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Polymer reinforced aerogels and composites A. Polyimide crosslinked aerogels B. Silica-polymethylmethacrylate composites

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POLYMER REINFORCED AEROGELS AND COMPOSITES

A. POLYIMIDE CROSSLINKED AEROGELS

B. SILICA-POLYMETHYLMETHACRYLATE COMPOSITES

by

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This thesis has been prepared in the form of a general introduction (Section 1) and two manuscripts. Papers I and II are written in the form of two articles that will be submitted for publication to the *Chemistry of Materials*.

ABSTRACT

Crosslinking of aerogels is a promising approach to combine the advantages of inorganic and polymeric materials. In the present study, two types of polyimide-silica hybrid aerogels, APTES-BTDA-MDA (mol ratio: 2:2:1) and APTES-BTDA-MDA (mol ratio: 2:3:2), were synthesized using a sol-gel process followed by heating in order to imidize the polyamic acid that is formed quickly and is covalently bonded to silica. The hybrid aerogels were made using 3-aminopropyltriethoxysilane (APTES) endcapped polyamic acids and tetramethoxysilane (TMOS) as precursors. Polyimide crosslinked aerogels were characterized by TGA, SEM, FT-IR, BET, solid state NMR and gas pycnometry. These hybrid aerogels exhibit high thermal stability and have potential applications in thermal insulation.

Silica-polymethylmethacrylate (PMMA) composites have been synthesized by in situ polymerization of methylmethacrylate (MMA) in the microstructure of silica gels by using an alkoxy derivative of 2,2′-azo-bis (isobutyronitrile) already bonded to silica. Composites with three different silica contents were synthesized and their thermal and mechanical properties were compared to neat PMMA and a composite prepared via mechanical dispersion of sol-gel silica nanoparticles in PMMA. Silica-PMMA composites were characterized by TGA, FT-IR, compression testing and solid state NMR. The PMMA composites exhibited considerable rise in thermal decomposition temperatures as compared to neat PMMA.

ACKNOWLEDGMENTS

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1. INTRODUCTION

1.1. POLYMER NANOCOMPOSITES

A major portion of modern plastics are polymer composites produced by reinforcement of polymers with a second organic or inorganic phase. The development of nylon-layer silicate nanocomposites at Toyota Inc. was probably the most important breakthrough in the field of polymer nanocomposites, which demonstrated a doubling of tensile modulus and strength without sacrificing impact resistance [1]. Moreover, the heat distortion temperature increases by up to 100 ^{0}C, which makes the nanocomposites useful for high temperature environments. Besides their improved properties, these nanocomposite materials can also be easily extruded or molded in the desired shape. Since high degrees of stiffness and strength are achieved with less dense inorganic material, the nanocomposites are much lighter compared to conventional polymer composites. In addition, the combination of excellent barrier and mechanical properties of nanocomposites may eliminate the need for a multipolymer layer design in packaging materials, enabling greater recycling of food and beverage packaging. There has been a significant development in the field of polymer nanocomposites with varying polymer matrices and inorganic nanoparticles. But, the combination of enhanced modulus, strength and toughness is a characteristic of only a fraction of polymer nanocomposites reported to date [2].

The mechanical and thermal properties of inorganic/organic nanocomposites are expected to be considerably improved after incorporating the inorganic material in the matrix. However, to get improved properties the inorganic phase must be efficiently dispersed in the matrix. The task of dispersing the inorganic material in the matrix is difficult, because the inorganic particles have a tendency to form agglomerates. Hence, as a remedy to the problem of agglomeration, use of surfactants and modification of the particle surface have been reported [63,64]. The synthesis of PMMA/clay nanocomposites via emulsion and *in situ* polymerization with 10% w/w clay montmorillonite modified with zwitterionic surfactant is also reported [48-52].

1.1.1. The Sol-Gel Process.
Aerogels are porous materials with very high internal void space. In the present work aerogels are prepared by low temperature

traditional sol-gel chemistry and thereafter drying of the resulting wet-gels using the supercritical fluid drying method. The gelation takes place by a process which involves formation of M-OH-M or M-O-M bridges between the metallic atoms M of the precursor molecules. In the present work, precursor molecules of silica were used to synthesize the aerogels. Hence the aerogels have a three dimensional network with silica as the backbone. The gelation process is equivalent to the polymerization process which occurs by formation of direct bonds between the carbon atoms of organic precursors [3,4]. The reactions of a typical silica sol-gel process are shown in Scheme 1.1 and the sol-gel processing of aerogels is illustrated in Figure 1.1.

Scheme 1.1 The reactions of a typical silica sol-gel process
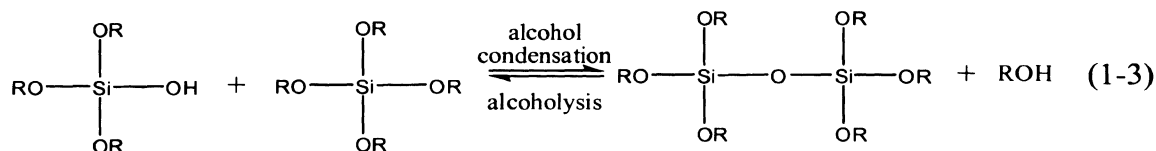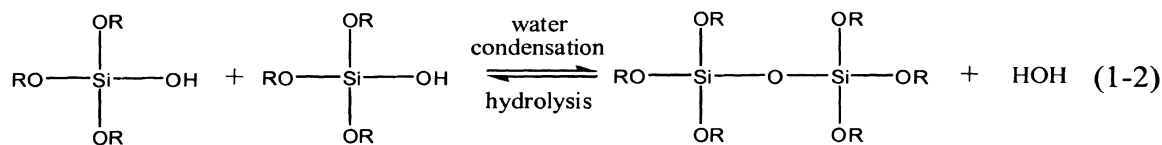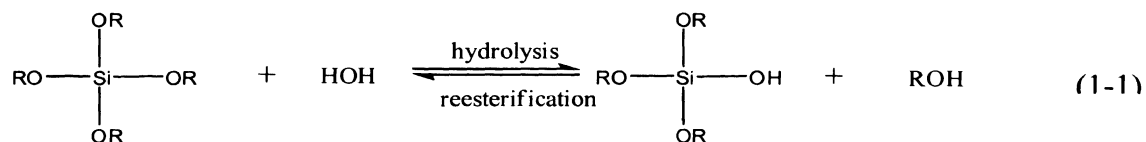
1.1.2. Polymer Crosslinked Aerogels. Silica is one of the most important fillers used to reinforce plastics and significant efforts have been devoted on making the organic (polymer) and inorganic (silica) phases compatible. Silica aerogel is a nanoporous low bulk-density, chemically inert form of silica with low thermal conductivity, excellent acoustic insulation properties. In spite of those excellent properties, the low strength of the native aerogels restricts their use for practical applications. Crosslinking silica

aerogels with polymers is a promising approach to enhance their mechanical strength. This was first achieved by utilizing the hydroxyl functionality on the surface of silica nanoparticles as a template for the conformal accumulation and polymerization of isocyanates. It was shown that the resulting isocyanate crosslinked aerogels could be up to 3 times more dense, but 300 times stronger in terms of the force it takes to break them in a three-point bending test [4].

```
┌─────────────────────────┐
│  Precursor(s), solvent(s),│
│   Water and Catalyst     │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│        Gelation          │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│         Aging            │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│        Washing           │
│   (solvent exchange      │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│     Drying process       │
│    (using SCF CO2        │
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│        Aerogel           │
└─────────────────────────┘
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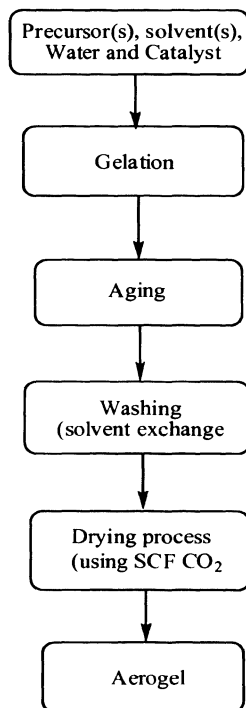
Figure 1.1 Sol-gel processing for aerogel formation

1.2. INTRODUCTION TO POLYIMIDES

Polyimides comprise a class of high performance polymeric materials with exceptionally high thermo-oxidative stability. Aromatic polyimides primarily consist of heterocyclic imide and aryl groups, linked sequentially by simple atoms or groups, as shown in Figure 1.2.

KAPTON™ repeat unit
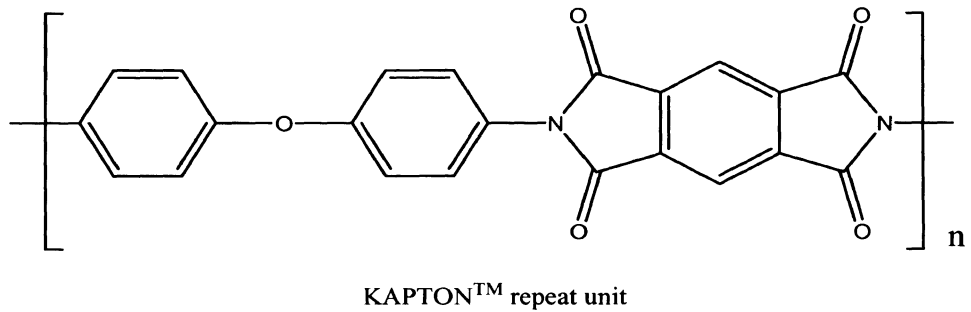
Figure 1.2 Chemical structure of a typical polyimide

The rigid structure of aromatic polyimides provides high glass transition temperatures (T_g >300 °C) and gives the polyimides good mechanical strength and high modulus. The linearity and stiffness of the backbone allow for molecular ordering. In turn, this phenomenon results in lower coefficients of thermal expansion (CTE) than those for thermoplastic polymers having coiled, flexible chains. Additionally, the morphology of long, linear ordered chains provides solvent resistance to the aromatic polyimides [45].

Polyimides are obtained in a two-step synthetic route (see Scheme 1.2). The first step is addition of an aromatic diamine to a dianhydride of a tetracarboxylic acid at room temperature in a strongly polar aprotic solvent (DMF, DMAc or NMP) to give a polyamic acid. The second step is polycondensation at 150-300 °C. The solvent evaporates and ring closure with intramolecular elimination of water gives the polyimide [15]. Condensation polyimides find major uses in thin films in electronics, wire coatings and polyimide tapes.

Scheme 1.2 Classic two-step polyimide synthesis

Dianhydride   Diamine

Step 1

Polyamic acid

Step 2
- H$_2$O
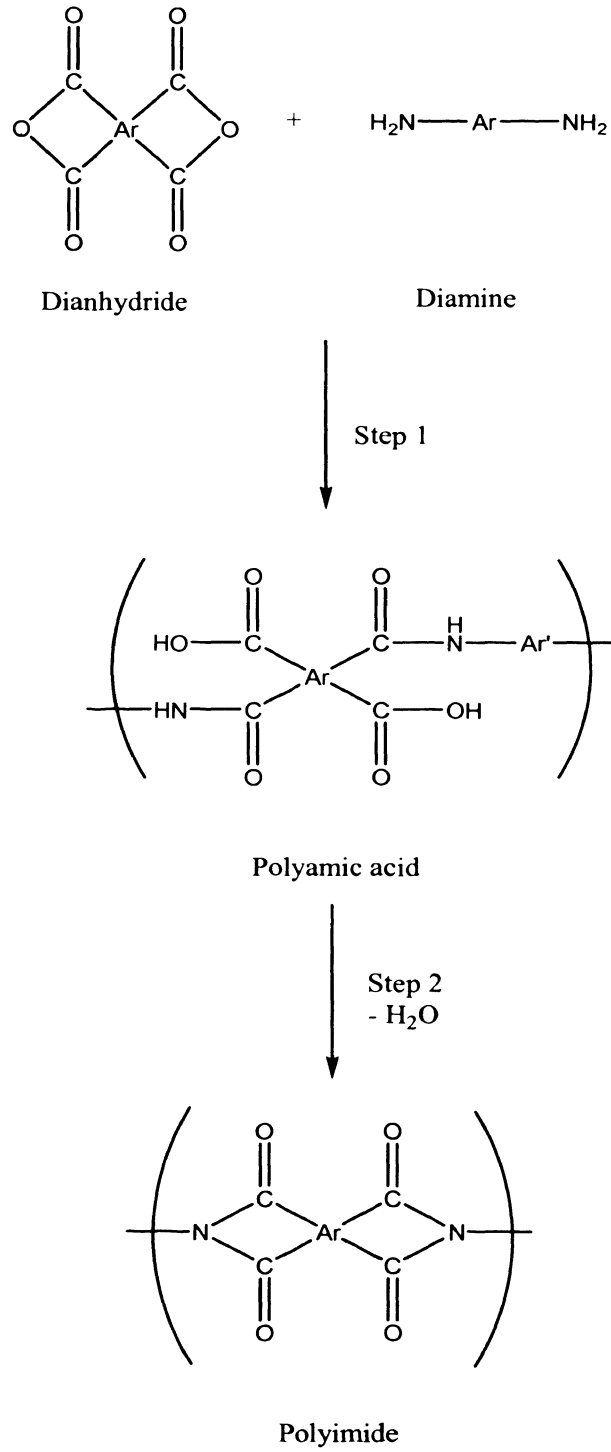
Polyimide

Some common dianhydrides and diamines used for the synthesis off polyimides are given below.
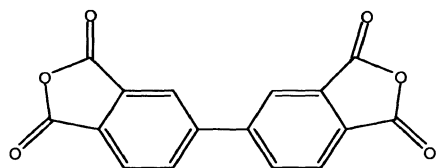
3.3'-4.4'-biphenyltetracarboxylic dianhydride (BPDA)   2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)
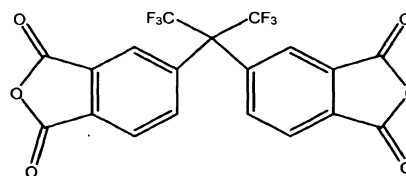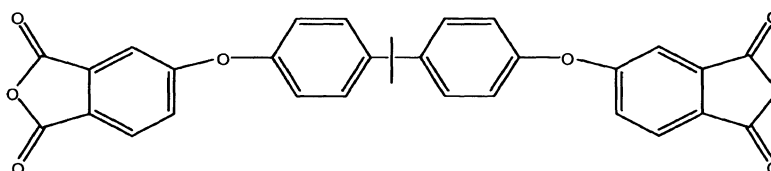
2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA)
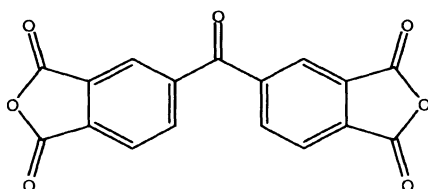
benzophenonetetracarboxylic dianhydride (BTDA)
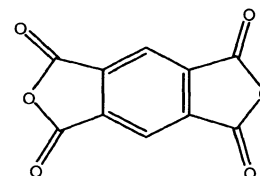
pyromellitic dianhydride (PMDA)
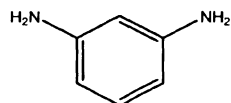
m-phenylene diamine (m-PDA)   4,4'-diaminophenyl sulfone (4,4'-DDS)   p-phenylene diamine (p-PDA)
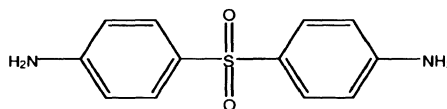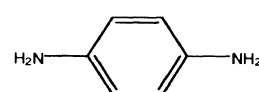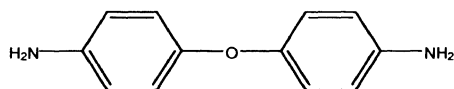
4,4'-oxydianiline (4,4'-ODA)   methylene dianiline (MDA)
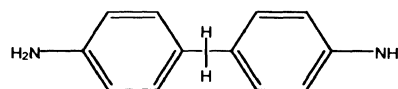
1.2.1. Endcapped Addition Polyimides. In spite of having excellent mechanical and thermal properties, the condensation polyimides did not gain popularity due to processability problems. The evolution of condensation byproducts (H_2O) and the low flow of the system render it difficult to process. As a result addition-curing polyimides were investigated in the early 1970's in an attempt to improve the processability of condensation polyimides without adversely affecting their stability and high-temperature performance. The development of "Polymerization of Monomer Reactant" (PMR) family of polyimides is the most notable progress in this area. PMR-15 was developed at NASA Lewis Research Center. For PMR-15, reinforcement fibers are impregnated with a solution of the dialkyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE), methylene dianiline (MDA), and the monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) in a low boiling solvent, typically methanol or ethanol. In the first step of this process, these monomers undergo imidization at temperature around 200 °C to yield short chain norbornyl end-capped polyimide oligomers with a molecular weight of 1500 g/mol. At temperatures above 300 °C, these oligomers undergo a cross-linking reaction involving the norbornyl endcap (see Scheme 1.3) [9-15].

Scheme 1.3 Preparation of PMR-15
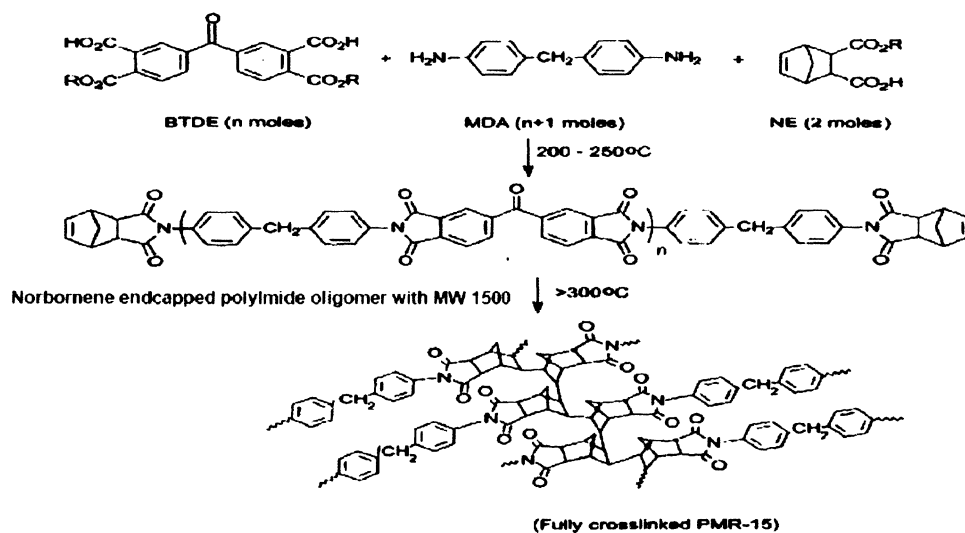
1.2.2. Involving Polyimides in the Sol-Gel Process. Hybrid materials offer the possibility of combining the advantages and overcoming the disadvantages of the individual components. Polyimide-silica hybrid films have been synthesized for applications in high temperature optoelectronic devices [3] Polyimide coated silica nanocomposites obtained by the sol-gel route are also reported [4]. The sol-gel process has been used as a chemical route to synthesize ceramics with high purity and controlled microstructure. The sol-gel reaction has also been used for synthesis of organic-inorganic hybrid materials in conjunction with polymeric materials. The process occurs in two steps, the first step being the hydrolysis of a metal alkoxide and the second the polycondensation of the hydrolysis products. The method allows one to combine the superior thermal stability, high refractive index, low thermal expansion coefficient with the superior toughness, ductility and processability of polymers [13,14]. Introduction of chemical bonds between the polyimide and silica should improve their compatibility and further improve their mechanical properties. Polyimide-silica hybrids can possibly prove to be good materials for high temperature applications.

1.3. SILICA/PMMA COMPOSITES

1.3.1. PMMA Composites. PMMA is an acronym for poly(methyl methacrylate), which is the product of the addition polymerization of methyl methacrylate monomer. PMMA is a material of interest due to its exceptional optical clarity, very good weatherability, impact resistance (can be machined) and excellent dimensional stability due to rigid polymer chains ($T_g = 105$ °C) [45]. The formation of PMMA occurs according to Scheme 1.4.

The combination of polymers and inorganic solid particles is of great interest for a number of existing and potential applications. Generally, the preparation of composites involves mechanical mixing of the polymer and the inorganic component to obtain a compound which can be molded in desired shapes by conventional extrusion and injection molding techniques. The composites consist of two phases viz. the matrix and the filler. The matrix holds the filler together and absorbs energy when under stress. The filler adds strength to the composite. PMMA is an important polymer for composites research due to its various desirable properties enumerated above and its compatibility

with numerous inorganic materials to form composites with improved mechanical and thermal properties [46-50].

Scheme 1.4 Free radical polymerization of MMA to give PMMA
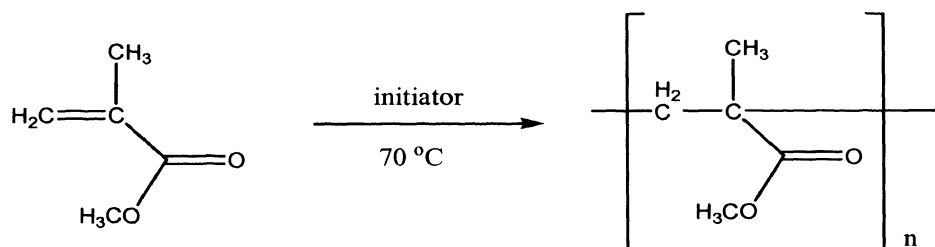
1.3.2. A Novel Method of Preparation of Silica/PMMA Composites. In the present study, monolithic, dense composites of poly(methyl methacrylate) and silica were prepared by using either silica gels or by dispersing silica in particulate form. In-situ bulk polymerization using a silica surface bound derivative of 2,2'-azobis (isobutyronitrile) called "silica-AIBN" was carried out in all the cases. Silica-AIBN cross-linking Agent (Compound 1) is an alkoxy derivative of 2,2'azobis(isobutyronitrile) and it was developed and synthesized in our laboratory [56].

The present work describes two methods for synthesis of polymer nanocomposites. One method is to incorporate polyimides in the sol-gel process to synthesize polyimide crosslinked aerogels with covalently bonded polyimide to the silica network. Two types of polyimide crosslinked aerogels were prepared having different mole ratios of the monomers.

Another method discusses synthesis of silica-PMMA nanocomposites prepared by *in situ* polymerization of MMA in the pores of silica gels using an alkoxy derivative of the 2,2'-azobis(isobutyronitrile) free radical initiator (shown in Figure 1.3) covalently covalently bonded to the silica surface. In the present work we have reported a novel method of preparation of silica-PMMA composites by circumventing the need for dispersing silica in PMMA. Three types of silica-PMMA composites with various silica contents were made by preparing gels with "silica-AIBN" initiator and thereafter

crosslinking them in MMA to get PMMA filled silica monoliths. Other type of composites were prepared by conventional mechanical dispersion of silica particles in PMMA pre-polymer remaining after synthesis of the former type of silica-PMMA composites. These two types of composites were compared to neat PMMA, also synthesized in our laboratory using the PMMA pre-polymer. The polymer nanocomposites are prepared in the quest to get materials with better mechanical and thermal properties than the polymers alone.
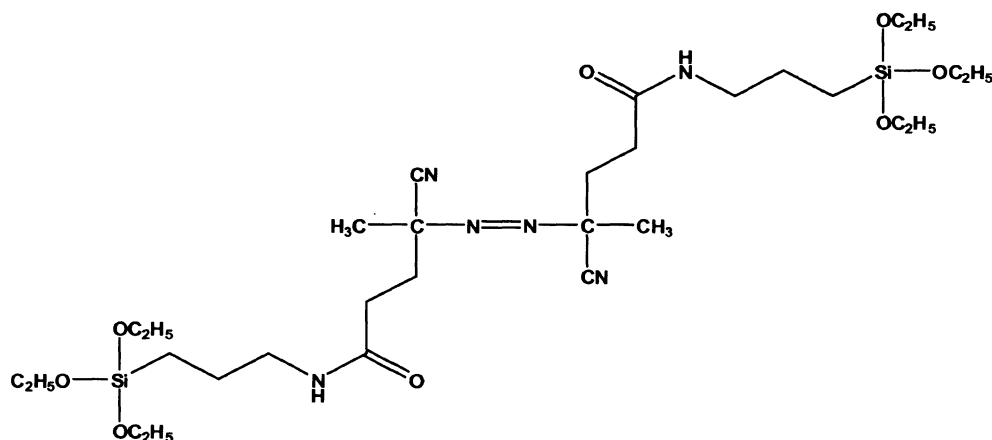
Figure 1.3. Chemical structure of silica-AIBN (compound 1):

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PAPER I

IN SITU POLYMERIZATION OF AMINOPROPYLTRIETHOXY-SILANE-ENDCAPPED POLYAMIC ACID ON THE MICROSTRUCTURE OF BASE-CATALYZED SILICA AEROGELS TO DERIVE POLYIMIDE CROSSLINKED SILICA AEROGELS WITH IMPROVED THERMAL STABILITY

1.   ABSTRACT

In this study, two types of polyimide-silica hybrid aerogels, ABM-PI 2:2:1 and ABM-PI 2:3:2, were synthesized by combining a sol-gel process with a silica surface-bound polyamic acid formation process, followed by heating in order to turn the polyamic acid into a polyimide covalently bonded to the silica surface. The hybrid aerogels were prepared by using 3-aminopropyltriethoxysilane (APTES) endcapped polyamic acid and tetramethoxysilane (TMOS) as silica precursors. TGA suggests that the two materials have good thermal stability. SEM indicates that ABM-PI 2:2:1 aerogels have a more open pore structure in comparison to ABM-PI 2:3:2. The skeletal densities of these hybrid aerogels are in the range of 1.60 to 1.68 g/cc. The BET surface area studies suggest that the ABM-PI 2:3:2 aerogels have a higher surface area than the ABM-PI 2:2:1 aerogels. N_2 adsorption isotherms confirm the mesoporous structure of both types of polyimide crosslinked aerogels. These hybrid aerogels have potential applications in thermal insulation.

2.   INTRODUCTION

Polyimides are a class of high-temperature/high performance polymers which are widely used for electronics and aerospace applications involving exposure to high temperatures. They are heterocyclic polymers that are attractive because of their outstanding mechanical and dielectric properties. Though polyimides find use in a number of applications, further development is required to meet the increasing demands on high performance materials. There is a need to produce composite materials that are

cost-effective, and can withstand temperatures above 300 °C for extended periods of time. Polyimides are commonly synthesized from dianhydrides and diamines in a two-stage process [25,26]. A soluble, high molecular weight polyamic acid is synthesized at ambient temperatures in the first stage, and is subsequently converted to fully crosslinked polyimide in the second stage.

Over the last two decades, the popularity of the sol-gel process has increased with regard to creation of novel inorganic-organic composite (hybrid) materials. The sol gel method can be used to generate reinforcing particles within a polymer matrix. Moreover, these hybrid sol-gel materials can provide unique properties which cannot be achieved by other materials [1,2]. The sol-gel method, due to its inexpensive nature, simple chemistry and compatibility with various polymeric materials presents a vista for development of hybrid materials which are of lower cost and possess better properties than the polymer alone.

A very common precursor in the sol gel process is tetramethoxysilane (TMOS). The tetra-functional nature of TMOS helps in achieving a highly crosslinked structure with Si-O-Si linkages in the backbone. In the inorganic/polymer hybrid materials the goal is to carry out the sol-gel reaction in the presence of the polyimide precursors. The polymeric component is provided with suitable functionality in order to be able to bond with the inorganic phase into a hybrid material that is classified as particle reinforced polymer [3-6].

The present investigation is based on the idea of combining the desirable materials properties of polyimides with those of silica aerogels to obtain crosslinked silica aerogels having chemically bonded silica and polyimides. To make the polyamic acid compatible with the sol, to avoid unnecessary side reactions and to chemically link polyimide on the sol-gel skeletal nanoparticles the polyamic acid was formulated with end-caps of 3-aminopropyltriethoxysilane [25-29], which are able to participate in sol-gel reactions with TMOS. This results in highly crosslinked three-dimensional networks with covalently bonded silica and polyimide moieties. In this study, silica/polyimide hybrid aerogels with two different mole ratios of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and methylene dianiline (MDA) were prepared. APTES was used as an endcapping agent in both cases. The mole ratios used were 2:2:1 and 2:3:2

(APTES:BTDA:MDA), and the resulting gels are named ABM-PI 2:2:1 and ABM-PI 2:3:2, respectively. Changing the mole ratios of BTDA and MDA changes the length of the polyimide tethers. The resulting aerogels were studied by a variety of methods.

3.   EXPERIMENTAL SECTION

Materials. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA, high purity, Chriskev Company) was dried under vacuum for 24 h at 160 °C before use. Methylene dianiline (MDA, 97%, Acros) was dried under vacuum at room temperature for 24 h. 3-Aminopropyltriethoxysilane (APTES, 99%, Acros), tetramethoxysilane (TMOS, 99%, Acros), 1-methyl 2-pyrollidinone (NMP, 99%, Aldrich), aqueous ammonia (NH_4OH, 28%, Aldrich) were used as received.

Reaction of BTDA and APTES. The 13C NMR spectra of the BTDA and APTES reaction mixture is illustrated in Figure 1.   The spectra were obtained immediately after mixing of BTDA and APTES in equimolar amount. It was observed that the reaction happens almost instantaneously at room temperature.

Preparation of Polyimide Crosslinked Aerogels. The flowchart for preparation of polyimide aerogels is illustrated in Figure 2. ABM-PI 2:2:1 and ABM-PI 2:3:2 aerogels were synthesized similarly, while the only difference was the mole ratios of BTDA and MDA. MDA was dissolved in 50 mL NMP. BTDA was added portionwise to the resultant solution over a period of 30 min under continuous stirring. Once a clear yellow solution of the polyamic acid was obtained, APTES was added and the solution was stirred for 1 h. This yields polyamic acid capped on both ends with APTES. To this silica/polyamic acid solution, TMOS was added and stirred continuously for 15 min. The sol was cooled in an ice bath. A solution of NMP, water and aqueous ammonia was prepared separately and was added to the silica/polyamic acid solution.

The molar ratio of H_2O and the alkoxy functional group of TMOS and APTES was kept at 1:1. The mixture was stirred for 1 min and transferred into plastic molds having 20 mm internal diameter. The gelation took place in 3-5 min; the gels were aged in their molds for 24 h. After aging, gels were removed from their molds and were transferred to glass vials just able to contain the gels. The gels are covered with NMP and

the vials with the gels covered with NMP are heated in a closed bottle at 180 °C for 24 h. At the end of the period gels were removed from the vials and were solvent-exchanged with acetone by washing for four times in 8 h intervals. The gels were then dried using supercritical fluid (SCF) CO_2 to afford polyimide crosslinked aerogels. The polyimide crosslinked aerogels are illustrated in Figure 3.
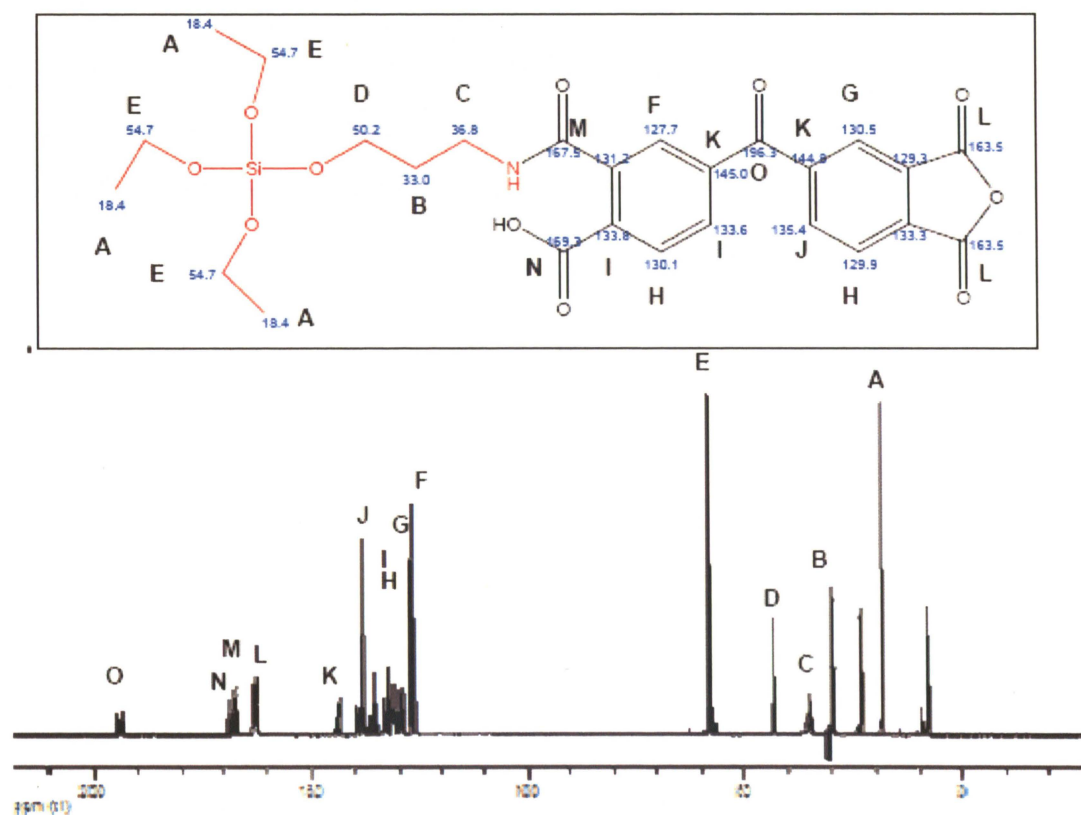
Figure 1 [13]C NMR spectrum in DMSO-*d6* of the reaction mixture of BTDA and APTES

MDA in NMP

Stirring 0.5 h

← **BTDA portionwise**

Stirring 0.5 h

← **APTES**

Stirring 1 h

APTES capped Polyamic acid —— **TMOS**

Mixing for 15 min

NMP, H$_2$O, NH$_4$OH

Mixing for 1 min

Molds

Aging for 24 h

Gels heated at 180 oC

4 Acetone washes

SCF drying
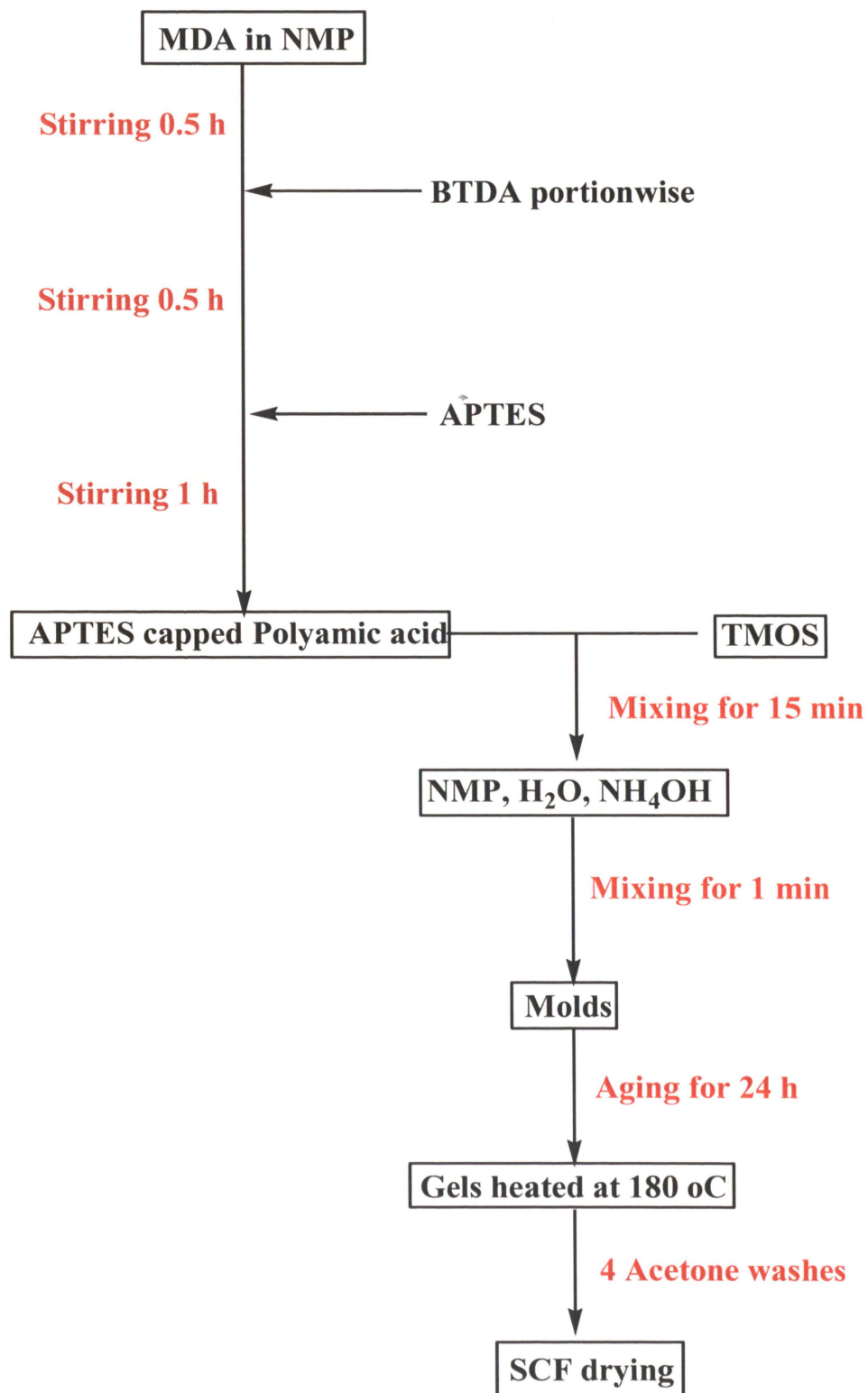
Figure 2 Preparation of polyimide crosslinked aerogels
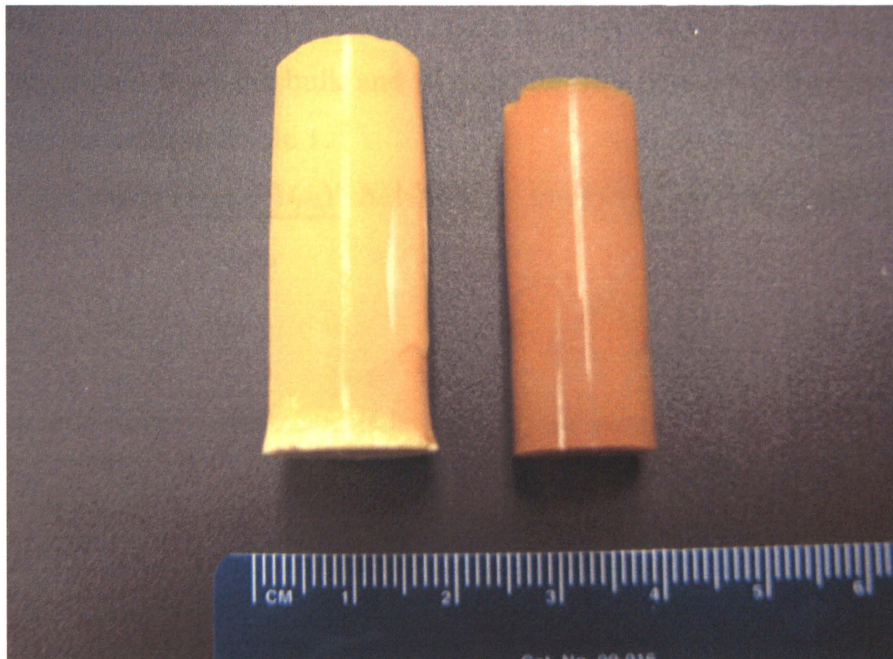
Figure 3 Polyimide aerogels A: ABM-PI 2:2:1; B: ABM-PI 2:3:3 (ABM-PI: APTES, BTDA, MDA polyimide)

Characterization. The aerogels were characterized for skeletal density on a Micromeritics AccupycII 1340 pycnometer. Bulk densities were calculated from the weight and physical dimensions of the samples.The mid IR spectra of the prepared polyimide crosslinked aerogels were recorded with NICOLET NEXUS 470 FT-IR. The SEM micrographs were taken with a HITACHI S 4700 FE-SEM which is a field emission type microscope. Thermogravimetric analysis (TGA) was carried out under air flow using a NETZSCH STA 409C/CD thermogravimetric analyzer. The BET surface area was measured using a Quantachrome Autosorb-1 Surface Area/Pore Distribution Analyzer. Solid state NMR was carried out on a Bruker Avance 300 Spectrometer.

4.   RESULTS AND DISCUSSION

Density Data. The bulk density and skeletal density data are presented in Table 1. The bulk density of ABM-PI 2:3:2 is higher than that for ABM-PI 2:2:1. On the other hand, the skeletal density of ABM-PI 2:2:1 is higher than that of ABM-PI 2:3:2 as

expected from the formulation for the relative silica and polymer content. The porosity of the samples is calculated from the bulk and skeletal density data according to eq. 1 and the results are also included in Table 1.

$$\Pi = \frac{(1/\rho_b - 1/\rho_s)}{1/\rho_b} \times 100\% \tag{1}$$

Table 1. Density data for polyimide aerogels

Material	Diameter (cm)	Bulk density, ρ_b (g/cc)	Skeletal density, ρ_s (g/cc)
ABM-PI 2:2:1	1.716 ± 0.002	0.234 ± 0.003	1.659 ± 0.004
ABM-PI 2:3:2	1.318 ± 0.003	0.481 ± 0.002	1.656 ± 0.003

Note: 20 mm inner diameter molds were used.

FT-IR Spectroscopy. Figure 4 shows the FTIR spectra of prepared polyimide crosslinked aerogels 2:2:1 and 2:3:2 (APTES: BTDA: MDA). The characteristic absorption bands of the imide group are observed at 727, 1378, 1728 and 1776 cm^{-1} for both samples is shown in Figure 4. The absorption band between 1000-1100 cm^{-1} is for the three dimensional Si-O-Si network in the aerogels. The absorptions between 3200-3700 cm^{-1} are assigned to Si-OH formed as a result of the hydrolysis of alkoxy species. This band is dominant in the ABM-PI 2:2:1 type and smaller in theABM-PI 2:3:2 type of aerogels. This is due to the relative difference in the quantities of silica and polyimide in these aerogels.

Solid State NMR. Figure 5 shows the ^{13}C CPMAS NMR spectra of the polyimide crosslinked aerogels. The ^{13}C CPMAS NMR spectra show resonances due to residual methoxy and ethoxy groups between 0-50 ppm. The resonances from the aromatic rings from BTDA and MDA are observed between 100-150 ppm. Three different carbonyl peaks were observed. The peaks at 167 and 168 ppm correspond to the carbons joining the nitrogen of the imide. The peak at 194 corresponds to the carbonyl bridge of BTDA. Figure 6 shows the ^{29}Si CPMAS NMR spectra of the polyimide crosslinked aerogels. The ^{29}Si CPMAS NMR suggests the covalent nature of bonding between the silica and

polyimide. The resonances in the range of -125 to -75 ppm are assigned to Q^4 (-105 ppm), Q^3 (-95 ppm) and Q^2 (-85 ppm) silicon atoms from TMOS. This indicates that the silicon atoms form four, three and two Si-O-Si bridges, respectively. The silicon atoms from APTES are linked through two or three Si-O-Si bridges. This is evident from the T^3 and T^2 silicon observed at -60 and -59 ppm, respectively.
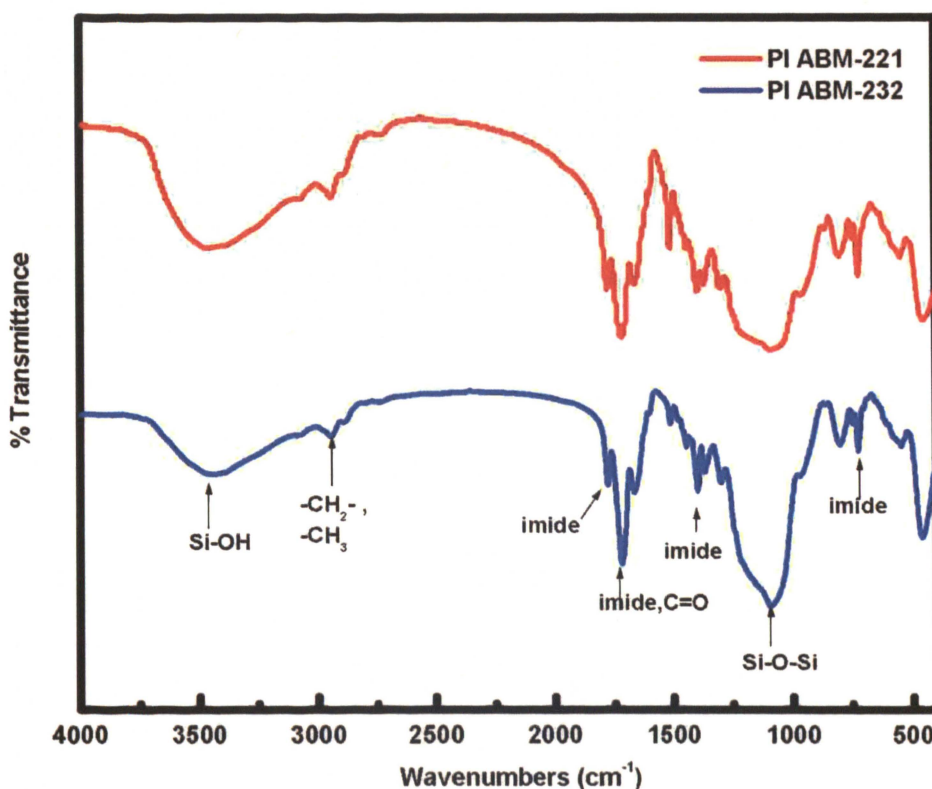
Figure 4 FTIR spectra of polyimide crosslinked aerogels ABM-PI 2:2:1 and ABM-PI 2:3:2

Scanning Electron Microscopy. Figures 7 and 8 show the FE-SEM micrographs of the two types of polyimide crosslinked aerogels of this study. It can be estimated from the micrograph that the silica particles are in the range of 15-20 nm in both types of aerogels. It can also be observed that the ABM-PI 2:2:1 type aerogels have a more porous structure of the two in agreement with results shown in Table 2.1.
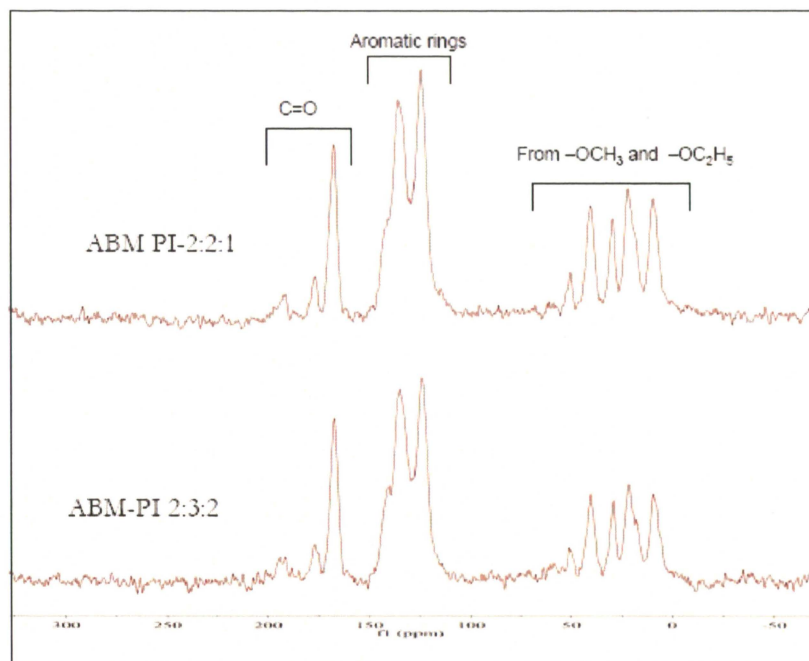
Figure 5 ^{13}C CPMAS NMR spectra of polyimide crosslinked aerogels
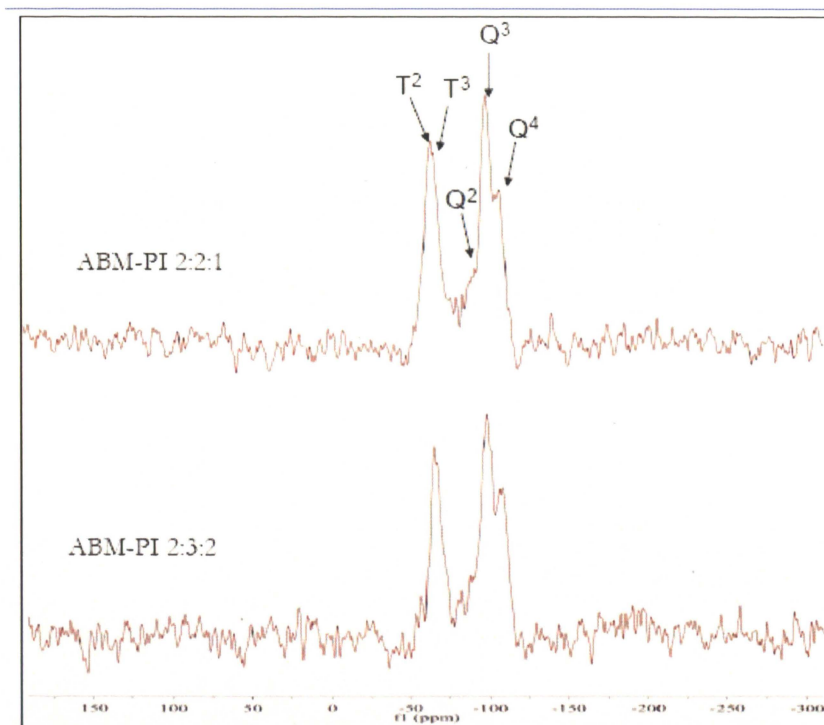
Figure 6 ^{29}Si CPMAS NMR spectra of polyimide crosslinked aerogels

S4700 10.0kV 6.0mm ×200k SE(M) 11/25/07   200nm
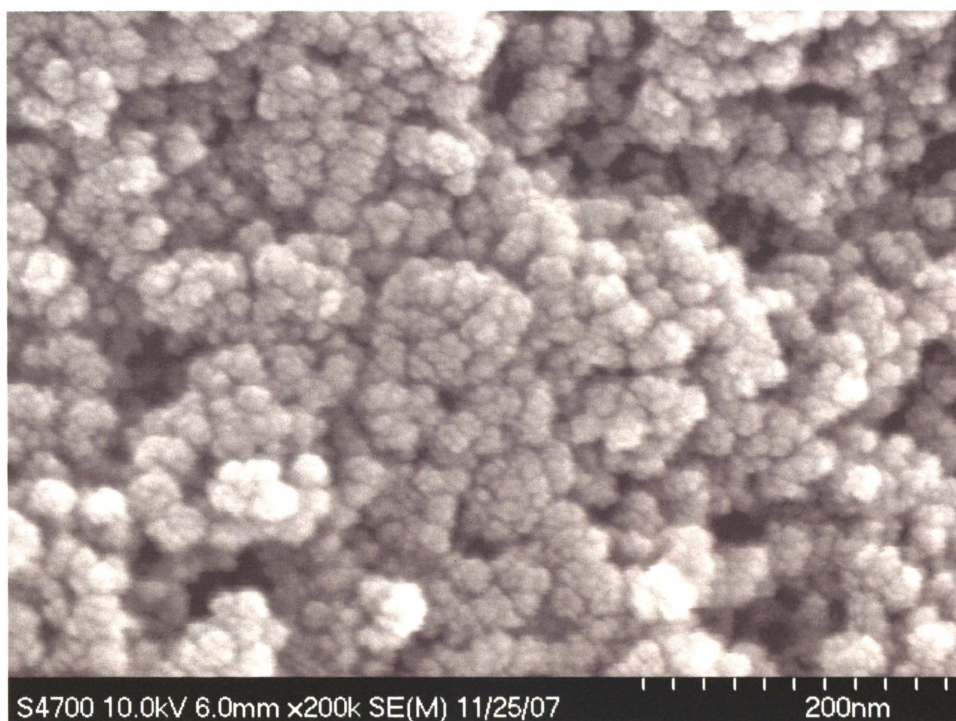
Figure 7 FE-SEM micrograph of ABM-PI 2:2:1 aerogels

S4700 10.0kV 7.8mm ×200k SE(M) 11/25/07   200nm
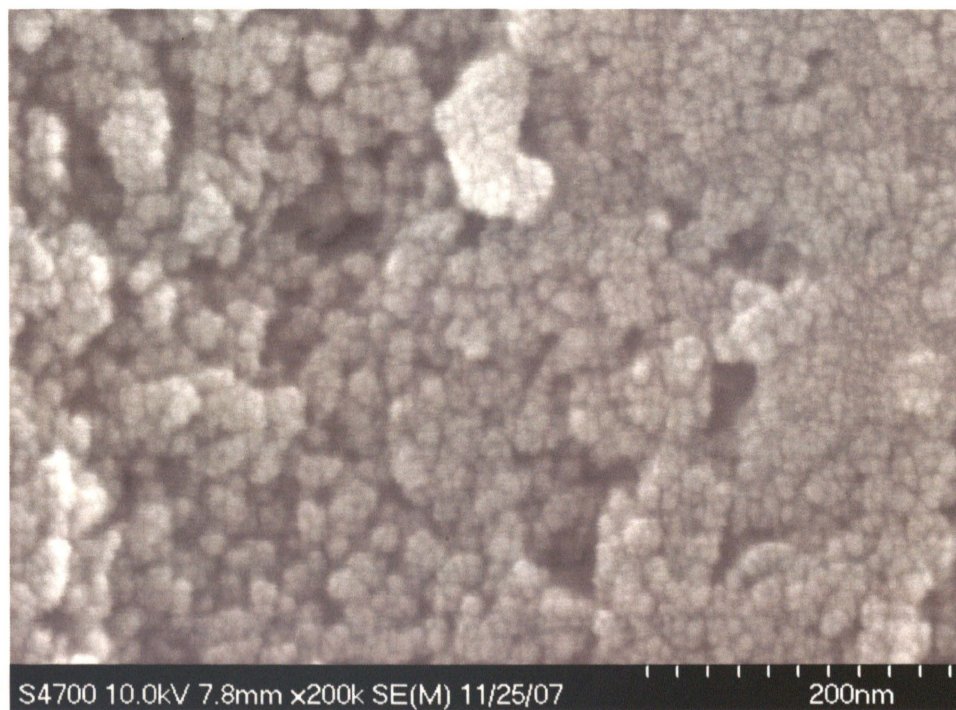
Figure 8 FE-SEM micrograph of ABM-PI 2:3:2 aerogels

Thermogravimetric Analysis. Figure 9 illustrates the TGA data for the polyimide crosslinked aerogels of this study at a heating rate of 20 $^\circ$C/min under nitrogen flow. The thermal decomposition temperature for both types of aerogels is higher than 450 $^\circ$C.
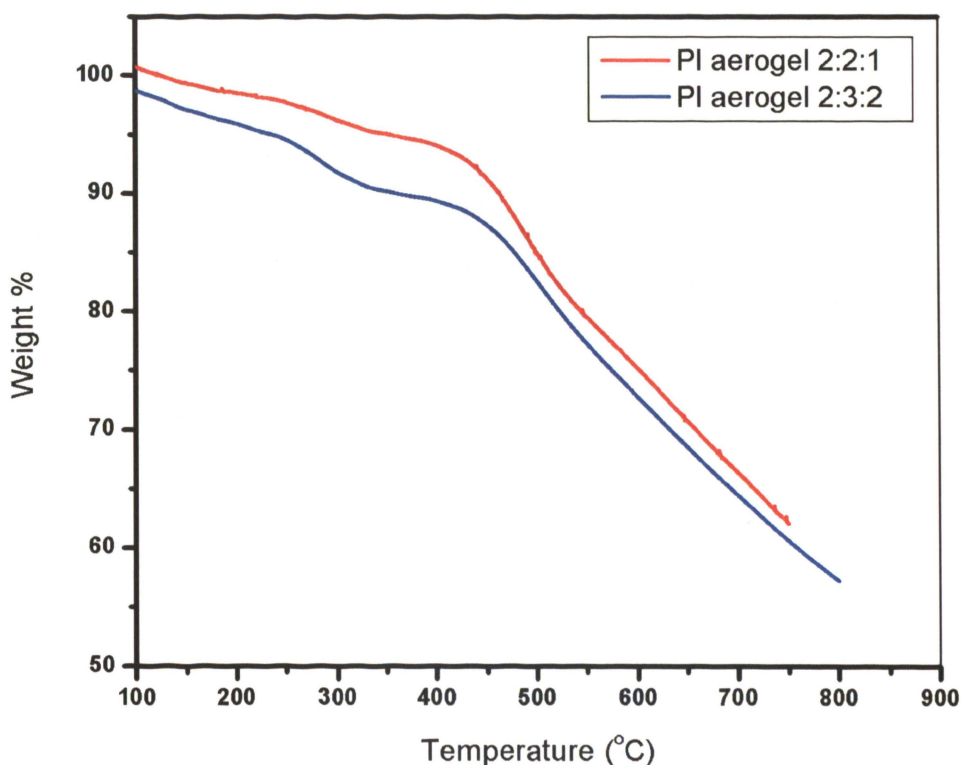
Figure 9 TGA curves for the polyimide crosslinked aerogels of this study

Nitrogen Sorption Porosimetry. Figures 10 and 11 illustrate the results for BET surface area of the aerogels. The shape of the BET isotherm for both the samples is characteristic for a mesoporous material with a Type IV isotherm and a H1 hysteresis loop. Table 2 summarizes results for both types of polyimide aerogels. The 2:3:2 type of polyimide aerogel has higher surface area than the 2:2:1 type. On the other hand, the ABM-PI 2:2:1 aerogels have higher pore volume and pore size than the ABM-PI 2:3:2 type.
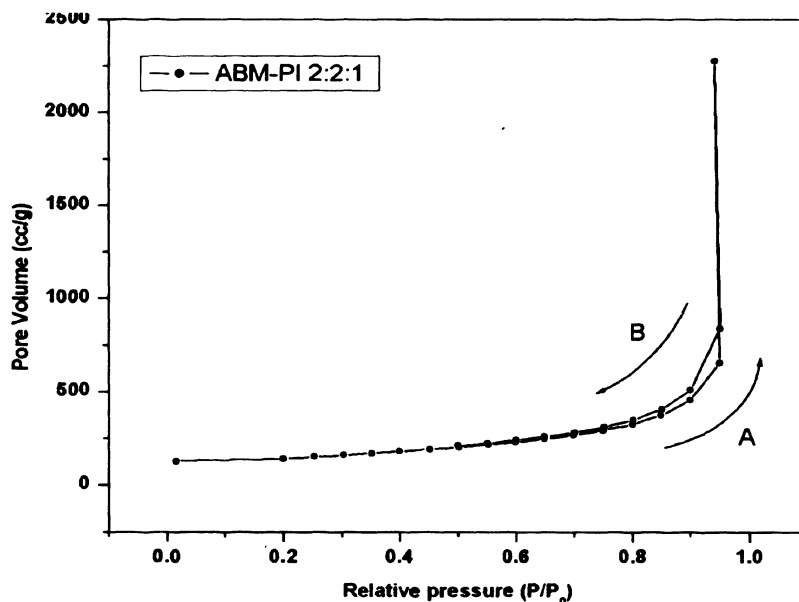
Figure 10 N_2 sorption isotherms of a ABM-PI 2:2:1 type polyimide aerogel sample. A: Adsorption; B: Desorption
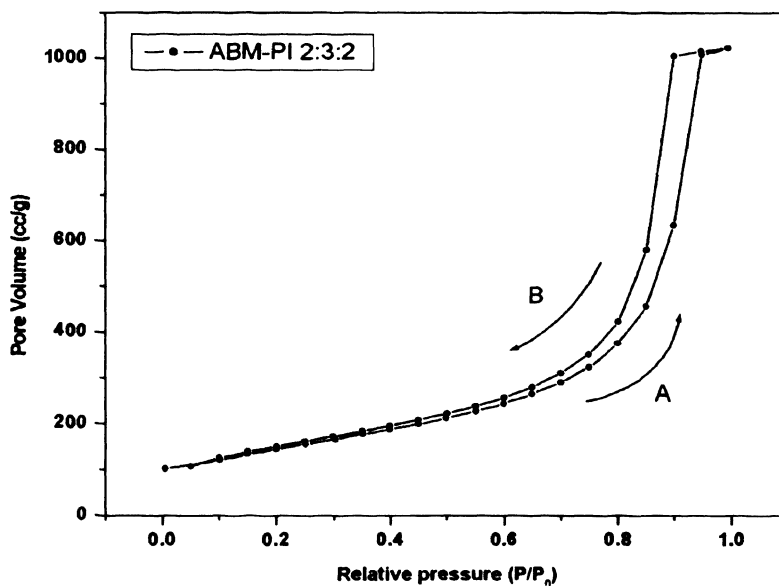
Figure 11 N_2 sorption isotherms of ABM-PI 2:3:2 type polyimide aerogel sample. A: Adsorption; B: Desorption

Table 2 Structural properties of polyimide aerogels

Sample	S_{BET} (m^2/g)	Pore Volume (cc/g)	Pore Size (nm)
ABM-PI 2:2:1	493.90	3.52	28.58
ABM-PI 2:3:2	530.30	1.58	11.96

5. CONCLUSIONS

In this study, polyimide crosslinked aerogels were successfully prepared by *in situ* polymerization of APTES endcapped polyamic acid by the sol-gel route. The prepared aerogels have polyimide coated silica nanoparticles. The presence of polyimide increases the thermal stability of the composite, while silica acts as filler which makes the composites cost-effective. The polyimide aerogels might be obtained in desired shapes and they have potential applications for manufacture of equipment requiring high thermal stability.

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PAPER II

.

SYNTHESIS OF COMPACT SILICA-PMMA COMPOSITES BY *IN SITU* POLYMERIZATION OF METHYL METHACRYLATE IN THE VOID SPACE OF MESOPOROUS SILICA BY EMPLOYING AN ALKOXY DERIVATIVE OF THE 2,2'- AZOBIS(ISOBUTYRONITRILE) FREE RADICAL INITIATOR COVALENTLY BONDED TO THE SILICA SURFACE

1.   ABSTRACT

Silica-PMMA composites have been synthesized by *in situ* polymerization of MMA in the void space of mesoporous silica gels by using an alkoxy derivative of 2,2'-azobis(isobutyronitrile) covalently bonded to the silica backbone. Composites with three different silica contents were synthesized and their thermal and mechanical properties were compared to neat PMMA and a composite prepared by conventional dispersion of silica particles in PMMA. The silica-PMMA composites were characterized by TGA, FT-IR, compression testing and solid state NMR. The PMMA composites exhibited considerable rise in thermal decomposition temperatures as compared to neat PMMA.

2.   INTRODUCTION

Inorganic particles-polymer composites have gained importance in the scientific and commercial fields due to their unique properties, which are not achievable by the polymers alone [1]. A considerable increase in performance with respect to thermal stability and mechanical strength can be achieved with the right combination of the inorganic particles and polymer. However, the inorganic particles have a tendency to form agglomerates and as a result they separate into discrete phases [2,3]. The problem of agglomeration is prominent when the size of the dispersed particles is under 50 nm; it is really difficult to get homogenous dispersion when the filling material is higher than 5% by weight [4]. This can have serious consequences on the mechanical and optical properties of the composites. To encounter the problem of agglomeration, polymer

composites have been reported to be synthesized by various routes. One way of making the nanoparticles compatible with the system is to change the functionality on the surface of the particles by chemical modification [1]. On the other hand, specific functional groups can be added to the polymer matrix by chemical modification [2]. Another method is to create nanoparticles within the polymer matrix by means of conventional sol-gel methods [3]. There are many reports on the preparation of inorganic particle-polymer composites by dispersion of nanoparticles in polymers [4-14], but there has been no report of synthesis of silica-PMMA composites by in situ polymerization of MMA in the void space of a mesoporous silica gel.

In the present study, monolithic and dense composites of poly(methyl methacrylate) and silica were prepared either by direct polymerization in the mesoporous void space of silica gels or by dispersing silica in particulate form in a the monomer undergoing polymerization. *In situ* bulk polymerization using a surface bound derivative of 2,2'-azobis(isobutyronitrile) called "silica-AIBN" was carried out in all cases. However, our focus is on our novel method of preparing silica-PMMA composites by circumventing the need for dispersion of silica in MMA. Three types of silica-PMMA composites with varying silica content were prepared by making gels incorporating the "silica-AIBN" initiator and thereafter crosslinking them in MMA to get PMMA-filled silica monoliths. Another type of composite was prepared by conventional mechanical dispersion of silica particles in PMMA pre-polymer remaining after synthesis of the former type of silica-PMMA composites. These two types of composites were compared to neat PMMA, also synthesized in our laboratory using the same PMMA pre-polymer.

3.   EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA) was purchased from Aldrich and was washed with a 5% (w/w) sodium hydroxide solution in water to remove the inhibitor, followed by distillation under reduced pressure. The silica gels were synthesized in lab by base catalyzed sol-gel route.   Tetramethoxysilane (TMOS, 99%, Acros), aqueous ammonia (NH$_4$OH, 28%, Aldrich) were used as received. The silane derivative of 2,2'-

azobis(isobutyronitrile), silica-AIBN (compound **1**) was synthesized in our laboratory [17]. Solvents were obtained from Fisher Scientific.

Preparation of PMMA/Si Composites. The different types of silica-PMMA composites made are illustrated in Figure 1. Syringes (Fisher Scientific, CAT no. 14-817-32, 25 ml, 20 mm inner diameter) were used as molds. The recipe given in Table 1 was scaled up to make 10 gels at a time with a volume of 20 mL each. "100% Silica" are gels obtained from 3.85 mL of silicate (TMOS in this case). Gelation takes place in 5-10 min at room temperature. The gels were aged for 24 h in their molds.

Figure 1 Silica-PMMA composites

Synthesis of PMMA filled silica-AIBN monolith termed "100% silica": (PMMA/Si-100%Si)

The Si-AIBN gels for making the PMMA/Si-100%Si composites were made according to the recipe given in Table 1.

Table 1. Recipe for making Si-AIBN gels with "100% silica"

	Vial A	Vial B
CH₃OH	4.5 ml (0.1112 moles)	4.5 ml (0.1112 moles)
TMOS	3.465 ml (0.0234 moles)	0
H₂O	0	1.5 ml (0.0833 moles)
NH₄OH	0	40 μl (0.00029 moles)
Silica-AIBN	0.8961 g (0.00130 moles)	0

Note: CH₃OH, HPLC grade supplied by Fisher scientific.

TMOS, 99% supplied by Acros organics.

H₂O, deionized.

NH₄OH 29.5% by weight supplied by Fisher Scientific.

Silica-AIBN synthesized in our laboratory [17].

The Si-AIBN gels were washed 5 times with acetone followed by 5 times with toluene. After the last washing with toluene, the gels were washed 5 times with inhibitor-free MMA. Glass jars of 100 mL supplied by Fisher Scientific, USA (catalogue number 06-414-1A) were used as containers for solvent exchange. In all washings, 100 mL of the wash solution was used. An interval of 24 h was given between the washings with occasional agitation. Finally, gels were heated in last MMA bath at 70 °C for 12 h. At the end of the 12 h period, MMA surrounding the gel became a viscous syrup; and the gel was enclosed in a shell of PMMA that extends beyond the original gel boundaries. The monolith was removed from the syrup, dried in the open air on the hood floor for 24 h and subsequently it was heated at 95 °C to complete the polymerization. The viscous syrup surrounding each monolith was saved for making other composites.

Synthesis of PMMA filled silica-AIBN monolith termed "50% silica":
(PMMA/Si-50%Si)

The PMMA/Si-50%Si composites were prepared by using the "Silica AIBN" gels made as per the recipe given in Table 2. The gels were further processed as described earlier.

Table 2. Recipe for making Si-AIBN gels with "50% silica"

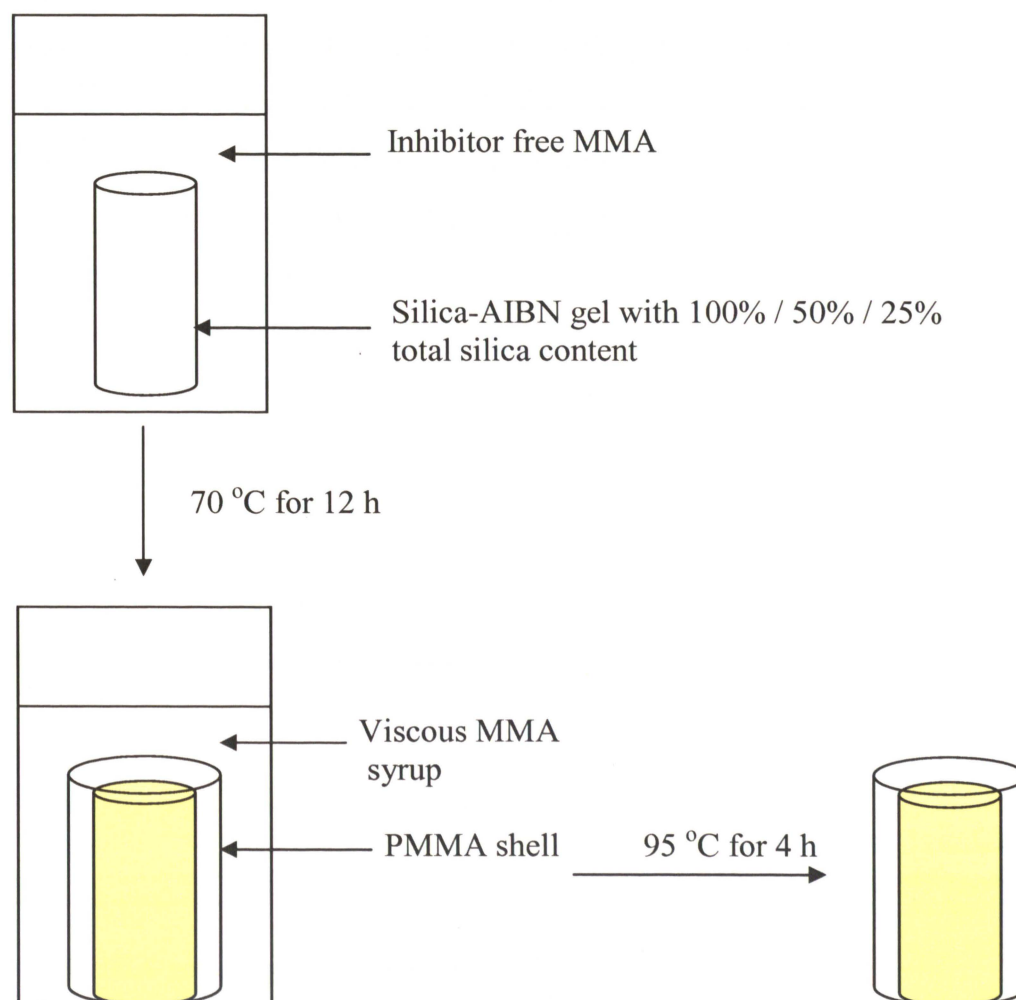|	Vial A	Vial B
CH₃OH	4.5 mL (0.1112 moles)	4.5 mL (0.1112 moles)
TMOS	1.732 mL (0.00117 moles)	0
H₂O	0	1.5 mL (0.0833 moles)
NH₄OH	0	40 μL (0.00029 moles)
Silica-AIBN	0.4480 g (0.00065 moles)	0

Synthesis of PMMA filled silica-AIBN monolith termed "25% silica":
(PMMA/Si-25%Si)

The PMMA/Si-25%Si composites were prepared by using the "Silica AIBN" gels made as per the recipe given in Table 3. The gels were further processed as described earlier.

Preparation of Neat PMMA. The neat PMMA monoliths were prepared according to the steps given in Figure 2. Several experiments were done to obtain PMMA monoliths. One approach was to heat the inhibitor-free MMA with AIBN (0.5, 0.29, 0.1, 0.05, 0.01 wt %) for 1 h at 70 °C. Bubble formation was noted, probably due to decomposition of AIBN. Another approach was to make a pre-polymer by heating MMA and AIBN (0.5, 0.29, 0.1, 0.05, 0.01 wt %) at 90 °C for 10 min. The viscous pre-polymer was then heated at 70 °C. A similar problem of bubbling was observed. As a third approach, inhibitor-free MMA was heated by itself to 130 °C for inducing thermal polymerization. Again bubbling was observed, this time probably due to boiling of MMA. The neat PMMA composites were prepared by heating the syrup obtained after synthesis of 100% Si composites. The syrup was heated for 48 h in 30 mL glass vial with 24.20 mm inner diameter at 70 °C. The lids were tightly closed during heating at 70 °C. Once a rubbery polymer was formed, the uncapped vials with the polymer inside were heated in tightly capped jars at 95 °C for 4 h to complete polymerization and hardening. This rendered clear, homogenous PMMA monoliths, which were obtained by breaking their glass molds.

Table 3. Recipe for making Si-AIBN gels with "25% silica"

	Vial A	Vial B
CH_3OH	4.5 mL (0.1112 moles)	4.5 ml (0.1112 moles)
TMOS	0.866 mL (0.00585 moles)	0
H_2O	0	1.5 mL (0.0833 moles)
NH_4OH	0	40 µL (0.00029 moles)
Silica-AIBN	0.224 g (.000325 moles)	0

Inhibitor free MMA

Silica-AIBN gel with 100% / 50% / 25% total silica content

70 °C for 12 h

Viscous MMA syrup

PMMA shell   95 °C for 4 h

Figure 2 Preparation of 100 %, 50 % and 25 % silica-PMMA composites

Preparation of PMMA Composites with Dispersed Silica Particles. The recipe given in Table 4 was scaled up to make ten gels with a volume of 20 mL each. The molds used for making those gels were 25 mL syringes with an inner diameter of 20 mm, supplied by FisherSci, USA. Gelation takes place in 5-10 min at room temperature. The gels were aged in their molds at room temperature for 24 h and washed 4 times with acetone at an interval of 24 h for each wash. Finally, gels were dried supercritically. The bulk density of the resulting aerogels was found out to be 0.234 ± 0.002 g/cc (average density of 5 aerogels) and they were crushed to fine powder in a SPEX 8000D Mixer/Mill supplied by SPEX Certiprep Group. The MMA-syrup obtained after synthesis of "100% Si" compo- sites was mixed with the silica fine powder. The total volume of the fine powder and MMA was kept at 20 mL. Vials (30 mL) with 24 mm inner diameter were used as molds. The mass of the fine powder used was equal to the mass of one silica aerogel, which was 2.391 ± 0.034 g (average mass of 5 aerogels). The MMA-syrup and the silica fine powder were mixed by shaking vigorously on a vortex mixer for effective wetting and dispersion. Subsequently, the resulting dispersion was heated at 75 °C in tightly closed vial for 48 h. The polymer was heated in the open mold placed in a tightly capped 100 mL jar at 95 °C for 4 h in a 100 mL tightly capped glass jar to complete polymerization.

Table 4 Recipe for making native silica aerogels

	Vial A	Vial B
CH_3OH	4.5 mL (0.1112 moles)	4.5 mL (0.1112 moles)
TMOS	3.465 mL (0.0234 moles)	0
H_2O	0	1.5 mL (0.0833 moles)
NH_4OH	0	40 μL (0.000297 moles)

Note: CH_3OH, HPLC grade supplied by Fisher scientific.

TMOS, 99% supplied by Acros organics.

H_2O, deionized

NH_4OH 29.5% by weight supplied by Fisher Scientific

MMA syrup

70 °C for 48 h

Rubbery PMMA
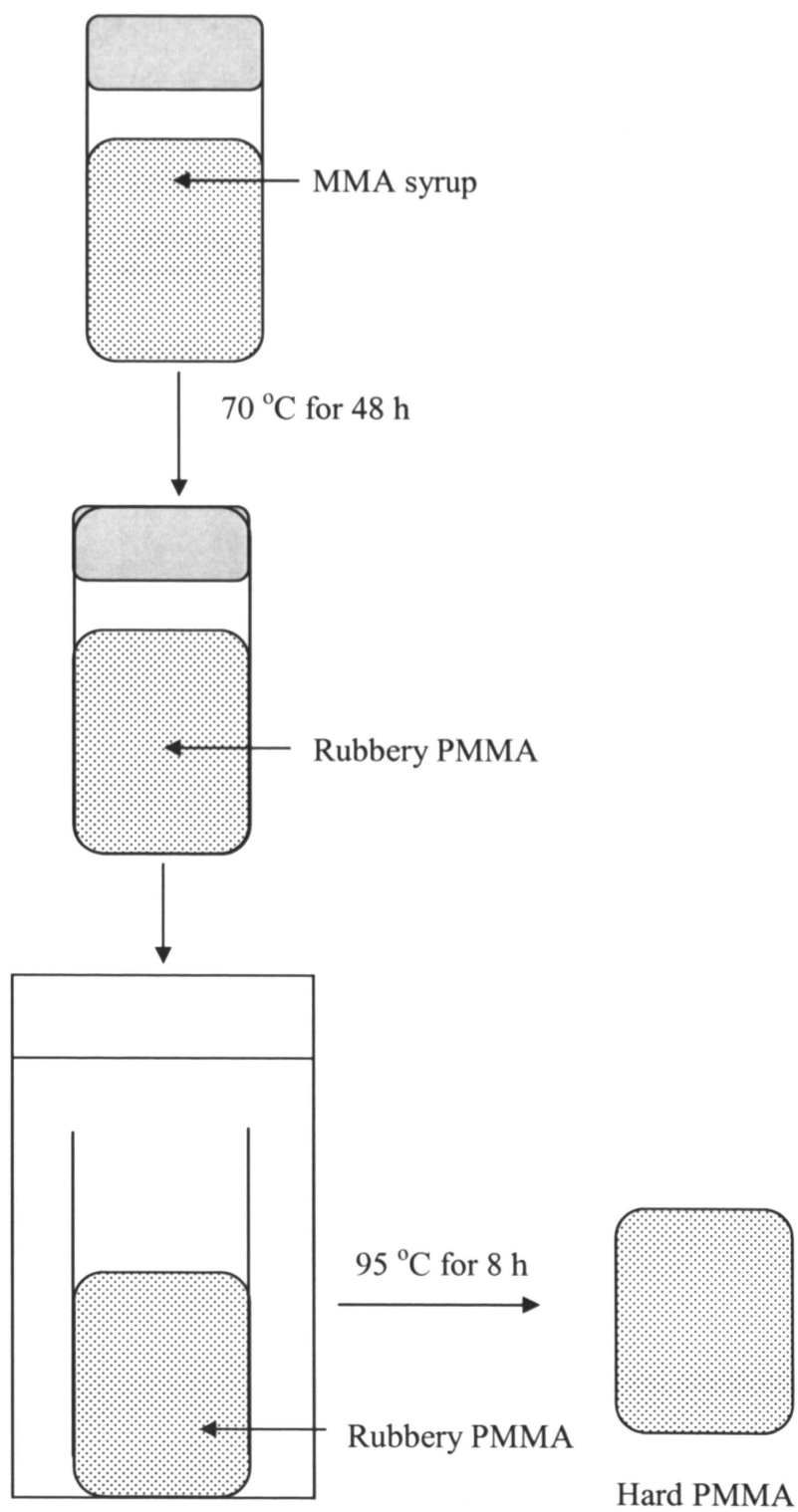
95 °C for 8 h

Rubbery PMMA

Hard PMMA

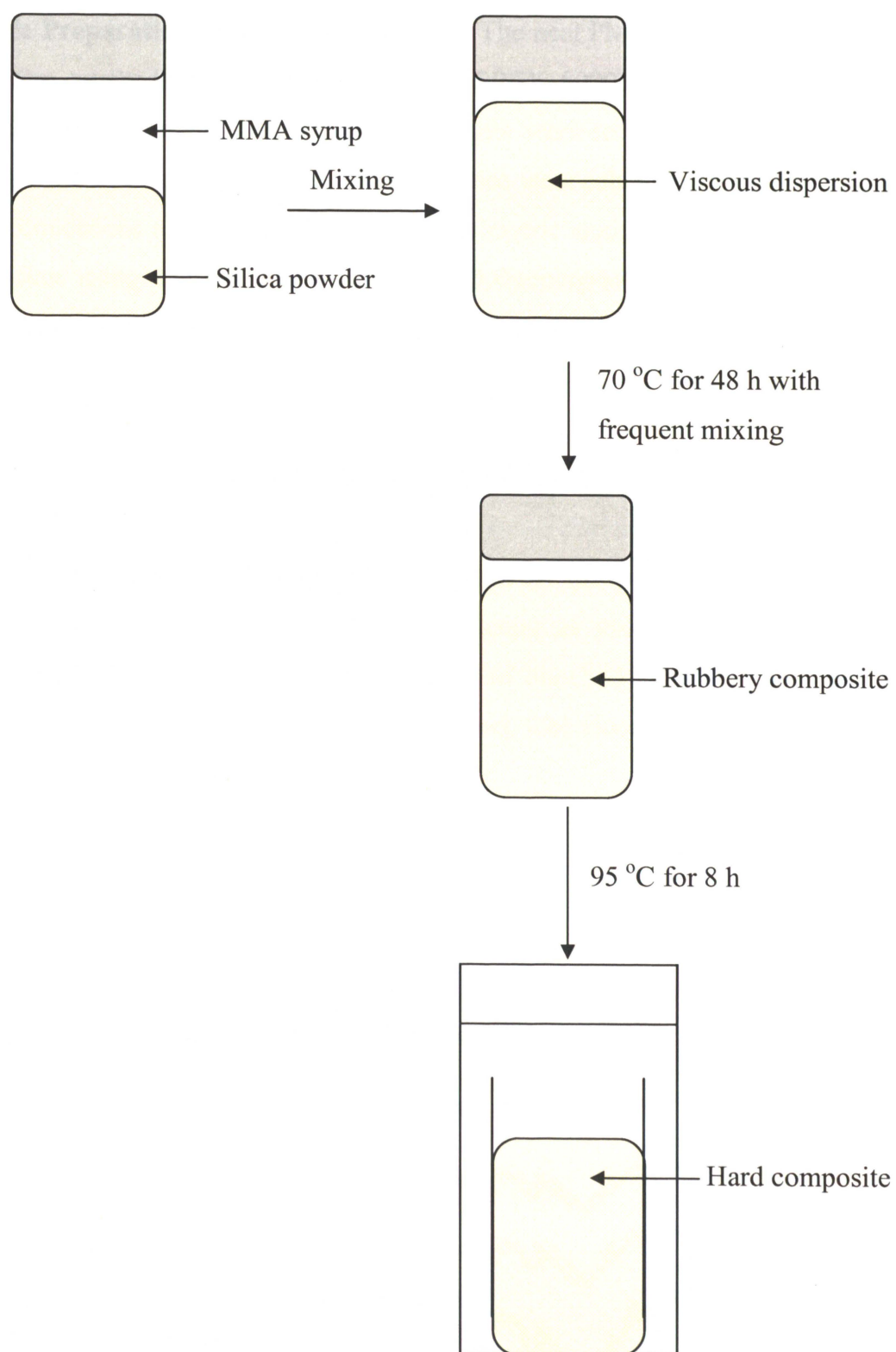**Figure 3** Preparation of neat PMMA monoliths

Figure 4 Preparation of silica-PMMA composite with silica particles dispersed in PMMA

Sample Preparation and Characterization. The neat PMMA and silica PMMA composites were crushed to fine powder using a SPEX 8000D Mixer/Mill. Mid IR spectra of the prepared polyimide crosslinked aerogels were recorded on a NICOLET NEXUS 470 FT-IR by using KBr pellets. Bulk densities were calculated from the weight and physical dimensions of the samples. Thermogravimetric analysis (TGA) was carried out under air flow using a NETZSCH STA 409C/CD thermogravimetric analyzer. Solid state NMR was carried out on a Bruker Avance 300 Spectrometer using magic angle spinning.

4.   RESULTS AND DISCUSSION

FT-IR Spectroscopy. The chemical structures of the prepared silica-PMMA composites were characterized with FT-IR spectroscopy as shown in Figure 5. The characteristic peaks of the stretching vibration bands of the C=O and C-H bonds in the PMMA segment at 1730 and 2950 cm^{-1} were observed. The characteristic vibration for Si-OH was observed between 3400-3500 cm^{-1}.
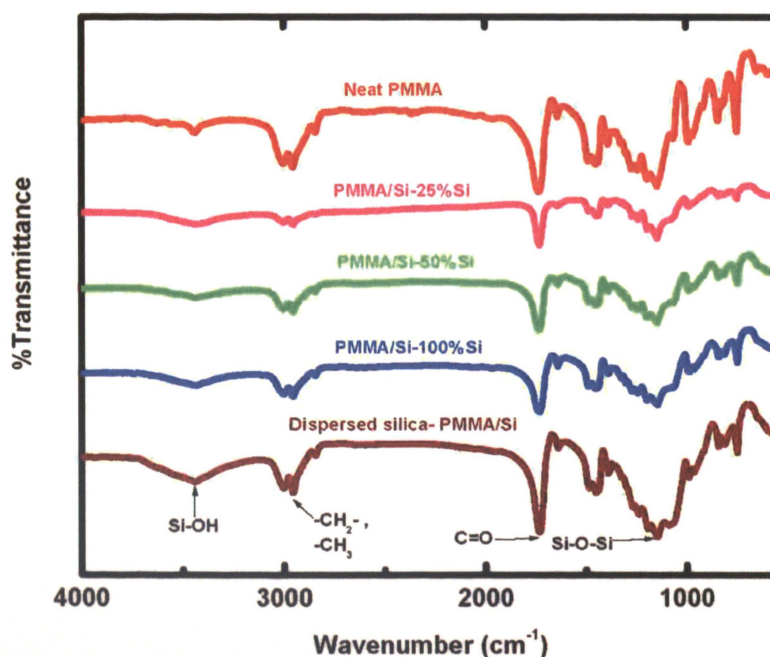

Figure 5 FT-IR spectra of silica-PMMA composites

Solid State NMR. The results of ^{13}C CPMAS NMR spectroscopy are illustrated in Figure 6. The resonances for carbon of the α- methyl group are seen at 15 ppm. A sharp peak for the quaternary carbon is seen at 45 ppm. The resonances for the carbon of the methyl group are observed at 55 ppm. The peak for the carbonyl of PMMA is observed at 177 ppm.

Thermogravimetric Analysis. The TGA curves of neat PMMA and silica-PMMA composites tested under the flow of nitrogen are shown in Figure 7. Three thermal decomposition stages for the neat PMMA and the composites can be found from these TGA curves. The first two decomposition steps correspond to the cleavage of head-to-head linkages and end-initiated vinyl-terminated PMMA. The third step of the thermal decomposition curve corresponds to the random scission of PMMA main chains [15,16]. The decomposition temperature increases considerably when silica is incorporated in the PMMA. The thermal decomposition temperature for the silica-PMMA composites is about 300 °C as opposed to 250 °C for neat PMMA. It was observed that the 50% silica-PMMA composites gave the highest thermal stability closely followed by the 100%, 25% and dispersed silica composites.

Density and Mechanical Testing. Uniaxial compression tests were performed on a MTS 810 Servo Hydraulic test system. Figure 8 shows the compressive stress strain curves for the silica-PMMA composite. A strain rate of 0.01 s^{-1} was used in all the cases. The density data and compressive testing results are given in Table 5. It was found that the strength of the composites with 25%, 50% and 100% silica did not vary significantly; the dispersed silica in PMMA sample showed the highest strength followed by neat PMMA.
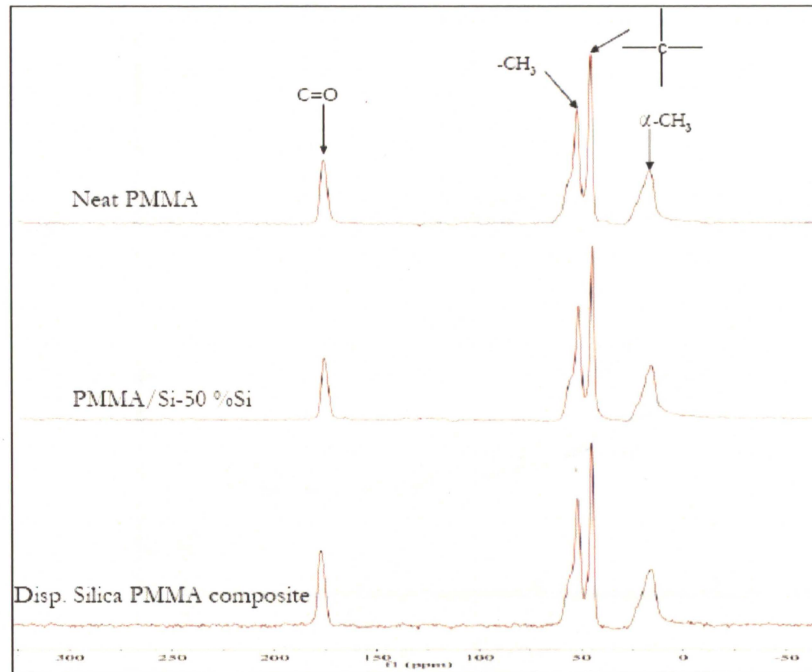
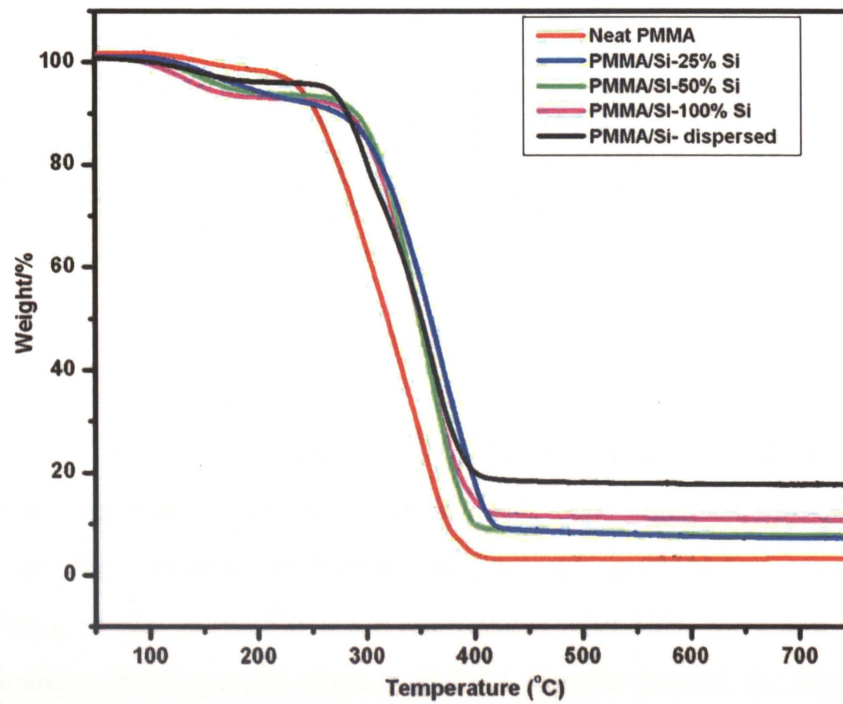**Figure 6** ^{13}C CP-MAS NMR spectra of neat PMMA, 50% silica-PMMA and silica dispersed in PMMA composites

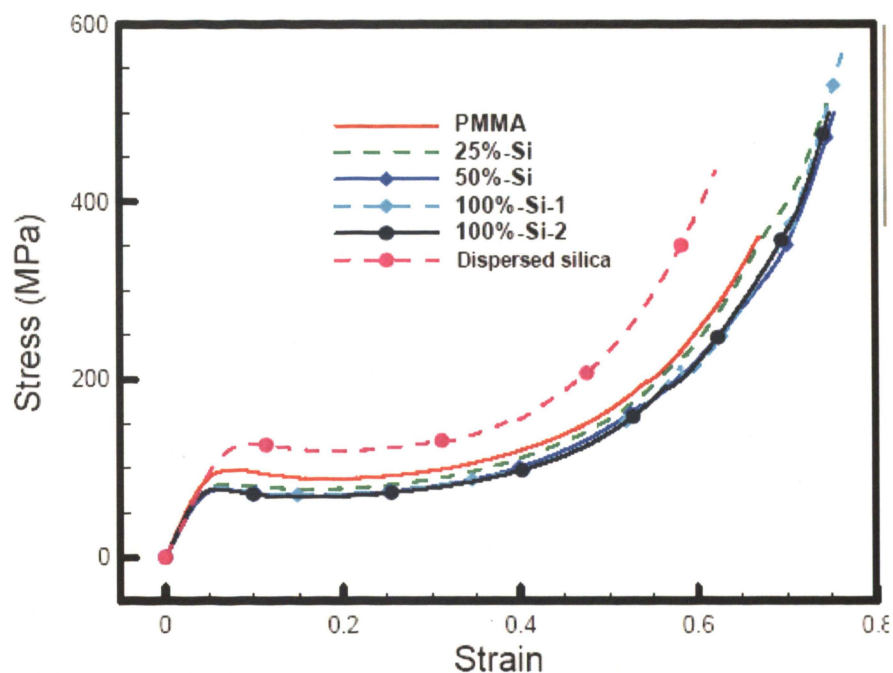**Figure 7** Thermal decomposition of silica-PMMA composites

Figure 8 Compressive stress-strain curves for neat PMMA and silica-PMMA composites

Table 5 Density and Mechanical testing data for silica-PMMA composites

Sample	diameter (cm)	Density ρ_b (g/cc)	Young's modulus (Gpa)	Comp. yield strength (Mpa)
Neat PMMA	2.331 ± 0.020	1.407 ± 0.019	2.29	95.84
PMMA/Si-25% Si	2.222 ± 0.014	1.057 ± 0.034	1.83	73.44
PMMA/Si-50% Si	2.208 ± 0.005	1.091 ± 0.021	1.84	66.02
PMMA/Si-100% Si	2.346 ± 0.111	1.134 ± 0.033	1.99	66.35
PMMA/Si dispersed Si	2.415 ± 0.013	0.940 ± 0.035	1.86	122.36

4.   CONCLUSIONS

In the present study, four different silica-PMMA composites were compared to neat PMMA by testing them by various methods. The TGA analyses showed significant improvements in the thermal properties of the silica-PMMA composites. The compressive testing results showed that the composites with 25%, 50% and 100% Si did not vary significantly; the dispersed silica in PMMA sample showed the highest strength followed by neat PMMA.

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VITA

Vishal U. Patil was born on May 16, 1981, in Jalgaon City, Maharashtra state, India. He received his B.Tech. in Chemical Technology from North Maharashtra University, Jalgaon in June 2002. He enrolled at the University of Missouri-Rolla (renamed as Missouri University of Science and Technology) in January 2006, and joined the research group of Professor Nicholas Leventis in March 2006. He received his M.S in Chemistry in May 2008.