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Electrical conductive properties of some composites of gum arabic biopolymer and magnetite nanoparticles

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DC electrical conductive properties of some composites of gum arabic biopolymer (host) and magnetite nanoparticles (guest) synthesized in different weight percentages have been studied as a function of temperature and applied bias voltage to explore the effect of the guest on the electrical conduction of the host. Two types of trap distributions (single discrete and exponential) have been found in these composites. The observed results show that the conductivity of the composites increases with increasing guest content along with a decrease in activation energy. Percolation theory has been employed for the analysis of the room temperature electrical conductivity enhancement with the variation of guest content. The activation energy and the pre-exponential factor values estimated following Arrhenius relation satisfies the compensation law.

Keywords: Gum arabic, Magnetite, Composites, Dark conductivity, Percolation, Compensation

1 Introduction

Natural biopolymers are considered to be the eco-friendly materials as opposed to synthetic polymers. Different research activities geared toward producing harmless products from biopolymers have intensified. Improved understanding of the properties of biopolymers allows for the design of different new eco-friendly materials that have enhanced physical properties and that make more efficient use of resources. Gum arabic is an inexpensive, hydrophilic, nontoxic, biocompatible and totally biodegradable polymer[1,2]. It is a natural complex polysaccharide derived from exudates of Acacia Senegal and Acacia seyal trees[2,3].

The electrical properties of a polymer can be suitably modified through incorporation of semiconductor nanoparticles into the polymer matrix[2-5], where the properties can easily be modified through the variation of size, shape and distribution of the nanoparticles by controlling the interfacial interactions between the nanostructured semiconductors and the polymers[6,7]. The primary interest in biopolymer composites is attributed to modify the electrical properties of the biopolymers due to incorporation of some nanoparticles. By choosing particular kind of matrix and filler nanoparticles, one can modify the desired properties of the composite for a particular application. The temperature dependence conductivity of polymer composites shows wide range of conduction mechanism depending on the nature of host, guest and interaction between host and guest materials. Polymer matrices with embedded nanomaterial materials as guest molecules have been widely used and studied as multifunctional materials. There are a few reports on the electrical properties on gum arabic and it's composites[2,3,8-10].

The choice of suitable guest molecules to modify the electrical property of the polymer is quite important. In this context, magnetite is one well known filler material that has attracted intensive interest in recent years due to different potential applications in various fields[11-14]. Magnetite is a common magnetic iron oxide that has a cubic inverse spinel structure with fcc close packed oxygen anions and Fe cations occupying interstitial tetrahedral and octahedral sites[15]. Due to its strong magnetic and semiconducting properties, magnetite has the potential for providing the desired magnetic and electrical properties to the final composite. The present study of dc electrical conduction property of the composites of gum arabic as host and magnetite as guest is aimed at understanding the effect of guest materials on the electrical conduction of the host. The nature of distribution of charge carrier traps in these composites and its dependence on the extent of guest

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molecule have been explored. The enhancement in the room temperature electrical conductivity of these composites due to increase in the guest content has been analyzed in the light of the percolation theory to understand the guest-modified electrical conduction property of the host matrix. Realization of the compensation law of electrical properties in these biopolymer composites to understand the guest-modified electrical conduction property of host polymer has also been explored.

2 Experimental Details

2.1 Synthesis of composites of gum arabic and magnetite nanoparticles

The materials used for synthesis were obtained from Sigma and were used as procured. Synthesis of composites of gum arabic (hereafter GA in short) and magnetite (Fe_3O_4) nanoparticles was done according to literature method[2,3]. The synthesis has two steps: (i) preparation of Fe_3O_4 nanoparticles and (ii) preparation of the biopolymer–nanoparticle composites.

The obtained Fe_3O_4 nanoparticles were characterized using powder X-ray diffractometer to be pure Fe_3O_4 and the particle size as obtained from XRD pattern is ~15 - 20 nm. The typical TEM image of the particles reveals that the average size of Fe_3O_4 nanocrystals is in the range 20 – 30 nm. The EDAX spectrum shows strong Fe and O peaks.

The GA-Fe_3O_4 composites were then prepared by adding appropriate amount of Fe_3O_4 powder thus prepared with aqueous GA solution under sonication at frequency of 33 kHz at ~50 °C for 1 h. The solution was then oven dried at 90-100 °C. The given sample name and compositions (given in parenthesis) of GA-Fe_3O_4 composites are as follows: GAF1 (1 g GA + 10 mg Fe_3O_4), GAF5 (1 g GA + 50 mg Fe_3O_4), GAF10 (1 g GA + 100 mg Fe_3O_4), GAF15 (1 g GA + 150 mg Fe_3O_4) whereas pure gum arabic and Fe_3O_4 are denoted by GAF0 and GAF100, respectively. As observed previously for synthesis of GA-CdS[2] and GA-ZnO[3] nanocomposites, a homogeneous composite of GA-Fe_3O_4 was formed.

2.2 Characterization

Electrical current through the biopolymer composites was measured as a function of temperature and applied bias voltage using the conventional sandwich cell technique with stainless steel and ITO coated glass as electrodes inside a suitably designed conductivity chamber under vacuum[16]. Electric current was measured with one Keithley 6514 electrometer and the bias voltage was applied from Aplab, India made dc Power Supply (L3205). Temperature of the sample cell was controlled by a circulator (Model no. Cool Tech 320, Thermos) and was measured using a Chromel-Alumel (K-type) thermocouple attached at the top of the metal electrode and a thermometer (MASTECH, model - MS8222H). The conductivity cell consisted of two junctions of stainless steel electrode/sample and conducting glass/sample. All the experiments were repeated to confirm the reproducibility.

3 Results and Discussion

The steady state electrical conductivity of polymeric materials is usually expressed by following Arrhenius relation[10]:

$$\sigma(T) = \sigma_0 \exp(-E/kT) \quad \ldots (1)$$

σ_0 being the pre-exponential factor which includes the charge carrier mobility and density of states, E is the activation energy and k is the Boltzmann constant. In the Ohmic region, the steady state current flowing in a semiconductor arises due to the drift of the thermal charge carriers present in the material. Ohmic current at a given temperature is given by[17]:

$$I_\Omega = n_0 q \mu (A/d) V \quad \ldots (2)$$

where n_0 is the thermally liberated free charge carrier density, q is the electronic charge, μ is the microscopic mobility and other symbols have their usual meaning. At sufficiently high bias voltages as the injected carrier density becomes greater than the free carrier density, the charge conduction is dominated by the injected charge carriers, i.e., the current becomes space charge limited (SCL). At a transition voltage (V_t) where conduction changes from Ohmic to SCL, the injected carrier density is equal to free carrier density[17]. In the high bias region usually a slope of 2 indicates shallow trapping level of charge carriers. Here the traps are confined in a single discrete energy level and the current is represented by:

$$I_{SCL} = (9/8)\, \varepsilon \mu \theta V^2/d^3 \quad \ldots (3)$$

θ being the ratio of the free carriers density to the total carrier density, ε is the dielectric constant, and μ is the microscopic mobility[17]. When the slopes are greater than 2, it suggests that the space charge

limited current is governed by the exponential trap distribution. This trap limited SCL current density is expressed as[17]:

$$I_{SCL} = q\mu N_C (VA/d)[\varepsilon_0 \varepsilon V/qd^2 N_t]^S \quad \ldots (4)$$

where N_C is the effective carrier density per unit energy range at conduction band edge, ε_0 is the free space permittivity, ε is the dielectric constant, and S the ratio of (T_C /T), here T_C and T are the characteristic temperature[12,18] of exponential trap distribution and ambient temperature, respectively. N_t is the total density of electronic levels given by $N_t = N_C k T_C$. Other parameters have their usual significance.

3.1 Current versus voltage characteristics

To find out the nature of the distribution of traps in the biopolymer and its composites the dark current of these samples at different steady sample cell temperatures were measured as a function of applied bias voltages. The logarithmic plots of the measured current against the bias voltage for GAF0, GAF5 and GAF100 samples at different sample cell temperatures are shown in Fig. 1 as representative ones. The value of slope (S) for linear regions has been evaluated for each plot. The sample current at lower voltages (V < 300 Volts) is Ohmic ($S_{Ohmic} \approx 1$), whereas at higher voltages (V > 300 Volts) the current is space charge limited. It is found that in space charge region the current is proportional to the square of the applied bias voltages for GAF0, GAF1, GAF5 and GAF10 samples whereas for the remaining sample, i.e., GAF15 and GAF100 the slope S_{SCL} is greater than 2. Thus the nature of trap-distributions in GAF0, GAF1, GAF5 and GAF10 samples is single discrete level type whereas that for GAF15 and GAF100 is exponential type[16,18].

Traps in these composites are due to the defects or presence of perturbing guest molecules in the lattice causing the change of polarization energy in the perturbed regions[19]. The characteristic temperature T_C of exponential distribution is calculated for the samples GAF15 and GAF100 sample from the slope S_{SCL} value (S_{SCL}= T_C / T +1) and is presented in Table 1. With increasing sample cell temperature the T_C values are found to linearly decrease for GAF15 and GAF100 samples. A lower T_C value indicates that either the structural defects are less or the presence of impurities is relatively low[18]. On the other hand, change in the nature of trap distribution of the host GA matrix by gradual increase of guest is interesting.

3.2 Current versus temperature characteristics

To estimate the activation energy (E) for GAF0 - GAF100 samples the current values (I) were measured as a function of temperature at constant voltage in the Ohmic region (Fig. 2). Experimentally

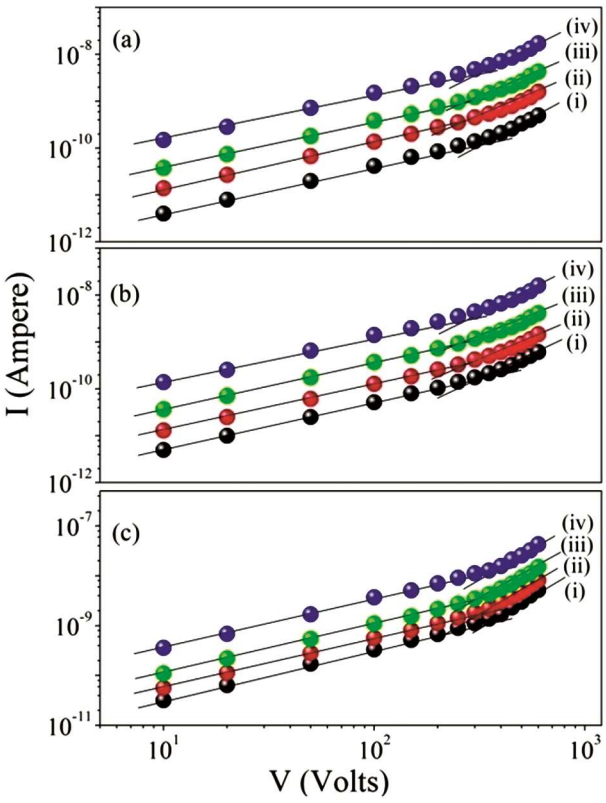

Fig. 1 — Plots of dark current versus voltage for (a) GAF0, (b) GAF5 and (c) GAF100 at different sample cell temperatures: (i) 300 K, (ii) 310 K, (iii) 320 K, (iv) 335 K. The solid lines are guide to the eyes.

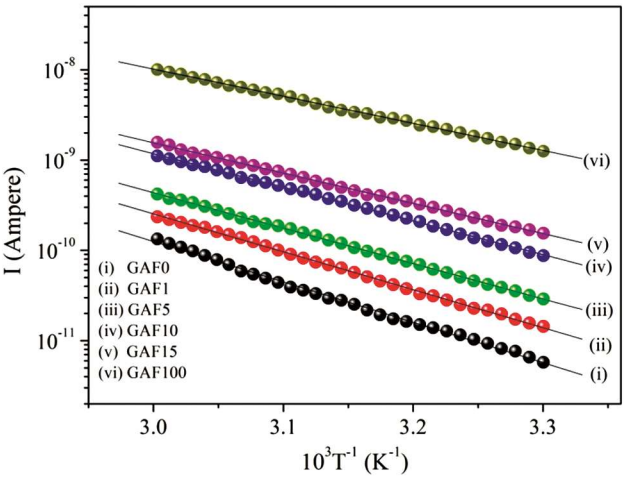

Fig. 2 — Temperature dependence of the current (I) in the Ohmic region for GAF0 – GAF100 samples.

Table 1 — Calculated values of characteristic temperature (T_c), activation energy (E), room temperature conductivity (σ_{RT}) and pre-exponential factor (σ_0) for GAF0 - GAF100 samples.

Sample	Sample temperature T (K)	T_c (K)	E (eV)	σ_{RT} (Ohm^{-1} cm^{-1})	σ_0 (Ohm^{-1} cm^{-1})
GAF0	300	-	0.89	5.5×10^{-15}	3.15
	310	-			
	320	-			
	335	-			
GAF1	300	-	0.83	1.3×10^{-14}	0.94
	310	-			
	320	-			
	335	-			
GAF5	300	-	0.78	3.0×10^{-14}	0.26
	310	-			
	320	-			
	335	-			
GAF10	300	-	0.74	8.5×10^{-14}	0.18
	310	-			
	320	-			
	335	-			
GAF15	300	423	0.67	1.7×10^{-13}	2.01×10^{-2}
	310	412.3			
	320	403.2			
	335	398.7			
GAF100	300	450	0.60	1.2×10^{-12}	1.05×10^{-2}
	310	434			
	320	416			
	335	408.7			

measured electrical currents were converted to electrical conductivity using the relation $\sigma(T) = I(T)d/AV$, where $\sigma(T)$ is conductivity at any absolute temperature T, $I(T)$ is measured current at temperature T, d is sample thickness/ inter-electrode separation, A is area of the sample cell and V is applied bias voltage. The activation energy values are calculated using Eq. (1) and are shown in Table 1. The room temperature conductivity (σ_{RT}) values are also noted for each sample and compared in Table 1. The σ_{RT} values are observed to increase with increasing amount of guest content in the host polymer matrix. It is also observed from Table 1 that the E values decrease with increase in the guest content. Activation energy describes the microstructure of a composite system being a function of the mean radius of the conducting particles and the mean inter-particle distance[20]. Thus, the growing size of the conductive network inside the composite and reduction of inter-particle distance by increasing the amount of guest content might have resulted in the observed decrease in the activation energy values and hence the increase in the conductivity.

3.3 Effect of guest on the electrical conductivity of host: Percolation

In this subsection we discuss the variation of σ_{RT} values of the composites as a function of guest content in the light of Kirkpatrick's model of percolation[21]. This model predicts the dc electrical conductivity of a nonconductive-conductive composite system based on the likelihood of contact between conductive particles within the composite[21,22]. The presently observed room temperature conductivity values of the composites are expressed as a power law equation given by[21]:

$$\sigma_{RT} = \sigma_g (\varphi - \varphi_c)^{\mu} \quad \ldots (5)$$

where σ_g is the guest conductivity which is a constant at a particular temperature, φ is the weight percentage of guest, φ_c is the percolation threshold and μ is the critical exponent. μ depends on the type of space

dimension of the network, and it is a characteristic value experimentally obtainable. The percolation threshold in the present case is described as the minimum quantity of the guest required to form a continuous network. The variation of σ_{RT} with φ obtained at room temperature is shown in Fig. 3. The solid curve is the fit of the observed data with Eq. (5).

The value of μ is calculated from the least-squares fitting method using Eq. (5), which gives a minimum residual (R). As both μ and φ_c values are unknown, we took certain values of φ_c and determined values of μ from that fitting and noted the least squares residual minimum. The set of φ_c and μ values for which the R value becomes the minimum was adopted as the most probable set[23]. Estimated value of φ_c is 0.88 % whereas the value of μ is 1.63 for the composites at room temperature. The critical exponent μ greater than 1 is believed to be independent of the details of the structure except the dimensionality of the space[24] and the value is close to 2 for three-dimensional space[24-27]. The guest particle size as well as the host-guest connectivity should be playing a crucial role in the conduction mechanism of these composites. Percolation theory could not explain very low values of percolation threshold. Non-equilibrium theory for the host-guest mixtures could explain the observations of low percolation threshold[28].

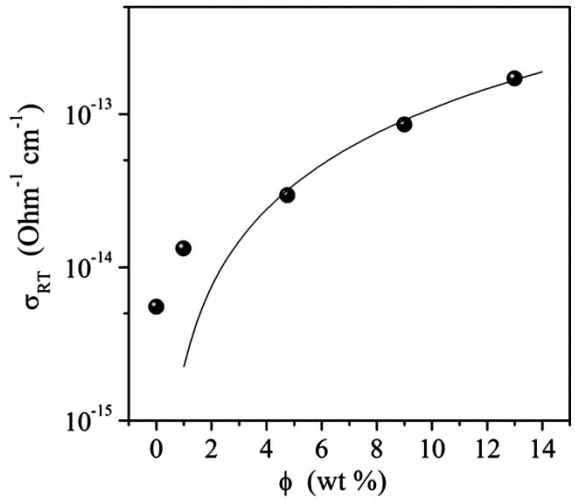

Fig. 3 — Variation of the room temperature electrical conductivity (σ_{RT}) with the weight percentage (φ) of guest for GAF0 - GAF15 samples. The solid curve is the fit of observed data with Eq. (5).

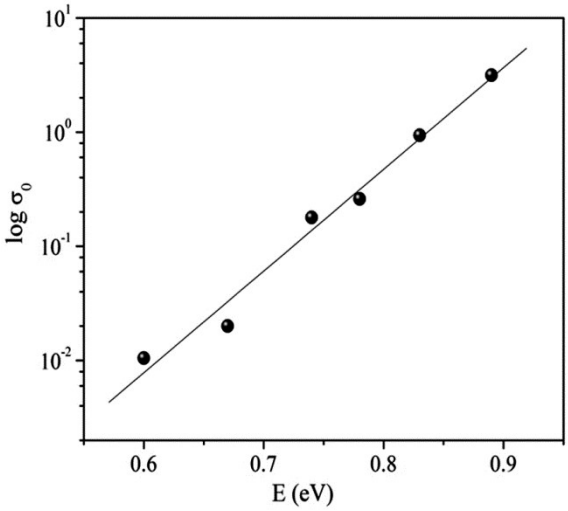

Fig. 4 — Variation of log σ_0 with activation energy (E) for GAF0 - GAF100 samples.

3.4 Compensation effect

The compensation law quite frequently observed to be valid in the case of electrical conduction in organic semiconductors has been an empirical relation[29]. According to this law if the electrical conductivity (σ) has an Arrhenius behavior as a function of temperature (T), like Eq. (1), then the pre-exponential factor σ_0 and the activation energy E are related by:

$$\sigma_0 = \sigma'_0 \exp(E / kT_0) \quad \ldots (6)$$

where σ'_0 and kT_0 are constants for a given class of materials. σ'_0 is often called the compensation characteristic pre-exponential factor, T_0 the compensation temperature and $kT_0 = E_0$ as the compensation characteristic energy. It has been observed in a wide range of materials which include single crystals[30], polycrystalline[31], amorphous[32], organic solids[33], etc.

Figure 4 shows the dependence of the pre-exponential factor, σ_0 values estimated for GAF0 - GAF100 samples using Eq. (1) (shown in Table 1) on the corresponding activation energy values, and this dependence can be well represented by Eq. (6). This establishes the fact that the compensation law is valid in case of the presently studied solid composites. From the slope and intercept of the plot one can calculate the values of T_0, kT_0 and σ'_0, and these are as follows: T_0 = 565 K, kT_0 = 49 meV, and σ_0' = 3.5×10^{-8} Ohm^{-1}cm^{-1}. The estimated value of the compensation energy kT_0 (= 49 meV) lies well within the expected range of kT_0 (25–100 meV) for the semiconductors[34]. On the other hand, the presently observed result indicate that σ_0 does not have constant value which is reflected from the band-transport model[35]. The large scatter (10^3~10^{12} Ohm^{-1} cm^{-1}) in the value of σ_0

observed in the present study (Table 1) means that σ_0 could not be treated as the microscopic conductivity. Instead, σ'_0 may have a physical meaning in terms of microscopic conductivity[36]. The very low values of σ'_0 (10^{-17}~10^{-3} Ohm^{-1} cm^{-1}) for organic semiconductors have been already reported[33,37]. In such materials the electrical transport is assumed to be dominated by electron tunneling through intermolecular barriers[38] which leads to small tunneling factor and thereby small σ'_0.

4 Conclusions

The electrical conductivity of some composites of biopolymer and inorganic nanoparticles has been studied as a function of temperature and applied bias voltage. The trap distribution of charge carriers in these composites has been estimated. It is found that the increase of the guest content changes the nature of trap distribution in these composites. The characteristic temperature is highly host/guest weight ratio dependent. Conductivity of these composites strongly depends on sample temperature, applied bias voltage and the weight percentage of the guest molecules. The activation energy of these samples is directly proportional to the guest content. Percolation concept has been applied to understand the electrical conduction in these composites. The compensation law has been found to be satisfied for the thermally activated conductivities in the composites. It is observed that there exists a strong correlation between electrical conductivity prefactor and activation energy. Thus, in the present study we observe that in the case of composites activation energy is compensated by a change in the pre-exponential factor in the Arrhenius equation. Magnetic characterization of these composites is getting our next interest.

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