A Unique Approach To Prepare Poly (Acrylamide –Co-Itaconic Acid) /Graphite Composite Polymer For Electrical Conducting Properties.

S .K. Bajpai[a*], S. Awasthi[b*] And Abhishek Dubey[b]

a. Polymer Research Lab, Dept.of chemistry, Govt. Model Science College, Jabalpur (M.P)-482001, India
b. Dept.of Physics, Govt. Model Science College, Jabalpur (M.P)-482001,
India.

Abstract

In this work a pH-sensitive poly(acrylamide-co-itaconic acid)/ graphite composite hydrogel is prepared by free radical initiated polymerization of monomers acrylamide(Am) and itaconic acid(IA) in the presence of settled graphite(Gt) particles using N,N'-methylene bisacrylamide(MB) as cross linker in aqueous medium. The SEM analysis revealed almost uniform distribution of grafite particles within the polymer matrix.For the same amount of graphite, the conductivity of hydrogel composite was observed to increase and later on decrease with amount of cross linker (MB) and monomers IA and Am.

Keywords: Graphite, , conductivity, cross linker.

INTRODUCTION

Recently, they have been considerable efforts made to prepare conducting polymers(CP) for using in a variety of applications such as fuel cells, super capacitor, dye sensitive solar cells and re-chargeable lithium batteries[1-2]. There are several reports which describe synthesis of conducting polymers using various types of chemical species of organic and inorganic origin such as aniline, pyrrole, copper, carbon etc [3-4]. However, looking to the excellent electrical conducting property of carbon based compounds like graphite and graphene, the current research works have mainly focused on these material to prepare conducting polymers. In fact, a variety of strategies have been followed to prepare conducting polymer composites. Recently, Fouad et al.[5] have reported synthesis of high density polyethylene/graphite nano composites using melt blending in a co-rotating intermeshing twin screw extrude. One-pot synthesis of conducting graphene-polymer composite has been recently reported by Eswaraiah et al.[6].The simultaneous reduction of graphite oxide, melting of the polymer and embedding of reduced graphite oxide nano flacks in polymer offer a new way of synthesizing graphene/ polymer composite. Similarly, Segerstrom et al[7].carried out a study to determine water sorption, water solubility, dimensional change caused by water storage, residual monomer ,and possible cytotoxic effect of heat-polymerized carbon-graphite fiber–reinforced composites with different fiber loadings based methyl methacrylate/ poly(methyl methacrylate) (MMA/PMMA). In a work by Fan et al.[8], few-layered graphene sheets, synthesized by direct current arc-discharge method using NH_3 as one of the buffer gases were dispersed in chitosan /acetic acid solutions to prepare films. The films were tested for mechanical properties and biocompatibility. In addition to the above mentioned conjoint instrumental techniques to prepare conducting polymer composites, there have also been relatively simpler methods proposed to synthesize conducting polymer composites. For example, Lin et al.[9] have reported synthesis of polyacrylate/ graphite hydrogel by a simple approach which involves free–radical initiated polymerization of potassium acrylate in the presence of graphite particles pre-dispersed in the reaction mixture. However, there exists some uncertainty regarding the almost homogeneous/ uniform distribution of graphite particles within the polymer network formed because the chances of settling down of graphite particles dusting the course of polymer formation can not be completely eliminated.

In the present work, we have developed a pH-sensitive polymer/ graphite composite hydrogel using an almost diffrent approach which totally eliminate the chances of agglomeration or non-uniform distribution of graphite within the polymer networks.

EXPERIMENTAL

Monomers acrylamide (Am) and itaconice acid (IA), the cross linker N,N'-methylene bisacrylamide (MB), the initiator potassium persulfate(KPS) were purchased from Hi Media Chemicals, Mumbai, India .The graphite micro powder (Gt), having a specific surface area larger than $80 m^2 g^{-1}$ and an average particle size smaller than 1.8×10^{-6}m was purchased form Merck Chemical, Mumbai, India and was dried at 60 °C for 4h prior to use. The monomer (Am) was re-crystallized in methanol to remove the inhibitor .The de-ionized water was used throughout the investigations.

Preparation of p(Am-co-IA)/Gt composite

The composite was prepared by free radical initiated aqueous polymerization of Am and IA in the presence of cross linker(MB)within the settled graphite column. For example, in a test-tube, 14.06 mili mol of Am, 384.3 micro mol of IA, 518.90 micro mol of crosslinker MB and lastly 295.9 micro mol of initiator KPS was dissolved in the above sequential manna is distilled water and the final volume was made up to 5.0 ml. To this ,a per-weighed quantity e.g. 1.7g of graphite powder was added slowly and carefully and then the above mixture was shaken vigorously for 5 min and allowed to stand till all the graphite powder was settled. The test-tube was now placed is an electric oven (Tempstar,India) at 70°C for a period of 2h.After the polymerization was over, the test-tube was taken out , broken and the cylindrical P(Am-co-IA)/Gt hydrogel composite was taken out, washed with distilled water and then cut into slices each one almost 2mm thick. The circular discs were equilibrated in water for 12h to remove the un-reacted salts, then finally dried till they attained constant weight. The Fig.1 shows the optical photograph of plain p(Am-co-IA) and p(Am-co-IA)/Gt composite discs.

Measurement of electrical conductivity

The electrical conductivity of composites discs measured using four probes method Five measurements were made and average values are reported.

RESULTS AND DISCUSSION

Preparation of p(Am-co-IA)/Gt composite :

As mentioned in the section introduction the preparation of polymer/ graphite composite by free-radical induced polymerization in the presence of dispersed graphite particles is a commonly adopted method. But the non-uniform distribution of graphite particles, on a micro scale level, may result in formation of gel composite having un-even physico-chemical and other related properties along the polymer network. However, in the present study, the polymerization of acrylamaid and itaconic acid takes place within the aqueous phase which is present within the settled graphite column. Therefore, the chances of inhomogeneous distribution of Gt particles within the polymer network are almost nil. Fig.2 shows the overall scheme of formation of polymer/ graphite composite. In order to ensure the uniformity in the graphite particles distribution along the polymer matrix, we carried out an experiment. The volume of various composite discs, obtained from same sample, was determined accurately using heptane as a non-solvent Then mass of each composite disc was measured accurately and finally density of all the samples was calculated using the density = mass/volume relationship. Finally, all the density values, obtained, were represented graphically as shown is Fig.3. All data points joined yielded a horizontal straight line thus indicating that all the sample had almost the same density.

SEM analysis of composite

The novelty in the proposed study is to ensure the uniform distribution of graphite particles within the polymer matrix. To confirm this SEM image of polymer/graphite composite was recorded as shown in Fig.4. It can be seen that there is fairly uniform distribution of particles within the polymer thus establishing the superiority of this method.

Effect of crosslinker on conductivity

In order to study effect of crosslinker concentration on conductivity of resulting composites , we prepared number of polymer/ Gt composites, containing different amount of crosslinker MB, in the range of 129.72 to 648.63 micro mol and measured their conductivity using four probe experiment. The results, as shown in Fig.5 reveal that electrical conductivity of composite increases with crosslinker concentration attains an optimum value of 279.16 S/cm at the crosslinker concentration, of 389.18 micro mol and then it begins to decrease with further increase in MB content. The observed findings may be explained as follows: When the amount of crosslinker MB is quite low, the loosely bonded three dimensional crosslinked network is formed, which is quite unable to put entrapped charcoal microparticles intact, thus resulting in low conductivity of the polymer composite. As the amount of crosslinker increased, more and more tightly crosslinked network is formed within the polymer matrix , thus holding the entrapped graphite particles more intact. This causes an increase in the conductivity and finally it attains an optimum value. However, as the concentration of crosslinkers is increased further, the number of crosslinkes increase and this reduces the free space available among the three-dimensional crosslinked segments and so the space available is small enough as compared to the size of the micro sized particles. This is turn causes the weakening of the inter-connectivities among graphite particles, thus causing a decrease inelectrical conductivity. Almost similar result have also been reported elsewhere[3].

Effect of IA content or conductivity

The effect of IA content in the polymer/ graphite composite on the electrical conductivity was investigated by measuring conductivity of various samples, containing varying moles of IA in the feed mixture, in the range of 230.59 to 1383.55 micro mol as shown in Fig.6. The results indicated that with the increase of IA content in the composite, electrical conductivity continues to increase, attains an optimum value of 193.43for 1152.95micro mol of IA, and then it begins to decrease with further increase in content of monomer acid. The results obtained may be explained on the basis of the fact that initially when IA content is low, the graphite particles that are present within the three dimensional networks are not much intact or have insufficient inter-particles connectivity. As the IA content increase, the presence of carboxylic acid groups causes an enhancement in the inter-segmental hydrogen bonding interactions which produce additional crosslinks within the polymer networks. As a results, the graphite particles have better connectivity with each other, thus resulting in enhancement in the electrical conductivity of the composite. However, beyond 193.43 micro mol concentration of IA, the further rise in IA content causes the mesh size of the polymer network sufficiently small enough so that the micrometer sized graphite particles are not well occupied in the three dimentional crosslinked networks and hence begin to lack of connecting channels. Finally, this result in decrease in the conductivity of the polymer of composite.

Similarly, the conductivity of polymer/graphite gel showed similar trend when content of other monomer Am was increased (Please see Fig.7). This can also be explained as follows : when amount of Am is sufficiently low, these is not enough network formation and this results is incapability of crosslinked segments to hold the micro sized graphite particles almost intact, thus causing low conductivity .On increasing the monomer content ,fairly high degree of polymerization occurs with fairly dense network This keeps the graphite particles almost intact and allows optimal conductivity. However, when Am content is further increased , the polymer fraction in the composite increases . Since Am is nonionic in nature , it causes a decrease is the conductivity of the resulting composite material.

CONCLUSION

From the above steady it may be concluded that poly (Am-co-IA)/ Gt composite , produced by free radical initiated polymerization of Am and IA in the presence of pre-settled graphite powder results in formation of composite with uniformly distributed Gt particles throughout the polymer matrix.. It conductivity changes with amount of crosslinker MB ,ones monomer Am and IA present in the feed mixture.

References

1. Lan, z.; Wu, J. H.; Wang, D. B.; Wao, s. c.; Lin, J. M. & Huang, V. F; Solar Energy 2006, ,90,1483.
2. Kato,T; Okazaki,A; Hayase,S. J.photobiology A:chemistry 2006, 179,42.
3. Lin,J.; Tang,Q.; Wu,J; Hao,S. Reactive and Funct. Polymer 2007,67,275.
4. Lin,J.; Tang,Q.; Wu,J. Reactive and Funct. Polymer 2007,67,489.
5. Tang,Q.; Wu,J.; Sun,H.; Lin,j.; Fan,s.; Hu,D. Carbohydrate polymers 2008, 74,215.
6. Fouad, H.; Elleithy, R. J. Mech , Behav. Biomed, Mater . 2011, 49(7),1376.
7. Eswarajah,V.; Balasubramaniam,K.; Ramprabhu,S. Nanoscale2012,4(4),1258.
8. Segerstrom,S.; Sandbargh-Englund,G.; Ruyter,E.L. Eur. J. Oral Sci. 2011, 11a(3), 246.
9. Fan, H; Wang, L.; Zhao,K.; Shi , Z. ; Jin , Z. ;and Ge, Z. Biomacromolecule ,2011, 11(9), 2345.

Captions

Figure 1. Optical photograph of (A) poly(Am-co-IA) and (B) poly(Am-co-IA)/Gt composite.
Figure 2. Schemes showing formation of poly(Am-co-IA)/Gt composite.
Figure 3. Test for uniform distribution of graphite powder within the polymer matrix.
Fig.4 SEM image of polymer/graphite composite
Figure 5. Effect concentration of MB in the feed mixture on electrical conductivity of the poly(Am-co-IA)/Gt composite.
Figure 6. Effect of monomer IA concentration in the feed mixture on electrical conductivity of the poly(Am-co-IA)/Gt composite.
Figure 7. Effect of Am concentration in the feed mixture on electrical conductivity of the poly(Am-co-IA)/Gt composite.

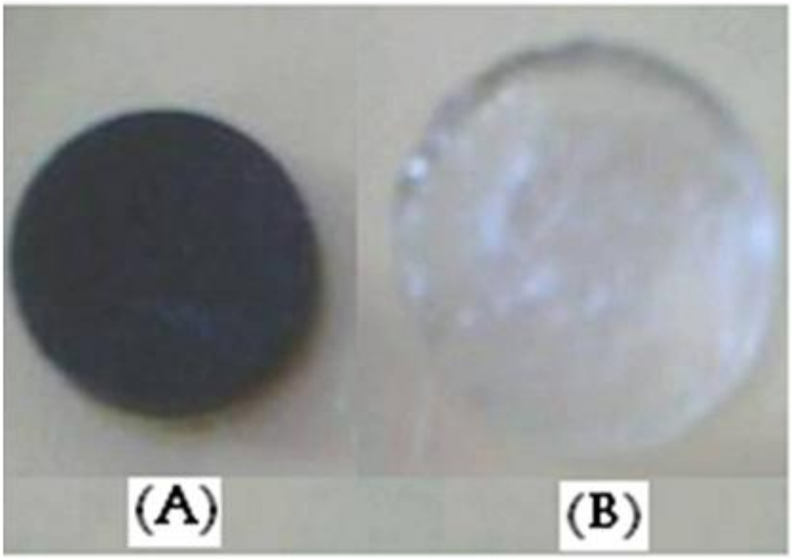

Fig.1

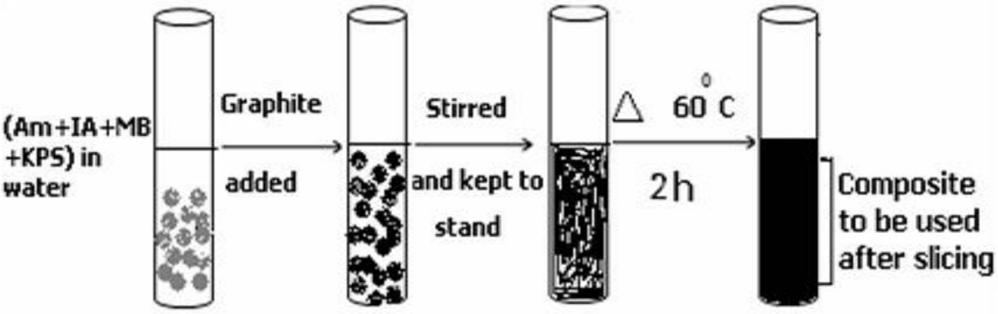

Fig.2

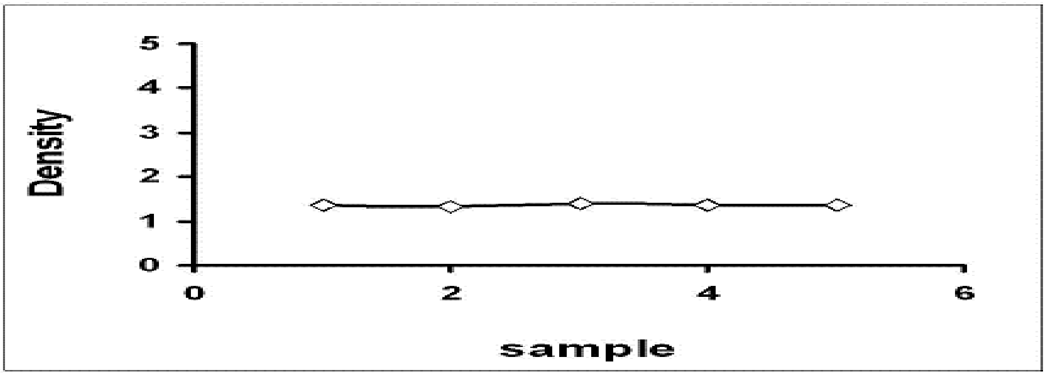

Fig.3

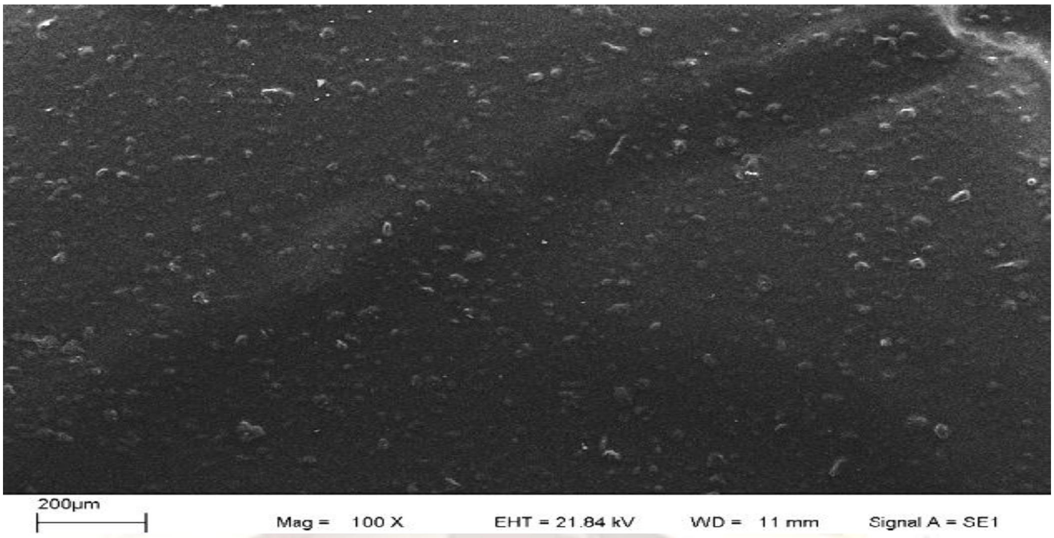

Fig.4

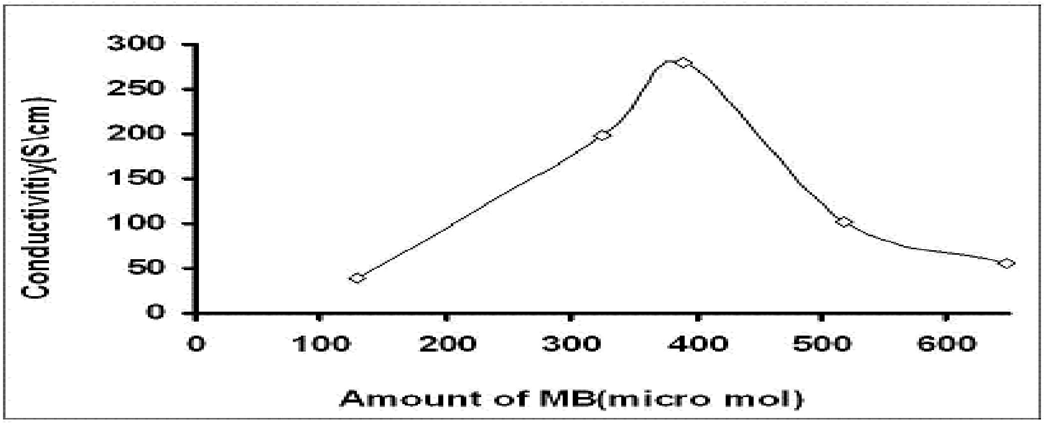

Fig.5

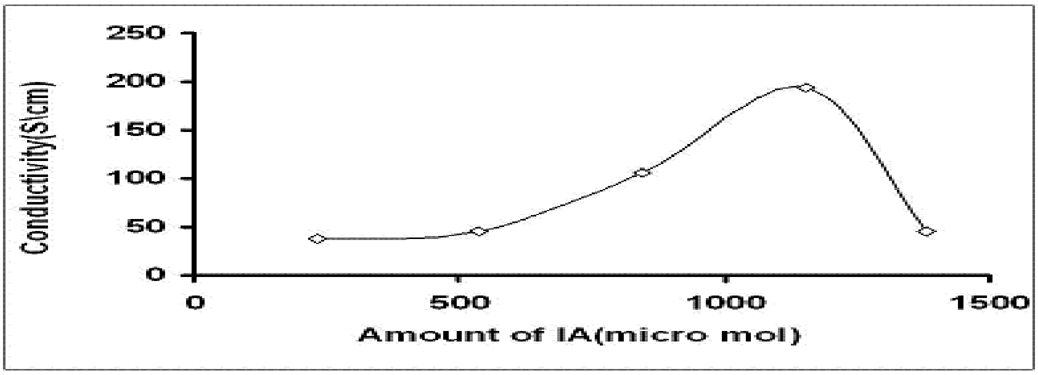

Fig.6

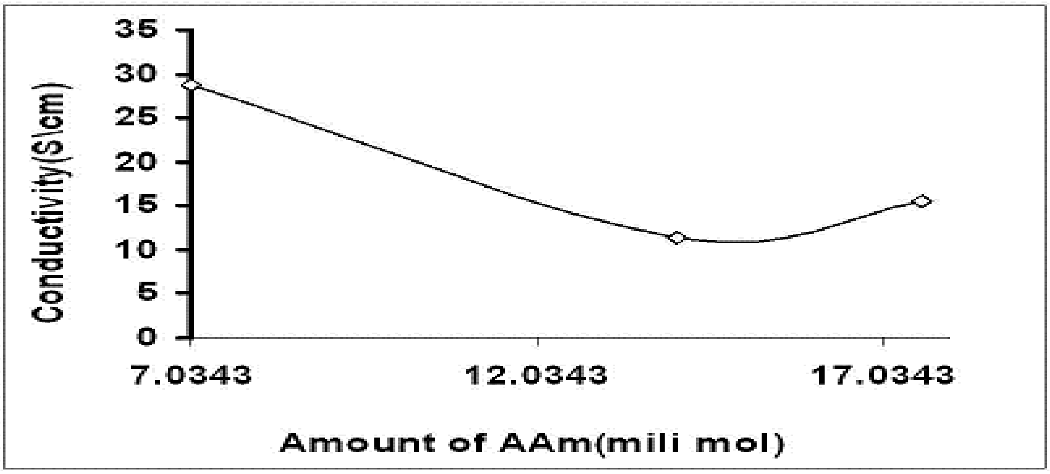
Conductivity(S\cm)
35
30
25
20
15
10
5
0
7.0343
12.0343
17.0343
Amount of AAm(mili mol)

Fig.7