Synthesis of highly translucent semiconducting thin films from elastomer nanoparticles

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Nanocomposites are advanced materials obtained by combining two or more solid phase, one which having at least one dimension in nano scale range. In this study conducting elastomer nanoparticles are prepared by solution doping method using a Lewis acid as dopant. Subsequently, these nanopowders are encapsulated by an intrinsically conducting polymer, polypyrrole by chemical root method to obtain rubber polypyrrole nano composite. Highly transparent conducting films are obtained by dispersing these nano composite in ethanol using poly vinyl pyrrolidone as a stabilizing agent. The I-V characterization studies satisfies the electrical conductivity of the composite. The UV-Vis spectroscopy gives an insight into the optical absorption properties of the composite. Further composite film characterizations satisfy the requirements of transparency and surface morphology for simple optoelectronic applications. The SEM picture shows that the conducting elastomeric nanoparticles are effectively dispersed in the PVP matrix.

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1. Introduction

The natural rubber, a member of poly butadiene family combines high tensile and tear strength with outstanding resistance fatigue. Also natural rubber retains its mechanical properties to a great extend at both elevated and low temperatures [1-2]. The natural rubber nanocomposites can be a potential candidate for various applications such as solar cells, LEDs, FETs etc. The nano composites can be based on binary combination of ceramics, metals and polymers, however polymer based Nanocomposites, that is the system based on continuous polymeric matrix embedding nano-sized domains of another solid, are most common systems. Nano sized semiconductor ceramics blended with thermoplastic polymers represent a new class of nano structured materials that can be exploited for a number of applications in different technological fields [3].

The efficient dispersion of particulate solids is of great importance in a number of industries such as pharmaceutical, bulk chemical and food. Powder dispersion is widely used to break up loose aggregate clusters as a means to determine particle size distribution; this can be achieved by using laser diffraction, time of flight techniques and microscopy method.

Dispersion of powders can be done in gas or liquid phase and a variety of theoretical and experimental researches are available which investigate liquid systems [4].

The ability to control dispersion of a wide range of powder from a friable to robust and free flowing to extremely cohesive material is an area of great interest and importance. It is recognized that the complete dispersion of fine cohesive powders especially in the size range below 20 µm is difficult due to the relatively large inter particle attractive forces namely Vander waal's force, electrostatic force etc [5] . Also the relative strength of these forces increases with decreasing particle size. Therefore a great amount of energy is required to deform and disintegrate the clusters completely to their primary constituents. Additionally particle morphology features such as shape and surface asperities also affect particle interaction and hence dispersion performance. It is reported that irregular shaped particles disperse more easily compared to spherical particles [6].

In the present study, the dispersion of Natural rubber/polypyrrole composite semi conducting nanoparticles are studied in presence of stabilizer PVP in the aqueous medium of ethanol. For obtaining contact free dispersion high speed stirring treatment is given to the aqueous medium. The alcoholic suspension is spin coated on the glass substrate to get the uniform thickness film. Particle size of the composite is measured to confirm the nano size of the composite. The obtained film satisfies the transparency conditions and electrical conductivity.

2. Experimental part

2.1. Preparation of natural rubber conducting powder

The natural rubber used for this study is Indian Standard NR, grade 3(ISNR 3) with a number average molecular weight of 3×10^5 is collected from Rubber research Institute, Kottayam. The dopant Antimony penta chloride (Aldrich), the solvent carbon tetra chloride (Merck) and Pyrrole (Merck) are used for study without further purification. The conducting natural rubber nanoparticles are prepared by solution doping keeping NR: $SbCl_5$ mole ratio as 1:2 under optimum experimental conditions. The deep black precipitate formed is filtered off and dried under vacuum to obtain a black insoluble powder.

2.2. Preparation of the Pyrrole coated NR conducting powder

Here explain a rational approach for the construction of nano meter sized core-shell particles of the following structure, a core of natural rubber conducting polymer is surrounded by a corona of polypyrrole. The corona, polypyrrole act as the matrix. A fine dispersion of conducting NR powder is made in demonized water using ultra sonication process. Pyrrole is added to the solution by keeping Pyrrole: NR ratio as 8:1. Polypyrrole is embedded via oxidation polymerization of monomer Pyrrole such that electrical percolating shell is formed around the NR nano powder. The pyrrole coated NR powder composite is filtered and dried under vacuum.

An efficient technique used to disaggregate the pyrrole composite is based on the dispersion of the powder into a low viscosity liquid phase such as ethanol at high speed. The aggregate periphery experiences the action of high friction force by the fast moving liquid. As a result of this fast movement the single particles detach from the periphery. The incompatibility of the surface characteristics of the nano particles can be improved by the addition of a surface modification agent. This method can be used also for disaggregating other types commercial nanopowders. To increase the stability of the prepared colloidal nanoparticles suspension a stabilizer is added. Poly vinyl Pyrrolidone (PVP) showed excellent surfactant characteristics. PVP is highly soluble in alcoholic solvents and it make uniform coating on each particle and produce stable colloidal systems. PVP is an optical plastic owing to the great transparency and refractive index close to the glass value. Due to this reason the PVP has been widely used in the optoelectronic field.

The optical absorption spectra of pristine rubber, $SbCl_5$ doped natural rubber powder and Pyrrole coated NR powder/PVP composite are taken by UV-Vis Spectrophotometer Varian Cary 5000. The I-V characteristics are made by using an electrometer. The surface characteristics are analyzed using JEOL 5600 model scanning electron microscope.

3. Result and discussion

When the colloidal suspension is dried by ethanol evaporation, uniform pyrrole coated NR powder /PVP composite film is obtained. The film is highly transparent in the visible spectral region as shown in Fig. (1). The transparency property of the sample enhances its application in the optoelectronic field. The optical absorption spectra of pristine rubber, $SbCl_5$ doped natural rubber powder and pyrrole coated NR powder/PVP composite are taken experimentally is shown Fig. 2. The optical absorption spectra of pristine state show no absorption in the visible domain.

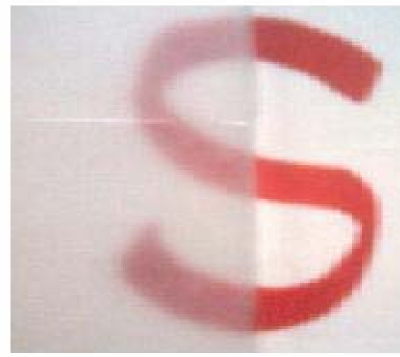

Fig. 1. Highly transparent conductive pyrrole coated NR powder /PVP composite film.

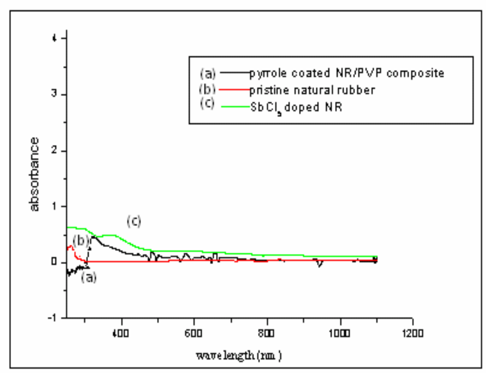

Fig. 2. Optical absorption spectra of (a) Pristine natural rubber, (b) $SbCl_5$ doped Natural rubber and pyrrole coated NR powder /PVP composite.

The natural rubber power prepared by $SbCl_5$ doping absorb strongly in UV/Vis region indicate the formation of conjugated sequence of, (-CH = CH) of various length along the polymer backbone. It is also evident from the wavelength positions that short conjugated sequences of five to six C=C bonds are also introduced into the natural rubber chains [7-15]. In the optical absorption spectra of pyrrole coated NR powder/PVP composite the absorption peak shown at the wavelength 450 nm indicate the presence of pyrrole in the composite and the absorption spectra shows less absorbance than the $SbCl_5$ doped Natural rubber powder[16-17].

The I-V characteristic of the NR/pyrrole composite is shown in Fig. 3. The linear behavior of the curve signifies the ohmic behavior of the composite. The ohmic nature of the curve suggests that the resistance of this composite is the same no matter the applied voltage is used to measure it.

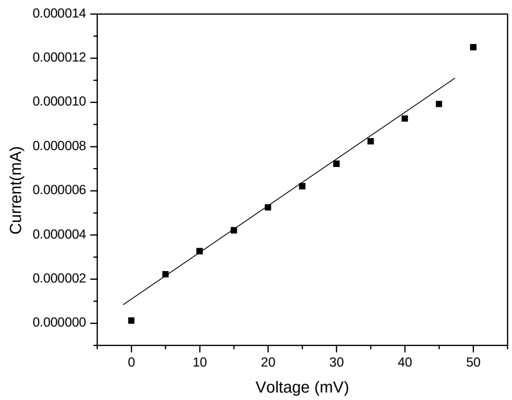

Fig. 3. I-V characteristics of pyrrole coated NR powder /PVP composite.

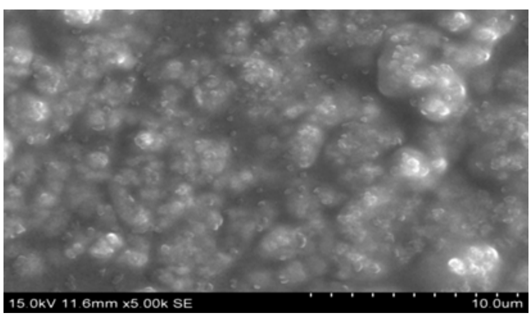

Fig. 4. SEM image of the pyrrole coated NR powder /PVP composite.

The morphology of the composite film is also investigated. The SEM picture shows that the conducting elastomeric nanoparticles are effectively dispersed in the PVP matrix. The PVP molecules absorbed on the elastomeric nanoparticles surfaces, prevents the nanoparticles from re-aggregation both in the dispersing medium and during solvent removal. Such an approach is described in polymeric micro particle separation, but it has been found to work with polymeric aggregates [16-19].

4. Conclusion

The obtained pyrrole coated NR powder /PVP composite films are electrically conductive and transparent in the visible spectral region. Since the films are transparent in the visible region, it can be used for a number of technological applications such as optoelectronic field.

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