MODIFICATION OF POLYPROPYLENE AND POLYSTYRENE USING NANOSILICA

Thesis submitted to the
Cochin University of Science and Technology

By

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In partial fulfillment of
the requirement for the award of the degree of

DOCTOR OF PHILOSOPHY
UNDER THE FACULTY OF TECHNOLOGY

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July 2008

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Certificate

Certified that, the thesis entitled 'MODIFICATION OF POLYPROPYLENE AND POLYSTYRENE USING NANOSILICA' *submitted to* Cochin University of Science *and* Technology *under the faculty of technology, by* Mrs.Renjanadevi.B, is *an authentic record of the original research carried* out *by her under my supervision and guidance. The thesis has fulfilled all the requirements as per regulations and no part of the results embodied has been submitted to any other* institution *for any other degree/diploma.*

Dr.K.E.George

Declaration

I hereby declare that, the thesis entitled 'MODIFICATION OF POLYPROPYLENE AND POLYSTYRENE USING NANOSILICA' submitted to Cochin University of Science and Technology, under the Faculty of technology, is based on the original research carried out by me under the supervision of Dr. K.E.George, professor, Dept. of Polymer Science and Rubber Technology, and no part of the results presented has been submitted to any other institution for any degree/diploma.

Renjanadevi.B

Cochin
5th July 2008

Acknowledgement

I would like to express my deep sense of gratitude to my supervising guide, Dr. K. E. George, Professor, Department of Polymer Science and Rubber Technology for his scholarly guidance and inspiration at every stage of this work. I am also thankful for the relentless support and care that he has given me during my research and also in my personal life.

I am grateful to Dr.Thomas Kurian, Head of the Department of Polymer Science and Rubber Technology for the help and the facilities offered by him during my research. I also extend my thanks to Dr. Rani Joseph, former Head of PSRT and all other staff members of the department, office staff for their timely help. I would like to place on record my thanks to Mrs. Girija, Librarian of the department library for her help and co-operation.

I would like to thank all the research scholars, past and present especially Mr. Thomas N.Abraham, Mr.Sinto, Mr. Parameswaran, Mrs. Bhuvaneswary, Ms. Saritha, Mr.Bipin Pal, Ms.Anna and Nimmi for their help and support. I am grateful to my students of 3rd semester M.Tech., GEC, Thrissur, especially Ms. Sreevidya, Mercy Anna Philip, Najuma and Beena for their help and co-operation.

I gratefully indebted to all my colleagues in the Department of Chemical Engg. Govt. Engg. College, Thrissur especially Prof. Dr. Lakshmikutty Amma, for all the help they have rendered to me. I would like to make a special mention to Dr.A.N.Chandran former HOD, Govt. Engg. College Thrissur and for his valuable suggestions at all times.

I am thankful to the Govt. of Kerala, The Director of technical Education, Principals of Government Engineering Colleges in Kozhikode and Thrissur for granting me permission to do research.

Finally I express my deepest sense of gratitude to my beloved family members, especially my husband and my children for their encouragement and moral support which helped me a lot in completing this study.

Renjanadevi. B

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PREFACE

Nanotechnology has received special attention in recent years as it offers a growing range of applications in many fields. Nanosilica is an attractive filler that be used for the modification of properties of polymers. This novel material has many unusual properties, such as a low thermal conductivity, refractive index, along with a high surface area and thermal stability. The addition of nanosilica particles to glassy polymers modify the permeability coefficients for several gases and vapours. Addition of very small amount of nanofillers brings about a large enhancement of the mechanical and thermal properties of the polymers. Utilization of nanosized organic-inorganic hybrid particles for advanced applications requires high quality with respect to chemical purity, homogeneity, morphology and a controlled state of agglomeration as well as low production costs. This lead to the production of surface modified silica particles and such modified nanofillers have generated great interest in scientific research and industrial development.

The present work focuses on the modification of the commonly used thermoplastics, polypropylene and polystyrene using nanosilica prepared from a cheap source of sodium silicate. Melt compounding technique has been used for nanocomposite preparation as it is simple and suited to injection moulding. Nanosilica in a polymer matrix provide significant enhancement in strength, stiffness and impact strength. Incorporation of silica particles in a polymer also improves its thermal stability. To achieve better dispersion of fillers in polymer matrices the mixing was done at different shear rates. The enhancement in material properties indicates that at higher shear rates there is greater interaction between particles and the matrix and it depends on filler concentration and type of polymer used. Nanosilica is a useful filler in thermoplastic polymers and has been applied in automotive applications, electronic appliances and consumer goods.

This thesis is divided into six chapters. General introduction to the topic is described in chapter 1. Salient features of polymer nanocomposites, their synthesis, properties and applications are presented. A review of relevant literature and the scope and objectives are also mentioned in this chapter.

The materials used and the various experimental method and techniques employed in the study are described in chapter 2. Preparation of nanocomposites by melt blending using Thermo Haake Rheocord, preparation of samples, evaluation of mechanical and thermal properties using UTM, Impact testing and characterization using DMA, TGA and DSC and morphology by SEM are described.

The preparation of nanosilica from a laboratory scale to a pilot plant scale is described in chapter 3. Generation of surface modified silica, evaluation of kinetic parameters of the synthesis reaction, scale up of the reactor and modeling of the reactor are also dealt with in this chapter.

The modification of the commodity thermoplastic, Polypropylene using nanosilica is described in chapter 4. Preparation of PP/silica nanocomposites, evaluation of mechanical properties, thermal and crystallization characteristics, water absorption and ageing resistance studies are also presented.

The modification of Polystyrene using synthesized nanosilica is described in chapter 5. The method of preparation of PS/silica nanocomposites, evaluation of mechanical properties (static and dynamic), thermal properties melt flow characteristics using Haake Rheocord, water absorption and ageing resistance of these nanocomposites are studied.

The summary and conclusions of the study are presented in chapter 6.

Chapter 1

Introduction

Polymers are widely used due to their ease of production, light weight and design flexibility and processability. However, polymers are of lower modulus and strength compared to metals and ceramics. One way to modify their properties is to reinforce polymer with particulate fillers. The common practice of embedding of inclusions in a polymer to make composites provides material properties not achieved by either phase alone. Hence polymer properties can be improved while maintaining their light weight and ductile nature. Modification of polymers can be done at relatively low filler content.

Over the past decade, the incorporation of fillers into a polymer matrix has produced a wide range of multifunctional properties like increasing the backbone stiffness , Catalytic activity and transport properties etc[1-3]. several effects on the polymer properties by the addition of silica includes change in mechanical properties due to reduction of polymer mobility and possible interaction between the phases involved. The main purpose of the filled polymer is to reduce cost, improve mechanical and thermal properties, reduce permeability to gases, reduce electrical conductivity etc.[4]. However the mechanical properties of the particle filled polymer composites depend strongly on the size, shape and uniformity of the dispersed fillers in the polymer matrix and interfacial adhesion between the polymer and the filler[5].

Commonly, smaller fillers are used to increase the surface area available for interaction with the matrix. However, in the case of micron sized fillers, content above 20% volume is required to optimally impact mechanical properties. At these higher concentrations the filler can detrimentally affect other benefits of polymers such as processability and appearance. With the advent of nanomaterials research, synthesis of inorganic nanoparticles, that is particles with one dimension in the nanosized regime is readily achievable [6]. Because of their smaller size, nanoparticles have an extremely high surface to volume ratio providing significantly more surface area for bonding with the matrix than micro sized fillers.

Hence polymers modified with nanoparticles fillers have been predicted to provided the most beneficial applications.

1.1 Commodity /standard plastics

1.1.1 Polypropylene

Polypropylene(PP) is the lightest of the common plastics, with a specific gravity of 0.9. PP, however, is harder and has a higher softening point, lower shrinkage and immunity to stress-cracking. It is a widely used standard plastic. Polypropylene is made by the polymerization of propylene monomer which is obtained from the cracking of petroleum products. The synthesis is much the same as that of HDPE by Ziegler process [7]. Due to the presence of the methyl group, the polymer can be isotactic, syndiotactic and atactic. The commercial type is isotactic. It has a higher softening point and hence articles made of it can be subject to many steam sterilizing operations. It has a higher brittle point. PP is readily degraded by UV radiation and heat. Stabilizers are blended into the resin to protect it against degradations. Its high tensile strength, elongation at break, high melting point and low density is advantageous in many applications. PP shows lower mould shrinkage than polyethylene.

Isotactic PP is an essentially linear, highly crystalline polymer, with a melting point of 165^0 C. PP has excellent electrical properties, chemical inertness and moisture resistance[8]. It is completely free from environmental stress cracking. However it is less stable than polyethylene. The material is used for injection moulding. PP film is used for packaging of a variety of products. In addition to the film, this plastic is moulded into domestic hollow ware, toys, bottles, automotive components such as distributor caps, disposable syringes for medical and veterinary use, battery cases, rope and carpeting[6].

Polypropylene Properties (General purpose)

Melt Flow, g/10min.	4 – 12
Tensile strength, MPa	35 – 34.8
Elongation, %	12 – 11
Flexural modulus,MPa	1724 – 1793
Rockwell hardness	99 – 100
Notched Izod impact strength at 23° C, J/m	37.3 – 42.7

1.1.2 Polystyrene (PS)

Polystyrene, like poly (vinyl chloride) (PVC) and Poly ethylene(PE) is a widely used low-cost thermoplastic. Because of the aromatic ring in the monomer, it does not crystallize. Two general types of PS are available which are general purpose and impact grades [7]. The impact type is obtained by blending with 5-10 % Poly butadiene rubber. However it is easily stress cracked and the solvent resistance is poor. The resin is rapidly degraded by sunlight. Its heat resistance is also limited. PS is obtained by the polymerization of styrene, by either bulk or suspension polymerization[8]. Commercial PS is a radically initiated atactic polymer. It is amorphous and transparent. Polystyrene being hydrophobic in nature, has very low moisture absorption good mouldability, dimensional stability and low moulding shrinkage and hence it is considered as an ideal polymer for injection moulding and for thermoforming. Polystyrene has poor outdoor weathering resistence and a tendency to yellowing and crazing on long use. The Tg of polystyrene is ~ 100^0C. Above Tg the polymer chain allows large-chain segment mobility, and hence it can be easily shaped into useful forms. Below Tg, PS possesses considerable mechanical strength, allowing it to be used in load bearing tasks. Since PS is nonpolar, chemically inert, resistant to water and easy to fabricate, it is preferred for electronic, medical, food packaging, optical appliance and automotive applications [8-9].

PS molecules can be oriented during fabrication. Modern processing equipment uses controlled orientation to produce tougher fabricated parts. Tensile strength may double and elongation may increase by up to two orders of magnitude, resulting in improved toughness. Toughening by orientation makes it to produce PS from which is widely used in insulation and food packaging. Pure PS have better ultraviolet stability. Anionic polymerization produces more thermally stable polymer. Because of its polymerization ease and its relatively simple linear structure, PS is one of the most thoroughly investigated polymers in the world [10].

1.2 Fillers

Fillers are usually solid additives mixed with plastics to improve material properties, to introduce specific characteristics, or to reduce the cost of the compound. In the case of mass volume biodegradable polymers, cost reduction has practical importance besides improvement in the mechanical properties. Fillers are inorganic or organic materials, and each group consists of fibrous and non fibrous types. Individual fillers are available in a number of grades differing in average particle size and size distribution, particle shape and porosity, chemical nature of the surface, and impurities. As a result of the presence of filler, hardness and stiffness are increased while impact and tensile strength are usually decreased[11-13]. Thakur et al.[14] have found that talc, which is commonly added as a filler, also acts as a nucleating agent for poly(lactide) and increases the number of spherulites in crystallization. Kolstad [15] concluded that 6 wt% talc gives a 500-fold increase in the nucleation density. Hiljanen-Vainio et al.[16] have recently enhanced the mechanical properties of lactic acid based poly(ester-urethane) via the addition of organic fillers.

Fillers are solid additives usually incorporated into the polymer mechanical for a variety of purposes of which the most important are reinforcement, increase in stiffness, reduction in material costs and improvements in processing[17]. Reinforcement in accompanied by stiffening or increasing in modulus. Fillers are also used to improve the optical thermal (thermal conductivity and co-efficiency of their thermal expansion), electrical, magnetic and flammability characteristics of the polymeric matrix.

The effectiveness of filler depends on its type, incorporation method loading and surface treatment. The presence and arrangements of filler particles of the matrix such as crystallinity and glass transition temperature.

1.2.1 Fillers for plastics

It can be divided as → Inactive fillers (Extender fillers)
→ Active fillers (Functional fillers)

Inactive fillers are used mainly to reduce the cost while functional fillers brings about a special change in properties. Among the fillers used are $CaCO_3$, china clay, talc and barium sulphate. Particle size and shape influence the properties of polymers such as tensile strength, modulus and hardness and anisotropy of the polymer. The chemical nature of the surface can have a vital effect. Mineral fillers improve the wetting of polymers to fillers and hence obtain better products[18]. Most recently coupling agents such as silane which in effect form a polymer shell around the surface of the particle and improve the wetting to the main polymer.

Reinforcing particulates effectively incorporated in elastomers significantly increases the tensile strength. Rubbery materials added in to rigid thermoplastics improve their toughness.

Fibrous fillers are also employed in plastics. Wood flone, Cotton flock, Macerated fabric and short length of Synthetic nylon fibres improve the impact strength of molding compositions. Inorganic fibres are also used in both thermoplastic and thermosetting resin to enhance the strength modulus and heat resistance of unfilled resin. Structurally filler particles can be globular rod like or plated type. Generally carbon black and silica particles are globular, while whiskers and fibers are ideal examples of unidirectional rod like fillers.

1.2.2 Nanofillers

Nanofillers are nanosized materials having at least one diamension of the order of nanometer(10^{-9}m) that are added to polymer matrices to promote specific, optical, electrical sensory, catalystic or mechanical properties [20-21]. Addition of nanofillers in polymers strongly increases the thermal and mechanical properties. However, it has been clearly been shown that the properties improvement is strongly related to the strength and well controlled dispersion state of nano fillers in the polymer matrix. Such fillers includes Carbon black, silicate, synthetic silica and talc. In most hybrid systems investigated so far, a nanofiller is added to a single homopolymer permitting uniform distribution of the nanofiller.

1.3 Synthetic Silica

Synthetic silicas are mainly amorphous silicon dioxide. The primary particles of size 10-100nm form aggregates (secondary particles) with 1-10 um average size. The silica products are named after their production process as formed, fused and precipitated. The surface area range between 50 and 800m^2/g. Due to their high abrasion resistance good grip and dusting qualities they can be used for making shoe outsoles and rubber goods and their optimal properties are used in battery separators. Nanosilica enhances polymer properties like flame retardency barrier properties/transparency and scratch resistance [22].

The basic raw material for the production of synthetic silicas is sand or quartz. The two main routes to these products are the 'wet' process starting from sodium silicate and 'thermal process using high temperature reactions[23]. The basic processes for the production of synthetic silicas are shown in fig 1.1.

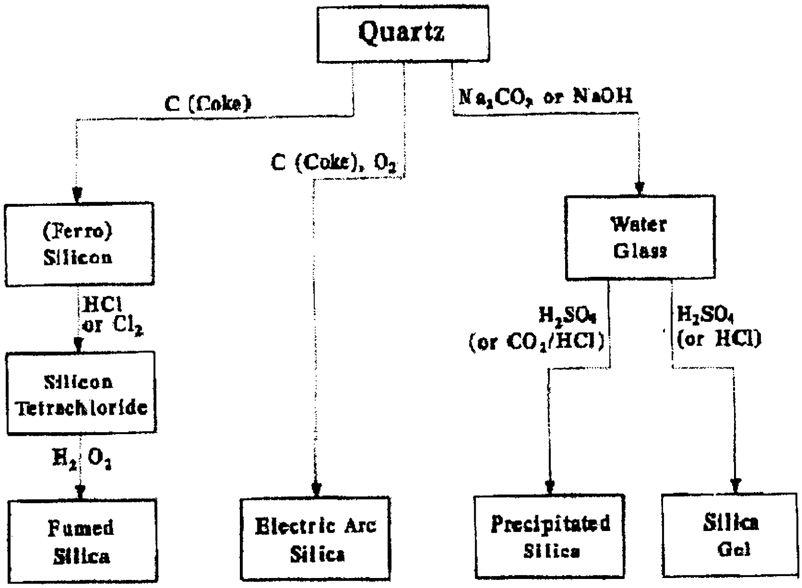


Fig 1.1 Basic processes for the production of synthetic silicas

Despite the apparent simplicity of these processes, the properties of silica products can vary within large range. Table 1.1 shows the properties of synthetic silicas.

Table 1.1 Properties of synthetic Silica

Type	Diameter of Primary Particles, (nm)	Specific surface area,(m^2g^{-1})	Tapped Density (g/cm^3)	Silanol group density, (SiOHnm^{-2})	Porosity
Fumed	7 – 40	50-500	50-120	2 – 4	Non porous (< $300m^2g^{-1}$)
Gel	2 – 10	300-1000	100-800	5 – 6	Very high
Precipitated	7-100	50-800	100-350	5 – 6	Low

1.3.1 Silicas produced by thermal processes

i) Fumed (pyrogenic) silicas

The insufficient reinforcement properties obtained with different precipitated products stimulated Dr. Harry Kloepfer, in the late 1930's to try a different approach to finding "white carbon". He developed a process similar to the one used for making channel blacks and used feedstock tar oil for a volatile compound, silicon tetrachloride. Sand or quartz is first reduced in an electric arc process to silicon metal, then the latter is chlorinated with chlorine or hydrogen chloride to silicon tetrachloride. It was burned in the presence of expensive hydrogen to give SiO_2 as per the following reaction.

$$SiCl_4+2H_2+O_2 \rightarrow SiO_2+ 4HCl$$

A new class of products with remarkable properties have been found. They were called 'aerosils': 'airborn' silicas also known as pyrogenic or fumed silicas.

They are excellent reinforcement fillers for silicon rubber. Some of the disadvantages include the high price and poor processability associated with normal rubber. However, these ultrapure and ultra-fine fumed silicas found, despite their high price, a continuously growing technical application in different industries.

Properties and applications

Fumed silicas are fluffy white powders of amorphous structure. The average diameter of the particles in the range of 7-40 nm, corresponding to BET surface areas between 380 and $50 m^2/g$.

Very important for the outstanding properties of fumed silicas as thickening, thixotropic, and reinforcing agents in liquids, plastic and elastic systems are the evenly distributed silanol groups on the silica surface and their ability to form hydrogen bonds. Hence they are used in coatings, printing inks, gelcoats, sealants, cosmetics, and toothpastes. They also find application as free-flow and anticaking agents. Reinforcement of silicones with fumed silica (30 wt%) can cause a substantial increase of tensile strength. In high-performance insulation composites, silica is the main component and advantage is taken of the micro porous structure formed by the void volume between the silica aggregates which hinders gas diffusion.

ii) Electric arc and Plasma silicas

Highly dispersed silicas are obtained by the electric arc processes[24]. The principle of the method is as follows. At temperatures >1000°C, quartz is reduced with coke to ~ at that temperature - volatile SiO which, in a second step, is oxidized with air or steam to silica again.

$$SiO_2 + C \rightarrow SiO + CO$$

$$SiO + CO + O_2 \rightarrow SiO_2 + CO_2$$

The energy intensive and the general performance of these products cannot compete with the fumed silicas. Their technical importance is low.

1.3.2 Silicas by wet processes

Silicas produced by the wet processes are the amorphous product groups of the precipitated silicas and the silica gels. 'Silica sols' are produced on a large commercial scale by de-ionizing dilute sodium silicate solution by means of cation exchangers, followed by concentration and stabilization with small amounts of alkali. They find application as binders, for example in the manufacture of cast mouldings and insulation composites, in granulation, and as polishing agents for silicon wafers.

1.3.3 Sources of silica

Sodium silicate, of formula Na_2SiO_3,is commercially produced by the reaction of soda ash and sand in a furnace. Also know as "water glass", sodium silicate is used as an adhesive (Suleman and Hamid 1997), detergent (Keeley 1983), and fire-retardant (Nassar, Fadali et al. 1999). In addition to sodium silicate, several organic silica precursors are available, such as tetraethoxysilane (TEOS), of formula $Si(OC_2H_5)_4$, and tetramethoxysilane (TMOS), of formula $Si\ (OCH_3)_4$.

Sodium silicate, is inexpensive and highly soluble in water. However, it has a high ionic strength, which may be problematic, and the gel must be extensively washed to remove the considerable amount of salt which forms. This gives a savings of more than 40 percent, compared to TEOS, which can be significant on an industrial scale.

1.3.4 The use of silica

Precipitated silica can be used in a variety of functions, including:

- Reinforcing elastomers to improve modulus, elongation, tear strength and abrasion resistance (shoes, joints, pipes, tires)
- Free-flow and anti-caking agent for powders (organic and inorganic chemicals, food and animal feed products).
- Adsorption as a carrier for liquid active ingredients (Vitamins A and E and choline chloride for animals, dispersants and surfactants)

- Optics to improve whiteness and opacity (paper, emulsion paints for buildings)
- Rheology as a thickening agent (glue, varnish, industrial paint, toothpaste)
- Structuring smooth surfaces to add roughness, adsorption and dulling of surfaces (any smooth surface and anti-blocking of plastic films and paper).
- Controlled abrasion (toothpaste, household polishing products).

1.4 Coupling Agent

A filler in a polymer cannot modify the properties unless there is a good adhesion between them. To achieve control over the functionality of the filler surface, modification and special treatments has frequently led to the development of appropriate methods and/or substances[25]. All surface treatments are designed to bond an organic molecule physically or chemically to the filler surface. Coupling agents are bifunctional molecules which are used to develop a chemical bond (Covalent bond) between the polymer and the filler. In physical treatment the filler surface is coated with organic molecules that are physically bonded (mostly waxes starches etc.) which will improve the filler incorporation and dispersion. The amount and type of treatment depends on its chemical activity and on the filler surface.

The use of coupling agents started in early 1940s. These materials were used in conjunction with glass fibres, marketed as volan A for use in polyester-glass reinforced plastics. Chemical bonding to the surface of the glass fibres occurs through Cr-O-Si links. Bonding occurs via polymerization reaction involving double bond in the polyester, in styrene monomer present as diluents and in the methacrylate groups present in the coupling agent.

After their introduction, the use of coupling agents continue to be of great importance. Coupling agents also helped to increase the adhesion of polymers to fillers and other additives. For example, silane coupling agents are tried with phenolics and thermoplastics. In these cases covalent bonding to the polymer do not occur. Table 1.2 lists some examples of coupling agents.

Coupling agents were also extended to use with particulate fillers like silicas, silicates and clays for use in rubbers[26-27]. These materials are added during compounding stage. Titanium coupling agents are used to couple fillers in PVC, unsaturated polyester resins and polypropelene etc. They have the general formula $(RO)_m\text{-Ti-}(OX\text{-}R\text{-}Y)_n$. Typical example is isopropyl tri (dioctyl pyrophosphide) titanate. Significant changes in properties can be achieved with very small quantities of these materials when compared with untreated polymers.

1.4.1 Silane coupling agents

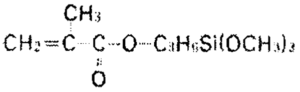
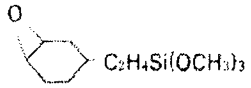
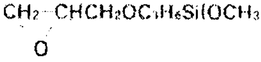
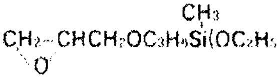
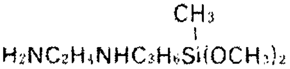
Silane coupling agents belong to a class of organosilane compounds having at least two reactive groups of different types bonded to the silicon atom in a molecule. One of the reactive groups of different types (eg. methoxy, ethoxy and silanolic hydroxy groups) are reactive with various inorganic materials such as glass, metals, silica sand to form a chemical bond with the surface of the inorganic material while the other of the reactive groups (ex, vinyl, epoxy, methacryl, amino and mercapto groups) are reactive with various kinds of organic materials or synthetic resins to form a chemical bond.

As a result of possessing these two types of reactive groups, silane coupling agents are capable of providing chemical bonding between an organic material and an inorganic material[28].

This unique property of silane coupling agents is utilized widely in the application of the silane coupling agents for the surface treatment of glass fiber products, performance improvement of fiber-reinforced plastics by the direct admixture to the synthetic resin, improvement of paints and other coating materials and adhesives, modification of surface properties of inorganic fillers, surface priming of various substrate materials, etc[29].

When a silane coupling agent is used in a thermosetting resin-based fiber-reinforced material, remarkable improvements are obtained in the mechanical and electrical properties of the material and the effect is more remarkable when the material is used in a wet or humid condition[30]. General properties of the silane coupling agents are given in Table 1.2.

Table 1.2 General Properties of Silane Coupling Agents

Classification	Chemical name	Structural Formula	Molecular weight	Specific gravity 25°C
Vinylsilane	Vinyltrichlorosilane	$CH_2 = CHSiCl_3$	161.5	1.26
	Vinyltris (ßmethoxyethoxy) silane	$CH_2 = CHSi(OC_2H_4OCH_3)_3$	280.4	1.04
	Vinyltriethoxysilane	$CH_2 = CHSi(OC_2H_5)_3$	190.3	0.90
	Vinyltrimethoxysilane	$CH_2 = CHSi(OCH_3)_3$	148.2	0.97
Acryloxy	3-metacryloxypropyl-trimethoxysilane	 $CH_2=\overset{CH_3}{C}-\underset{\underset{O}{\|}}{C}-O-C_3H_6Si(OCH_3)_3$	248.4	1.04
Epoxysilane	ß-(3,4 epoxycyclohexyl)-ethyltrimethoxysilane		246.4	1.06
	r-glycidoxypropyl-trimethoxysilane	 $\underset{O}{CH_2-CH}CH_2OC_3H_6Si(OCH_3)_3$	236.3	1.07
	r-glycidoxypropyl-methylidiethoxysilane	 $\underset{O}{CH_2-CH}CH_2OC_3H_6\overset{CH_3}{Si}(OC_2H_5)_2$	248.4	0.98
Aminosilane	N-ß (aminoethyl)-r-aminopropyl-trimethoxysilane	$H_2NC_2H_4NHC_3H_6Si(OCH_3)_3$	222.4	1.02
	N-ß (aminoethyl)-r-aminopropyl-methyldimethoxysilane	 $H_2NC_2H_4NHC_3H_6\overset{\overset{CH_3}{\vert}}{Si}(OCH_3)_2$	206.4	0.97
	3-aminopropyl-triethoxysilane	$H_2NC_3H_6Si(OC_2H_5)_3$	221.4	0.94
	N-phenyl-r-aminopropyl-trimethoxysilane	$C_6H_5NHC_3H_6Si(OCH_3)_3$	255.4	1.07
Others	r-mercaptopropyl-trimethoxysilane	$HSC_3H_6Si(OCH_3)_3$	196.4	1.06
	r-chloropropyl-trimethoxysilane	$ClC_3H_5Si(OCH_3)_3$	198.7	1.08

Application of silane coupling agents to thermoplastic resin-based fiber-reinforced materials is also actively performed along with the efforts to develop a silane coupling agent having further enhanced coupling effects.

1.5 Composites

Broadly defined, composites are materials with two or more distinct components that combine to yield characteristics superior to those of the individual constituents [31-32]. Although this definition can apply to such ordinary building materials as plywood, concrete, and bricks, within the aerospace industry the term composite generally refers to the fibre-reinforced metal, polymer, and ceramic products that have come into use since World War II. These materials consist of fibres (such as glass, graphite, silicon carbide, or aramid) that are embedded in a matrix , for example, aluminum, epoxy, or silicon nitride.

In the late 1950s a revolution in materials development occurred in response to the space program's need for lightweight, thermally stable materials. Boron-tungsten filaments, carbon-graphite fibres, and organic aramid fibres proved to be strong, stiff, and light, but one problem with using them as fibres were of limited value in any construction other than rope, which can bear loads in only one direction. Materials scientists needed to develop a way to make them useful under all loading conditions, and this led to the development of composites. While the structural value of a bundle of fibres is low, the strength of individual fibres can be harnessed if they are embedded in a matrix that acts as an adhesive, binding the fibres and lending solidity to the material. The matrix also protects the fibres from environmental stress and physical damage, which can initiate cracks. In addition, while the strength and stiffness of the composite remain largely a function of the reinforcing material—that is, the fibres—the matrix can contribute other properties, such as thermal and electrical conductivity and, most important, thermal stability. Finally, fibre-matrix combination reduces the potential for complete fracture. In a monolithic (or single) material, a crack, once started, generally continues to propagate until the material fails; in a composite, if one fibre in an assemblage fails, the crack may not extend to the other fibres, so the damage is limited.

To some extent, the composite-materials engineer is trying to mimic structures made spontaneously by plants and animals. A tree, for example, is made of a fibre-reinforced material whose strength is derived from cellulose fibres that grow in directions that match the weight of the branches. Similarly, many organisms naturally fabricate "bioceramics," such as those found in shells, teeth, and bones. While the designers of composites for the aerospace industry would like to copy some of the features of bioceramics production—room-temperature processing and net-shape products, for example—they do not want to be constrained by slow processing methods and limited fibre and matrix material choices. In addition, unlike a mollusk, which has to produce only one shell, the composites manufacturer has to use rapid, repeatable processing methods that can fabricate hundreds or even thousands of parts.

Modern composites are generally classified into three categories according to the matrix material: polymer, metal, or ceramic. Since polymeric materials tend to degrade at elevated temperatures, polymer-matrix composites (PMCs) are restricted to secondary structures in which operating temperatures are lower than 300° C (570° F). For higher temperatures, metal-matrix and ceramic-matrix composites are required[33].

1.5.1 Polymer-matrix composites

PMCs are of two broad types, thermosets and thermoplastics. Thermosets are solidified by irreversible chemical reactions, in which the molecules in the polymer "cross-link," or form connected chains. The most common thermosetting matrix materials for high-performance composites used in the aerospace industry are the epoxies. Thermoplastics, on the other hand, are melted and then solidified, a process that can be repeated numerous times for reprocessing. Although the manufacturing technologies for thermoplastics are generally not as well developed as those for thermosets. Thermoplastics offer several advantages. First, they do not have the shelf-life problem associated with thermosets, which require freezer storage to halt the irreversible curing process that begins at room temperature. Second, they are more desirable from an environmental point of view, as they can be recycled. They also exhibit higher fracture toughness and better resistance to solvent attack. Unfortunately, thermoplastics are more expensive, and they generally do not resist heat as well as thermosets; however, strides are being made in developing thermoplastics with higher melting temperatures. Overall, thermoplastics offer a greater choice of processing approaches, so that the process can be determined by the scale and rate of production required and by the size of the component.

A variety of reinforcements can be used with both thermoset and thermoplastic PMCs, including particles, whiskers (very fine single crystals), discontinuous (short) fibres, continuous fibres, and textile preforms (made by braiding, weaving, or knitting fibres together in specified designs).

Continuous fibres are more efficient at resisting loads than short ones, but it is more difficult to fabricate complex shapes from materials containing continuous fibres than from short-fibre or particle-reinforced materials. To aid in processing, most high-performance composites are strengthened with filaments that are bundled into yarns. Each yarn, or tow, contains thousands of filaments, each of which has a diameter of approximately 10 micrometres (0.01 millimetre, or 0.0004 inch).

Depending on the application and on the type of load to be applied to the composite part, the reinforcement can be random, unidirectional (aligned in a single direction), or multidirectional (oriented in two or three dimensions). If the load is uniaxial, the fibres are all aligned in the load direction to gain maximum benefit of their stiffness and strength. However, for multidirectional loading (for example, in aircraft skins), the fibres must be oriented in a variety of directions. This is often accomplished by stacking layers (or lamina) of continuous-fibre systems.

The most common form of material used for the fabrication of composite structures is the preimpregnated tape, or "prepreg." There are two categories of prepreg: tapes, generally 75 millimetres (3 inches) or less in width, intended for fabrication in automated, computer-controlled tape-laying machines; and "broad goods," usually several metres in dimension, intended for hand lay-up and large sheet applications. To make prepregs, fibres are subjected to a surface treatment so that the resin will adhere to them. They are then placed in a resin bath and rolled into tapes or sheets.

To fabricate the composite, the manufacturer "lays up" the prepreg according to the reinforcement needs of the application. This has traditionally been done by hand, with successive layers of a broad-goods laminate stacked over a tool in the shape of the desired part in such a way as to accommodate the anticipated loads. However, efforts are now being directed toward automated fibre-placement methods in order to reduce costs and ensure quality and repeatability. Automated fibre-placement processes fall into two categories, tape laying and filament winding. The tape-laying process involves the use of devices that control the placement of narrow prepreg tapes over tooling with the contours of the desired part and along paths prescribed by the design requirements of the structure. The width of the tape determines the "sharpness" of the turns required to place the fibres in the prescribed direction—*i.e.,* wide tapes are used for gradual turns, while narrow tapes are required for the sharp turns associated with more complex shapes.

1.5.2 Metal-matrix and ceramic-matrix composites

The requirement that finished parts be able to operate at temperatures high enough to melt or degrade a polymer matrix creates the need for other types of matrix materials, often metals. Metal matrices offer not only high-temperature resistance but also strength and ductility, or "bendability," which increases toughness. The main problems with metal-matrix composites (MMCs) are that even the lightest metals are heavier than polymers, and they are very complex to process. MMCs can be used in such areas as the skin of a hypersonic aircraft, but on wing edges and in engines temperatures often exceed the melting point of metals. For the latter applications, ceramic-matrix composites (CMCs) are seeing increasing use, although the technology for CMCs is less mature than that for PMCs. Ceramics consist of alumina, silica, zirconia, and other elements refined from fine earth and sand or of synthetic materials, such as silicon nitride or silicon carbide. The desirable properties of ceramics include superior heat resistance and low abrasive and corrosive properties. Their primary drawback is brittleness, which can be reduced by reinforcing with fibres or whiskers. The reinforcement material can be a metal or ceramic.

Unlike polymers and metals, which can be processed by techniques that involve melting (or softening) followed by solidification, high-temperature ceramics cannot be melted. They are generally produced by some variation of sintering, a technique that renders a combination of materials into a coherent mass by heating to high temperatures without complete melting. If continuous fibres or textile weaves (as opposed to short fibres or whiskers) are involved, sintering is preceded by impregnating the assembly of fibres with a slurry of ceramic particles dispersed in a liquid. A major benefit of using CMCs in aircraft engines is that they allow higher operating temperatures and thus greater combustion efficiency, leading to reduced fuel consumption. An additional benefit is derived from the low density of CMCs, which translates into substantial weight savings.

1.5.3 Other advanced composites

Carbon-carbon composites are closely related to CMCs but differ in the methods by which they are produced. Carbon-carbon composites consist of semicrystalline carbon fibres embedded in a matrix of amorphous carbon. The composite begins as a PMC, with semicrystalline carbon fibres impregnated with a polymeric phenolic resin. The resin-soaked system is heated in an inert atmosphere to pyrolyze, or char, the polymer to a carbon residue. The composite is re-impregnated with polymer, and the pyrolysis is repeated. Continued repetition of this impregnation/pyrolysis process yields a structure with minimal voids. Carbon-carbon composites retain their strength at 2,500° C (4,500° F) and are used in the nose cones of reentry vehicles. However, because they are vulnerable to oxidation at such high temperatures, they must be protected by a thin layer of ceramic.

Efforts are also being directed toward the development of "smart," or responsive, materials. Representing another attempt to mimic certain characteristics of living organisms, smart materials, with their built-in sensors and actuators, would react to their external environment by bringing on a desired response. This would be done by linking the mechanical, electrical, and magnetic properties of these materials. For example, piezoelectric materials generate an electrical current when they are bent; conversely, when an electrical current is passed through these materials, they stiffen. This property can be used to suppress vibration: the electrical current generated during vibration could be detected, amplified, and sent back, causing the material to stiffen and stop vibrating.

1.6 Nanotechnology

The relentless development of new technologies are continually transforming the social, legal and ethical parameters. Even during the 1980's when its prospects could be faintly discerned by just a few researchers [34,35], nanotechnology promised a second industrial revolution. No wonder, total worldwide R&D spending on nanotechnology in 2004, was an estimated US# 8600 million and continues to rise rapidly[36].The expenditure is remarkable, coming despite the fact that 'the relatively small number of applications that have made it through to industrial application represent evolutionary rather than revolutionary advances[37]. Together with information technology, biotechnology and cognitive science, nanotechnology is expected to radically alter the human condition within a short span of time, probably not exceeding two decades.

Nanotechnology is not a single process; neither does it involve a specific type of material instead the term nanotechnology covers all aspects of the production of devices and systems by manipulating matter at the nanoscale. The ability to manipulate matter and processes at the nanoscale undoubtedly exists in many academic and industrial laboratories, at least one relevant dimension must lie between one and 100nm, according to the definition of nanoscale by the US national research council[38].

Nanotechnology is being classified into three types. The industrial use of nanoparticles in automobile paints and cosmetics exemplifies incremental nanotechnology. Nanoscale sensors exploiting quantum dots and carbon nanotubes represent evolutionary nanotechnology , but their development is still in the embryonic stage. Radical nanotechnology, as envisioned in sci-fi thrillers such as Michael Crichton's prey, does not seem viable in the next several decades.

Material properties at the nanoscale differ from those in bulk because of extremely large surface area per unit volume at the nanoscale. Quantum effects also come into paly at the nanoscale. Nanoscale properties and effects should transform current practices in integrated electronics, optoelectronics and medicine. But translation from laboratory to mass manufacturing is currently fraught with significant challenges, and reliable manipulation of matter at the nanoscale in a desirable manner remains difficult to implement economically.

Little data exists on the hazards of nanotechnology. Because small amounts if nanomaterials are expected to be handled outside the workplace a panel of experts convened by the Royal Society of London and the Royal Academy of Engineeringconcluded that the risk to general public is minimal. However, the risk to nanoindustrial workers from inhalation as well as by skin penetration could be high, and toxicological studies should be undertaken soon. There is also the risk of spontaneous combustion of nanomaterials due to the large surface-to-volume ratio.

Nanotechnolgy is emerging at a crucial stage of global civilization. A remarkable convergence of nanotechnology, biotechnology and information technology is occurring. Among the extremely pleasant prospects of their symbiosis are new medical treatments , both preventive and curative: monitoring systems for buildings, dams, ships, aircrafts, and other structures vulnerable to natural calamities and terroristic acts; energy-efficient production systems that produce little wastes and so on. The convergence of three technologies, along with progress in cognition science, also raises prospects that can be horrifying to contemplate.

1.6.1 Nanoparticles, Method of preparation

Nanoparticles offer the advantages of narrow particle size distribution, high surface area, homogeneous pure and improved properties. Nanoparticles are obtained from available natural sources and generally they need to be treated because the physical mixture of polymer and nanoparticles may not form a composite; a separation into discrete phases may take place. The poor physical interaction between the organic and inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the filler particles result in the formation of nanocomposites which exhibit unique higher properties than conventional composites[39-43].

Solids with nanosize particle size cannot be prepared or treated by traditional methods simply because the reactants are not mixed on the atomic scale. Alternate methods used for their synthesis include hydrothermal, sol-gel, Pechini, chemical vapour deposition, and microwave synthesis. These methods are based on atomic scale mixing of reactants, in gas ,liquid, or even solid phases. Most of these are low temperature methods, although finally firing may be required at high temperatures especially for ceramic type products.

1.6.1.1 *Hydrothermal synthesis*

Hydrothermal reactions are usually performed in closed vessels. The reactants are either dissolved or suspended in a known amount of water and are transferred to acid digestion reactors or autoclaves. Under hydrothermal conditions, reactants otherwise difficult to dissolve can go into solution and reprecipitate.

1.6.1.2 *Sol-Gel synthesis*

Sol-Gel synthesis is a very viable alternate method to produce nanocrystalline elemental,alloy and composite powders in an efficient and cost effective manner. Nanocrystalline powders could be consolidated at much lower pressures and temperatures.

Polymerized complex method

Wet chemical method using polymeric precursor based on the Pechini process has been employed to prepare a wide vaiety of ceramic oxides. The process offers several advantages for processing ceramic powders such as direct and precise control of stochiometry, uniform mixing of multicomponents on a molecular scale, and homogeneity.

1.6.1.3 *Chemical Vapour Deposition*

Chemical Vapour Deposition (CVD) may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapour phase[44]. It is a versatile process suitable process suitable for the manufacturing of coatings, powders, fibres, and monolithic components.

1.6.4 *Microwave synthesis*

Recently, there has been a growing interest in heating and sintering of ceramics by microwaves. The field of application in the use of microwave processing spans a number of fields from food processing to medical applications to chemical processing. Major areas of research in microwave processing for ceramics includes microwave material interaction, dielectric characterization, microwave equipment design, new material development, sintering, joining, and modeling. A microwave chemical deposition unit is used for the fabrication of carbon nanotubes and coils. It consists of a microwave magnetron, circulator, four- stub tuner, waveguide, cavity, etc.

1.6.1.5 *High-energy Ball Milling process*

Ball milling has been utilized in various industries to perform size reduction for a long time. Recently materials with novel microstructures and properties have been synthesized successfully via high-energy ball milling processes. Although different terms have been used to describe the high energy ball milling processes, three terms are used to distinguish powder-particle behaviour during milling: mechanical alloying (MA), mechanical milling (MM), and mechanochemical synthesis (MS). There are some inhernt advantages in processing nanomaterials via high-energy ball milling techniques, such as excellent versatility, scalability, and cost effectiveness. Therfore high-eneergy ball milling techniques are well suited for manufacturing large quantity of nanomaterials.

1.7 Nanocomposites

The term "nanocomposite" describes a two – phase material where one of the phases has at least one dimension in the nanometer (10^{-9}m) range. Nanotechnology is now recognized as one of the most promising areas for technological development in the 21st century. In material research, the development of polymer nanocomposits is rapidly expanding research activity.

Polymer nanocomposites (PNC) are polymers (thermoplastics, thermosets) that have been reinforced with small quantities (less than 5 % by weight) of nano sized particles having high aspect ratios. PNCs are considered as it is an attractive conventional filled polymers or polymer blends[46,47,48]. PNCs contain substantially less filler (1-5 vol. %) and thus there is a greater retention of the inherent processability of the neat resin.
Properties of PNCs

Properties that have been shown to exhibit substantial improvements includes:

- Mechanical strength, modulus and diamensional stability.
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance

- Light weight
- Electrical conductivity
- Optical clarity in comparison to conventional filled polymers.

The nanocomposites have many applications. Due to higher stiffness, weight saving, improved surface quality, less brittle in low temperatures, and easily recyclable they can be used in automotive parts.

An epoxy based nanocomposites produced a transparent, super-tough and highly abrasion resistant and chemical resistant coating for transparent substrate. Other benefits are they donot craze, crack or shatter upon impact, flame resistant and effective barrier against moisture and oxygen. Potential commercial applications are protective eyewear and vehicle wind-shields etc.

Addition of nanofillers will greatly improve flame retardancy of polymer resins[49]. The nanofillers delay ignition, reduce smoke emissions, eliminate dripping of the molten polymer by formation of a strong stable character. Some applications of the flame retardant nanocomposites are wire and cable covers, battery jars and interior decoration materials.

1.7.1 Types of nanocomposites

Depending on how many dimensions of the dispersed phase are in the nanometer range, three different nanocomposites.

1. Nanocomposites that can be reinforced by isodimentional nanofillers which have three dimensions in the nanometre range such as precipitated silica, spherical silica nanoparticles obtained by in-situ sol-gel methods or by polymerization promoted directly from their surface.

2. Nanocomposites which can be reinforced by fillers which have only two dimensions in the nanometer scale. For example polymer matrices reinforced by cellulose whiskers or carbon nanotubes.
3. The third type of nanocomposites corresponds to the case were the reinforcing phase, in the shape of platelets, has only one dimension on a nano level. Polymer layered silicate nanocomposites belong to this class.

1.7.1.1 *Hybrid organic/inorganic composites*

Polymer-based organic/inorganic nanocomposites have gained increasing attention in the field of materials science [50,51]. Numerous synthesis procedures are available including evaporation of elemental metal with its deposition on a polymeric matrix, plasma-induced polymerisation, etc. Reviews are found in [52,53]. Sol- gel processing, which includes two approaches: hydrolysis of the metal alkoxydes and then poly-condensation of the hydrolysed intermediates is a well-known method to prepare nanocomposites [54-56]. The following methods have been lately employed to prepared nanocomposites:

1.7.1.2 *In-situ intercalative polymerisation*

In-situ intercalative polymerization usually implies polymer interaction with clays. The ability of intercalating polymer into silica layers was first obtained by the Toyota group [57]. Using the inherent characteristics of the alumino-silicate layer (e.g. swelling behaviour and cation exchange), the inorganic phase could be evenly dispersed on a nanometer scale, generating strong interaction between the inorganic and organic phases. The material developed by Toyota's researches was found to have considerable improved properties, as compared to ordinary nylon-6. Through the addition of only 5 wt% clay higher tensile strength (40%), flexural strength (126%) and heat distortion (from 65°C to 152°C) were achieved. More research has been reported to incorporate clays into a polymer using nylon [58].

Nanocomposites of nylons have focused on the intercalation method used to prepare nylon/clay nanocomposites. How the clay particles achieve these feats is not well understood. The effect seems to be related to the clay's surface area, the extent of dispersion of the clay in the matrix and/or aspect ratio. Many different polymer matrices have been reinforced with clays. Matrices researched include polyamides, epoxy resins, polystyrene, polyurethanes, polypropylene, etc. To date, only few clay nanocomposites have been successfully brought into the realm of commercial application [59-69]. This method, however, is only suitable for clay minerals.

1.7.1.3 *In-situ polymerisation*

In-situ polymerisation is a method in which fillers or reinforcements are dispersed in a monomer first and then the mixture is polymerized using a technique similar to bulk polymerisation [70-72]. Ou et al. [73,74] reported on the preparation of nylon-6/silica nanocomposites by this method, in which silica was pre-treated with aminobutyric acid (modified silica). Scanning Electron Microscopy pictures revealed that silica was quite well dispersed in the polymer matrix and that the addition of silica increased the Tg and crystallization rate of the nylon-6 matrix. The mechanical properties of nylon-6/unmodified silica nanocomposites decreased gradually with the increment of silica content, whereas those of the nylon-6/modified silica system had maximum values at 5 wt% silica content. The feasibility of this method, however, is for polymers able to have an open polymerisation, such as caprolactam, and where the composite can remain stable at high temperatures.

1.7.1.4 *Atom transfer radical polymerisation (ATRP)*

The synthesis of hybrid organic/inorganic nanoparticles has been performed using ATRP. A monolayer of a silane was attached to the surface of 55 nm silica nanoparticles [75-76]. The modified nanoparticles were used as macro-initiators for styrene, resulting in a controlled living polymer from the nanoparticle surface. A good review of this method can be found in [77].

The use of microwave radiation has been used to polymerize polyamides in a rapid and efficient way. The polycondensation is achieved in the presence of a small amount of a polar organic medium that acts as a primary microwave absorber. The reaction gives a high viscosity value for the polyamide in a shorter polymerisation time than the conventional external heating [78-80]. So far, there are several polymers successfully made throughout this method, such as nylon and inorganic materials, but no hybrid compounds have been found in the literature yet.

1.7.1.5 *Nylon-6-Silica nanocomposites*

State-of-the-art nylon-6/silica composites are presently formed through an in-situ polymerisation process (vide supra). Typically, such reactions require a catalyst and the silica particles require a surface pre-treatment. The solid particles are then dispersed in e-caprolactam (monomer) and the mixture is heated at relatively high temperatures (> 200°C) to form nylon-6 through a ring opening polymerisation (ROP) mechanism. However, due to the thermal energy originating from the heating process, sol particles collide which lead to aggregation and grain growth of the silica particles. The phenomenon becomes particularly problematic when the silica particles are below 50 nm in diameter [82]. Furthermore, such a process is limited to the family of nylons that rely on a ROP mechanism, where the monomer can act as polymer precursor. The method is therefore not amenable to nylons where a condensation mechanism is involved (e.g. nylon-6,6).

More recently, silane treatment has been applied to the preparation of nylon-6/nano-SiO_2 composites, with 4% of silica content, through In-situ polymerisation. The results revealed that the reactivity of the silica remained in both treated and not treated silica. In addition, dynamical and mechanical tests showed an improvement of strength and toughness of the composite materials. The activity of silica fillers depends upon the chemical structure of the silica surface. A way to modify the hydrophilic character of the silica is silane coupling, in which agents are used [83,84]. More of the PA6-SiO_2 nanocomposites obtained so far have used powder-state silica. Rusu [85] prepared the nanocomposite through In-situ polymerization by uniaxially rotational moulding. The effects of addition of unmodified and modified silica's on the physical and mechanical properties of PA6 nanocomposites were also investigated.

1.7.2 Nanocomposites based on sol-gel process

The sol-gel process generally begins with a reaction between a metal oxide precursors [$M(OR)_n$] and water, were M is a network forming element and R is an alkyl group. Although Zr, Ti, Al oxides have been utilized as the inorganic components[86],the majority of the nanocomposites incorporate silica from TEOS. Hydrolysis and condensation of the alkoxide are the two major steps to produce an inorganic network in the presence of an acidic or basic catalysts. For TEOS, the rate of hydrolysis is high under an acid environment in relative to the rate of condensation and this promotes the development of linear or polymer like structures while high rate of condensation promotes star-like or particulate structures. Generally, acid catalyzed nanocomposites have high tensile strength , while basic catalyzed nanocomposites have the best elastic properties but lower tensile strength. Therefore, slight changes in the experimental parameters like pH, concentration, temperature, nature of solvent etc. lead to variations in the resulting supramolecular structure.

The polymer- inorganic hybrid by the sol-gel process is formed by either a polymer dispersed into an inorganic matrix at high proportion of an inorganic component or inorganic particles dispersed in a polymer matrix in a lower proportion of inorganic component. These materials exhibit properties which are dependent largely on the ratio of inorganic/inorganic content. The organic polymer flexibility, low density, toughness and formability, whereas the inorganic component usually imparts excellent mechanical and optical properties such as modulus, strength, surface hardness, transparency and high refractive index. The properties rely on the nature of the interface between organic and inorganic components and the interactions between them. Sanchez and Ribot categorized these hybrids into two main classes. Class I corresponds to the systems where there exists no covalent or iono-covalent bonding interactions between the organic and inorganic components. In these systems, the inorganic and organic components interact only weakly through H-bonding ,Vander Waal's forces or electrostatic forces. In class II, at least a fraction of the organic and inorganic components are linked through strong chemical bonds like covalent, iono-covalent or Lewis acid-base bonding.

In order to improve the dispersion between the usually hydrophobic polymer and the hydrophilic nanofillers (like silica or silicate) are often modified by attaching some organic substituents and then composite is made using this modified materials. Generally polar polymers are used without further modification to generate organic-inorganic components. Wen and Wikes[87] reviewed the polymers employed for the preparation of hybrid composites using sol-gel technique. Recent researches focuses on the development of in-situ generated hybrids, where the organic and inorganic components are allowed to grow simultaneously. Most commonly used polymers are acrylates and methacrylates etc. and inorganic components are targeted for optical and optoelectrinic applications. Apart from the polymer/silica hybrids, other hybrids based on TI, Zr, Al etc have also been reported.

1.7.3 Nanocomposites using carbon nanotubes

Carbon nanotubes (CNTs) were discovered incidentally in 1991[88]. Carbon nanotubes are long thin cylinders of carbon that are unique for their size, shape and remarkable physical and electrical properties. The carbon nanotubes are used as reinforcing fibres to impart unique properties to the polymer matrix. Depending upon the number of cabon shells in CNTs they can be classified as single walled nanotubes (SWNTs) and multiwalled nanotubes(MWNTs)CNTs hold promise for the development of fundamentally new material systems. Some of the application areas of CNTs are listed below [89,90].

a) Additives in polymers

b) catalysts

c) Electromagnetic wave absorption and shielding

d) Lithium-battery anodes

e) Hydrogen storage

f) Nanotube composites

g) Electronic field emitters for cathode ray lighting element, flat panel display and gas discharge tubes in telecom networks

h) viii)Reinforcements in composites

i) ix)Super capacitor

1.7.4 Polymer-Layered silicate nanocomposites

Polymer-layered silicate composites are ideally divided into three general types.

a) Conventional composites or microcomposites where layered silicate acts as a conventional filler.

b) Intercalate nanocomposite consisting of a regular insertion of the polymer in between the silicate layers and

c) Exfoliated or delaminated nanocomposites where 1nm thick layers are dispersed in the matrix, forming a monolithic structure on the microscale.

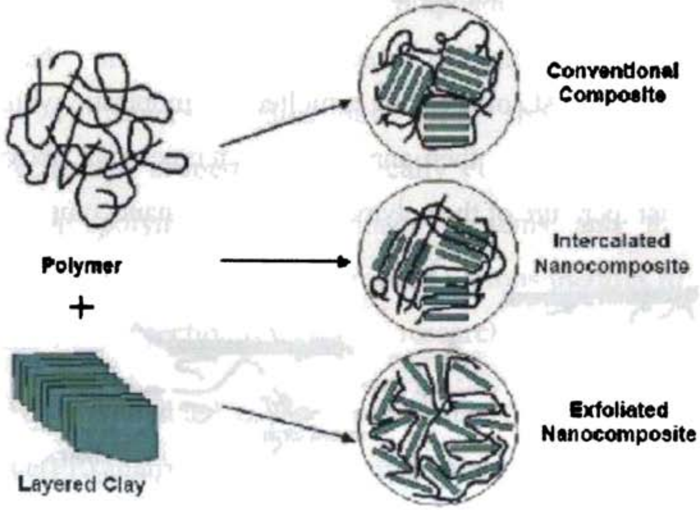


Fig.1.2 Polymer-layered nanocomposites

1.7.4.1 *Synthesis of polymer-layered silicate nanocomposites*

The three methods of preparation of clay-polymer nanocomposites are

i) **In-situ polymerization** was the first method to synthesize clay-polymer nanocomposites based on polyamide 6. Nowadays it is the conventional process used to [90] synthesize thermoset – layered silicate nanocomposites.

ii) **Solution casting**

The method consist to solubilize polymer in an organic solvent, then the clay is dispersed in the obtained solution and subsequently the solvent is evaporated, usually under vacuum. Nanocomposites based on high density poly ethylene(HDPE), polyimide and nematic liquid . Crystal polymers have been synthesized by this method. The major advantage of this method is that it synthesizes of intercalated nanocomposites based on polymers with low or even no polarity is possible[91,92]. However, the "solution" approach is difficult to apply in industry due to problems associated with the use of large quantities of solvent.

iii) **Melt intercalation**

This strategy consists of blending a molten thermoplastic with an organic silicate. The mixture is then annealed at a temperature above the glass transition temperature of the polymer and forms a nanocomposite.

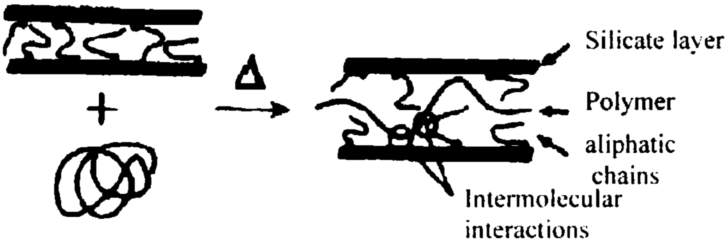


Fig.1.3 Schematic depicting the intercalation process

The melt intercalation process has become increasingly popular because of its great potential application with rapid processing methods such as injection moulding.

1.7.5 Nanocomposite characterization review

Modification of polymers can also be done successfully by incorporating fillers. Nanofillers belong to a class of new generation fillers and compared to conventional fillers, they have at least one characteristic length scale of the order of nanometer, a thickness one billionth of meter (10^{-9}m).

The following is a general review of the effect of a few conventional fillers on the properties of plastics. In polyamides, silica increases the tear strength and improves extrudability and surface finish. Stiffness, strength, hardness heat distortion characteristics, dimensional stability and surface finish are improved by mica and talc.

While there has been a great amount of experimental work that has taken place in the area of polymer nanocomposites, a consensus has not yet been reached on how nanosized inclusions affect mechanical properties(93,94). Several studies have been shown that reduced size improves mechanical properties, specifically elastic modulus[95,96] These studies vary in polymer nanocomposite systems and the mechanical properties characterized. The studies propose various theories to explain their results. The following section reviews the research and results.

Chan,et al.[97] embedded calcium carbonate ($CaCO_3$)nanoparticles in a polypropylene(PP) matrix to study the nucleation effect of the nanoparticles and their impact on mechanical properties of the nanocomposite. The study dispersed the nanoparticles via melt mixing and achieved average particle size of 44nm. Good dispersion of particles was achieved at 4.8% and 9.2% volume fractions, but many aggregates were found at 13.2%. Nano-sized $CaCO_3$ inclusions in the matrix, however, showed little improvement in mechanical properties. The improved modulus increases with volume fraction, the yield stress and tensile strength decreased with increased volume fraction, while the ultimate strain does not change with volume fraction.

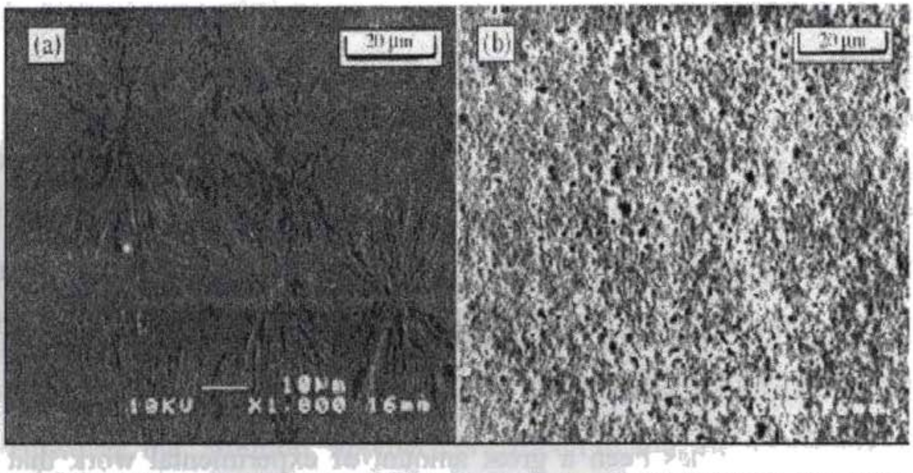


Figure 1.4 Pure polypropylene and (b) polypropylene with 9.2% volume filler (Chan et al. 2002).

The study assumed the increase in modulus was due to a strong interaction between the polymer and filler, caused by the large interfacial area between them, resulting in reinforcing and nucleating effects have a counter-balancing force on the mechanical properties. Strong interaction increases the yield strength and tensile strength but decreases the ultimate strain. But the strong nucleating effect reduces the size of the spherulites which has the opposite effect, decreasing the yield strength and tensile strength but increasing the ultimate strain. They propose the dispersion of nanoparticles is critical as shown by the large impact on mechanical properties of the lower volume percent samples, in which they confirmed better dispersion.

Shelly,et al. showed that in a nylon-6 system with 2 % and 5% weight fraction clay platelets, modulus increases 200% for larger weight fraction (5%), yield strength increases 175% and ultimate strain slightly decreases(98). For smaller weight fraction (2%) ,the increase in effective elastic modulus was 40% over the modulus of the pure polymer system. The same system with a lower weight fraction showed lower increases in modulus and yield strength but showed a slight increase in ultimate strain. The platelets had a surface area of 100nm^2 with a thickness of 1nm and were found to have good interaction with the matrix.

In a different study, silica nanoparticles of 17, 30, and 80 nm size were embedded in a polyamide-6 matrix.(99 : The elastic modulus was higher for the nanocomposites than for the pure system but showed little variation with particle size. Consistent with the polyamide system presented above, the yield stress increased with increasing filler concentration and increased slightly as the size of the particles decreased. Ultimate strain decreased greatly, however, as concentration increased and particle size decreased. The study observed a filler size effect on the filler dispersion and suggests a possible existence of an optimal size for the reinforcing particles. The debonding process was examined to explain the differences in the mechanical properties between the particle sizes as shown in Fig. 1.5. The study suggests that the 12 nm particles tend to gather into aggregates and a multiple debonding process results from debonding around each individual particle. The aggregates, therefore, act like large soft particles during the deformation process. The 50 nm particles are well distributed, however, and would preferentially undergo a single debonding process. The debonding theory was also used to explain why the volume of the polymer nanocomposites increased, with the greatest increase occurring in systems with the smallest particles.

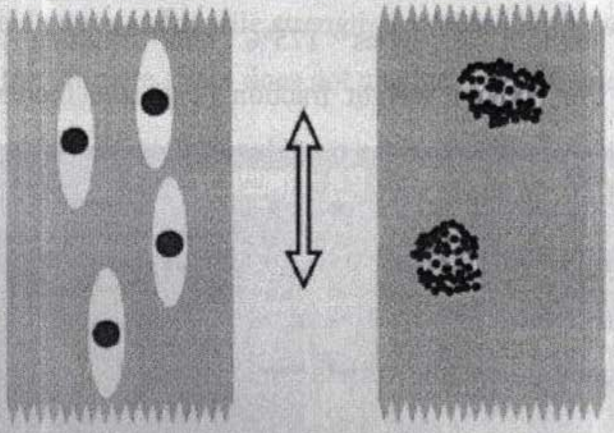


Fig.1.5 Schematic representation of the debonding process.

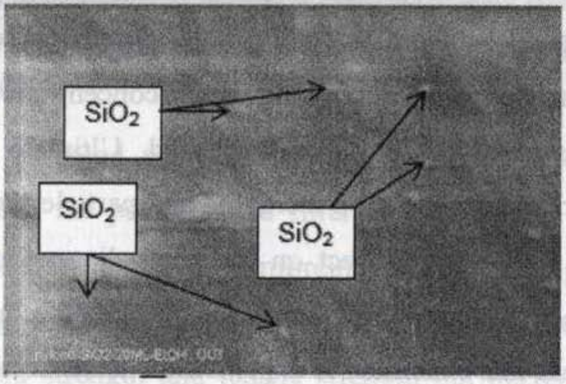


Fig.1.6. Silica nanoparticles dispersed in the polymer matrix (PA6-2).

Other research has shown that elastic modulus increases or changes inconsistently with reduced dimensionality. [100,101] Petrovic, et al. directly compared the mechanical properties of polyurethane-based composites formed using nano-size (10-20nm) silica fillers against the properties of the composites formed using micro-size(1.4um) silica fillers. The study provided mixed results. Mechanical and structural properties were examined as a function of filler concentration, 10-50% weight fraction. Samples with nanopartic;les showed lower modulus than samples with micro particles at less than 40 % weight fraction, but higher modulus at 40% and 50% weight fraction. Both nanosilica-filled and micro silica –filled composites showed increase in elastic modulus with increasing filler concentration in the glassy and rubber states but the changes was less predictable in the nanocomposites. The tensile strength increased for nanocomposites but decreased for micro-composites above 20% weight fraction, but varied little between the micro and nano-sized particles below 20% weight fraction. Ultimate strain increased 600 % with nanofiller but increased only slightly with microfiller. Glass transition temperatures, T_g, were inconsistent across measurement methods. DSC showed no dependence on filer concentration or filler type. However, TMA, DTMA, and DEA showed T_g increased with increasing filler concentration for both nano and micro fillers, but showed a slightly higher increase with nanofillers. This study also observed a decreasing composite density, that is, an increase in volume, with nanofillers as compared to micron fillers. The study proposed that the results stemmed from chemical/physical interaction between the filler and the matrix and geometric constrains imposed by the close proximity of the filler particles.

In this same study, Petrovic,et al. investigated the impact of the nanoparticles fillers on composite hardness. Hardness is an important property for characterizing elastomers. Hardness increased consistently with micro silica across all concentration. Hardness increased only slightly for nanosilica on low concentration then decreased at higher concentration. Interestingly, other studies have shown an increase in hardness with the addition of nanoparticles.

Ash, et al.[102] Performed mechanical and thermal characterization of PMMA-alumina nanocomposites with 40nm particles of varying concentration from 0–10weight fraction. The nanocomposites in this study were synthesized via free radical polymerization. The elastic modulus for all nanocomposite concentration were lower than for pure PMMA. At the lowest filler content, there was a sharp initial drop in elastic modulus followed by a steady increase as concentration increased, but never reaching the level of the pure system in addition, strain-to-failure for 5% weight fraction increased by around 800% over the pure system. However the ultimate stress of the pure system was higher than for the composite as shown in the fig.1.7.

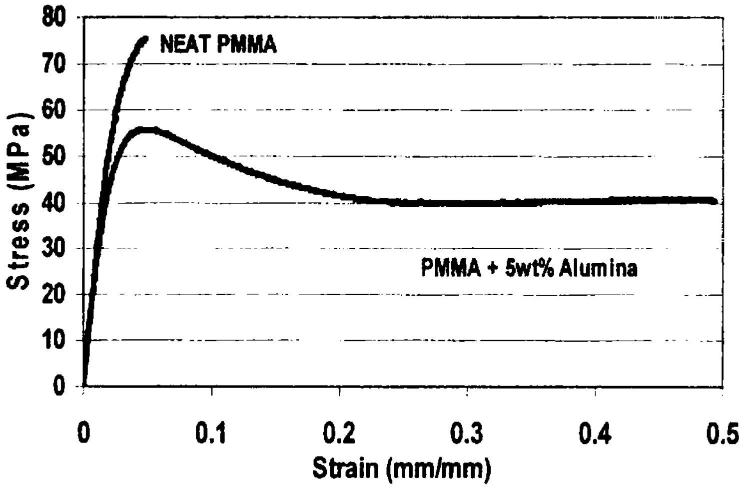


Fig.1.7. Stress strain curve for PMMA and alumina

In this study T_g decreased ~ 20^{0}c for the composite systems as compared to the pure system. The researcher related this decrease in T_g to that observed in thin films as function of film thickness and interfacial properties in which higher chain mobility at the interfaces results in lower T_g. If the polymer were not bound to the particles, a matrix with many voids result in very high interfacial area. A system of this type has the characteristic of a thin polymer film with a large surface to volume ratio.

Analysis of SEM images of the fracture surfaces showed good dispersion of particles and suggested a different fracture mechanism between the pure and nanocomposite systems. The pure surfaces show crazing that leads to brittle fracture. The fracture surfaces of the nanocomposites does not shows attributing crazing, suggesting that the mode of failure has been altered from crazing to homogeneous yield. The study proposes that minimal bonding exist between the nanoparticles and the surrounding system allowing voids surrounding nanoparticles to expand, which prevent crazing.

The crystallinity of crystalline and semi crystalline polymers is not effected very much by the addition of nanoparticles. There may be some changes in particular nanocomposite systems,but overall no major differences in crystallinity of nanocomposites versus neat polymers were observed in any of the systems examined. On the other hand, the glass transition temperature was influenced by the addition of nanoparticles. When there is a good filler Particle interaction, the glass transition temperature tends to increase with a decrease in particle size for amorphous polymers. For crystalline polymers, the transition temperature decreases with an increase in particle concentration. For an amorphous system with poor filler-polymer interfacial interaction, the glass transition temperature decreased overall. Thus, while the degree of crystallinity is not significantly affected by the presence of particles, the glass transition temperature is very dependent overall [102].

Ray and Okamoto (2003) [103] presented a brief discussion about heat distortion temperature (HDT) of nanocomposites. HDT of a polymeric material is an index of heat resistance towards applied load. Most of the nanocomposite studies report HDT as a function of clay content, characterized by the procedure given in ASTM D-648 (see figure 1.7). Ray and Okamoto state that increasing of HDT due to clay dispersion is a very important property improvement for any polymeric material, not only from application or industrial point of view, but also because it is very difficult to achieve similar HDT enhancements by chemical modification or reinforcement by conventional filler.

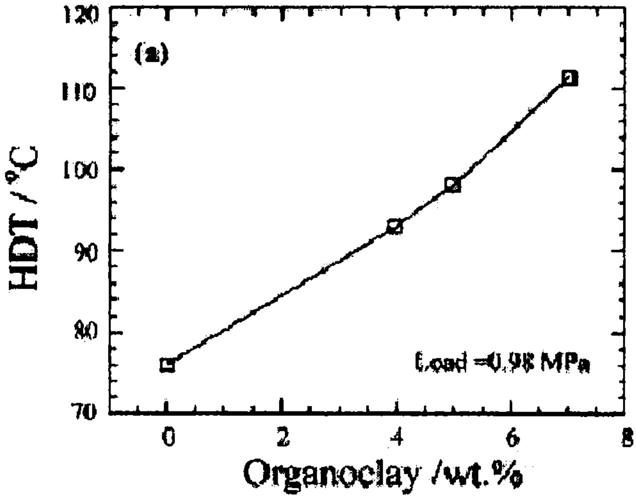


Fig. 1.7. Organoclay (wt%) dependence of HDT (Ray and Okamoto, 2003).

Tidjani (2005)[104] found a dramatic reduction in peak heat release rate for the nanocomposites compared to pure polypropylene-graft-maleic anhydride and its hybrid. He states that the improved flammability happens in the condensed phase and is not likely to be due to a higher thermal stability of the nanocomposite. The impermeability of the silicate layers in the polymer, which reduced the diffusion of gases in the nanocomposites, may participate in the reduction of the flammability.

Using an intercalated thermoplastic polyolefin (TPO)/organoclay nanocomposite with maleic anhydride functionalized PP as a compatibilizer, Mishra et al. (2005)[105], established that the compatibilizer not only enhances the intercalation of the polymer chain inside the clay gallery but also changes the thermoplastic elastomer composition (which is very important for end use application) of the TPO/clay nanocomposite. The tensile modulus as well as storage modulus of TPO/organoclay nanocomposite was substantially higher over a 20% talc based microcomposite.

From the point of view of gas barrier properties, nanocomposites offer interesting features. Ray and Okamoto (2003)[106] proposed that clays increase the barrier properties by creating a maze or "tortuous path" (see Figure 14) that retards the progress of the gas molecules through the matrix resin.

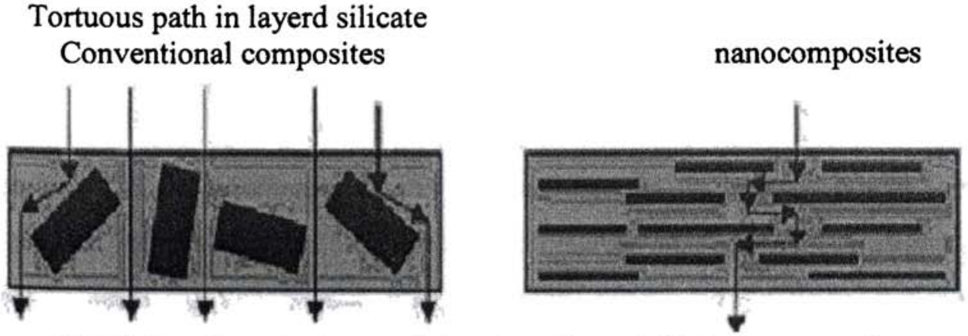


Fig.1.8 Formation of tortuous path in polymer/layered silicate nanocomposites

1.7.6 Applications of nanocomposites

In the field of coating systems, Fischer (2003),[107] reported that permeability of the nanocomposites coatings for water vapour markedly decreased with respect to the non-modified coating; a decrease of the water vapour permeability by a factor of 15 has been measured. This points to the presence of a strong bonding of the methylene blue to the clay platelets. Clay particles are homogeneously dispersed in the coating matrix, thus resulting in a fully transparent coating.

Inorganic–organic composites based on organoalkoxysilanes and other alkoxides have demonstrated their usefulness for hard coatings on eye-glass lenses. It has been shown that the addition of nanoparticles, especially in combination with epoxy silanes, which act as an inorganic as well as an organic crosslinking agent, leads to a substantial increase of the abrasion resistance of such systems without losing any transparency. Also, nanocomposites have been developed for the fabrication of low surface free energy coatings. With nanoparticles incorporated into the matrix, high abrasion resistance can be obtained. To promote good adhesion to different substrates, like metals, ceramics and plastics, adhesion promoters have been added (Schmidt, 2001)[108].

Mechanical properties of CNTs suggest that they may be used as reinforcing fibers in high-toughness nanocomposites, where stiffness, strength and low weight are important considerations. There are numerous possible applications; some examples are aerospace structural panels, sporting goods, ultra-lightweight thin-walled space structures for use in space, and high stiffness-to-weight space mirror substrates. Applications relating to nonlinear optics include protection of optical sensors from high-intensity laser beams. Additional applications involving the optical and electronic properties are electronemitting flat-panel displays, electromechanical actuators, light-emitting diodes; supercapacitors, field-effect transistors, subpicosecond optical switches and optical limiters (Breuer and Sundarraraj, 2004)[10[illegible]]. Conducting polymer structures can be constructed at low loadings of nanotube fillers.

Nanocomposites offer improvements over conventional composites in mechanical, thermal, electrical and barrier properties. Furthermore, they can reduce flammability significantly and maintain the transparency of the polymer matrix. In the case of layered silicate (clay) nanocomposites, loading levels of 2 to 5% by weight result in mechanical properties similar to those found in conventional composites with 30 to 40% reinforcing material (Denault J., Labrecque B., 2004)[110]. These attractive characteristics already suggest a variety of possible industrial applications for polymer nanocomposites (Wypych and Satyanarayana, 2005):

- automotive (gas tanks, bumpers, interior and exterior panels)
- construction (building sections and structural panels)
- aerospace (flame retardant panels and high performance components)
- electrical and electronics (electrical components and printed circuit boards)
- food packaging (containers and wrapping films)

1.8 Scope and objectives of the present study

Polypropylene and polystyrene are two widely used commercial thermoplastics. Polypropylene is the lightest major thermoplastic, with a density of 0.9g/cm^3. Its high crystallinity imparts the polymer high tensile strength, stiffness but low toughness. PP can be produced in either isotactic or atactic form. It has excellent electrical properties and chemical inertness. However PP has some limitations when used as an engineering material. It has low service temperature and stability to heat ,light and oxidation when compared to other linear polymers like poly ethylene (PE),Ethylene-propylene diene rubber (EPDM) etc. Polystyrene on the other hand has good mouldability, dimensional stability etc., but it is brittle and has low impact strength. In order to overcome the limitations and to convert these plastics into a more versatile engineering materials several methods are used. One method is to improve their mechanical properties like strength, stiffness etc., by modifying using with particulate fillers. The addition of nanofillers to polymers can bring dramatic changes in the properties of polymers when compared to their micro scale counterparts. This is because nanoparticles possess large surface area . Hence the introduction of suitable nanomaterials to polypropylene and polystyrene that can be synthesized effectively and economically is proposed to be investigated.

There are many types of nano materials that has been used to modify polymers. This include metal oxides such as SiO_2,TiO_2, Al_2O_3,ZnO etc. Among this silica is one of the attractive materials as it offers excellent thermal stability and is chosen as the potential modifier for the above thermoplastics. But silica particles usually have less interaction with PP and PS due to its polarity. Hence to improve the interaction between nonpolar polymers and polar silica a coupling agent is used. It is proposed to study the effect of coupling agents.

The specific objectives of the present study are

i) Synthesis of silica in nanoscale from a relatively cheap source, sodium silicate using PVA as surfactant and characterization of the material by different techniques such as TEM, SEM, FTIR, TGA, XRD and EDX.

ii) Preparation of PP/Silica and PS/Silica nanocomposites by melt mixing method.

iii) Characterization of the composites using mechanical (both static & dynamic) and thermal measurements.

iv) Surface modification of nanosilica particles using a silane coupling agent such as vinyl triethoxy silane (VTES).

v) Comparison of the performance of PP/Silica and PS/Silica nanocomposites prepared using modified and unmodified particles with conventional PP/Silica and PS/Silica nanocomposites.

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Chapter 2

Materials and Methods

The materials used and the experimental methods adopted in the present work are given in this chapter.

2.1 Materials used

a) Polypropylene homopolymer (PP)

REPOL H200MH, Melt Flow Index of 20g/10 min, was supplied by Reliance Industries Ltd., Mumbai, India.

b) Polystyrene (PS)

PS grade LGG 104, Melt Flow Index of 18g/min, was supplied by LG Plastics.

c) Sodium Silicate

Solution of Sodium silicate (60%) obtained from M/S Minnar Chemicals,Kochi was used.

d) Hydrochloric acid

AR Hydrochloric acid manufactured by M/S Loba chemicals with an acidimetric assay of 35-38% was used.

e) Ammonia

AR grade ammonia manufactured by M/S Spectrum chemicals, Kochi with an assay of about 25% ammonia and specific gravity of 0.91 was used.

f) Poly Vinyl Alcohol

Poly Vinyl Alcohol manufactured by M/S Polex Laboratories was used.

g) Vinyl triethoxy silane (98%) was supplied by Lancaster east gate, England was used.

2.2 Preparation of nanocomposites

Traditional routes to prepare nanocomposites are

- In-Situ polymerization
- Solution casting
- Melt mixing

In this study melt mixing method was used, because it has the following advantages.

- An environmentally benign one
- All types of polymers can be used
- Compatible with practicing polymer processing operations
- Most popular method for industrial applications

2.2.1 Melt mixing

A Thermo Haake Rheometer (Rheocord 600p) was used for melt compounding [1-3]. Torque rheometers are well suited for formulating various polymer systems and studying the flow behaviour, thermal sensitivity, shear sensitivity and batch compounding. The mixing chamber has a volumetric capacity of $69cm^3$ and was fitted with roller type rotors for mixing. The rotors rotate in opposite directions in order to effect a shearing action on the material mostly by shearing the material against the walls of the mixing chamber. The rotors have chevrons which perform additional mixing by churning the material and moving it back and forth through the mixing chamber. The granules in the desired proportion are fed to the mixing chamber through a vertical chute with a ram. There is a small clearance between the rotors which rotate at different speeds at the chamber wall. In these clearances dispersive mixing takes place. The shape and motion of rotors ensure that all particles undergo high intensive shearing flow in the clearances.

The mixer consists of three sections and each section is heated and controlled by its own heater and temperature controller. It is designed to maintain accurate and uniform temperature profiles throughout the mixer. Since mechanical dissipation heat is developed in the small gap between rotors and chamber, the heat conducts to the centre bowl and raises the set temperature. In this case, the heater and the centre bowl is automatically shut off and circulation of cooling air is activated.

To make a composite material the pure material is fed into the mixing chamber first and mixing is done with a constant rotor speed for 3min. Then the weighed silica particles are fed into the chamber and the mixing is continued for another 5min.The temperature selected depends on the material. In all cases the torque stabilized to constant value in the selected mixing conditions. The rpm and temperature are automatically controlled at the set values and the torque and energy required for blending are recorded as a function of time.

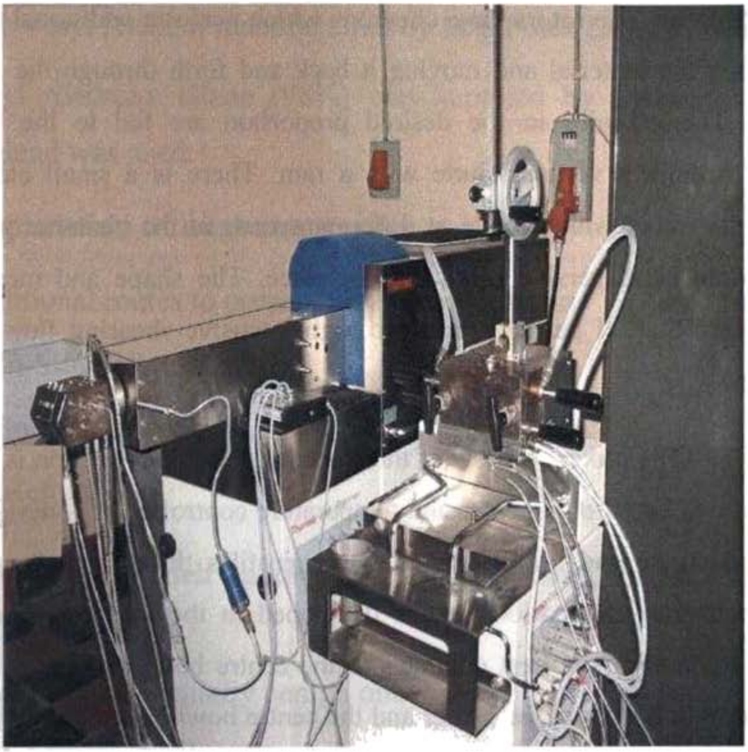

Fig.2.1. Thermo Haake Rheocord

2.2.2 Preparation of Test Specimens

The compound from the mixer was immediately passed through a laboratory size two roll mill and the resulting sheets were cut into small pieces. The test specimens[4] were prepared using a semi-automatic plunger type injection moulding machine. The melt temperature was set to be automatically controlled in the injection moulding machine.

Tensile test samples of size conforming to ASTM-D-638 were moulded using the moulds which were fabricated. The length of the jaws at the start of each test was fixed to be 40 mm.

Specimens were moulded at identical conditions and the properties were taken as the average property of six test samples. The temperatures were set according to the melt temperatures of the material and the injection pressure and holding time were adjusted to get the best properties.

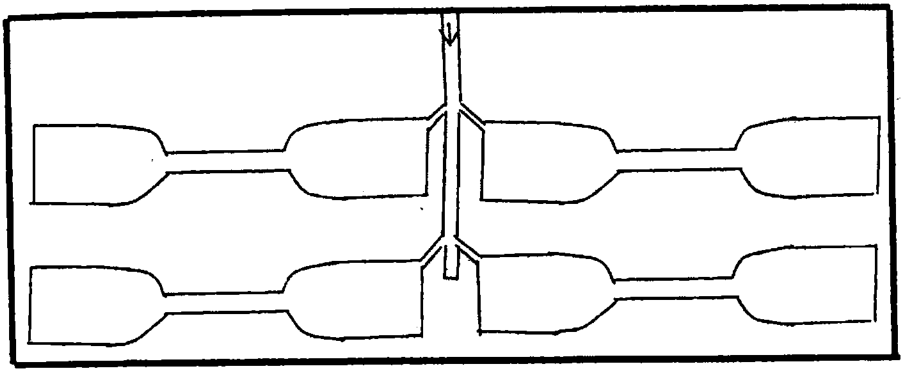

Fig.2.2 Mould for preparing tensile test samples

2.3 Determination of mechanical properties

2.3.1 Tensile properties

Mechanical properties of the injection moulded samples of both PP-silica and PS-Silica nanocomposites were studied using a Universal Testing Machine (UTM, Shimadzu, model AG-1) with a load cell of 10kN capacity. The specimens used were dumb-bell shaped. The gauge length between the jaws at the start of each test was adjusted to 40mm and the measurements were carried out at a crosshead speed of 50mm/min.Average of at least six sample measurements were taken to represent each data point.

2.3.2 Flexural properties

The flexural properties of the nanocomposites were measured by a three point loading system using universal testing machine as per ASTM-D-790. Rectangular shaped specimens were used for the flexural test and testing was done at a crosshead speed of 5 mm/min.

The flexural strength is determined using the relation

$$S = 3PL/2bd^2$$

where S is the flexural strength, P is the maximum load at the moment of break, b= width of the specimen, L= length of the span and d = thickness of the specimen. The flexural modulus is calculated from the slope of the initial portion of the stress-strain curve[5].

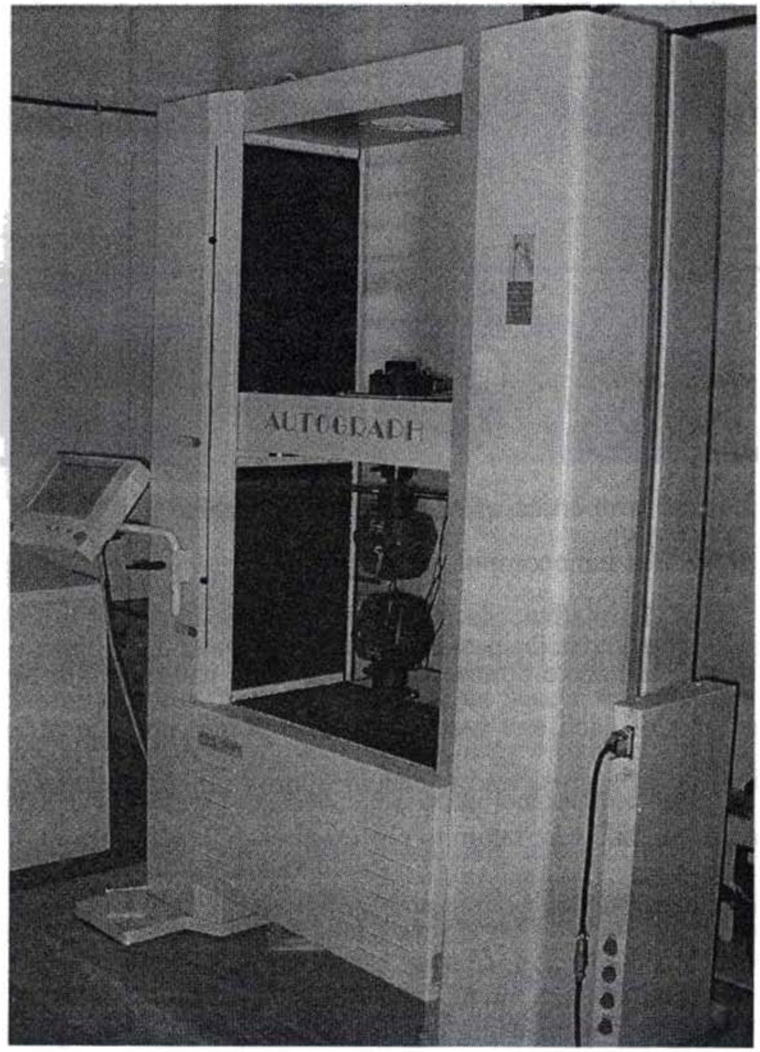

Fig.2.3 Universal Testing Machine

2.3.3 Impact strength

The impact properties of polymeric materials are directly related to the overall toughness of the material. Toughness is defined as the ability of the polymer to absorb applied energy. The area under the stress strain curve is directly proportional to the toughness of the material. Impact strength is a measure of toughness. The higher the impact strength of the material, the higher the toughness and vice versa. Impact resistance is the ability of the material to resist breaking under a shock loading or the ability to resist fracture under stress applied at high speed.

Several methods are used to measure the impact resistance of plastics-Izod, charpy, Gardner, tensile impact, and many others. The Izod impact strength is the most common test for impact strength measurement.

The Izod impact strength of the injection moulded samples was determined as per ASTM-D-256 The samples were rectangular strips of dimensions 12x10x3 mm. The dimensions of an impact specimen are shown in the fig.2.4.

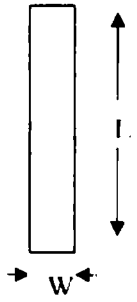

Fig.2.4 Impact test specimen

The izod impact strength of cast specimens was determined using impact testing machine model RESIL IMPACTOR. The striking velocity and capacity of the hammer was 3.46m/s and 1.037J respectively. It is shown in the fig.2.5.

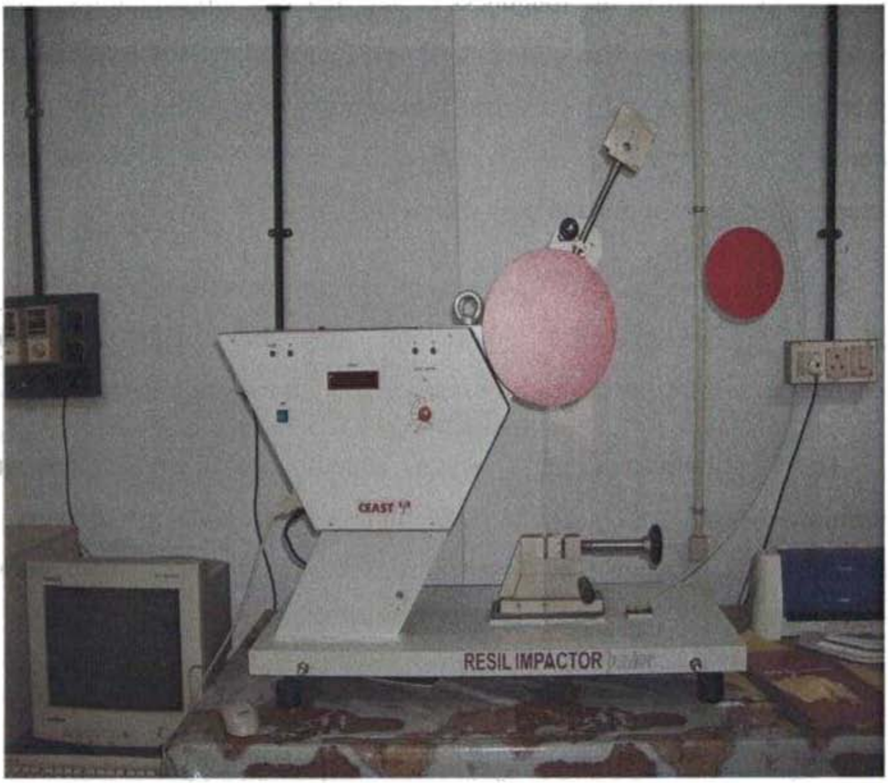

Fig.2.5 Impact testing machine

A pendulum swings on its track and strike the sample. The energy lost as the pendulum continues on its path was measured from the distance of its follow through. The impact energy and striking load was directly read from the tester.

Impact strength = Impact energy(J) / Thickness(m)

2.4 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis involves the determination of dynamic mechanical properties of polymers and their assemblies. In order to determine the dynamical properties such as dynamic modulus E' and the loss modulus E" and the damping or internal friction tan $\delta = E''/E'$. The response of the material to periodic forces is measured [6]. Generally the dynamic measurements are carried out over a frequency range at a constant temperature or over a temperature range at constant frequency. The commonly used temperature range for DMA of polymeric materials is from 10^{-2} to 10^{6} Hz[7].

Dynamic Mechanical Analyzer (DMA Q-800, TA instruments) was used to study the effect of silica nanoparticles on the viscoelastic properties of both PP and PS. Rectangular shaped specimens of dimension35mmx4mmx2mm were used. DMA tests were conducted at a constant frequency of 1Hz.A temperature ramp was run from 30°C to 120°C at 2.5°C/min to get an overview of the thermo mechanical behaviour of the samples. At each temperature the material was deformed at constant amplitude of 10µm over a frequency of 1 Hz. The dynamic storage modulus, loss modulus and tan δ (loss modulus/storage modulus) were measured.

2.5 Thermo Gravimetric Analysis (TGA)

Thermogravimetric analysis is a technique by which the mass of the sample is monitored as a function of temperature or time, while the substance is subjected to a controlled temperature programme[7].

Thermal stability of the polymer-Silica composites were analyzed using TGA Q-50 of TA instruments. Approximately 5mg of the samples were heated at a rate of 20°C/min from ambient temperature to 800°C. The chamber was continuously swept with N_2 at a rate of 90 ml/min.

2.6 Water absorption characteristics

Water absorption characteristics of plastics depend largely upon the basic type and functional composition of a material. These characteristics can be altered by the addition of additives such as fillers, glass, fibers and plasticizers. The specimens (~25mm x 25mm) were conditioned in an oven for 24 hr at 50°C and weighed, and then the long term immersion procedure outlined in ASTM D1895 was followed. The specimens were immersed in water and the wet weight was determined at specified intervals until it become saturated. The percentage water absorption was calculated with the following equation

$$\%\,\text{Water uptake} = \frac{\text{Final weight} - \text{Initial weight}}{\text{Initial weight}} \times 100$$

The results reported are average of six measurements.

2.7 Differential Scanning Colorimetry

Differential scanning colorimetry is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to controlled temperature program.

It is one of the most widely accepted techniques of thermal analysis for studying the crystallization characteristics of polymers and their composites[8-10]. The materials, as they undergo changes in chemical and physical properties, which are detected by transducers, which the changes into electrical signals that are collected and analyzed to give thermograms. In DSC, the crystallization characterizations are studied from the heat flows associated with the corresponding transitions as a function of temperature.

2.8 Melt Rheology

Melt flow measurements using Haake Rheocord

The rheological measurements were measured using Haake rheocord since it represents the real processing equipment. This is widely used in characterizing the polymer flow behaviour by measuring viscosity related torque caused by the resistance of the material to the shearing action of the plasticizing process.

The Rheomix mixer was calibrated to obtain flow curves from the torque C and rotor speed values N by using the calculation method of Blyler and Daane [11].Goodrich and Porter [12] succeeded in converting the torque rheometer data into fundamental rheological units for materials that exhibit Newtonian behaviour. Based on this Blyler and Daane developed the following equation for Non-Newtonian mateials,

$$M=C(n)\,KS^n$$

where M is the torque, K and n are famous parameters of the Power law equation, S is the rpm and C(n) is a characteristic constant which is determinable but depends on other constants.

$$\tau = K\gamma^n$$

where K is a parameter which depends on temperature and is given by,

$$K= K_0\, e^{-\Delta E/RT}$$

ΔE is the activation energy. R is the gas constant and K_0 is a constant.

Bousmina et al.[13] who assume that the flow in the Rheomix device is the same in a double Couette system. It leads to the following equations:

$\gamma = 0.45N$ and $\tau = 7500.C$

where τ is the shear rate (s^{-1}), N the rotation speed (rpm), γ the shear stress (Pa), C the torque (N.m).

Lee and Purdon in their work derived an equation identical to that derived by Blyler and Daane. They predicted that constant C(n) was related to two experimental constants and can be determined experimentally[14]. The relation between rheocord torque and rotor speed were separately related to the shear stress and shear strain of the polymer melt in the rheocord. Thus these data can be used for both Newtonian and Non-Newtonian materials as per the following procedure.

a) A plot of log M Vs log S at constant temperature is made for a polymer melt using the measurements from Haake. This is identical to the plot of log τ vs log γ .Consequently the power law index is obtained from the slope.

b) The Haake Rheocord can be calibrated using melts of known K and n to determine C(n) and can be used to characterize a polymer.

c) The energy required to plasticize a polymer for a given time can also be determined from the area under the torque-time curve at a preset temperature for the specified period of time as per the following relation,

$$W = 2\pi n \int_{t_1}^{t_2} M dt$$

where W is the energy, n is the number of revolutions of the rotor per minute, t_1 and t_2 are the initial and final time respectively and M is the torque in Nm.

2.9 Morphological studies- Scanning Electron Microscopy

Scanning electron microscope (JEOL JSM 840 A) was used to investigate the morphology of the fractured surfaces [15].In this technique, an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photo multiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in a cathode ray tube and photographed using black and white film. The SEM observations reported in the present study were made on the fracture surfaces of the tensile specimens. Thin specimens were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position, the stub with the sample was placed in an E-101 ion-sputtering unit for gold coating of the sample to make it conducting. The gold-coated sample was used for SEM analyses.

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Chapter 3

Nanosilica - Synthesis and Characterization

3.1 Introduction

In the past few years, nanomaterials have attracted tremendous international interest, investment and effort both in scientific research and in industrial development because of their potential applications in various fields. Nanostructured composite materials, when using organic polymer and inorganic fillers, represent a merger between traditional organic and inorganic materials, resulting in compositions that are truly hybrid. Organic-inorganic composites with nanoscale dimensions are of growing interest because of their unique properties, and numerous potential applications such as enhancement of conductivity [4,5], toughness [6], optical activity [7,8], catalytic activity [9], chemical selectivity [10,11] etc. In these materials, inorganic and organic components are mixed or hybridised at nanometer scale with virtually any composition leading to the formation of hybrid/nanocomposite materials [12-22].

Silica has been used in different polymers as a reinforcement material. Examples are in methacrylate [23-26], polyimide [27-28], polyamide [29], rubbery epoxies [30], and acrylic [31]. The specific function of the filler is based on the specific resin system, particle size, surface area, loading and surface modification. Because of the high bond energy in the Si-O bond, SiO_2 has extremely high thermal stability. SiO_2 also possesses a very low thermal expansion coefficient. The silica containing nanocomposites show remarkable barrier properties to gases and moisture as well as very good resistance to staining [32-34].

Several methods are used to produce nanosilica from various sources [6-12][35-41]. Bomal. et.al. reported a process for preparing precipitated silica comprising reacting a silicate with an acidifying agent to produce a suspension of precipitated silica and, then, separating and drying the suspension to obtain the precipitated silica as a dried product.The silica obtained has a good dispersibility and very satisfactory reinforcing properties. It also relates to new precipitated silicas which are in the form of powder, of substantially spherical beads or of granules, these silicas being characterized by the fact that they have a BET specific surface of between 90 and 250m.^{2} /g.Another study by Teofil Jesionowski studied preparation of amorphous silica via precipitation reaction from aqueous solution of sodium metasilicate and hydrochloric acid in emulsion medium, focusing on determination to optimize the dispersive and morphological properties of silicas. It is revealed that the properties of silicas precipitated from emulsion systems depend on several variables but the amount and concentration of the applied reagents and pH of the emulsion are of critical importance. Kim, Liu and Zachariah have suggested that the aerosol- assisted sol-gel method to produce nanosilica. In this method, Tetra ethoxy silane(TEOS),water and ethanol were allowed to react. Sufficient hydrolysis time was given and then the solution was aerosolized with sodium chloride. Sodium chloride was employed both as an agent to accelerate the kinetics of silica generation and as a templating medium to support the formation and stability of pore structures. Ahamed et al, have synthesized nanosilica from rice hull. The method involved acid digestion, combustion at 700°C and then milling to produce nanosilica. Kotoki et. al prepared poly vinyl alcohol/silica nanocomposite starting from sodium silicate with dilute hydrochloric acid as catalysts in poly vinyl alcohol. This is a sol-gel method in which the acid plays a catalytic role in enhancing sol-gel condensation of silicon alkoxides within the PVA. The reaction was carried out at 60°C and pH maintained between 1-2.The reaction mixture was passed through cation exchange resin amberlite for the removal of sodium ions. After 24 hrs at ambient temperature it gelled and the samples were dried for 48 hrs at 47°C.

3.1.1 Silica

Silicon is the second most abundant element on earth, after oxygen, making up approximately 25 percent of the earth's crust by weight; largely found in the form of oxides such as sand and clay (Winter 2003). Silica, in its pure form is colorless to white. Silica is widely and abundantly distributed throughout the earth, both in the pure state and in silicates, (e.g., in quartz, agate, amethyst, chalcedony, flint, jasper, onyx and rock crystal), opal, sand, sandstone, clay, granite and many other rocks. Silica occurs in several forms and is insoluble in water, slightly soluble in alkalies and soluble in dilute hydrofluoric acid.

3.1.2 Types of silica

Commercially available silicas can be broadly classified as Crystalline silicon dioxide, Non -Crystalline, fumed silica, precipitated silica, silica gel and Colloidal silica.

Crystalline silicon dioxide : Crystalline silicon dioxide is one of the most commonly encountered substances in both daily life and in electronics manufacturing. Crystalline silicon dioxide (in several forms: quartz, cristobalite, tridymite) is an important constituent of a great many minerals and gemstones, both in pure form and mixed with related oxides. Beach sand is mostly silica. Crystalline silicas show discrete reflections in X-ray diffraction from the internal planes formed by the orderly pattern of atoms. The working of silica into glass (usually by the addition of natron -- sodium oxide -- to lower the melting point) has been known since antiquity, with polished glass lenses in eyeglasses and optical instruments dating back more than 5 centuries.

Non-Crystalline silicon dioxide : Non-crystalline, or amorphous silica, is usually prepared by vapor-phase hydrolysis , precipitation or other processes that ensure the absence of crystalline free silica. Three forms of synthetic amorphous silica are classified according to their method of preparation: silica gel (silica G), precipitated silica (silica P) and fumed silica (silica F). There are several naturally-occurring and synthetic amorphous silicas, namely diatomaceous earth, precipitated silica, silica gel, fumed silica and silica fume (thermally generated). In amorphous silica, X-rays are scattered randomly and no discrete reflections are seen. All types of amorphous silica can be converted to crystalline forms when heated to a sufficiently high temperature.

Fumed silica : Fumed silica is derived from vapor-phase hydrolysis of a silicon-bearing halide, such as silicon tetrachloride. It is the byproduct of a high-temperature process when elemental silicon is produced by reacting coke and silica sand (crystalline) in an electric arc furnace. It offers primary particles with diameters from 5 to 40 nm., as well as a low density of silanols, and very few impurities.

Precipitated silica : in precipitated silica, the reaction mixture is held in the alkaline pH region, and offers limited aggregates of primary particles with a diameter of >5 n.m., and specific surface area (<350 m^2.g). The production of precipitated silica starts with the reaction of an alkaline silicate solution with a mineral acid. Sulfuric acid and sodium silicate solutions are added simultaneously with agitation to water. The resulting white precipitate is filtered, washed and dried in the manufacturing process. Precipitated silica's basic characteristics, which can be altered during the precipitation process, are particle size distribution, porosity, specific surface area and purity.

Silica gel: for silica gel, the reaction mixture is held in the acidic pH region, and here precipitated silica means a three-dimensional network of particles with low diameter (3 nm.), with a high specific surface area (>350 m^2/g). Packets of silica gel are found in all sorts of products because silica gel adsorbs and holds water vapor. In fact, you will find little silica gel packets in anything that would be affected by excess moisture or condensation. Silica gel is nearly harmless and that is why you find it in food products. Silica gel can adsorb about 40% of its weight in moisture and can take the relative humidity in a closed container down to about 40%. Once saturated you can drive the moisture off and reuse silica gel by heating it above 300 degrees F.

Colloidal silica: Colloidal silica has found widespread use for diverse materials in many industries. It is an aqueous, colloidal dispersion of chemically inert silica particles. The particles cut effectively, without deformation, because they combine individual crystals with a large exposed surface area and a high pH activation. Colloidal silica has been used successfully on a variety of materials including aluminium and aluminium alloys, titanium and titanium alloys, copper and copper alloys, lead and lead alloys, zirconium alloys, semiconductors, printed circuit boards, steels and coal.

3.1.3 Methods of production

3.1.3.1 *The sol-gel process*

Sol-gel technology has been used extensively in the synthesis of nano silica. as illustrated in Figure 1-1. A sol, by definition, is a suspension of solid particles, with size between 1-1000 nm, in a liquid continuous phase. The sol-gel process refers to the creation of a continuous, solid network through a change of interactions between the colloidal particles; changing the systems characteristics from that of a liquid to that of a gel. The result is a bi-continuous system composed of the continuous, interpenetrating solid and liquid phases. The overall sol-gel process, as the name implies, usually involves two stages: precursors initially form high molecular weight but still soluble oligomeric intermediates, a sol, and the intermediates further link together to form a three-dimensional cross linked network, a gel. The precursors for a sol-gel reaction could be either inorganic salts or organic compounds, such as metal alkoxides.

In general, sol-gel process involves a transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The starting materials used in the preparation of the "sol" are usually inorganic metal salts or metal organic compounds such as metal alkoxides. The first metal alkoxide was prepared from $SiCl_4$ and alcohol by Ebelmen in 1844, who found that the compound gelled on exposure to ambient environment. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a "sol". When the "sol" is cast into a mold, a wet "gel" will form. With further drying and heat-treatment, the "gel" is converted into dense ceramic or glass particles[42-43]. The whole process is illustrated in Figure 3.1.

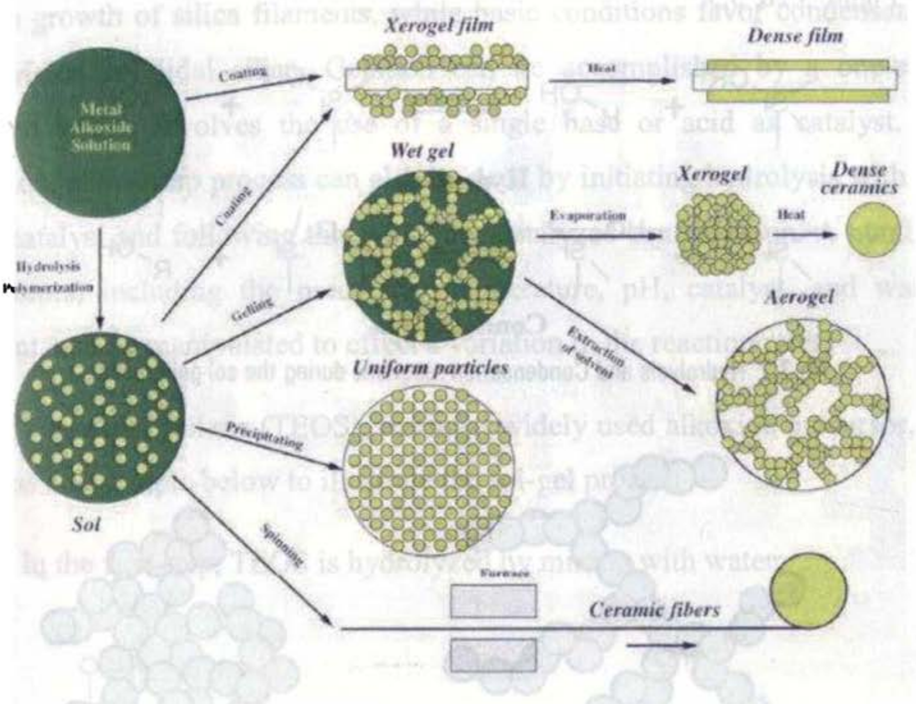


Fig. 3.1 Sol-gel process and their products.

3.1.3.2 *Sol-Gel Reactions*

The synthesis of silica gel is easily carried out through either an acid or base catalyzed reaction.The precursors for a sol-gel reaction could be either inorganic salts or organic compounds, known as metal alkoxides. Compared with inorganic salts, reactions of alkoxide precursors have easily controlled reaction kinetics and generate byproducts of alcohols and water, which can be readily removed during the drying process.

The sol-gel process consists of three basic steps: 1) gelation; 2) ageing; and 3) drying. During gelation, the synthesis of silica polymers occurs through the simultaneous hydrolysis and condensation reactions represented in Figure 3.2& 3.3.

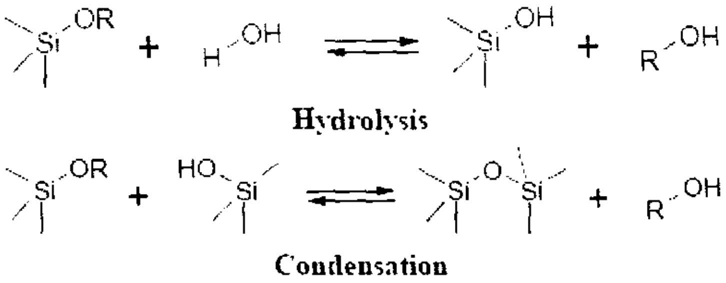


Fig 3.2 Hydrolysis and Condensation reactions during the sol-gel process

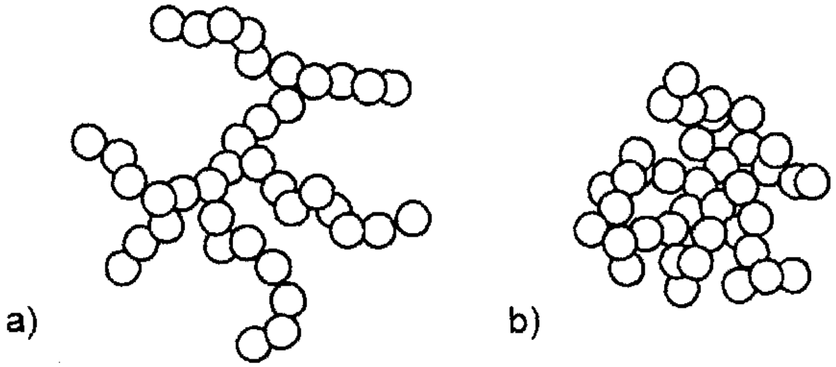


Fig.3.3 Silica gel network formation by (a) acid and (b) base catalyzed hydrolysis and condensation.

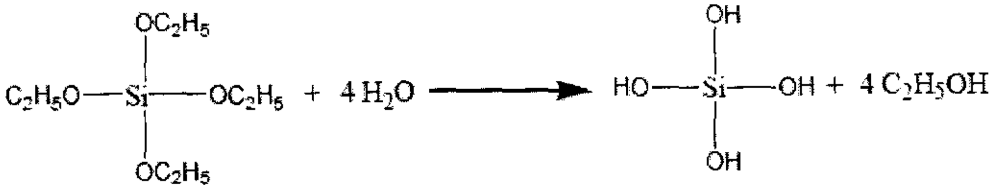
3.1.3.3 *Effect of catalysts*

The fact that the hydrolysis and condensation of alkoxysilicates can be accelerated by using both acids and bases allows for a variety of catalysts to be used in this process. Both hydrolysis and condensation depend greatly on the pH value of the reacting mixture.

Condensation between the precursors results in the formation of a 3-dimensional network, or gel, which grows to encapsulate the solvent phase. It is the relative rates of hydrolysis and condensation that determines the properties of the silica gel formed. Acidic conditions favor hydrolysis leading to the growth of silica filaments, while basic conditions favor condensation and yields colloidal silica. Gelation can be accomplished by a one-step process which involves the use of a single base or acid as catalyst. In addition, a two-step process can also be used by initiating hydrolysis with an acid catalyst and following this with base-catalyzed condensation. A number of factors, including the precursor, temperature, pH, catalyst, and water content, can be manipulated to effect a variation in the reaction rates.

Tetraethoxysilane (TEOS), the most widely used alkoxide precursor, is used as an example below to illustrate the sol-gel process

In the first step, TEOS is hydrolyzed by mixing with water:



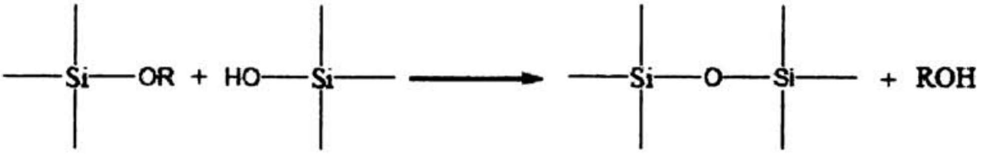
$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH$$

In this reaction, either an acid or a base can serve as catalyst.

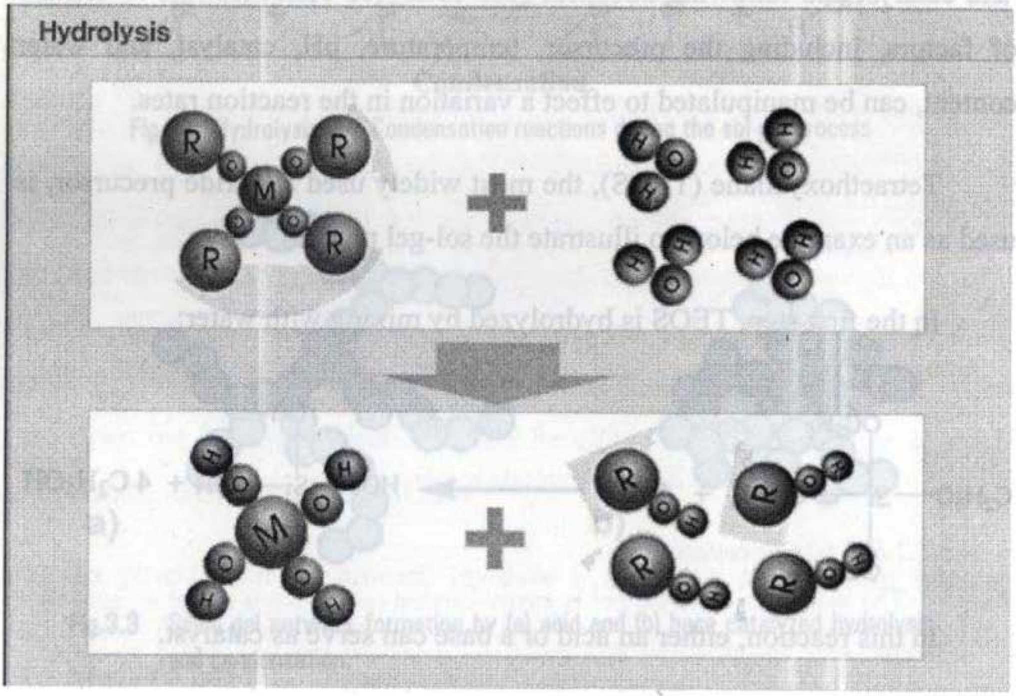
The silanols, i.e., hydrolyzed TEOS undergoes further condensation reaction forming siloxane bonds, that is the second step of the sol-gel process:

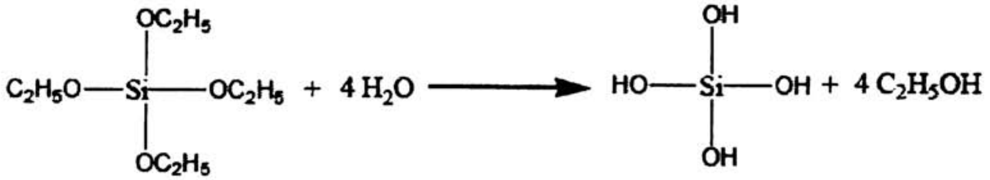
$$\equiv Si-OH + HO-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

or



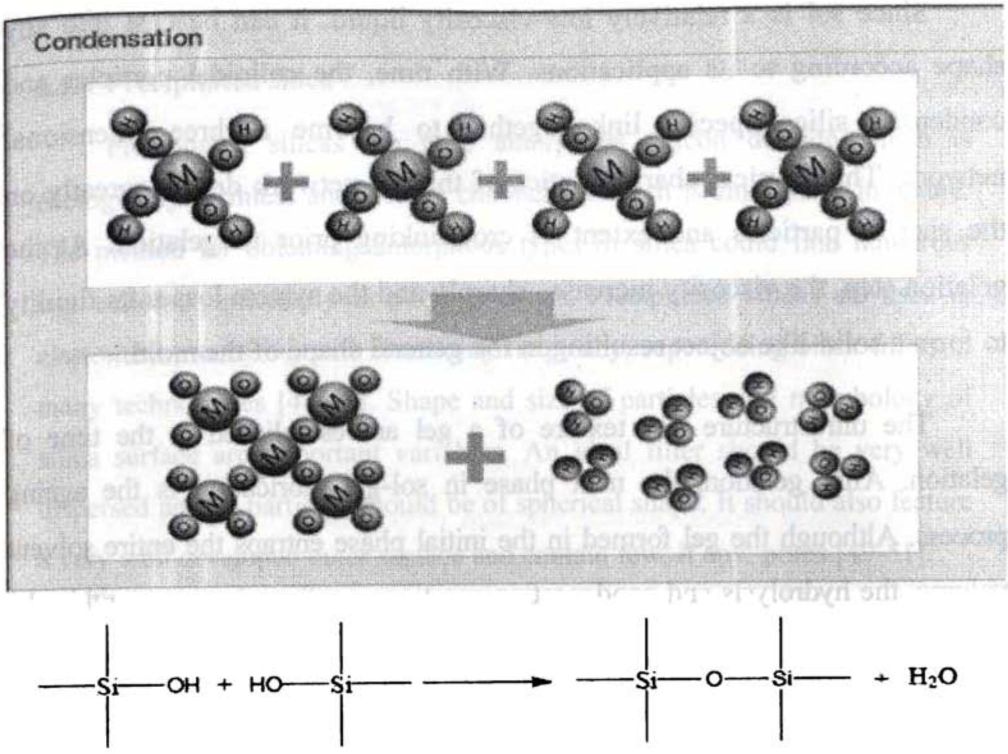
$$\equiv Si-OR + HO-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + ROH$$





$$Si(OC_2H_5)_4 + 4\,H_2O \longrightarrow Si(OH)_4 + 4\,C_2H_5OH$$

(a)



(b)

Fig. 3.4 Diagrams of sol-gel reactions: (a) Hydrolysis reaction; (b) Condensation reaction.

Linkage of additional $Si(OH)_4$ tetrahedra occurs as a polycondensation reaction and eventually results in a three dimensional SiO_2 network. The water and alcohol byproduct molecules generated from the reactions remain in the pores of the silica's three dimensional networks. They can also, as most often done, be removed during the reaction.

The hydrolysis and polycondensation reactions happen at numerous sites within the TEOS and water mixture upon mixing. When sufficient interconnected Si-O-Si bonds are formed in region they respond cooperatively as colloidal particles, e. g. a sol. The size of the sol particles and the cross linking within the particles depend upon the pH and $[H_2O]/Si(OR)_4$ ratio in the solution.

Since sol is a relatively low-viscosity liquid, it can be cast into any shape according to its applications. With time, the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend greatly on the size of particles and extent of crosslinking prior to gelation. At the gelation step, the viscosity increases sharply and the system losses its fluidity to form a solid-like object resulting in the general shape of the mold.

The ultrastructure and texture of a gel are established at the time of gelation. After gelation, the next phase in sol-gel fabrication is the ageing process. Although the gel formed in the initial phase entraps the entire solvent volume, the hydrolysis and condensation reactions continue to occur within the gel (Scherer1988). During this phase, some gel shrinkage is seen along with a corresponding expulsion of solvent. Gels of desired densities can be obtained by simply varying the ageing time (Kistler 1937).Typically, an application for silica gel requires the removal of the solvent phase and this is the final stage of the sol-gel process – the drying step. Drying conditions can have a significant effect on the final gel properties. In drying, as the liquid is removed from the gel, a liquid-vapor interface is developed within the gel and this creates significant capillary pressures as described by the La Place equation:

$$\Delta \mathrm{p} = \frac{2\gamma(\cos\theta)}{\mathrm{r}}$$

where Δp is the capillary pressure difference, γ is the specific surface energy of the liquid-vapor interface, θ is the contact angle, and r is the pore radius. With a pore radius on the nanometer scale, the large stresses generated can result in permanent shrinkage of the gels.

3.1.4 Precipitated silica

Precipitated silicas are pure amorphous silicon dioxide which is ecologically harmless and inert in chemical sense. It is amorphous in nature. The method for obtaining amorphous types of silica could find numerous applications, particularly as polymer fillers. Precipitated silicas are used in elastomers processing with increasing frequency, superceding black fillers in many technologies [44-48]. Shape and size of particles and morphology of silica surface are important variables. An ideal filler should be very well dispersed and its particles should be of spherical shape. It should also feature a very well developed outer surface and contain few, if any, pores [49-51].

Properties of the applied silicas are listed in Table 1.

Table 3.1

Parameter	Silica industrial by-product	Precipitated silica
SiO_2, %	83, 5	89,0
Water loss, %	2, 2	4, 8
pH of water suspension	6, 2	6, 5
Specific weight	2.01	2.12
Particle size, nm	120	25
Bulk density, g/dm^3	290	75
Packing density,g/dm^3	440	210
Water absorption, g/100g	320	650
Dibutyl phthalate absorption, g/100g	100	100

3.1.4.1 *Manufacture*

Precipitated silicas are produced by chemical reactions and precipitation, which is achieved by neutralizing a solution of sodium silicate with an acid, often sulfuric acid. The by-product, sodium sulfate, is eliminated via filtration. The remaining silica is then dried and formed based on its final application. The precipitation stage determined the microscopic particle morphology for most of the silica's application properties.Key precipitated silica manufacturing process stages include precipitation, filtration, drying and milling.

During the precipitation stage, product properties may be varied through changes in composition and ratio of reactants, reaction time, temperature and concentration. The important characteristics that result from the precipitation process include physical properties such as structure (oil absorption and compressibility), and chemical properties such as pH, silanol group density and optical properties.

During filtration, drying and milling, salts formed during the precipitation stage are washed out, and depending on the product, the solids content of the filter cake can range from 15-30 percent. As a result, drying is a major cost component in manufacturing precipitated silica.

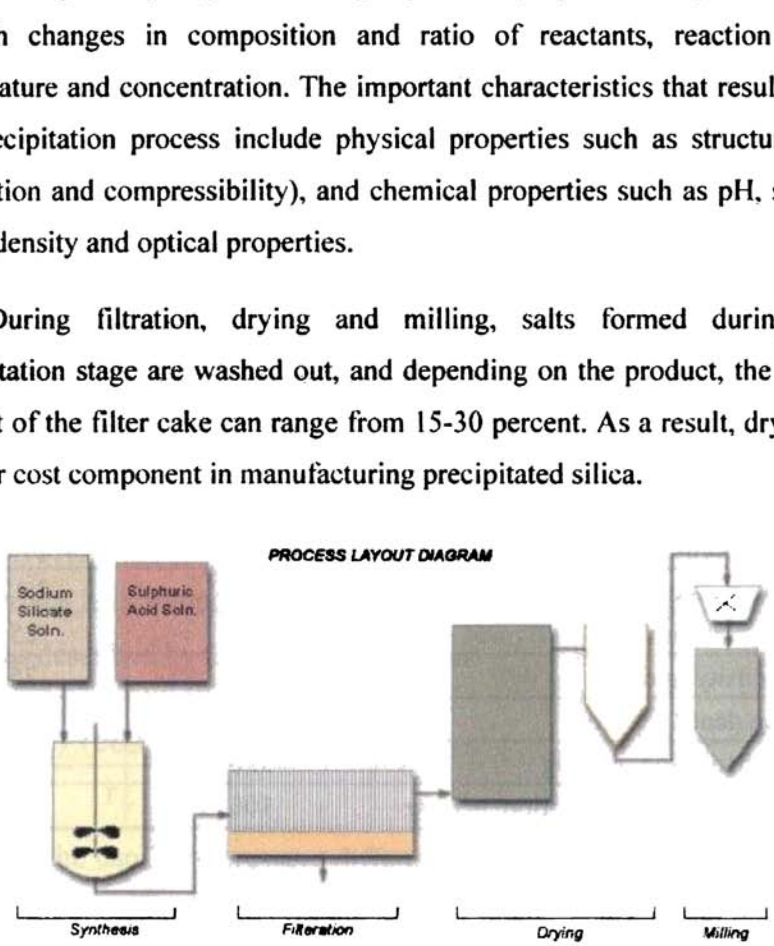


Fig.3.5 Typical flow diagram for the manufacture of silica from sodium silicate.

3.2 Experimental

Precipitation was chosen for the study for the following reason.

a) It involves the use of commonly available sodium silicate and mineral acids.

b) It is possible to produce nanosized silica particles by proper modification and control of conditions.

c) It does not require very long gelation and drying time as required for sol-gel process.

d) Limited choice of solvents that can prevent phase separation during reaction with the organosilanes.

e) The catalyst used in the sol-gel process may remain as impurities.

f) Silica synthesized by the sol-gel process was observed to contain many lattice defects.

g) The impurities would be easily removed by washing with distilled water.

The method adopted in this study is based on the work of Kotoky and Dolui on the PVA/Silica nanocomposite. In the mentioned work, PVA material was used to synthesize nanosilica , which remains in the material to form PVA/Silica composite with sodium silicate and HCl as the starting material. Since in the present work, the required product is nanosilica and not the PVA/Silica nanocomposite, the amount of PVA is reduced to a lower mole ratio. As alkaline medium supports the precipitation reaction and also ammonia reacts with sodium silicate to produce silica, a slightly alkaline medium can be maintained by adding ammonia.

The reaction medium was stirred continuously for a period of 2 hours and the temperature was maintained at 60°C.This serves two purposes.

a. It enables uniform PVA distribution in the reaction solution, so that it could act as a matrix to collect the formed particles. In the absence of heating PVA agglomerates out in the reaction medium.

b. It also enables the conversion of silicic acid formed by the reaction between HCl and Sodium silicate into silica.

The reactions are given below.

$$Na_2SiO_3+2\ HCl \longrightarrow SiO_3+ 2NaCl$$

$$H_2SiO_3 \longrightarrow SiO_2+ H_2O$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

$$Na_2SiO_3+2\ NH_4Cl+2H_2O \longrightarrow H_2SiO_3+2NaCl+2NH_4OH$$

The acid plays a catalytic role in enhancing the co-condensation of silicon oxides within the PVA matrix. Acid provides extensive Hydrogen bonding to both the polymer and the developing polysilicate network enabling system homogeneity.

It is expected that the addition of PVA would produce a matrix into which synthesized silica would be incorporated, thus producing silica in the nano scale .The interaction between the hydroxyl groups of PVA and the hydroxyl groups of silanol from hydrolyzed silica would result in co-condensation.

The synthesized silica after complete drying is proposed to be calcined to remove the PVA matrix and hence obtaining purer silica. Since the end use of the synthesized silica is to produce nanocomposite with polymer, no effort is proposed to be made to remove PVA. The presence of organic molecule (PVA) eliminates the need for the usage of coupling agent during nanocomposite preparation.

3.2.1 Preparation of Chemicals

Sodium silicate solution of two different concentrations, 15% and 30% were prepared for the study.

Hydrochloric acid of strength 3.5N was used.

AR grade ammonia was used as such without any dilution.

Poly Vinyl Alcohol of 1%, 5% were used in the experiments.

The optimized reaction conditions include the concentration of sodium silicate as 15%, HCl of 3.5N and 1% PVA solution.

3.2.2 Procedure

The reaction was initially conducted on a laboratory scale with a reactor with a reactor volume of 500cm^3 for studying the kinetics and later developed into a large scale, based on a total volume of 8 litres to get a more uniform product that can be used for polymer modification.

The required quantities of sodium silicate, HCl, PVA and ammonia in the mole ratio 1:1.96:0.000286: 0.00615 was prepared.

A homogeneous mixture of 3.5N HCl, 1% PVA and ammonia in the desired ratio was made initially and it is then added to Sodium silicate solution (15%) with constant stirring and a constant heat supply of 60°C. During the addition of chemicals, there was instant solidification at one point and stirring becomes difficult. So distilled water was added to keep the reaction mixture in a 40% slurry form. The reaction mixture was stirred continuously for a 2 hours. After the stirring, heat supply was cut off and the reaction mixture was kept at room temperature and the reaction was allowed to continue. After the completion of reaction time, the resultant slurry was kept at room temperature for 24 hrs. It was then filtered, washed, dried at a temperature of 100°C for 5hrs and then milled to produce fine particles.

3.2.3 Experimental set up

The experimental set up consists of the following parts.

a) Reactor
b) Stirring and heating arrangement
c) Filtration assembly
d) Drying assembly

Reactor

The experiments were carried out initially on a laboratory scale and then to a large scale. In a small scale a 250 ml borosil beaker was used as reactor but in a large scale a stainless steel cylindrical vessel with a volume of 20 litres is being used.

Stirring cum heating arrangement

For experiments on a large scale, a motor driven stirrer with two sets of blades was used to provide necessary agitation of the slurry. The reactor was kept in a constant temperature bath which was set for 60°C.The speed of the stirrer can be varied from 0-100 rpm. The speed of the stirrer was varied from 30 rpm to 60 rpm based on the concentration of the slurry and the optimum was found to be 40 rpm.

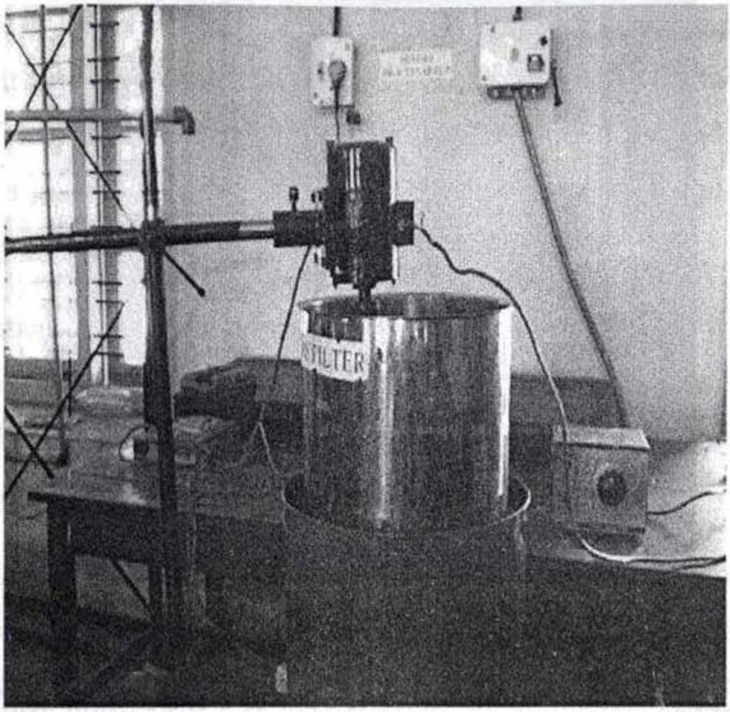


Fig.3.6 Synthesis of Silica

Filtration assembly

Vacuum filtration was done using a leaf filter. The filtration assembly consists of the following parts.

a) The cylindrical vessel containing the slurry
b) Stirrer
c) Leaf filter covered with filter cloth
d) Graduated jar
e) Tubing
f) Stop cocks 1& 2
g) Mercury manometer
h) Vacuum pump

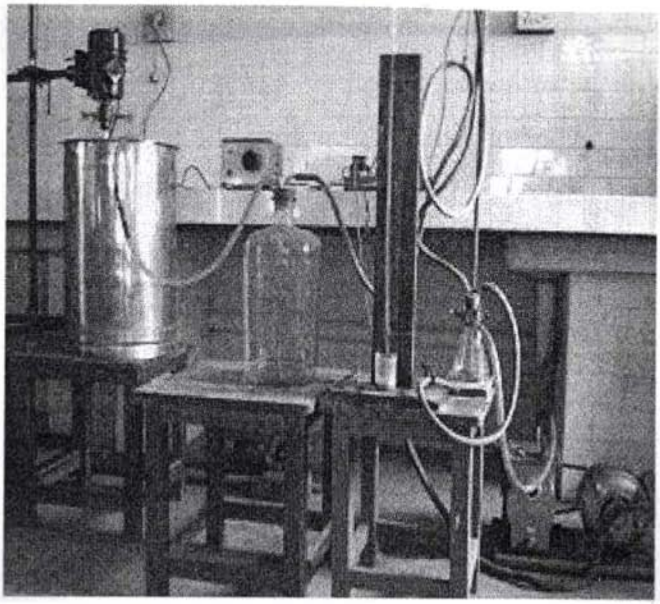


Fig.3.7 Filtration assembly

The vessel containing the slurry is kept as a suspension using a stirrer. Keeping stop cock 1(which is nearer to the leaf) vacuum is made to develop inside the jar using a vacuum pump and it is measured using a manometer. Vacuum is kept at a particular value, i.e. about 30 cm Hg using stop cock 2.

Now stop cock1 is opened. Now vacuum will enter the filter. Due to the pressure difference filtrate will be sucked into the graduated jar. The cake will be deposited on the surface of the leaf. It is lifted up when it is full and the cake is dislodged and dipped into the slurry again. This is repeated till almost all the silica particles in the slurry have been removed. A small portion of the wet cake deposited is taken, dried and weighed.

Drying assembly

Hot air oven with a temperature setting adjustable to 300°C was used. The oven maintains the set point by turning on and off the hot air circulation through the drying chamber. The oven was given the required temperature set point and it was ensured that the temperature was achieved by means of the indicator. The cake obtained after filtration was scrapped out and spread out evenly on a glass plate using a glass rod. Glass plate was then placed in the middle tray of the oven and dried for the required time.

Filtration was done using a leaf filter and the cakes obtained were washed with distilled water several times and then dried in an oven at a temperature of 120°C for 5 hours. Dried cakes are then ground to obtain fine powder of silica.

3.2.4 Surface modification of silica

Explanation of the reinforcing action of fillers in polymers would require consideration of several factors which affect polymer properties, including chemical character of a polymer and a filler, type of filler, polymer-filler phase relation, polymer adhesion to filler's surface, conditions of polymer formation in the presence of a filler and other. The surface modification should be considered in order to improve chemical affinity of the silica to elastomer. Several modifying compounds and on various ways of inducing filler surface modification are reported [52-56].

Silane coupling agents are a very attractive group of compounds capable of promoting reciprocal action of silica fillers and elastomers [56-59].

Activity of silica fillers reflects to a significant extent the chemical character of their surface. The latter may be altered using various reactions which lead to chemical bonds between functional groups, a modifying substance and a filler. With this aim, coupling agents of silane [60-62], borate [63] or titanate [64-65] are used. The application of silane coupling agents is principally aimed at decreasing the hydrophilic character of silicas and at introducing onto the surface of silica, particles of new functional organic groups capable of reacting with the polymer.

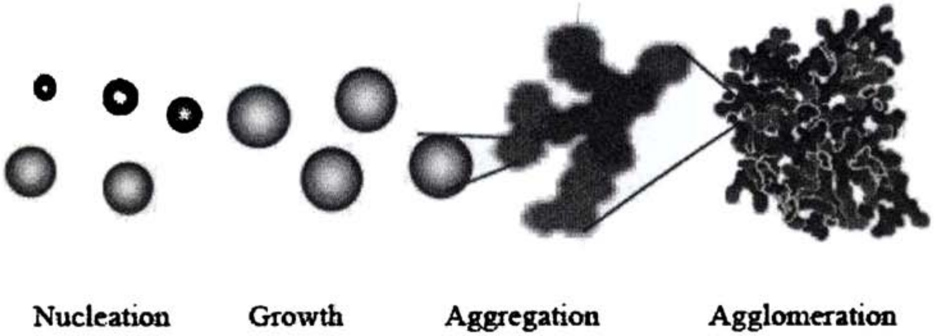


Fig.3.8 Stages of colloidal growth of precipitated silica.

Figure 1 shows schematically the processes that are believed to be active during synthesis along with the structural features resulting from complex growth processes active during synthesis. We can control both the structure of the aggregate/agglomerate and to optimize the structure for effective reinforcement by interfacial modification during the synthesis.

3.2.5 Modification Procedure

The procedure for the surface modification of silica particles are outlined in figure 2.The basic steps involved are hydrolysis and condensation of organoalkoxysilanes. This was done by the addition of HNO_3 and NH_4OH as catalysts. The silica particles (0.1g/ml) with agitation and sonication were dispersed homogeneously in an aqueous solution with agitation and sonication. A dilute solution of HNO_3 was added to the dispersion. In the acidic condition an organoalkoxysilane (0.2M) was added to the silica dispersion and the mixture was stirred at 60°C for 3 minutes for the hydrolysis. Then in the basic condition resulting from the addition of NH_4OH solution the mixture was stirred continuously at 60°C for 1 hour for the condensation. The surface modified particles thus obtained were filtered, washed with distilled water. The particles were then dried overnight in a drying oven at 120°C.

The modified particles were then characterized by various techniques such as TEM, SEM, FTIR,TGA etc.

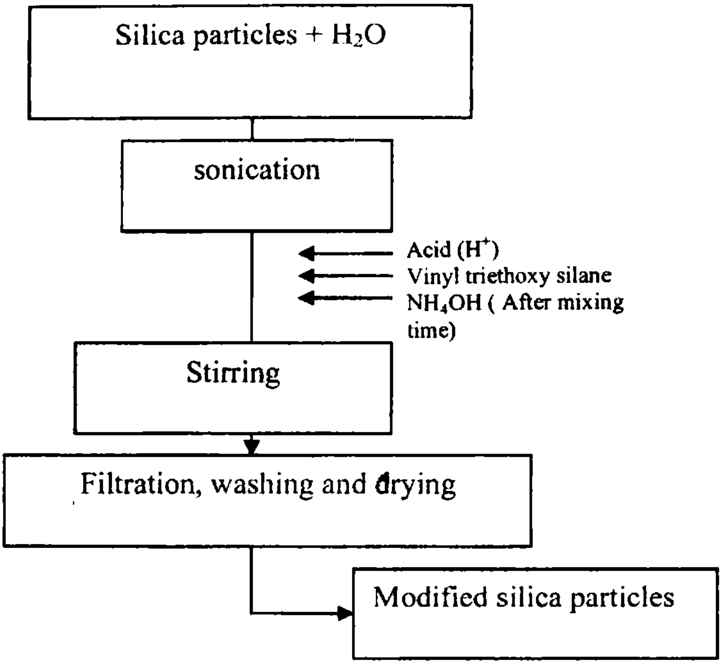


Fig.3.9 Flow chart for the surface modification of silica particles.

3.2.6 Characterization

The characterization of synthesized silica particles were done using various techniques which are described below.

3.2.6.1 *Bulk density*

Determination of bulk density of the material was done as per ASTM-D-1895. Two important terms used are apparent density and bulk density.

Apparent density is the weight per unit volume of a material including voids inherent in the material. Bulk density is defined as the weight per unit volume of a material. It is primarily used for pellets. The test can provide a gross measure of particle size and dispersion, which can effect material flow consistency and reflect packaging quantity.

Apparent density

Measuring cup, a cylindrical cup of 100+0.5 ml capacity having a diameter equal to half of the height. For e.g. 39.9 mm inside diameter by 79.8 mm inside height.

Funnel, having a 9.5 mm diameter opening at the bottom and mounted at a height 38 mm above the measuring cup.

Apparent density value is recorded as g/cm^3.

Specimen: Powder or Pellets

Procedure

Close the small end of the funnel with hand or a suitable flat strip and pour 115± 5 cm^3 samples into the funnel. Open the bottom of the funnel quickly and allow the material to flow freely into the cup. If caking occurs in the funnel, the material may be loosened with a glass rod. After the material has passed through the funnel immediately scrap off the excess on the top of the cup with a straight edge without shaking the cup. Weigh the material cup to the nearest 0.1g. Calculate the weight in grams of 1cm^3 of the material.

3.2.6.2 *Energy dispersive X-ray spectrometer*

The chemical stochiometry of silica nanoparticles is investigated with EDX, (EDS,HITACHI, S-2400).

3.2.6.3 *Surface area*

Surface area of the silica nanoparticles were measured using BET method. Surface area analysis was done using Micromeritics BJH surface analyzer. Model 060 Gemini 2360 instrument (liquid $N_{2,}$77K). Measurements were carried out at liquid nitrogen atmosphere.

Surface area is determined by the equation,

$S_{BET} = 4.353\ V_m$

Where S_{BET} is the surface area in m^2/g and V_m is the moalr volume of adsorbate gas (N_2) at STP.

3.2.6.4 *X-Ray diffraction (XRD)*

Particle size of the sample was determined using X-Ray diffraction (XRD) technique. XRD patterns were collected using Bruker, AXS D8 advance diffractometer at the wavelength CuKα = 1.54°A, a tube voltage of 40 KV and the tube current of 25 mA.

Crystallite size is calculated using Scherrer equation,

$L_{hkl} = k\lambda / \beta \cos \theta$

Where L_{hkl} is the crystallite size perpendicular to the direction of the (hkl) crystal plane,

β - half width of the diffraction peak

k- constant factor of the crystal shape = 0.9

λ- wavelength of the incident X-ray

θ- half of the Bragg angle (degree)

3.2.6.5 *Fourier transform infrared spectroscopy*

The shape of a spectrum can be qualitatively interpreted into the compound responsible for the spectrum. Ultraviolet and visible spectra of solutions contain generally featureless information for identifying the compound, but infrared spectra show a great deal of peak characteristics of the compound, which allows the identification by matching known spectra of the compound.

Fourier transform infrared spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are the indication of the band structures and structural geometry in the molecule. FTIR absorption spectra were collected using Thermo Avtar 370 spectrometer.

3.2.6.6 *Transmission electron microscopy*

The morphology and particle size of nanosilica were observed using transmission electron microscope (TEM). The TEM images were taken on Philips TEM CM 200 model.

3.2.6.7 *Scanning electron microscopy*

Scanning electron microscope (Cambridge Instruments, S 360 Stereo scanner-version V02-01, England) was used to investigate the morphology of the nanosilica sample.

3.2.6.8 *Thermogravimetric analysis*

Thermo gravimetric analyzer (TGA, Q-50, TA Instruments) was used to study the thermal stability of nanosilica. Approximately 5 mg of the samples were heated at a rate of 20^{0} C/min to $800^{o}C$.The chamber was continuously swept with nitrogen gas at the rate of 60ml/min.

3.2.7 Kinetic studies on synthesis of nanosilica from sodium silicate

Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals. The selection of a reaction system that operates in the safest and most efficient manner can be considered economically feasible. So a study on the chemical kinetic principles associated in the synthesis of silica will lead to the design of a better process that can meet our requirements on a large scale.

Chemical kinetics is concerned with the rate at which the chemical reactions take place, the mechanism and rate- limiting steps that can the reaction process[66]. In order to design a process it is important to have knowledge of the chemical and physical behaviour of the fluids within the reactor.

As a first step towards design, it is necessary to account for the various chemical species entering and leaving a reaction system. This is achieved through overall material balance on individual species in the reacting system. Then the design equations for common industrial reactors are developed.

3.2.7.1 *Classification of reactions and definition of reaction rate*

There are many ways of classifying chemical reactions. The wide classification is based on the number and types of phases involved. That is, they are classified into two types.

i) Homogeneous and ii) Heterogeneous

A reaction is homogeneous if it take place in one phase alone. Eg : most gas phase reactions, most liquid phase reactions which are non-catalytic or catalytic in nature.

A heterogeneous reaction is one which requires the presence of at least two phases to proceed, at that rate.

Reaction rate

There are several ways of expressing a reaction rate. For this we must select one reaction component and define the rate in terms of this component i.

If the rate of change in the number of moles of this component due to reaction is dNi/dt , then based on unit volume of reacting fluid,

$$r_i = \frac{1}{V}.\left(\frac{dNi}{dt}\right) = \text{moles i formed/(volume of fluid)(time)}$$

There are many variables that may affect the rate of a chemical reaction. In homogeneous system the temperature, pressure and composition are important variables. But in heterogeneous reactions due to the more number of phases involved we must consider the heat and mass transfer effects also.

The rate equation

Consider the single phase reaction,

$$A\,A + b\,B \rightarrow r\,R + s\,S$$

The most useful measure of the reaction rate for reactant A is then

$$-r_A = \frac{1}{V}.\left(\frac{dNi}{dt}\right) = \text{(amount of A disappearing) /(volume) (time) ,[mol/m}^3\text{.s]}$$

where $-r_A$ is the rate of disappearance of A.

The rates of reactions of all materials are related by $-r_A/a = -r_B/b = r_R/r = r_S/s$

The rate of reaction is influenced by composition and the energy or temperature of the material.

Thus $-r_A$ = f [(temp. dependent terms). (Concn.dependent terms)]

Example, $-r_A = kC_A^a$

$= k_0\, e^{-E/RT}.\ C_A^a$

where $k = k_0\, e^{-E/RT}$ and E is the activation energy.

Simple reactor types

The various types of ideal reactors used for homogeneous and for isothermal and non- isothermal operations are,

a) Batch Reactor (BR)

b) Plug Flow Reactor (PFR)

c) Mixed Flow Reactor (MFR)

Batch reactor

In batch reactor, the reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged.This is an unsteady state operation where the composition changes with time, however at any instant the composition throughout the reactor is uniform.

Plug flow reactor

In plug flow reactor the pattern of flow is considered as plug flow. There is no mixing in the axial direction inside the reactor though there may be lateral mixing of fluid elements. The residence time of all elements of fluid in the reactor is same.

Mixed flow reactor

This is another ideal steady state flow reactor. The other names of this reactor are the back mix reactor, continuous stirred tank reactor etc. In this reactor the contents are well stirred and uniform throughout and the exit stream has the same composition as the fluid within the reactor.

Batch reactor- Performance Equation

A batch reactor has neither inflow nor outflow of reactants or products while the reaction is being carried out.

A material balance equation written for component A which is taken as the limiting component is given below.

Input = Output + disappearance + accumulation ....(1)

0	= 0	+	rate of loss of reactant A within the reactor due to chemical reaction	+	rate of accumulation of reactant A within the reactor

or

$$(-r_A).V \frac{\text{(moles of A reacting).}}{\text{(time)(vol. of fluid)}} \text{(vol. of fluid)} = -dN_A/dt \text{ moles/time}$$

$$\text{i.e. } (-r_A).V = \frac{d}{dt}[N_{Ao}(1-x_A)]$$

$$= N_{Ao}\frac{dx_A}{dt} \quad \text{..(2)}$$

Rearranging and integrating gives,

$$t = N_{Ao}\int_0^{x_A} \frac{dx_A}{(-r_A)V} \quad \text{..(3)}$$

If the fluid density remains constant, eq.(3) becomes,

$$t = C_{Ao} \int_{o}^{x_A} \frac{dx_A}{(-r_A)} \quad \text{...} (4)$$

$$t = -\int_{C_{Ao}}^{C_A} \frac{dc_A}{(-r_A)} \text{ for } \varepsilon_A = 0 \quad \text{.......................................} (5)$$

Space time and Space velocity

Space time and space velocity are the proper performance measures of flow reactors. Space time (τ) is defined as the time required to process one reactor volume of feed at specified conditions. Space velocity (s) is the number of reactor volumes of feed at specified conditions which can be treated in unit time. Both these terms are related as,

$\tau = 1/s$

τ has the unit of time.

s has the unit of $(\text{time})^{-1}$.

$\tau = 1/s = C_{Ao}V/F_{Ao}$

where C_{Ao} is the initial concentration of A,(moles of A entering)/(volume of feed),

V is the volume of the reactor, (m^3)

F_{Ao} is the feed rate (moles of A entering/time)

$\tau = V/v_0$ = (reactor volume)/ (vol. feed rate)

3.2.7.2 *Collection and analysis of reactor data*

Batch reactors are used to determine rate law parameters for homogeneous reactions. This is usually done by measuring concentration as a function of time and then using either differential or integral method of analysis to determine the reaction order 'n' and specific reaction rate , k.

Differential method of Rate analysis

For irreversible reactions of the type involved in the synthesis of silica, it is possible to determine the reaction order 'n' and specific rate constant 'k' by differential method. This method is applicable when the reaction conditions are such that the rate is essentially a function of the concentration of only one reactant.

For the irreversible reaction

$A + B \rightarrow$ products

With the rate law

$-r_A = k\, C_A^{a}\, C_B^{b}$

where a and b are both unknown, then reaction could be first run in excess of B so that C_B remains constant during the course of reaction and

$-r_A = k'\, C_A^{a}$ where $k' = k\, C_B^{b}$

In the same manner b is also found out.

Now consider the reaction involved in the synthesis of silica. In the reaction between sodium silicate and hydrochloric acid it is assumed that the reaction rate is proportional to the concentration of HCl and all the calculations are based on the amount of HCl converted during synthesis.

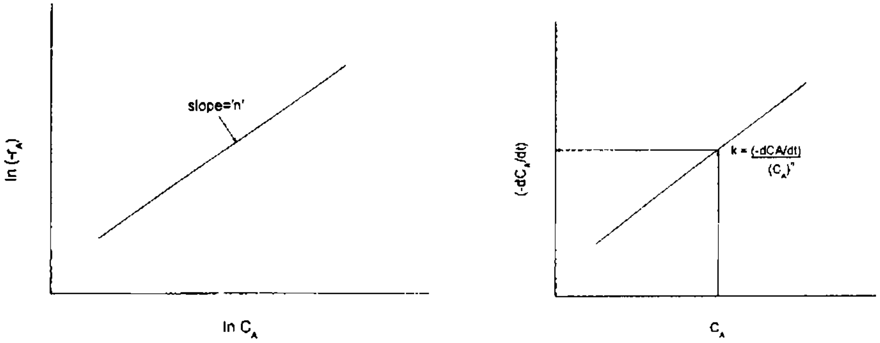
The reaction is carried out isothermally in a constant volume batch reactor and the concentration recorded as a function of time.

Then, $(-r_A) = (-dC_A/dt) = kC_A^n$. .... (6)

Taking logaritham of both sides of equation (6),

$\ln(-dC_A/dt) = \ln k + n \ln C_A$ .... (7)

Now plot ln $(-dC_A/dt)$ as a function of C_A and determine the slope which will be the order of the reaction. See the fig.3.10 (a)&(b) given below.



(a) (b)

Fig.3.10(a)&(b) Determination of rate constant and reaction order by differential method.

The specific reaction rate can be found by first choosing a concentration in the plot, say C_A and then finding the corresponding value of $(-dC_A/dt)$. After raising C_A to the nth power, divide $(-dC_A/dt)$ to determine k.

$$k = \frac{\frac{-dC_A}{dt}}{C_A^{\,n}}$$

The values of $(-dC_A/dt)$ can be found either graphically or by numerical methods. In graphical method, plot C_A vs time. Draw tangents at various points and find the slopes. This gives the values of $(-dC_A/dt)$.

Integral method

To determine the reaction order by this method, guess the reaction order and integrate the differential equation used to model the batch system. If the order we assume is correct the appropriate plot of concentration-time data should be linear. The integral method is used most often to evaluate the specific reaction rate constants at different temperatures and to determine the activation energy.

In the integral method, the rate data should be a function of concentration corresponding to a particular rate law that is linear with time.

For a second order reaction,

$$\frac{-dC_A}{dt} = kC_A^{\,2} \quad \text{.......} \quad (8)$$

Rearranging and integrating eq.(8),

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^{\,2}} = k\int_{0}^{t} dt$$

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = kt$$

In this case a plot of $\frac{1}{C_A} - \frac{1}{C_{Ao}}$ vs t yield a straight line with slope k.

The unit of k for nth order reactions is $(\text{time})^{-1}(\text{concentration})^{1-n}$.

3.2.7.3 *Estimation Methods*

The amount of HCl reacted was estimated by titration method using NaOH solution and phenolphthalein indicator. Known volumes of sample collected from the reactor were titrated against 0.035N NaOH solution. The end point is pink colour. This procedure was continued till the concentration of HCl that remain unconverted in the reaction mixture was almost constant.

3.3 Results and discussion

3.3.1 Characterization

3.3.1.1 *Bulk density*

The primary identification of the material was done by determining the bulk density of the material. The samples prepared in the lab are characterized by determining the bulk densities and it is given in the table.3.3

Table 3.2 Densities of silica samples.

Sample name	Bulk density (g/cm^3)
Commercial silica	1.03
Sample 1	1.39
Sample 2	1.0

3.3.1.2 *Energy dispersive X-Ray spectrometer*

The nanosilica prepared was found to have less amount of impurities. The EDX spectrum of samples 1& 2 are given in the figures 3.9&3.10.The percentage of Si in the nanosilica samples prepared in the laboratory are listed in table 3.2. A similar spectrum is obtained for commercial silica.

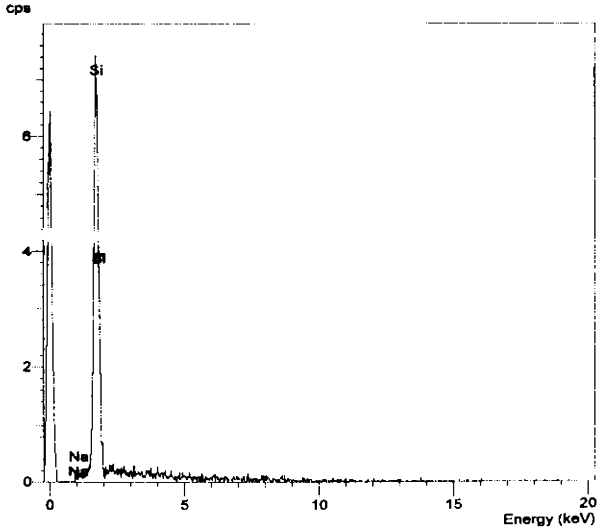


Fig.3.9 EDX spectrum of nanosilica sample 1.

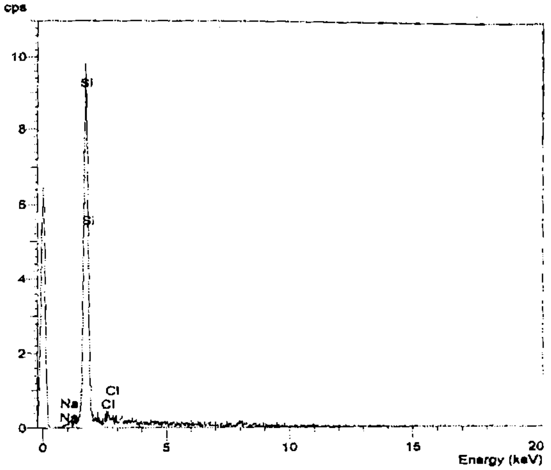


Fig.3.10 EDX spectrum of nanosilica sample 2

Sample name	Si	
	Atomic %	Element %
Sample 1	96.86	97.03
Sample 2	98.54	99.01
Commercial silica	98.12	98.8

3.3.1.3 Surface area

Representative samples were selected from those prepared with and without modification for surface area determination. Table 3.4 shows surface area for commercial nanosilica, Sample1 and Sample 2.

Table 3.4 Surface areas of silica samples.

Sl.No.	Samples	Surface area (m^2/g)
1	Commercial silica	175
2	Sample 1	180
3	Sample 2	278

It is clear that surface area of silica prepared in the lab is more than commercial silica. Also the surface modified particles have greater surface than the other samples.

3.3.1.4 *XRD Studies*

The XRD patterns of silica samples are given in figures 3.11(a)&(b). Since silica is amorphous there is no sharp peaks observed. From the one which is seen at an angle of 22° the crystallite size was determined as 24 nm.

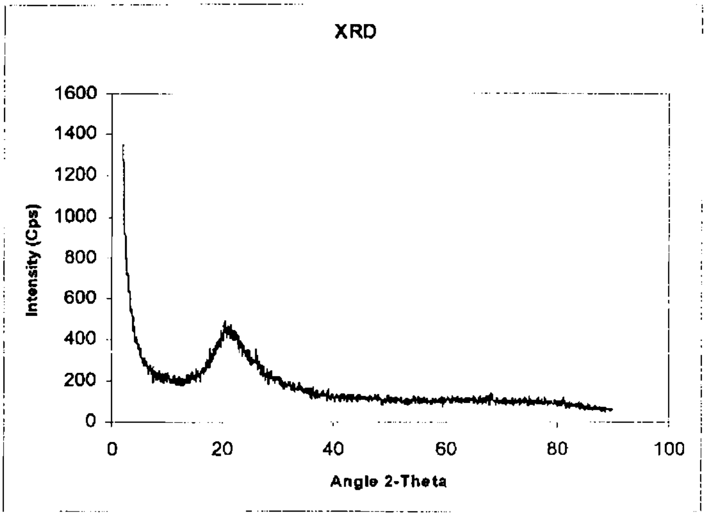


Fig.3.11(a). XRD patterns of commercial silica.

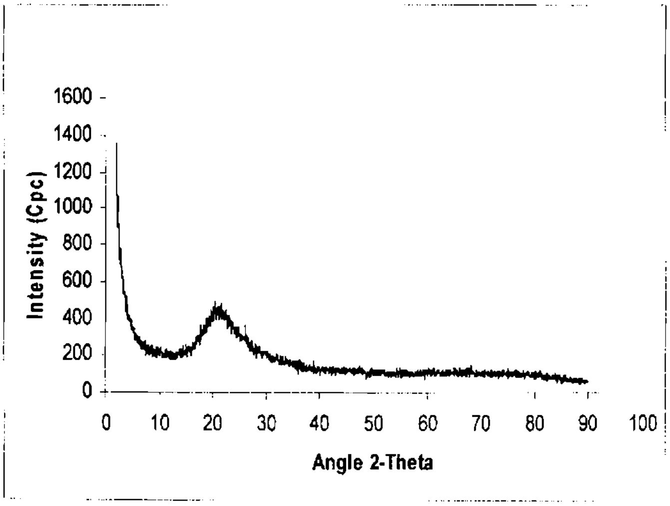


Fig3.11(b). XRD patterns of sample1.

3.3.1.5 *IR spectroscopy*

The IR spectrum of different samples of silica are shown in the fig.3.12(a),(b)&(c).

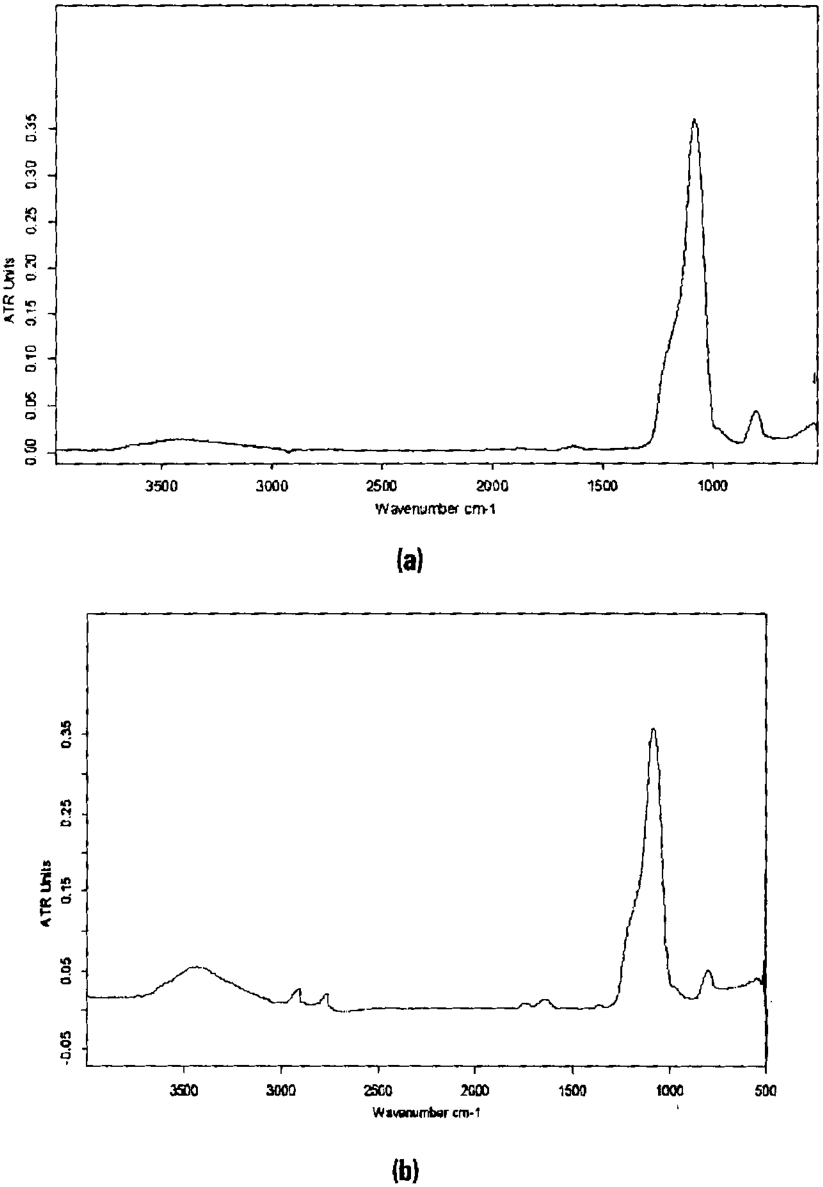


Fig.3.12 IR spectrum of (a) Commercial Silica (b) modified silica

The IR spectra give only qualitative (and not quantitative) information about a sample By comparison of the corresponding peaks, it can be concluded that all samples consist predominantly of silicon oxide. The IR spectrum of commercial and unmodified silica showed a characteristic peak around 1085 cm^{-1} which is due to the Si-O bond. There are no peaks in the region of 1500 – 3000 cm^{-1}. However, the second sample shows two small peaks in the viscinity of 3000°A. This means that organo groups have been attached to silica as a result of modification.

3.3.1.6 *Scanning electron microscopy*

Scanning electron microscopy (SEM) allows the visualization of materials at very high magnifications. Depending on the instrument and materials properties, it is capable of providing resolutions down to the nanometer scale .

The surface morphology as determined by scanning electron microscopy reveals that the method of preparation has a significant effect on the structure and shape of the particles. It is clear from the figure that the silica particles prepared have spherical shape. The effect of modification is also evident from the SEM pictures. The commercial silica particles is found to be present in the form of agglomerates when compared to modified silica particles which is identical to that of unmodified silica.

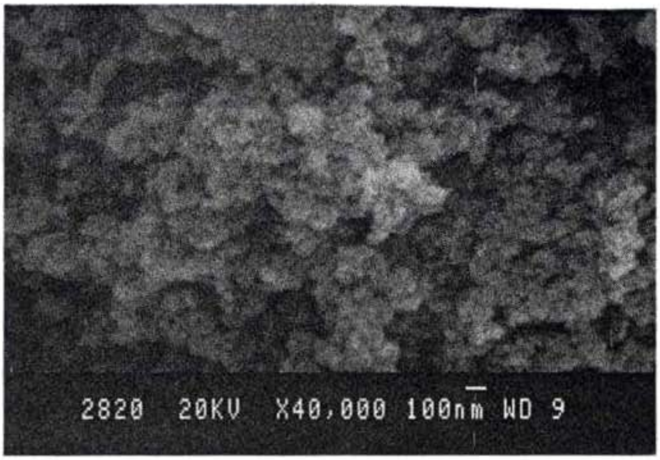


Fig3.13 SEM picture of modified silica

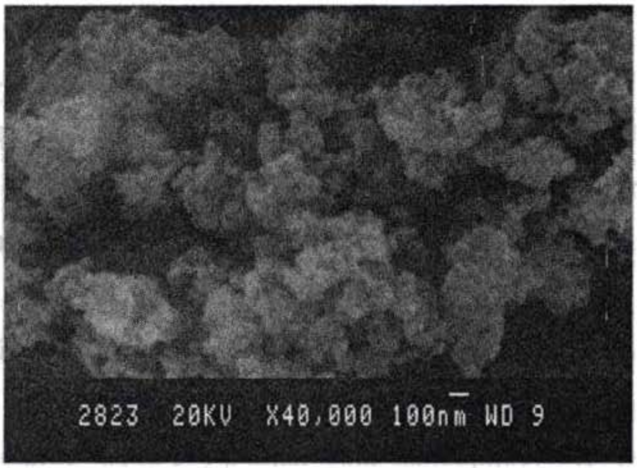


Fig.3.14 SEM picture of unmodified silica

3.3.1.7 *Transmission electron microscopy*

The TEM image of the different silica samples is given in figure 3.15. The size of the particles was determined from the scale bar given in the picture. The average size of the particles was calculated and found to be equal to 15 nm. The corresponding diffraction pattern is also shown in fig.3.16 and it is identical to that of amorphous particles.

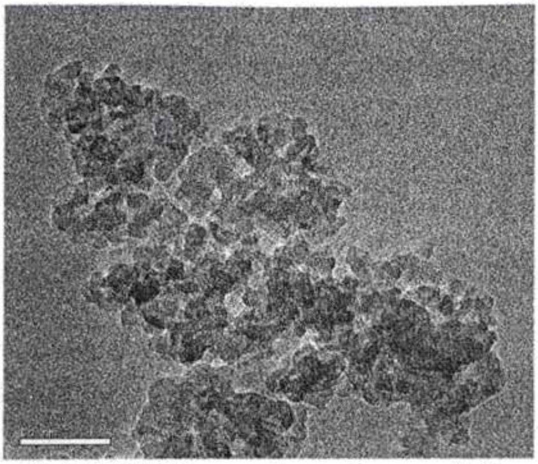


Fig.3.15 TEM image of nanosilica sample 1

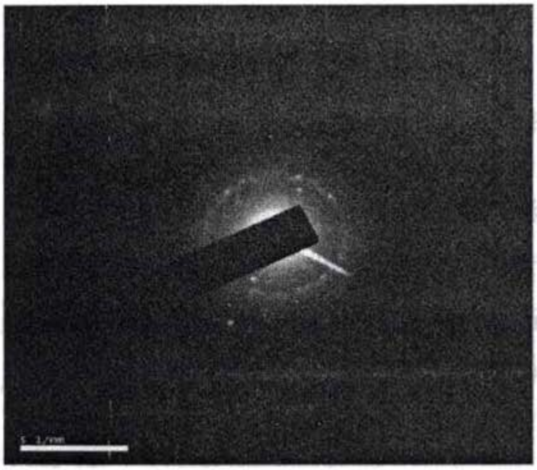


Fig.3.16 Diffraction pattern of silica sample.

3.3.1.8 *Thermogravimetric analysis*

Thermogravimetric analysis of the synthesized silica and commercial silica nanoparticles was done to check the thermal stability. The changes occurring during the heat treatment are given the fig.3.17.TGA shows that there was no peaks which may be due to the perfect drying of the samples prior to Thermal analysis. The nanosilica sample 2 shows very good thermal stability even at higher temperatures.

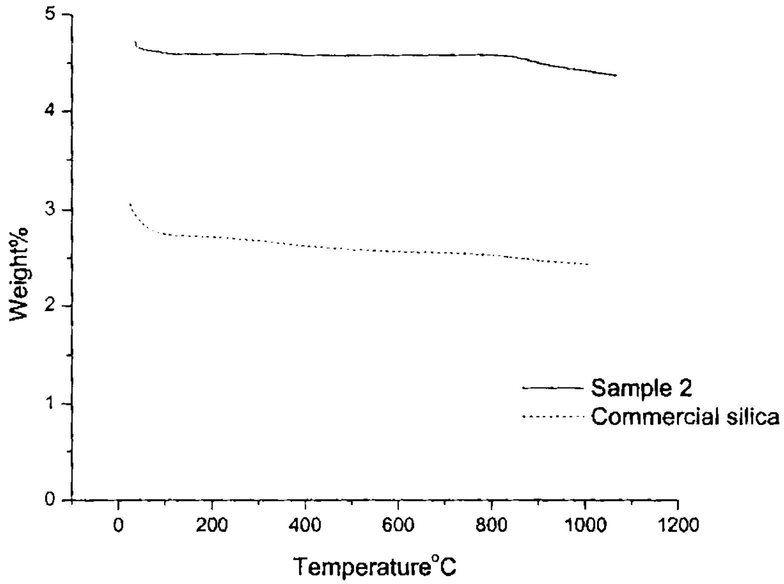


Fig.3.17 Thermogravimetric traces of nanosilica samples

3.3.2 Determination of kinetic parameters

In the reaction between sodium silicate and HCl the rate of reaction depends on the amount of HCl converted. Hence to evaluate the rate constant k, the concentration of HCl in the reaction medium is determined at definite intervals.

The information necessary for finding out the performance of the reactor used for silica synthesis are the rate constant and order of the reaction [67-69]. Based on this data the process can be scaled up to industrial level which can offer great potential for using silica for polymer modification.

The rate constant for the reaction of sodium silicate with HCl is determined based on the observation that the acid plays a significant role in the formation of silica particles. The concentration of HCl is used as a measure to find the reaction order and rate constant. The rate constant for the reaction is found out by estimating amount of HCl converted with time. The concentrations of sodium and ammonia are assumed to be constant during the course of reaction. The reaction rate is written to be of the form,

$$-r_A = k\, C_A^n \qquad (9)$$

where $-r_A$ = rate of disappearance of HCl with time = $-dC_A/dt$

C_A is the concentration of HCl, mol/litre

k = rate constant for the reaction, litre/mol.min

n = order of the reaction.

Taking logarithm on both sides of equation (1),

$$\ln -r_A = \ln k + n \ln C_A \qquad (10)$$

A plot of $\ln -r_A$ vs $\ln C_A$ is made. The slope and intercept of the straight line obtained is determined. From these, the values of rate constant 'k' and reaction order 'n' are found out. The ($-dC_A/dt$) values are obtained either numerically or by graphical method [70-71]. In the graphical method C_A vs time is plotted [72]. The slopes of the tangents drawn at various points in curve are taken as $-dC_A/dt$.

The plot of concentration vs time is shown in fig. 3.18. From this graph $-dC_A/dt$ is calculated and are listed in Table3.4

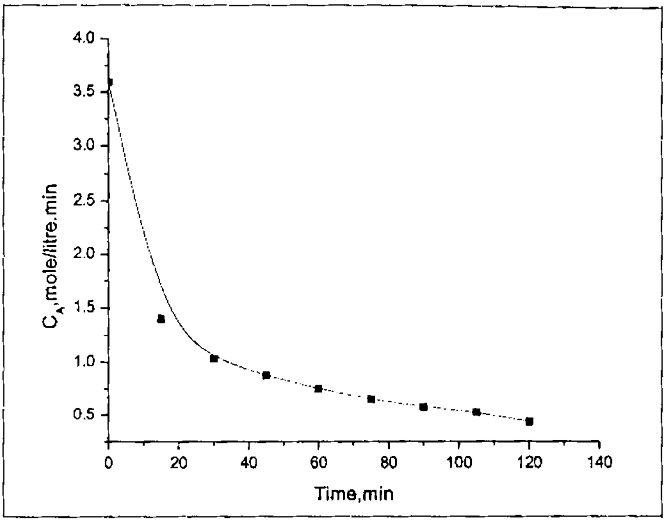


Fig.3.18 plot of concentration vs time

Table.3.4 Concentration-time data

Time, minutes	C_A mol/litre.min	(dC_A/dt)
0	3.591	0.24
15	1.401	0.042
30	1.033	0.013
45	0.875	0.009
60	0.75	0.006
75	0.645	0.004
90	0.578	0.003
105	0.526	0.002
120	0.438	0.001

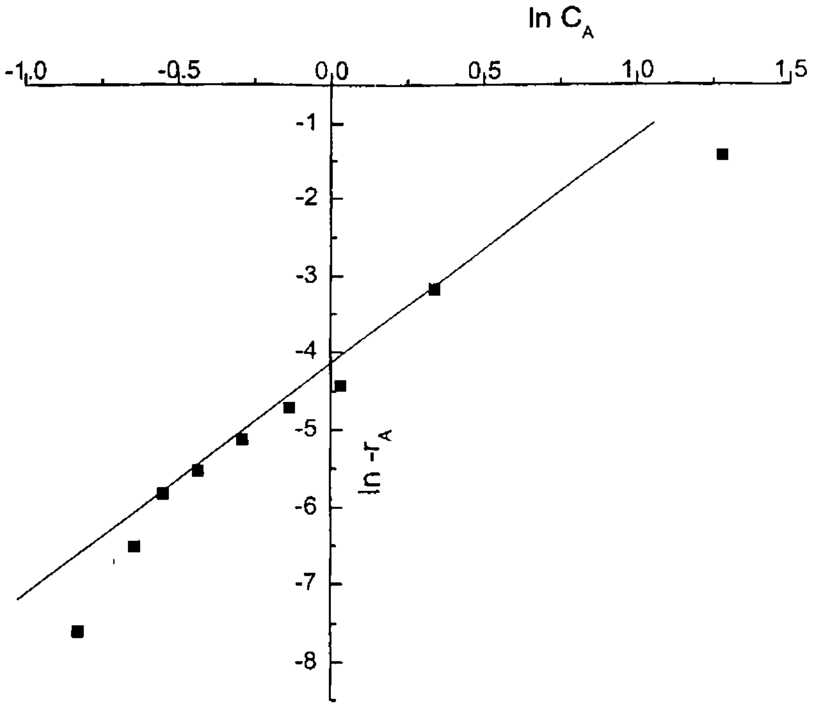


Fig.3.19 Shows the plot of ln $-r_A$ vs ln C_A.

The plot of ln $-r_A$ vs ln C_A is shown in fig.3.19. The plot is a straight line and the slope of this line is equal to 2 which show that the reaction is of second order. Also from the intercept the value of the rate constant is found to be 0.0166 litre/mol.min.

3.3.2.1 *Determination of k by Non-linear least squares analysis*

This is a useful method to determine the rate law parameters [73-74]. In non-linear least squares analysis we search for those parameter values that minimize the sum of squares of the differences between the measured values and the calculated values for all the data points. Here we make estimates of parameter values such as reaction order and specific rate constants in order to calculate the rate of reaction, r_c. Then search for those values that minimize the sum of the squared differences of the measured reaction rate, r_m , and the calculated reaction rates, r_c. Now select the value if the parameters such that sum of (r_m-$r_c)^2$ is minimum. The variance is calculated according to the equation,

$$\sigma = \frac{S^2}{(N-K)} = \sum \frac{(r_{im} - r_{ic})^2}{N - K}$$

where N - is the number of runs

K - Number of parameters to be determined.

r_{im} - measured reaction rate for run i

r_{ic}- calculated reaction rate for run i

Now consider the silica synthesis reaction, the rate equation is assumed to be of the form $-r_A = k\, C_A{}^n$ where k is the reaction rate and n is the reaction order. For these parameters values were chosen and the rate is calculated as r_{ic} at each concentration at which an experimental point was taken. Then the sum of the squares of the difference (r_{im}- r_{ic}) was found out. This procedure is continued by further varying k and n until their best values, that is, those values that minimize the sum of squares. The values of k and n that minimize the sum of squares were taken as the theoretical values and the data were tabulated in table.3.5. It was then compared with the experimental values and the percentage error is determined. This is shown in fig.3.20

Table 3.5 Minimizing the sum of the squared differences

Data			**Trial 1 k = 1, n=1**		**Trial 2 k = 0.017, n = 3**		**Trial3 k = 0.05, n = 3**		**Trial4 k =.15, n = 2**		**Trial 5 k = 0.017, n = 2**	
Run	C_A	r_m	$r_m - r_c$	$(r_m - r_c)^2$	$r_m - r_c$	$(r_m - r_c)^2$	$r_m - r_c$	$(r_m - r_c)^2$	$r_m - r_c$	$(r_m - r_c)^2$	$r_m - r_c$	$(r_m - r_c)^2$
1	3.59	0.24	-3.35	11.22	2.073	4.299	-0.404	0.1635	-0.021	4.37×10^{-4}	-0.547	0.229
2	1.40	0.042	1.359	1.85	0.096	9.14×10^{-3}	-0.056	3.2×10^{-3}	8.6×10^{-3}	7.12×10^{-5}	4.8×10^{-3}	2.29×10^{-5}
3	1.03	0.013	1.021	1.04	0.042	1.78×10^{-5}	-0.040	1.63×10^{-3}	5.16×10^{-3}	2.66×10^{-5}	5.8×10^{-3}	3.33×10^{-5}
4.	0.88	0.009	0.866	0.75	0.025	6×10^{-4}	-0.029	8.6×10^{-4}	4.02×10^{-3}	1.61×10^{-5}	2.39×10^{-3}	5.7×10^{-6}
5.	0.75	0.006	0.744	0.55	0.015	2.28×10^{-4}	0.022	4.9×10^{-4}	3.56×10^{-3}	1.27×10^{-5}	1.17×10^{-3}	1.37×10^{-6}
6.	0.65	0.004	0.644	0.42	9.6×10^{-3}	9.23×10^{-5}	0.017	2.89×10^{-4}	3.14×10^{-3}	9.86×10^{-6}	6.28×10^{-4}	3.4×10^{-7}
7.	0.58	0.003	0.575	0.33	6.65×10^{-3}	4.43×10^{-5}	0.014	1.88×10^{-4}	2.68×10^{-3}	7.18×10^{-6}	2.83×10^{-4}	7.99×10^{-8}
8.	0.53	0.002	0.525	0.28	5.78×10^{-3}	3.34×10^{-5}	0.012	1.52×10^{-4}	3.2×10^{-3}	1.03×10^{-5}	9.74×10^{-4}	9.48×10^{-7}
9.	0.44	0.001	0.438	0.19	3.7×10^{-3}	1.37×10^{-5}	0.009	8.27×10^{-5}	2.76×10^{-3}	7.63×10^{-6}	9.28×10^{-4}	8.62×10^{-7}
				16.63		4.299		0.17		2.61×10^{-3}		0.402
			$S_1^2 = 16.63$ $\sigma_1^2 = \frac{16.63}{2}$ $= 8.315$		$S_2^2 = 4.299$ $\sigma_2^2 = 2.15$		$S_3^2 = \frac{0.17}{2}$ $\sigma_3^2 = 0.085$		$S_4^2 = 2.61 \text{ X } 10^{-3}$ $\sigma_4^2 = \frac{0.00261}{2}$ $= 0.0013$		$S_5^2 = 0.402$ $\sigma_5^2 = 0.201$	

Trial No: 4 gives the lowest value for σ^2. Hence it is chosen

∴Theoretical value of rate constant k is takes as = 0.017 litre/mole.min

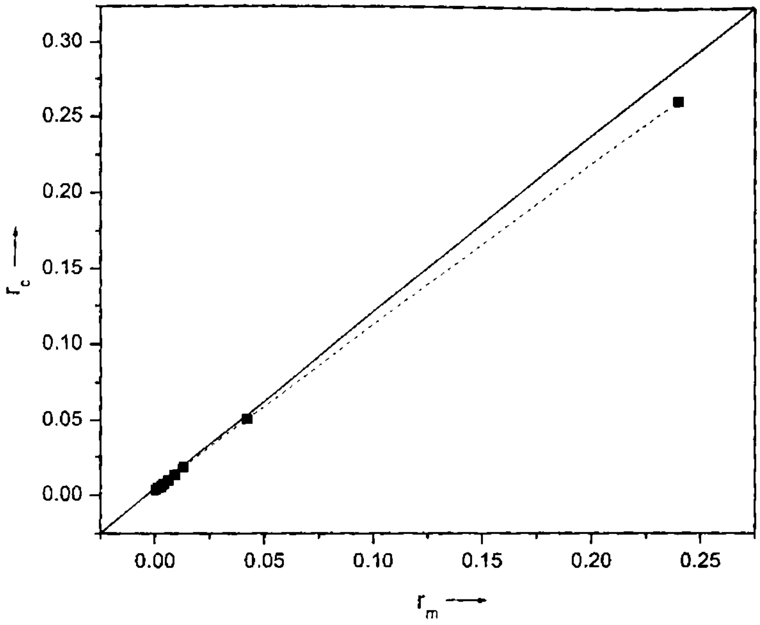


Fig.3.20 Plot of measured rate versus calculated rate.

From the figure, the percentage error was determined from the extent of deviation of the line with the 45° diagonal,where the rates have equal values. The deviation is calculated as 6.25% which is satisfactory as it is less than 10%.

3.3.3 Scale up and reactor modeling

After optimizing the parameters for the synthesis of silica , the next step was to produce it in a large scale for polymer modification. Scale up of laboratory experiments to pilot plant or full scale production is usually done based on laboratory data . To make this successful, a thorough understanding of the chemical kinetics is required. In this work, after determining the specific reaction rate, k, from a batch experiment we used it in the design of a full-scale reactor.

3.3.3.1 *Characteristic behaviour of reactors*

The design equation developed for three basic types of reactors are based on the assumption that the reaction mixture behaviour according to the ideal flow patterns characteristic of such reactors.

Although practical reactors can not completely fulfill these assumptions, many cases may be approximated by ideal react oral models without any serious error being introduced. On the other hand, there are a number of cases in which deviation from ideal reactor becomes so significance that an excessively large error good result if the design were based entirely on ideal models. Such deviations can some times be taken care of by introducing correction factors in to the ideal reactor models, but purely empirical methods of scale up and design are also frequently employed.

In addition to the non- ideal behaviour, those reactors characteristic that govern the degree of conversion and the product composition should also be considered. They include reactor type and size, reaction temperature and pressure.

3.3.3.2 *Non- ideal flow*

Deviation from ideality assumed in developing the basic reactor design equations are presenting practical reactors and the extent of non-ideality often varies considerably, depending on the scale and type of reactor. Important types of deviation from two ideal flow reactors are

Deviation from plug-flow reactor

a) Channeling of the reacting fluid through the catalyst packing and the presence of stagnant fluid pockets.

b) The presence of velocity and temperature gradients in the radial direction, and

c) The presence of stagnant fluid pockets.

Deviation from back-mix reactor

a) Short-circuiting and bypassing of the reacting fluid. That is certain portions of the fluid may proceed directly from the feed inlet to the product discharge port with out mixing with the contents of the reactor.

b) Internal recycling of the fluid.

c) The presence of stagnant fluid pockets.

3.3.3.3 *Characterization of non-ideal flow*

Deviations from ideality imply that the different portions of reacting fluid follow separate flow patterns through the reaction vessels, resulting in a wide distribution of residence times. Such deviations from ideality represent inefficiency in the reactor performance and cause reduction in the production capacity. To alleviate this condition, there are various methods used to characterize the magnitude of deviation - the so called stimulus-response techniques that utilize a tracer.

Three typical techniques of introducing a tracer into the reaction vessel are the step input, the pulse input and the cyclic input. The information thus obtained is applicable to the determination of conversion in a reactor, either directly or in combination with one of the several mathematical models proposed to account for non-ideal flow condition.

3.3.3.4 *Residence time distribution (RTD)*

Information obtainable from the stimulus techniques by using a tracer is the distribution of residence times for various elements of reacting fluid.

RTD of a reactor is a characteristic of mixing that occurs in a chemical reactor. The RTD exhibited by a given reactor yields distinctive clues to the type of mixing occurring within it and is one of the most informative characterizations of the reactor.

The distribution of times for the stream of fluid leaving the vessel is called the residence time distribution, RTD or exit age distribution E of the fluid. E has the unit of time^{-1}.

It is convenient to represent the RTD in such a way that the area under the curve is unity or

$$\int_{0}^{\infty} E\,dt = 1$$

Tracer response curves

Two types of response curves are obtained from the tracer experiment. In both curves, a dimensionless tracer signal (or concentration) C/C_0 is plotted against dimensionless time τ. C_0 is the input concentration, whereas C is the tracer concentration measured at the exit. The response curve to a step input is termed an F-curve. The second type, called a C-curve is the response to a pulse tracer injection.

The method of obtaining the RTD from the tracor experiments is shown in the following relation

$$E = C = \left(\frac{C}{C_o}\right)_{\text{step input}}$$

$$E = \frac{dF}{dt} = \frac{d}{d\tau}\left(\frac{C}{C_o}\right)_{\text{step input}}$$

Application of residence time distribution data

The RTD data resulting from the tracer experiment can be used to predict the performance of the reactor with good accuracy only for processes involving first order reactions. For reactions other than first order tracer data alone is not sufficient to determine its performance, in addition to RTD, an adequate model of the non ideal reactor flow pattern and knowledge of the quality of mixing or “degree of segregation” are required to characterize a reactor properly.

a. RTD in ideal reactors

RTDs in batch reactors

The RTDs in plug flow reactors and batch reactors are simplest to consider. All the atoms leaving such reactors have spent precisely the same amount of time within the reactors. The distribution function in such a case is a spike of infinite height and zero width, whose area is equal to 1; It occurs at $t=V/v$ or $\theta=1$ where θ is the dimensionless time. Mathematically, this spike is represented by the dirac delta function.

$$E(t) = (t - \tau)$$

The dirac delta function has the following properties.

$$\delta(x) = 0 \left\{ 0 \text{ when } x \neq 0, \infty \text{ when } x=0. \right.$$

b. Single CSTR-RTD

In an ideal CSTR the concentration of any substance in the effluent stream is identical to the concentration within the reactor. Hence RTD is obtained by taking material balance on an inert tracor that has been injected as a pulse at time t=o into a CSTR. The material balance equation is given below.

$$\text{In - out} = \text{accumulation} \tag{11}$$

$$0 - VC = \frac{V.dc}{dt} \tag{12}$$

where V is the volume of the reactor, v is the volumetric flow rate and C is the concentration of the tracer either in the effluent or in the reactor.

Separating the variables and integrating eq.(2) with C=Co at t=0 yields

$$C(t) = C_0\, e^{-t/\tau} \tag{13}$$

This relationship gives the concentration of the tracer in the effluent at time t.

E(t) for an ideal CSTR is given by

$$E(t) = C(t) \frac{C(t)}{\int_0^{\infty} C(t)dt} \tag{14}$$

$$= \frac{C_0\, e^{-t/\tau}}{\int_0^{\infty} C(t)dt} \tag{15}$$

In terms of the dimensionless parameter θ,

$E(\theta) = e^{-\theta}$ where $\theta = t/\tau$ ....(6)

c. Reactor modeling with RTD

There are many situations in which the fluid in a reactor is neither well mixed nor approximates plug flow. So various models were developed and used for predicting conversion in real reactors based on the information obtained from RTD. These models are classified according to the number of adjustable parameters that are extracted from RTD data and are given below.

1) Zero adjustable parameters
    a. Segregation model
    b. Maximum mixedness model
2) One adjustable parameter model
    a. Tanks -in-series model
    b. Dispersion model
3) Two adjustable parameter model

Real reactors modeled as combinations of ideal reactors.

The mixing of reacting species is one of the major factors controlling the behaviour of chemical reactors. For reactions of first order the conversion is independent of concentration. Consequently mixing with the surrounding molecules is not important. Therefore once the RTD is determined we can predict conversion that will be achieved in real reactor provided that specific reaction rate for the first order is known. For reactions of higher order models used must contain information about micromixing in addition to that of macromixing. Macromixing produces a distribution of residence times without specifying how molecules of different ages encounter one another in the reactor.

A fluid in which globules of a given age do not mix with other globules is called a macro fluid, while a fluid in which molecules are free to move everywhere is called a microfluid. These two extremes of late and early mixing are referred to as complete segregation and maximum mixedness respectively.

Segregation model

In a CSTR, the entering fluid is assumed to be distributed uniformly throughout the reacting mixture. The mixing is assumed to take place even on the microscale, the elements of different ages mix together thoroughly to form a completely micromixed fluid. If the fluid elements of different ages do not mix together at all, the elements remain segregated from each other and the fluid is termed completely segregated.

In a segregated flow model, we visualize the flow through the reactor to consists of a series of globules. They do not interchange material with other globules in the fluid during their period of residence in the reaction environment. In addition each globule spends a different amount of time in the reactor. The principles of this model are based on clumping all the molecules that have same residence time in the reactor into the same globule. The reactor performance was first described by Danckwertz & Zweitering.

Because there is no molecular interchange between globules, each acts essentially as its own batch reactor. The reaction time in any one of these batch reactors is equal to the time that the particular globule spends in the reaction environment given by the E function.

Thus fluid elements have different compositions. The mean composition in the exit stream will have to account for these two factors, the kinetics and the RTD.

$$\left(\begin{array}{l}\text{Mean concentration}\\ \text{Of reactant in the exit}\\ \text{stream}\end{array}\right)=\left(\begin{array}{l}\text{concentration of}\\ \text{reactant remaining}\\ \text{in an element of age}\\ \text{between}\\ \text{t and t +dt}\end{array}\right)\left(\begin{array}{l}\text{fraction of exit}\\ \text{stream which is of}\\ \text{age between t and}\\ \text{t + dt}\end{array}\right)$$

In symbols this becomes,

$$\left(\frac{C_A}{C_{Ao}}\right)_{\text{at exit}}=\int_o^{\infty}\left(\frac{C_A}{C_{Ao}}\right)_{\text{for an element of age t}}\text{Edt}$$

or in terms of conversion,

$$X_A=\int_0^{\infty}X_{A\ \text{element}}\,\text{Edt}$$

$$\left(\frac{C_A}{C_A}\right)_{\text{all age intevals}}=\sum\left(\frac{C_A}{C_{Ao}}\right)_{\text{element}}.\text{E}\,\Delta\text{t}$$

For a second order reaction taking place in a batch reactor the conversion is given by the equation,

$$\left(\frac{C_A}{C_{Ao}}\right)_{\text{all age intevals}}=\frac{1}{1+k\,C_{Ao}t}$$

For an nth order reaction,

$$\left(\frac{C_A}{C_{Ao}}\right)_{element} = \left[1+(n-1)CAo^{n-1}\,kt\right]^{\frac{1}{(n-1)}}$$

The steps involved in the scale up are discussed below.

1. A mole balance on a batch reactor that is well mixed is

$$\frac{dC_A}{dt} = r_A$$

1. The rate law was assumed as $-r_A = kC_A^2$

2. Combining the rate law and the mole balance,

$$\frac{-dC_A}{dt} = k\,C^2{}_A$$

For isothermal operation, the equation can be integrated,

$$\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A{}^2} = \int_o^t kdt$$

Integrating yields,

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = kt$$

A plot of $(1/C_A - 1/C_{Ao})$ versus time yields a straight line with slope equal to k.

The value of k determined from previous experiment was 0.0166mole/litre.min can be used here. Hence the rate law becomes

$-r_A = 0.0166\ C_A$

3. This rate law was used in the design of CSTR.

For a batch reactor, the mean residence time is calculated as follows.

In terms of conversion,

$$C_{Ao} \int \frac{dx_A}{(1 - x_A)^2}$$

Integrated equation is,

$$\frac{1}{kC_{Ao}} \frac{x_A}{(1 - x_A)}$$

= 1x0.878 / (0.122x0.0166x3.59x60)

= 2.04 hours.

The results of the kinetic studies obtained from a batch reactor are used for finding out the conversion in a CSTR.

The residence time distribution function, E, is calculated using the equation,

$$E = 1/\tau .\ e^{-t/\tau}$$

The batch equation for a second order reaction is,

$$\left(\frac{C_A}{C_{Ao}}\right)_{\text{element}} = \frac{1}{1+kC_{Ao}t}$$

Table.3.6

t, min	$E = 1/\tau . e^{-t/\tau}$	$(C_A/C_{Ao})_{element}$	$(C_A/C_{Ao})_{element}.E.\Delta t$
0	0.0083	1	0
15	0.0073	1.862	0.0592
30	0.0065	2.723	0.0358
45	0.0057	2.585	0.0333
60	0.0050	3.446	0.0219
75	0.0045	5.308	0.0127
90	0.0039	6.169	0.0095
105	0.0034	7.031	0.0074
120	0.0030	7.893	0.0058

$\Sigma(C_A/C_{Ao})_{element} .E.\Delta t = 0.186$

From the table,

$C_A/C_{Ao}) = \Sigma(C_A/C_{Ao})_{element} .E.\Delta t$

$= 0.186$

Therefore conversion in a CSTR is,

$X_A = 1 - 0.186 = 0.814$

$= 81.4\%$

3.4 Conclusions

Silica particles can be prepared from sodium silicate by precipitation method in poly(vinyl alcohol) medium. The size of the silica particles obtained is found to be in the nanoscale from TEM analysis. The average size of the particles is 15nm.This is lower than the commercial silica particles as it is obvious from the surface area values. SEM studies revealed the influence of reaction parameters during synthesis. Unmodified particles exist as small agglomerates when compared to modified particles. Thermogravimetry shows the thermal behaviour and purity of the product formed. XRD pattern revealed that the prepared silica samples are amorphous.

Kinetic studies on synthesis reaction provided important information required for the design of reactors for producing silica in a large scale for polymer modification.. The value of the reaction rate constant k is determined from a batch experiment as 0.0166 litre/mole.min which is found to be consistent with the theoretical methods. The reaction is found to be of second order and these data can be used for analyzing the performance of the continuous reactors used for the synthesizing silica on a large scale.

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Chapter 4

Modification of Polyropylene using Nanosilica

4.1 Introduction

Polymers belong to a class of material that can offer significant advantages due to their potential for modification. With the emergence of nanotechnology a major shift occurred towards modifying polymers with nanoparticles. Polymer based nanocomposites in which inorganic nanoparticles are dispersed in organic polymer matrices have attracted material scientists' attention owing to their unique properties resulting from the nanoscale microstructure [1-4].

There are many ways to modify a polymer. Incorporation of fillers of various types and different kinds of fibers. Polypropylene (PP) is a crystalline polymer which is very versatile in nature and hence it is widely used thermoplastic material [5]. Even though it is the highest turnover plastic it has some limitations. Inorganic fillers can be added to PP, leading to a composite system, which combines the advantage of the two phases it is composed off. Modification of PP by nanoparticles can markedly enhance the mechanical properties [6-10]. Silica filled polymers, fulfills some of these needs and has been a frontier research area. It has been gaining importance in automotive applications, electrical & electronic engg. appliances and consumer goods[11-13]. However the extent of improvement depends on the properties of the components, by the shape of the filler phase, size, degree of dispersion and by the nature of the interface between the phases. An important property of the interface which can greatly affect mechanical behaviour is the strength of the adhesive bond between the phases.

Over the past decade, incorporation of fillers into the polymer matrix has produced a wide range of multifunctional properties such as backbone stiffness, higher rigidities and thermal stability, modified electrical properties, reduced permeability to gases and liquids and reduced cost [27-29]. Introduction of nanoparticles into a polymer changes the intermolecular interaction of the matrix. One of the attractive characteristics of the nanoparticles is the extremely large surface area. However, homogeneous dispersion of nanoparticles in polymers is very difficult because the particles possessing high surface energy tend to agglomerate during melt blending, which is the most convenient technique for mass production of nanocomposites with cost effectiveness.

The inorganic fillers usually have high surface energy. The hydrophobic polymer and the hydrophilic filler cause a significant problem in enhancing the adhesion between the filler and the matrix. This problem can be overcome by increasing the affinity between the two phases. For example in-situ polymerization, use of silane coupling agents and other strategies [30]. Filler in a polymer cannot modify the properties unless there is good adhesion between them. To achieve control over the functionality of the filler surface, modification and special treatments are designed to bond an organic molecule physically or chemically to the filler surface. Coupling agents are bifunctional molecules which are used to develop a chemical bond (covalent bond) between the polymer and the filler [31-32].

Mineral fillers such as talc and silica are frequently used with polypropylene (PP) as extenders to reduce costs, increase stiffness and decrease shrinkage. However, the non-polar nature of PP limits its adhesion and compatibility with other materials, and therefore a variety of organic compounds, including fatty acids, phosphate esters, silanes and titanates, have been employed as coupling agents to improve interfacial interaction, adhesion and dispersion between the filler and matrix.

Surface-modified silica particles have generated intense interest in a wide range of application fields. The modification of inorganic silica particles with organics leads to the production of organic-inorganic hybrid particles in which the organic components may be chemically bonded to a silica matrix. Somewhat similar to inorganic silicate glasses, the structure of the silica network can be modified by the presence of organic groups. The mechanical, electrical and optical properties of the resulting organic-inorganic hybrid particles are then governed by the type and concentration of the organics used. Furthermore, the utilization of nano sized organic-inorganic hybrid particles for the production of advanced ceramic materials requires high quality with respect to chemical purity, homogeneity, morphology, and a controlled state of agglomeration as well as low production costs. Thus, a large number of methods have been developed to satisfy these requirements.

For improving the polymer – silica interaction, modifying nanoparticles with a coupling agent such as vinyl triethoxy silane (VTES)is proposed to be tried. The properties of the composites prepared with both modified and unmodified nanosilica are proposed to be compared. Effect of mixing shear on the dispersion state of nanosilica in pp is also proposed to investigated.

4.2 Experimental

4.2.1 Materials used

PP REPOL 200 MH, with a melt flow index of 20g/10 min, was supplied by Reliance Industries Ltd., Mumbai, India.

Nano silica: Silica synthesized from sodium silicate using acid hydrolysis method [14]. Precipitated silica could be prepared in nano scale by controlling the reaction conditions. The method utilizes only commonly available chemicals and impurities could be easily removed by washing with distilled water.

4.2.2 Preparation of nanocomposites

Nanosilica reinforced PP composites were prepared by melt blending [15]. The concentration of nanosilica was varied from 0-3 wt%. The mixing of PP with both unmodified and modified nanosilica was done in a Haake mixer (Haake rheocord 600) at 180°C and at different rotor speeds of 30,50, 70 and 90 rpm. The variation of torque with time was monitored. The resulting compound was hot pressed into thin sheets and cut into pieces. Dumb bell and rectangular shaped specimens were prepared by injection moulding in a semi automatic injection moulding machine.

The tensile test samples of size conforming to ASTM-D-638 was tested in a Universal Testing Machine (Shimadsu) at a crosshead speed of 50 mm/min and flexural properties of the composites were measured by three point loading system using the Universal Testing Machine as per ASTM-D-790.The morphology of the tensile fractured surface was also investigated using Scanning Electron Microscope (SEM).

4.3 Results and Discussion

4.3.1 Torque variation

The variation of mixing torque with time at different filler concentrations is given in Fig.4.1 & 4.2. A mixing time of 8.5 minutes was sufficient since the torque stabilized to a constant value during this time in all cases. The temperature of mixing chamber was fixed as 180^0C. There is no reduction in torque up to the mixing time. The stabilization of the torque is an indication of the attainment of a stable structure after a good level of mixing. This indicates that there is no appreciable degradation taking place during this time. The values of torque changes with increase in the concentration of silica particles added. The varitation of torque with time of PP/silica nanocomposites, at different shear rates are shown in fig 4.3.

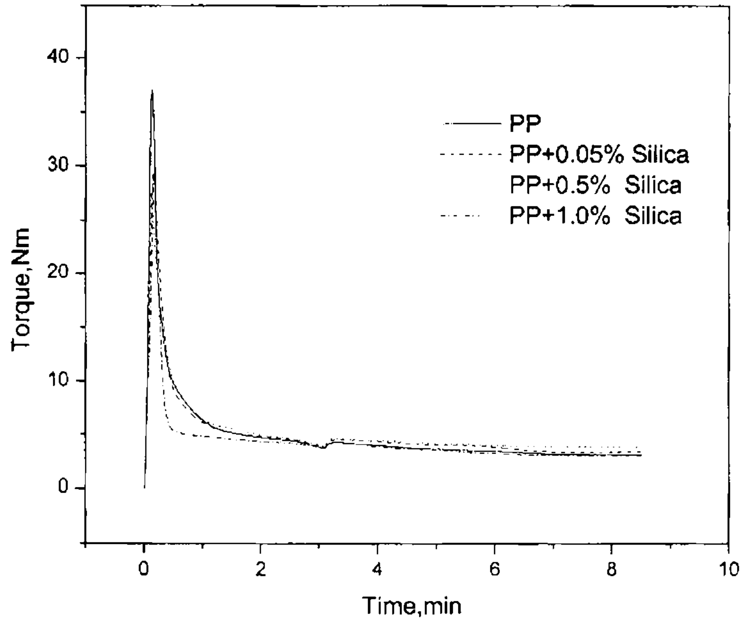


Fig.4.1 Variation of torque with time of PP/silica nanocomposites at 70 rpm

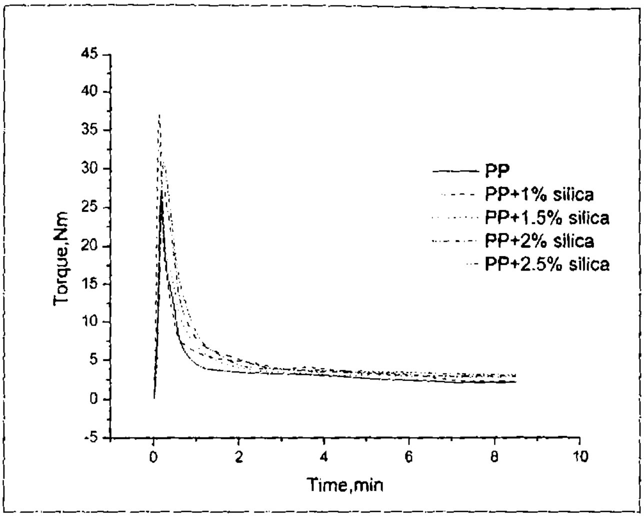


Fig.4.2. Variation of torque with time of PP/silica nanocomposites at 90 rpm

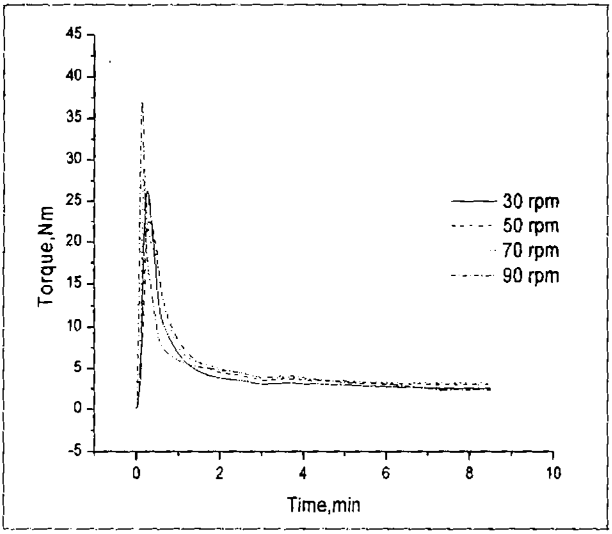


Fig.4.3 Variation of torque with time of PP/silica nanocomposites at different shear rates

The variation of mixing torque with time of mixing of modified silica in PP is shown in the fig.4.4. In this case also the mixing time was fixed as 8.5 minutes since the torque got stabilized by this time.

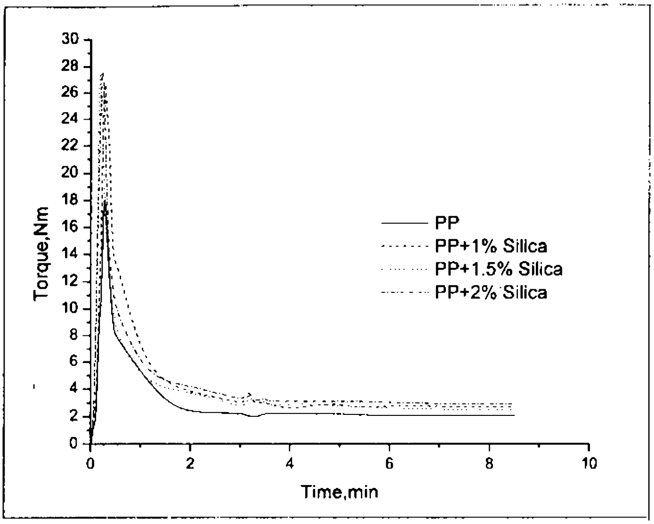


Fig.4.4. Variation of torque with time of PP/ modified silica nano composites

The variation of torque with time at different rotor speeds of 30, 50 and 70 rpm is shown in fig 4.5. As seen in the figure there is a slight increase in torque as the speed is changed to higher values.

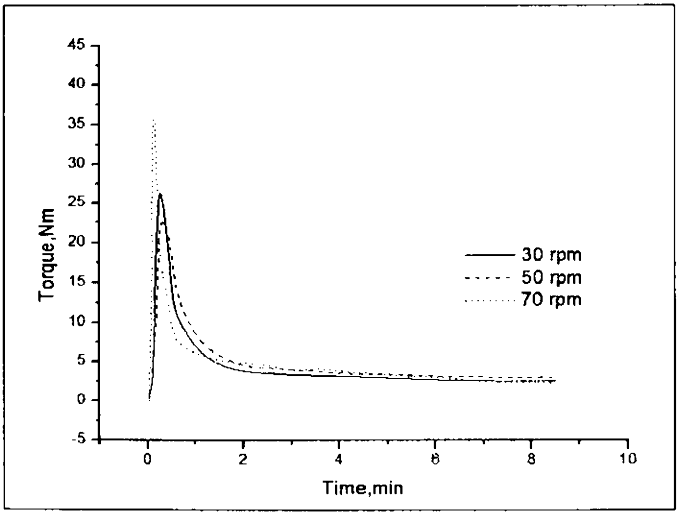


Fig.4.5 Variation of torque with time of PP + 1% silica at different rotor speeds

4.3.2 Tensile properties of nanosilica modified PP

4.3.2.1 *Effect of filler concentration*

The influence of filler concentration on the tensile properties of the composites is shown in Fig.4.6 & Fig. 4.7. For this study the concentration of silica particles in the matrix was varied from 0 to 3wt% of PP.

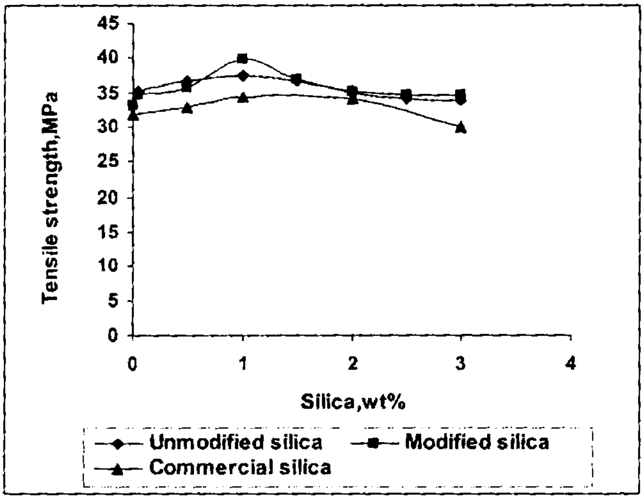


Fig.4.6 Variation of tensile strength of PP/silica composites with silica content.

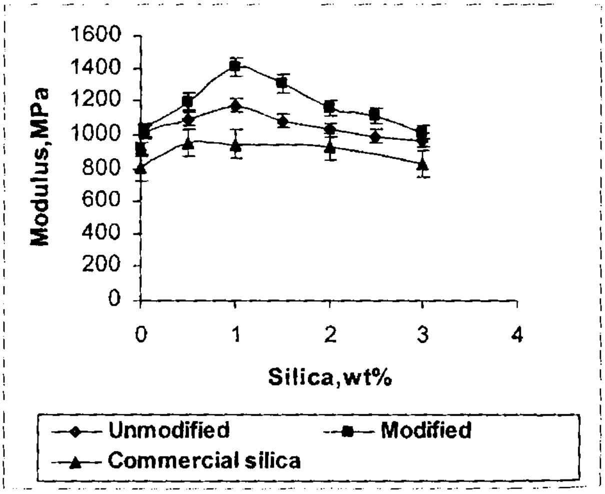


Fig.4.7 Variation of modulus of PP/silica composites with silica content.

As shown in Fig.6&7 the properties are on the increase and a maximum value was obtained at 1 wt% silica. At this composition interaction of the nanoparticles with PP is very effective and this causes an enhancement in mechanical properties [16]. After that there is a gradual reduction in strength values. This may be due to the highly crystalline nature of PP and at higher compositions there is a tendency for the silica nano particles to aggregate and processing becomes difficult. The tensile strength, modulus improved by approximately 14 and 33% respectively with unmodified silica particles. The corresponding values for modified nanosilica/PP composites are 20% and 44% respectively. The nanocomposites with commercial silica show only marginal increase in both strength and modulus values. The effects of unmodified nanosilica on the mechanical properties of PP are summarized in table 4.1.

Table 4.1 Tensile properties of PP/Silica nanocomposites

Silica Concen-tration,wt%	**Tensile strength,MP$_a$**	**Modulus, GP$_a$**	**% strain**	**Impact strength, J/m**
0	33.01	0.977	7.97	325
0.05	35.11	1.012	8.33	414.42
0.5	36.68	1.093	9.06	440.32
1.0	37.58	1.171	8.86	591.1
1.5	36.7	1.080	7.62	581.61
2.0	34.8	1.030	7.5	552.09
2.5	34.24	0.989	7.26	549.03
3.0	34	0.968	7.07	423.17

In a composite material the interfacial stress transfer efficiency and extent of induced deformation determines the mechanical performance. In general, particulate composites exhibit a reduced tensile strength and elongation to break due to weak interfacial adhesion. However, when bonding between fillers and matrix is strong enough then we can expect considerable improvement in tensile yield strength when compared to unfilled matrix. As shown in Fig. (1) it is evident that a good adhesion is associated with the modified nanosilica/PP composite. An enhancement of 6 % is found in tensile strength and 21% in modulus by modification using VTES when compared with those using unmodified particles. This may be due to the modification of silica surface by the coupling agent and the maximum values are obtained at a composition of 1 wt% after which there is not much change. A similar trend is also observed in the case of modulus. From this we can see that there is particular filler content for a particular polymer-filler system in which the properties are found to be optimum. The decrease in these properties after this composition may be due to the tendency of the silica particles to agglomerate within the polymer matrix and hence resulting in poor dispersion. The tensile properties of modified nanosilica/PP composites are listed in table.4.2.The results indicate that for effective reinforcement only 1% nanosilica is required. The modification of silica using silane coupling agent resulted in improved bonding of the nanosilica with the polymer matrix. An enhancement of 6% more in tensile strength and 20% in modulus with modified silica was also obtained. This again supports the fact that nanosilica can be a suitable reinforcing agent for PP. The elongation to break was found to be increasing with silica concentration up to this concentration. These results show that the improvement in properties due to better adhesion between the nanosilica and PP.

Table 4.2. Tensile properties of PP/ modified silica nanocomposites

Silica Concen-tration,wt%	Tensile strength,MP$_a$	Modulus, GP$_a$	% strain	Impact strength, J/m
0	33.01	0.97	7.97	325
0.05	34.60	1.02	8.76	427.84
0.5	35.80	1.19	10.11	440.32
1.0	39.72	1.41	9.34	731.5
1.5	37.04	1.30	7.76	712.7
2.0	35.17	1.15	7.68	615.24
2.5	34.70	1.11	7.42	487.16
3.0	34.57	1.01	7.28	473.28

4.3.2.2 *Effect of shear rate*

The effect of mixing shear on the tensile strength and modulus of PP/unmodified silica nanocomposites are shown in Fig.4.8 & 4.9. The PP containing 1 wt% silica shows the highest strength. Also these properties increase with shear rate up to 70 rpm. The tensile strength increases by 14% and 20% and modulus values by 41% and 20% respectively when compared with the values at 30 rpm. From the results, it is evident that an additional increase of 4% more in tensile strength and 32% in modulus was also obtained with VTES modified nanosilica. At 90 rpm the improvement is not significant when compared with those at 70 rpm. This may be due to the poor interaction of silica particles with the matrix at this speed. Hence the optimum speed of the rotors has been fixed as 70 rpm. The effect of coupling agent on the tensile properties of PP is given in the fig.4.10 & 4.11.

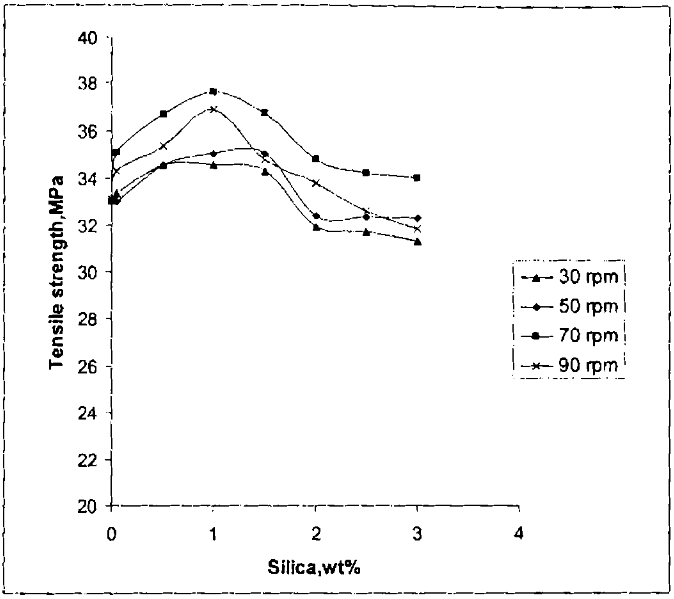


Fig.4.8 Effect of mixing shear on the tensile strength of PP/silica nanocomposites

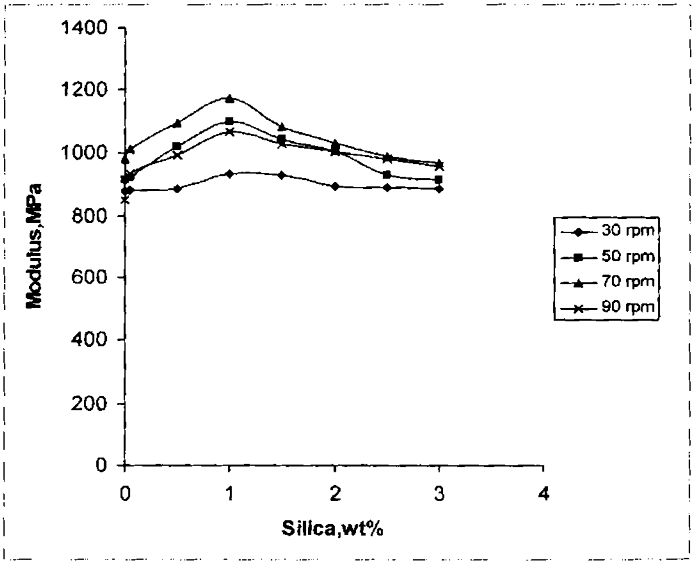


Fig.4.9 Effect of mixing shear on the modulus of PP/silica nanocomposites

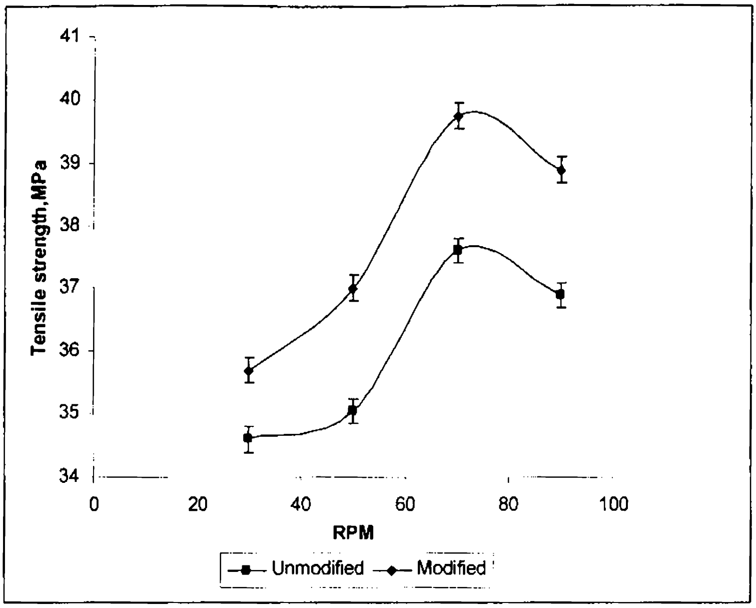


Fig.4.10 Comparison of tensile strength of PP/Silica nanocomposites

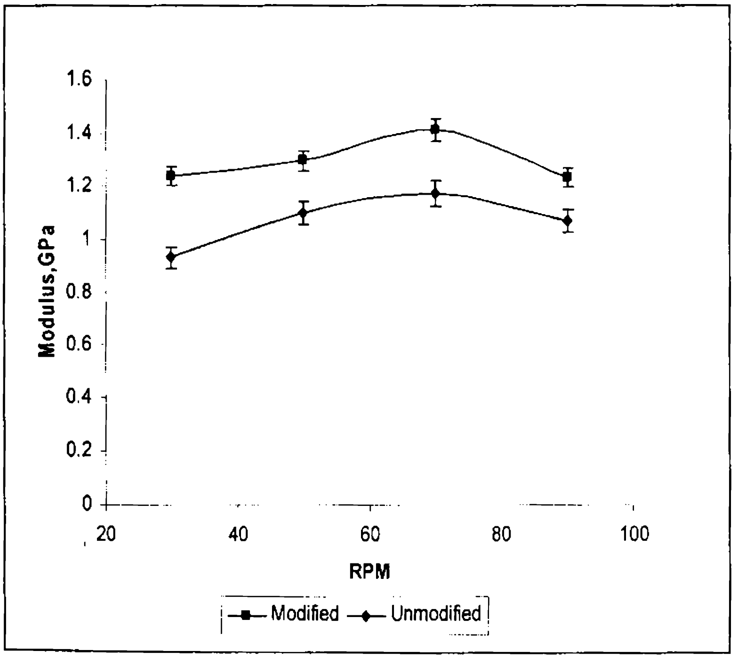


Fig.4.11 Comparison of modulus of PP/Silica nanocomposites

4.3.3 Flexural properties of nanosilica modified PP

The influence of both unmodified and modified nanosilica concentration on the flexural properties of PP is given in Figures 4.12 & 4.13 respectively. There is a considerable increase in flexural strength and modulus of PP/nanosilica composites. The figures also show that the concentration of silica that can be added to PP to obtain maximum values in flexural loads in both cases is again 1%. At this composition, the flexural strength increases by 31% and modulus by 66% for composites prepared with unmodified silica. By using a coupling agent the increase in strength and modulus is about 37% and 68%. This indicate that the additional increase is due to the better attachment of the nanosilica with the polymer through the coupling agent VTES. The modification has resulted in enhancing the adhesion between the hydrophobic PP and the hydrophilic silica particles.

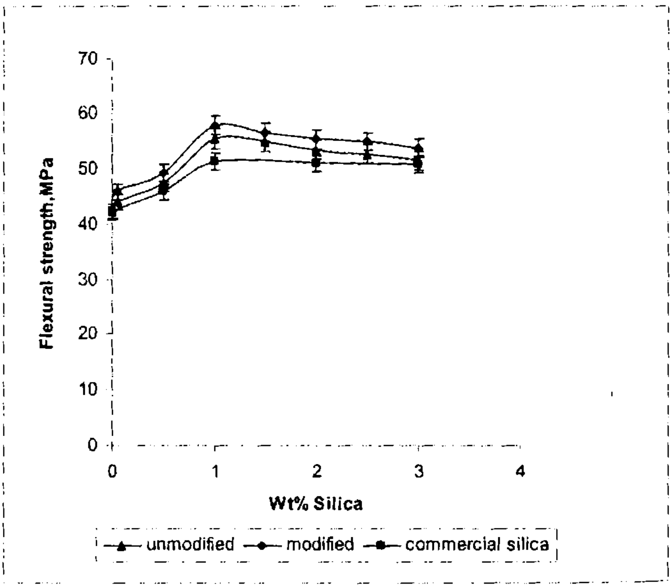


Fig 4.12. Variation of flexural strength of PP/Silica nanocomposites.

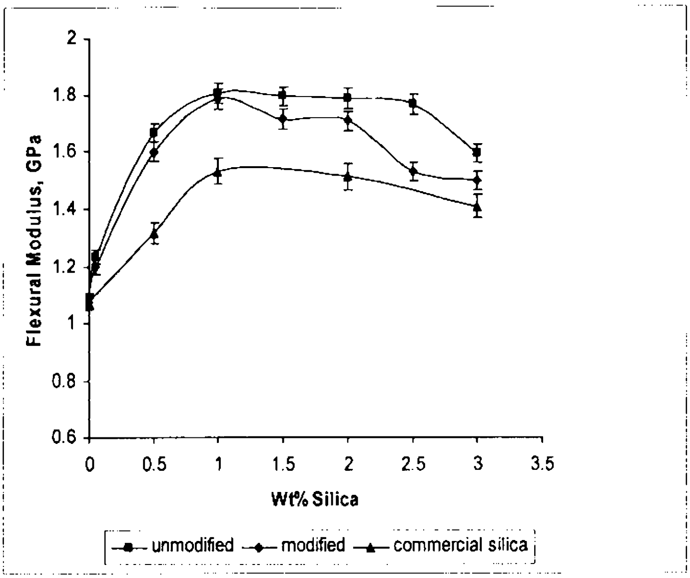


Fig 4.13 Variation of flexural modulus of PS/Silica nanocomposites

The effect of mixing shear on flexural strength and modulus on PP/silica nanocomposites is shown in fig 4.14 & 4.15. The flexural strength and modulus also found to be increasing gradually with increase in shear rates and the maximum values are obtained at 70 rpm. This increase in properties obviously due to the improved dispersion resulting from the high shear rates involved in mixing. However property again decreases when the speed of rotors are increased to 90 rpm. This indicates that both the nanosilica concentration and the shear rates play a significant role in the possible enhancement in properties. The variation of flexural modulus of both modified and unmodified silica/PP nanocomposites is given in fig.4.16. It is clear that the flexural modulus is improved by the use of coupling agent.

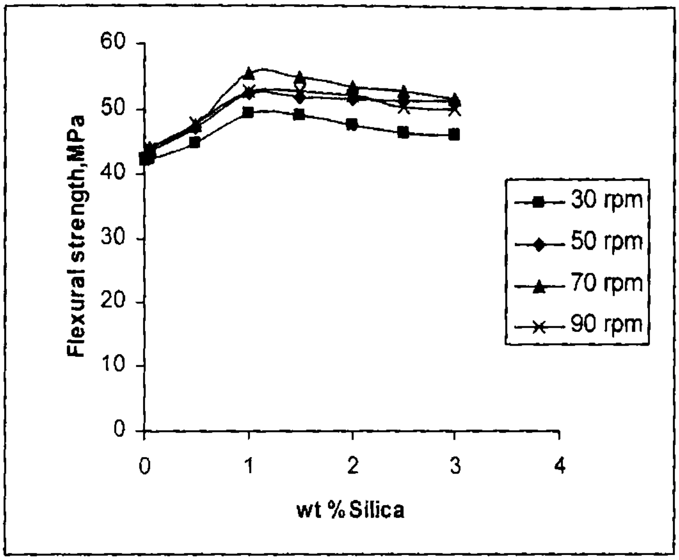


Fig.4.14 Variation of flexural strength of PP-Silica nanocomposites at different shear rates.

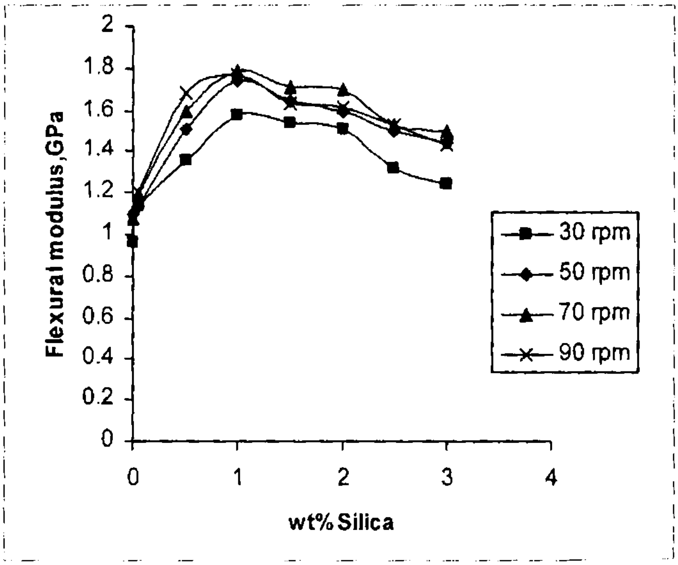


Fig.4.15 Variation of flexural modulus of PP-Silica nanocomposites at different shear rates.

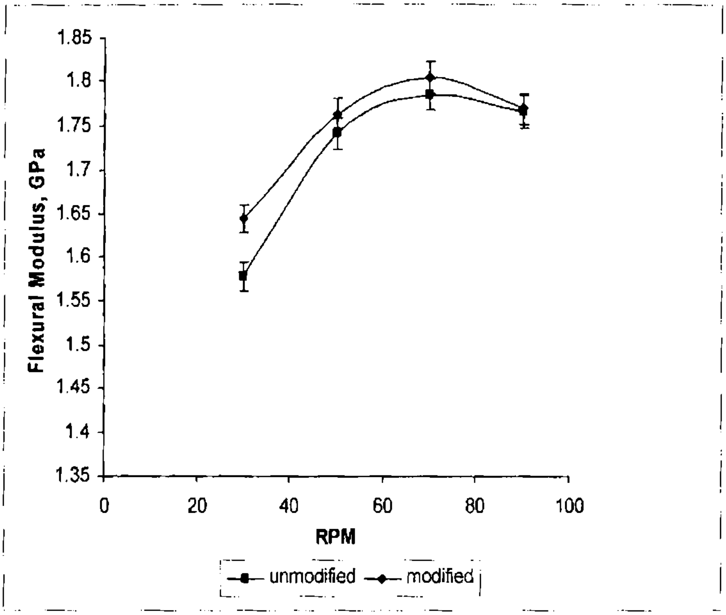


Fig.4.16 Comparison of flexural modulus of PP-Silica nanocomposites at different shear rates.

4.3.4 Impact strength

The toughness of both commodity and engineering plastics under impact loading and low temperatures can be improved by several means. One method is the incorporation of rubber particles but this causes a reduction in elastic modulus of the material [17-18]. The impact strength of composites is more complex than that of unfilled polymers because of the role played by the filler particles and the interface. For a material to be very tough and to have a high impact strength in general there must be some mechanism for spreading the stored energy to be absorbed. The material falls in a brittle manner and the impact strength is low.

The use of rigid fillers to toughen polymers has also been received considerable attention [19-26]. This approach may lead to rigid and tough composites. Argon and Cohen proposed that for toughening to occur in rigid filler systems, the particles must rebound from the matrix creating voids around the particles and allowing the intra particle ligaments deform plastically. On the other hand voids also decreases the fracture strain and the overall toughness of the material.

Recently the use of nanoparticles has been suggested to improve the toughness of the polymers especially PP. The major challenge associated with the use of nanoparticles is the adhesion between the particles and the matrix. If the particle-matrix adhesion is low, then the toughness is improved because this will favour debonding. But for smaller particles debonding is more difficult to occur. It is also necessary to prevent particles agglomeration and void coalescence. Because of their small size, these particles show a strong tendency to agglomerate.

The focus of the study is to investigate the effect of nanosilica, synthesized by the precipitation method on the toughness of PP in addition to other mechanical properties such as elastic modulus, tensile strength etc.

4.3.4.1 *Effect of filler concentration on impact strength of PP*

The effect of filler concentration on impact strength of PP is shown in fig.4.17

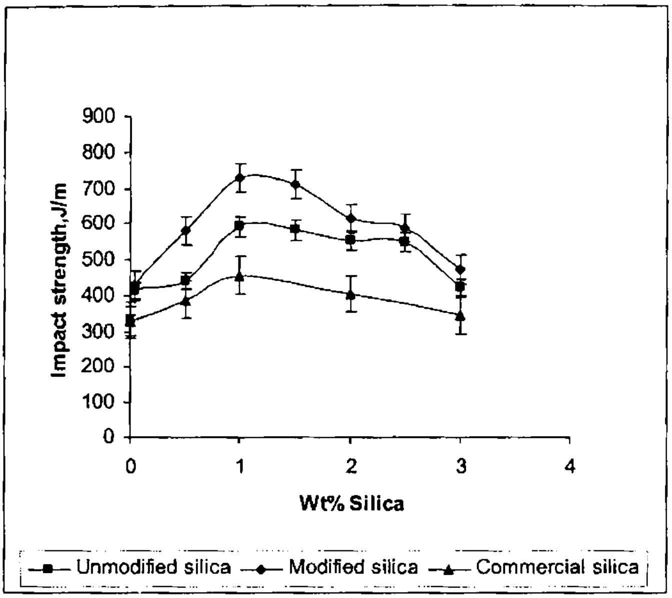
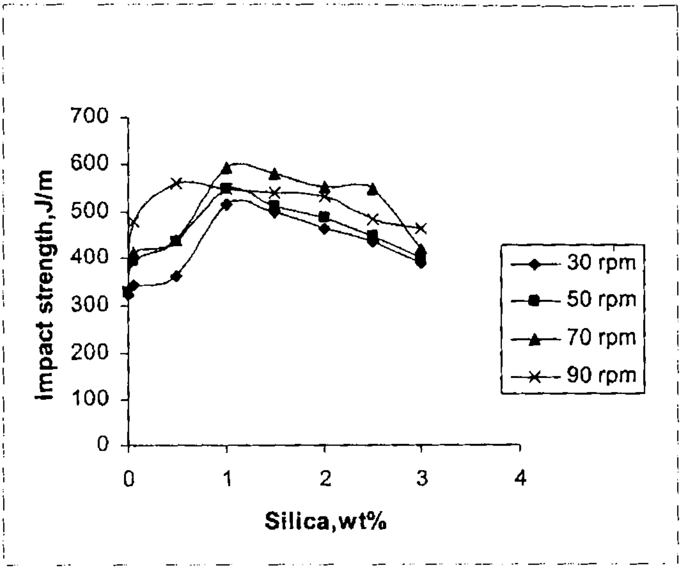


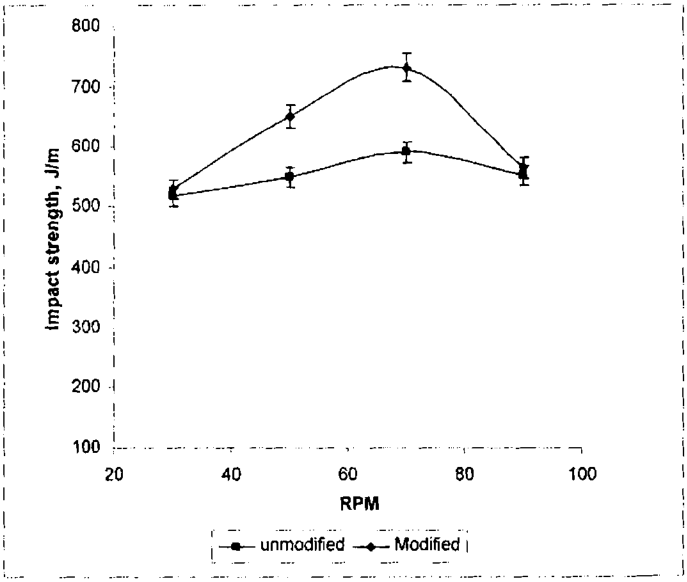
Fig 4.17 Effect of filler concentration on impact strength.

The impact strength of PP is found maximum at 1% silica in this case also. While the influence of filler particles on tensile strength is limited, its effect on impact strength is much higher. With unmodified silica, the increase in impact strength is about 82% and with coupling agent modified nanosilica, the enhancement in impact strength is 125%.This may be due to the action of coupling agent which improved the compatibility between the filler and the polymer [33]. The higher is the resistance to separation between the two phases the higher are the stresses that can be applied before it breaks. Hence impact strength increases. For concentrations higher than 1% silica, there is a crowding of silica particles within the matrix. This may cause creation of voids and increased size of the filler particles. The presence of voids will cause the disintegration of the composite and the resistance to separation under the given load reduces. The enhancement in properties with commercial silica is not much when compared to the other two types.

4.3.4.2 *Effect of shear rate on impact strength*



(a)



(b)

Fig.4.18 (a) & (b) Impact strength of PP/Silica nanocomposites at different shear rates.

The effect of mixing speed on impact strength of PP is given in Fig.4.18(a). As seen from the graph the impact strength increases from 30 rpm to 70 rpm and also with silica concentration up to 1%. At 90 rpm the maximum strength is attained at an earlier concentration of nanosilica. i.e. at 0.5%. This may be because of the higher crystallinity of PP and higher shear involved in mixing. The reason for the increase in toughness may be due to the improved filler dispersion within the PP matrix when the shear rate increases. The agglomerates that formed may be broken as shear rate is increased to higher values thus improving the dispersion.

The comparison of impact strength of both modified and unmodified silica/PP nanocomposites at different shear rates is shown in Fig 4.18(b). As seen from the figure the impact strength increases considerably with increased shear rates up to 70 rpm in both cases. At 90 rpm the values show a decline. This is more prominent in the composites made of modified nanosilica.

4.3.5 Rheological measurements using Torque Rheometer

The Rheological interpretation of the measurements was based on the analysis of Blyler and Daane [34].They extended the work of Goodrich and Porter to Non-Newtonian materials and developed the relation,

$$M = C(n)\,KS^n ,$$

where M is the torque and S is the rpm, K and C(n) are calibration constants whose value can be determined using melts of known values of K and C(n).

The torque values from the Haake rheometer was plotted against rpm and is given in fig.4.19. The plot is identical to the shear stress versus shear strain diagram. The plot consists of a set of parallel lines which indicates that the power law indices for the pure polymers and their compounds are identical. The values of the parameter n is given in table 4.2.

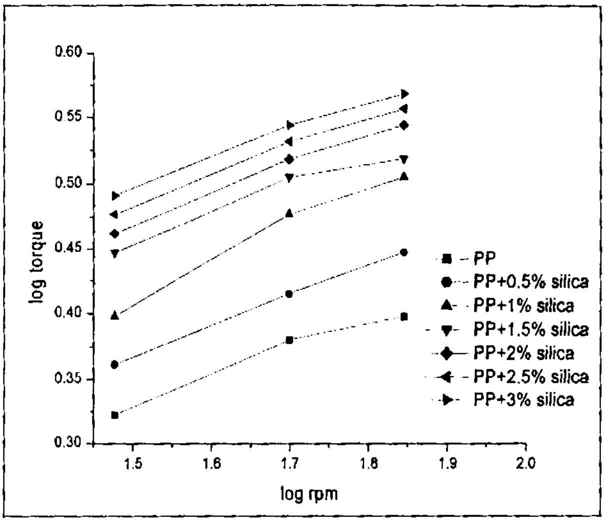


Fig 4.19 Variation of torque with rpm for PP/Silica nanocomposites.

Table 4.3 Power law index values for PP/Silica nanocomposites.

Material	**Power law index ‘n’**
PP + 0% silica	0.25
PP + 0.5% silica	0.24
PP +1.0% silica	0.29
PP +1.5% silica	0.26
PP +2.0% silica	0.25
PP +2.5% silica	0.24
PP +3.0% silica	0.29

4.3.6 Water absorption characteristics

The water absorption characteristics of the PP/Silica nanocomposites is shown in fig.4.20. It is observed that the water absorbing tendency progressively decreases with increasing silica loading[35].PP+1% Silica composite exhibits lower water uptake than pure PP. Lower water absorption is also a significant property improvement. The nanosilica particles in the PP matrix impede the penetration of water molecules and this leads to decreased water absorption. At higher compositions >1% silica particles shows a tendency to aggregation and there is a corresponding increase in the property.

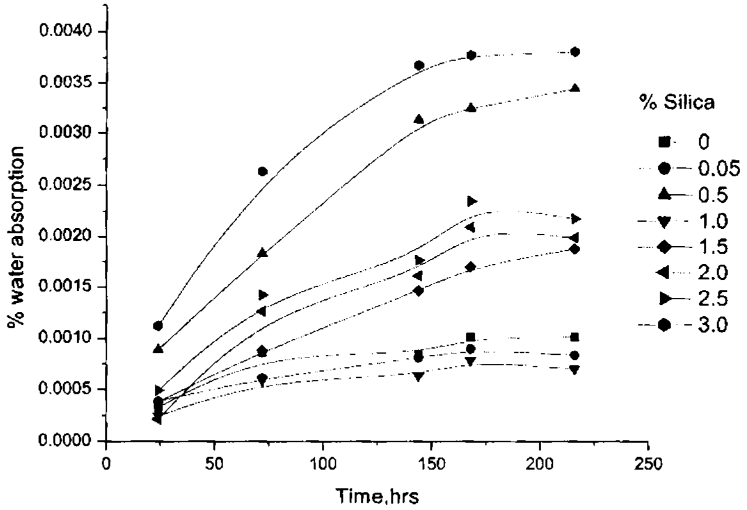


Fig.4.20 Water absorption characteristics of PP/Silica nanocomposites.

The % water uptake of PP+1% Silica composite at different shear rates of 30, 50, and 70 rpm as shown in fig 4.21. It indicates that the tendency decreases as shear rate increased to higher values and optimum values are obtained at 70 rpm. This may be because of the improved dispersion at this shear rate.

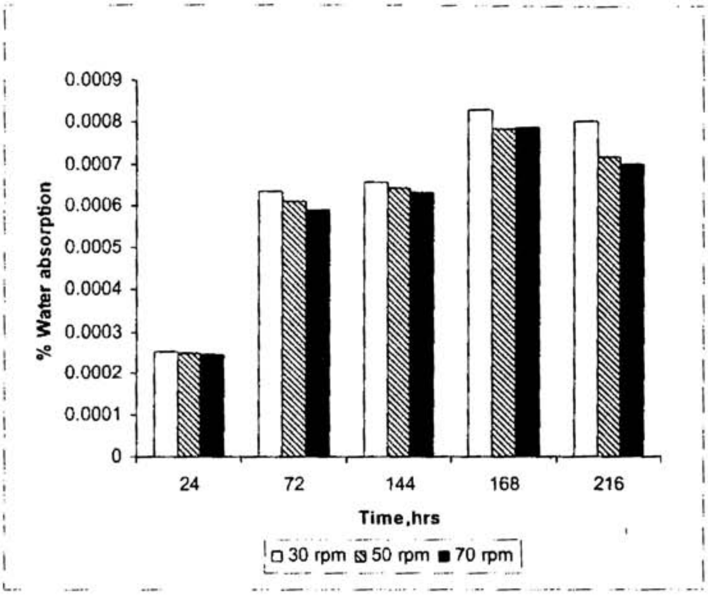


Fig.4.21 Water uptake characteristics of PP/Silica nanocomposites at three different rpm.

4.3.7 Ageing studies

4.3.7.1 *Effect of ageing on tensile properties*

The effect of laboratory ageing of PP/Silica nanocomposites are shown in figures 4.22,4.23& 4.24.From the figures it is evident that there is no significant reduction in the properties such as tensile strength and modulus. This means that the nanosilica filled PP remains stable in ageing. The pattern of changes is similar for composites made of both modified and unmodified silica. In the case of elongation at break, there is considerable reduction in values for aged samples when compared with those with no ageing. This means that the composites become more brittle with ageing.

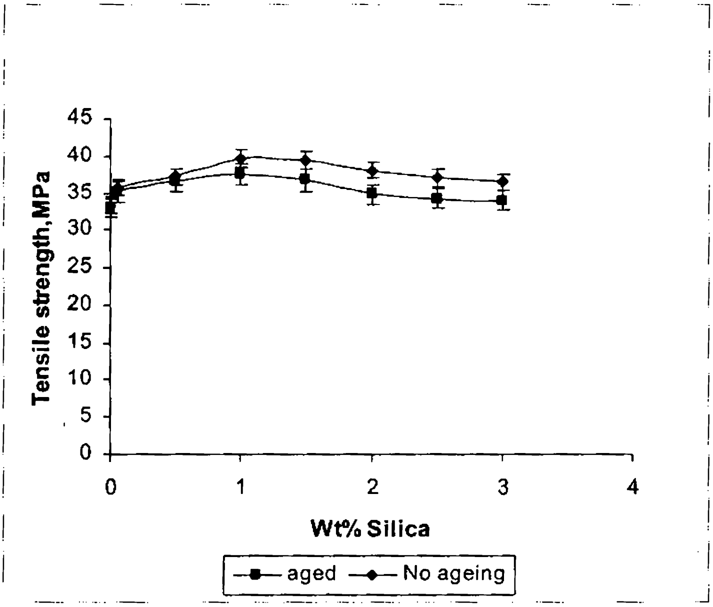


Fig.4.22 Comparison of tensile strength of aged PP/Silica nanocomposites

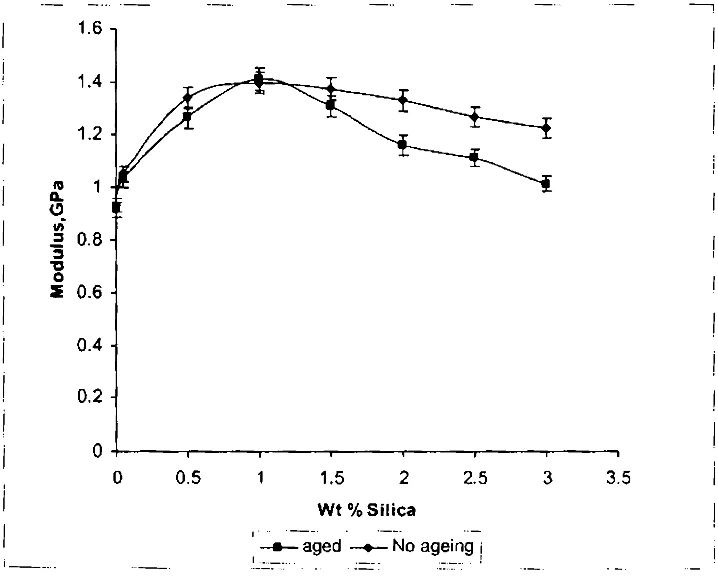


Fig.4.23 Comparison of modulus of aged PP/Silica nanocomposites

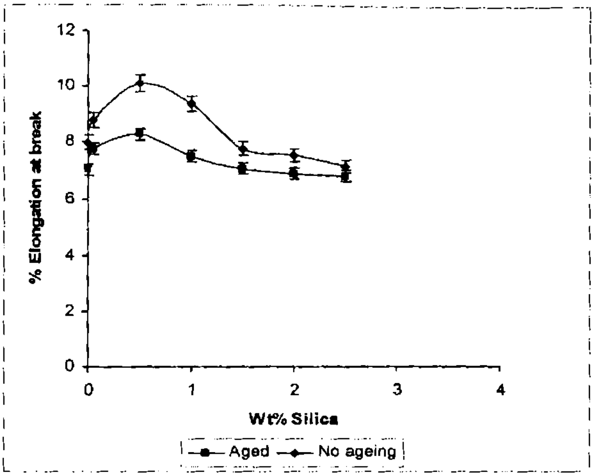
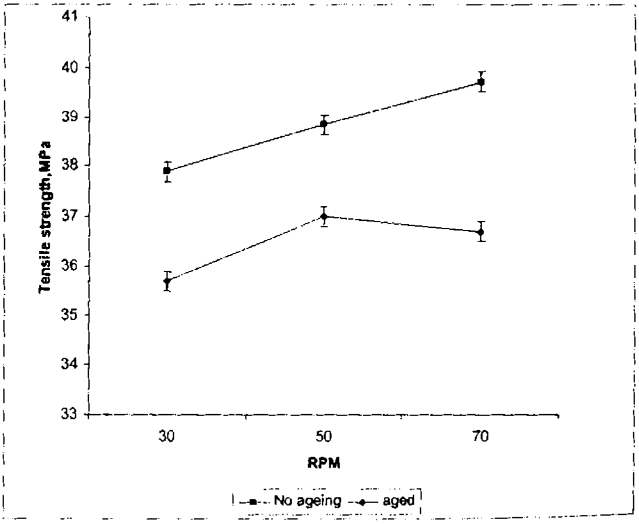


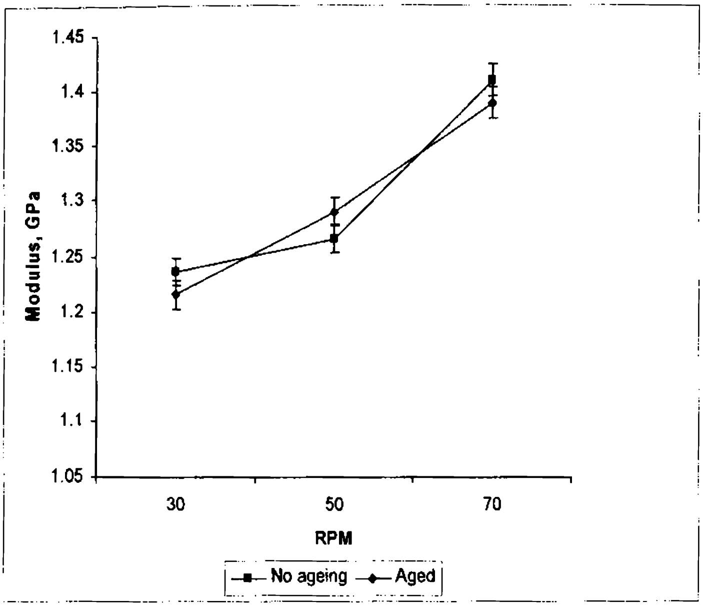
Fig.4.24 Comparison of % elongation at break of aged PP/Silica nanocomposites

4.3.7.2 *Effect of shear rate on tensile properties of aged samples*

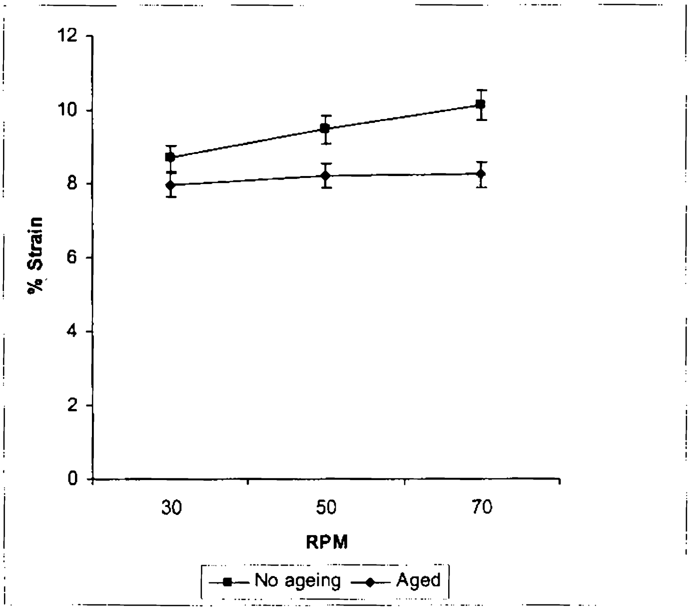
The effect of ageing on the tensile properties of samples made at different shear rates of mixing from 30 rpm to 70 rpm is shown in fig. 4.25 (a) to (c). The properties show a similar behaviour as that of samples with no ageing. This shows that there is no considerable degradation of the samples.



(a)



(b)



(c)

Fig.4.25 Comparison of effect of shear rate on (a) tensile strength (b) modulus (c) % elongation at break of aged PP/Silica nanocomposites

4.3.8 Morphological studies

The Scanning electron micrograph of the fractured surfaces of tensile test specimens may give an insight into the morphological structure of the polymer nanocomposites. SEM images were taken on a JEOL JSM 840 operated at an acceleration voltage between 10 and 15 kV. The SEM pictures of the fractured surfaces of pure PP and its composites are given in figures 4.26(a) to (d).

Agglomerates of nanosilica particles are found in fig.4.26(b). The thread like structures in figure 4.26(c) indicates that the fracture occurred due to matrix yielding. Fig .4.26(d) shows that no large agglomerates are present and the nanosilica particles more evenly dispersed when compared with those other figures.

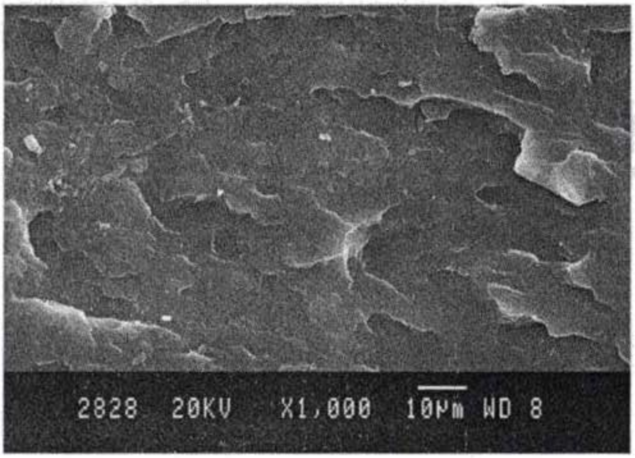


Fig.4.26 (a) Fracture surface of pure PP

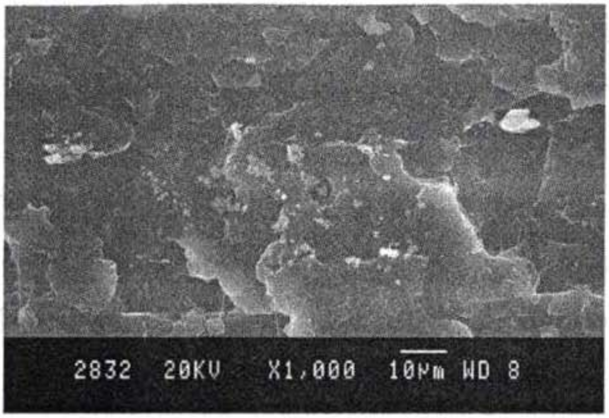


Fig.4.26 (b) PP+ 1% nanosilica at 30 rpm

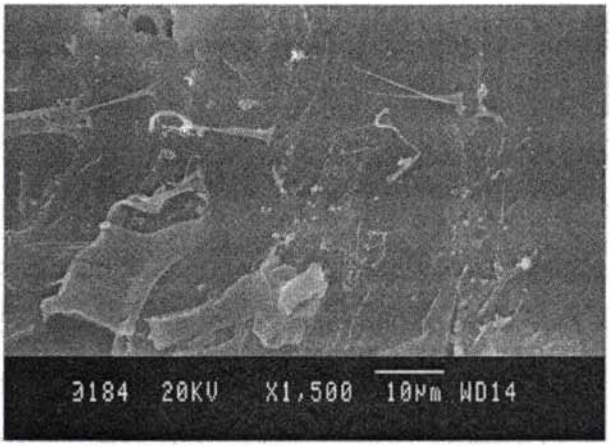


Fig.4.26 (c) PP+1% nanosilica at 50 rpm

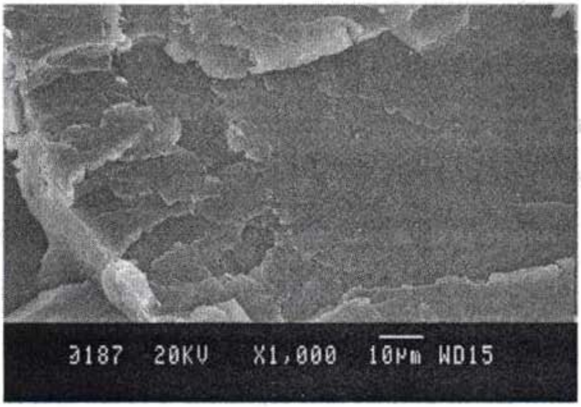


Fig.4.26 (d) PP+ 1% nanosilica at 70 rpm

Fig.4.26 (a) to (d): SEM images of fracture surfaces of PP and PP/Silica nanocomposites.

4.3.9 Thermogravimetric analysis

Polymer compounds considerably vary in their thermal stability. In order to process any specific polymer its thermal stability characteristics should be investigated. Thermal analysis is considered as an important analytical method in understanding the structure- property relationship and mastering the technology for the industrial production of different polymeric materials.

It is well known that thermal stability of the material can be improved by adding inorganic nanofillers [36-41].However the inorganic nanofillers have poor dispersibility in the polymer matrix because of their surface properties. Several methods have been attempted to improve dispersion. One approach is the use of a coupling agent to improve the interfacial adhesion between the inorganic nanofillers and the polymer matrix. Chi-Ming Chan *et.al.* reported that $CaCO_3$ particles in polypropylene(PP) improved the thermal stability of PP. In another study by Li *et. al* and Bagheri starch was used as a filler in PP which prevented the thermal degradation of PP and also improving the flame retardant properties.

The thermal stability of the composites was analyzed by thermogravimetry and derivative thermogravimetry. This was done using TGA Q 50 (TA instruments) at a heating rate of 10°C/min from room temperature to 800°C in a nitrogen environment. Differential scanning colorimetry was done using DSC Q 100 (TA) instruments to study the effect of silica nanoparticles on the crystallization characteristics of PP. All samples were dried prior to measurements and analysis was carried out using nitrogen atmosphere using standard aluminum pans. The samples were exposed to heating at a rate of 20°C/min to 200°C holding for 10 min and then cooling to

30°C at a rate of 20°C/min during which peak of crystallization exotherm was noted as the crystallization temperature T_c. The heat of fusion (ΔH_m) and heat of crystallization ΔH_c were determined from the areas of the melting and crystallization peaks respectively.

Typical TG curves obtained at a heating rate of 10°C/min for pure PP and PP+1% silica at different rpm are shown in the figure 4.27 The thermal decomposition take place at a programmed temperature range of 30-800°C.The temperature of onset of degradation, T_{onset} and the temperature at which maximum degradation occurs T_{max} and the residue obtained are given in table 4.4. In the figure the curves correspond to single stage degradation with well defined initial and final degradation temperatures. The onset of degradation for pure PP is 355°C while that containing 1% silica at 70 rpm is 410°C. The T_{max} increases from 389°C to 479°C. Hence the PP/Silica nanocomposites have improved thermal stability.

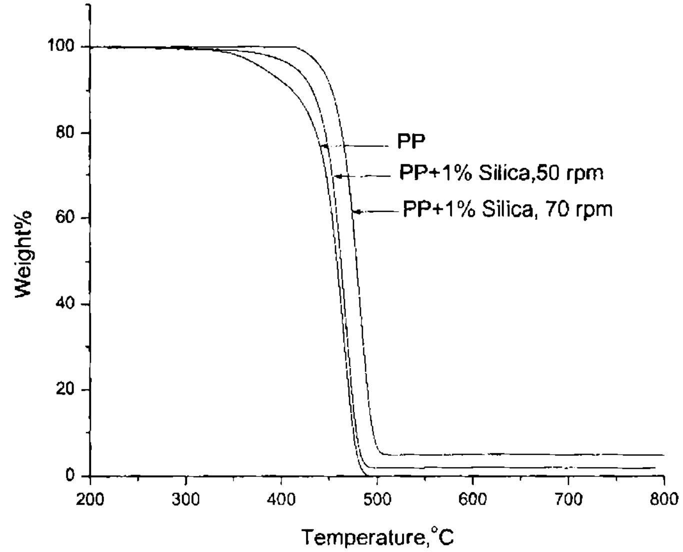


Fig.4.27 Thermogravimetric traces of PP-modified silica nanocomposites.

The TG curves for PP/modified nanosilica composites are indicated in fig.4.28.These curves also confirm that PP/nanosilica composites have better thermal stability when compared to neat PP.

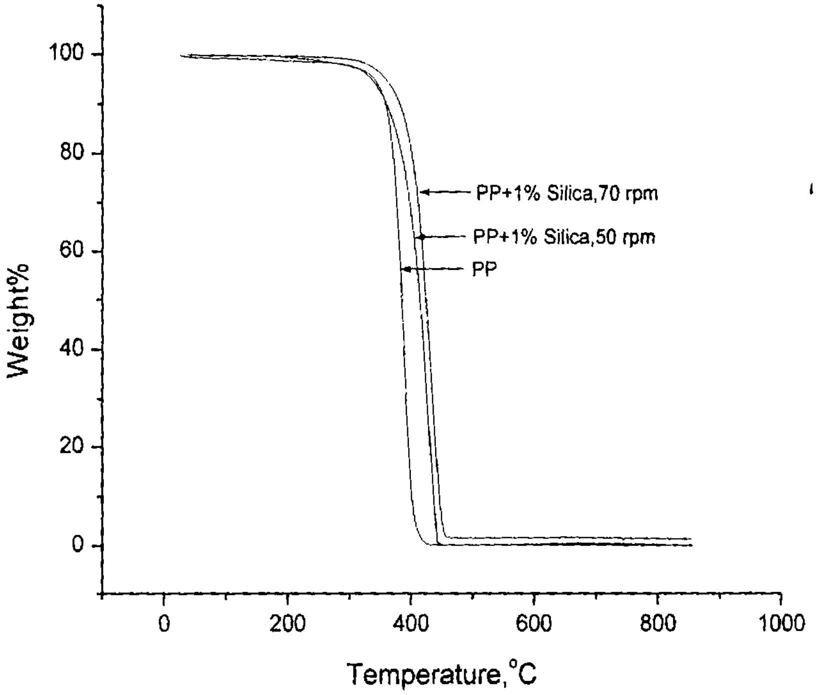


Fig.4.28 Thermo gravimetric traces of PP-unmodified silica nanocomposites

Thermogravimetric traces of PP/Commercial silica nanocomposites are given in Fig.4.29.The nanocomposites are thermally stable. However, there is no attractive changes in the onset and maximum degradation temperatures. Hence thermal stability of these composites remains unaffected.

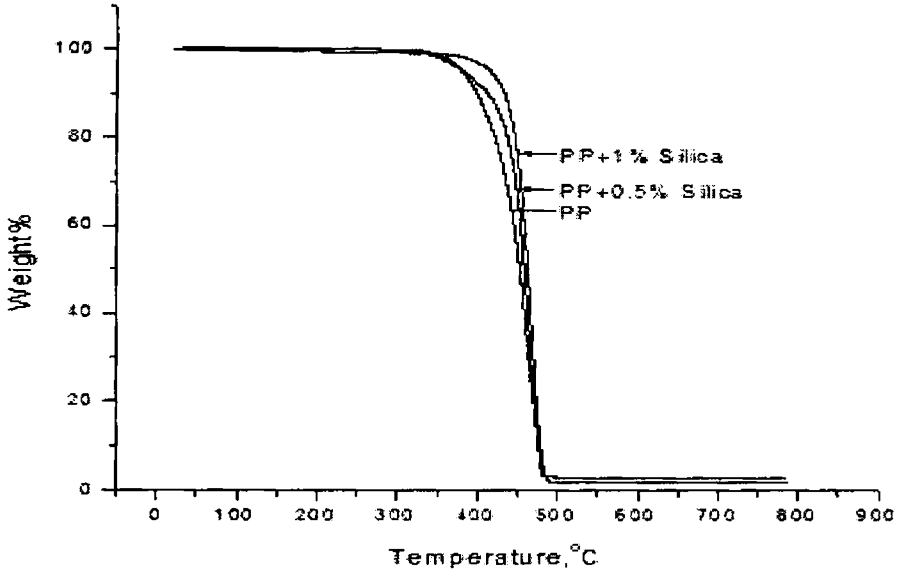


Fig.4.29 Thermo gravimetric traces of PP-Commercial silica nanocomposites

Table 4.4 Degradation characteristics of PP-Silica nanocomposites.

Sample	**T_{onset} (°C)**	**T_{max} (°C)**	**Residue obtained at 600°C (%)**	**Peak rate of decompositon (%/min)**
PP	355	389	0.0885	2.72
PP+1% Silica (50rpm),	369	429	1.807	2.69
PP+1% Silica(70 rpm)	380	432	3.173	1.96
PP+1% Silica (50 rpm) Modified	383	463	2.023	2.54
PP+1% Silica (70 rpm) Modified	410	479	5.003	1.36

4.3.10 Differential Scanning Colorimetry (DSC)

The presence of inorganic filler also affects the crystallization behaviour of the polymer. Hence it is important to study the crystallization kinetics of a semi crystalline polymer which determines the final properties of a polymeric product. Differential Scanning Colorimetry (DSC) is an important tool for studying the crystallization and thermal behaviour of PP/Silica composites [42]. In DSC the heat flow rate associated with a thermal event is measured as a function of time and temperature, allowing us to obtain qualitative information regarding the melting and phase transitions of the composites [43-49].

The changes in the crystallinity of the PP/Silica samples were studied by differential scanning colorimetry. The DSC provides the information about the crystallinity aspects that has occurred in the polymer as a result of thermo mechanical processing. These curves provide the various parameters in crystallization such as peak crystallization temperature (T_c), degree of crystallinity (X_c), crystallization enthalpy (ΔH) etc.

Fig 4.30 indicates that for a given cooling rate, peak crystallization temperature (T_c) is slightly higher than PP. This means that the addition of silica particles in PP matrix increases the crystallization rate of PP [50]. T_c of composites containing 1% silica particles is 4.26^{0}C higher than that obtained for pure PP which again shows an increase in the crystallization rate. The crystallization temperature T_c, crystallization enthalpy and the degree of crystallinity are given in table 4.5.

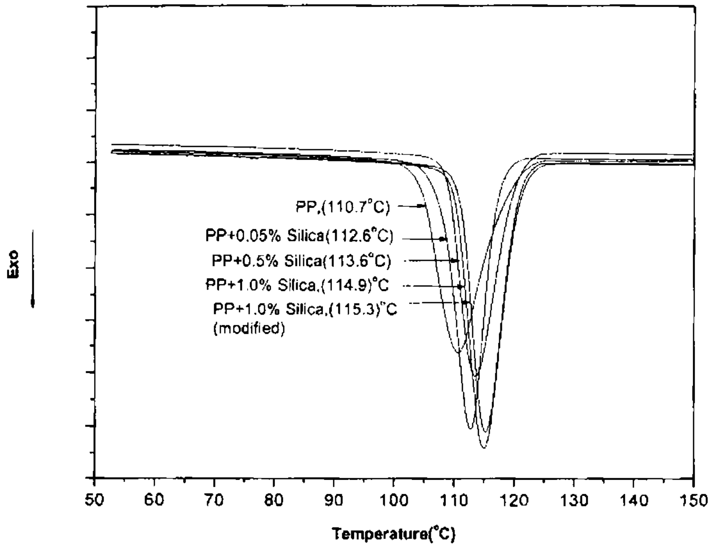


Fig.4.30 DSC thermograms of PP/Silica nanocomposites

Table 4.5 Crystallisation characteristics of PP/Silica nanocomposites.

Sample	Tc (°C)	Xc (%)	ΔH (J/g)
PP	110.7	45.66	82.03
PP+0.05wt% Nanosilica	112.8	44.79	79.65
PP+0.5wt% Nanosilica	113.6	45.62	81.54
PP+1wt% Nanosilica	114.9	45.38	79.89
PP+1wt% Nanosilica (modified)	115.3	44.01	77.5

Fig.4.31 shows the DSC thermograms for PP containing 1% Silica at different rpm. It is evident that the crystallization temperature increases with increase in shear rate.

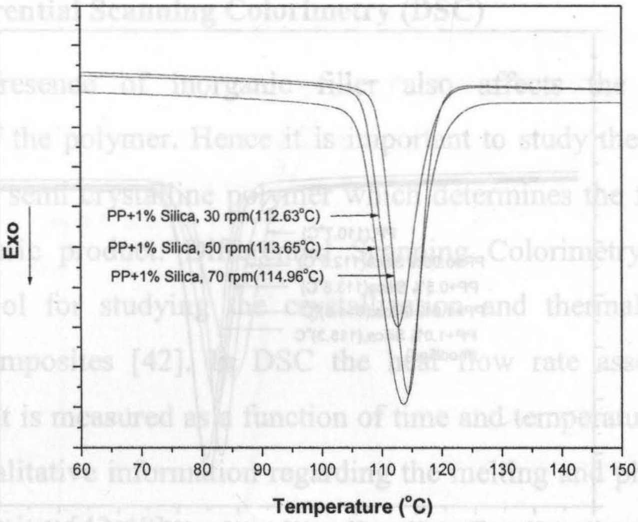


Fig.4.31 DSC thermograms of PP + 1% Silica nanocomposite at different rpm.

4.3.11 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical characteristics of the PP/Silica composites were also studied using Dynamic Mechanical Analysis (DMA).It is essential to know the behaviour of the material under dynamic loading conditions when the materials are put into different applications[50]. The dynamic modulus, loss modulus tan δ of the composites prepared by employing both modified and unmodified silica nanoparticles has been studied in this work.

A dynamic mechanical analyzer DMA Q 800 of TA instruments was made use of for measuring the storage modulus and mechanical damping (tan δ).

The variation of storage modulus with temperature for pure PP and PP/Silica composites are shown in fig 4.32 (a)&(b). It is evident that at this composition there is an increase in storage modulus. This may be due to the improved stiffness resulting from the addition of nanoparticles. An increase in storage modulus in PP/ZnO nanocomposites is also reported earlier [51].

The values of storage modulus also increases with increase in shear rates and the highest values are provided by the composites prepared at 70 rpm.

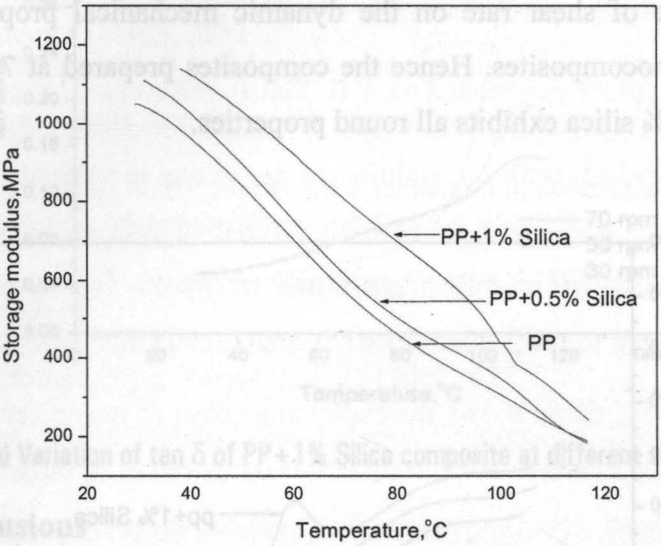


Fig.4.32 (a) Variation of storage modulus of PP/Silica nanocomposites.

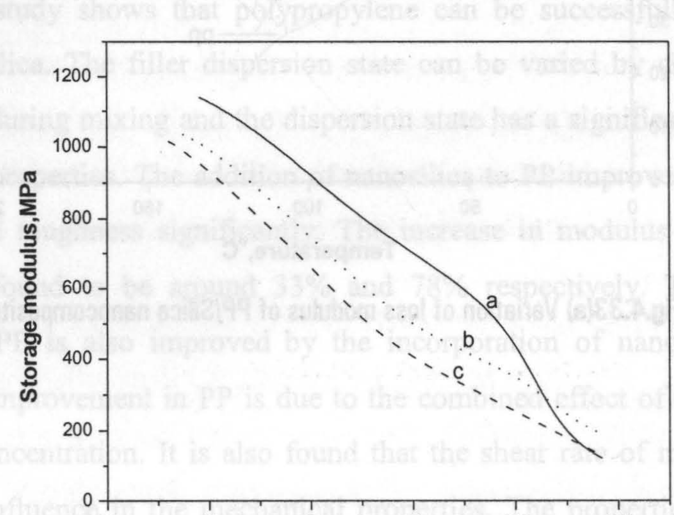


Fig.4.32(b) Variation of storage modulus of PP + 1% Silica at different shear rates.

a: *PP+1%Silica at 70 rpm,* b: *PP+1%Silica at 50 rpm* c: *PP+1%Silica at 30 rpm*

The variation of loss factor and tan δ with temperature for pure PP and PP+1%Silica nanocomposites are shown in fig 4.33 (a)&(b). It is observed that the addition of silica particles to PP reduces the loss factor. It also shows the influence of shear rate on the dynamic mechanical properties of the PP/Silica nanocomposites. Hence the composites prepared at 70 rpm which consists of 1% silica exhibits all round properties.

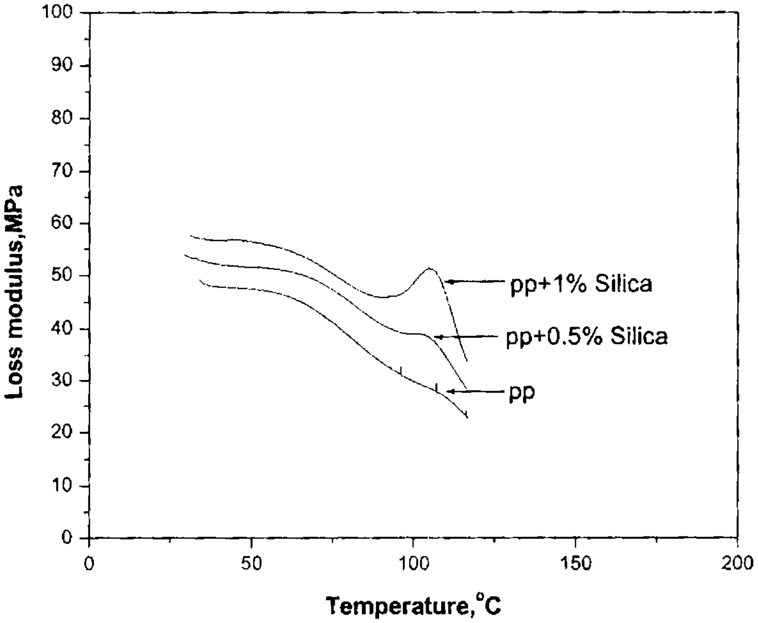


Fig.4.33(a) Variation of loss modulus of PP/Silica nanocomposites

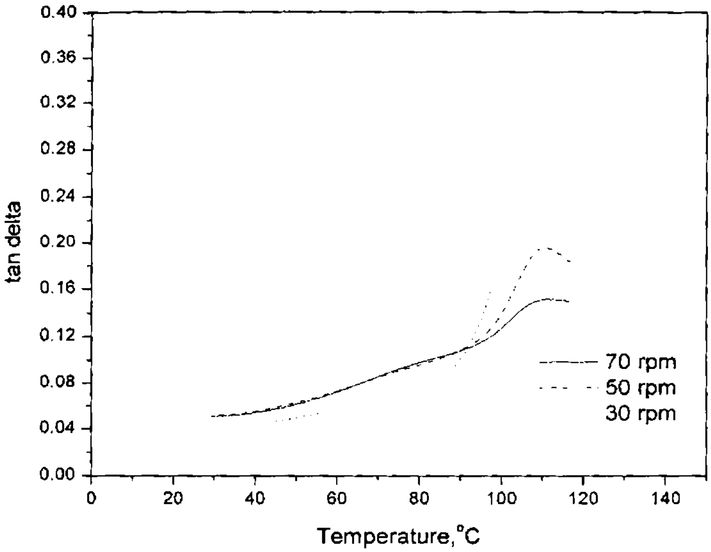


Fig.4.33 (b) Variation of tan δ of PP+1% Silica composite at different shear rates.

4.4 Conclusions

The study shows that polypropylene can be successfully modified using nanosilica. The filler dispersion state can be varied by changing the rotor speed during mixing and the dispersion state has a significant effect on mechanical properties. The addition of nanosilica to PP improves the elastic modulus and toughness significantly. The increase in modulus and impact strength is found to be around 33% and 78% respectively. The thermal stability of PP is also improved by the incorporation of nanosilica. This shows that improvement in PP is due to the combined effect of crystallinity and filler concentration. It is also found that the shear rate of mixing has a significant influence in the mechanical properties. The properties gradually increases as the shear rate increases and the maximum values are obtained at 70 rpm. The incorporation of commercial silica in PP is not giving fruitful results. This may be because of the poor interaction of the particles with the polymer matrix.

The following conclusions can be drawn from the thermal behaviour of PP modified with nanosilica.

- Thermogravimetric analysis shows that both PP and PP/silica composites exhibit single step degradation behaviour and are similar. There is marginal increase in the onset and maximum degradation temperatures with the addition of nanosilica in PP matrix. Hence the thermal stability has been improved. Furthermore, the thermal behaviour of modified nanosilica in PP is very attractive when compared to the performance of commercial silica particles in PP.
- The DSC curve shows the nucleating effect of nanosilica. In this case also the increase in crystallization temperature is only marginal. As the shear rate increases there is corresponding change in the crystallization temperatures.
- DMA of PP/Silica composites show that the composites have better dynamic load bearing capacity than pure PP. It also shows that the composite containing 1% silica has the high value and the best results are obtained for the composites prepared at 70 rpm.

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Chapter 5

Modification of Polystyrene using Nanosilica

5.1 Introduction

Polymers are widely used due to their ease of production, light weight and ductile nature. However polymers have lower modulus and strength compared to metals and ceramics. One way to improve their mechanical properties is to reinforce the polymers with nanofillers[1-4].Modification of polymers with inorganic fillers of nano scale dimension has received considerable attention in recent years [5-6]. Mechanical properties of polymers can be improved by incorporating nanoparticles. The desire for state-of-the-art materials give rise to the development of organic-inorganic nanocomposites with unique properties not found in conventional composites. Common polymer composites usually involve a high amount of inorganic filler (more than 10% by wt) for imparting desired mechanical properties. This would detrimentally affect some important properties of matrix polymers such as processability, appearance, density and ageing performance. Therefore a composite with improved performance with low particle concentration is highly desired. The development of such materials is currently a research area of great interest. However, nanoparticles cannot be compounded with polymers like conventional particulate fillers, which have been employed in plastics industry on a large scale since many years. Therefore, special techniques are now a days used for their preparation[7-14].

The extremely high surface area is one of the most attractive characteristics of nanoparticles because it facilitates in creating a great amount of interface in a composite. Smaller particle size means the size will approach the size of the polymer molecule, and there is greater probability of significant polymer segment particle interaction. Therefore, extra interfacial interaction between additives and polymer matrix will be expected, and it will not be the case for micron-scale additives. Improved bonding between polymer and the reinforcing agent leads to improved mechanical properties [15-17]. In order to reach this improvement, a homogeneous dispersion of the particles in the polymer matrix is required. However, nanoparticles cannot be compounded with polymers like conventional particulate fillers, which have been employed in plastics industry on a large scale since many years. Therefore, special techniques are now a day used for their preparation. If the nanoparticles are not dispersed properly, the nano particle agglomerates may split under a stress and a premature failure of the materials can thus take place.. The enhanced properties are presumably due to the synergetic effects of the nano scale structure and the maximized interaction between the fillers and the polymer molecule.

Polymer composites are widely used in various applications such as transportation vehicles, construction materials, electronics & sporting goods and consumer products. These composites are often filled with natural or synthetic inorganic particles. The main purpose of the filled polymer is to reduce cost, and at the same time enhance their mechanical and thermal properties while reducing the permeability to gas. (eg. oxygen, water) and electrical conductivity. In order to achieve this good dispersion of the filler in the polymer matrix is necessary and it depends on the interfacial adhesion between the filler and the polymer. The interfacial adhesion may be improved by the modification of fillers with surfactants, dispersants or coupling agents which have been found to be reasonably effective [18-19].

Polystyrene can be modified with nanosilica and silicate particles to improve its mechanical& thermal properties [20-21]. Several studies have reported in literature which relates to a nano scale dispersion of inorganic silicate particle in PS matrix [22-23].One study by Stephane et.al reports on the synthesis of PS/Silica nanocomposites by emulsion polymerization of styrene in presence of silica particles previously modified by γ-methacryloxy propyl triethoxy silane (MPS). Grafting was performed by the addition of MPS to aqueous silica suspension in the presence of an anionic surfactant under basic conditions. In another study radical polymerization of styrene with vinyl groups onto surfaces of the nano sized silica via solvent polymerization method was developed. n-Methacryloxy propyl triethoxy silane groups onto the surfaces of the nano sized silica in organic matrices. The addition of the nano sized silica also improved the thermal stability of PS [24].

However modifying PS with nanosilica prepared by precipitation method has not been evaluated. Hence an attempt is made to analyze the possible impact of nanosilica on the overall performance of this polymer. This study is proposed to be focused on the preparation of new PS-Silica composites that show enhanced mechanical and thermal properties. The silica particles are also proposed to be modified with an organo alkoxy silane such as VTES to improve the polymer-filler interaction. The effect of the mixing shear to break down the nano particle agglomerate and hence achieve a well dispersed nanocomposite is also proposed to be investigated.

5.2 Experimental

5.2.1 Materials used:

Polystyrene: PS grade LGG 104 was supplied by LG Plastics with MFI 18g/min

Nanosilica: silica nanoparticles were prepared from sodium silicate by precipitation using dilute HCl. The reaction conditions were optimized to produce uniform sized particles. The method used is very cost effective since it utilizes only commonly available chemicals [25].

5.2.2 Preparation of PS/Silica nanocomposite

PS/Silica composites were prepared by melt blending. In Haake mixture (Haake Rheocord 600) at different shear rates varying from 30 rpm to 90 rpm. The variation of torque with time of mixing was measured. The compound from the mixture was then pressed into sheets and cut into small pieces. The material is then injection moulded in semi automatic laboratory injection moulding machine to obtain specimens for tensile and impact tests.

The tensile test was done as per ASTM-D-638 in universal testing machine (Shimadsu) at a cross head speed of 50mm/min. Flexural properties of the composites were measured by 3 point loading system using the universal testing machine as per ASTM-D-790. The morphology of the tensile fractured surface was also investigated using Scanning Electron Microscope (SEM).

5.3 Results and discussion

5.3.1 Torque studies

The variation of mixing torque with time at different filler concentrations is shown in figure 5.1. The mixing time was fixed as 8.5 min since the torque leveled of during this time. This indicates that a stable structure is obtained after this level of mixing. The temperature of mixing chamber was kept at 180°C.Initially the torque rises to a maximum value due to charging of PS and after that it decreases due to melting and then levels off.

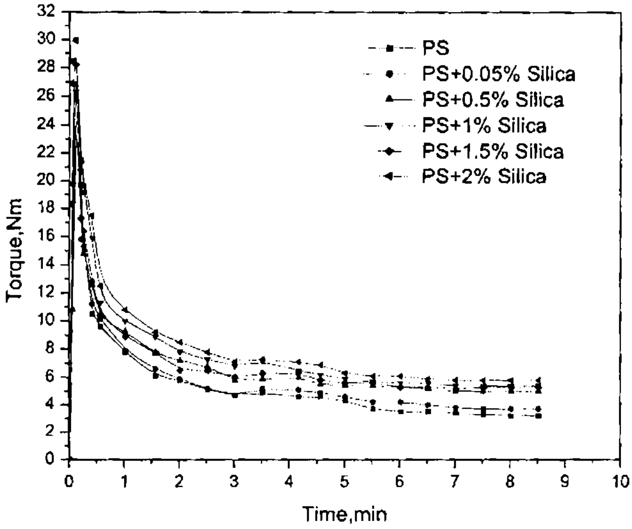
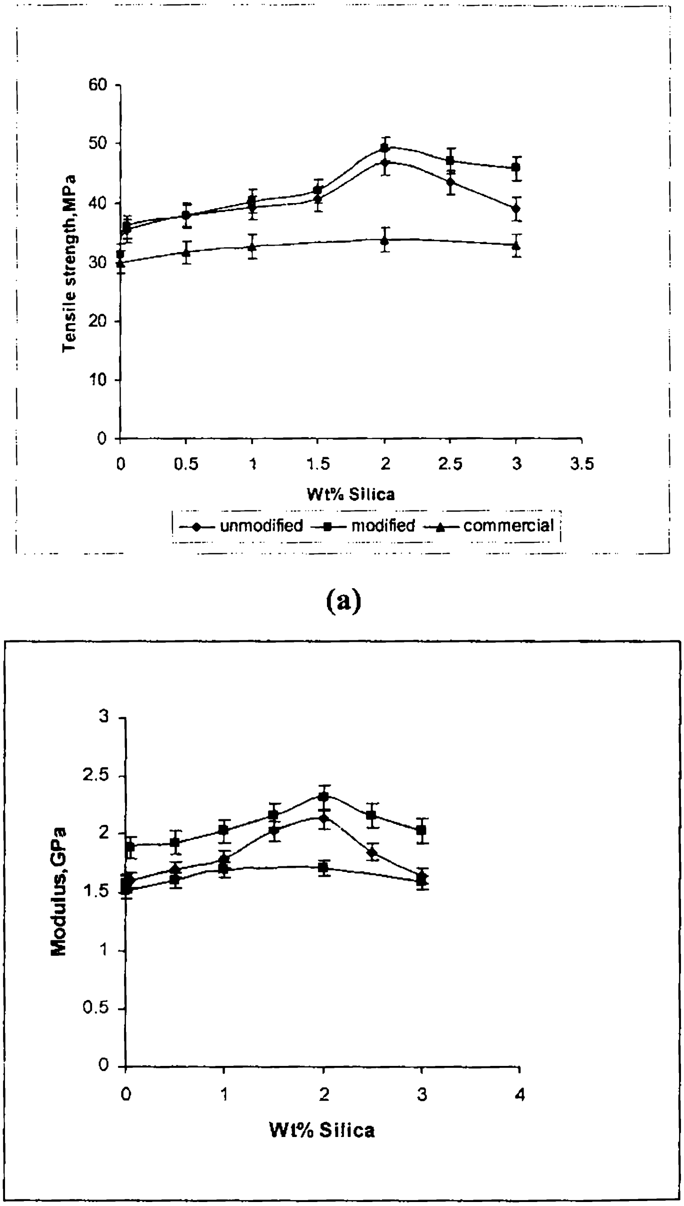


Fig.5.1 Variation of torque with time for PS/silica nanocomposites

The variation of torque for PS/ nanosilica composites made of both unmodified and modified nanosilica at different shear rates are shown in the fig.5.2 (a) & (b). It is observed that as the rotor speed increases the torque also varies accordingly and a stable structure is obtained after sufficient level of mixing in all the cases. In this case also mixing time was 8.5 minutes. The stable level of torque indicates that the material has been homogenized by this time.

5.3.2 Tensile properties of nanosilica modified PS

5.3.2.1 *Effect of filler concentration*



(a)

(b)

Fig.5.3 Comparison of (a) tensile strength (b) modulus of PS/Silica nanocomposites

Table.5.1 Tensile & impact properties of PS/unmodified silica nanocomposites.

Silica Concen-tration,wt%	Tensile strength,MP$_a$	Modulus, GP$_a$	% strain	Impact strength, J/m
0	31.2	1.58	2.19	229
0.05	35.34	1.60	2.77	250.0
0.5	37.91	1.69	3.15	281.9
1.0	39.32	1.78	3.49	325.8
1.5	40.76	2.02	3.7	363
2.0	46.79	2.12	3.99	383.1
2.5	43.44	1.84	3.117	283.3
3.0	39.062	1.63	2.887	212

Table.5.2 Tensile & impact properties of PS/modified silica nanocomposites

Silica Concen-tration,wt%	Tensile strength, MP$_a$	Modulus, GP$_a$	% strain	Impact strength, J/m
0	31.2	1.58	2.19	229
0.05	36.1	1.88	2.79	244.7
0.5	38.03	1.92	3.23	290
1.0	40.36	2.02	3.68	344.2
1.5	42.11	2.15	3.78	382
2.0	49.03	2.31	4.01	407.6
2.5	47.04	2.15	3.89	404.6
3.0	45.8	2.02	3.66	383

The stress-strain curve for pure PS and PS/silica nanocomposites are shown in the fig.5.4. The area under the stress-strain curve increases due to energy absorption. Thus it is evident that satisfactory reinforcement has been taken place with the addition of nanosilica in the PS matrix.

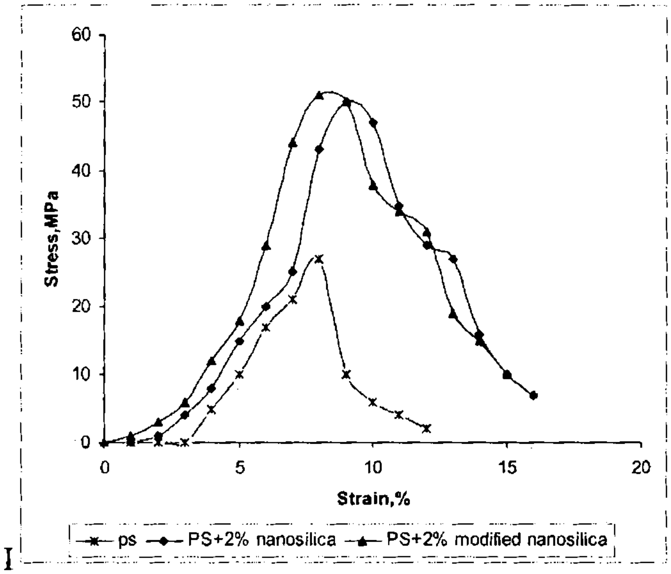
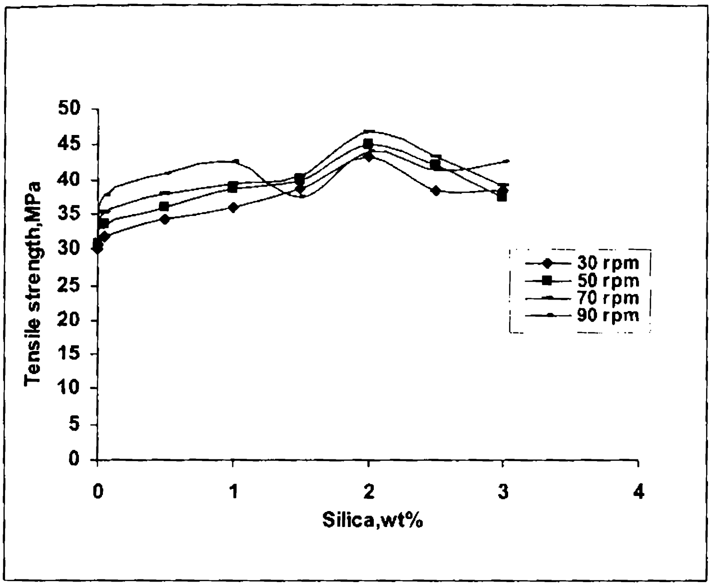


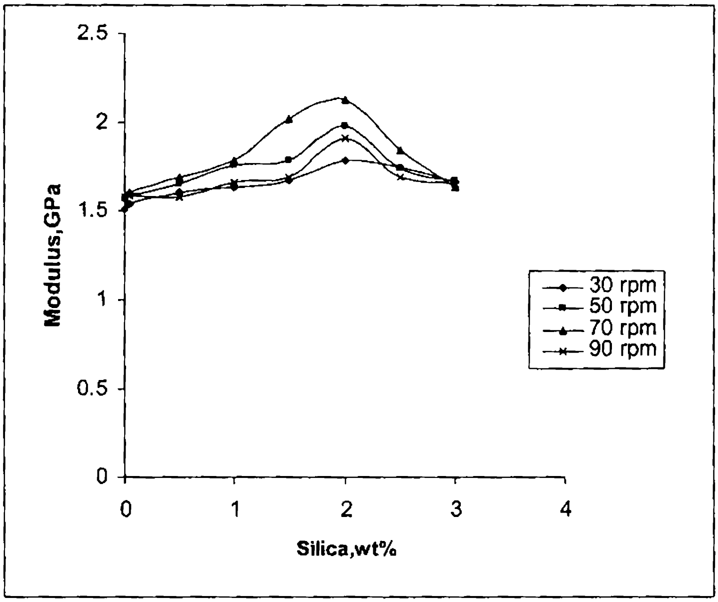
Fig.5.4 Stress-strain curve for PS and PS/Silica nanocomposites.

5.3.2.2 *Effect of shear rate*

The effect of mixing shear on tensile strength and modulus of PS/Silica composites is given in figures 5.5 & 5.6.(a)&(b).It is observed that PS containing 2% silica particles shows maximum values in both properties. It is also evident that the properties increase with increase in shear rates up to 70 rpm. At 90 rpm the increase in properties is not significant and is lower than that at 70 rpm. The decrease in values is rapid at higher silica loadings. This may be due to the tendency of the silica particles to form aggregates and thus affecting the quality of dispersion.



(a)



(b)

Fig.5.5 Effect of silica on (a) tensile strength (b) modulus of PS/Silica nanocomposites at different shear rates.

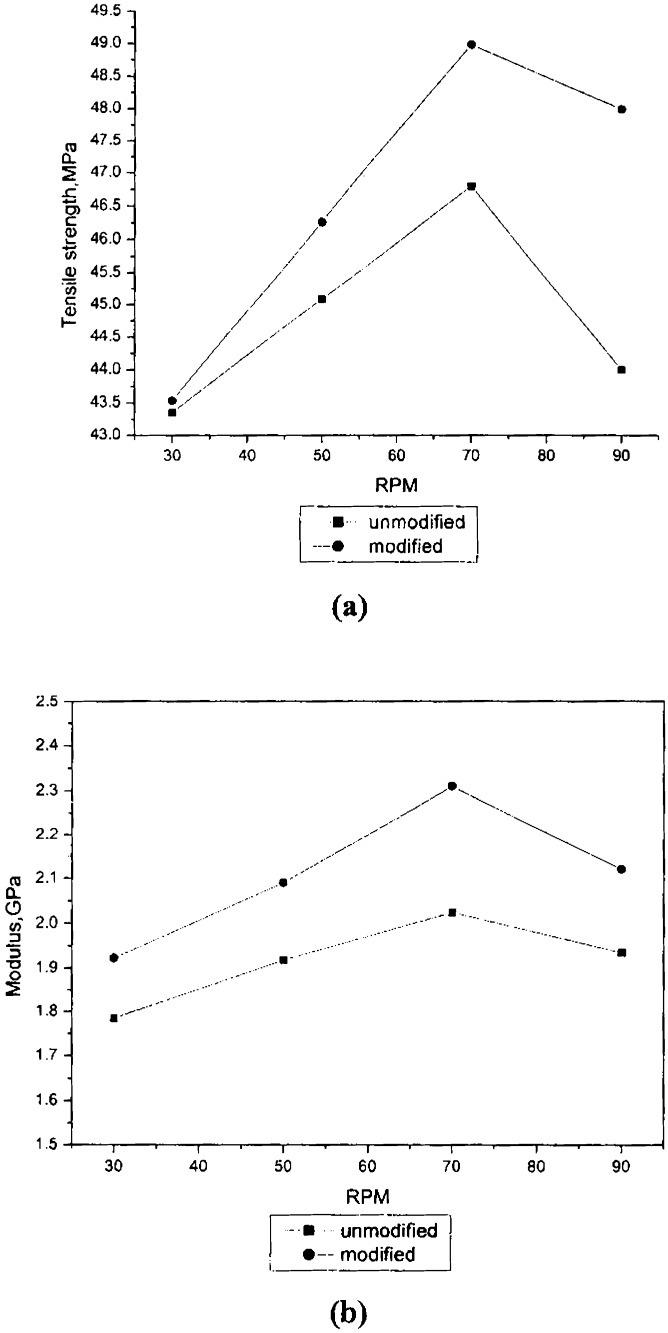


Fig.5.6 Comparison of (a) tensile strength (b) modulus of PS+1%Silica nanocomposites at different shear rates

5.3.3 Flexural properties of nanosilica modified PS

5.3.3.1 *Effect of filler concentration*

A comparison of flexural strength and modulus of PS/Silica nanocomposites using both unmodified and modified silica is shown Fig.5.7& 5.8. With the addition of 2 wt% silica in PS the flexural strength and modulus increases by 28% and 22% respectively for unmodified silica and 30 and 29% for modified silica. The properties increases steadily at the level of 2% and remain almost constant at higher compositions for modified silica while there is a decline in values for unmodified silica. This means that a satisfactory reinforcement can be obtained with the incorporation of nanosilica in PS matrix. This may be because of the high aspect ratio and homogeneity of the nanosilica particles. Chen et al. also reported a similar behaviour with nano ZnO reinforced PS [28].

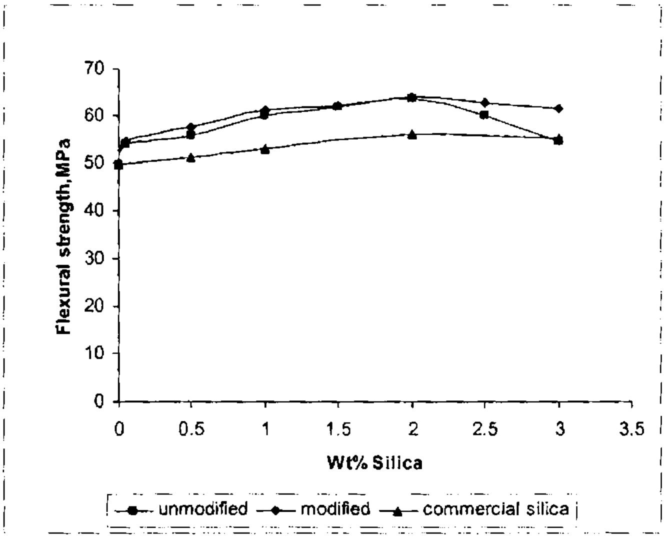


Fig.5.7 Variation of tensile strength of PS/silica nanocomposites

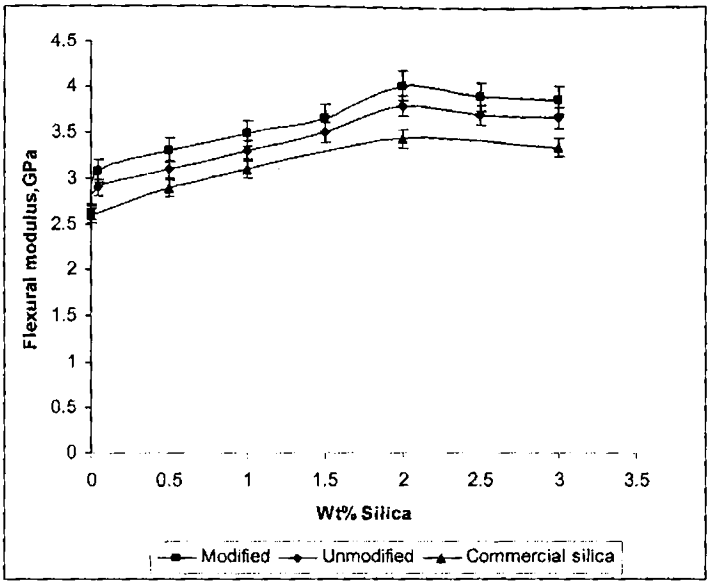


Fig.5.8 Variation of modulus of PS/silica nanocomposites

5.3.3.2 *Effect of shear rate*

The variation in flexural strength and flexural modulus of modified silica nano composites with change in mixing shear are shown the figures 5.9&10. The properties are exhibiting maximum values at the shear rate of 70 rpm and thus it is evident that there is a proper dispersion of nanosilica in PS matrix at this mixing speed. The increase in both flexural strength and modulus is about 5% and 7% respectively when compared with the values at 30 rpm. Almost same level of improvement has occurred due to the action of coupling agent. Thus it is clear that proper reinforcement in PS can be obtained with very small amount of nanosilica and the action is further exemplified by surface modification of silica particles.

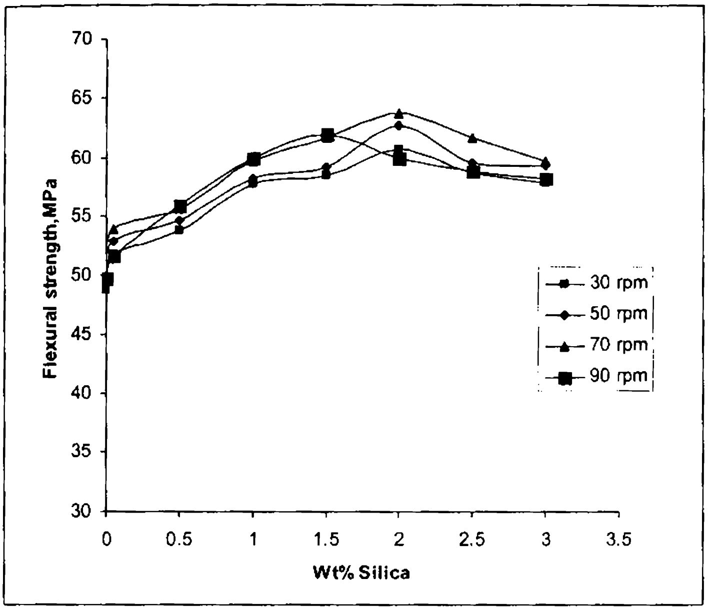


Fig.5.9 Variation of flexural strength of PS/silica nanocomposites at different rpm

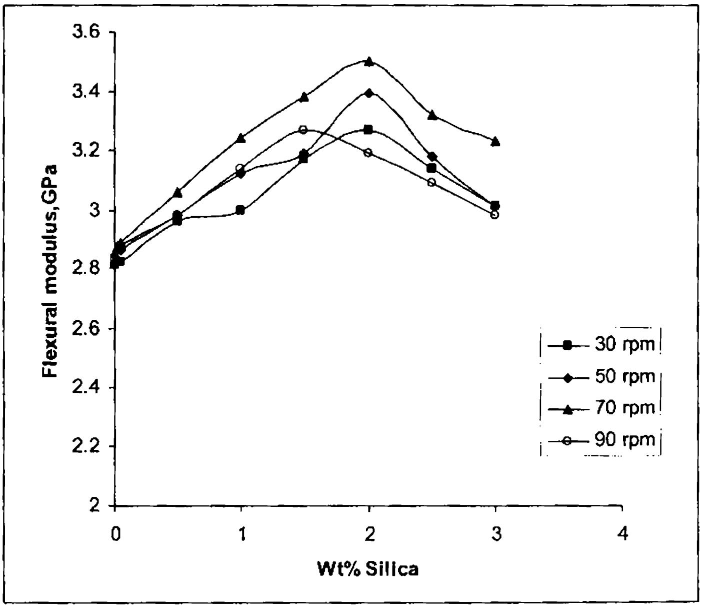


Fig.5.10 Variation of flexural modulus of PS/silica nanocomposites at different rpm

The effect shear rate of mixing on the flexural strength and modulus are given in the figures 5.11&12. As the filler content increases the flexural properties increases in this case also. The values changes with change in shear rates. There is a gradual rise in properties with increase in shear rates and as in the earlier case the maximum values are obtained at 70 rpm. The dispersion of nanosilica in PS matrix could be improved by increasing the shear during mixing. As it is seen the highest values are at 70 rpm. The increase is about 7% more than the values at 30 rpm. The agglomerates formed may be broken down by the shear force involved in mixing resulting in good dispersion. But at the highest shear rate the properties again show a decrease and this may be because of the combined effect of filler concentration and high speed of the rotors.

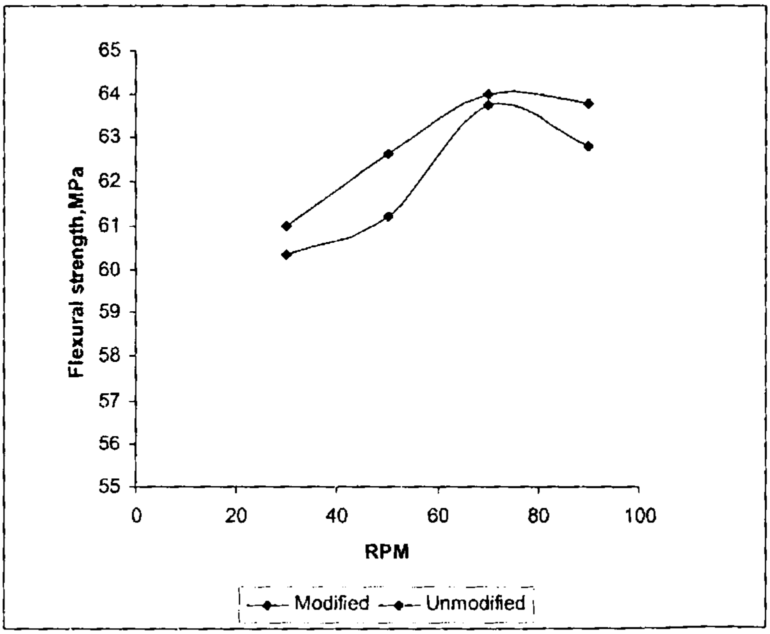


Fig.5.11 Effect of shear rate on flexural strength of PS/Silica nanocomposites

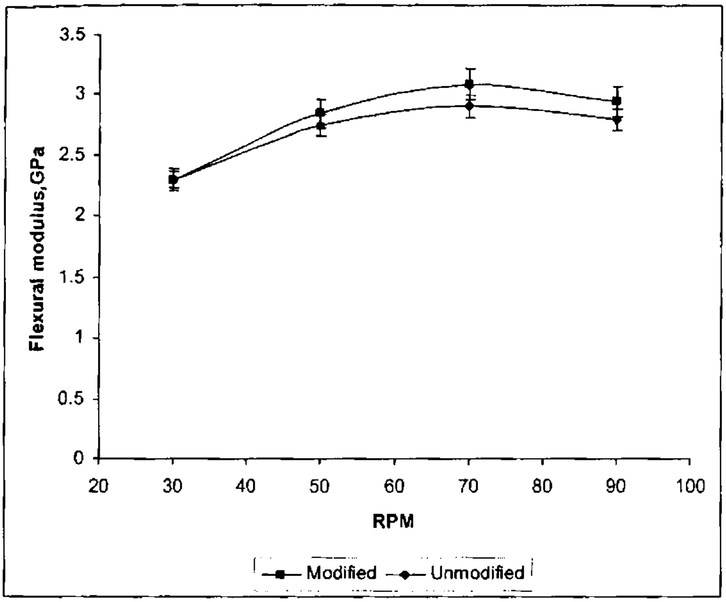


Fig.5.12 Effect of shear rate on flexural modulus of PS/Silica nanocomposites

5.3.4 Impact strength

Rigid fillers in a rigid polymer generally decrease the impact strength of a polymer [29].But there are exceptions for this. It is not surprising that impact strength of brittle polymers decreases on the addition of rigid fillers since the impact strength should correlate with the area under the stress-strain curve. The impact strength increases as particle size decreases as long as agglomeration does not occur. At very small particle size, the impact strength decreases with particle size because of extensive agglomeration. Thus the impact strength may go through a maximum as particle size is changed.

If the matrix is a glassy polymer and the filler is much softer the filler deforms and crazes initiate at about 33^0 down from the pole where the triaxial stresses are highest [30]. But once initiated they grow toward and propagates along, the equatorial direction. As a result rigid polymers filled with elastomeric particles are capable of having very high impact strength if good adhesion exists between phases. Brittle polymers such as PS can be converted to high impact materials by the addition of rubber. There is a reduction in modulus of elasticity, and of breaking strength but the increase in elongation to break, and the ability to dissipate large amount of energy is much better and this compensates for the reduced strength and stiffness. Several studies have undertaken to improve the impact strength of polystyrene by the addition of rubber. The present work is focused on modifying PS with nanosilica and to investigate its influence on impact strength.

5.3.4.1 *Effect of filler loading*

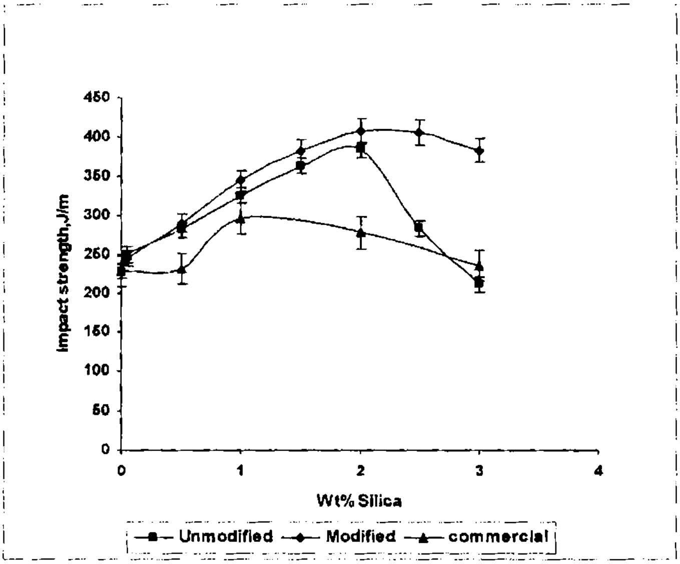


Fig.5.13 Variation of impact strength of PS/Silica nanocomposites with silica content.

The effect of filler loading on unnotched impact strength of PS is shown in fig.5.13. The influence of both modified and unmodified was compared. There is a gradual increase in impact strength with the addition of nanosilica up to 2% in both cases. The impact strength increases to about

68% when compared to that of pure PS for unmodified silica particles. This suggests that for a nanocomposite subject to impact loading, the interfacial regions are able to resist crack propagation effectively than the polymer matrix. This can be because of the large surface area provided by the nanoparticles and improved dispersion in PS. PS+2% Silica composite is showing maximum improvement in impact strength. At higher silica loading the property decreases. This may be because of the presence of voids as agglomerates of silica particles are formed, which leads to the disintegration of the composite. For large particles, poor adhesion with the matrix will create voids and the size of the voids is determined by the particle size. Hence the resistance to separation under the given load reduces and impact strength decreases. The increase in impact strength due to the addition of vinyl triethoxy silane modified silica is about 9%. In this case the bonding between nanosilica and the PS resisted the propagation of the crack more effectively and hence impact strength is improved.

5.3.4.2 *Effect of shear rate*

The influence of mixing shear on impact strength of PS/ nanosilica composites is shown in Fig.5.14 & 15. As the shear rate increases the property increases and the maximum values are obtained at 70 rpm. The improvement is about 65% when compared with that at 30 rpm for modified silica. This demonstrates that the quality of dispersion is improved by raising the mixing shear to higher values. The property again decreases when the shear rate increased to 90rpm. At this speed the adhesion between the silica particles and the matrix is not proper thus affecting the quality of dispersion. Hence, the impact strength decreases. A comparison of unnotched impact strength of both modified and unmodified nanosilica/PS composites is shown in fig.5.15. For coupling agent modified nanosilica/PS composites the enhancement in toughness is more. About 6% more increase is obtained with modified silica at the shear rate of 70 rpm.

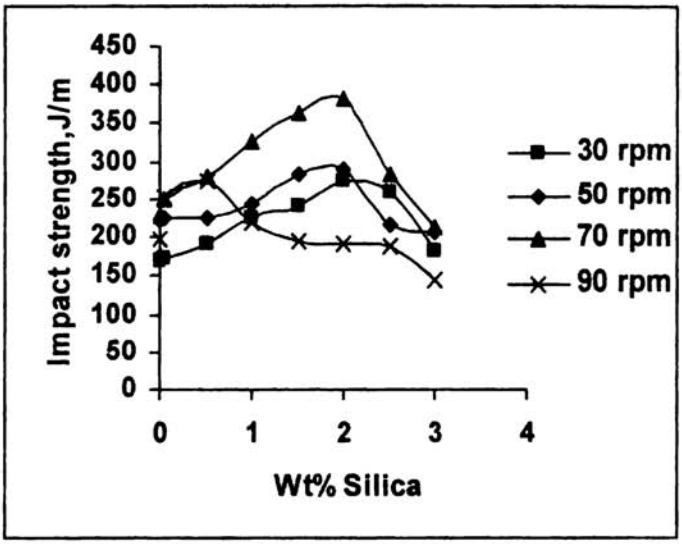


Fig.5.14 Effect of shear rate on PS/Silica nanocomposites at different rpm.

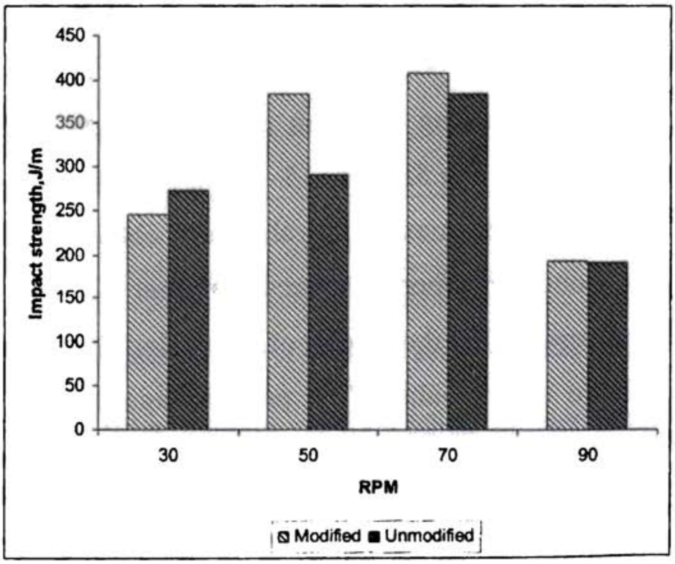
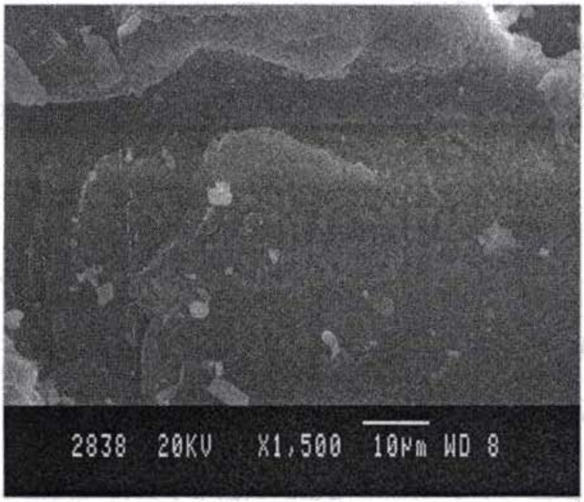


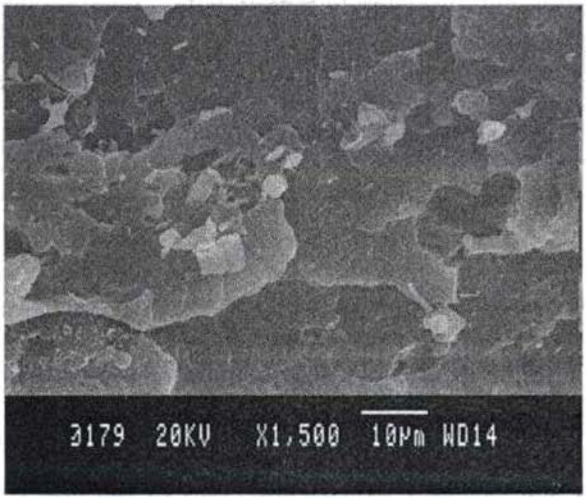
Fig.5.15 Comparison of impact strength of PS/Silica nanocomposites at different rpm.

5.3.5 Morphology

The morphology of PS/Silica nanocomposites are studied to understand the various properties. The SEM pictures of the fractured surfaces were taken and given the figures 5.16(a) to(d).Agglomerates are seen in fig.5.16(b). Figures 5.16(c) &(d) show no presence of agglomerates and thus it is evident that the dispersion is improved.



(a)



(b)

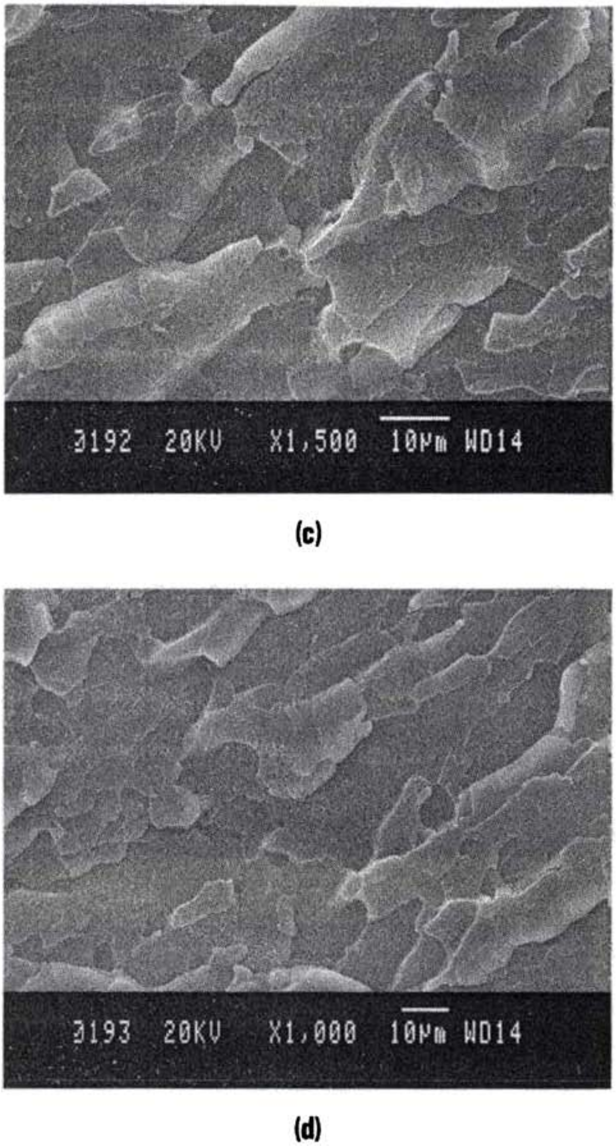


Fig.5.16 Fracture surface of (a) neat PS (b) PS-unmodified silica nanocomposites at 30 rpm (c) PS-unmodified silica at 50 rpm (d) PS-modified silica at 70 rpm.

5.3.6 Rheological measurements using torque rheometer

Fig.5.17 is a plot of log torque v/s log rpm for various loadings of surface modified nanosilica. It consists of a set of parallel straight line which envisages that the power law indices for the pure polystyrene and its composites are identical. The values of the power law indices (n) are determined [31] and given in table 5.3.

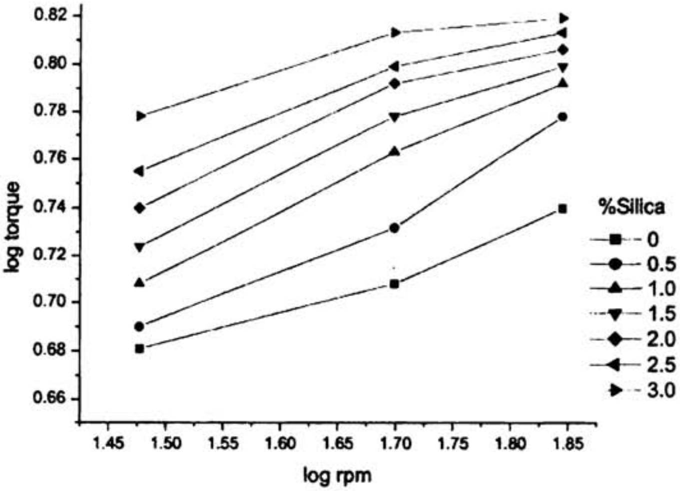


Fig.5.17 Log torque vs log rpm for PS/Silica nanocomposites

Table 5.3 Power law indices for PS/nanosilica composites at three different rpm

Material	Power law index 'n'		
	30 rpm	50 rpm	70 rpm
PS + 0% silica	0.455	0.411	0.40
PS + 0.05% silica	0.461	0.426	0.41
PS + 0.5% silica	0.467	0.444	0.424
PS +1.0% silica	0.473	0.453	0.428
PS +1.5% silica	0.485	0.461	0.432
PS +2.0% silica	0.495	0.465	0.436
PS +2.5% silica	0.505	0.473	0.44
PS +3.0% silica	0.521	0.485	0.46

5.3.7 Water absorption characteristics

The water absorption characteristics of PS/silica nanocomposites are shown in fig.5.18&19. The water absorption tendency decreases with increase in silica concentration up to 2% silica when compared to that of pure PS. This is because the silica particles fills up the free volume of the polymer matrix and prevent the penetration of water molecules. But when the concentration exceeds 2% there will be a change towards higher water absorption due to crowding of silica particles with in the matrix.

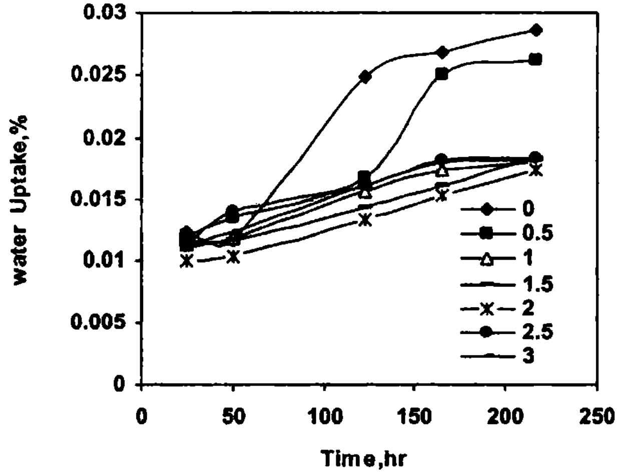


Fig.5.18 Water uptake characteristics of PS/Silica nanocomposites.

The % water uptake varies with mixing shear also. From fig. 5.19.,it is clear that the composites prepared at 70 rpm have lower water absorption when compared with 30 and 50 rpm. This may be because of the good dispersion of the silica particles at this shear rate. Since nanosilica particles posses a large surface area a great amount of interface is created between the particles and the polymer matrix. This will be reducing the permeation of water molecules and hence there is a decline in the property.

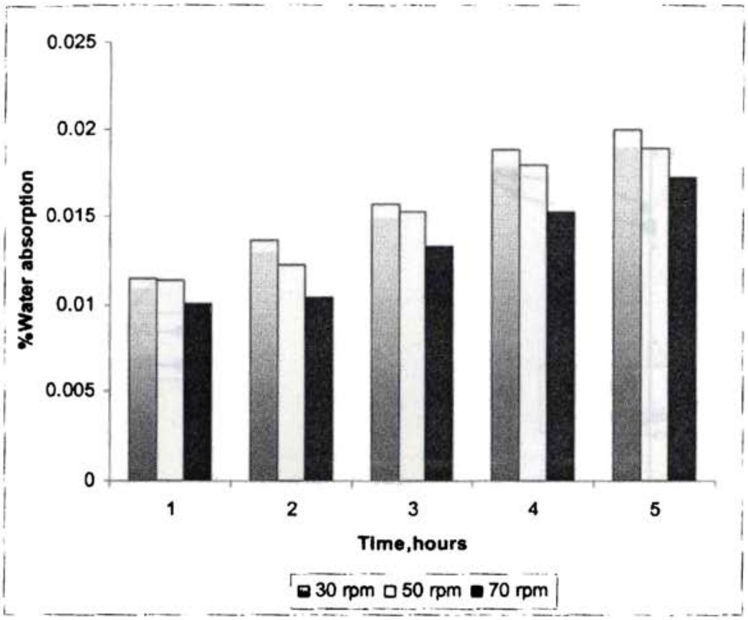


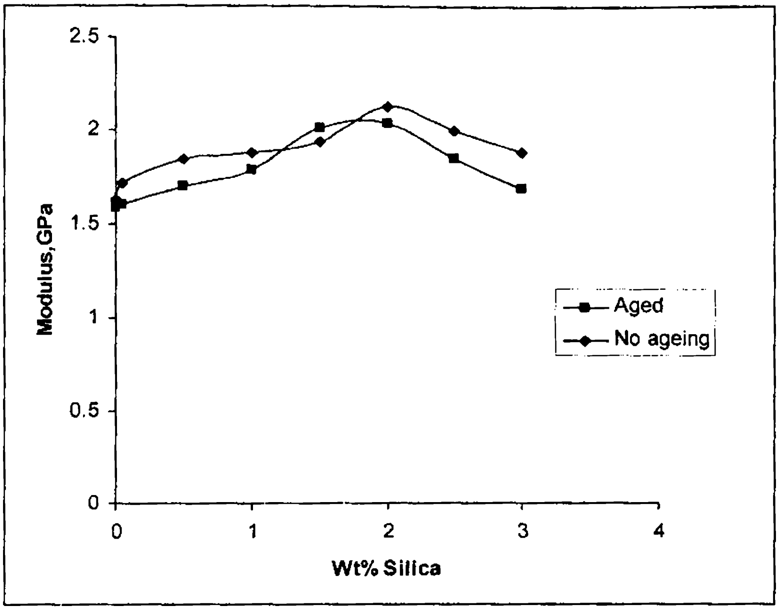
Fig.5.19 Water uptake characteristics of PS/Silica nanocomposites at three different rpm.

5.3.8 Ageing studies

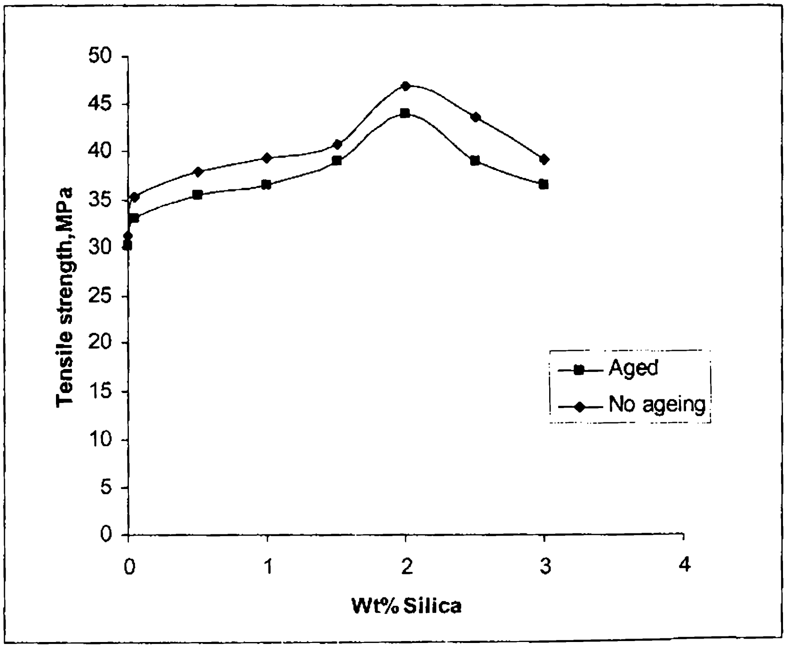
5.3.8.1 *Effect of filler concentration*

Figures 5.20(a)to(c) show the results of laboratory ageing of PS/Silica nanocomposites.

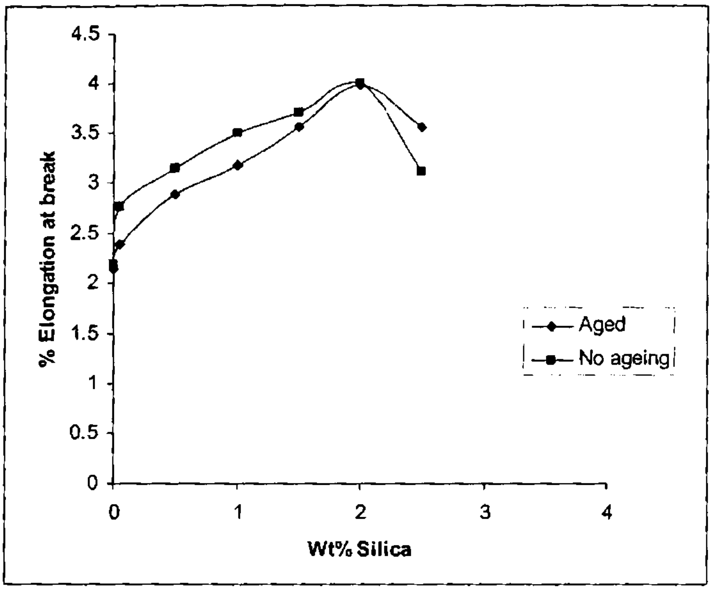
The plots reveal that the nanosilica filled PP remains stable in ageing. The tensile properties like strength, modulus, % elongation at break show no considerable reduction in values for aged samples when compared with those with no ageing. The pattern of variation is also similar to that of samples with no ageing.


Modulus,GPa
2.5
2
1.5
1
0.5
0
0
1
2
3
4
Wt% Silica
Aged
No ageing

(a)


Tensile strength,MPa
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
4
Wt% Silica
Aged
No ageing

(b)



(c)

Fig.5.20 Comparison of (a) tensile strength (b) modulus (c) % elongation at break of aged PS/Silica nanocomposites

5.3.8.2 *Effect of shear rate*

The effect of shear rate on the tensile properties of aged PS/Silica composites using unmodified silica is indicated in fig.5.21(a)to(c). The samples prepared at 70 rpm have better ageing resistance when compared to those at 30 rpm. A similar behaviour is also obtained with modified nanosilica.

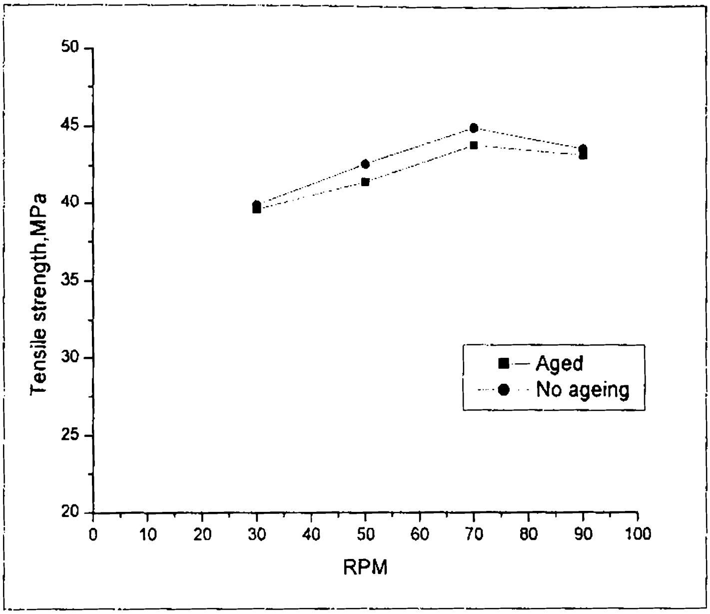


Fig. 5.21(a) Variation of tensile strength of PS/silica nanocomposites at different rpm

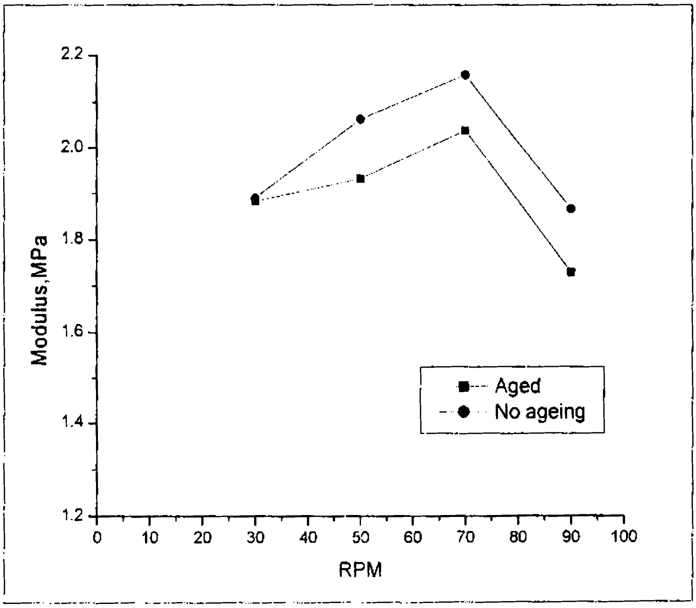


Fig. 5.21(b) Variation of modulus of PS/silica nanocomposites at different rpm

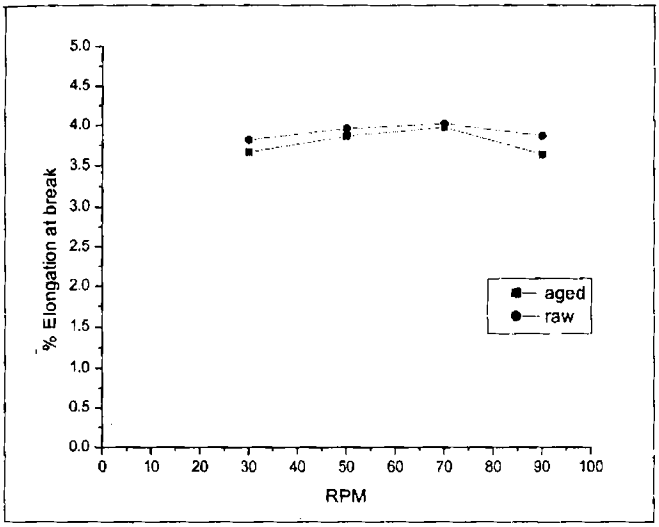


Fig. 5.21(c) Variation of % elongation at break of PS/silica nanocomposites at different rpm

5.3.9 Thermogravimetric Analysis

The properties of polymeric materials are not solely determined by the chemical structure of the polymer chain molecules but equally well by the processing step, viz. the orientation of the molecules in the final product. The majority of the synthetic polymers are processed via the melt, the so called thermoplasts. Next to chemistry and processing, the final properties can be tuned by additives. In fact a plastic product is often a polymer plus additive, notably in engg., applications. The incorporation of fillers into a polymer matrix can bring about changes in mechanical and thermal characteristics of the resulting composites.

It is known that the addition of very small amount of fillers brings about a large enhancement in the mechanical and thermal properties of the polymer [32-35]. TGA was used to study the degradation of polystyrene modified with nanosilica. The study carried out by Bok Nam Jang *et.al.* was based on the degradation pathway of PS modified by the presence of clay[36].. The present work is focused on the evaluation of the thermal properties of PS modified with nanosilica by employing techniques such as thermogravimetry and differential thermogravimetry.

The TGA thermograms of pure PS and PS modified with nanosilica containing 2wt% silica at different rpm are shown in fig.5.22. The curves shows that the decomposition temperature of PS modified with nanosilica shifted towards higher temperature range than that of pure PS which indicates that the nanocomposite exhibits higher thermal stability [40-42].This improved thermal stability is attributed to the fact that the silica particles form a dense layer and it can confine PS chains inside this layer due to the good interaction between them. The temperature of onset of degradation, T_{onset} , is the temperature at which the rate of decomposition is 10% and temperature at which the rate of decomposition is maximum is the T_{max}. The peak degradation temperature, T_{onset}, T_{max} and the residue values obtained for PS/Silica nanocomposites are given in Table 5.4.

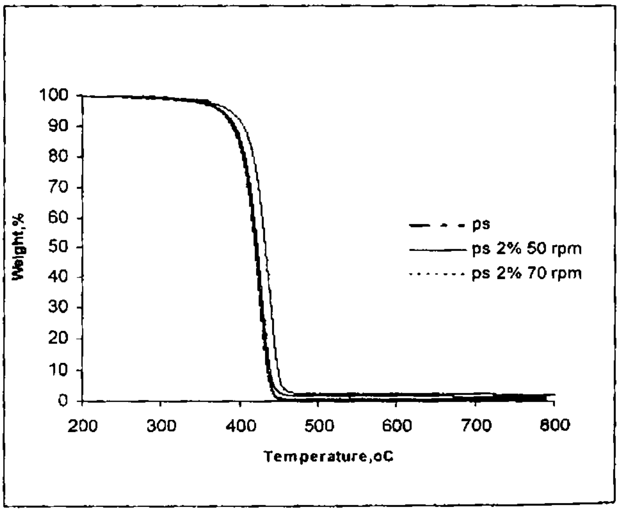


Fig.5.22 Thermogravimetric traces of PS-Silica nanocomposites

The composites showed a higher degradation temperature compared with the virgin materials and an increased degradation temperature was found with increasing silica content in the polystyrene matrix. This result is similar to the trends found in PMMA/silica nanocomposites, which suggests that the inclusion of nanosilica has improved the thermal stability of the polystyrene matrix.

Table 5.4. T_{onset} and T_{max} values for thermal degradation of PS nanocomposites

Sample	T_{onset} °C	T_{max} °C	Peak rate of decomposition, (%/min)	Residue at 800°C
PS(neat)	343.08	416.23	2.783	0.556
PS/SiO_2 50 rpm	349.33	421.15	2.438	1.407
PS/SiO_2 70 rpm	355.49	422.63	1.526	1.893

The thermal stability of PS/Commercial silica samples are shown in fig.5.23.It is clear that the stability remains unaffected by the addition of commercial particles. The interfacial area provided by the commercial silica particles are much less when compared to others. Therefore the expected improvement in thermal stability is not obtained.

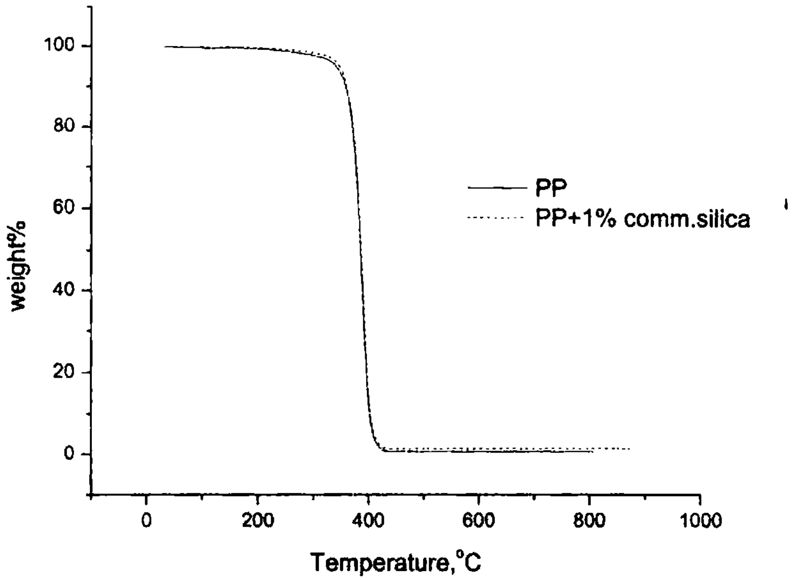


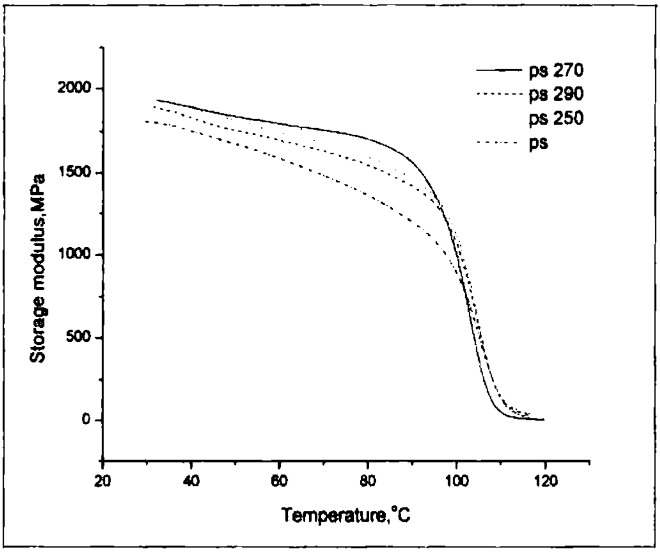
Fig.5.23 Thermogravimetric traces of PS/Commercial silica nanocomposites

5.3.10 Dynamic Mechanical Analysis

Dynamic Mechanical properties were measured using DMAQ 800 of TA instruments at a heating rate of 2.5°C/min with amplitude of 10μm at a frequency of 1Hz.

The results of Dynamic Mechanical analysis PS/silica nanocomposites as a function of temperature, at three different shear rates are shown in Fig 5.24.The storage modulus of polystyrene increases upon modification with nanosilica [37-38]. The increase in storage modulus is due to the stiffness induced by the increased interaction between the silica particles and the polymer. The DMA further confirms the effect of mixing shear on the storage modulus. The maximum storage modulus was obtained for the nanocomposites at 70 rpm. This may be due to the better adhesion of silica particles within PS matrix at this mixing speed.

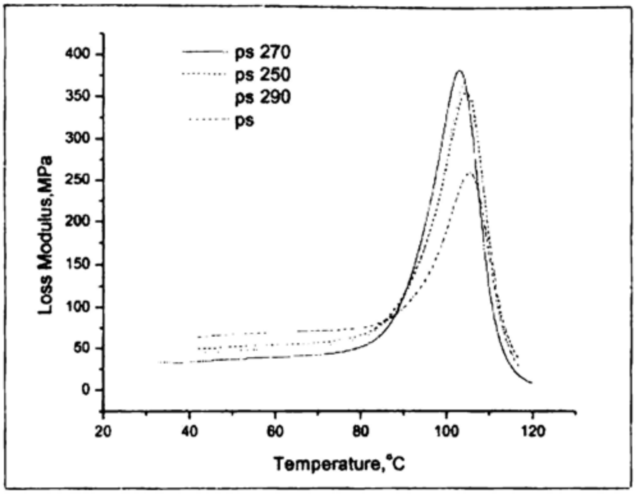
It is evident that increasing the speed of the rotor to above 70 rpm has no significant change in storage modulus.



ps 250: ps+2% silica,50 rpm ps270: ps+ 2% silica,70 rpm ps290: ps+2% silica,90 rpm

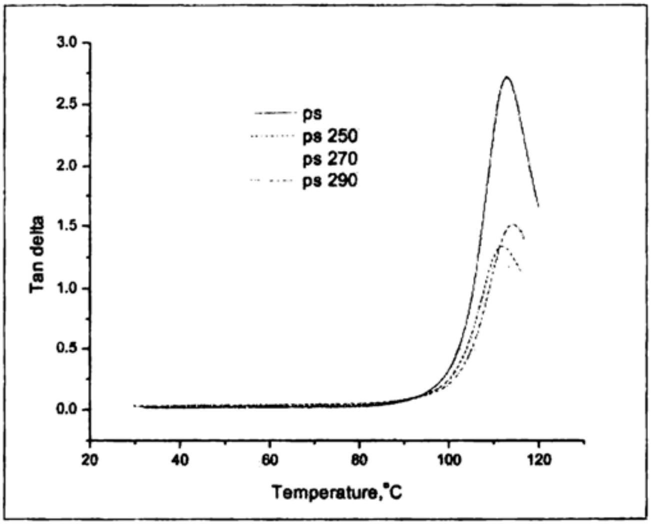
Fig.5.24. Variation of storage modulus with temperature of PS/Silica nanocomposites at three different shear rates.

The loss modulus of the PS/Silica nanocomposites as a function of temperature is also obtained from the DMA results and is depicted in the fig.5.25. It is observed that the loss modulus decreases upon modification of PS with nanosilica. This type of behaviour is also reported for PS/ nano ZnO systems [39].The influence of shear rate also evident in the plot. As the shear rate is increased the loss modulus decreases.



ps 250: ps+2% silica,50 rpm   ps270: ps+ 2% silica,70 rpm   ps290: ps+2% silica,90 rpm

Fig.5.25 Variation of Loss modulus with temperature of PS/Silica nanocomposites at three different shear rates.



ps 250: ps+2% silica,50 rpm   ps270: ps+ 2% silica,70 rpm   ps290: ps+2% silica,90 rpm

Fig.5.26 Variation of tan δ with temperature of PS/Silica nanocomposites at three different shear rates.

The variations of tan δ with temperature for pure and modified PS are given in fig 5.26. It is observed that the tan δ peak height decreased due to the addition of nanosilica particles. There is a slight change in glass transition temperature (T_g) is observed, only 2°C when compared to that of pure PS.

5.4 Conclusions

The study shows that nanosilica is a potential reinforcing agent for polystyrene and that filler dispersion state in the matrix can be varied by changing the mixing shear. The addition of nanosilica improves the elastic modulus up to 34 %.With only 1 wt% silica in the nanocomposite, the tensile strength improves by 25%, which is remarkable for organic/inorganic composites since the same phenomena cannot be found when macro-size additives are used. A significant improvement in toughness is also obtained with modification with silica and change in dispersion states. An improvement up to 78% is noted from the Izod impact tests. This is the contribution of the soft interface between silica and PS when a flexible surface modifier is used. The improvement of mechanical properties suggests a strong interfacial interaction between the organic phase and the inorganic phase, with silica serving as reinforcement sites instead of mechanical failure sites.

Thermogravimetric analysis shows that both PS and modified PS exhibit single step degradation behaviour. There are significant changes in the onset and maximum degradation temperatures. This indicates the better thermal stability of the modified PS. TGA study also shows that the thermal stability of the polymer is enhanced by surface modification of silica nanoparticles through a coupling agent.

Dynamic mechanical analysis of pure and modified PS shows that the composites have improved storage modulus and loss modulus. From this it is evident that the modified PS has improved dynamic load bearing capacity than pure PS. It is also observed that the PS+2% Silica composite prepared at 70 rpm exhibits all round properties.

A comparison of the mechanical and thermal properties of the modified PS with and without coupling agent has been carried out. The results dictate that incorporation of nanosilica in PS matrix through a silane coupling agent (VTES) produce better reinforcement than unmodified nanosilica. This level of reinforcement can be brought out by a small fraction (2%) of nanosilica. The study using commercial silica fillers indicate that its impact on the mechanical and thermal properties are limited.

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Chapter 6

Summary and Conclusions

Modification of polymers using nanomaterials is a challenging area. The most striking feature of the nanomaterials is their large surface area and low concentration which produces remarkable improvement in the properties of polymers. Nanofillers in polymers offer several advantages in addition to the reinforcing effect. Nanosilica, known as 'white carbon' is a potential reinforcing agent for polymers.

The present study was undertaken to modify the performance characteristics of two important commodity plastics, polypropylene and polystyrene using nanosilica. Nanosilica used for modification was synthesized in the laboratory from sodium silicate.

In the first stage of the work, nanosilica was prepared from sodium silicate by acid- hydrolysis method. The usual procedure is to prepare silica by sol-gel method starting from TEOS. But this is an expensive method and the catalyst used may remain as impurity. In the present study silica was prepared from sodium silicate through the use of poly vinyl alcohol which act as a matrix to condense the silica particles, thus producing uniform structured particles. Silica was produced in a large scale in a batch reactor for incorporation in polymers. The kinetic studies on the synthesis reaction helped to evaluate the reaction parameters rate constant 'k' and reaction order 'n'. Modeling of the reactor revealed the conversion in a real continuous reactor. Synthesized silica has been characterized by using techniques such as EDX, XRD, TEM, SEM TGA and FTIR.

Next stage of the study was to modify the polymers using nanosilica. This included the preparation of PP/nanosilica and PS/nanosilica composites. Melt compounding method was adopted because of its versatility and commercial importance.

The mechanical and thermal properties of PP significantly improved on modification with nanosilica. PP. With unmodified silica particles about 20% increase in modulus and the 82% in impact strength is obtained. Interaction between the nanosilica and PP could be improved on surface modification of nanosilica by the addition of a coupling agent, vinyl triethoxy silane (VTES). With the addition of the coupling agent tensile strength improved by 20% and modulus by 44%. A remarkable improvement in toughness was also obtained through the use of a coupling agent. The dispersion of nanosilica particles in PP could be improved by increasing the mixing shear rate to the high values. The dynamic mechanical properties of the nanocomposites revealed that a small concentration of nanosilica is sufficient to improve the storage modulus. The storage modulus improved by around 40%upon addition of nanosilica. This is due to the stiffening effect of the filler particles and efficient stress transfer between them and the polymer metrix. The loss factor curves indicate that the T_g of the composites is not significantly affected by the incorporation of nanoparticles. Thermogravimetric analysis show that the PP/silica nanocomposites have better thermal stability than PP. Differential scanning calorimetric studies reveal that silica nanoparticles act as effective nucleating agents for PP melt crystallization. PP/Silica nanocomposites show a decrease in water absorption tendency which further decreased upon silica particle modification. The comparison of the performance with commercial nanosilica reveal that, the nanosilica particle synthesized in this study have better performance characteristics and hence, they can be promising candidates for modification of polypropylene.

The last stage of the work was modification of polystyrene with synthesized nanosilica particles. The PS/nanosilica composites were prepared by melt mixing method. The mechanical properties of the composites reveal that a filler concentration of 2wt.% increased the strength to 50% and impact strength to 68% with unmodified silica particles. With modification of silica the strength improves further by 7%, modulus 12% and impact strength 11%. The dynamic mechanical analysis revealed that the composites prepared with both modified and unmodified silica particles have better load bearing capacity than pure PS. The tan delta curves show a slight change in Tg values with unmodified silica particles. The thermogravimetric analysis reveals that the PS nanosilica composites provided enhanced thermal stability. It is also found that the thermal stability increases with higher shear rate and the maximum stability is attained for composites prepared at 70 rpm.

Water absorption characteristics of the PS/nanosilica composites show a decrease in water absorption tendency up to 2 wt% after which a slight increase in values due to crowding of particles in the matrix. Water absorption is also minimum for composites prepared at 70 rpm. A decrease of 6% is observed at this shear rate.

The study shows that nanosilica to be a potential modifier for both in a crystalline plastic like PP and amorphous plastic like PS. The improvement in impact strength is most significant in PP while that the improvement in tensile strength is most significant for PS.

List of Abbreviations

ASTM - American Society for Testing Materials
BET - Brunauer, Emmett, and Teller
BR - Batch reactor
CNT - Carbon nanotubes
CSTR - Continuous Stirred Tank Reactor
DMA - Dynamic Mechanical Analysis
DSC - Differential Scanning Calorimetry
EDX - Energy Dispersive X-ray Spectrometer
HCL - Hydrochloric acid
HDPE - High Density Poly ethylene
MFI - Melt Flow Index
MFR - Mixed Flow Reactor
MPS - Methacryloxy propyl triethoxy silane
PE - Poly ethylene
PFR - Plug Flow Reactor
PMMA - Poly (methyl methacrylate)
PNC - Polymer Nano Composites
PP - Polypropylene
PS - Polystyrene
PVA - Poly (vinyl alcohol)
PVC - Poly (vinyl chloride)
RTD - Residence Time Distribution
SEM - Scanning Electron Microscope
TEM - Transmission Electron Microscope
TEOS - Tetra ethoxy vinyl silane
TMOS - Tetra methoxy silane
TGA - Thermogravimetric analysis
UTM - Universal Testing Machine
VTES - Vinyl Triethoxy Silane

LIST OF SYMBOLS

C - Concentration
E' - Storage Modulus
E'' - Loss Modulus

t - time
k - specific reaction rate
r_A - Reaction rate for Component A
F_{Ao} - Initial Molar feed rate
E - Residence time distribution function
T - Temperature
T_c - Crystallization Temperature
T_g - Glass transition temperature
T_{onset} - Temperature of Onset of Degradation
T_{max} - Maximum degradation temperature
ΔH_c - Enthalpy of Crystallization
X_c - Percentage Crystallinity
Wt% - weight percentage
e - Exponential
τ - Space time
θ - Angle; diamensionless time
Δ - Wavelength
∞ - Infinity
r - Shear rate
M - Torque
n - Power
V - Volume of reactor,
V_m - Molar volume.
v - volumetric flow rate
C_{Ao} - Initial concentration of component A
C_A - Final concentration of component A
Δt - Time interval
N - Rotation Speed, Normality
ΔE - Activation Energy
R - Universal gas constant
ΔP - Capillary pressure difference
r - Radius
nm - Nanometer
β - Half width of diffraction peak
s - Space Velocity
ε - Density of the mixture

Publications and Presentations

- Modification of polystyrene, using nanosilica for improvement in mechanical properties. Renjanadevi. B, K.E. George; progress in Rubber, Plastic & Recycling technology (Accepted) .

- Modification of polypropylene using nanosilica. Renjanadevi. B , K.E.George (submitted).

- Kinetic studies on synthesis of nanosilica using PVA as surfactant. Renjanadevi. B, K.E.George (to be submitted).

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- Renjanadevi.B & K. E. George, International Conference on 'Materials for Future', ICMF - 2008 Jan. 17 - 19, 2008, Govt. Engg. College, Thrissur, India.

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