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A STUDY ON POLY ACRYLIC ACID-SILVER POLYMER COMPOSITES

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ABSTRACT

Polymer metal composites comprising poly acrylic acid (PAA) and silver particles have been synthesized by chemical methods and their spectroscopic thermal properties are investigated under different conditions. Chemical interaction between silver metal particles and PAA has been confirmed by spectroscopic techniques i.e., optical absorption and FTIR methods. Due to the presence of silver particles in PAA matrix, thermal stability of PAA is found to increase as per DSC studies. With the interaction of Ag concentration, metal particle-polymer interactions are found to increase. As a result thermal stability of resultant composites is further increased. Scanning electron microscope suggests that the silver particles are found to PAA matrix.

KEYWORDS: PAA, PAA-Ag, FTIR Spectra, SEM, ESR Spectra and SEM.

Polymers and metals are expected to come into contact in many areas of science and technology like fuel cells and electric applications. Therefore it is very important to study polymer-metal particle interaction (1, 2). Ion exchange properties of synthetic and natural polymer are an important aspect due to their applications in different branches of science and technology. Rivas at al (3) have reported that complexes of water soluble polymers are used to separate metal ions from dilute solutions. For example hazardous traces of arsenic can be retended by the composite consisting of poly acrylic acid – tin .These authors (3) have synthesized PAA complexes with different composition of tin and investigated their chemical, thermal and morphological properties.

The Sn^{2+} ions are reported to be co-ordinate through 2-4 carboxylate groups by bendate structure (3). In other papers Rivas at al (4), and Ni et al (5) have reported on synthesis and characterization of complexes of poly acrylic acid with different metal ions (4,5) and investigated their chemico-physical properties. Abdelaziz and Abbel Razek (6) have investigated thermal and optical properties of polymethyl methacrylate / Silver nitrate film using XRD,FTIR,DSC techniques. T_g of the polymer is reported to decrease with increase of $AgNO_3$ concentration. These authors have observed optical absorption band corresponding to surface plasma at 280-480nm.

Though composites of PAA with different metals are reported in literature, such studies of PAA-silver metal composites is attempted by vary few authors. In this context, the author have synthesized PAA-Ag^{2+} complexes by chemical methods and investigated their spectroscopic, thermal and morphological properties

EXPERIMENTAL

PAA-Ag polymer metal composites have been synthesized by solution casting techniques described by Lauter at al (7) and Yang at al (8). The complexes are in powder form. Optical absorption spectra are taken for dilute solutions of complex in the wave length region of 200- 800nm on Shimadzu spectrophotometer with water as blank. Fourier transform infrared spectra are recorded on Perkin Elmer spectrometer in pellet form. DSC thermo grams are recorded on TA Q-10 model Calorimeter. For this purpose, about 2-3 mg of complex was sealed in aluminum pan and heated from room temperature (RT) to 350^0C with a heating rate of 10^0C/minute. Empty aluminum pan is kept as reference and nitrogen gas is flushed throughout the experiment to avoid oxidation of the sample. To record Scanning electron micro graphs of the complex the sample is fixed on cylindrical stub covered with carbon strip. The surface of the sample was gold coated with sputtering unit and morphology was examined with a Carl Zeiss Scanning electron microscope.

RESULTS AND DISCUSSION

Optical Absorption Spectroscopic Studies

Optical absorption spectra of PAA-Ag complex is as shown in Fig.1. An absorption band around 280nm was observed. The UV absorption band in the 270-290nm region corresponds to π-π^* transition and arise due to either C=O and or C=C functional groups present in the molecular system. Since PAA contain C=O groups are in its structure, presence of 280 nm band is expected. Upon complexation carbonyl groups of PAA are expected to

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interact with the silver ions and shift/change in the band position and intensity of 280 nm band is expected.

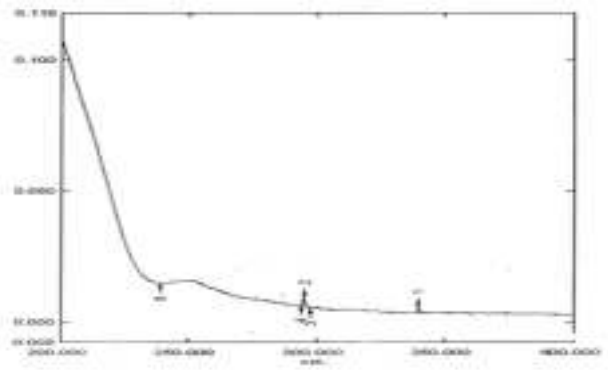


Figure 1: Optical absorption spectra of composite

Further an additional optical absorption band around 400nm is observed for the complex, which is assigned to be due to surface Plasmon resonance, a typical behavior of metallic nano- particles. These results suggest the interaction of reactive group's polymers interact with silver icon to form silver particles. Due to agglomeration of some of the metal particles presence at 350 nm corresponding to plasma resonance of bulk silver optical absorption band is expected. Coloration of the sample is due to SP excitation of nanoparticles, which gives optical absorption band in the region of 390-500 nm and these nanoparticles has spherical geometry.

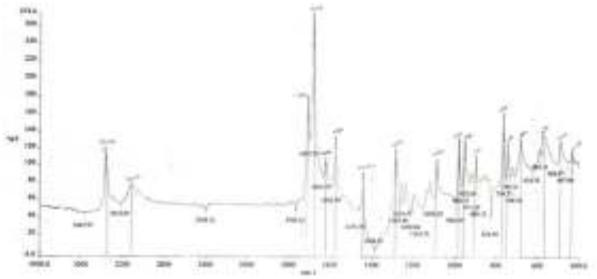


Figure 2: FTIR Spectrum of poly acrylic acid

Figure 3: FTIR Spectrum of PAA-Ag Complex

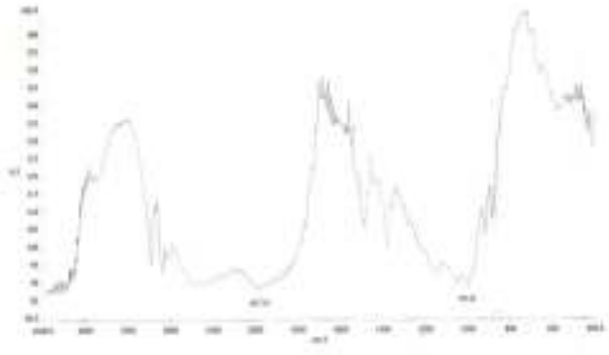


Figure 4: FTIR Spectrum of PAA-Ag Complex with more Ag content.

FTIR Studies

FTIR spectra PAA and PAA Ag composites are as shown in Fig 2,3 and 4.The spectra of homo polymers compose various absorption bands characteristic of molecular groups present in the polymer. They are listed in table 2.1.FTIR absorption bands centered around 3340, 2920, 1760, 1450, 1270, 1080, 960, 770, 750 ,660,570,490,450 cm^{-1} are observed. For PAA complexes, the band position and intensity is found to be altered. On increasing the band intensity are markably effected.

Among these bands the 3500-3300cm^{-1} band is assigned to OH stretching vibration. Due to complexation a decrease in its intensity is observed suggesting that OH-metal ion interaction. Such types of interactions are previously observed (10).The new absorption band is 400-200 cm^{-1} are due to charge transfer reaction between polymer ion and the dopant. The 985 cm^{-1} absorption band is due to NO_3 groups(11). Upon increasing the concentration of $AgNO_3$, the following changes have been observed.

1) The 3500-3300 cm^{-1} band completely vanished.
2) Intensity of 1760 cm^{-1} band is also decreases
3) The absorption band is in the range of 1090-1010 cm^{-1} was assigned to C-H out off plane deformation that arose from molecular interaction. The band sharpened and shifted to higher frequencies.

Table 1:

S.No	Band Position (cm^{-1})	Intensity	Assignment
1.	3400-3210	Strong	OH group
2.	2980	Weak	CH_2/CH_3 group
3.	1762	Weak	C=O vibrations
4.	1697	Very strong	C=O vibrations-C-O-C/C=O
5.	1635	Very strong	C=O vibrations
6.	1592	Medium	COO^-
7.	1470	Weak	CH_2/CH_3 group
8.	1384	Weak	CH_2/CH_3 group
9.	1265	Medium	CH_2/CH moieties

Due to interaction of metal ions with COOH groups of the polymer some of the other absorption bands are also observed to shift with a reduction in intensity. As such the 1697 and 1760 cm^{-1} absorption bands of PAA are found to shift towards lower wavelengths confirming the polymer metal interaction (8). When silver nitrate is added to PAA, the silver ions interact and bound to macro molecular chains by electro static interaction. Due to the presence of electron rich oxygen atoms of carbonyl and hydroxyl group present in PAA, such interactions are highly probable (12, 13). With increase of $AgNO_3$ concentration, more and more interactions occurs causing a reduction in intensity of 1650, 1750cm^{-1} absorption bands as observed from the observed FTIR spectra.

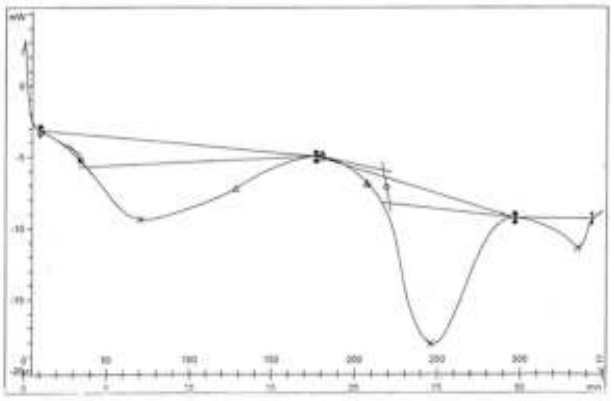


Figure 5: DSC thermogram of poly acrylic acid

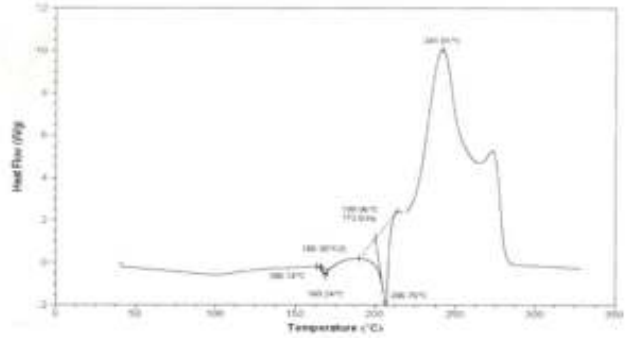


Figure 6: DSC thermogram of PAA-Ag Complex

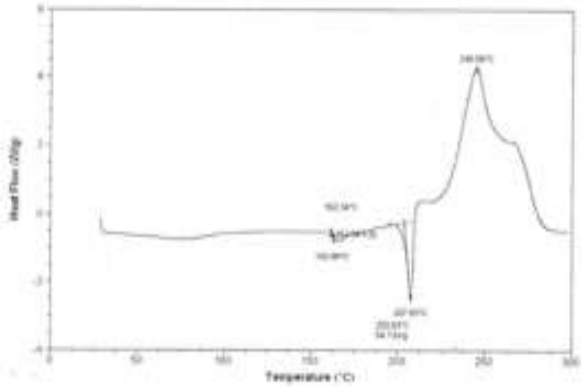


Figure 7: DSC thermogram of PAA-Ag Complex with more Ag content

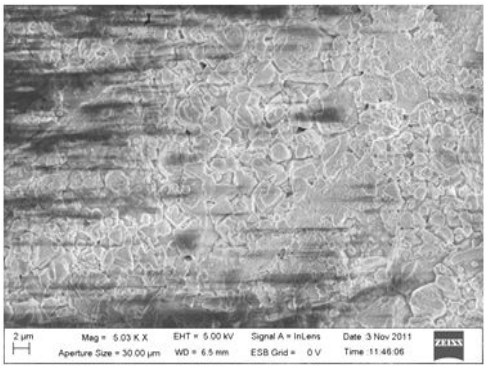
Thermal Studies

DSC thermo gram of PAA, PAA-Ag complex are as shown in figure 5, 6 and 7. Poly acrylic acid showed a well defined endothermic peak, centered around 202^0 C and exothermic peaks at 310^0 C 438^0 C. Presence of nano sized metal particles into polymer matrices causes

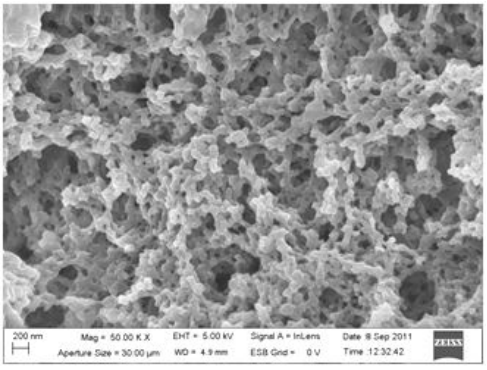
increase in the thermal stability causing a delay thermal degradation (12). While thermo grams of complex indicates shifting of endothermic peak to 206^0 C and exothermic peak at 240^0 C as shown in figure 3. Shifting of endothermic peak to higher temperature is attributed to the presence of metal particles in the polymer network. Therefore thermal stability of complex is improved then the homo polymer. With the increase of Ag content, the endothermic peak shifted to 207^0 C, indicating higher thermal stability.

Morphology Studies

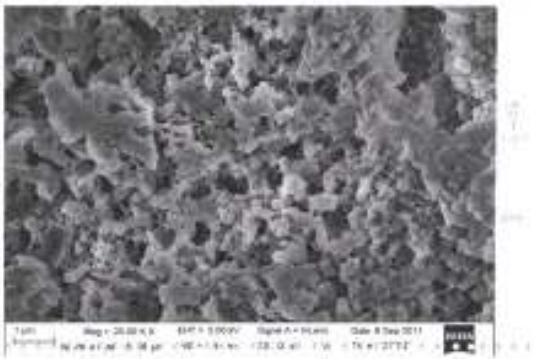
To assess the surface morphology of composites, SEM micrographs are recorded under different conditions as shown in figure a to h in Fig 8. The metal particles are bound to the polymer matrix and sum of them are lie on the polymer surface indicating some molecular interaction have taken place. With the increase of silver content more interaction occurs showing that the silver particles are bond to PAA matrix very strong. Further agglomeration of silver particles on the surface of PAA is also visible (b, c, d). With the increase of reaction temperature, the particles gradually decreases (e, f, g, h, i).



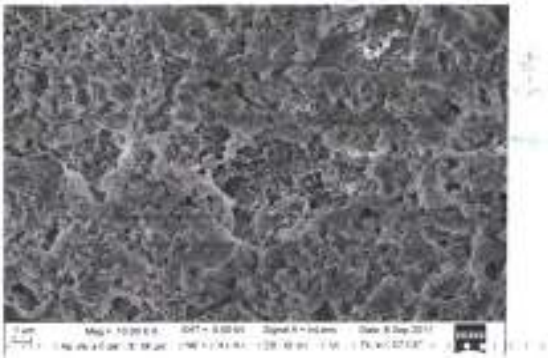
(a)



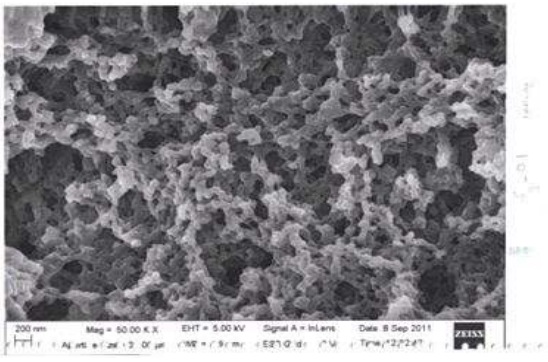
(b)



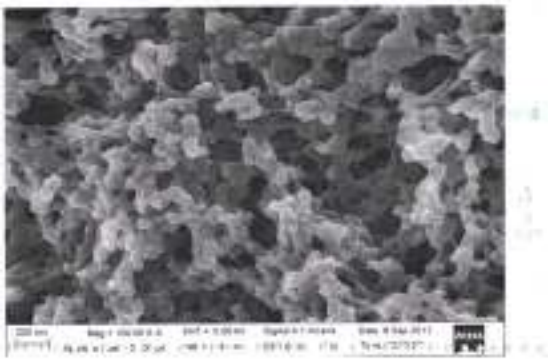
(c)



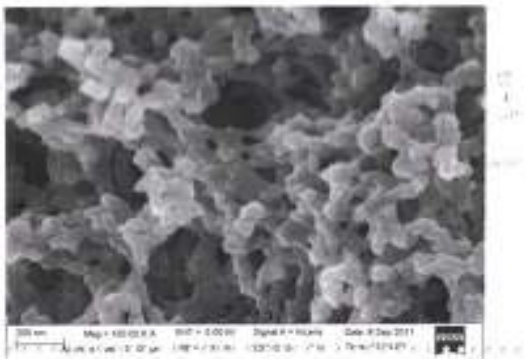
(d)



(e)

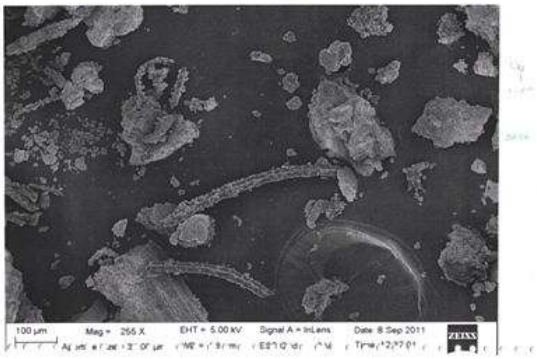


(f)



(g)

(h)



(i)

Figure 8: SEM micrographs of complex under different conditions, (a) PAA matrix (b) PAA with Ag less content (c) and (d) PAA with more Ag content (e), (f), (g), (h) and (i) effect of increase in reaction with temperature+

CONCLUSION

In conclusion carboxyl groups of PAA interact with the silver particles and form complexes as evidence from UV, FTIR studies. The PAA silver complex exhibit better thermal stability than the homo polymer. This has been attributed to the molecular interaction of PAA and silver particles.

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