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Studies on Effect of Doping Alumina Nanoparticles in ION Conducting Polymer Nanocomposites

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Abstract

In this study the polymer composite specimen has been prepared by using polymer Polyvinyl- pyrrolidone (PVP) a Potassium iodide (KI) and alumina nanoparticles. The polymer composite specimens were developed by using solution cast techniques. The main objective of the project is to study microstructure, XRD, ionic conductivity, ionic transference number, glass transition temperature using DSC, microhardness and tensile properties of the polymer nanocomposite specimen. The results revealed conductivity as well as tensile strength increased of the polymer nanocomposite increased with concentration of alumina nanoparticles where as tensile strength reduced. The polymer electrolyte can be used in photovoltaic cell

Keywords: SEM, XRD, DSC, ionic conductivity and tensile test.

Introduction

A new type of polymer nano composite was produced using as the polymer matrix. A method was developed to allow to be used as the polymer matrix in polymer nanocomposites. Physical analysis of the samples, including X-ray diffraction and scanning electron microscopy, has validated the creation of a true nano composite material. The nano composite material displays enhanced mechanical properties which indicate some degree of improved tensile strength and hardness from the original polymer. The thermal characteristics of the nano composite material were analyzed by thermo gravimetric analysis. The nanocomposites were produced as film, Preliminary testing of the effect of the nanoparticles on the strength of the polymer matrix was performed. A unique small scale nano composite material was created to support this work.

Mechanical properties of polymer nanocomposites are expected to be higher than pure polymers because the second component filler has higher mechanical properties. Advantages of polymer nanocomposites containing uniformly dispersed Alumina layers in a PVP polymer matrix, Higher the degree of exfoliation, larger is the improvement in properties. Intercalated particles, having a less important aspect ratio, play a minor role. It is observed mechanical properties of nanocomposites are better than that of pure polymers. They also attribute the improvement of property is due to dispersion of particles. The improved mechanical property is also observed in different nanocomposites by different groups.[1-3]

Objective of Study

Considerable academic and industrial research has focused on developing advanced polymer nanocomposites using nanometer-scale fillers to achieve desirable polymer properties such as high mechanical, thermal properties. The extremely large surface area of nano-fillers affords increases in these properties and other performance characteristics of the polymer composites with relatively small amounts of loading compared to that of micrometer-scale fillers. Among many potential types of fillers, Nano materials and salts have attracted much interest due to their commercial availability and mechanical strength and conductivity respectively. By achieving well-dispersed aluminum oxides morphology in polymer matrices with nanometer scale dimension of particles, it has been demonstrated that these polymer nanocomposites can exhibit unique properties compared to conventional polymer composites. With rapid expansion of photopolymer applications due to many advantages in processing and performance aspects, some recent research has studied polymer nanocomposites based on doping and blending systems in pursuing a new category of advanced materials. While significant improvement in various performances of polymers by incorporating nanometer-

scale dispersion of aluminum oxides particles has been demonstrated, few studies have been performed for understanding the fundamental factors in the aluminum oxides dispersion process and its impacts on polymerization behavior as well as final nanocomposite properties [4-6].

Methodology
The following steps are carried in this work
a. Fabrication of PVP + Potassium Iodide + aluminum oxides polymer nano composite
b. To evaluate the mechanical properties of polymer nano composite specimen
c. To evaluate the physical properties of polymer nano composite specimen
d. Micro-structural study of polymer nano composite specimen

Synthesis of Polymer Nano Composites
The steps involved in preparation of PVP+KI polymer composite specimen by solution casting method is as follows and prepared specimen

- The inner surface of conical flask is cleaned with soft brush and cloth by using acetone. A silicon spray is applied on the cleaned surface.
- After that a sample is prepared using 1g weight of PVP and 10,20,30,40mg weight of Potassium Iodide(KI) using an 4ml water as a solvent in a conical flask
- The mixture of PVP+ water is poured into a conical flask.
- The mixture is stirred in a magnetic stirrer at a speed of 500rpm with temperature of 323K by using a magnetic bellet for 15 minutes.
- After stirring, Potassium Iodide is added to mixer stirred at a speed of 500rpm with temperature of 323K by using a magnetic bellet for 30 minutes.
- After stirring , Nano Aluminum oxides and water mixed and poured into above conical flask and stirred at a speed of 500rpm for 1.15 minutes
- The mixture of PVP+ KI+ water+ nano aluminum oxides is poured in petridish and the sample is allowed to solidify in open atmosphere.
- The samples were cut into a proper size.
- The mechanical properties and structural behavior of the polymer composite specimen are tested. Table1 shows different Nanocomposite system considered

Table 1: Different Nanocomposite system

NANOCOMPOSITE SYSTEM
PVP + KI (30%)+ Al_2O_3 (4%)
PVP + KI (30%)+ Al_2O_3 (8%)
PVP + KI (30%) + Al_2O_3 (12%)
PVP + KI (30%)+ Al_2O_3 (16%)

Scanning Electron Micrography
The SEM gives the idea of the crystalline nature of spherulite with amorphous boundary of the polymer nano composites. Spherulites are spherical microcrystalline regions inside non-branched linear polymers. Their formation is associated with crystallization of polymers from the melt and is controlled by several parameters such as the number of nucleation sites, structure of the polymer molecules, cooling rate, etc
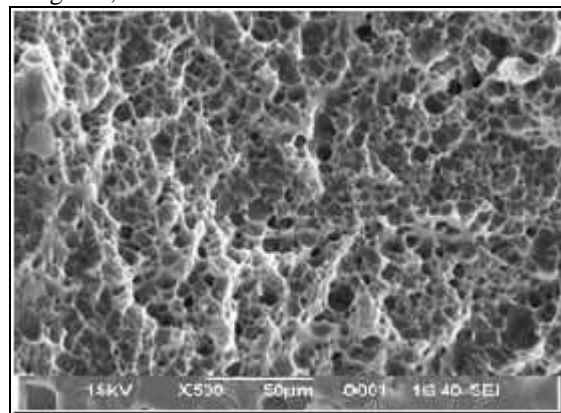

Fig 1 SEM Image of PVP + 30%KI polymer

Fig 1 shows the structure of Potassium Iodide in Polymer composite. The black color dots represent the salt structure and white color shows the polymer structure. The salt completes dissolved in distilled water and uniformly distributed in PVP polymer.
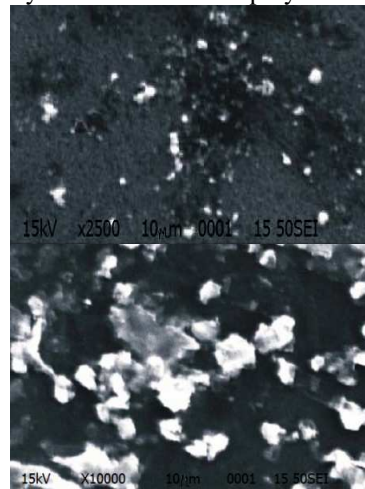
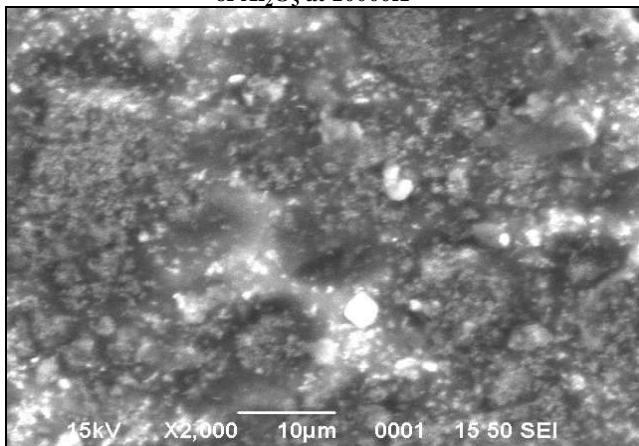**Fig 2 SEM Image of Al$_2$O$_3$ at 2500X   Fig 3 SEM Image of Al$_2$O$_3$ at 10000X**

Fig 4 SEM Image of PVP/16% Al$_2$O$_3$ polymer Nanocomposites

Fig 2 and Fig 4 shows the structure of Al$_2$O$_3$ Nanopowder at different magnification. Fig 4 shows comparative SEM scans at high resolution of a portion of the polymer nano composites which indicates distribution of nano powder in polymer composites which shows in white dots.

The SEM gives the idea of the crystalline nature of spherulite with amorphous boundary of the polymer nano composites.   Spherulites are spherical microcrystalline regions   inside   non-branched linear polymers.   Their   formation   is   associated with crystallization of polymers from the melt and is controlled by several parameters such as the number of nucleation sites, structure of the polymer molecules, cooling rate, etc

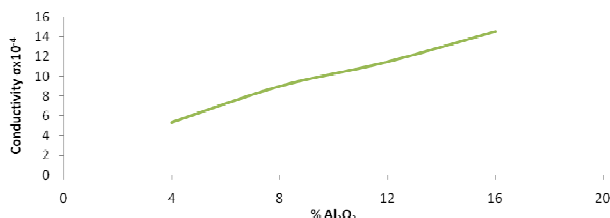## Conductivity   Studies   on   Polymer Nanocomposites

Fig 5 Conductivity v/s % Al$_2$O$_3$ in polymer composites

Fig 5 shows the variation of ionic conductivity with change in percentage of Al$_2$O$_3$ nano powder in polymer composites. From the Fig 5 it's clear that the conductivity increase and resistance decrease with increase in Al$_2$O$_3$ nano powder concentration in polymer composite. The 16% Al$_2$O$_3$ nano powder shows the highest conductivity compared to other concentration. This plot indicates that the polymer nano composites

comprising PVP, KI (salt) and Al$_2$O$_3$ nano particles exhibits the maximum ionic conductivity at room temperature at 16% of nano material by weight as shown in table 6.2. It can be seen that the electrical conductivity of the polymer nanocomposites vary with % of nano particles loading. When the content of aluminum oxides is 16 g/100 g PVP, the ionic conductivity of the polymer nano composites prepared is significantly higher than that of the corresponding polymer composites prepared because of the better exfoliation and the dispersion of nano particles. We conclude that the electrical conductivity depends on the competition between the nano particle loading and the dispersion This indicates that a required Ionic conductivity could be by either improving the dispersion of nano particles at a low loading amount, or increasing nano partcile loading that might cause poor dispersion.

ION Transference Number

Transference   number   measurements   of   the PVP+KI and PVP+KI+ Al$_2$O$_3$ Nano composites polymer systems were made by means of solution casting technique. In this technique, the dc current is monitored as a function of the time on application of a fixed dc voltage across the cell: polymer composite and PVP+KI+ Al$_2$O$_3$ Nano composite. After polarization of the cell with 9 V dc, the current v/s time plot was obtained.
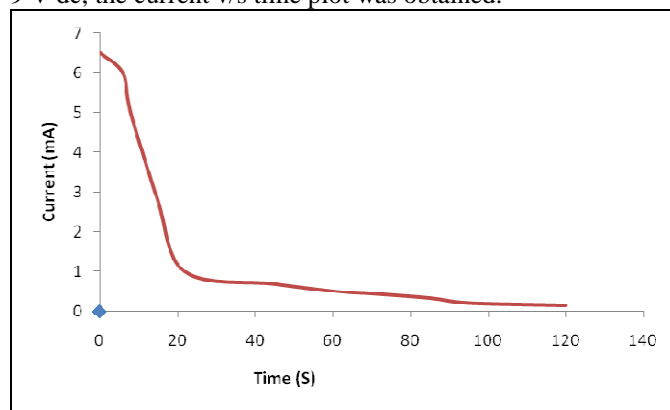

Fig 6 Current V/s Time characteristics for polymer composite (PVP+KI (30%))
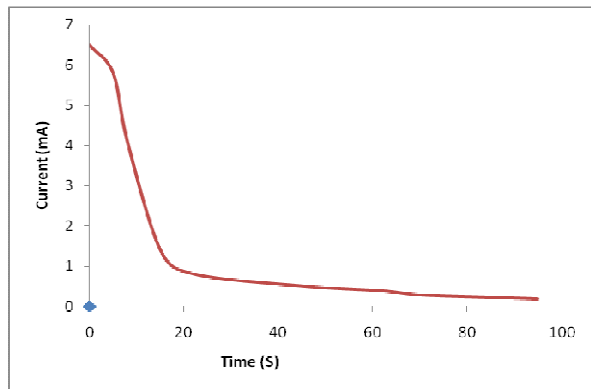
Fig 7 Current V/s Time characteristics for nano composite (PVP+KI(30%)+ Al$_2$O$_3$ (16%))

After polarizing the electrolyte, the transference number t$_{ion}$ was calculated from the initial current I$_i$ and the final residual current I$_f$, i.e.

$$t_{ion} = (I_i - I_f) \, / \, I_i$$
$$t_{ele} = 1 - t_{ion}$$

From the figure 6 and fig 7 we can conclude that current decrease as time increase. At this instance it is consider at 20 sec current in Polymer nano composites is more than that of polymer composites which indicates conductivity is more

Table 2 : Ion Transference number calculation

Specimen	Transference Number	
	T(ion)	T(electrical)
Pure PVP	-	-
PVP+KI(30%)	0.9753	0.0247
PVP+KI(30%)+Al$_2$O$_3$(16%)	0.9815	0.0185

Table 2 indicates that the charge transport in these polymer electrolyte films is predominantly due to ions; only a negligible contribution comes from the electrons.

Differential Scanning Calorimetry (DSC)

Thermal analyses were performed using a DSC instrument (Mettler). The instrument was calibrated with indium and Zinc standards and the analyses were conducted under a nitrogen flow rate of ca. 20 mL/min. The sample was heated sequentially from 30°C to 300°C. The glass transition temperature (Tg) was obtained as the inflection point of the heat capacity jump recorded at a heating rate of 20° C/min.

Fig.8 and 9 shows DSC thermo gram of the synthesized polymer nanocomposites sample and only PVP polymer. The actual Tg value of pure PVP is 110°C. The complexes show a single Tg indicating the compatibility of the polymers. The incorporation of KI

salt and Al$_2$O$_3$ nano powder to the polymer blend matrix decreases the Tg value, and is minimum for 16wt.% Al$_2$O$_3$ nano powder content the Tg valve is 82.3°C.
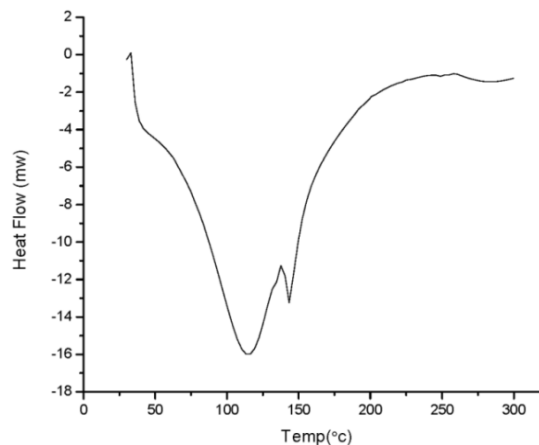

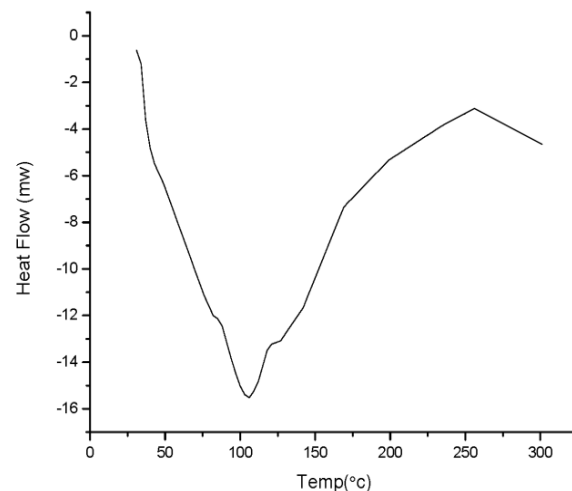**Fig: 8 DSC curves for 16% polymer nanocomposites**

Fig 9 DSC curves for pure PVP polymer

This observation suggests the increase of crystallinity of the complexes because of the presence of excess nano powder. It is also evident from conductivity studies that the conductivity of the complexes increases with increase of salt concentration and decreases for higher concentration of nano powder due to formation of ion cluster. This is in good agreement with TGA results.

PVP is a more water-soluble polymer because the tertiary amide carbonyl groups exhibit stronger Lewis basic character (dipole moment: ca. 4 D) .Therefore, it seems reasonable to expect that PVP possesses a higher value of Tg (110°C) primarily because of its strong intermolecular dipole-dipole interactions, even though other factors may also contribute. The presence of sail and nano powder at a relative low concentration reduces

the degree of self-association of the PVP units and results in lower values of Tg   because the electron donor groups of PVP interact, through ion-dipole interaction, with the electron acceptor species (i.e., the Ki^+ cat ions). As a result, two competitive interactions exist: self association of PVP through dipole-dipole interactions and ion-dipole interactions between Ni^+ cat ion and the carbonyl groups of PVP.

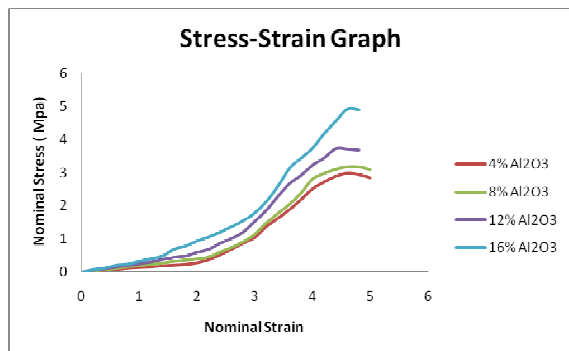## Tensile Test of PVP/KI/AL$_2$O$_3$ Composite

Fig 10 Stress Strain curve for different of percentage of nano powder in polymer

The addition of Nano particles is seen to increase both the modulus and the strength polymer nano composites. Also, the toughness (area under the stress–strain curve before rupture) increased significantly.Fig.10 show the tensile strength (the maximum stress in the stress–strain curve, MPa) and Young's modulus (the slope of the stress–strain curve in the low strain region) as a function of nano particle volume content. Both the tensile strength and Young's modulus increased with the increase of functionalized particle loading. Compared to the pure polymer, the strength and the Young's modulus of the 16% vol% filled nanocomposites sample increased by approximately 108%% and 99%, respectively. The fictionalization of the nanoparticles was observed to have more effect on the Young's modulus.

Micro Hardness Test

Table 3 : Micro Hardness for Polymer Nanocomposites

Specimen	Load grams	Load (kgf)	d1 (mm)	d2 (mm)	d*= (d1 + d2)/2 (mm)	Scaling Factor d = d*0.1154	H V =1.854F/d^2 (kgf/mm^2)
PVP	100	100xE^{-3}	0.7412	0.7802	0.7616	0.08790	24
PVP+KI+ Al$_2$O$_3$ (12%)	100	100xE^{-3}	0.5739	0.5914	0.5827	0.06724	41
PVP+KI+ Al$_2$O$_3$ 16%)	100	100xE^{-3}	0.5392	0.5610	0.5501	0.06348	46

Table 3 shows the micro hardness of PVP/KI/ Al$_2$O$_3$ nanocomposites as a function of Al$_2$O$_3$ content and KI. The hardness of composite at 12 wt% Al$_2$O$_3$ increases from 24 kg/mm^2 for the pure PVP and 41 for polymer nano composite. The hardness of micro composite at 16 wt% Al$_2$O$_3$ increases to 46 kg/mm^2. Moreover, relatively uniform distribution of Al$_2$O$_3$ particles and decrease in inter particle distance with increasing particle loading in the matrix results in increase of resistance to indentation of Polymer Nano composites. For a given volume fraction, nanoparticles are much closer to each other compared to micro particles in the matrix, and hence, nanoparticles will resist more strongly the penetration of the indentation in the matrix. This results in higher micro hardness for nanocomposites than that of polymer at a constant volume fraction of particles. Due to this, hard Al$_2$O$_3$ particles are pressed into the comparatively soft PVP matrix rather than being plastically deformed under the applied load during the indentation test. Moreover, due to much lower maximum packing factor of the Al$_2$O$_3$ particles under applied pressure, micro- or nanocomposites could not resist the indent penetration in proportion of Al$_2$O$_3$ content. The micro hardness increases with increasing Al$_2$O$_3$ content due to the increase in crystallinity of the PVP fraction in composite and higher micro hardness of Al$_2$O$_3$ compared to pure PVP (24 kg/mm^2).

Conclusions

        Various samples of conductive polymer composite were prepared by taking different

compositions of KI (i.e. 10, 20, 30, 40, 50) and were characterized by different experimental techniques such as X-ray diffraction technique, Scanning electron microscopy, Optical microscopy, Thermo gravimetric Analysis, Ionic conductivity, Tensile test.. Aluminum oxides powder was used as an alternative material to improve the ionic conductivity, mechanical properties and thermal properties of the PVP polymer matrix composites. Al_2O_3 have another advantage on polymeric composite to possess Dielectric properties as well. The following conclusions were drawn from the present study:

➢ X–ray diffraction (XRD) studies implied the higher degree of amorphous nature of the polymer electrolytes by reducing the intensity of characteristic peaks. The higher amorphous region is further verified in coherence length study. XRD patterns of PVP polymer nanocomposites doped Al_2O_3 showed the decrease of intensity of peaks corresponding to pure Al_2O_3 with the increase of nano powder wt% ratio suggesting a decrease in the crystallinity of the complex.

➢ OM and SEM is used to investigate the morphology of the samples. By analyzing the OM and SEM images, Distribution of salt in samples were verified, the higher porosity revealed the improved ionic migration in the sample. SEM image of PVP/KI Composite reveled presence of distinct spirulites in the sample.

➢ 16 wt% of aluminum oxides nanoparticles effected a change in the mechanical properties of the original polymer. The ideal additive amount appears to be around 16wt% of nano particles to the polymer

➢ Ionic Conductivity increases as the percentage of alumina nanoparticles increases.

➢ DSC studies inferred the improved thermal properties of samples. The excellent thermal stability of the polymer electrolyte where their stability is up to 200 °C.

➢ The ionic transport number data in the PVP polymer nanocomposites doped Al_2O_3 films indicate that the conduction is due to ions rather than electrons.

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