

Novel Copolymer for SiO₂ Nanoparticles Dispersion

V. Sorna Gowri, Luís Almeida, Teresa Amorim, Noémia Carneiro, António Pedro Souto, Maria Fátima Esteves

Department of Textile Engineering, University of Minho, Guimaraes, Portugal

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ABSTRACT: High performance polymers exhibiting multifunctional characteristics can be achieved by the introduction of inorganic nanoparticles like SiO₂ into the functional polymers. In the present work a copolymer epoxy poly(dimethylacrylamide) was synthesized to disperse the SiO₂ nanoparticles. The aim of the work is to develop a new method/process/material for the dispersion of nanoparticles and evaluating the performance of these composites. FT-IR studies of the polymer adsorbed SiO₂ nanoparticles confirmed that the polymer molecules chain was anchored on the surface of the SiO₂ nanoparticles. The improved interfa-

cial interaction between the particles and polymer enhanced the thermal properties of the composites. The results also show the newly synthesized polymer disperse the nanoparticles well as evidenced by SEM analysis, the uniformly dispersed SiO₂ nanoparticles in the polymer matrix and the particles almost remained in their original shape and size even after incorporation in to the polymer matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1553–1561, 2012

Key words: block copolymers; dispersions; FT-IR; thermal properties

INTRODUCTION

Polymer nanocomposites are a special class of materials having unique properties and wide applications potential in diverse area.^{1–4} One main reason for using nanoparticles in polymer composites is the large surface to volume ratio. The large surface area increases the number of particles matrix interaction, thus increasing the effects on the overall materials properties. It has been demonstrated that a well-dispersed system generally yields more desirable composite properties. Particle agglomeration decreases materials performance by the inclusion of voids that act as preferential site for failure. Particles especially in nano scale (less than 100 nm) tend to agglomerate due to the dominant intermolecular Van der Waals interaction between them.

The incorporation of nanoparticles could improve the properties of polymer matrix when compared with neat polymer at the same time imparting the functional properties of nanoparticles in the system. The nanoparticles have high surface energy due to large surface area and it is difficult to disperse them in any organic solvent and functional polymers, which is very essential for many applications of

these nanoparticles as nanofinishings.^{5–8} Therefore, it is necessary to use surface modifiers, dispersant to enhance the dispersion of nanoparticles before adding them to any solvent, or functional polymers in making nanofinishings to prevent the formation of agglomerated nanoparticles. A surface modification improves the dispersion stability of nanoparticles in nanofinishings. In general surface modification of nanoparticles can be carried out by either chemical or physical methods. Silane coupling agents are the most widely used type of chemical modifying agents. Surface modification based on physical interaction is usually implemented by using surfactants or macromolecular adsorption on the surface of nanoparticles.⁹ SiO₂ nanoparticles were modified with steric acid to improve their dispersion and the adhesion between the filler and polymer matrix.¹⁰ Nano-size silica was modified with oleic acid which was bonded to the silica surface with single hydrogen bond.^{11,12} There are two advantages of performing surface treatments based surface modifications. One is to decrease apparent interaction between nanoparticles using polymer coatings. The other is to increase wettability between particles surface and matrix using chemical structure similar to polymer matrix. Then treated particles were dispersed into the polymer matrix to prepare organic/inorganic composites.

Silica is a substance of acidic and hydrophilic character,^{13,14} reflecting its surface structure comprising silanol (=S–OH) and siloxane (=Si–O–Si=) groups.^{13–15} A pronounced hydrophilicity of silica used as polymer filler may induce problems of

Correspondence to: V. S. Gowri (gowrisorna@yahoo.com).

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miscibility of organic and inorganic phases. To enhance the silica affinity to the polymer matrix, the former is modified with adhesion promoters of other substances capable of reacting on its surface. Adhesion of these compounds on silica also results in hydrophobicity of the surface and sometimes improves the physical, chemical, mechanical and thermal properties of the composites.¹⁶ The interaction between the polymer and inorganic material may be strong (covalent or ionic interaction) and weak Van der Waals forces, hydrogen bonds or hydrophilic-hydrophobic equilibrium.^{17–21} A significant step in the formation of well dispersed silica was found to be preliminary hydrophobisation of silica nanoparticles surface using block copolymers. These compounds not only enhance the chemical affinity of the functionalized polymers to the surface of the silica but also prevent undesirable agglomeration of the silica particles.

The adsorption of polymers on oxide nanoparticles and its application in preparing organic/inorganic composites have been the subject of intensive theoretical and experimental studies. Yu et al.²² have reported that the mono dispersed CeO₂ nanoparticles were stabilized by the adsorption of a block copolymer of poly(ethylene glycol) and poly(acrylic acid). Lin et al.²³ prepared stable aqueous Fe₃O₄ dispersion with average particles size of 10 nm by using poly(acrylic acid) as modifier. Chibouski et al.²⁴ investigated the adsorption of poly(vinyl alcohol) on the Al₂O₃ surface. Polyacrylamide adsorption behavior on surface of silica nanoparticles has been studied by Samoshina et al.²⁵ PVP was used as a surface modifier for the dispersion of metal particles in polymers.^{26,27} The desorption problem is overcome in our approach by using statistical copolymers as it is known that the polar polymers adsorb almost irreversibly on different inorganic surfaces by not only one but a large number of binding sites.²⁸

Our goal was to develop an universal method for making surface modified inorganic SiO₂ nanoparticles compatibilized for blending into a polymer matrix. In this article, we present the synthesis and properties of epoxy poly(dimethylacrylamide) copolymers and explore the possibility of using them in the dispersion of SiO₂ nanoparticles through surface modification. The morphology of composites was studied by SEM and highly inorganic and organic components of the composites were studied by FT-IR. Not only did we expect a good dispersion effect on silica nanoparticles but also an improved compatibilization of the nanoparticles with other functional polymers due to the hydrophobic parts of the copolymers used for dispersion. The free epoxy groups of the polymer provide additional functionality in the particle surface.

EXPERIMENTAL

Materials

Ammonium persulphate and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were from E-Merck, Germany. *N,N*-dimethylacrylamide was from Sigma-Aldrich. Allyl glycidyl ether was from Acros Organics, NJ. Nanosilica was from Sigma-Aldrich. Water and all solvents were of analytical grade.

Synthesis of epoxy poly(dimethylacrylamide)

The polymerization reaction was carried out in a two necked, round bottom flask equipped with nitrogen inlet tube. *N,N*-dimethylacrylamide (0.4 mol/L) and 0.008 mol/L of allyl glycidyl ether were dissolved in distilled water and then after purging with purified nitrogen gas, solutions of TEMED and ammonium persulphate were added to catalyze the reaction at a final concentration of 0.14% v/v and 0.056% w/v respectively. The mixture was left to polymerize overnight at room temperature. The resulting polymer was lyophilized and gave white solids.

Activation of SiO₂ nanoparticles

The surface activation of SiO₂ nanoparticles was done by washing the SiO₂ nanoparticles with an alkaline solution (1 mol/L sodium hydroxide) for 10 min and then washed with distilled water for 15 min to remove all sodium ions and dried at 120°C. This left the surface of the particles saturated with silanol groups to allow reaction with polymer.

Preparation of epoxy poly(dimethylacrylamide)-SiO₂ nanocomposites

Films of epoxy poly(dimethylacrylamide)-SiO₂ nanocomposites were prepared by simple casting procedures from aqueous solutions. One percent solution of nanocomposite was prepared by dissolving the activated SiO₂ in 1% polymer solution under ultrasonification. The composite film was cured at 60°C for 6 h.

Gel permeation chromatography (GPC)

Ten milligrams of polymer was dissolved in 500 μL of 0.1M NaNO₃ aqueous solution at 20°C during 60 min and further filtered through a 0.4 μm filter reaching a sample concentration of about 2%. The gel permeation chromatography (GPC) analysis has been carried out using two PL aquagel-OH MIXED 8 μm 300 × 7.5 mm columns protected by a PL aquagel-OH Guard 8 μm precolumn on a PL-GPC 110 system (Polymer Laboratories, UK). The

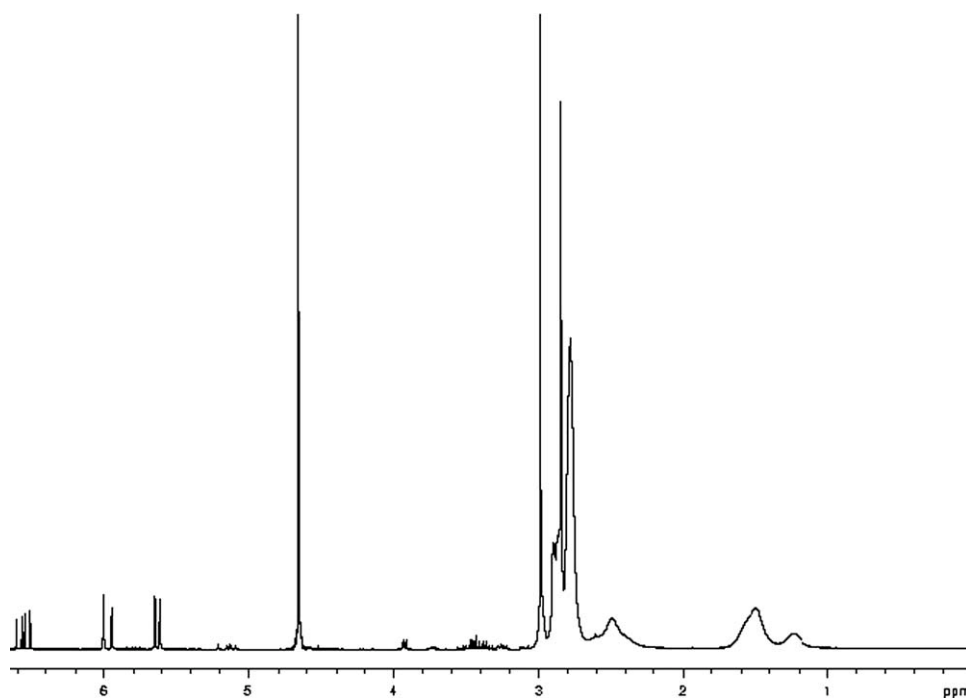


Figure 1 ¹H-NMR of epoxy poly(dimethylacrylamide).

columns, injector system and the detector (RI) were maintained at 35°C during the analysis. The eluent (0.1M NaNO₃) was pumped at a flow rate of 0.9 mL/min. The analytical columns were calibrated with pullulans (Polymer Laboratories, UK) in the range 1.7 to 300.0 kDa. The injected volume was 100 μL.

FT-IR spectroscopy

FT-IR spectra were obtained using FT-IR spectroscopy with Nicolet Avatar 360 spectrophotometer using KBr tablets. All the samples were dried under reduced pressure for 24 h before collecting their spectra. The resolution of each spectrum was 2 cm⁻¹

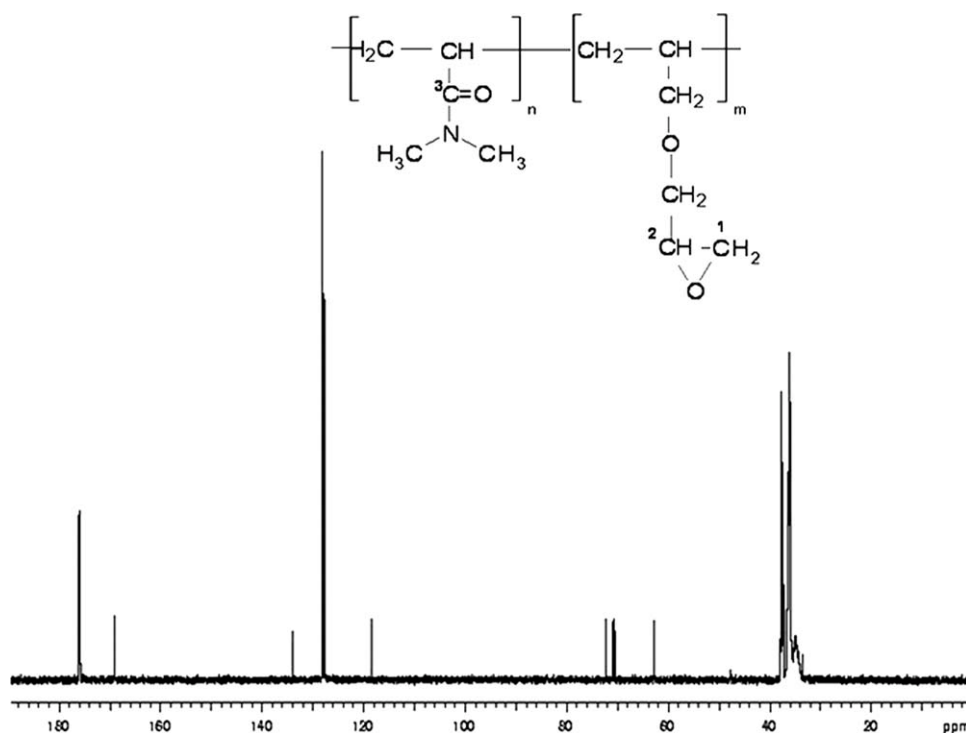


Figure 2 ¹³C-NMR of epoxy poly(dimethylacrylamide).

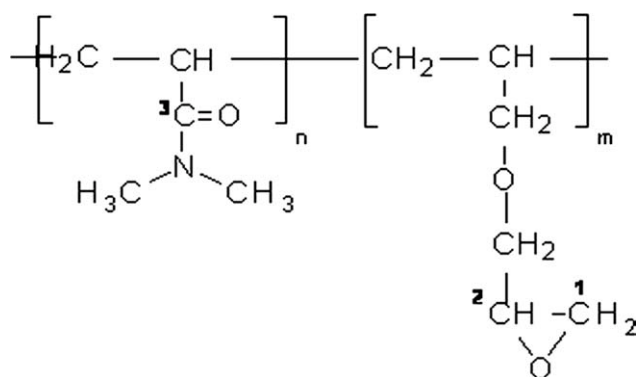


Figure 3 Structure of epoxy poly(dimethylacrylamide).

and the number of co added scans was 64. The spectra presented were base line corrected and converted to the transmission mode.

NMR spectroscopy

The NMR analysis of polymer was done using Varian Unity Plus 300 Model. The frequency used for ^{13}C -NMR of the polymer is 75.4 MHz, and for ^1H NMR is 300 MHz.

Contact angle measurement

Contact angle measurements were carried out in OCA 20, Data Physics Instruments GmbH, Filderstadt apparatus using distilled water. For contact angle measurement we used plasma treated silicon wafers to simplify the procedure. The plasma treatment was done by the flow of oxygen (80%) at $40\text{ cm}^3/\text{min}$ and Argon (6%) at $30\text{ cm}^3/\text{min}$ for 15 min (0.03 A, 50 KHz, and 60 V). SiO_2 is formed when silicon wafer is exposed to oxygen. The plasma treatment of silicon wafers forms a layer of SiO_2 on the surface of the silicon wafer. After plasma treatment the polymer solutions (1% w/v) were dropped on the surface of the

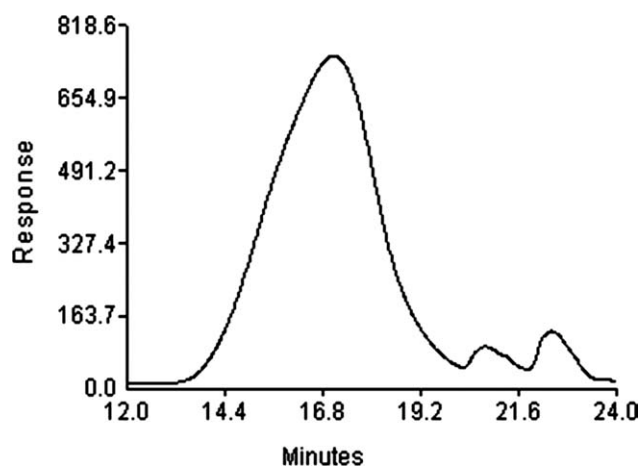


Figure 4 GPC chromatogram of epoxy poly(dimethylacrylamide).

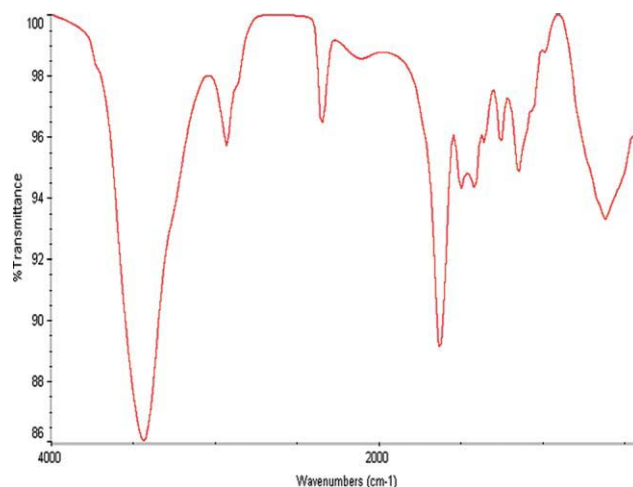


Figure 5 FT-IR spectrum of epoxy poly(dimethylacrylamide). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treated wafers and spin coated before the contact angle measurement. The surfaces of wafers and polymer adsorbed wafers were dried by pure nitrogen gas before measurement. Then a drop of pure water was dropped on the wafer surface and the contact angle of silica surface and polymer adsorbed surface were gained by contact angle measurement equipment.

Differential scanning calorimetry

T_g of the polymer and polymer adsorbed silica were evaluated using differential scanning calorimeter (DSC). Each sample (5 mg) was loaded onto a DSC aluminum crucible cell (Mettler Toledo International) heated under nitrogen at a constant heating rate of $10^\circ\text{C}/\text{min}$. The samples were heated first to 250°C and kept for 3 min in the hermetic cell to remove the thermal history. The samples were then

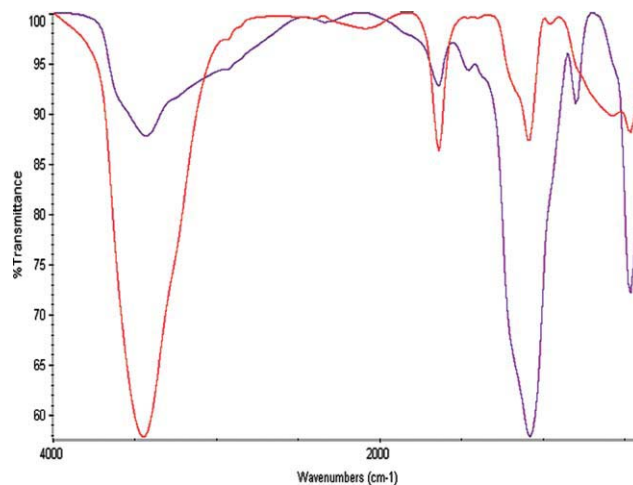


Figure 6 FT-IR of raw silica (a) and activated silica (b) nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
FT-IR Characteristic Peaks of Silica and Activated Silica

Material	Peak assignment (cm ⁻¹)				
	Si—OH vibration (stretching)	—OH bending (molecular H ₂ O)	Si—O—Si assymmetric stretching vibration	Si—O (H—...H ₂ O) bending	Si—O bond rocking
Nanosilica	~ 3432	~ 1641	~ 1080	~ 800	~ 466
Activated nanosilica	~ 3449	~ 1638	~ 1087	~ 963	~ 467

cooled to 30°C at the rate of 20°C/min and then a second heating was performed at the rate of 20°C/min to 250°C. The results from the second heating thermogram were recorded.

Thermogravimetric analysis

Thermogravimetric analysis was carried out with Universal TA instruments-500. Samples (11 ± 0.5 mg) were placed in platinum crucibles. An empty platinum crucible was used as reference. Samples were heated from ambient temperature to 900°C in a 60 mL/min flow of N₂ with heating rate of 20°C/min. Continual records of sample temperature, sample weight, its first derivatives, and heat flow were taken.

Scanning electron microscopy

SEM study was carried out using Nano SEM (Model: FEI Nova 200, FEG/SEM). Silicon wafers were used as model flat substrate after washing with piranha solution.

RESULTS AND DISCUSSIONS

Characterization of epoxy poly(dimethylacrylamide)

NMR analysis of epoxy poly(dimethylacrylamide)

The proton and ¹³C-NMR (D₂O) of the epoxy poly(dimethylacrylamide) are shown in Figures 1 and 2. The polymer has a polydimethyl acrylamide backbone with oxirane groups attached to the skeleton. The structure of the polymer is shown in Figure 3.

In ¹H-NMR spectrum the peaks at 1.6 ppm (C1) and 2.8 ppm (C2) are due to the protons of the oxirane ring. In ¹³C-NMR, the peaks around 176 to 169 ppm are due to the carbonyl groups (C3) of PDMA backbone and peaks around 38 to 33 ppm are due to methyl groups.

GPC analysis of epoxy poly(dimethylacrylamide)

Polymer sample was analyzed on the interval between 13 and 20 min and the GPC chromatogram of the polymer is shown in Figure 4 (small peaks at 21 and 23 min are salts or contaminations), the weight-average molecular weight (*M_w*) was of

617,000 Da and the number-average molecular weight (*M_n*) was of 154,000 Da.

FT-IR spectrum of pure polymer epoxy poly(dimethylacrylamide)

The FT-IR spectrum of epoxy poly(dimethylacrylamide) is shown in Figure 5. The characteristic FT-IR peaks of polymers at 1628 cm⁻¹ for carbonyl group and 1497 cm⁻¹ is due to C—H bending vibrations indication of the methyl group attached to nitrogen and 1255 cm⁻¹ is the characteristic absorption of C—O—C groups. A peak at 2931 cm⁻¹ is due to —CH₂ group. A small peak around 920 cm⁻¹ is due to oxirane groups of the polymer.

FT-IR of silica and activated silica nanoparticles

The purpose of surface activation of silica nanoparticles is to increase the concentration of —OH group on the surface of the nanoparticles. The silica nanoparticles have limited number of hydroxyl groups present on its surface. In this activation the concentration of hydroxyl groups on the surface of the silica was induced by treatment with NaOH. FT-IR spectra of silica and activated silica nanoparticles are shown in Figure 6. The FT-IR spectrum of nanosilica shows strong absorption at 1080 cm⁻¹ attributed to

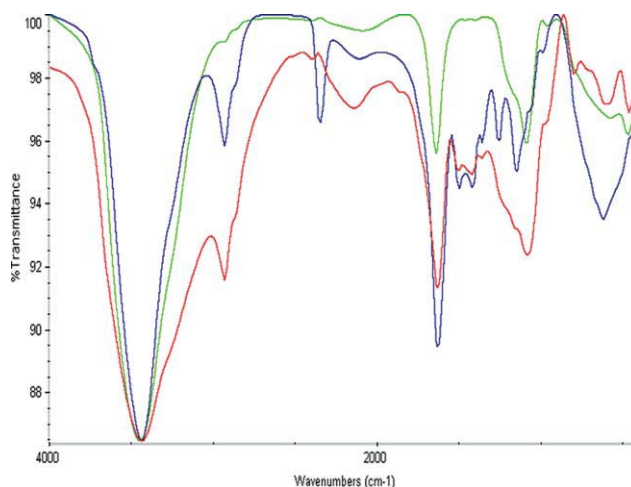


Figure 7 FT-IR Spectra of silica (a) polymer (b) and polymer adsorbed silica (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
FT-IR Characteristic Peaks of Epoxy Poly(dimethyl acrylamide) and Polymer Adsorbed Silica

Material	Peak assignment (cm^{-1})				
	$-\text{CH}_2$	$\text{C}=\text{O}$	$\text{C}-\text{H}$ bending	$\text{C}-\text{N}$ stretching	$\text{Si}-\text{O}-\text{Si}$ asymmetric stretching vibration
Epoxy poly(dimethylacrylamide)	~ 2931	~ 1628	~ 1497	~ 1147	–
Silica-polymer composite	~ 2932	~ 1630	~ 1422	–	~ 1081

$\text{Si}-\text{O}-\text{Si}$ siloxane groups and broad peak with maximum at 3432 cm^{-1} attributed to the surface hydroxyl groups. Assignment of IR bands of activated and untreated silica is shown in Table I. It was observed that the absorbance of $\text{Si}-\text{O}-\text{Si}$ peak becomes weaker for the spectrum of silica activated by NaOH. This may be due to the breaking of the siloxane groups after activation process. Furthermore, the silanol band at 3400 cm^{-1} for activated silica becomes broader and deeper after surface activation as compared with raw nanosilica. It can be concluded that activated silica with NaOH introduces more $-\text{OH}$ groups on the silica surface as conformed by FT-IR.

Characterization of polymer and polymer adsorbed silica

The FT-IR spectra of polymer and polymer adsorbed silica are shown in Figure 7. The characteristic peaks of the polymer and polymer adsorbed silica are shown in the Table II. The peak shifts related to the $\text{C}-\text{H}$ bending, $-\text{CH}_2$ and $\text{C}=\text{O}$ show clear interaction between silica and the polymer.

There are two possible mechanisms for the absorption of polymer on the silica surface. One is the formation of weak secondary interactions namely hydrogen bonds of Van der Waals interaction, the second is the formation of covalent linkages between surface silanols and the oxirane rings on the polymer. FT-IR analysis of earlier studies indicates that the adsorption of the polymer on the silica surface does not involve covalent bonds between the polymer and the silica surface.²⁹ Polymers with amide groups

have been found to be the most suitable for the preparation of nanocomposites with silica due to the $-\text{NHCO}-$ groups in the polymer chain which very easily form hydrogen bonds with silanol groups.^{30,31} Earlier studies showed that shift in peaks of FT-IR spectra of nanoparticles and the nanocomposites are due to strong interaction of polymer and nanoparticles through hydrogen bonding.^{32,33}

Contact angle measurement

The Figure 8(a,b) shows the contact angle measurement on plasma treated silicon wafer and polymer adsorbed silicon surfaces. When silica wafers are exposed to oxygen the SiO_2 is formed. The plasma treatment of silicon wafers forms a layer of SiO_2 on the surface of the silicon wafers. The thickness of the layer of silicon replaced by SiO_2 is about 44% of the thickness of the SiO_2 layer produced.³⁴ The contact angle on plasma treated silicon wafer is 26° and the contact angle on polymer adsorbed silicon surface is 78° . The water contact angle increases dramatically after treatment with the polymer. This phenomenon is attributed to the hydrophobicity of the different substitutes on the nitrogen atom of the dimethylacrylamide. According to the FT-IR and contact angle measurements we presented an adsorbing model of the polymer on silica surface as shown in Figure 9. In this model, the polymer was adsorbed on silica surface through the formation of hydrogen bond between oxygen atom on the carbonyl group of acrylamide part and hydroxyl group of the silica surface, which is similar to that described in earlier works.^{29,35} By the increased hydrophobicity of the

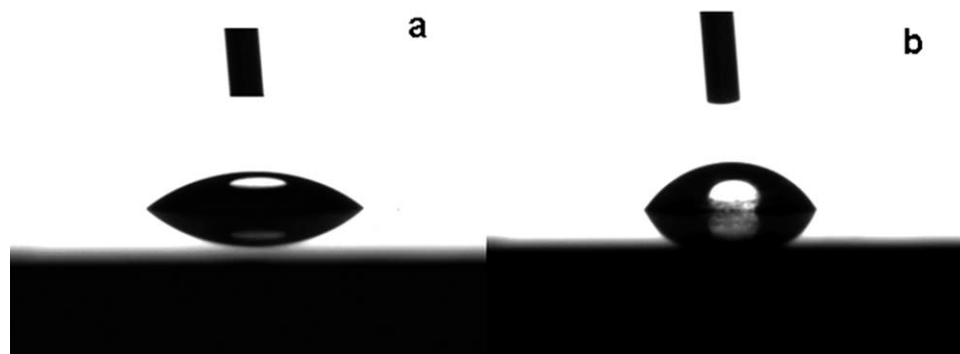


Figure 8 Contact angle measurement on silica surface (a) and polymer adsorbed surface (b).

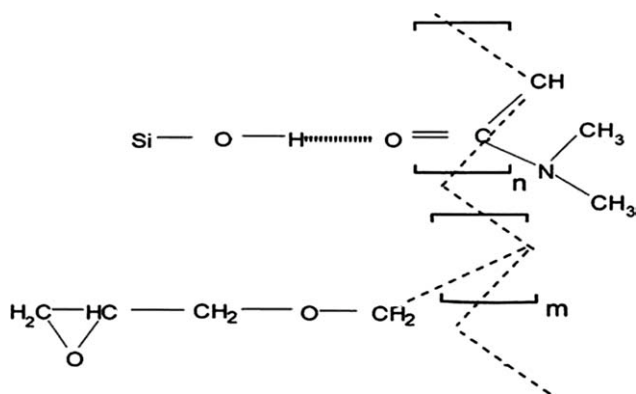


Figure 9 Adsorbing model of the polymer on silica surface.

polymer adsorbed particles they are expected to be completely redispersed in any organic medium. The adsorption of polymer on silica surface was mainly dependent on the hydrogen bonding associated with the substitutions on the nitrogen atom of the polymer. The methyl group on nitrogen atom may be intensifying the hydrogen bonding through the *p*_r-conjugation effect between nitrogen atom and hydroxyl group. When the polymer was adsorbed on silica surface the hydrophobic groups on nitrogen would tend to approach the silica surface and release solvent molecules (H₂O)³⁶ and then this could hinder the water molecules replacing the polymer molecules adsorbed on silica surface.

Thermal stability of composites

Glass transition temperatures (*T*_g) of polymer and polymer adsorbed silica were investigated by DSC. The thermo scan profiles were shown in Figure 10.

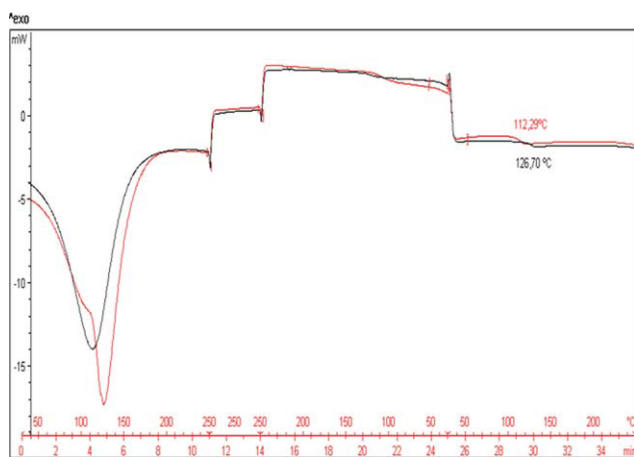


Figure 10 DSC thermogram curves of pure polymer (a) and polymer adsorbed silica (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It can be found from the analysis that neat polymer has *T*_g at 112.29°C. However, the polymer adsorbed silica exhibits *T*_g at 126.70°C. These results show that the polymer adsorbed silica has higher *T*_g due to the strong interaction between the silica network and the polymer. Thus strong interaction limits the movement/motion of the polymer chain segments due to increase rigidity structure of the polymer. Specifically the polymer segments that were close to the SiO₂ surface were more constrained by the surface than remote segments thus requiring more energy to pass from a glassy to rubbery state.^{37,38}

The thermal decomposition behavior of epoxy poly(dimethylacrylamide)-silica composites films was investigated by TGA at heating rate of 20°C/min as shown in Figure 11. It was found that polymer and composites decomposed in a single stage (main degradation stage). The major weight loss of the composite is attributed to the decomposition of the polymer. Pure SiO₂ does not present any abrupt decrease in weight and only a slight decrease in weight at about 100°C appears due to the removal of absorbed water.³⁹ The data of the degradation temperature were collected from derivative thermogravimetric curves (DTG, not shown). It was found that thermal decomposition temperature (*T*_d) of polymer is 398.91°C. The *T*_d of SiO₂ polymer composite is 415.42°C. The composite has *T*_d value higher than pure polymer by about 17°C. Since nanosilica exhibits good thermal stability even at 800°C the weight loss of the composite is resulting mainly from the polymer matrix. It seems that the polymer chain adsorbed or trapped in the network of the nanocomposite is protected from thermo-oxidation process and this hinders the process of degradation. The composite films therefore show better thermal stability as compared to the pure polymer.

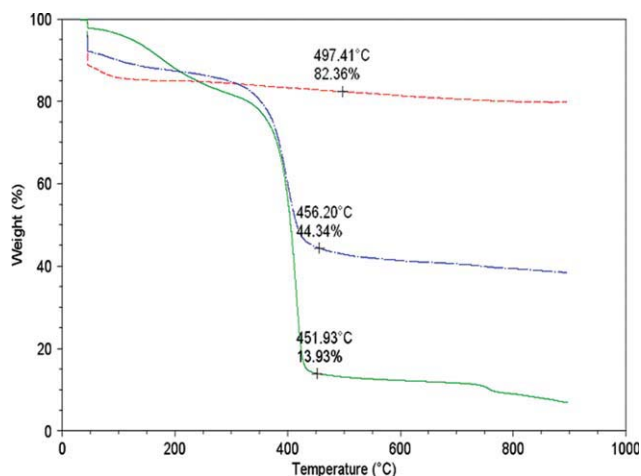


Figure 11 TGA curves for silica (a), polymer adsorbed silica (b), and polymer (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

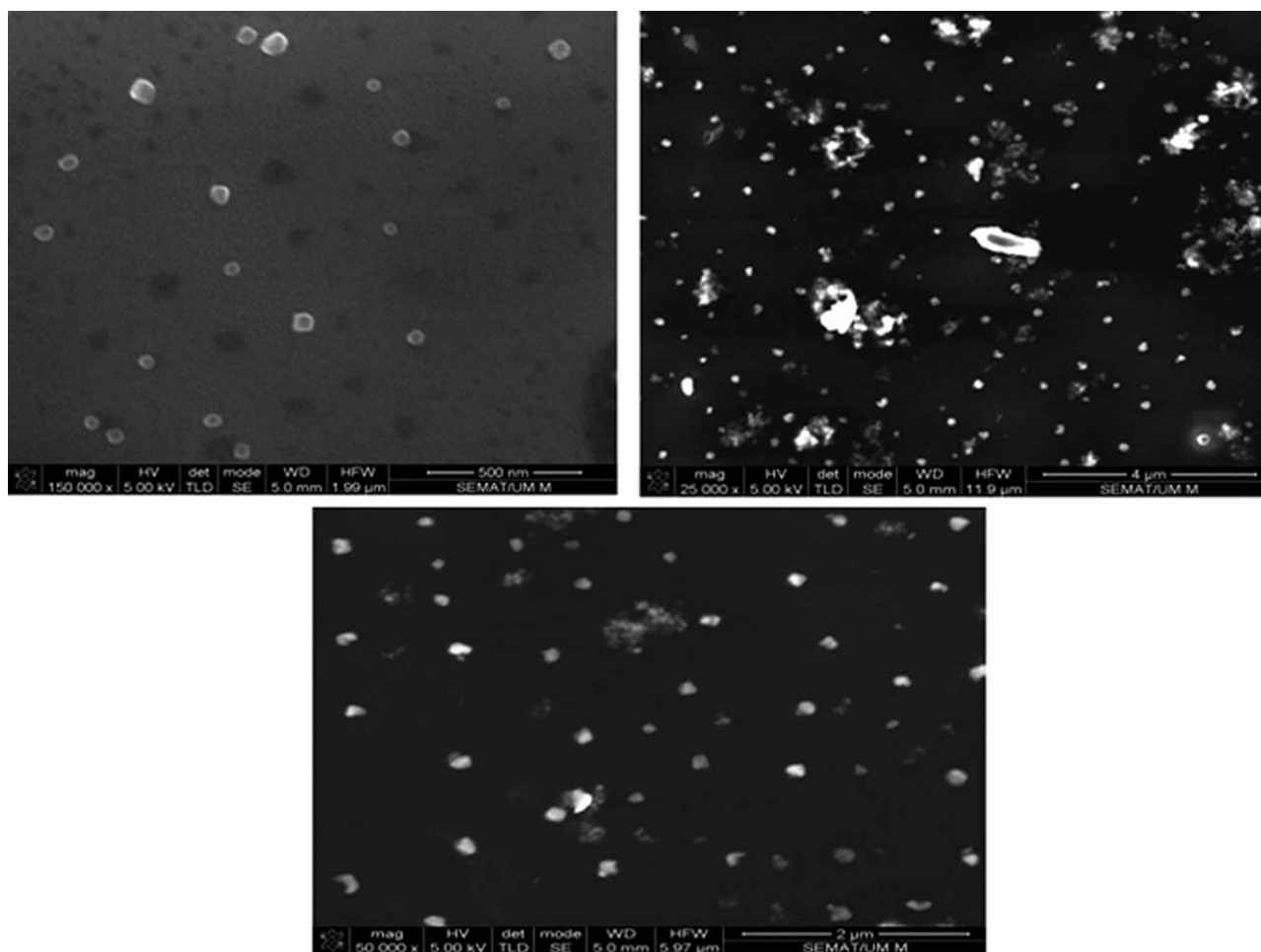


Figure 12 (a) SEM of silica nanoparticles, (b) SEM of polymer adsorbed raw silica, and (c) SEM of polymer adsorbed activated silica.

SEM analysis

SEM images of the silica particles and its dispersion in polymer are shown in Figures 11(a), 12(b,c). The silica particles have uniform size and spherical shape. It was observed that there was no agglomeration of the particles in nanocomposites with both activated and untreated silica composites. The size of the pure silica particles is in the range of 87 to 93 nm and the size in the polymer dispersion with activated silica is 104 to 115 nm, while the size range in the polymer dispersion with untreated silica is 128 to 209 nm, as measured from SEM analysis. The size of particles in activated silica composites is slightly larger than the composites with untreated silica. It was also very important to observe that though both activated and untreated silica showed good dispersion in the polymer, the dispersion is more uniform in dispersion with activated silica.

CONCLUSIONS

The preparation of nanocomposites in industrial scale is still difficult to achieve. There are many

methods for their preparation, but an universal easy and efficient process allowing a perfect distribution of the inorganic particles in a polymer matrix is a challenge. This is mainly due to the difficulties in fulfilling all requirements such as good compatibility and high degree of entanglement between polymer matrix and polymer chains attached to the surface of the inorganic particles. In this work we demonstrated that an excellent surface modification can be achieved by adsorption of copolymers as stabilizers on activated silica surface:

FT-IR studies confirmed that the polymer molecules chain was anchored on the surface of the SiO_2 nanoparticles.

The contact angle and FT-IR measurements showed that the adsorption of polymers on silica surface derived from the formation of hydrogen bond from the hydrophobic effects of substituents on nitrogen atom. These hydrophobic groups could hinder water molecules replacing the adsorbed polymer molecules and markedly improved the dispersion of SiO_2 nanoparticles in polymer. This

observation is supported by the fact that the contact angle increases dramatically after polymer adsorption on the silica surface.

The improved interfacial interaction between the particles and polymer enhanced the thermal properties. The glass transition temperature of the polymer is increased with the addition of silica nanoparticles to the polymer.

The present study shows that interphase chemical links between the silica network and the polymer chain prevent the agglomeration of silica nanoparticles making them their distribution more homogeneous in polymer as evidenced by SEM analysis.

With this new procedure, we have created a tool to obtain a broad range of new inorganic/organic hybrid materials in a very easy way.

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