

Synthesis and Characterization of Novel Saponified Guar-Graft-Poly(acrylonitrile)/Silica Nanocomposite Materials

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ABSTRACT: The combination of carbohydrates with silicon-based ceramic materials offers attractive means of production for high performance materials. Present article describes the synthesis of novel nanocomposites out of SiO₂ and saponified guar-graft-poly(acrylonitrile) (SG). Tetraethoxysilane was used as the precursor for silica and growth of SiO₂ phase was allowed concurrently in the presence of SG. The material so obtained was thermally treated at 80°C, 160°C, 500°C, and 900°C to study the effect of thermal curing on its properties. During the curing process, silanol surface groups of silica globules reacted to create the

reinforced SiO₂-SG substance. It was observed that at 900°C, the SiO₂ phase crystallized out in tetragonal shape (similar to Cristobalite form of silica) in presence of SG. The chemical, structural and textural characteristics of the composites were determined by FTIR, XRD, TGA-DTA, SEM and BET studies. The materials were also evaluated as efficient Zn²⁺ metal binder. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 536–544, 2007

Key words: saponified guar-graft-poly(acrylonitrile); silica; sol-gel method; metal ion binder

INTRODUCTION

Organic–inorganic composites of organic polymers and silica constitute an important class of advanced materials. Most of the polymeric materials used for making such hybrids are derived from continuously depleting petrochemical resources. Materials with high performance from renewable sources and with sufficient shelf life coupled with their ultimate biodegradability are the need of the day. Silicate-filled polymer composites often exhibit remarkable improvement in mechanical, thermal, and physicochemical properties when compared with pure polymers and their conventional microcomposites due to the nano-level interactions with the polymer matrix. Thus, the biopolymer silica composites prepared by the sol-gel processes in aqueous solutions, owing to their promising properties, are of special interest.^{1–5} Tetramethoxysilane (TMOS)⁶ and tetraethoxysilane (TEOS)⁷ are currently used as precursors. Sol-gel syn-

thesis of composite materials^{8–11} allows the production of materials in which it is possible to control both particle size and shape and sometimes even the final packing of the colloidal particles. The combined organic–inorganic characteristics of the composites represent an improvement upon some of the thermal, mechanical, and porosity properties of the substance compared with the homologous characteristics of the lone individual organic and inorganic components.

It has been observed that polysaccharides can serve as a template for silica generated *in situ* by the sol-gel processes, thus manipulating its synthesis as well as properties and structure. The polysaccharides promoted silica polymerization¹² through acceleration and catalysis of processes. Their effect is explicable by the formation of hydrogen bonds between hydroxyl groups of macromolecules and silanols generated by the hydrolysis of precursor.

Guar gum is a commercially available, industrially important^{13,14} polysaccharide material having backbone of β-D (1 → 4) mannopyranosyl units with α-D-galactopyranosyl units as side chains. Though tremendously used in industry, guar gum is rarely used in its natural form due to its quick biodegradation.^{15,16} Grafting of vinyl monomers significantly improves its shelf life⁵ and the grafted guar gum finds various commercial applications.¹⁷ Grafting of poly(acrylonitrile) on to guar gum followed by its saponification offer grafted material bearing —COOH/—CONH₂ groups^{18,19} and potentially such material is

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expected to be good metal ion binder. However, being water soluble, it cannot be used and recycled as metal ion binder under aqueous conditions. Making its composite with silica may potentially offer materials with efficient metal ion binding properties because of (i) the reactive functionalities present in saponified poly(acrylonitrile) grafted guar gum (SG) and the fact that (ii) porosity, water insolubility are outstanding thermal properties of silica.²⁰

In the present study, composites of silica and saponified poly(acrylonitrile) grafted guar gum were synthesized by sol-gel method using TEOS as silica precursor. Condensation polymerization of TEOS was allowed in presence of saponified poly(acrylonitrile) grafted guar gum and the material thus obtained was thermally treated to various temperatures. The effect of thermal treatment on the composite was studied in terms of its structure and metal ion binding capacity. Comparative evaluation of the nanocomposite was also made with silica synthesized under similar conditions by dehydration condensation of TEOS in the absence of polysaccharide. The metal ion adsorption capacity of the materials was investigated using the batch technique with Zn ions in aqueous solutions, at room temperature.

EXPERIMENTAL

Purification of the guar gum

The guar gum was purified¹⁶ by barium complexing, preparing 2.5% (w/v) aqueous solution of the gum by continuous stirring with water for 12 h at 60°C and precipitating with saturated barium hydroxide solution. The complex was separated by centrifugation and taken in 1M CH₃COOH, stirred for 8 h, centrifuged and precipitated with EtOH to get pure gum. The pure gum was finally washed with 70, 80, 90, 95% ethanol and dried.

Preparation of the functionalized biopolymer

Grafting method

Guar gum (2.0 g) was taken with acrylonitrile (26×10^{-2} M) and ascorbic acid (2.3×10^{-2} M) in 500 mL water in a 1-L flask and thermostated at $(35 \pm 0.2)^\circ\text{C}$. After 30 min potassium persulphate (10×10^{-3} M) was added. Total volume of the reaction mixture was kept constant to 500 mL and grafting was allowed for 1 h. Guar-graft-poly(acrylonitrile) was separated¹⁷ from polyacrylonitrile (PAN) by pouring the reaction mixture into a large quantity of DMF. The graft copolymer was washed well with DMF to remove adhered homopolymer if any. %Grafting (%G) and %efficiency (%E) were calculated using eqs. (1) and (2) and were found to be 110 and 31.89% respectively.

$$\% \text{Grafting } (\%G) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\% \text{Efficiency } (\%E) = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 denote respectively, the weight of the grafted guar gum, the weight of original gum, and weight of the monomer used.

Intrinsic viscosity and molecular weight of grafted PAN chains

Homopolymer-free graft copolymer samples were hydrolyzed in 2M HCl for 2 h to depolymerize the polysaccharide chains. The residue (consisting mainly of PAN chains), was washed well with water and ethanol, dried in air, and weighed. The PAN chains were extracted for 24 h at 20°C in DMF. After filtration, the PAN solutions were used for measuring the intrinsic viscosity.²⁰ The intrinsic viscosity (η) of the polymer solution was measured in water at $(30 \pm 0.2)^\circ\text{C}$ using an Ubbelohde viscometer. The flow time was measured for solutions at five different concentrations and the intrinsic viscosity was calculated.

Hydrolysis of guar-graft-poly(acrylonitrile)

Sample of the guar-grafted-poly(acrylonitrile) was hydrolyzed²¹ in aqueous alkali. Grafted sample (2 g on dry basis) was dispersed in 1% NaOH at 100°C for 1.5 h. After hydrolysis the sample (SG) was precipitated in 600 mL methanol, washed with methanol and ethanol, dried and weighed.

Preparation of composite materials²²

Saponified poly(acrylonitrile) grafted guar gum (1.0 g) was dissolved in 10 mL of distilled water. Separately, TEOS (2.5 mL) was also dissolved in ethanol (2.5 mL). A third solution incorporating 1.75 mL of 12N ammonium hydroxide was prepared separately. Afterwards, the three solutions were rapidly poured together into a reaction glass flask and kept under gentle stirring for 18 h at room temperature to grow monodisperse SiO₂ particles, within the modified biopolymer medium, which was subsequently washed several times with distilled water. The ensuing mixture was then subjected to slow evaporation at 80°C for about 4.5 h until a dry material was obtained (H1). This thermal process not only brought about further and ultimate growth of the SiO₂ particles but also interaction between the silanol surface groups of silica particles and the end groups available at the biomaterial surface. H1 thus obtained was further thermally treated inside a furnace at 160°C for 24 h (H2) followed by treatment at 500°C for 2 h (H3). H3 was further treated at 900°C for 2 h (H4).

Preparation of silica oligomer²³

NH₄OH solution (12N; 3.5 mL) was added to TEOS (5 mL) dissolved in ethanol (5 mL) in a 50-mL conical flask and stirred for 18 h at 32°C followed by 3 h stirring at 80°C, whereupon the reaction mixture becomes completely dry. The dry product was washed well with distilled water, filtered, and dried. The oligomer (SO) was an amorphous white powder. Like the hybrids, SO was also thermally treated at 160°C (S1), 500°C (S2), and 900°C (S3) inside a muffle furnace.

Study Zn²⁺ ions adsorption by the composite²⁴

To reaction flasks thermostatically maintained at (30 ± 0.2)°C were added 100 mg of the material as adsorbent and 50 mL of aqueous solution of 2 mM zinc ions and the systems were maintained at (30 ± 0.2)°C in an incubator shaker at 180 rpm. After 1 h the mixtures were filtered and the amounts of the adsorbed metal ions (mmol) were determined by titration with 0.01M EDTA using Eriochrome Black-T as indicator. The amount of metal ions adsorbed per gram of the polymer was calculated by difference between the initial and final number of millimoles in the solutions (Table II). The recovered materials after leaching with 2M HCl and washing several times with distilled water were dried and recycled for another two cycles for the Zn²⁺ ion binding as described above; the results are compiled in Table III.

Instrumental analysis

Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer making KBr mulls in reflectance mode. Tetra ethoxyorthosilicate (98% TEOS; Aldrich) was used as silica precursor. NH₄OH (30% NH₃; Merck) was used. Acrylonitrile (E. Merck) was distilled in a stream of nitrogen before use. Ascorbic acid and potassium persulfate (BDH, analar grade) were used without further purification. Commercial sample of guar (Merck) after purification was used. X-ray diffraction (XRD) was carried out on Rigaku D/MAX-2200 X-ray powder diffractometer.

TABLE I
Particle Size (As Measured by Particle Size Analyzer) and Surface Area of the Hybrids As Estimated Size on BET Analysis

S. no.	Sample	Particle size range (μm)	Surface area (m ² /g) by BET
1	H4	95–120	156.90
2	H3	37–106	113.54
3	H2	40–127	36.96
4	H1	101–102	3.77
5	SO	1–90	2.55
6	SG	79–149 and 157–201	1.20

TABLE II
Change in the Average Crystallite Size of the Hybrids and Silica Oligomers

S. no.	Sample	Temperature in °C	Average crystallite size in nm as estimated by XRD
1	GN	–	18.7
2	SG	–	18.9
3	H1	80	>100
4	H2	160	9.9
5	H3	500	15.5
6	H4	900	19.1
7	SO	80	19.1
8	S1	160	14.1
9	S2	500	13.8
10	S3	900	13.8

Wavelength used to compute d-spacing was 1.54,056 Å (Cu/K-alpha 1). Average crystallite sizes (from XRD) for the crystalline materials were calculated by FWHM using Scherrer formula, and for amorphous materials using software JADE/6.5. TGA was done at Perkin-Elmer TGA-7 at a heating rate of 10°C per min under nitrogen atmosphere. BET studies were done on Coulter SA3100 with sample weight 0.1182 g, out gas temperature 45°C and out gas time 30 min respectively, while particle size was determined by Fritsch particle sizer analysette 22 instrument. SEM analysis was done on EDAX, FEI Quanta 200 machine. Temperature treatment of the hybrid was done in PhoenixTM Microwave Muffle Furnace.

RESULTS AND DISCUSSION

Poly(acrylonitrile) grafted guar gum sample with 110% grafting was saponified for making silica composite. To find out the average molecular weight of grafted poly(acrylonitrile) chains (PAN) in poly(acrylonitrile) grafted guar gum (GN), the graft copolymer was subjected to acid hydrolysis and the separated PAN was dissolved in DMF. The flow time was measured for solutions at five different concentrations and the intrinsic viscosity was calculated by plotting η_{sp} versus C and η_{inh} versus C and then taking the common intercept at $C = 0$ of the best-fitted straight line through the two sets of points. Here C represents polymer concentrations in g/dL. The η_{sp} and η_{inh} are specific and inherent viscosities and were calculated from the relation $\eta_{sp} = \eta_{rel} - 1$ and $\eta_{inh} = \ln \eta_{rel}/C$. The number average molecular weight M_n value was calculated from the following relation²

$$[\eta] = 3.92 \times 10^{-4} \times \overline{M}_n^{0.75} \quad (3)$$

Its intrinsic viscosity $[\eta]$ was found to be 1.0 dL/g, which indicated that average molecular weight (\overline{M}_n) of the grafted PAN chains was 3.48×10^4 .

TABLE III
Zn²⁺ Ion Adsorption of the Hybrids Materials and Silica Oligomers in Comparison with Guar Gum and Modified Guar Gum

Sample	Adsorption of Zn ²⁺ ions in meq/g	Adsorption of Zn ²⁺ ions in meq/g after 1st desorption	Adsorption of Zn ²⁺ ions in meq/g after 2nd desorption
Guar gum	0.40	–	–
Guar-graft-PAN	0.74	–	–
SG	1.20	–	–
H1	1.7	1.68	1.58
H2	2.46	2.44	2.34
H3	3.16	3.14	3.10
H4	3.36	3.34	3.28
SO	1.16	1.12	1.00
S1	0.94	0.90	0.65
S2	0.62	0.60	0.46
S3	0.40	0.36	0.22

The commonly accepted mechanism for the formation of silica hybrid materials includes three main stages; hydrolysis of the precursor, condensation of the formed monomers to produce oligomers arranged as sol particles, and crosslinking of the sol particles leading to sol–gel transition. This occurs as a set of chemical reactions²⁵ that are initiated by a catalyst in the precursor solution.

The addition of the saponified poly(acrylonitrile) grafted guar (SG) to the precursor solution modifies the sol–gel process. Polysaccharide macromolecules promote the mineralization, that is, nucleation and growth of the silicon compound. They manifest themselves as a template for the silica generated in the mixed system due to the hydrogen bonding between the hydroxyl groups at silanols and COOH/–CONH₂ groups at the modified polysaccharide surface. Linked silanol groups can further hydrolyze and then participate in the condensation reaction. Thus the polysaccharide promotes both the mineralization in the mixed system and also serves as a template for the generated inorganic component. This is clearly observed by visualizing the difference in the physical state of the materials obtained by polymerization of the TEOS itself and by the thermal curing of the hybrid at 900°C. On treating the hybrid at 900°C, most of the SG portion is decomposed and the residual SG templates silica to crystallize out into a tetragonal system. However when silica oligomer synthesized by dehydration condensation of TEOS (without SG) is treated thermally to such temperatures, it does not crystallize out; rather it remains amorphous throughout up to 900°C, indicating that the polysaccharide molecules template and direct the silica crystallization in the tetragonal shape.

The above-considered results suggest that polysaccharide macromolecules work as a template for silicate generated by TEOS in the biopolymer solution. This means that their catalytic effect might be related

to the interactions with silanols (Si–OH) produced in the course of hydrolysis of the precursor.

The formation of the composites with silica and polysaccharide can thus be presented by three stages: Hydrolysis of the precursor, condensation of the formed monomers on the macromolecule through linkage of –OH by hydrogen bonds and polycondensation of the linked silanol molecules with silanols or precursor monomers.

Characterization of hybrid

The IR spectra of the guar-graft-poly(acrylonitrile) (GN) show $\nu_{\max} = 2242 \text{ cm}^{-1}$ due to stretching of CN

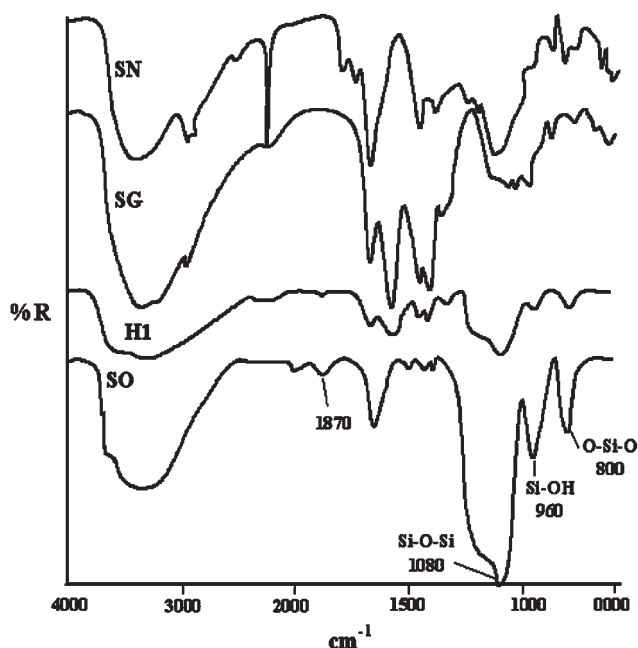


Figure 1 IR spectra of (GN) guar-g-PAN, (SG) base hydrolyzed PAN, (H1) hybrid treated at 80°C, (SO) silica oligomer.

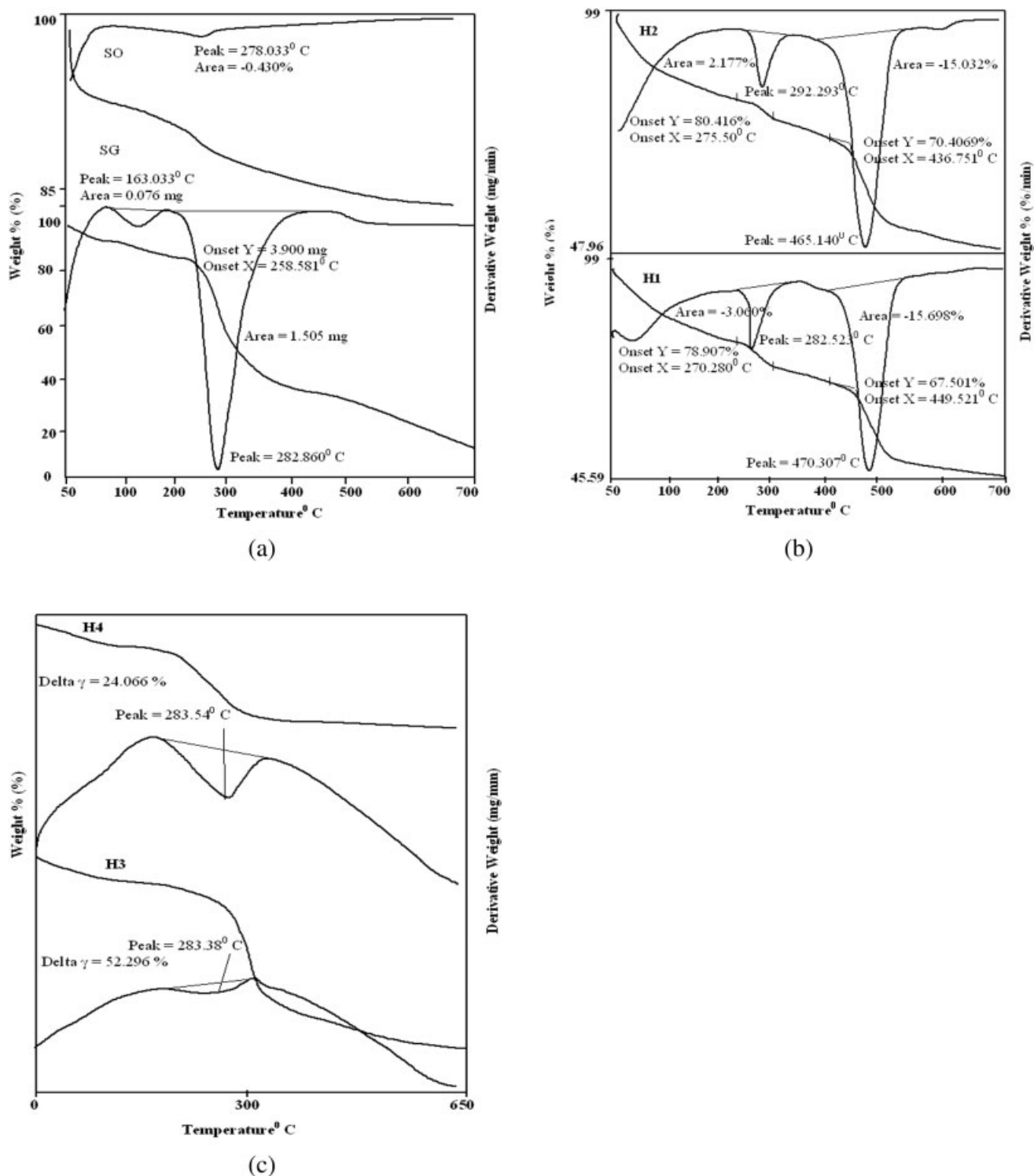


Figure 2 (a) TGA of (SO) silica oligomer, (SG) saponified guar-g-PAN; (b) TGA of hybrids: (H1) treated at 80°C, (H2) treated at 160°C; (c) TGA of hybrids: (H3) treated at 500°C, (H4) treated at 900°C.

group confirming poly(acrylonitrile) grafting at guar gum, while in base hydrolyzed guar-graft-poly(acrylonitrile) (SG) ν_{\max} at 2242 cm^{-1} disappeared and show $\nu_{\max} = 1667 \text{ cm}^{-1}$ due to C=O stretching of the amide groups resulting from the saponification of the nitrile (Fig. 1). In the composite material, the absorption

bands at 3300–3500 cm^{-1} were attributed to stretching mode of water and hydroxyl. The inorganic component can be identified from the Si—O—Si modes observed below 1250 cm^{-1} , the typical silica overtone bands at $\sim 1870 \text{ cm}^{-1}$ and the silanol stretching bands above 3500 cm^{-1} . IR spectra of the composite¹⁰

showed a ν_{\max} in the vicinity of 960 cm⁻¹ (due to Si—O bonds of Si—OH groups) as a shoulder of the intense absorption peak around 1080, which can be assigned to the asymmetric stretching vibration of the Si—O bonds of Si—O—Si bridges while ν_{\max} at 800 cm⁻¹ is due to the symmetric stretching of Si—O—Si bonds. In silica oligomer (SO), peaks due to Si—OH, Si—O, and O—Si—O bonds are observed at 1100, 954, and 799 cm⁻¹ respectively.

TGA curves of the hybrids are compared with the saponified guar-graft-poly(acrylonitrile) (SG) and silica oligomer (SO) [Fig. 2(a)]. Silica oligomer (SO) showed a single peak at 278°C with a weight loss of 11.5%, which is due to the loss of bound water. The total weight loss observed was 15% up to 700°C for SO. However SG showed two endothermic peaks at 163°C and 282°C with a total weight loss of 81% up to 700°C. The first peak was due to the loss of the adhered water and second peak indicated the decomposition of the SG.

The hybrid materials (H1 and H2) showed [Fig. 2(b)] thermal stability compared to parent polysaccharide material (SG). It appears that SG is impregnated in silica matrix in two ways and shows decomposition in two stages. In H1 two endothermic peaks were observed one at 282°C and the other at 470°C with a total weight loss of 54.41% up to 700°C. The first peak is due to loss of the SG that is strongly entrapped deep inside the ensuing silica matrix, resulting in 21.1% weight loss; the second peak may be due to the loss of SG which is bonded to the silica matrix and therefore is decomposed at higher temperature and results in 11.4% weight loss. The DTA curve of H2 also showed two endothermic peaks at 292°C and 465°C with a total weight loss of 52% up to 700°C. The first peak is due to the loss of the entrapped SG, resulting in 20% weight loss, and the second peak is due to the decomposition of the bonded SG (with silica matrix) resulting in 10% weight loss. Compared with H1, the first peak in H2 was seen at a relatively higher temperature (292°C), which may be due to the syneresis of the silica gel which causes tighter entrapping of SG in the silica cage. The first peak at 283°C persists in H3 and H4 also whereas the second peak around 470 is no more seen in hybrids (H3, H4) treated at high temperatures [Fig. 2(c)]. This is because SG bound to the silica matrix is completely decomposed at higher temperatures (perhaps it is much exposed for decomposition) whereas the physically entrapped SG remains partly entangled to the matrix even after thermal curing at 500°C and 900°C. However the entrapped SG after decomposition of the bound SG gets exposed so goes off fast as evident by 52% weight loss in H3 at 283°C. However the presence of SG is still seen in H4 (which is decomposing at 283°C), decomposition of which results in to 24% weight loss again. The residual SG

in the silica matrix directs the silica to crystallize out in the form similar to crystobalite²⁶ (XRD of H4).

XRD of the GN shows crystalline areas at 2 θ 16.8, 20 20.08, 20 21.13, 20 23.56, 20 26.16, 20 28.21, 20 29.52, 20 30.69, 20 35.61, 20 36.92, 20 37.68, 20 40.38, 20 43.18, and 20 54.077, due to the presence of poly(acrylonitrile) grafts on the guar gum. Saponification of the GN significantly reduces the crystalline areas and just show amorphous peak with two humps at 2 θ 16.72 and 20 19.94 while XRD of the silica oligomer indicates amorphous nature.

XRD of the hybrid (H1) shows intermediate pattern and in it two humps are observed at 2 θ 9.4° and 20 22.44°, while H2 shows completely amorphous nature. XRD of H3 shows amorphous curve with a developing hump between 2 θ 30° and 20 40°, indicating that the crystallization of the silica triggers at 500°C and it gets fully crystallized at 900°C. It is clear from Figure 3 that on thermal curing, peaks gradually sharpened and in H4 (treated at 900°C), several crystalline peaks are observed, three strongest peaks are at 2 θ 21.98° (*d*-value 4.0720), 20 31.414° (*d*-value 2.8454), and 20 36.019° (*d*-value 2.4914), corresponding to *hkl* values, (100), (102), (200) respectively, indicating tetragonal shape (c.f. crystalline form: crystobalite). It is probably due to ordering within the siloxane domains with thermal curing that is evidenced by crystalline sharp peaks in the XRD of H4, where as H2 show broad hallow typical to amorphous materials. In H3 the hallow is sharpened at and a additional hump is observed at 2 θ 28–36° [Fig. 3(b)]. This is further confirmed by SEM picture where more ordered and symmetrical texture of material is seen in H4 as compared with H2 and H3 (Fig. 4), while SO, on treating thermally at 160°C (S1), 500°C (S2), and 900°C (S3) remains amorphous through out [Fig. 3(c)].

In the SEM picture of the silica oligomer (prepared in the absence of the polysaccharide in the initial solution), solid particles are seen which are connected with each other forming a three-dimensional network. This structure is typical of silica nanocomposite materials being in agreement as noticed by other authors²⁷ (Fig. 4). SEM picture of the saponified guar-graft-poly(acrylonitrile) (SG) also show the particles to be spherical and agglomerated. In the hybrid (H1) silica network is being formed at agglomerated SG surface. H1 clearly shows silica networking at SG surface (where clusters of agglomerated SG particles are easily seen). On further curing at 500°C, decomposition of the SG molecules takes place (TGA show that bound SG decompose below 500°C) and results in mesoporous structure. Further dehydration condensation and ordering in the siloxane domains takes place on heating the material at 900°C leading to a crystalline microporous structure (H4).

Crystallite size of the particles of the hybrid material first decreases slightly on heat treatment which

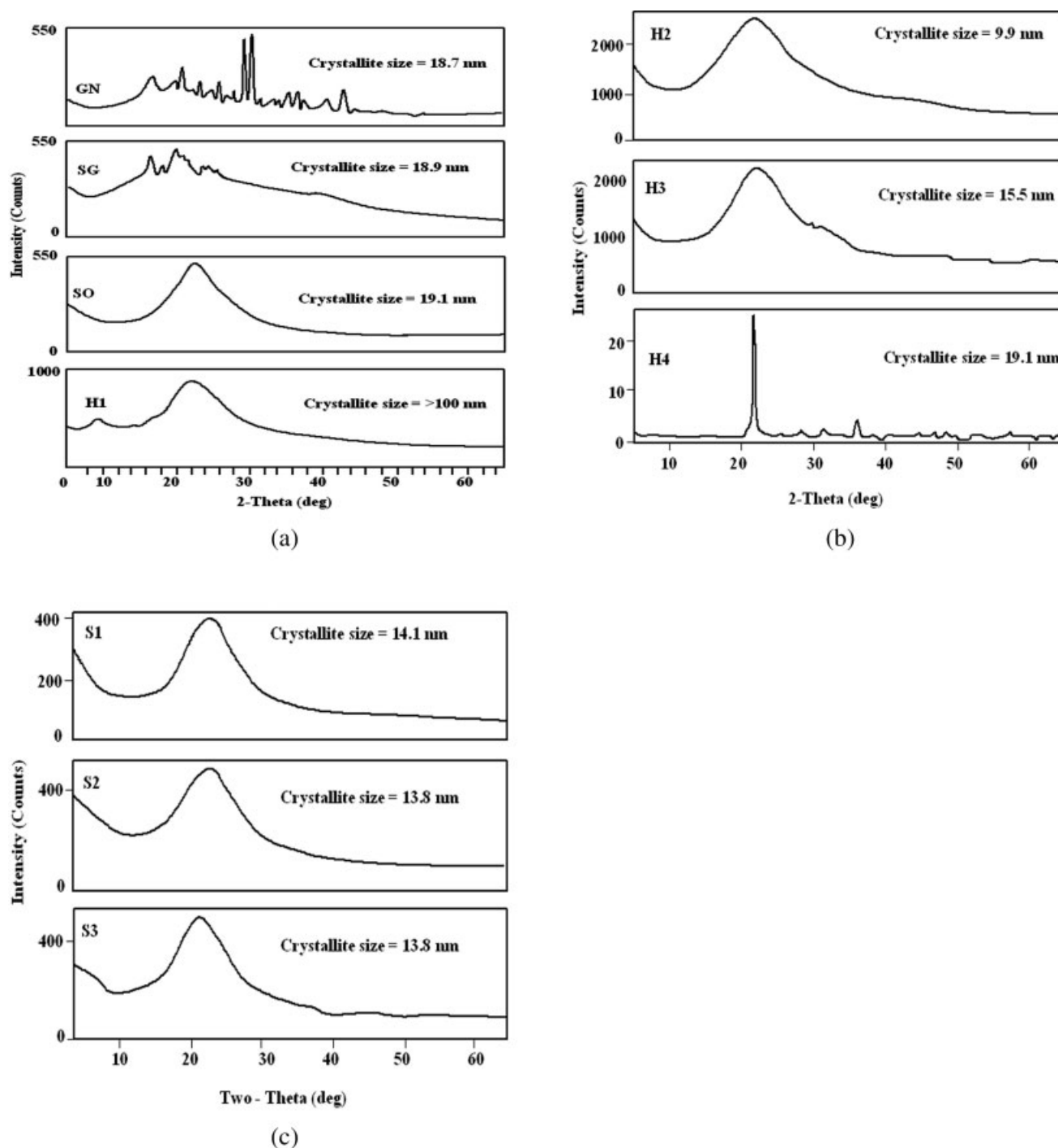


Figure 3 (a) XRD of (GN) guar-g-PAN, (SG) Saponified Guar-g-PAN, (SO) silica oligomer, (H1) hybrid at 80°C; (b) XRD of (H2) hybrid treated at 160°C, (H3) hybrid treated at 500°C, (H4) hybrid treated 900°C; (c) XRD of (S1) treated at 160°C, (S2) treated at 500°C, (S3) treated 900°C.

however increases on treating the samples at 900°C due to clustering of the particles resulting from the dehydration condensation of the silanol groups at the silica. On being heat treated, SG is partly decomposed, exposing the available silanol groups for dehydration condensation (Table II).

The BET analysis showed the surface area for the hybrids treated 900°C (H4) and 500°C (H3) to be

156.90 m²/g and 113.54 m²/g respectively, while the samples treated at 160°C (H2) and 80°C (H1) had a surface area of 36.96 m²/g and 3.77 m²/g respectively. Surface areas for the SG and SO are lower than H1 (Table I).

Average particle sizes as revealed by particle size analyzer (Table I) and XRD (Table II) show that on heat treatment, particle size of the hybrid decrease

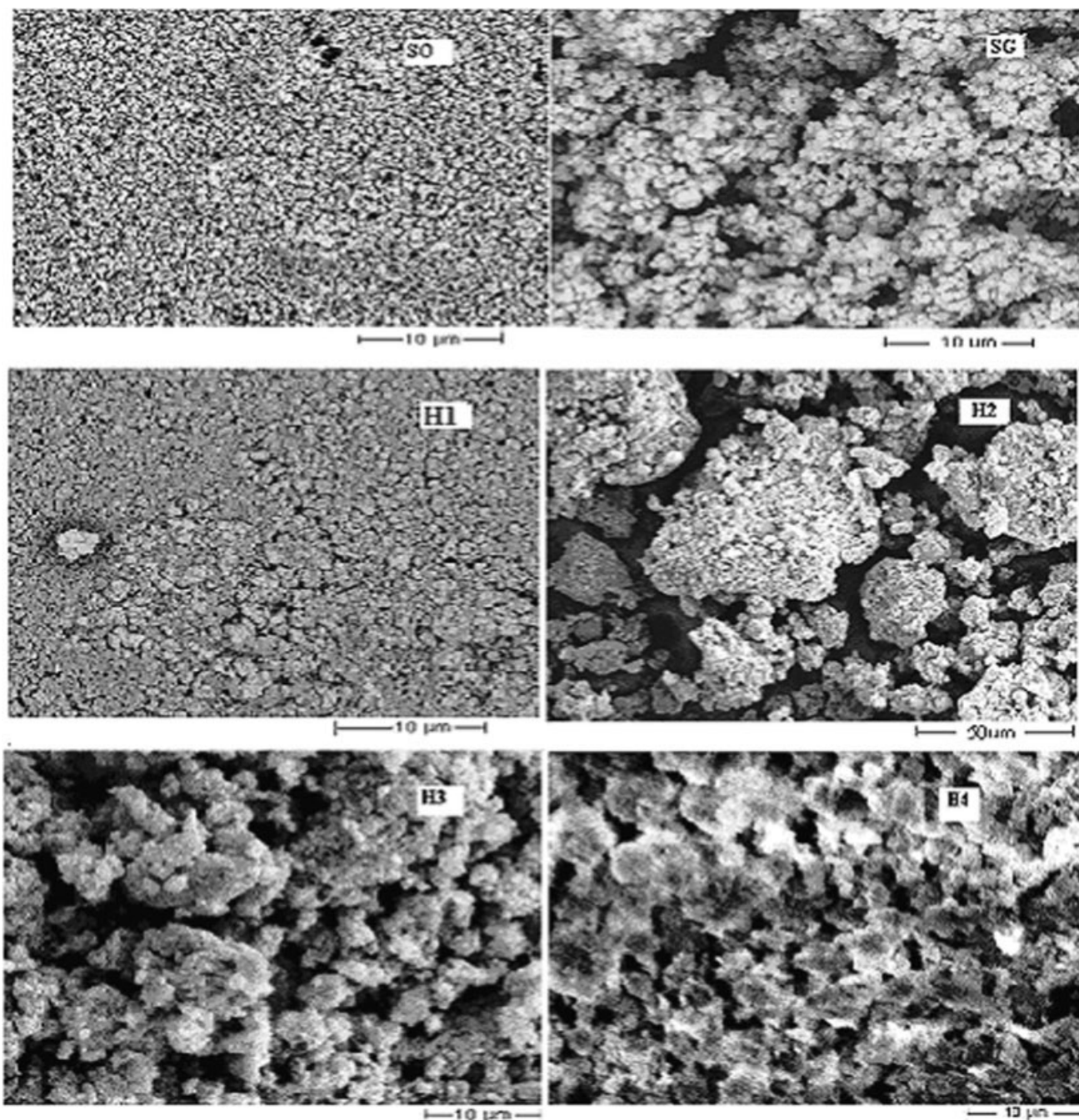


Figure 4 SEM picture of (SG) Saponified Guar-g-PAN, (SO) Silica Oligomer; hybrid, (H1) treated at 80°C, hybrid (H2) treated at 160°C, (H3) treated at 500°C, (H4) treated at 900°C.

first and then increases slightly. While for silica oligomer heat treatment first decreases the average size due to syneresis and then it becomes constant. Heat treatment of the hybrid at 500°C and 900°C slightly increases the average particle sizes this may be due to the aggregation of the particles, since at such temperatures SG is partly lost and the available silanol groups are now more exposed for the dehydration condensation. The particles appear to be highly porous²⁸ and aggregated due to which the size

by particle size analyzer was estimated to be larger than that indicated by XRD (Table II).

Adsorption ability of the hybrid material for adsorption of the Zn²⁺ ions

Metal binding capacity of guar is markedly increased by the presence of polyacrylonitrile grafts, which provide additional metal binding sites. Since hydroxyl groups of guar are highly hydrated and are not free

as adsorption sites, the nitrile groups on graft copolymer are the sites responsible for metal ion adsorption. On base hydrolysis of the material though potentially metal binding should increase due to availability of $-\text{COOH}/\text{CONH}_2$, the material cannot be exploited for metal ion binding as it dissolves under aqueous conditions. On making hybrid of the saponified poly (acrylonitrile) grafted guar with silica the water solubility is lost and such hybrid materials were found to have much better adsorbing power for the Zn^{2+} ions due to the porosity and presence of appropriate functionalities. For 2 mM Zn^{2+} ion solution, the samples treated for 500°C (H3) and 900°C (H4) showed the absorption of 3.36 and 3.16 meq/g, while the hybrid treated at 160°C (H2) and 80°C (H1) showed adsorption of 2.46 meq/g and 1.70 meq/g respectively, in comparison to just 0.40 meq/g adsorption for guar, 0.74 meq/g for guar-graft-poly(acrylonitrile) and 1.20 for saponified Guar-g-PAN (SG). Almost a three fold increase in adsorption capacities was observed when SG was changed to H4. Table III summarizes the Zn^{2+} ion adsorption of the hybrid materials. The materials after use were desorbed to remove the zinc ions and reused for metal ion binding. The stripping solution used was 2M HCl. The recycled materials showed nearly the same adsorption as that of the originals (Table III) in the first cycle with a marginal decrease in the second cycle. Guar-g-poly(acrylonitrile), saponified guar-graft-poly(acrylonitrile) and guar gum could not be recovered for reuse as these materials dissolve during their use in the first cycle itself. Under similar conditions when S3 was reused, the adsorption capacities were reduced to almost half by the end of 2nd cycle.

Metal ion binding can be attributed to the presence of $\text{COOH}/\text{CONH}_2$ groups and the increased porosity and surface area of the material on treating the material to high temperature.

CONCLUSIONS

Novel nanocomposites out of SiO_2 and saponified guar-graft-poly(acrylonitrile) (SG) were synthesized using a simple sol-gel process. On treating the composite thermally at 900°C, its SG-part decomposes, templating the left over silica to crystallize out in to tetragonal cristobalite form (polymorph of quartz). However, silica synthesized under similar conditions by dehydration condensation of TEOS in absence of SG remained amorphous up to 900°C. The synthesized composite materials were also evaluated as efficient zinc ion binder. Zinc ions could be easily stripped off from the used material by washing with acid and used again for two cycles without any signi-

ficant change in adsorption capacities. Potentially these novel nanocomposites may find commercial application as washable filters in the removal of metal ions from wastewater and as solid support for the catalyst in organic synthesis.

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