Electrical Conductivity of Polyvinyl Alcohol Films filled with Multiwall Carbon Nanotubes

Zainab Al-Ramadhan
Al-Mustansiriyah University
College of Education, Physics Department

Abstract

Efficient and inexpensive ways for the preparation of conductive PVAFilms were developed via a simple solution dispersion method. Multiwall carbon nanotube was used as filler in this research to achieve conductivity in PVA films. Well dispersion was achieved with the PVA solution. The conductivity increased from $10^{-13}(\Omega\text{-cm})^{-1}$ to $9x10^{-12}$ $(\Omega\text{-cm})^{-1}$ with filling ratio 3wt% and 6wt%. High conductivity was achieved at 12%; it reached $8.7x\ 10^{-4}(\Omega\text{-cm})^{-1}$. The activation energy was decreased with ratios 3% and 6% and it became negative at 12wt% which indicates a metallic behavior of the films.

Introduction

The electrical insulating behavior of most polymeric materials is well known. However, conductive fillers can be incorporated as a second phase into these matrices, leading to an increase in the conductivity of the resulting composites. The properties of these composites are mainly varied with the filler content. When the filler content reaches a critical value(the so-called percolation threshold), a sharp transition in the conductivity of the composites occurs with slight increase of the filler content. Nano size fillers significantly modify the properties of polymer composites and even generate certain new properties that cannot be derived from conventional fillers[1]. Generally, the resultant nanocomposites display enhanced optical, mechanical, magnetic and optoelectronic properties. Therefore, the composites have been widely used in the various fields such as military equipments, safety, protective garments, automotive, aerospace, electronics and optical devices[2,3].

Polyvinyl alcohol (PVA) is a good insulating material with low conductivity and hence is of importance to microelectronic industry. Its electrical conductivity depends on the thermally generated carriers and also the addition of suitable dopants[4].

The main objectives pertaining this research were to come up with efficient ways for the preparation of carbon Nano filler(carbon Nano fiber, exfoliated graphite, carbon black, and multiwall carbon nanotube) based composites and adhesives, and to explore the electrical conductivity of the prepared structures which can be used as thick films devices.

Experimental

The matrix polymer used in the present study is PVA. It is rigid polymer, fine solid poweder Mw=14.000, supplied from Petkim company(Turkey). The PVA material was added to distilled water at room temperature. Water bath method was used for heating the solution to prevent thermal decomposition of polymer. The hot solution was stirred until the polymer is completely dissolved and forming a clear viscous solution. The above viscous solution was treated by adding carbon Nano-tubes $(CNT)_s$ in different weights to prepare different ratios of PVA-$(CNT)_s$. $(CNT)_s$ were supplied from show a Denko chem. corporation. The process of sonication is one that shoots ultrasonic waves at the sample; therefore aiding dispersion of the filler and creating a more homogenous solution, then casted onto plates and left to dry in airfor three days. The thickness of the films ranging from 200-210µm. Thickness measurements were made using a micrometer.

Measurements

The conductivity of the Nano composite films was measured using three points probe testing device according to ASTM method(D257), the voltage passing through the Nano composite films was recorded as well as the current. The resistances of the sample filmswere obtained using ohm's law and consequently the conductivity data obtained.

- $$\text{Resistivity} = \frac{V}{I}\left(\frac{\text{Electrodes Circular Area(A)}}{\text{Film Thickness}}\right)$$

-Conductivity=1/Resistivity ρ

- $$A = \frac{D^2\pi}{4}$$

Diameter D =1.82cm^2

Results and Discussion

The observed variation of electrical conductivity of Nano composites with$(CNT)_s$ concentration is illustrated in figure (1). For very low $(CNT)_s$ contents, the conductivity gradually increases. It is very interesting to notice thatfor the films of 3% and 6% concentration, very lowconductivity data were recorded. This is due to the fact that not enough filler was added to establish a network with the PVA matrix or system. At 12% the carbon nanotubes connected to form a network therefore is making the film conductive[5]. The σ of the composites increases for more than nine orders at the percolation threshold of 12% of $(CNT)_s$Content. This percolation threshold signifies the critical volume fraction at which the filler particles within the matrix get closer and form linkages, the conductivity elements of the paths are either making physical contacts between themselves or are separated by very small distances across which the electrons can tunnel.

A surprising property of filled polymer composites is their conductivity profile as a function of filler concentration. It is found that their conductivity does not increase continuously but show a sudden jump to higher conductivity values at certain filler concentration, this critical filler concentration is called percolation threshold[6, 7].

In order to illustrate the variation of (σ_{Dc}) values with temperature, these were plotted in figure (2). It was seen that σ_{Dc} increased with increasing temperature, this behavior can be attributed to the thermal movement of ions and molecules [8].

The relationship between $\ln\sigma$ and $\frac{1}{T}$ are shown in figure (3). In order to calculate the values of activation energies the following equation were used.

$$\sigma = \sigma_0 \exp\left(\frac{-E_{ac}}{KT}\right)$$

Figure(4) shows the activation energies versus concentration. The high activation energy value for PVA sample without additive(control) can be attributed to the thermal movement of the macromolecules, whereas the low activation energy values for PVA composites (3% and 6%) can be attributed to the electronic conduction mechanism. It has been reported that for this kinds of composites ionic, electronic or even mixed conducting processes are possible. At 12% the activation energy becomes negative which indicates that the Nano composite becomes conductive.

Conclusion

It is found that the polyvinyl alcohol films prepared by a solution dispersion method can be stable and of less cost to produce. In addition highly conductive films produced when filler concentration of 12wt% with multiwall carbon nanotubes was achieved.

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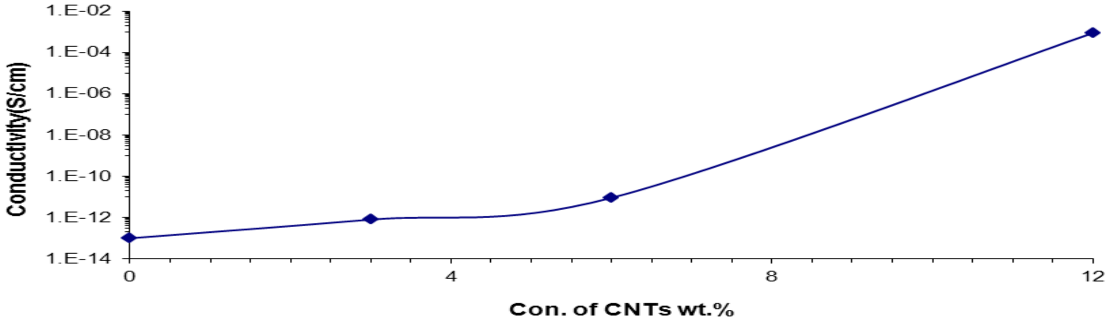

FIG.1
Variation of D.C electrical conductivity with CNTs wt.% concentration for (PVA-CNTs) composite.

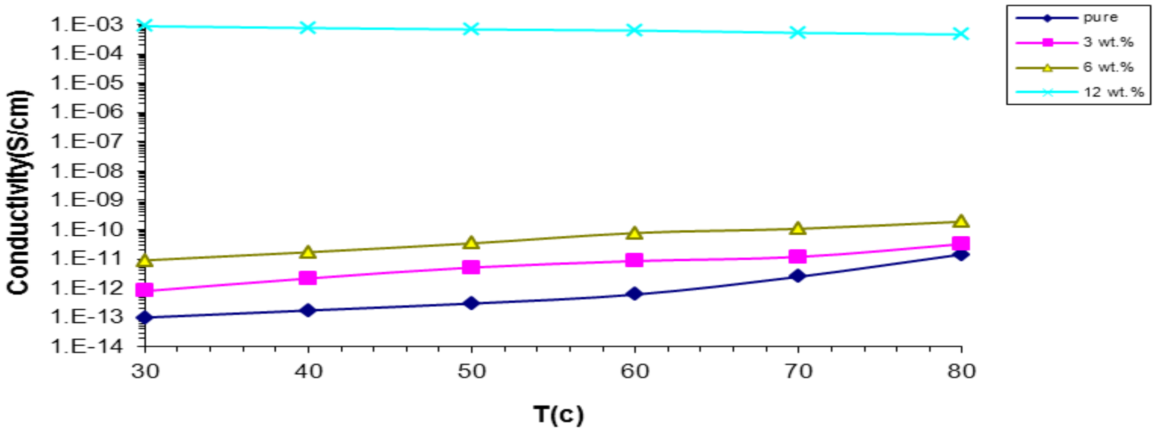

FIG.2
Variation of D.C electrical conductivity with temperature for(PVA-CNTs)

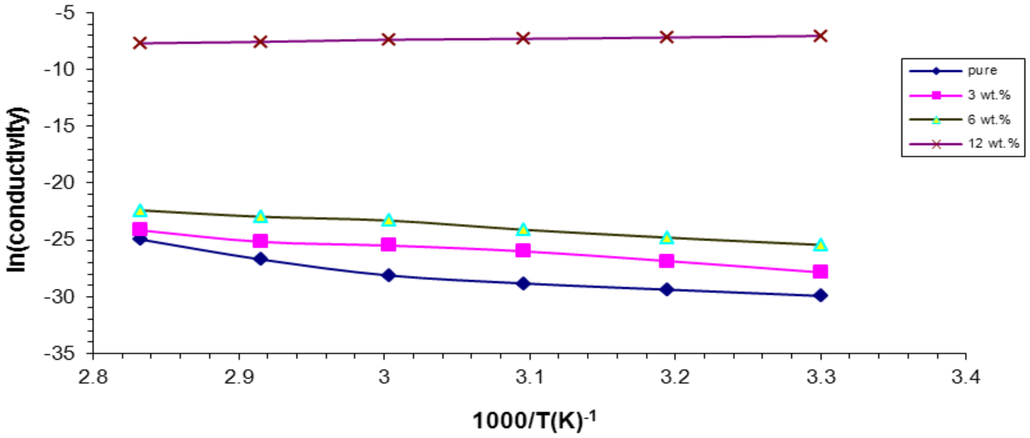

FIG.3
Variation of D.C electrical conductivity with resprocal absoute temperature for (PVA-CNTs) composite.

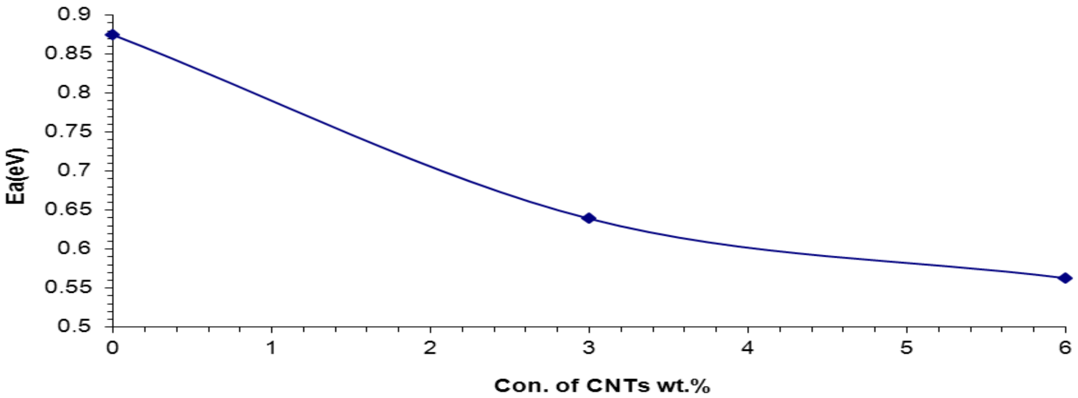

FIG.4
Variation activation energy for D.C electrical conductivity with CNTs wt.% concentration for (PVA-CNTs) composite

الخلاصة:

تم تطوير طرق فعالة وغير مكلفة لتحضير افلام بولي كحول الفاينيل الموصلة بواسطة طريقة تفريق المحلول البسيطة. تم استخدام انابيب الكاربون متعددة الطبقات النانوية كمواد حشو مع بولي كحول الفاينيل. تحقق التفريق الجيد مع محلول بولي كحول الفاينيل. اذ لوحظ زيادة التوصيلية من $(\Omega\text{-cm})^{-1}$ 10^{-13} الى $9\text{x}10^{-12}$ $(\Omega\text{-cm})^{-1}$ مع نسب الحشو 3wt% و6wt% ، حصلنا على توصيلية عالية عند النسبة 12% حيث وصلت قيمة التوصيلية الى $8.7\text{x}10^{-4}$ $(\Omega\text{-cm})^{-1}$. كذلك لاحظنا ان قيمة طاقة التنشيط قلت مع النسب 3wt% و 6wt% واصبحت سالبة عند النسبة 12 % وهذا يدل على السلوك المعدني للفلم.