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Development of Thermal and Electrical Properties of Poly(vinyl alcohol)/ Poly(ethylene glycol) Based on solid Electrolyte and Nanocomposite

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ABSTRACT

Polymer Nano composites and lithium polymer electrolytes are always scientifically speaking. It is formed by dissolving Multiwalled carbon nanotubes(MWNT) and lithium salt in poly(ethylene glycol), poly(vinyl alcohol) blends with the aim of developing new types of polymer composite characterized by enhanced thermal stability, as well as by improved electrical properties. The interaction of the MWNT and LiNO3 with the polymer blend were confirmed by a Fourier transform infrared (FTIR) spectroscopy study. The thermal properties of the polymer blend with the MWNT were carried out by means of differential scanning calorimetry (DSC). It is evident from DSC that the polymer/MWNT had a decreased of Tm and heat crystalline fusion(ΔHc) with of increased MWNT. Scanning electron microscopy is used to study the dispersion of the MWNT and LiNO3 in the polymer blend. Electrical conductivity was observed for PVA/PEG/MWNT containing 0.40 wt % MWNT was 7.98 X10-7S/cm where the PVA/PEG was 8.31 X10-8S/cm also electrical conductivity of PVA/PEG/LiNO3 containing 40wt % was 1.02 X10-7S/cm. Relative changes in the conductivity of blends with different concentrations and temperatures are analyzed.

INTRODUCTION

In recent years solid polymer electrolytes have become a subject of great interest due to their potential applications in rechargeable batteries, fuel cells, sensors, electrochromic display devices, smart windows and other applications(1,2).

The development of solid polymer electrolytes with high ionic conductivity at ambient and sub-ambient temperature has been made extensively due to its potential applications in electrochemical devices, such as high energy-density batteries, electrochromic devices and chemical sensors(3,1). The PVA based lithium salts complexed electrolytes for the application in electric double layer capacitors was studied. Magnesium acetate $Mg(CH_3COO)_2$ and magnesium nitrate $Mg(NO_3)_2$are mixed in equal wt% and are used as the salt for this system(4). Most of the solid polymer electrolytes are reported based on alkali metal salts(5), alkaline earth and other divalent and trivalent metal salts (6). Polyethylene glycol (PEG) based composite gel electrolytes using polyvinyl alcohol (PVA) as guest polymer have been synthesized with 1M solution of ammonium thiocyanate (NH_4SCN) in dimethylsulfoxide(DMSO)(7). In addition to the discovery of carbon nanotubes (CNT) in 1991(8) which was the realization of their unique physical properties including mechanical, thermal, and electrical, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these properties(9,10,11).

CNT owing to their outstanding electrical conductivity, small diameter, light weight, high aspect ratio, high thermal and air stabilities, are superior fillers for electrically conductive polymer composites. One of the main reasons for the incorporation of conductive nanoparticles into a polymer matrix is the production of conductive materials ambiguous new applications, such as electromagnetic interference (EMI) shielding, electrostatic dissipation and gas sensors(12,13).

Electrical conductivity can be explained by the established percolation theory(14) with an onset of the conductivity when a critical filler concentration commonly named percolation threshold is reached to form conductive pathways. The percolation threshold of nanotubes filled composites primarily is dependent on the processing methods, eventually on the dispersion of the SWNT or MWNT in a matrix. Direct blend of carbon nanotubes and a thermoplastic polymer by melt processing results in a high threshold since the dispersion of the very thin tubes is not facile(15).

Miscible polymer blends are attractive host materials to which CNT can be inserted because this type of mixture has a degree of mixing down to the molecular level. Many literature reports deal with the addition of CNT as fillers into polymer matrices; however, just a few researchers have investigated the effect of adding CNT to a polymer matrix specifically formed by a miscible polymer blend. Because of CNT are typically insoluble in organic solvents and severely bundled, their homogeneous dispersion in a desired polymer matrix is difficult to achieve. The dissolution of CNT in common organic solvents has been described(16–18). We investigate the effects of different ratios of MWNT and $LiNO_3$ on the morphology, thermal and electrical properties of PVA/PEG blends. The interaction of the MWNT and $LiNO_3$ with the polymer blend were confirmed by a Fourier transform infrared (FTIR) spectroscopy study.

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA) of molecular weight 67000 was supplied by Fluka, Polyethylene glycol (PEG) with an average molecular weight of 3500-4500 and melting point (mp=58-64◦C) was obtained from Scharlu, dimethylsulfoxide (DMSO) was supplied by Aldrich with purity 99.9%. Multi-walled carbon nanotubes (MWNT) with diameter 10 nm, length 0.1–10 micron and purity 90%, was supplied by Nanocyl S. A, Lithium Nitrate ($LiNO_3$) was supplied by Merck.

Preparations

The blends were prepared by solution casting using DMSO as solvent. In the first part of the work PVA/PEG were blended in several weight percent ratios and dissolved in DMSO. The solutions are stirred overnight and then poured into glass dishes and allowed to evaporate at 120 °C under vacuum.. The selected weight ratio PVA:PEG (50:50) was selected for the second part of the experiments. Here, different weights of MWNT (0.1, 0.2, 0.3, 0.4wt %) and (10, 20, 30, 40 wt %) from $LiNO_3$ were mixed into the chosen ratio of PVA/PEG.

Instruments

Differential scanning calorimetry (model-DSC-910) was used to measure the thermal properties for prepared samples. The sample was heated at a scanning rate of 10°C/min from 20 to 500 °C under a nitrogen gas.

FTIR spectra (SHIMADZU, FT-IR Spectrometer, Scimitar) was used to measure the polymer blends and its composites carried out with KBr pellets

SEM (JSM-6380 LA) used to examine the surface morphology and microstructure or to investigate the inner microstructure from fracture cross-sections.

RESULTS AND DISCUSSIONS

The DSC thermal analysis results for PVA/PEG(1:1) and PVA/PEG(1:1) + 0.1wt% MWNT are shown in Figures 1 and 2 respectively show typical DSC curves of PVA/PEG and PVA/PEG/MWNT Nano composite at the range from 20–500°C. The results and the area of heat crystalline fusion (ΔHc), Tm, and thermal degradation of PVA/PEG blend, and PVA/PEG/MWNT, were shown in Table 1.

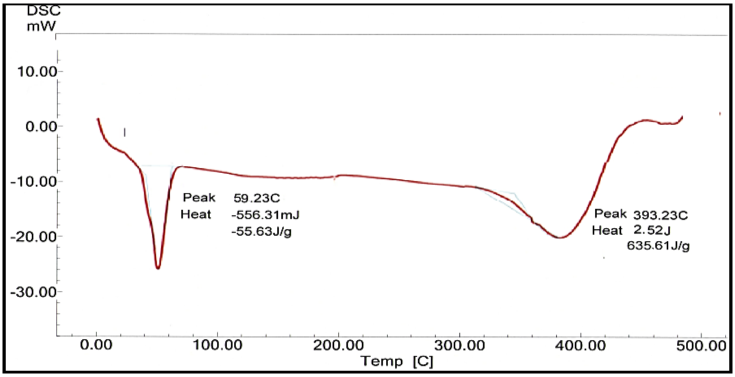


Figure 1: DSC curve of PVA/PEG blend (1:1).

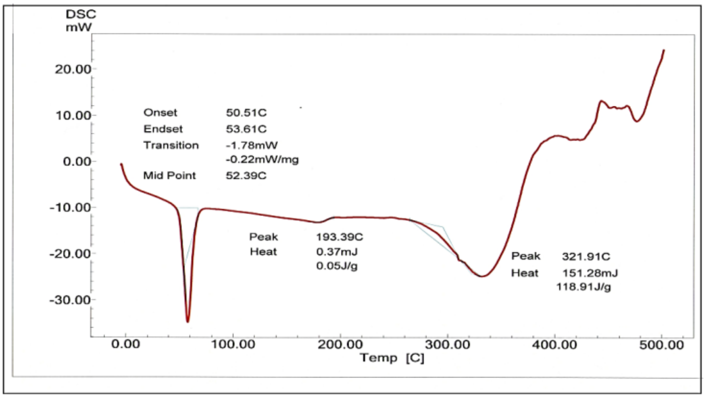


Figure 2: DSC curve of PVA/PEG blend (1:1)+ 0.1wt%MWNT.

The DSC of PEG shows an endothermic peak at 62.21ºC with a Heat of fusion of 186.57 J/g. with increased the ratios of PVA in the blends from (186.57J/g) for a net PEG to (55.63J/g), (24.63J/g) and (3.91J/g) for the ratios (1:1), (2:1) and (3:1) of PVA in the blend. This behaviors clearly observed with the decreased in the area of melting crystalline peaks.

The T_m was about (59.56ºC) and (57.86ºC) respectively for the higher ratio of PEG with (1:2) and (1:3). The heat of crystalline fusion of blend (ΔH_c) increased as the PEG content increased from (55.63 J/g) in equal ratio to (135.45J/g) for (1:3) PVA/PEG in blend. Higher arise in the heat of fusion indicates a higher crystallinity of the PEG in blend composites.

The effect of the MWNT composition on the thermal degradation T_d values of the PEG/PVA/MWNT; there was an apparent decrease in the T_d of the PEG/PVA film from 339.23ºC to approximately 321.19ºC in content of MWNT(1:1) and decrease with increasing MWNT content (0.1–0.2 wt %). Also T_m increasing when increased of MWNT contents (0.1–0.2 wt %) from 50.51 to 57.68ºC. This decrease in the crystallinity was due to the nanotubes impeded the crystallization formation(19).

Figure 3 Shown the FTIR spectra of the PVA/PEG/MWNT composites were analyzed to confirm the interaction between the polymer blends and the MWNT. The PVA/PEG blend (1:1) spectrum shows absorbance peak of (OH) at 3440 and shifted to 3384cm^{-1} for PVA /PEG/MWNT(20) these change were more broadened in (b, and c) and disappearance in (d, and e) with increases of MWNT content. The (PVA/PEG) band, originally appearing at 1600 cm^{-1}, shifted slightly to 1640 cm^{-1} for the PVA/PEG/MWNT composite which demonstrates a small shift of the (PVA/PEG) and OH peaks following the MWNT embedding compared PVA/PEG blend.

Table 1: The results of DSC curves for all samples (Tm, ΔHC, ΔHm, Td).

Compound	ΔH_C [J/g]	T_m [ºC]	ΔH_m [J/g]	Thermal degradation Td [ºC]
PVA	-439.61	224.35	-	-
PEG	-186.57	62.21	-	-
PVA/PEG (1:1)	-55.63	59.23	635.61	393.23
PVA/PEG (2:1)	-24.63	54.53	-	-
PVA/PEG (3:1)	-3.91	55.51	-	
PVA/PEG (1:2)	-129.61	59.56	-	-
PVA/PEG (1:3)	-135.45	57.86	-	-
PVA/PEG (1:1)+ (0.1wt.%)MWNT	-	50.51	118.91	321.19
PVA/PEG (1:1)+ (0.2wt.%)MWNT	-76.76	57.68	85.26	310.24

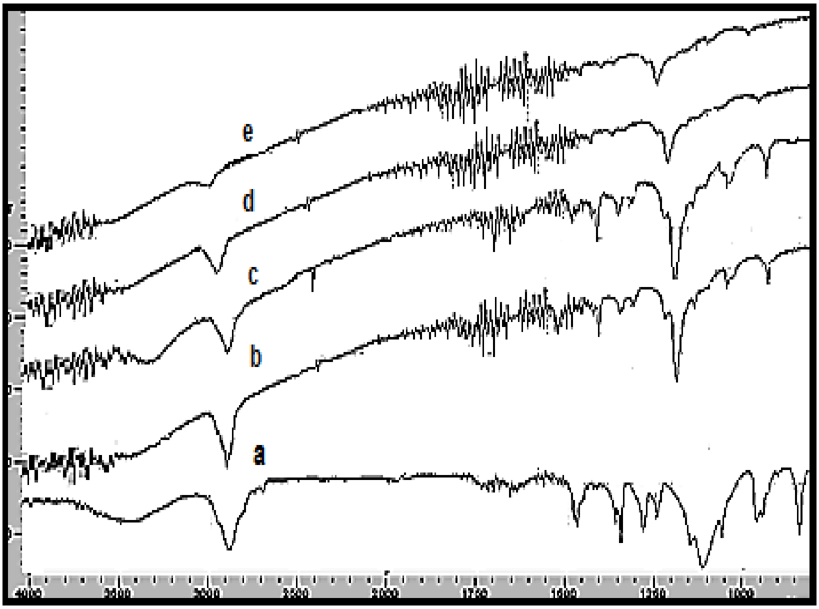


Figure 3: FTIR spectrum for (a)[(PVA/PEG)blend(1:1)], [(b, c, d, e) for blend(1:1)+ (0.1, 0.2 , 0.3 and 0.4wt.%) of MWNT respectively.

The FTIR spectra of the PVA/PEG/$LiNO_3$ blends were analyzed to confirm the interaction between the polymer blends and the $LiNO_3$. The PVA/PEG/$LiNO_3$ spectrum shows absorbance peaks at 2741 cm^{-1} of (-CH_2), 3440 cm^{-1} of (-OH), to blend of (PVA/PEG), characteristic of the polymer composite. The inset in Figure 4 demonstrates a change (-OH) band from3450 to more broadened in (b, c) and disappearance in (d,e) with increases of $LiNO_3$ concentrations. The peak for (C-O-) can be observed this change at ~(1248)cm^{-1}which shift to ~(1253,1257)$cm^{-1}$and from ~(1344)cm^{-1} to ~(1347-1352)cm^{-1} in

(b) to (c)respectively, this change due to coordination of lithium ions to the oxygen atom which has been reported elsewhere (21,22). The absorption peak can be de-convoluted into two components centered at about ~(685 and 750) cm^{-1}, respectively. The band at ~(685) cm^{-1} is attributable to the free NO_3^- and the (750,776) cm^{-1} mode is assigned to the ion-pair formation or the contact of NO_3^- with lithium ion. The ratio of peak areas in (685) and (750,776) cm^{-1} can be used as an index of the degree of ionization of the lithium salt in the polymer blend electrolytes(23).

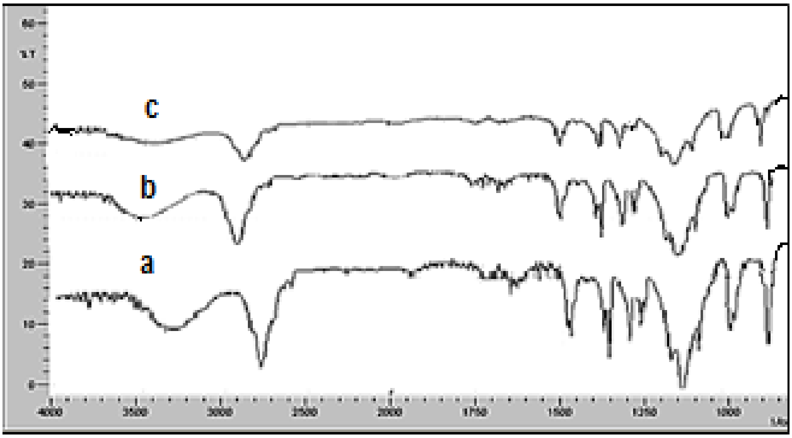
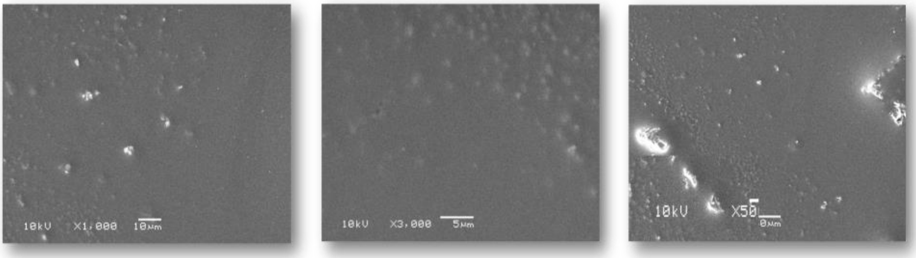


Figure 4: FTIR spectrum for (a)[(PVA/PEG)blend(1:1)], [(b,c)]for blend(1:1)+ (10,and 40wt.%) of $LiNO_3$ salt respectively.

The morphology of PVA/PEG films and MWNT dispersion in PVA/PEG composite films were observed by scanning electron microscopy (SEM) to determine miscibility of polymer blends. The uniformity of the dispersion of the solution cast films of PVA and PEG ratio (1:1), PVA/PEG with $LiNO_3$ and PVA/PEG with MWNT blend compositions were examined through SEM and the corresponding micrographs are as shown in Figure5(a, b and c). Figure5, b shows that in the PVA/PEG blend (1:1) with (0.4wt.%) of MWNT was observed network structure and relatively good dispersion of MWNT in PVA/PEG(1:1) blend. The similar result by electron microscopy was shown improve uniformity of the PEG/nano composite(24). Whereas Figure 5, c shows the PVA/PEG blend(1:1) with (10wt.%) of $LiNO_3$ salt, which shows that the size of spherules have been reduced and dispersed completely and showed single phase while adding $LiNO_3$ content to the blend as observed in previous literature(25).



(a) (b) (c)

Figure(5):a; SEM for (PVA/PEG)blend (1:1), b; SEM for (PVA/PEG)blend(1:1)+0.4 wt.% MWNT, c; SEM for (PVA/PEG)blend (1:1) +10 wt.% $LiNO_3$.

The measurements of the ionic conductivity of the PVA/PEG blend (1:1) and PVA/PEG/MWNT composites were carried out at different concentrations in the temperature range (303 – 343) K.

The conductivity activation energy of the polymer composite at 303K were calculated by using flowing equation

$$\sigma = \sigma_o \exp\left[\frac{-E_a}{k\,T}\right]$$

Whereas Ea is the conductivity activation energy, K is Boltzmann's constant, and σ_o is the pre-exponential factor and includes the charge carrier mobility and density of state

Conductivity activation energy for PVA/PEG/$LiNO_3$ has been calculated in the same way connectivity for calculating for PVA/PEG/MWNT in accordance of above equation. The semi logarithmic plots of Ln σ vs. T^{-1} illustrated in figure 6. Activation energy Ea values of 325.23 and 296.3 m.ev for PVA/PEG and PVA/PEG/$LiNO_3$, respectively. The corresponding values of activation energies are shown in Table 2. For all compositions of PVA/PEG blend with $LiNO_3$ salt, the conductivity increases with increase of temperature. It was for PVA/PEG without Lithium salts about 8.3×10^{-8} S/cm at 303K and about 9.68×10^{-8} S/cm at 343K. The increase of temperature causes the increase in conductivity due to the increase of free volume and their respective ionic and segmental mobilities. This increase in free volume would facilitate the motion of ionic charges(26). However, the conductivity is found to increase with increase of salt content which was added to blend and showed conductivities range from 8.66×10^{-8}S/cm to1.02×10^{-7} S/cm at 303K for different salt ratios. It was also found that the activation energy values increased with increasing concentration of $LiNO_3$.This may be due to the fact that the addition of salt forms charge transfer complexes in the host lattice(27). These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice, resulting in a decrease of activation energy.

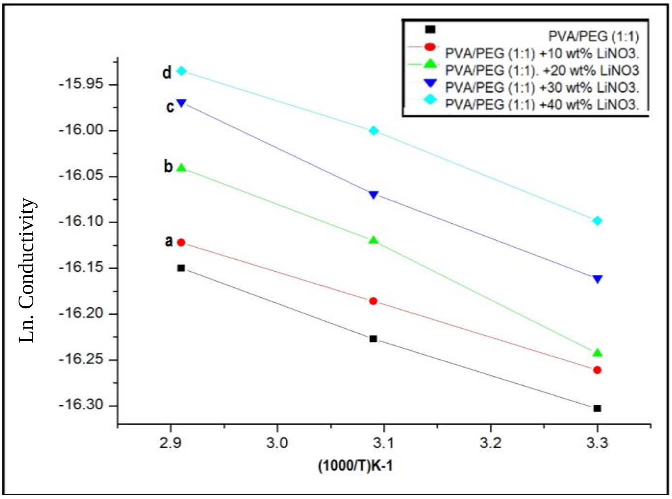


Figure 6: Arrhenius plots of PVA/PEG/$LiNO_3$ composites with (a) 10 wt %., (b) 20wt %, (c) 30 wt %, (d) 40 wt % of $LiNO_3$.

Table 5: Activation energy for PVA/PEG/$LiNO_3$ electrolyte.

Compound	σ (S/cm)	Ea (m.eV)
(PVA/PEG) blend (1:1).	8.31×10^{-8}	325.23
blend (1:1) +10wt.% $LiNO_3$ salt.	8.66×10^{-8}	296.3
blend (1:1) +20wt.% $LiNO_3$salt.	8.82×10^{-8}	432.1
blend (1:1) +30wt.% $LiNO_3$ salt.	9.58×10^{-8}	408
blend (1:1) +40wt.% $LiNO_3$salt.	1.02×10^{-7}	348.5

Conductivity of a neat PVA/PEG has increased by two orders from 1. 8.3×10^{-8} s/cm at 303K to 9.66×10^{-8} S/cm when (0.1wt%) MWNT was added, where a value of activation energy Ea decreased from 325.46 to 167.1 respectively . Generally, activation energy Ea values, still low with further increase of MWNT content in composite, as shown in Table 3. A sharp increase of conductivity was observed at 0.3wt%. The main factor influencing in conductivity for composite was the concentration of the filler particles. At low filler content the conducting particles are separated and the electric current is low(28). While at filler content increase the percolation threshold appears. So, the conductivity rises over several orders. Conductivity for composite increases with an increase of MWNT content Up to (0.4wt%) MWNT in blend, the conductivity increases to [7.98×10^{-7} S/cm] at the same temperature which increased by (two orders) of magnitude as compared with pure PVA which is about 10^{-10}S/cm, and one orders of magnitude compared with neat PVA/PEG. This result also shows improvement in conductivity when added MWNT to blend comparison with PVA/MWNT composite which observed by Literature(29) .

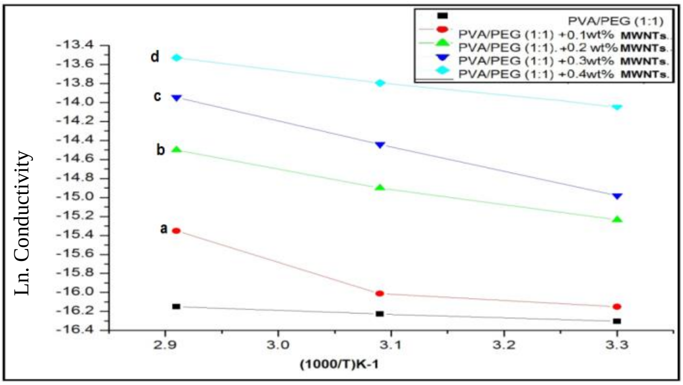


Figure 7: Arrhenius plots of PVA/PEG/MWNT composites with (a) 0.1 wt%, (b) 0.2 wt %, (c) 0.3 wt % and (d) 0.4 wt % of MWNT.

Table 3: Activation energy for PVA/PEG/MWNT composites.

Compound	σ (S/cm)	Ea (m.eV)
(PVA/PEG)blend (1:1)	8.31×10^{-8}	325.23
blend(1:1)+(0.1wt.%) MWNT	9.66×10^{-8}	167.1
blend(1:1)+(0.2wt.%) MWNT	2.42×10^{-7}	155.8
blend(1:1)+(0.3wt.%) MWNT	3.12×10^{-7}	220
blend(1:1)+(0.4wt.%) MWNT	7.98×10^{-7}	108.6

CONCLUSION

The studied Poly(vinyl alcohol)/Poly(ethylene glycol) composites containing Multiwalled carbon nanotubes or $LiNO_3$ have been successfully prepared through solution cast method.

The thermal properties, morphology and interaction between studied polymers have been characterized by using DSC, SEM and FTIR. The PEG showed miscible with the high molecular weight PVA and show that the PVA/PEG blend with ratio (1:3) has greater enthalpy (135.45J/g) than blend with (3:1) which was (3.91 J/g) and the blend was appeared thermal stability (393.23°C) for an equal ratio .The SEM technique indicates that, the PVA/PEG with an equal ratio in blend were given network structure, relatively good dispersion, and sizes of spherules have been reduced. It was confirmed by appearance of newly peak and shifted the wave numbers for other peaks in FT-IR spectrum.

Composites were produced by solution mixing of PVA/PEG with different weight ratios of $LiNO_3$ and MWNT. The addition of 40wt.% $LiNO_3$ exhibits an improving in conductivity with a value of 1.07×10^{-7} S/cm by one ordered magnitude. It was found that the electrical conductivity of PVA/PEG(1:1) is 8.66xl0^{-8}S/cm where the highest electrical conductivity was observed for PVA/PEG/MWNT containing 0.40wt.% MWNT with a conductivity of 7.98×10^{-7} S/cm. In comparing with PVA/PEG/$LiNO_3$ (40wt.% $LiNO_3$) and PVA/PEG/MWNT (0.40 wt.% MWNT), it was found that the electrical conductivity improved by one ordered magnitude and two ordered magnitude respectively.

As a result, the thermal and electrical properties of PVA/PEG/MWNT composites are significantly better than PVA/PEG blends and PVA/PEG/$LiNO_3$. These composites promise a new opportunity for the design of low cost polymer composites for numerous future applications such as solar energy utilization, sensors and electronic devices.

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تطوير الخصائص الحرارية والكهربائية للبولي (فينيل الكحول) / بولي (جلايكول الإثيلين) معتمداً على الالكتورليت والخلائط النانوية

عبدالله الحسام و نايف الطيار و جميل قاسم

قسم الكيمياء ، كلية العلوم التطبيقية ، جامعة ذمار ، ذمار ، اليمن

ملخص

نظرا لتزايد الاهتمام بمركبات النانو بوليمر وبوليمرات املاح الليثيوم الاليكتروليتية فقد تم تحضير خلائط بوليمرية وذلك بإذابة كل من (MWNT) و ملح نترات الليثيوم كلا على حده في خليط البولي إيثلين جليكول مع البولي فينيل الكحول (PVA/PEG) بهدف تطوير وتعزيز صفات هذا الخليط البوليمري كزيادة الاستقرار الحراري وتحسين الصفات الكهربائية. تداخل وتشابك كلا من (MWNT) و ملح نترات الليثيوم كلا على حده في خليط البولي إيثلين جليكول مع البولي فينيل الكحول تم اثباته بواسطة طيف الاشعة تحت الحمراء (FTIR) . الصفات الحرارية لخليط البوليمر مع (MWNT) قد تم دراستها بواسطة المسح الحراري المسعري (DSC) والذي بين ان قيم (Tm , ΔH_c) تتناقص مع زيادة نسبة (MWNT) في الخليط. المسح الاليكتروني الميكروسكوبي (SEM) استخدم لدراسة انتشار وتوزيع ($MWNT$, $LiNO_3$) في الخليط البوليمري. التغيرات النسبية في التوصيلية الكهربائية للمخاليط البوليمرية المحضرة بنسب تراكيز مختلفة لكل من ($MWNT$, $LiNO_3$) وعند درجات حرارة متغيرة تم دراستها والتي اوضحت تحسن في التوصيلية الكهربائية عنها في خليط (PVA/PEG) بمفرده.