Synthetic Strategies towards Silica/Poly (Acrylamide-Co-Acrylic Acid) Composites

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Abstract. Herein, we are reporting increased thermal properties and self-sustaining ability of polymer compositions with silica. The composite of poly (acrylamide-co-acrylic acid) [P(AM-co-AA)] with silica created intermolecular interactions. The formation of a composite has confirmed by FTIR spectroscopy, DSC, TGA, and FE-SEM analysis. The silica particles were homogeneously distributed in the P(AM-co-AA). The incorporation of silica particles gives rise to the enhancement of thermal stability due to the strong interactions between silica and poly (acrylamide-co-acrylic acid) polymer.

Graphical Abstract
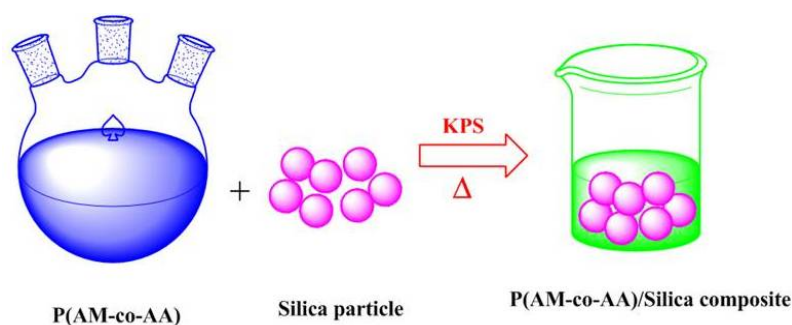
Keywords: Poly(acrylamide-co-acrylic acid), silica particles, composite, thermal stability

1 Introduction

Polymer composites have been widely studied over a long period of time and over the past few decades, organic polymer–inorganic oxide filler composites have replaced a lot of the conventional polymers in application fields. They are generally organic polymer composites filled with inorganic fillers. Their properties combine the advantages of the inorganic filler material (i. e., rigidity, thermal stability) and of the organic polymer (i.e., flexibility, ductility, process ability) [1]. In addition to such functionalization, composition can successfully reinforce materials; a characteristic example is natural rubbers reinforced by carbon black and silica for practical utilizing as tire materials.

Although the composites strategy is useful for the design of relatively hard functional materials, it is not simple to recognize soft composite materials because of the strong interactions at the interface that decrease the polymer chain mobility [2]. A successful way to improve mechanical properties of a polymer is to create their composites or blend with other polymers that have better mechanical properties for the intended applications [3]. Schmidt et al. synthesised conductive composites of polymer using the biologically active polysaccharide hyaluronic acid (HA) as the dopant in order to create biomaterials for tissue engineering and wound-healing applications [4].

Among inorganic oxide fillers, silica particles have received much attention due to their well-defined ordered structure, high surface area, cost-effective production, and the ease of surface modification [5]. In the polymer composition with silica particles, this can improve thermal properties and self-sustaining

ability under working environmental conditions. The modification of silica particles leads to better hydrophobic interactions with the polymer and unusual unique properties when compared with unmodified hydrophilic fillers [6, 7]. Porous silica materials with the large specific surface area, high pore volume and tunable pore size are of great interest for academia and industry due to their applications in adsorption, catalysis [8, 9], separation processes [10], drug, delivery systems [11, 12] and gas storage [13, 14.] The possibility of using polymer-silica composites to tailor the textural properties of silica could potentially be of considerable value for new silica applications within the above mentioned fields of interest [15]. The performance of silica materials in many applications requires controlling their morphology and the pore structure. The properties of the composite material may be adjusted by varying the type of inorganic filler, filler size, filler content and blending methods [16]. In addition, the compatibility between the filler surface and the polymer matrix is also an important factor [17].

A three-dimensional cross linked system is formed from a hydrophilic polymer, referred to as a hydrogels, which swells and absorbs water causing the network to swell in solution [18]. Polymeric hydrogels are of great interest for biomaterials applications because of their biocompatibility [19]. These are amongst most attractive classes of "soft matters" with several established and many more possible applications. On the other hand, swelling is limited to rubber like behaviour due to presence of crosslink or strong physical interactions between polymeric chains [20].

The motivation of the current research was to use the silica to prepare silica/P(AM-co-AA) composite by free radical polymerization. This manuscript focuses on more recent trend in the development of silica/polymer composites: materials, synthesis and characterizations of polymer/silica composites.

2   Experimental

2.1   Chemicals and Instrumentations

Acrylamide, tetraethoxysilane (TEOS), ammonia, and ethanol were obtained from Spetrochem Pvt. Ltd., Mumbai, India. Acrylic acid and potassium persulphate (KPS) were purchased from S.D. Fine Chem. Ltd, Mumbai, India.

The infrared spectra of the sample were recorded on a Shimadzu FTIR-8400 frequency range from 400 to $4000cm^{-1}$ using KBr flakes.

The morphology of the dried sample was examined using S-4800 (SEM) JEOL JSM 6360 & JEOL JSM 5400 in voltage range of 0.5 to 30 kV instrument after coating the sample with gold film.

Raw materials and polymer composite were analyzed by Differential Scanning Calorimetry (DSC) on Perkin elmer DSC 4000 10 ℃/min. in temperature from 0 to 300 ℃ in steam of nitrogen atmosphere.

Thermal stability was determined by Thermal Gravimetric Analysis (TGA) on Perkin elmer TGA 4000 10 ℃/min.

2.2 Preparation of Silica Particles

Silica particles were prepared by the stober process [21]. In 200 mL beaker tetraethoxysilance (TEOS) was dissolved in ethanol. In another 200 mL beaker mixture of ammonia, water and ethanol was prepared in 1:1:1 ratio. In this beaker, solution of TEOS was added slowly with constant stirring the mixture for 24 hrs. The obtained white precipitate was seapareted by centrifugation the high speed. The obtained silica particles were dried at room temperature.

2.3 Preparation of Polymer Composites

P(AM-co-AA) hydrogels were prepared by free radical polymerization of acrylamide and acrylic acid in water. Acrylamide (5 g) was dissolved in 20 mL of double distilled water in a 250 mL three neck round bottom flask equipped with a stirrer, condenser, and thermometer. Acrylic acid (2 mL) was added to the reaction mixture and stirred at room temperature for 10 min. Silica particles were added to reaction mixture, which was heated at 64℃ with stirring for 30 min. Potassium persulphate (0.2 g) was added as a radical initiator into reaction mass for polymerization at constant stirring. The resulting hydrogel was cooled at room temperature.
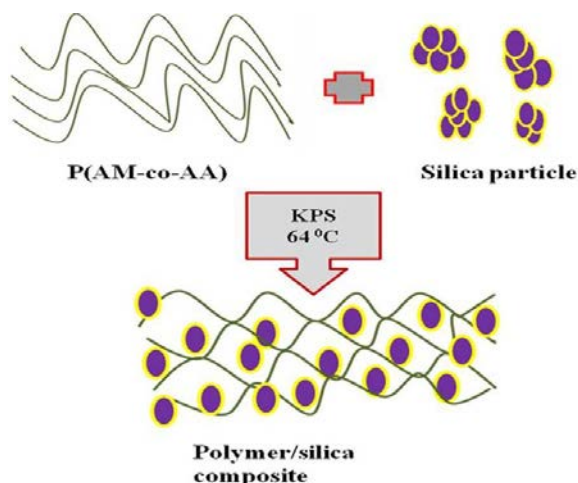
Figure 1. Scheme of P(AM-co-AA)/ silica composite

3   Results and Discussion

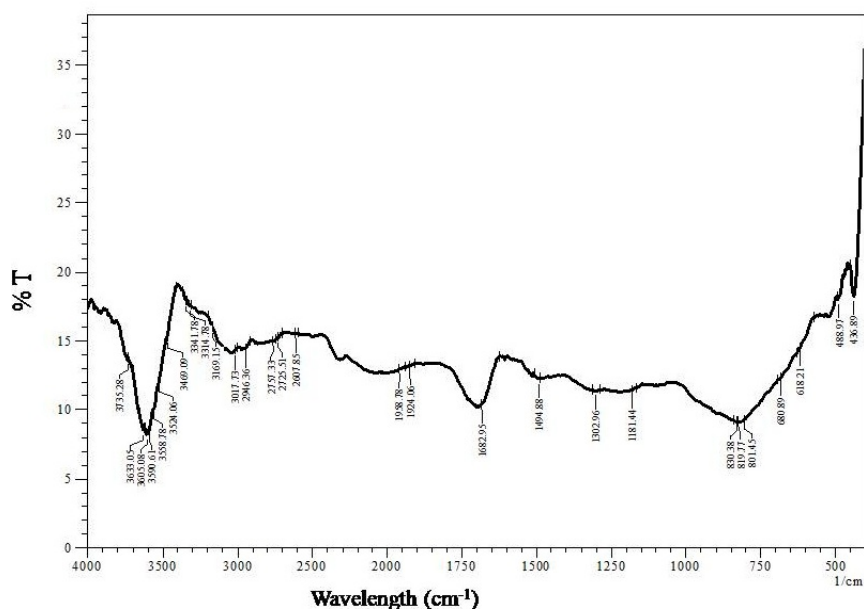## 3.1   FTIR Analysis of Polymer P(AM-co-AA)

Figure 2. FTIR analysis of P(AM-co-AA) polymer

The infrared spectra of P(AM-co-AA) is given in Fig. 2. The midrange band in the range of 3633-3451 cm^{-1} are results due to –NH$_2$ from acrylamide, the presence of water in hydrogel and the acidic –OH of polymer. The C-H stretching band is confirmed by presence of band at 2950 cm^{-1} due to asymmetric stretching vibrations of –CH$_2$ groups in polymer. The amide carbonyl is observed at 1683 cm^{-1}, The band found in between 800-400 cm^{-1} is due to bending occurring from NH and OH groups [22].
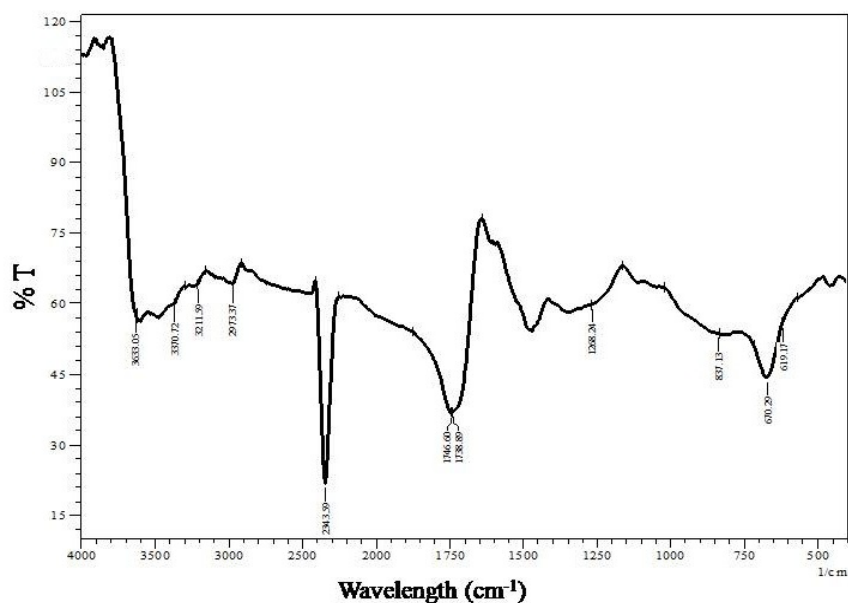
Figure 3. FTIR analysis of P(AM-co-AA)/silica composites material

The infrared spectra of silica composites are given in Fig. 3. The midrange bands in the range of 3633-3451 cm^{-1} and decreases up to the 2973 cm^{-1} are due to intermolecular hydrogen bonding between polymer and silica. The silica particles are confirmed by presence of band at 2343 cm^{-1}. The amide carbonyl is seen at 1746 cm^{-1}. The bands found between 800-600 cm^{-1} are due to bending occurring from NH and OH groups [23].

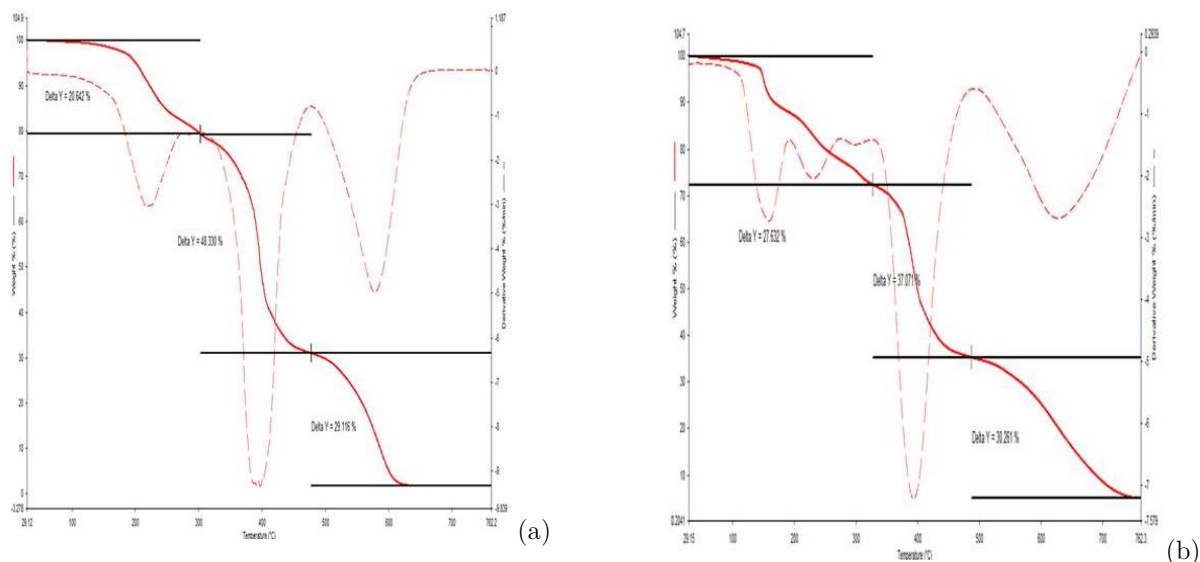## 3.2   Thermal Stability of Polymeric Compounds

Figure 4. Thermal gravimetric analysis of (a) P(AM-co-AA) polymer (b) P(AM-co-AA) silica composites material

Thermal stability of P(AM-co-AA) and polymer silica composite were studied by thermogravimetric analysis (TGA) and thermograms are depicted in Fig. 4. The theromogram of (a) P(AM-co-AA)

exhibited the first step weight loss as a consequence of moisture present. The second step observed in the range of 200 to 350 ℃ may be due to the release of ammonia by imidazation or CH_4 in the polymer with weight loss 48.3 %. The third step mass loss seen in between 350 to 490 ℃ is concerned with the carboxylate group present in polymer chain with mass loss 29.11 %. The polymer backbone degradation of P(AM-co-AA) occurred in fourth step which is in the range of 490 to 600 ℃ [22]. Figure (b) of polymer silica composites shows three stages of degradation, the first degradation starts from 20 to 320 ℃ due to moisture, approximately 27.632 % weight loss. The second degradation occurs between 320 to 490 ℃ due to the breaking of polymer chain with 37.071 % weight loss. The final degradation starts from 490 to 720 ℃ due to degradation and char of composites and a 30.261 % weight loss. It means the formation of the polymer composite has changes from 620 to 750 ℃ relative to the thermal properties of polymer [24].

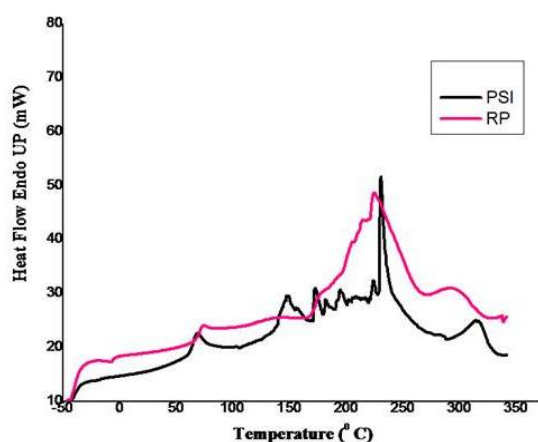### 3.3 Differential Scanning Calorimetric Analysis

Figure 5. Differential scanning calorimeter of P(AM-co-AA)[RP] and P(AM-co-AA)/ silica composites (PSI)

The DSC curves for P(AM-co-AA), and P(AM-co-AA)/silica composite are represented in Fig. 5 under the temperature range of -50 ℃ to 350 ℃ in a steam of nitrogen on thermal analysis. From Fig. 5 we concluded that the P(AM-co-AA) shows the glass transition temperature at 75 ℃ and the curve of P(AM-co-AA) showing a characteristic endothermic peak at 220 ℃ is corresponding to its decomposition while in case of the silica composite the glass transition temperature is at 70 ℃ and a broad peak is converted into a sharp endothermic peak at 230 ℃. This thermal property is due to intermolecular interactions and supports the formation of polymer composite [25].

3.4 Surface Characterization

One of the most important properties that must be considered when studying a hydrogel is its microstructure morphology. Fig. 6(a) shows the silica particles having the spherical shape and is in aggregation form. Figure (b) shows the secondary electron images of P(AM-co-AA) in the water-saturated state. This observation verified that the synthesized polymer structure of P(AM-co-AA) has a porous structure with effective pore sizes in the 150- 250 nm range. It is proposed that these pores are region of water permeation and interactions sites between external stimuli and the hydrophilic groups of the hydrogel. These pores are produced from water evaporation at the time of hydrogel synthesis. The morphology of the composite was studied by scanning electron microscopy in Fig. 6(c). From this image it can be seen that composites have smooth surfaces and the micrographs show the porous nature with a very small amount of silica particle composited in its pore and surface of the sample[26].
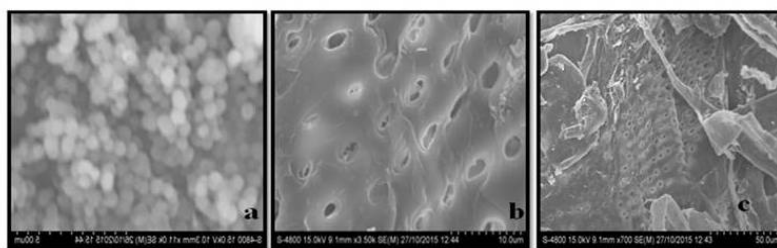
Figure 6. Morphology of a) Silica particles b) P(AM-co-AA) polymer c) P(AM-co-AA) silica composites

3.5 Elemental Analysis

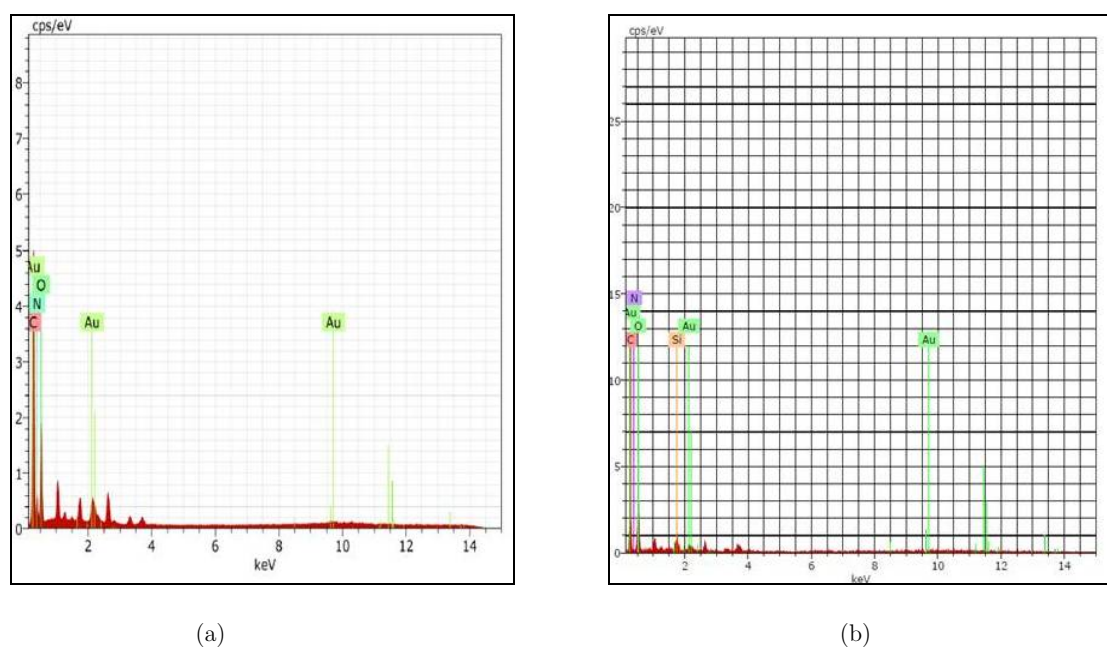(a)   (b)

Figure 7. EDAX analysis of polymeric compounds

From the EDXS analysis in Fig. 7(a), it is clear that the synthesized polymer is non-conducting and contains the carbon, oxygen and nitrogen as the major elements in the composition proving that the synthesized polymer is P(AM-co-AA) while EDXS analysis in Fig. 7(b), indicates carbon, oxygen, nitrogen and silica as the composite material in the synthesized polymer composite [24,25,26,27].

4   Conclusion

Herein we demonstrate the synthesis of a composite polymer where the polymer chains are not directly bonded but rather mechanically interlocked to the silica surfaces. The silica particles were homogeneously distributed in the P(AM-co-AA). For obtaining the optimum properties for the composites, requires an excellent homogeneous dispersion of the fillers i.e silica, as the tendency of the silica particles to agglomerate can seriously affect the achievable properties. Therefore, to provide a strong interfacial interaction between the inorganic particles and the polymer matrix, silica fillers must have suitably modified surfaces.

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