

Morphological and Electrical properties of Polyvinylpyrrolidone/Multi-walled Carbon Nanotubes Nanocomposite with Graphene

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ABSTRACT

Keywords

Polyvinylpyrrolidone, MWCNT, graphene, DC electrical conductivity

The solution casting method was used to prepare a polyvinylpyrrolidone (PVP)/Multi-walled carbon nanotubes (MWCNTs) nanocomposite with Graphene (Gr). Field Effect Scanning Electron Microscope (FESEM) and Fourier Transformer Infrared (FTIR) were used to characterize the surface morphology and optical properties of samples. FESEM images revealed a uniform distribution of graphene within the PVP-MWCNT nanocomposite. The FTIR spectra confirmed the nanocomposite information is successful with appearing the presence of primary distinct peaks belonging to vibration groups that describe the prepared samples.. Furthermore, found that the DC electrical conductivity of the prepared nanocomposites increases with increasing MWCNT concentration which is due to hopping conduction.

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1. Introduction

Polymers and polymer composites are widely used in industry. When compared to metals and metallic alloys, polymer-based materials are specifically and preferentially used in machine design due to advantages such as lightness, chemical resistance, ease of processing, and recycling. However, unreinforced polymers have some drawbacks in terms of mechanical and thermal properties. To improve some of the physical properties of polymers, various fibers such as glass fiber [1, 2], carbon fiber [3, 4], and aramid [5] are introduced, as well as particles with varying particle shape and size. In recent years, carbon-based nanomaterials (for example, carbon nanotubes-CNT, carbon nanofibers-CNF, and graphene derivatives) have emerged as the most important fillers for improving the physical properties of polymers [4,5]. Carbon nanotubes' superior structural and physical properties, such as one-dimensional (1D) geometry, extremely high aspect ratio, modulus of elasticity (200–1000 GPa) and strength (200–900 GPa), electrical and thermal conductivity, make them ideal candidates for nanofillers in advanced polymer nanocomposites [6–8]. Single-walled or multi-walled carbon nanotube (SWCNT or MWCNT) filled polymer composites can be created using in-situ polymerization, solution mixture, or melt-mixing (extrusion and injection) techniques [9]. Graphene (Gr) is a two-dimensional honeycomb lattice made up of a single atomic layer of sp²-bonded carbon atoms that has garnered attention due to its odd physical properties [10]. Because of their remarkable physical properties, such as extreme electrical conductivity, equal thermal stability, and excellent mechanical efficiency, graphene and carbon nanotubes (CNTs) have prompted tremendous interest and involvement in science [11,12]. The cast solution method, in particular, provides a cost-effective process for preparing polymer nanocomposite, allowing for both fast production and environmental benefits as a solvent-free route [13,14]. Polymer composites, on the other hand, have been identified as a promising candidate for use with CNT and Gr because they may result in improved properties [15]. However, due to the difficulty of the melting process, it is difficult to obtain a homogeneous solution of polymer, CNT, and Gr. Polyvinylpyrrolidone (PVP) is an amorphous, nontoxic, versatile polymer with excellent binding properties and high stability [16]. It is soluble in water and many polar solvents, including ethanol, making it simple to prepare [17]. To their good applications in sensors, membrane and optoelectronic devices, in this work an investigation of the effect of MWCNT addition on the morphological, and electrical properties of PVP-MWCNT nanocomposites, in the presence of Gr, that have MWCNT concentrations within the



range of (0.1, 0.25, 0.5, 0.75 and 1wt%) were prepared using solution casting method. morphological, and electrical properties of nanocomposite samples were characterized.

2. Materials and Methods

PVP was supplied by Sigma-Aldrich with average molecular weight of 40000g/mol, purity >95 wt% was purchased from Neutrino. Gr platelet nanopowder with thickness 608nm and average particle diameter 15 μ m was supplied by Skyspring nanomaterials Inc. The nanocomposite was prepared in an aqueous suspension using ethanol. 4gm of PVP was dissolved in 40ml of ethanol and sonicated with energy 30 kHz for 40 min in order to have clear and dense solution. MWCNT were prepared, by dissolving in 20ml of ethanol and stirred for about 6 hours at room temperature before it's stirred with PVP for about 24 hours. Then Gr powder (0.05mg) was added to the nanocomposite during the stirring and sonicated for 48 hours. Many nanocomposites with different concentrations of MWCNT (0.1, 0.25, 0.5, 0.75 and 1wt%) were prepared. The resulting samples were dropped on glass substrates with dimension of (2.5x2.5) cm for characterization. The structural properties of the samples were investigated using Fourier transformer infrared (FTIR) spectroscopy (type- Shimadzu 8400) in the frequency range 4000-400 cm^{-1} by pelletizing a homogenized powder of the synthesized samples and KBr. The surface morphology of prepared samples was studied using Field Emission-scanning electron microscope (FESEM), the electrical conductivity has been measured as a function of temperature for the samples over the range (303-423K) using sensitive digital electrometer type Keithley (616), (Mettler U10 oven made in Germany).

3. Results and discussion

The purpose of FTIR spectroscopy is to examine multi-component functional groups and provide helpful information about the mechanism of interaction and the content of the material phase in a variety of bond types found in all samples. Fig.1 shows FTIR absorption spectra of the nanocomposites. In the wave number range from 2900 - 3600 cm^{-1} the bands correspond to the outer phase vibration oscillation of hydroxyl group (O-H). The position of the bands at 771, 1242, 1413, 1606 cm^{-1} correspond to C-O bending, C-O stretching of hydroxyl group, and C=O stretching vibrations of carboxyl group, respectively [18]. By increasing the MWCNT concentrations the intensities of the peaks have been increased and broadened which means the increase in the interlayer spacing between the polymer chains. It is known that the wavenumber shifts of IR bands evidence the change in the potential energy distribution along the polymeric



chain due to the filling or doping, this can give an indication that the MWCNT can penetrate the carbonyl group of PVP [19].

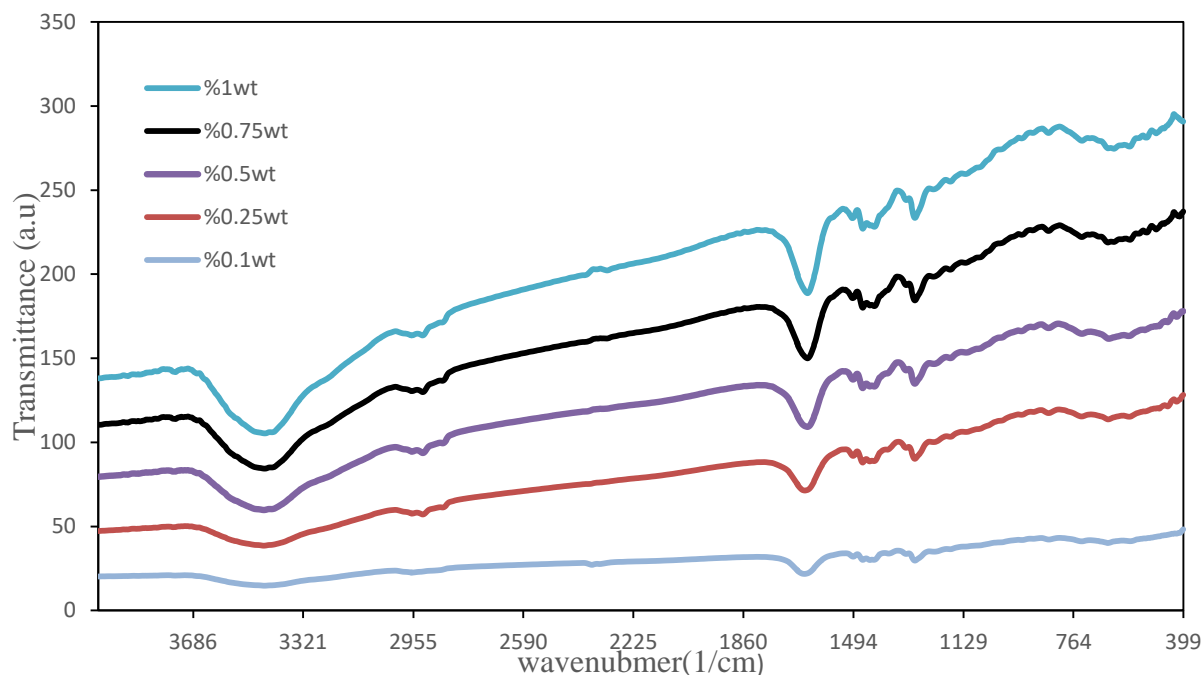


Figure 1: FTIR for the nanocomposites.

In general, FESEM is commonly used to examine the compatibility of various components of a film, as well as to detect phase separations and interfaces. Figure 2 (a,b,c,d) shows the FESEM images of PVP/MWCNT nanocomposite with Gr samples with 0.1, 0.25, 0.75 and 1wt%. Figure 2 shows a uniform dispersion of MWCNT and Gr within the PVP matrix with hemispherical shape and average size around $0.3\mu\text{m}$ indicating a strong interaction happened. In higher concentrations (0.75 and 1wt%) MWCNT began to aggregate since the adhesion decreases with the polymer [13].

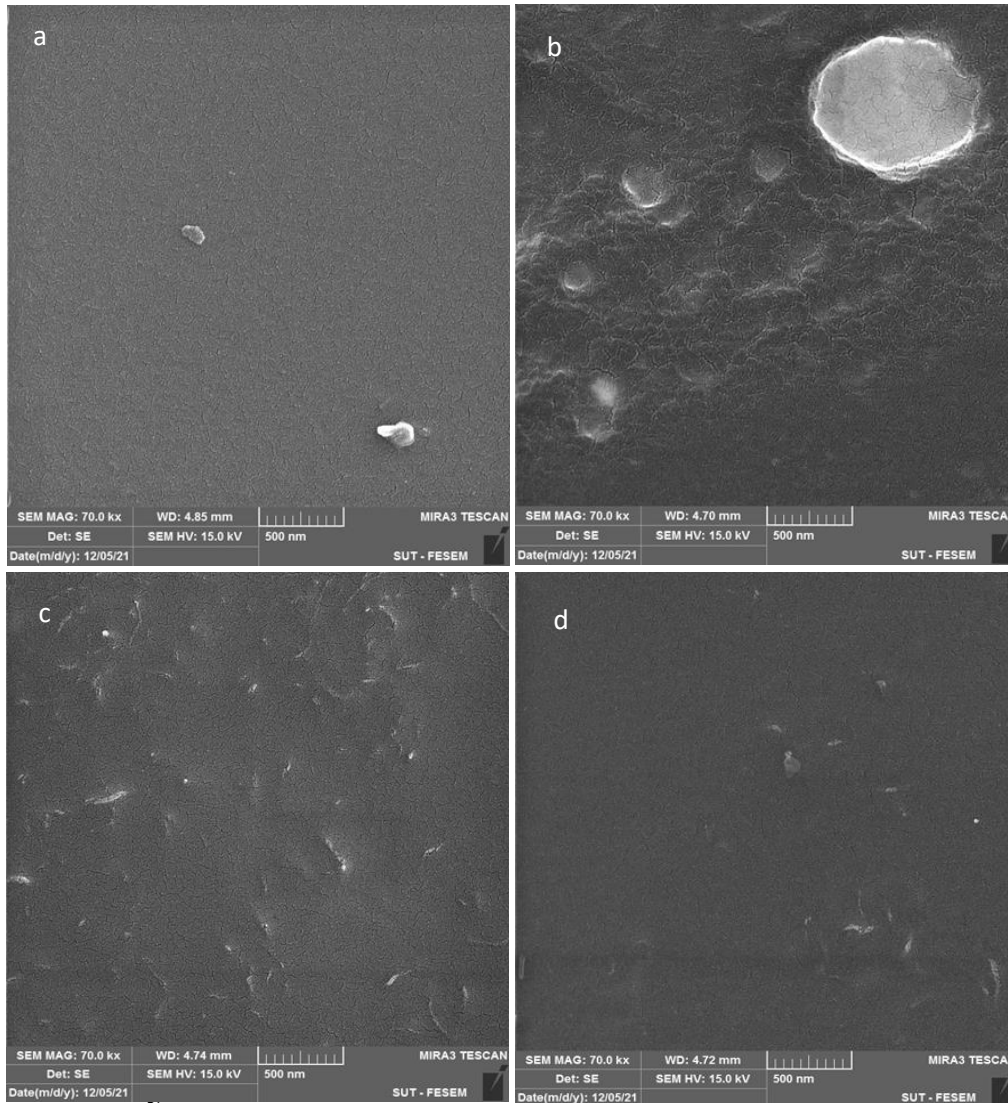


Figure 2: FESEM of PVP/MWCNT nanocomposite with Gr a) 0.1 b) 0.5 c) 0.75 d)1wt% of MWCNT.

Figure 3 shows the plot of $\ln \sigma_{dc}$ and $1000/T$ at 0.25, 0.5, 0.75, and 1wt% of MWCNTs and for range of temp. 303-423K. The linear behavior indicates that a thermally activated process follows the Arrhenius relationship:

$$\sigma_{dc} = \sigma_0 \exp(-E_{dc}/K_B T) \dots\dots\dots 1$$

where σ_0 is the pre-exponential factor, E_{dc} is the thermal activation energy for DC conductivity. Figure 3 shows the effects of temperatures on the electrical conductivity of nanocomposite for different MWCNT concentrations. The conductivity of the nanocomposites increase with

temperature increases; wherein 0.25wt% σ_{dc} was equal to $1.507 (\Omega^{-1} \cdot \text{cm}^{-1})$, and for the other wt% concentration the conductivity still increase slightly from 1.623, 1.856 to $1.899 (\Omega^{-1} \cdot \text{cm}^{-1})$, as illustrate in figure 4. This can be explained as the molecules undergo a phase transition when the temperature rises, they are likely to slide over each other to allow electrical conductions. The data show an increase in conductivity. The formation of conductive pathways occurs when the weight percent of MWCNTs exceeds a certain proportion, known as the percolation threshold, resulting in conductivity [20]. At low concentration of MWCNTS, the distance between particles (MWCNTs) is high, resulting in reduced conductivity. At higher nanoscale inclusions, the percolation threshold exists, and in the absence of a conductive channel, polymeric materials are commonly referred to be insulators [21,22]. MWCNT at high concentration tend to agglomerate due to the absence of the dispersion and interfacial interactions, and as a result, obstruct the formation of conductive pathways [22]. Therefore, a good dispersion is required to establish the conductivity pathway in the nanocomposite.

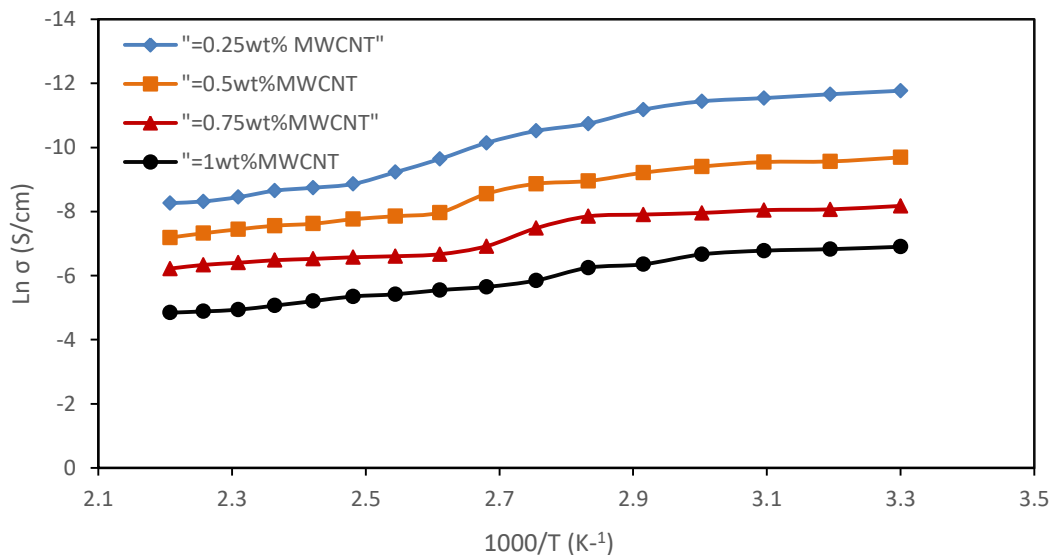


Figure 3: DC conductivity of the nanocomposite vs. reciprocal temperature.



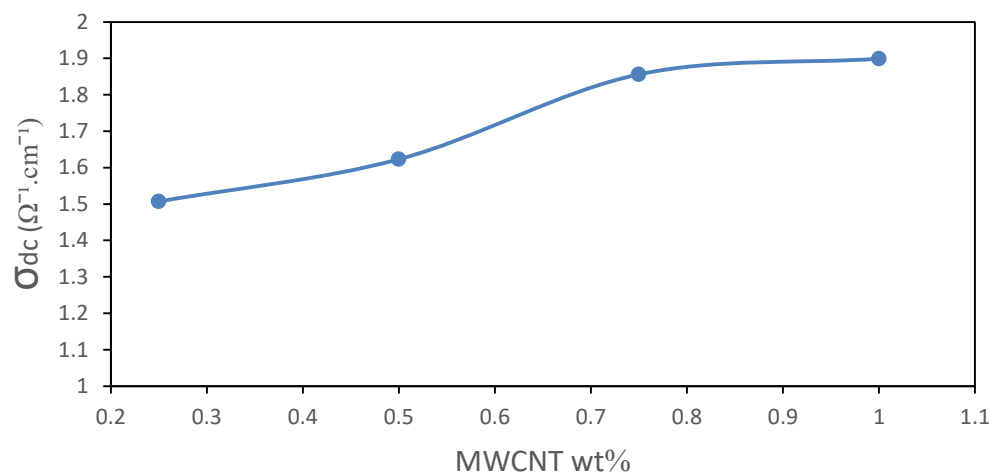


Figure 4: DC conductivity of the nanocomposite vs MWCNT concentrations.

Because of the mechanism of heating the polymer above room temperature is thermally induced, the resistance versus temperature behavior of the nanocomposite can be explained by their activation energy values. Figure 5 shows the plot of energy with MWCNT concentrations (0.25, 0.5, 0.75, and 1wt%). It shows a decrease in the activation energy as the MWCNT concentration increase; this might be due to the aggregation of the CNT and Gr.

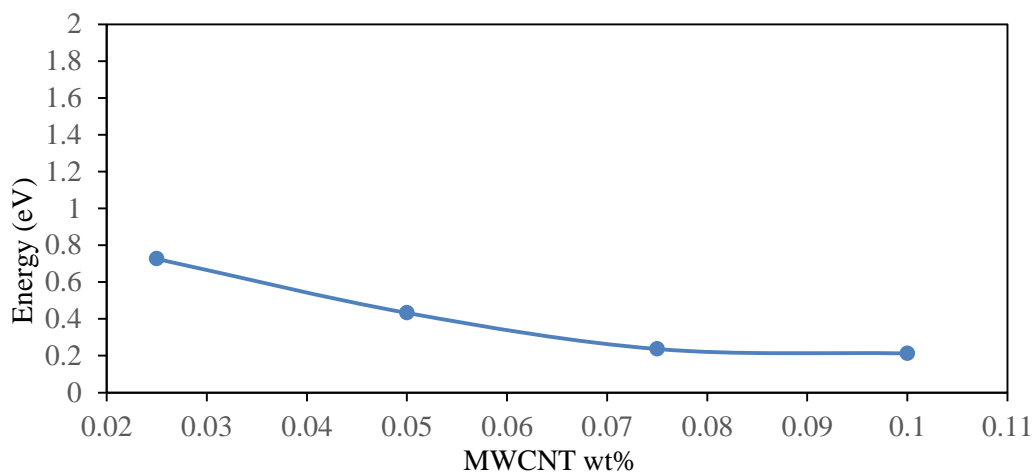


Figure 5: Activation energy vs MWCNT concentrations for nanocomposite.



4. Conclusions

A casting method was employed to prepare PVP/MWCNT nanocomposite with Gr at room temperature. Their morphological and electrical properties were investigated. FTIR analysis indicates the formation of intermolecular interaction between the PVP, MWCNT and Gr. FESEM images appeared the homogenous nature of the prepared samples without aggregation. An enhancement of electrical conductivity was shown after increasing the amount of MWCNT which indicate the hopping mechanism was dominated. As a result, it is possible to conclude that these nanocomposites are promising candidates for use in various engineering applications.

References

- [1] P. Morampudi, K.K. Namala, Y.K. Gajjela, M. Barath, G. Prudhvi, Review on glass fiber reinforced polymer composites, *Mater. Today Proc.*, 43(2021)314–319, doi.org/10.1016/j.matpr.2020.11.669.
- [2] AY. Chen, S. Baehr, A. Turner, Z. Zhang, G.X. Gu, Carbon-fiber reinforced polymer composites: A comparison of manufacturing methods on mechanical properties, *Int. J. Lightweight Mater. Manuf.*, 4 (2021)468-479, doi.org/10.1016/j.ijlmm.2021.04.001
- [3] K. Şahin, J.K. Clawson, J. Singletary, I. Chasiotis, Shear strength of homopolymer and copolymer aramid fibers, *Polymer*, 186, (2020)122034, [10.1016/j.polymer.2019.122034](https://doi.org/10.1016/j.polymer.2019.122034)
- [4] E.T. Abdullah, S.M. Hassan, R.S. Ahmed, Electrical Properties of Polyaniline/Functionalized Multi Walled Carbon Nanotubes Nanocomposite, *Int. J. Curr. Eng. Technol.*, 6(2016)617-621. <https://doi.org/10.1088/1742-6596/1178/1/012032>
- [5] A. Eitan, F.T. Fisher, R. Andrews, L.C. Brinson, L.S. Schadler, Reinforcement mechanisms in MWCNT-filled polycarbonate, *Compos. Sci. Technol.*, 66(2006)1159–1170, [10.1016/j.compscitech.2005.10.004](https://doi.org/10.1016/j.compscitech.2005.10.004)
- [6] J. Simon, E. Flahaut, and M. Golzio, Overview of Carbon Nanotubes for Biomedical Applications, *J. Mater.*,12(2019)1-21, [10.3390/ma12040624](https://doi.org/10.3390/ma12040624).
- [7] S. Iijima, Helical microtubules of graphite carbon, *Nature*, 354(1991)56-58, <https://doi.org/10.1038/354056a0>.
- [8] B. Zaidi,, N. Smida, M.G. Altho baiti, A.G. Aldajani , S.D. Almdhaibri, Polymer/Carbon Nanotube Based Nanocomposites for Photovoltaic Application: Functionalization, Structural, and Optical Properties, *Polymers*, 14(2022)1093-1119 <https://doi.org/10.3390/polym14061093>.
- [9] M. Ates, A.A. Eker, B. Eker , Carbon nanotube-based nanocomposites and their applications, *J Adhes. Sci. Technol.*, 31(2017)1977-1997, <https://doi.org/10.1080/01694243.2017.1295625>



- [10] B.G. Nassef, G.A. Nassef, M.A. Daha, Graphene and Its Industrial Applications – A Review, *Int. J. Mater. Eng.*, 10(2020)1-12, <https://doi.org/10.5923/j.ijme.20201001.01>.
- [11] K.K. Gangu, S. Maddila, S.B. Mukkamala, S.B. Jonnalagadda, Characteristics of MOF, MWCNT and graphene containing materials for hydrogen storage: A review, *J. Energy Chem.*, 30 (2019)132-144, <https://doi.org/10.1016/j.jechem.2018.04.012>.
- [12] A.R. Singh and V.D. Deshpande, Preparation and characterization of solution cast films of PET, reorganized PET and their MWNT nanocomposites, *Carbon Mat.*, 2012 (CCM12) AIP Conf. Proc. 1538(2013)190-195, <https://doi.org/10.1063/1.4810055>.
- [13] N.A. Ali, S.I. Hussein, T.B. Asafa, A.M. Abd-Elnaiem, Mechanical Properties and Electrical Conductivity of Poly(methyl methacrylate)/Multi-walled Carbon Nanotubes Composites, *Iran J Sci. Technol. Trans. Sci.*, 44(2020)1567–1576, <https://doi.org/10.1007/s40995-020-00948-7>
- [14] A.Venkataraman, E.V. Amadi, Y. Chen, C. Papadopoulos. Carbon Nanotube Assembly and Integration for Applications. *Nanoscale Res Lett.*, 14 (2019)220, <https://doi.org/10.1186/s11671-019-3046-3>.
- [15] B.M. Itapu, A.H. Jayatissa, A Review in Graphene/Polymer Composites, *Chem. Sci. Int. J.*, 23(2018)1-16, <https://doi.org/10.9734/CSJI/2018/41031>.
- [16] P. Boonsuk, K. Kaewtatip, S. Chantarak, A. Kelarakis, and C. Chaibundit, Super-tough biodegradable poly(vinyl alcohol)/poly(vinyl pyrrolidone) blends plasticized by glycerol and sorbitol, *J. Appl. Polym. Sci.*, 135,(2018)1–22, <https://doi.org/10.1002/app.46406>
- [17] L. Sun, G. Wang, C. Zhang, Q. Jin, Y. Song, "On the rheological properties of multi-walled carbon nano-polyvinylpyrrolidone/silicon-based shear thickening fluid" *Nanotechnol. Rev.*, 10 (2021)1339-1348, <https://doi.org/10.1515/ntrev-2021-0087>.
- [18] S.M. Omran, E.T. Abdullah, Preparation and Characterization of Polyvinylpyrrolidone/Multi-walled Carbon Nanotubes Nanocomposite hybrid with Graphene, *Bas. J. Sci.*, 39(2021) 253-264, <https://basjsci.net/index.php/bsj/article/view/116>
- [19] H.M. Zidana, E.M. Abdelrazek, A. M. Abdelghany, Ahmed E.Tarabiah, Characterization and some physical studies of PVA/PVP filled with MWCNTs, *J J. Mater. Res. Technol.*, 8(2019)904-913, <https://doi.org/10.1016/j.jmrt.2018.04.023>.
- [20] L. Wang, L. Zhang, M. Tian, Improved polyvinylpyrrolidone (PVP)/graphite nanocomposites by solution compounding and spray drying,” *Polym. Adv. Technol.*, 23(2012)652–659, <https://doi.org/10.1002/pat.1940>.
- [21] W.S. Khan, R. Asmatulu, M. M. Eltabey, Electrical and Thermal Characterization of Electrospun PVP Nanocomposite Fibers, *J. Nanomater.*, 2013(2013)1-9, <https://doi.org/10.1155/2013/160931>.



- [22] E. M. Abdelrazek, A. M. Abdelghany, A. E. Tarabiah, H. M. Zidan, AC conductivity and dielectric characteristics of PVA/PVP nanocomposite filled with MWCNTs, J. Mater. Sci., Mater. Electron., 30(2019)15521–15533 <https://doi.org/10.1007/s10854-019-01929-2>

الخصائص المورفولوجية والكهربائية للبولي فينيل بيروليدون / الأنابيب النانوية الكربونية متعددة الجدران مع الجرافين

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المستخلص

تم استخدام طريقة الصب بالمحلول لإنشاء مركب نانوي بولي فينيل بيروليدون / (PVP) أنابيب نانوية كربونية متعددة الجدران (MWCNTs) مع الجرافين (Gr). تم استخدام تأثير المسح المجهر الإلكتروني (FESEM) والأشعة تحت الحمراء لمحول فورييه (FTIR) لتوصيف العينات. تظهر النتائج أن معلومات المركب النانوي ناجحة ، حيث يُظهر FTIR وجود قمم مميزة أولية تنتمي إلى مجموعات الاهتزاز التي تصف العينات المحضرة. كشفت صور FESEM أيضاً عن توزيع موحد للجرافين داخل المركب النانوي. PVP-MWCNT تزداد الموصلية الكهربائية للتيار المستمر للمركبات النانوية مع زيادة تركيز MWCNT ، والذي يرجع إلى التوصيل بالتتط.

