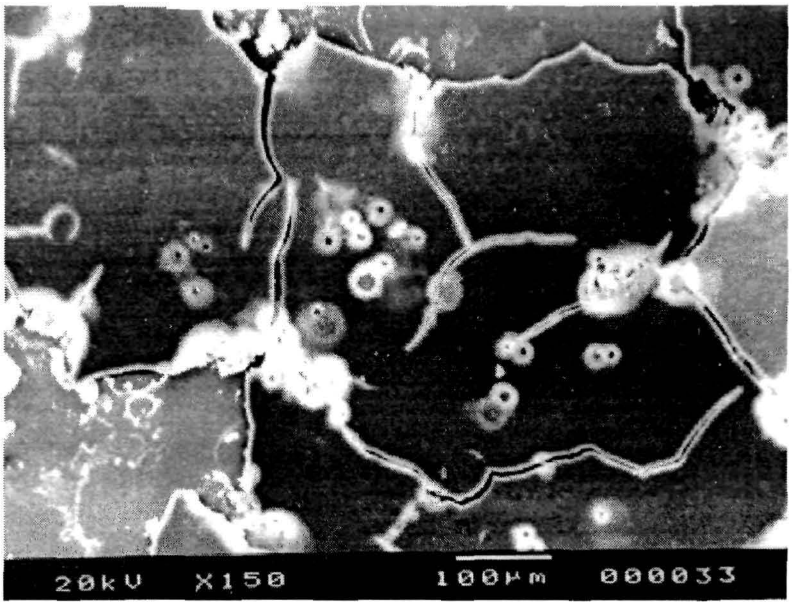


Fig. 3.5a: SEM micrograph for the composition
0.028PS:0.001TEOS:0.0014HCl:0.0793toluene

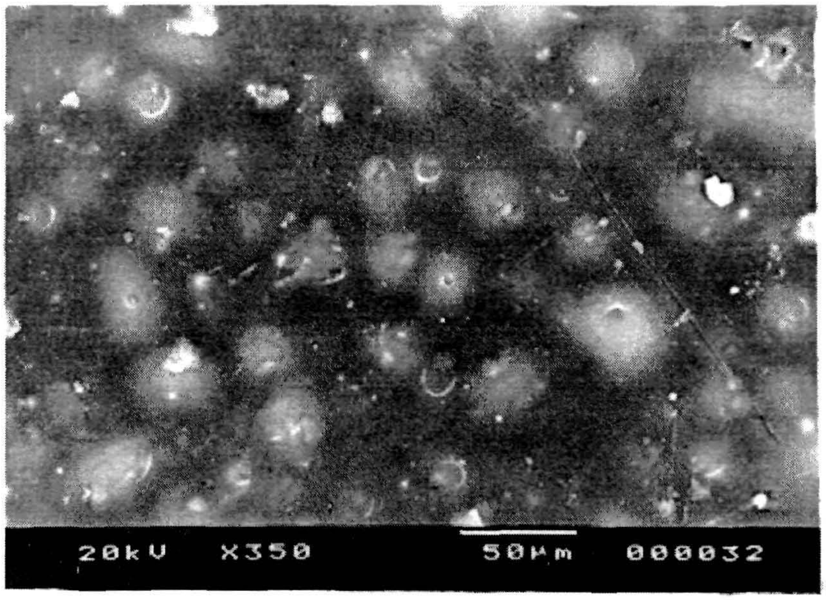


Fig. 3.5b.SEM micrograph for the composition
0.028PSMVSA:0.0036TEOS:0.007HCl:0.0793toluene

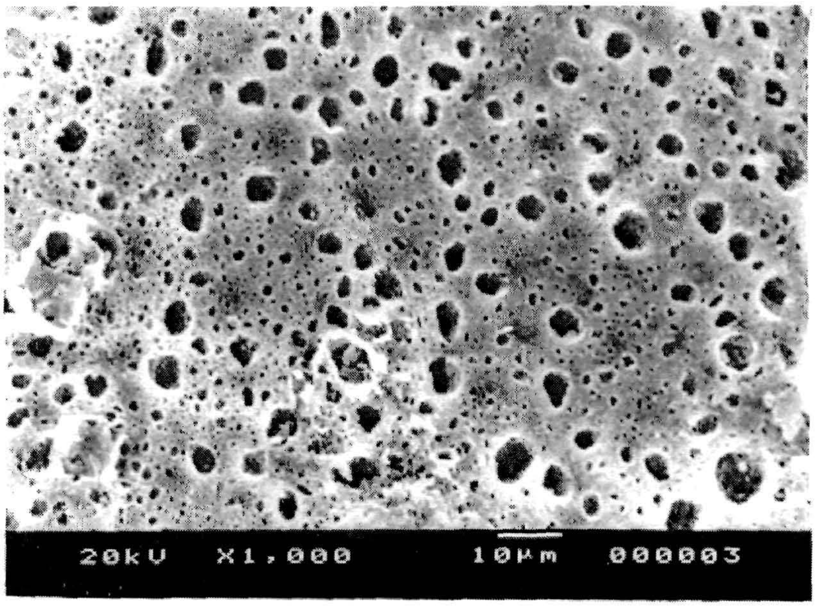


Fig.3.5c.SEM micrograph for the composition 0.028PSMVSB :0.0036TEOS:0.005HCl:0.0793toluene

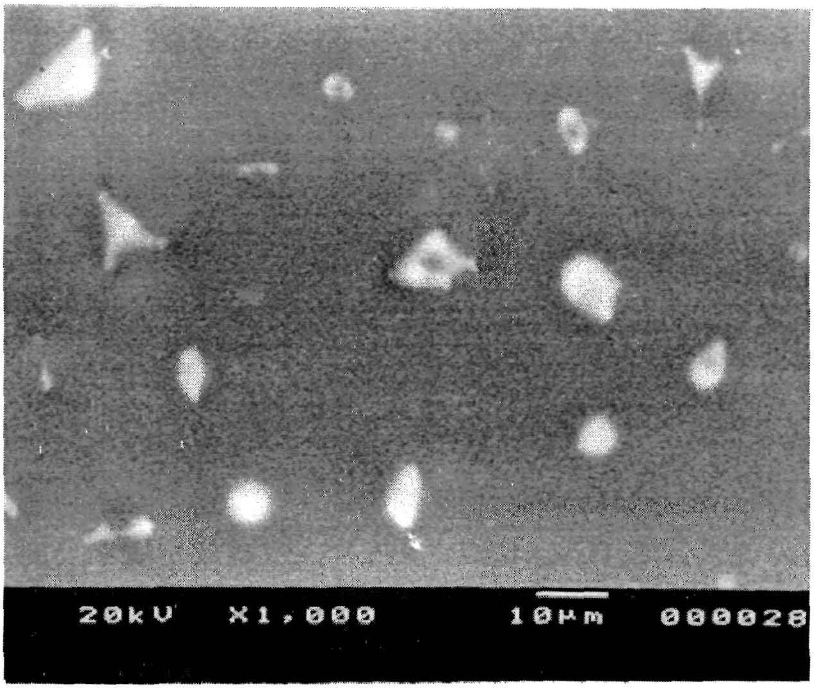


Fig.3.5d. SEM micrograph for the composition 0.028PSMVSC: 4.02x10-4TEOS:1.8x10-3HCl:0.0793THF

Table 3.3. Composition of sol-gel mixtures, morphology and thermal properties of the copolymers and composites

SL	sample	mole ratio of polymer :TEOS:HCL:toluene	TEOS ml	HCl ml	Physical appearance	Appearance under SEM	T_{id} C	Residue at 700C (%)
1	PS	pure polymer	0	0	transp	smooth surface	150	0
2	PS	0 067 0 001 0 0014 0 0793	0 1	4	phase separated	phase separated	176	0 25
3	**PSMVSA**	**pure copolymer**	**0**	**0**	**transp**	**smooth surface**	**200**	**0.25**
4	PSMVSA	0 0288 0 001 0 0014 0 0793	0 1	4	transp	no visible phase separation	215	0 25
5	PSMVSA	0 0288 0 0025 0 0007 0 0793	0 1	3	transp	no visible phase separation	220	2 5
6	PSMVSA	0 0288 0 0031 0 0007 0 0793	0 35	1 15	transp	no visible phase separation	230	5
7	PSMVSA	0 0288 0 0036 0 0007 0 0793	0 42	1 15	transp	no visible phase separation	180	6
8	**PSMVSB**	**pure copolymer**	**0**	**0**	**transp**	**smooth surface**	**220**	**0.5**
9	PSMVSB	0 0288 0 001 0 0005 0 0793	0 1	2 5	transp	no visible phase separation	225	6
10	PSMVSB	0 0288 0 0025 0 0012 0 0793	0 35	1 5	transp	no visible phase separation	220	2 5
11	PSMVSB	0 0288 0 0031 0 0007 0 0793	0 42	1 5	transp	no visible phase separation	230	5
12	PSMVSB	0 0288 0 0036 0 0005 0 0793	0 5	1 25	transp	phase separation visible	220	6
13	**PSMVSC**	**pure copolymer**	**0**	**0**	**transp**	**smooth surface**	**225**	**0.8**
14	PSMVSC	0 028 1 56x10^{-4} 2 7x10^{-3} 0 0793	0 5	1	transp	no visible phase separation	230	6 5
15	PSMVSC	0 028 1 87x10^{-4} 2 52x10^{-3} 0 0793	0 1	2	transp	no visible phase separation	250	6 8
16	PSMVSC	0 028 2 23x10^{-4} 2 43x10^{-3} 0 0793	0 35	1 5	transp	no visible phase separation	310	7
17	PSMVSC	0 028 2 68x10^{-4} 2 25x10^{3} 0 0793	0 42	1 4	transp	no visible phase separation	310	7
18	PSMVSC	0 028 3 12x10^{-4} 1 5x10^{-3} 0 0793	0 5	1 35	transp	no visible phase separation	316	7
19	PSMVSC	0 028 3 57x10^{-4} 1 8x10^{-3} 0 0793	0 6	1 25	transp	no visible phase separation	320	7
20	PSMVSC	0 028 4 02x10^{-4} 1 8x10^{-3} 0 0793	0 7	1 2	transp	no visible phase separation	330	7
21	PSMVSC	0 028 3 57x10^{-4} 1 8x10^{-3} 0 0793	0 8	1	transp	no phase separation	340	7
22	PSMVSC	0 028 4 02x10^{-4} 1 8x10^{-3} 0 0793	0 9	1	hazy	no visible phase separation	376	7

T_{id} = Initial decomposition temperature, transp = transparent, ml of TEOS and HCl are shown as 0,0 for the samples without silica, and 0 028 mole of copolymers PSMVS in 0 0793 ml of toluene were used in all cases

Factors affecting the dispersion characteristics within polymer /copolymer matrix:

In the absence of the silylating monomer, gel formation proceeds only through condensation of Si –OH of TEOS. In the presence of the silylating monomer, gel formation proceeds through two ways i) Condensation of Si – OH of TEOS and ii) Condensation of Si-OH of TEOS and Si-OH of polymer. This helps in uniformity of dispersion of silica within silylated polymer. In sol formation, the first step is the hydrolysis of TEOS and the second stage is its condensation forming Si-O –Si linkages. In gelation stage extended networks of Si-O-Si forms. The polymer viscosity is a significant factor in the formation of a homogenous sol-gel mixture from the organic and inorganic components. The viscosity affects the tendency for co-condensation of silica within the polymer matrix.

TGA analysis:

Table 3.3 shows the initial decomposition temperatures(T_{id}) for the polymers and their composites. The T_{id}s were obtained by second differentiation of integral TGA curves [Fig. 3.6]. moisture. The pure copolymers PSMVSA, PSMVSB and PSMVSC have an T_{id} value between 210C-250C. For the composites, the T_{id}s gradually increases with higher proportions of TEOS. The TGA curves for the composites derived from PSMVSC shows the highest extent of thermal stability with T_{id} value reaching upto 370C. The enhancement in thermal stability of the composites could be attributed to the interaction force between silane functionalized polystyrene and silica network. TGA analysis for copolymers PSMVSA, PSMVSB and PSMVSC showed residue (at 700C) of 0.45%, 0.5% and 0.8% respectively due to incorporated silane. TGA analysis for composites derived from copolymers PSMVSA and PSMVSB showed a residue of ~6%.

DSC analysis: The DSC curves are shown in the Fig.3.7. The copolymer PSMVS (curve a) shows three transitions within the temperature range 70-300C [Table3.4]. The first transition may be related to loss of moisture and the second may be for Tg. With the incorporation of the silica phase, the polymer becomes hydrophobic. This is reflected in the DSC curves. The first transition at 70C found in the copolymers is not found in the composites (curves b, c, d and e). Also with an increase in silica content, the second transition temperature gradually increases. The increase in Tg of the composites is due to restriction of chain motion in the composites imposed by crosslinks with the silica network [7].

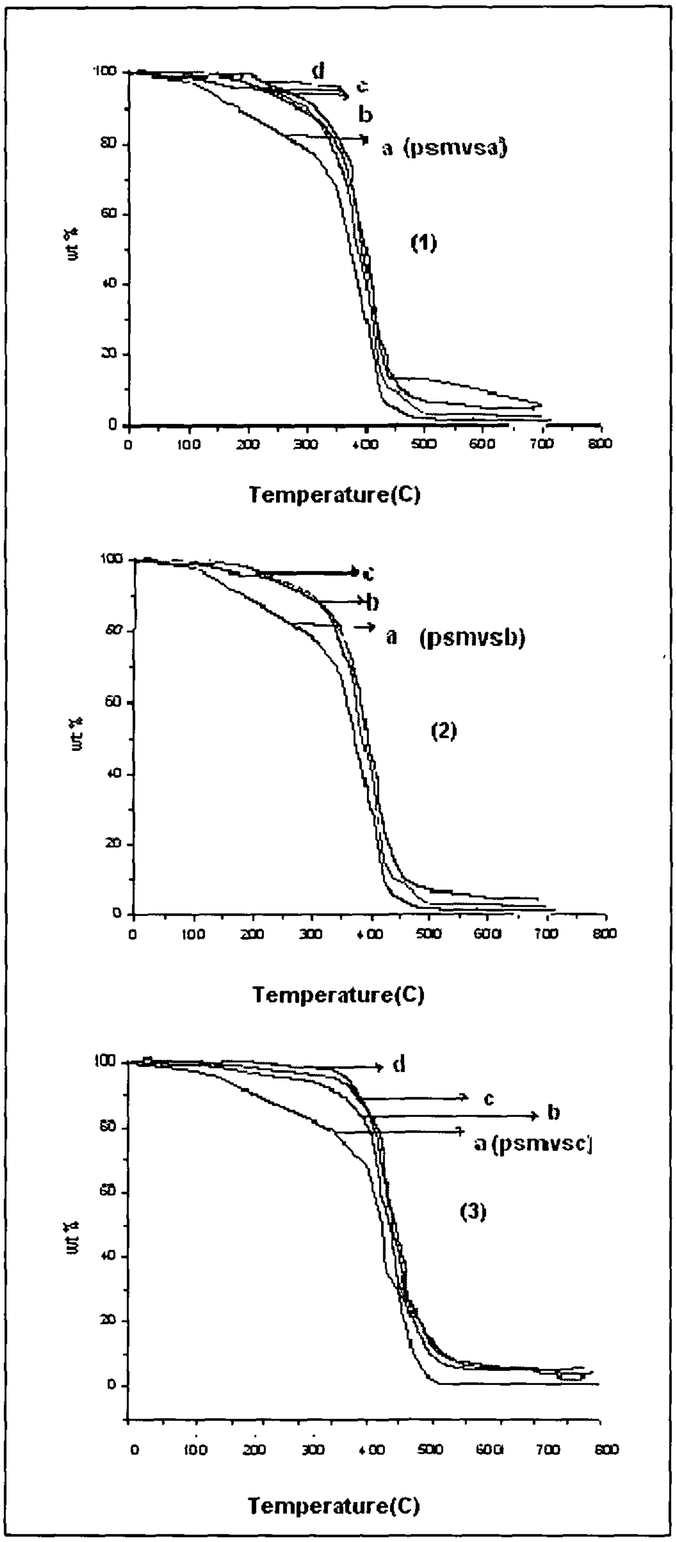


Fig. 3.6. TGA curves for PSMVSA and its composites(1), PSMVSB and its composites(2) and PSMVSC and its composites (3).

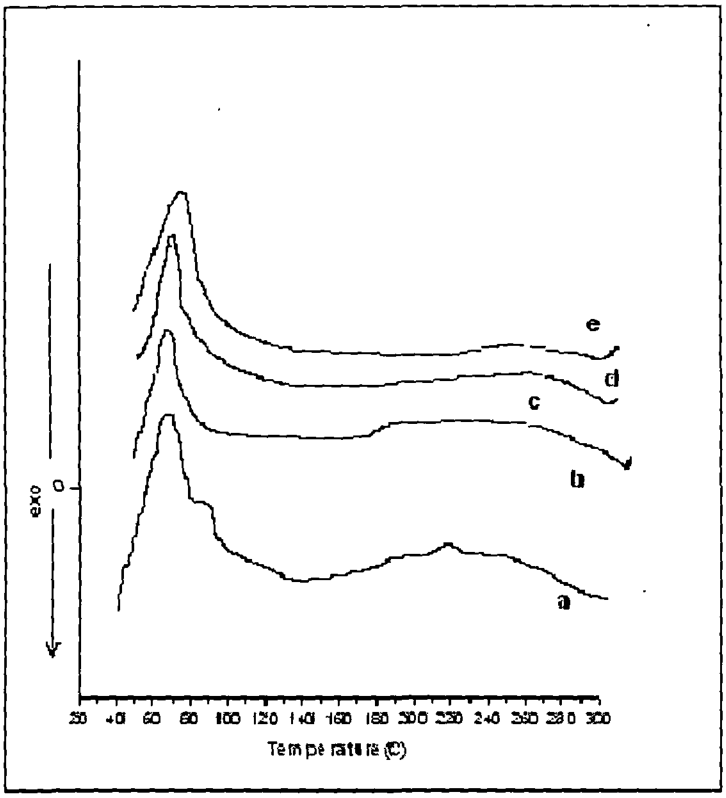


Fig.3.7. DSC curve for copolymer PSMVSC (curvea) and its composites (b, c, d and e)

Table3.4: Inflection temperatures for copolymers and composites as obtained from DSC curves.

*SL	**DSC** curve	**inflection (C)and ΔCp (kJ/mole) for first transition**	**inflection (C)and ΔCp (kJ/mole) for second transition**	**inflection (C)and Δ Cp (kJ/mole) for third transition**
1	a	76.1C, 1.946	134.1C, 0.693	217C, 0.392
2	b	139C, 0.664	231.7C, 0.038	Not observed
3	c	150C, 0.269	230C, 0.050	Not observed
4	d	180C, 0.261	250C, 0.214	Not observed
5	e	244C, 0.298	265C, 0.358	Not observed

* SL 1 (DSC curve a) is for PSMVSC and SL 2-5 (DSC curves b, c, d, e) are for PSMVSC/silica composites in order of increasing silica content

Water uptake experiment: The relative rate of water absorption under saturated conditions was measured by initially drying the films in a vacuum oven at 50 ° C for 12 hours, immersing the films in distilled water, and then measuring the weight change until it became constant. Water absorption by polystyrene under saturated conditions was 0.77%. For silylated copolymers PSMVSA, PSMVSB and PSMVSC this further decreased to 0..3%. Water uptake for composites derived from polystyrene and silica was ~0.45 % while that for composites derived from copolymers PSMVSA,PSMVSB and PSMVSC varied from 0.156 % and 0.145% .

3.5. Conclusion

Hybrid organic-inorganic composites were derived from TEOS and polymers polystyrene and copolymers of styrene with methylvinyldichlorosilane. The SEM micrographs have revealed that the dispersion of silica within the polymer matrix obtained by the in-situ hydrolysis of tetraethylorthosilicate is superior in the case of silane functionalised copolymers as compared to the pure polymers. TGA analysis has revealed that the thermal stability of the composite film is higher than the pure polymer. Moreover the tendency for moisture absorption for the composite film is lower than the pure polymer. The ratio by volume of the silylating monomer, methylvinyldichlorosilane, and the co-monomer styrene, viscosity of the resultant copolymer, and the ratio of copolymer solution to tetraethylorthosilicate solution were the significant factors affecting the uniformity of dispersion of silica within the polymer matrix.

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CHAPTER 4

Synthesis of polystyrene-butyl acrylate /silica hybrid composites by the sol-gel method

4.1. Introduction

This chapter reports the synthesis and characterization of sol-gel derived hybrid composites with styrene-butyl acrylate (PSBUA) copolymer as the polymer matrix and silica as the inorganic phase.

In the previous chapter we had discussed the synthesis of hybrid composites with a polystyrene matrix. It was found that non-phase separated composites could not be prepared with polystyrene alone due to its brittle nature. Therefore the polymer was silylated with a silylating monomer to enhance its compatibility with silica. The effect of the various reaction parameters on the bulk properties of the composites were discussed in that chapter.

The brittleness of polystyrene may be reduced by the incorporation of a flexible component such as butyl acrylate. In this chapter we have attempted to study the effect of this flexibilisation in the synthesis of sol-gel derived hybrid composites with silica.

The styrene butyl acrylate copolymer was subsequently functionalized with a silylating monomer for the synthesis of hybrid composites with silica.

The optical. morphological, thermal and water uptake properties of these composite were characterized.

A comparison amongst the four different hybrid systems viz. polystyrene/silica, silylated polystyrene/silica, polystyrene-silica/silica and silylated polystyrene-butylacrylate /silica has been made in this chapter.

4.2. Experimental

Raw materials: Styrene (Merck-Schuchardt) was purified by removing inhibitor with sodium hydroxide solution followed by drying over molecular sieves. Tetraethylorthosilicate (TEOS), (Merck-Schuchardt), methylvinyldichlorosilane (Fluka), benzoyl peroxide (S.d fine chem) and butyl acrylate (S.d fine chem) were used as received.

Synthesis of copolymers from styrene and butyl acrylate (PSBUA):

11 ml (.095 mol) of inhibitor free styrene was taken along with 20 ml of purified xylene in a three necked round bottomed flask fitted with a condenser, a N_2 inlet and a guard tube. 6 ml (0.042mole) of butyl acrylate was added with stirring over a period of 30 minutes. Temp was raised to 65C and 0.15g benzoyl peroxide initiator was added. The reaction was carried out at 65C for 10 hr .The copolymer PSBUA was precipitated in methanol.

Synthesis of copolymers from styrene, butylacrylate and methylvinyldichlorosilane (PSBUAMVS):

The copolymers were synthesized by varying the proportion of monomers. A typical reaction is given below:

11 ml of inhibitor free styrene (0.087 mole) and 6 ml of butyl acrylate (0.41mole) were taken together in 20 ml of xylene in a three necked round bottomed flask fitted with a N_2 inlet and a condenser. 1 ml (0.07 mole) of methyl vinyl dichlorosilane (MVS) was added drop wise with constant stirring over a period of 15 minutes. Initiator, benzoyl peroxide was added at 60C and polymerization was continued for 12 hrs. The copolymer (PSBUAMVS) was then precipitated in methanol. It was purified by dissolving in THF and then reprecipitating in methanol.

Preparation of colloidally stable sol from tetraethyl orthosilicate (TEOS) solution:

Sol-gel mixtures were prepared using TEOS, HCl (1N) and tetrahydrofuran(THF). 1N HCl was added with constant stirring at 60C to the TEOS solution in THF. Addition of acid catalyst was stopped just prior to the point of gelation, which was taken to be the point at which the mixture became thick and viscous. The amount of acid catalyst necessary for the preparation of colloidally stable required was noted.

Preparation of sol-gel mixtures from TEOS in THF in presence of solution of copolymer and composite films thereof:

A typical procedure for the synthesis of sol-gel mixtures from the copolymers and TEOS is given below:

TEOS solution was added with stirring to the solution of copolymer in THF to form a homogeneous mixture. Then the acid catalyst 1N HCl (amount of which was determined from the previous experiment) was added slowly with stirring at a temperature of 60C. The solution was stirred at 60C for 30 minutes to carry out the in-situ acid hydrolysis of TEOS.within copolymer solution. The sol-gel mixtures were then poured over glass plates to give composite films. The plates were then dried in air at 30C over a period of 72 hours and finally dried in the oven at 60C for 5hr.

4.3. Characterization

FTIR: The copolymers were dried and ground for FTIR analysis. The composite films were cast over glass plates. A Nicolet USA Impact 401 FTIR spectrophotometer was used for the analysis.

NMR analysis: 1HNMR ($CDCl_3$) and 13 C NMR ($DMSOd_6$) was carried out in a 400 MHz Brucker NMR spectrometer.

GPC analysis: GPC analysis for the copolymers were carried out using GPC (Water, USA, Model 515) solvent delivery system at a flow rate of 1 ml/min through a set of three ultrastyregel columns. Analysis was done at controlled temperature at 45C using HPLC grade tetrahydrofuran (THF) as eluent.

Viscosity: The viscosity of a 0.5% solution in THF was measured using Ubbellohde viscometer at 30C and reported in terms of inherent viscosity η = (ln t/$t_{0)}$/ c dl g^{-1}, where 't_o' is the time taken by the solvent THF and

' t 'is the time taken by the solution, and c is the concentration of the polymer solution.

TGA analysis: TGA analysis for the copolymer and composites were carried out in a PYRIS1 thermogravimetric analyzer (Shelton, USA). The samples were preheated at 40C and the analysis was carried out in nitrogen atmosphere at a heating rate of 10C per minute within a temperature range of 50C to 700C.

DSC analysis: DSC analysis for the copolymers and composite samples were carried out using a Diamond DSC instrument (Perkin Elmer, USA). The samples were preheated at 40C and the analysis was carried out in nitrogen atmosphere at a heating rate of 10C per minute within a temperature range of 70C to 300C.

SEM analysis: The samples for scanning electron microscopy were prepared in the form of thin film on glass plates. The samples were kept in desiccators for 2 hours and then coated with gold. The tests were conducted using a Scanning Electron Microscope (Jeol, Japan). The magnification and acceleration voltages varied from 20KVx150 to 20KVx1000.

4.4. Results and Discussion

Synthesis of copolymers: Copolymers were synthesized from styrene, butylacrylate (BUA) and methylvinyldichlorosilane (MVS) using the concentrations listed in Table4.1. Molecular weight and inherent viscosities of the copolymers are also listed in Table 4.1. Molecular weights of copolymers are in the range of 34,000-40,000 g/mole and inherent viscosities are in the range of 0.49-0.52dlg^{-1} [Table 4.1].

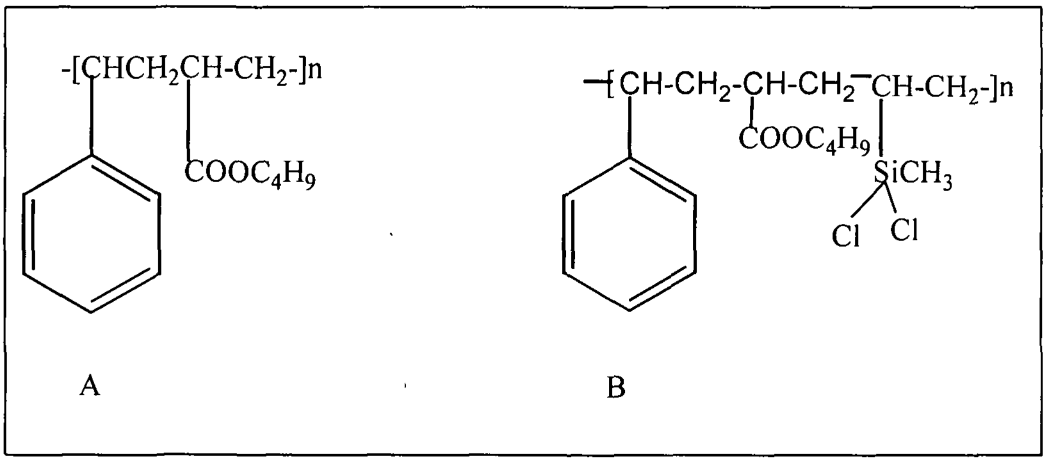


Fig. 4.1. Repeat unit of PSBUA (A) and PSBUAMVS(B)

Table 4.1. Composition of copolymers and their molecular weight

Polymerization temperature: 55-60C; Initiator: Benzoyl peroxide, 0/9g; Time: 7-8 hrs

SL	Sample	styrene mole	butyl acrylate mole	mvs mole	yield wt%	$\overline{Mn}$ g/mole	Mw/$\overline{Mn}$	Inherent viscosity of soln in CHCl3 dl/g
1	PSBUAMVSA	0.095mol	0.042	0	~95	40,000	1.8	~0.52
2	PSBUAMVSB	0.095mol	0.042	0.006	~95	35,000	2.2	~0.50
3	PSBUAMVSC	0.095mol	0.042	0.125	~95	34,572	1.79	~0.49

Structure analysis of copolymers:

Copolymer derived from styrene and butyl acrylate (PSBUA): In the 1H NMR of PSBUA copolymer [Fig.4.2] (δ, ppm, CDCl3) δ value at 3.75 is due to alkyl protons attached to –$COOC_4H_9$, δ value at 2.7 is due to –CH attached to –$COOC_4H_9$, δ value around 1.2-1.8 is due to alkane protons and δ value from 6.05 to 7.21 is due to aromatic protons [1]. In the 13CNMR of S-BUA, [Fig.4.2] δ values at 13,19, 30, 41, 63 are due to alkane C incorporated from the butyl group; δ values at 126, 127, 128,143 and 145 are due to aromatic C [1].

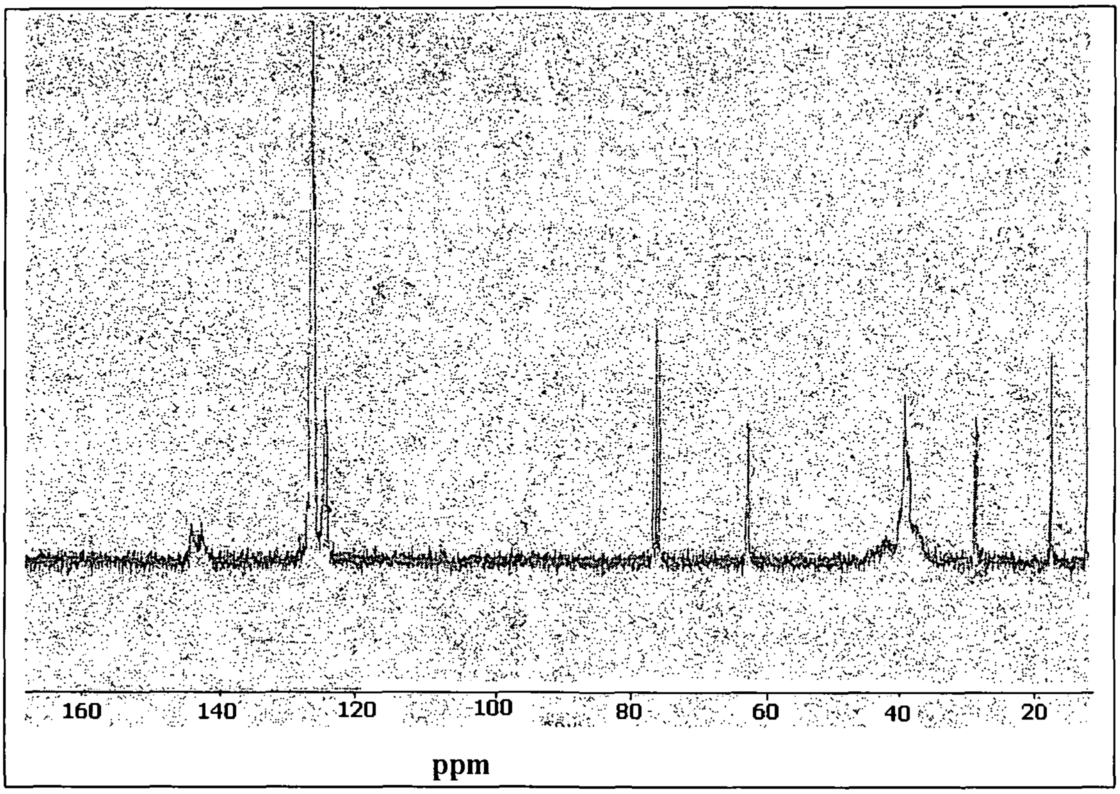


Fig. 4.3. 13CNMR of copolymer PSBUA

Copolymer derived from styrene, butylacrylate, methylvinyldichlorosilane (PSBUAMVS): The 1HNMR spectrum [Fig. 4.4] points to the following different proton environments. The aromatic protons appear at δ 7.1- 6.64; δ 4.17 is due to butyl group attached to COO; δ 2.7 due to CH attached to $COOC_4H_9$; δ 1.2 to 1.8 due to alkane protons [1].

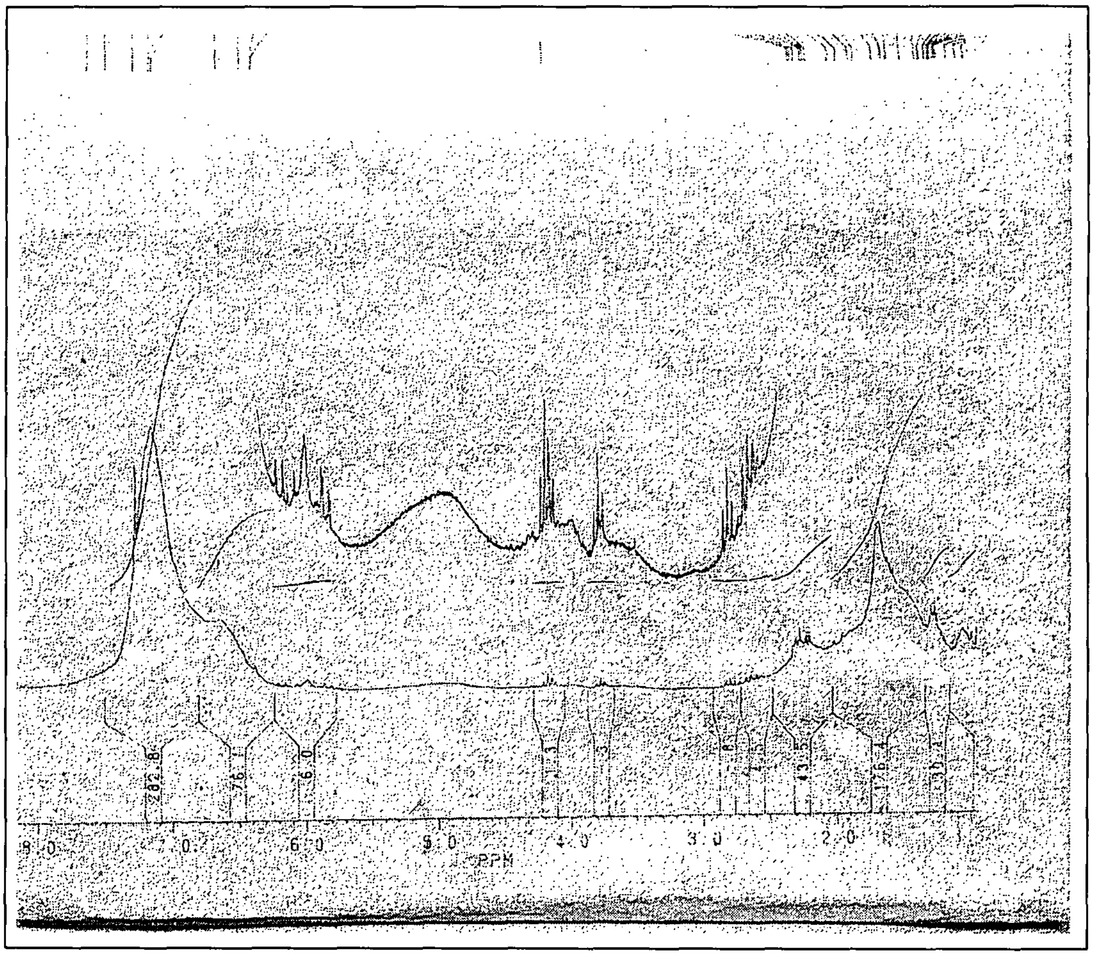


Fig.4.4.1H NMR of copolymer PSBUAMVS

FTIR analysis: In the spectrum of the copolymer PSMVSBUA [Fig.4.5, curve a], we find the characteristic peaks due to polystyrene moiety, that is, at 3027 cm^{-1}; (alkeneC-H stretch due to monosubstituted vinyl group), 2851 cm^{-1} (alkane C-H stretch), 1594 cm^{-1} (aromatic C-C multiple bond stretch), 1447 cm^{-1} and 1490 cm^{-1} (alkane CH_2 bending), 906 cm^{-1} (alkene C-H bending due to monosubstituted vinyl group), 753 cm^{-1} (aromatic C-H stretch) [2]. There is a sharp band at 1723 cm^{-1} which probably arises due to the COO-stretching vibration from the butyl acrylate group bending due to monosubstituted vinyl group), 753 cm^{-1} (aromatic C-H stretch) [2]. In the spectrum of the copolymer PSBUAMVS, in addition to bands due to the styrene repeat units, a sharp band appears at 1267 cm^{-1} due to Si-CH_3 stretching frequency [2]. But the band at 906 cm^{-1} diminishes in intensity in the copolymer spectrum. This shows substitution at the vinyl group. The bands at 538 cm^{-1} and 440 cm^{-1} might be due to Si-Cl stretching vibration [2]. The band at 1723 cm^{-1} indicates the presence of the butylacrylate moiety.

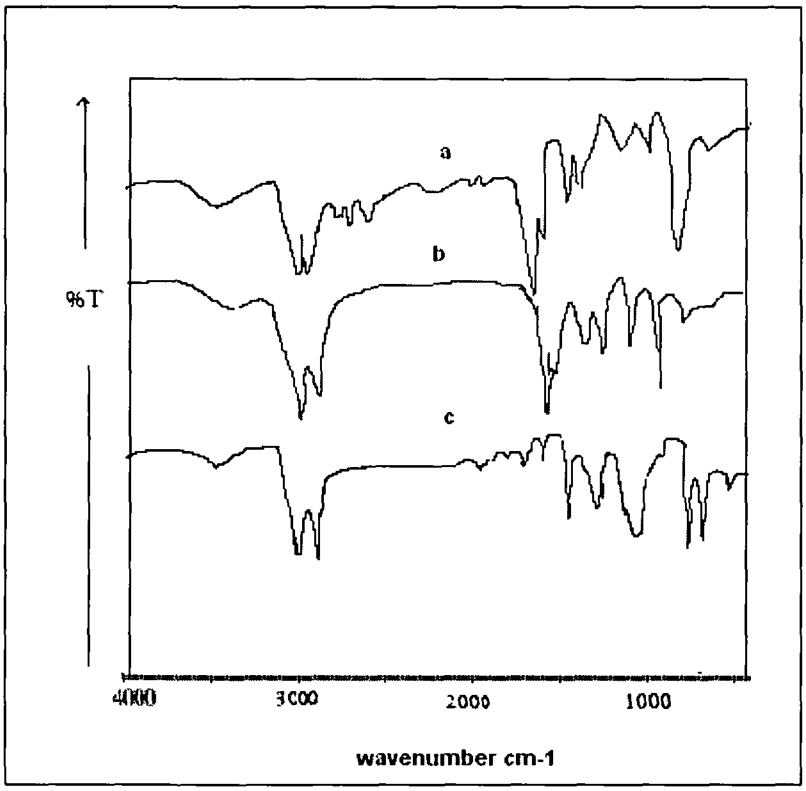


Fig.4.5. FTIR of PSBUAMVS(a), hydrolyzed TEOS(b) and PSBUAMVS composite

Preparation of colloidally stable sol from TEOS solution and in-situ acid hydrolysis of TEOS in the copolymer matrices:

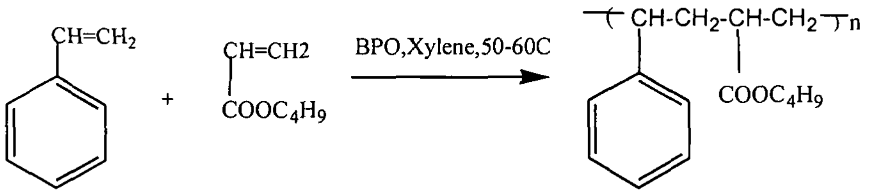
Scheme 4 in Fig. 4.6 shows the sol-gel reaction and composite formation of copolymers with silica. The mole ratios of polymer: TEOS: HCl: THF: H2O used for the sol-gel synthesis are given in Table 4.2. The amount of acid catalyst (1NHCl) required to form the sol decreased with an increase in the concentration of TEOS. The reason may be attributed to the fact that aggregation of silica particles to form sol increases with an increase in the silica concentration. As the silane content in the copolymers increased, the amount of TEOS in the mixture could be increased.

Composite films from the sol-gel mixtures:

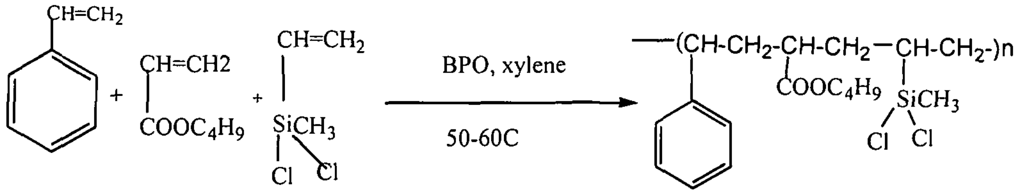
The sol-gel mixtures were cast onto glass plates and allowed to dry at 30°C for 72 hours. The composition, appearance and morphological characteristics of the composite materials are listed in Table 4.2. The optical transparency can be used as an initial criterion for the formation of a homogeneous phase of both inorganic and organic constituents. When macroscopic phase separation occurs, products look opaque because the large domain size in the inorganic oxide causes light scattering in the system [3]. These composite films were analyzed by FTIR, SEM, TGA, and DSC.

Scheme4

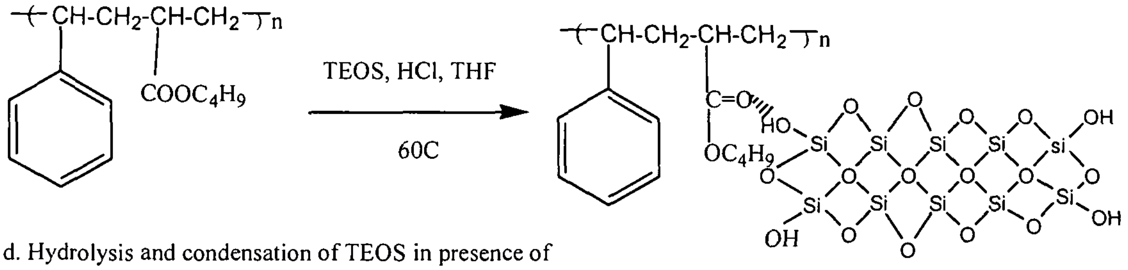
a. Synthesis of copolymer from styrene and Butylacrylate(PSBUA)



b. Synthesis of copolymer from styryene, butylacrylate and methylvinyldichlorosilane (PSBUAMVS)



c. Hydrolysis and condensation of TEOS in presence of PSBUA



d. Hydrolysis and condensation of TEOS in presence of PSBUAMVS

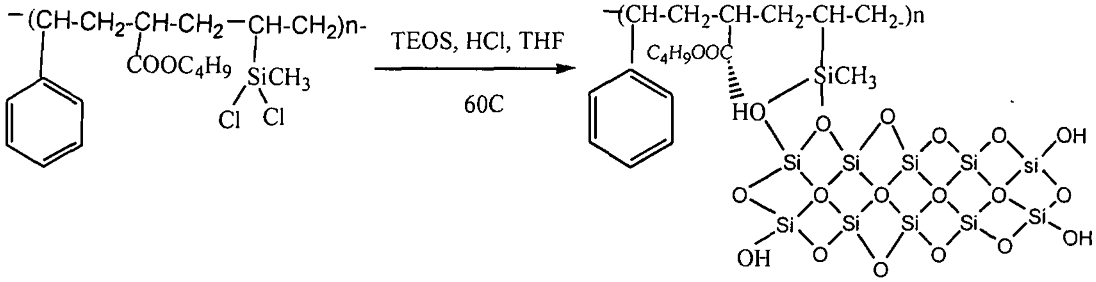


Fig.4.6. Synthesis of copolymers PSBUA and PSBUAMVS and hydrolysis and condensation of TEOS in presence of copolymers

FTIR analysis for silica, copolymers and the composites:

In the spectrum of silica [Fig.4.5b] there is a broad split band covering frequencies at 1037 cm^{-1}, 1085 $cm^{-1}$and 1166 cm^{-1}, which may be due to Si-O-Si linkage along with any remaining Si-O-CH_2R, if present. There is also a band at 963 cm^{-1}, possibly due to unhydrolyzed Si-O-C_2H_5 group.

In the spectrum of the composite [Fig.4.5c], the band at 963 cm^{-1} is found to disappear which might possibly be due to crosslinking with silica. A broadened band in the region 1070-1150 cm^{-1} is observed which is possibly due to crosslinked Si-O-Si linkages. In addition to the typical bands from the polystyrene component, there is a band at 1267 cm^{-1} which comes from the Si-CH_3 stretching frequency in the copolymer. The spectra for the copolymer PSMVSBUA and PSMVSBUA/silica composites are similar to the above except that there is an additional sharp band at 1723 cm^{-1} which probably arises due to the COO-stretching vibration from the butyl acrylate group.

Morphological study of the composites under scanning electron microscopy (SEM): For the sol-gel composites derived from the copolymers of styrene and butylacrylate (PSBUA), 0.38 ml TEOS can be added externally to 7g of the copolymer without phase separation during preparation [Table 4.2, SL 2]. The physical appearance of the sample is transparent and the SEM micrographs do not show phase separation, but a polymer/silica interface is clearly visible [Fig.4.7a]. Non-phase separated compositions could not be prepared with Polystyrene and silica [Fig.3.5a in Chapter3]. The introduction of the butyl acrylate component enhances compatibilisation with silica thereby preventing phase separation. The butyl acrylate acts as an internal plasticizer, reducing the brittleness of Polystyrene.

For the copolymers PSBUAMVSA and PSBUAMVSB, which contained both butyl acrylate and the silylating monomer methylvinyldichlorosilane (MVS), a higher amount of TEOS can be added without phase separation during preparation [Table 4.2 SL 2-15]. With copolymer PSBUAMVSA [SL 2, Table 4.2], optically transparent composites are obtained upto an external addition of 0.7ml of TEOS in the copolymer, beyond which, haziness appears in the sample. The SEM micrographs for the compositions showing optical transparency are smooth, with no clear polymer/silica interface [Fig. 4.7b], unlike the PSBUA/silica composites [Fig.4.7a]. This is due to the higher degree of interfacial cohesion possible with the silica network because of the presence of the silylating monomer MVS.

The copolymer PSBUAMVSB which contains a higher proportion of the silylating monomer MVS [Table 4.2 SL 11], incorporates a higher volume of TEOS without phase separation during preparation. Optical transparency is maintained for an addition of 1.8 ml TEOS in 7g of the copolymer PSBUAMVSB, beyond which haziness appears in the samples.

Table: 4.2 : Morphological properties for the copolymers and composites

SL	sample	ml TEOS	ml HCl	mole ratio of polymer :TEOS:HCL:toluene	physical appearance	appearance under SEM
1	PSBUA	0	0	**pure copolymer**	**transparent**	**no phase separation**
2	PSBUA	0 38	1	3 19x10^{3}1 56x10^{3}2x10^{4}0 123	transparent	no phase separation
3	PSBUAMVSA	0	0	**pure copolymer**	**transparent**	**no phase separation**
4	PSBUAMVSA	0 38	1	2 86x10^{3}1 56x10^{3}4 93x10^{-5}0 123	transparent	no phase separation
5	PSBUAMVSA	0 5	1	2 86x10^{3}2 23x10^{3}4 93x10-5 0 123	transparent	no phase separation
6	PSBUAMVSA	0 63	0 8	2 86x10^{3}3 12x10^{3}3 9x10^{-5}0 123	transparent	no phase separation
7	PSBUAMVSA	0 76	0 8	2 86x10^{3}3 576x10^{3}5x10^{-5}0 123	transparent	no phase separation
8	PSBUAMVSA	0 88	0 8	2 86x10^{3}4 34x10^{3}4x10^{-5}0 123	transparent	no phase separation
9	PSBUAMVSA	1 0132	0 7	2 86x10^{3}5 2x10^{3}3 4x10^{-5}0 123	transparent	no phase separation
10	PSBUAMVSA	1 3	0 65	2 86x10^{3}5 64x10^{3}3 2x10^{-5}0 123	hazy	spherical particles
11	PSBUAMVSB	0	0	**pure copolymer**	**transparent**	**no phase separation**
12	PSBUAMVSB	1 4	0 6	2 86x10^{3}6 5x10^{3}2 95x10^{-5}0 123	transparent	no phase separation
13	PSBUAMVSB	1 6	0 5	2 86x10^{3} 7 15x10-3 2 46x10^{-5}0 123	transparent	no phase separation
14	PSBUAMVSB	1 8	0 3	2 86x10^{3}8 24x10-3 1 47x10^{5}0 123	transparent	no phase separation
15	PSBUAMVSB	2	0 3	2 86x10^{3}8 94x10 3 1 47x10^{-5}0 123	hazy	spherical particles

- ml of TEOS and HCl are shown as 0,0 for the samples without silica
- 0 028 mole of copolymer PSMVS and 0 0123 mole of THF were used in all cases

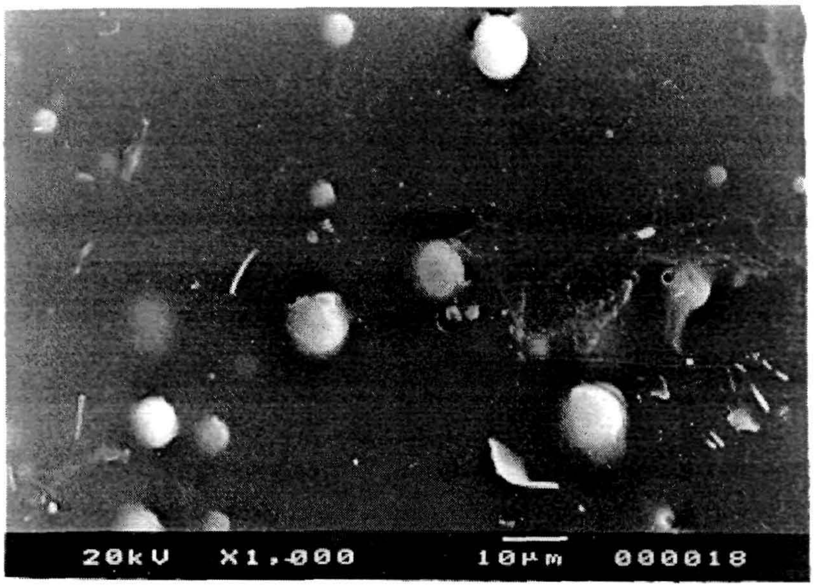


Fig.4.7a. SEM micrograph for the composition 3.19x10-3PSBUA: 1.56x10-3TEOS:2x10-4HCl:0.123THF

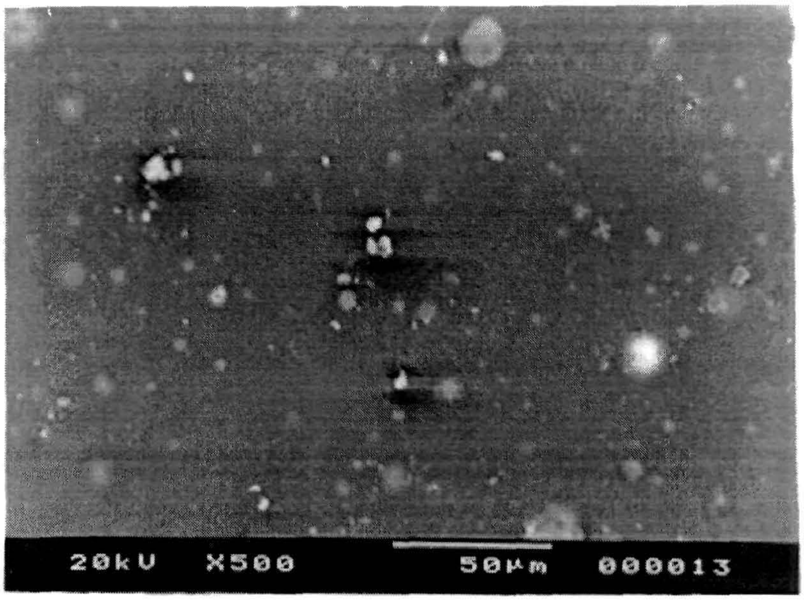


Fig.4.7b. SEM micrograph for the composition 2.86x10-3PSBUAMVS:4.34x10-3:3TEOS.2x10-5HCL:0.123 THF

The SEM micrographs for the compositions showing optical transparency [Fig.4.7c], show a greater degree of interfacial cohesion between the silica and the polymer phase because of the higher proportion of the silylating monomer in this copolymer. An addition of 2ml TEOS in 7g of this copolymer produces a slight haziness in this sample[Table 4.2, SL 15]. The SEM micrograph for this composition shows the presence of hollow and spherical silica particles [Fig. 4.7d]. Fig.4.7e shows the SEM micrograph for this composition at a higher magnification.

An explanation of the observed morphological characteristics may be given as follows: It has been reported that small, stable particles are produced under low pH conditions where hydrolysis is fast and condensation is relatively slow [3]. At low pH there are a large number of nucleation sites due to rapid hydrolysis, which depletes the solution of TEOS monomers, and small particles (2-4nm) are formed. These species can then aggregate, via a cluster cluster growth mechanism, to form oligomers. Polymerization is slow in this pH range so further particle growth is almost negligible. These chains may then adopt spherical shapes, which are not densified. At higher silica percentages the individual spheres become sufficiently large to become visible, at lower percentages, the sizes remain below 100A^0 and therefore smooth morphologies are produced [3]. According to Yoldas et al, concentrating the reaction solution results in significant polymerization if silanol groups are present [4].

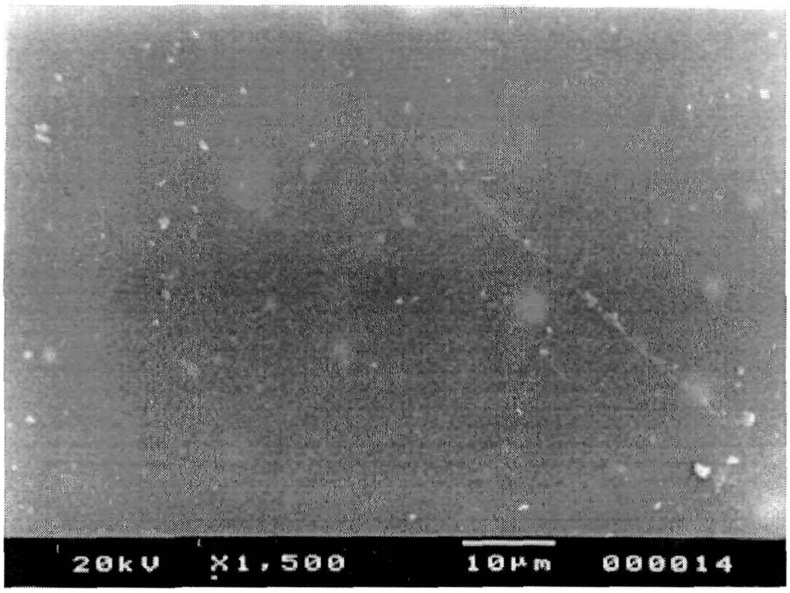


Fig.4.7c. SEM micrograph for the composition0.019 PSBUAMVSB: 6.5x10-3 TEOS:2.95x10-3HCl:0.123THF

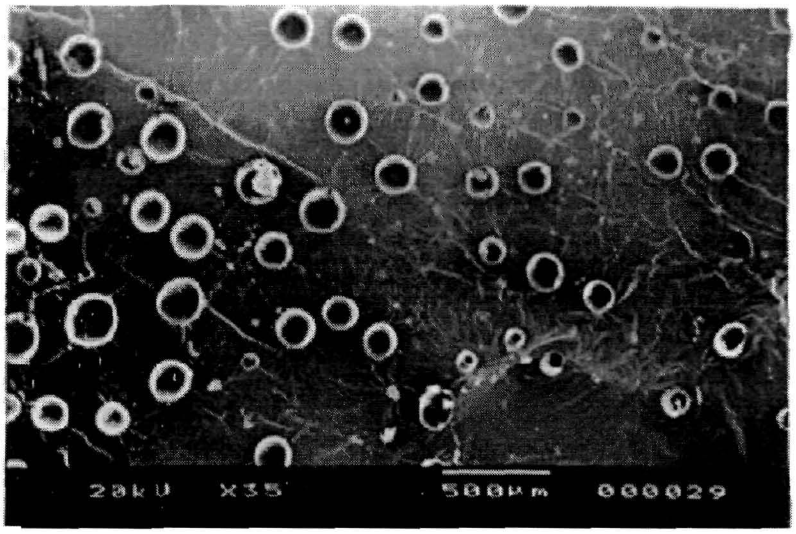


Fig.4.7d . SEM micrograph for the composition 2.86x10-3PSBUAMVSB: 8.94x10-3TEOS:1.47x10-5HCL:0.123THF

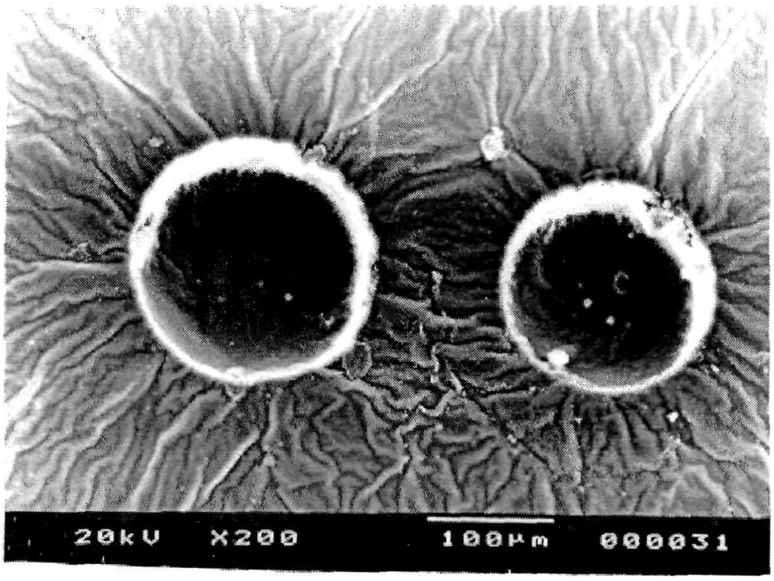


Fig.4.7 e SEM micrograph for the composition 2.86x10-3PSBUAMVSB: 8.94x10-3TEOS:1.47x10-5HCL:0.123THF

Examination of the sol-gel molar compositions in Table 4.2 shows that concentration of the medium increases with increase in ml of TEOS because the amount of the solvent (THF) remains the same. Another explanation for the formation of these hollow spherical particles could be that gels composed of larger particles are formed from solutions with higher HCl content and lower H_2O content [5]. As the particle size increases, the transparency of the resultant dried gel is lost and the bulk density of the gel increases [5]. That is also the reason why haziness appears in the samples and hollow spherical particles are visible under SEM. Because of the small amount of water used in the hydrolysis reaction in the starting solutions that give large particles, a large number of unhydrolyzed alkoxy groups are left on the polymerized species. These alkoxy groups give rise to the lipophilic nature of the polymerized species [4]. This was also evident from the residues obtained from TGA analysis [Table 4.3, SL 14-15], where the silica content at 700C is less than that at 550C and 600C . This is due to incomplete hydrolysis of the alkoxy groups.

It has been stated that there are two dominant effects which establish the reinforcing nature of the SiO_2 phase, the concentration of adhesion points between the polymer and silica surface, which depends on particle size and concentration, and the chemical character of the surface, which is a function of pH [3]. It appears that in presence of the butyl acrylate component in the copolymers PSBUAMVS, co-condensation was more dominant than with

PSMVS, which is why smooth morphologies at higher silica loadings was possible.

With higher percentages of MVS (upto2ml) in the copolymer derived from styrene, butyl acrylate and MVS, the extent of TEOS loading was further enhanced. It may be inferred from the above studies that,

i. Flexibilization of the Polystyrene backbone enhanced compatibilization with silica.

ii. Flexibilization coupled with silane functionalization greatly increased the extent of silica loading.

TGA analysis: The TGA curves are shown in Fig. 4.8. The curves for the composite samples show a more steady degradation pattern as compared to the composites. The Tids were obtained by second differentiation of integral TGA curves. The initial decomposition temperature (Tid) for the composites is generally higher than for the copolymers [Table 4.3]. Therefore thermal stability has been found to be enhanced on incorporation of silica in the copolymers. For the composites, the Ti gradually increases with higher proportions of TEOS in the composites. The enhancement in thermal stability of the composites could be attributed to the interaction force between silane functionalized polystyrene and silica network [5]. The silica content in the copolymers are obtained from residues in the TGA curves. For higher silica content in the copolymers PSBUAMVSB, the residue at 550C and 600C are higher than the residues at 700C [Table 4.3, SL 14 and 15]. This may be due to incomplete hydrolysis of TEOS.

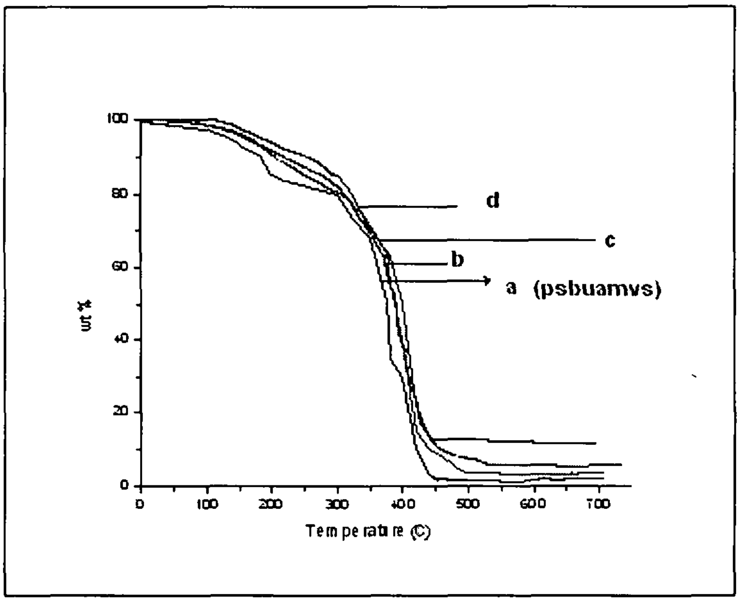


Fig. 4.8. TGA curves for copolymer PSBUAMVSB (curve a) and its composites (b, c and d.)

DSC analysis: DSC curves are shown in for the copolymers and composites. The DSC measurements were carried out in the temperature range 70C to 300C. In the DSC curve for PSBUA [Fig.4.9], the inflection for the first transition is at 82.2C. Another transition with a smaller value of ΔCp is observed around 122C.

For the copolymer PSBUAMVSA and PSBUAMVSB, there are two transitions, one at ~ 105C and the other at ~ 250C. In the composites derived from PSBUAMVSA and PSBUAMVSB, the first transition is observed around 125C and the second between 220C to 250C. The breadth of the endothermic transition is found to decrease with an increase in the silica content in the composites.

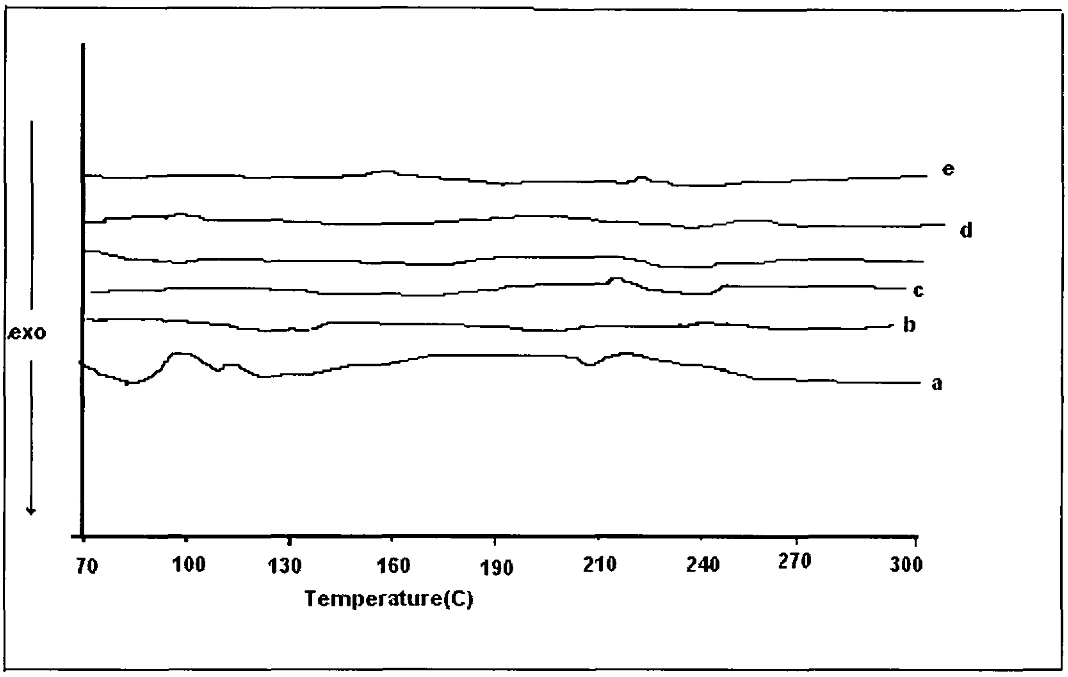


Fig.4.9. DSC curves for copolymer PSBUAMVSB (curve a) and its composites (curves b, c, d and e)

Table 4.3. Thermal properties from TGA analysis for the copolymers and composites

SL	sample	mole ratio of polymer :TEOS:HCl:THF	*T_{id} C	Residue at 550C (%)	Residue at 600C (%)	Residue at 700C (%)
1	PSBUA	**pure copolymer**	**170**	-	-	-
2	PSBUA	3 19x10^{3} 1 56x10^{3} 2x10^{4} 0 123	176	2.5	2.5	2
3	PSBUAMVSA	**pure copolymer**	**200**	**0.5**	**0.5**	**0.5**
4	PSBUAMVSA	3 19x10^{-3} 1 87x10^{3} 2x10^{-4} 0 123	210	5	5	5
5	PSBUAMVSA	2 86x10^{-3} 2 23x10^{3} 9 86x10^{5}0 123	215	5	5	5
6	PSBUAMVSA	2 68x10^{3} 3 12x10^{3} 7 5x10^{-5} 0 123	210	6	6	6
7	PSBUAMVSA	2 86x10^{-3} 3 576x10^{3} 5x10^{5} 0 123	220	6 6	6 6	6 6
8	PSBUAMVSA	2 86x10^{-3} 4 34x10^{3} 4x10^{5} 0 123	215	6	6	6
9	PSBUAMVSA	2 86x10^{-3} 5 2x10^{-3} 4x10^{5} 0 123	225	7	7	7
10	PSBUAMVSA	2 86x10^{3} 5 64x10^{3} 3 75x10^{-5} 0 123	230	7 5	7 5	7 5
11	PSBUAMVSB	**pure copolymer**	**180**	**0.8**	**0.8**	**0.8**
12	PSBUAMVSB	2 86x10^{-3} 7 15x10^{-3} 4x10^{5} 0 123	230	8	8	8
13	PSBUAMVSB	2 86x10^{-3} 8 04x10^{-3} 4 5x10^{-5} 0 123	250	8	8	8
14	PSBUAMVSB	2 86x10^{-3} 8 24x10^{-3} 5x10^{-5} 0 123	250	9	9	8
15	PSBUAMVSB	2 86x10^{3} 8 94x10^{-3} 5x10^{5} 0 123	280	12 8	10	8 5

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* T_{id} = Initial degradation temperature

Water uptake: As a result of incorporation of butyl acrylate in the copolymers, water sensitivity increases as compared to Polystyrene, but after incorporation of silica, the water uptake again decreases. The water uptake for PSBUA copolymer was 0.5%, for PSBUAMVSA and PSBUAMVSB copolymers it was ~ 0.45% and for the composites it varied between 0.4 to 0.35%. The composites with higher silica content showed a continuous decrease in the water uptake.

Comparison of the properties derived from polystyrene(PS), PSMVS, PSBUA and PSBUAMVS with silica: To summarize and compare the results of Chapter 3 and Chapter 4, comparison data has been incorporated in Table 4.4.

Table 4.4. Comparison of the physical properties of PS/silica, PSMVS/silica, PSBUA/silica, PSBUAMVS/silica

SL	Sample	$\overline{Mn}$ copolymer	TEOS ml	physical appearance	morphology under SEM	Tid C	water uptake %
1	PS/silica	~ 70,000	0.1	phase separated	visible phase separation	220	0.50
2	PSMVSA/silica	50,000	0.4	transparent	no phase separation	230	0.4
3	PSMVSB/silica	63,000	0.5	hazy	visible phase separation	250	0.25
4	PSMVSC/silica	34,000	0.9	transparent	no phase separation	376	0.15
5	PSBUA/silica	40,000	0.25	transparent	interface visible	220	0.5
6	PSBUAMVSA/silica	~35,000	1	transparent	no phase separation	230	0.45
7	PSBUAMVSA/silica	~35,000	1.3	hazy	silica particles visible	250	0.4
8	PSBUAMVSB/silica	~35,000	1.3	transparent	no phase separation	270	0.4
9	PSBUAMVSB/silica	~35,000	2	hazy	hollow spherical silica	285	0.35

The data presented in Table 4.4 may be discussed as follows.

Optical transparency and morphology of the composites: For the sol-gel composites derived from copolymer of styrene and butyl acrylate (PSBUA), synthesis of optically transparent, non-phase separated composites was possible for an external addition of 0.38ml TEOS in7g of the copolymer whereas non-phase separated composites could not be produced from polystyrene and silica. For the composites derived from silane functionalized polystyrene and silica (PSMVS), optically transparent composite films were obtained upto an addition of 0.7ml TEOS in 7g of copolymer. For the composites derived from silane functionalized copolymer of styrene and butylacrylate (PSBUAMVS), upto 1.8 ml of TEOS could be incorporated in 7g of copolymer to produce optically transparent composites Amongst the four systems polystyrene(PS)/silca polystyrene-butylacrylate (PSBUA)/silica, silane functionalized polystyrene (PSMVS)/silica and silane functionalized polystyrene-butylacrylate (PSBUAMVS)/silica, the highest amount of silica loading was possible in the composites derived with the copolymer PSBUAMVSB and silica.

The composites derived with the copolymers that were functionalized with the silylating monomer methylvinyldichlorosilane (MVS) (PSMVSA, PSMVSB, PSMVSC, PSBUAMVSA, PSBUAMVSB) showed smooth morphologies under SEM with no clear polymer/silica interface at low concentrations of silica. At higher silica and acid concentrations hollow and spherical silica particles become visible in the copolymers derived with PSBUAMVSB/silica [Fig.4.7d and 4.7e]].

The copolymer molecular weight was found to influence the extent of silica loading in the sol-gel hybrid composites. In the composites derived with PSMVSB, although the silane content was higher than PSMVSA, the composite morphologies were less smooth. This was due to the higher viscosity of the medium . With the lower Mn values it was possible to produce smooth morphologies with higher silane content and silica content in the copolymers.

Thermal stability: The thermal stability of the films was found to increase with an increase in the silane content in the copolymers and silica content in the composites. Amongst the four systems polystyrene/silica, polystyrene-butylacrylate (PSBUA)/silica, silane functionalized polystyrene (PSMVS)/silica and silane functionalized polystyrene-butyl acrylate (PSBUAMVS)/silica, thermal stability was found to be higher for composites derived with silane functionalized polystyrene and silica (PSMVS). Between the copolymers PSMVSA, PSMVSB and PSMVSC, thermal stability was the highest [Initial degradation temperature (T_{Id}) was of the order of 320C-370C] for the composites derived with the copolymer containing the highest amounts of the silylating monomer and silica content. (PSMVSC with 7% silica). The presence of the internal plasticizer butyl acrylate in the composites derived with the copolymers PSBUAMVS lowered the Tg values in the compositions. Therefore the improvement in thermal stability was not as high although the silica content in these composites was higher than composites derived with PSMVSC.

Water uptake: In all the four systems PS/silica, PSBUA/silica, PSMVS/silica and PSBUAMVS/silica, the water uptake percentage decreases with an increase in the silica content. Amongst these three systems water uptake percentage is lowest for the composites derived with silane functionalized polystyrene and silica (PSMVS). This is similar to the trend shown by the thermal stability of the composites. Water uptake percentage percentage follows the order PSBUA/silica > PSBUAMVS/silica> PSMVS/silica.

The comparison shows that incorporation of an internal plasticizer enhances the silica loading and optical properties but at the cost of water resistance and thermal stability.

4.5. Conclusion

Polymer /silica hybrid composites were prepared by the in-situ acid hydrolysis of TEOS within copolymers of polystyrene, viz. styrene-butyl acrylate and styrene-butylacrylate-methylvinyldichlorosilane by optimization of reaction parameters such as temperature and catalyst concentration . NMR spectroscopy results established the structure of copolymers. FTIR and TGA results showed the crosslinking of silica within the copolymer matrices. TGA and DSC results showed enhancement of thermal stability in the hybrid composites, which may be attributed to interactions between the polymer chain and silica network and uniform distribution of silica in the copolymer matrices. A higher loading of silica was possible in the copolymer obtained from styrene, butyl acrylate and methylvinyldichlorosilane as compared to the copolymers obtained from only styrene and methylvinyldichlorosilane (MVS). This fact showed that addition of butyl acrylate enhanced compatibilisation of silica with the Polystyrene copolymer matrix. The SEM results also showed that the styrene-butyl acrylate copolymers could produce crack free composites, whereas crack free composites with Polystyrene and silica could not be produced. This means that flexibilisation of the Polystyrene backbone with butyl acrylate obviates the necessity of silane functionalisation if silica is to be loaded at low percentages. Comparison of physical properties for the composites derived from from the four different systems Polystyrene/silica, Polystyrne-butylacryalte/silica, silylated Polystyrene/silica and silylated polystyrene-butylacrylate/silica showed that incorporation of an internal plasticizer enhances the silica loading and optical properties but at the cost of water resistance and thermal stability. These hybrid composites may find potential applications as sol-gel coatings, which can impart many useful properties to materials such as thermal, mechanical or chemical stability, wear protection and durability.

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CHAPTER 5

CONCLUSION

5.1. Introduction

We have synthesized polymer-inorganic hybrid composites by the sol-gel method. The findings of the previous chapters may be summarized and discussed as follows.

5.2.1 PVA/silica and PAA/silica hybrid composites

In the synthesis of PVA/silica hybrid composites, the concentration of PVA and sodium silicate used in the sol-gel mixtures are crucial in determining the maximum amount of silica that could be incorporated in the PVA matrices while retaining the flexibility and transparency in the composites. With 6% PVA (w/v), a maximum of 23% silica could be incorporated but with 11.5% PVA (w/v), a maximum of 16% silica could be incorporated.

Scanning electron microscopy (SEM) showed that for the PVA/silica composites, the dispersion characteristics are affected by viscosity of the sol-gel mixture and concentration of silica in mixture. The dispersion characteristics affect the bulk properties. For example, the elongation at break is maximum for the PVA/silica composite in which there was no large scale aggregation of silica particles (18% silica dispersed in 8.5%

PVA (w/v). The tensile strength was found to increase with an increase in the silica content. The maximum value of tensile strength (37.75Mpa) was obtained for the composition 16% silica in 11.5% (w/v) PVA.

For the PAA/silica composites, the SEM micrographs showed the silica to be distributed in an even manner throughout the PAA matrix. With an increase in the silica content in the composites, there is a growth and densification of silica particles within the matrix. This is in contrast to the dispersion of silica within the PVA matrix where a random distribution of lumps or aggregates is observed. This is possibly due to a difference in the mode of structural evolution of the silica sol within the PAA and PVA matrices.

The thermal stability of the hybrid composites PVA/silica and PAA/silica are found to increase with an increase in the silica content in the hybrids and the water uptake is found to decrease with an increase in the silica content.

The formation of colloidally stable sol through optimization of reaction parameters helped to attain better properties in the composites.

5.2.2. Polystyrene/silica hybrid composites

Non-phase separated composites could not be synthesized from polystyrene and silica. For the composites derived from silane functionalized polystyrene and silica (PSMVS), optically transparent composite films were obtained with ~ 7% silica loading in the composites.

The incorporation of the silylating monomer enhances the dispersion characteristics as well as the silica loading. The thermal stability of the films was found to increase with an increase in the silane content in the copolymers and silica content in the composites. On incorporation of the silica phase, the polymer becomes hydrophobic. The increase in Tg of the composites is due to restriction in chain motion in the composites imposed by crosslinking with the silica network. Water uptake measurements also showed that the water uptake decreased to a great extent on incorporation of the silica phase. The ratio by volume of the silylating monomer, (methylvinyldichlorosilane) and the co monomer styrene, viscosity of the resultant copolymer and the ratio of copolymer solution to TEOS solution were the significant factors affecting the uniformity of dispersion of silica within the polymer matrix.

5.2.2. Polystyrene-butylacrylate/silica hybrid composites

Composites without phase separation could be derived from copolymer of styrene and butyl acrylate (PSBUA). Thermal stability for PSBUA composites was enhanced in comparison to the copolymer.

For the composites derived from silane functionalized copolymer of styrene and butylacrylate (PSBUAMVS), higher proportion of silica (~10%) could be loaded to produce optically transparent composites.

The thermal stability of PSBUAMVS/silica composites was higher with respect to the pure copolymer. The extent of improvement in thermal stability, however, was less than that with hybrid composites derived from silane functionalized polystyrene (PSMVS/silica) due to the presence of butylacrylate which acts as an internal plasticizer. The water uptake in PSBUAMVS composites also decreased with incorporation of silica phase.

Amongst the three systems polystyrene-butyl acrylate (PSBUA)/silica, silane functionalized polystyrene (PSMVS)/silica and silane functionalized polystyrene-butylacrylate (PSBUAMVS)/silica, the highest amount of silica loading was possible in the composites derived from PSBUAMVS.

It was observed that the dispersion of silica within the polymer matrices and the bulk properties of the composites are decided by an interplay of various factors such as the nature and type of the polymer backbone, nature and concentration of the silica precursor, viscosity of the sol-gel reaction mixture, pH of the medium etc. Comparison of the SEM micrographs for the PVA/silica, PAA/silica, PS/silica, silane functionalized PS/silica, PSBUA/silica and silane functionalized PSBUA/silica showed that there was better compatibility between the silica and polymer phase in the silane functionalized systems. The SEM micrographs for the silane functionalized polymer/silica systems do not show clear polymer/silica interfacial separation. Flexibilization of the polymer backbone also helps in enhancing compatibility with the silica phase.

5.4. Scope of further work

PVA is an attractive candidate for the preparation of membranes because of its high water permeability and good film forming abilities. The PVA/silica composites synthesized by us showed a variation in water uptake with variation in the silica content in the composites. Therefore there is the possibility of synthesizing materials with controlled compositions for use as water permselective membranes. Recently a great deal of attention has been devoted towards the preparation of environmentally compatible materials for a wide range of applications. Application of PVA hydrogels have been proposed, particularly in the biomedical field, because of their inherent low toxicity, bioinertness, good biocompatibility and desirable physical properties such as elastic properties and good swelling in water. PVA/silica composites synthesized with sodium silicate might have an edge over those synthesized from (TEOS) because sodium silicate does not generate alcohol. Alcohol is detrimental for use with protein and cells. There is scope for the development of polymer/silica hybrid composites by using hydrophilic polymers such as PVA and silicate glasses that would have bioactivity. i.e. a degree of interaction between biomaterial and host tissue, controlled by the chemical and structural properties of the materials. Reaction parameters such as choice of solvent, catalyst, temperature, etc. will have to be optimized in the process of synthesis of the hybrids. The effects of the phase content of the inorganic and the polymeric components on the final bulk properties of the composites such as tensile strength, elasticity, thermal stability, cross link density and hydrogel behaviour will have to be studied and the possibilities of the biomedical applications of these materials will have to be tested.

The formation of hollow spherical silica particles in the composites derived with PSBUAMVS/silica opens up the possibilities of synthesis of hybrid materials with uniform pore sizes in systems of this type. Fabrication of materials into hollow and spherical particle promises scope for a wide variety of applications such as catalysis and separation.

Publications

A. Journals

1. Kotoky, Tapasi and Dolui, S.K. *Synthesis and characterization of Polyvinylalcohol (PVA)/silica hybrid composites derived through the sol-gel method in aqueous medium: Effect of acid content, silica content and viscosity of PVA on the dispersion characteristics of silica and the physical properties of the composites.* Journal of Sol-Gel Science and Technology 2004, 29, 107-114.

2. Kotoky, Tapasi; Ray, B.C; Dolui, S.K. *Synthesis and Characterization of Hybrid-Organic Inorganic Composites derived from polystyrene/copolymers of styrene and methyl vinyldichlorosilane with silica through the sol-gel method.* Journal of Polymer Materials 2003, 20, 257-265.

3. Kotoky,Tapasi and Dolui,S.K. *Synthesis and Characterization of Polystyrene/Silica Hybrid Organic- Inorganic Composites by the in-situ Sol-gel method: Effect of introduction of a flexible butyl acrylate component into the silane functionalized Polystyrene backbone.* (Communicated to the Journal of Composites Science and Technology).

B. Proceedings

1. Kotoky, Tapasi and Dolui, S.K. *Synthesis and Characterisation of Composites derived through the in-situ Sol-Gel method from Tetraethylorthosilicate and Copolymers of Polystyrene/silane functionalised Polystyrene* . Proceedings of POLYCHAR (International Conference on Advanced Polymer Materials, (POLYCHAR-12), Portugal. (Jan 6th-9th, 2004)

2. Kotoky, Tapasi and Dolui, S.K. *Synthesis and Characterization of Polyvinyl alcohol/silica hybrid organic-inorganic composites* . Proceedings of the Frontiers in Materials Science and Technology (FMST 02), I.I.T Kharagpur, Feb 22nd -24th, 2002.