



Synthesis and Characterization of CNT/PVA Nanocomposites for Electrical, Thermal and Morphological Properties

Gulfam Nasar^{1*}, Uzma Khalil², Muhammad Saleem Khan³, Qaisar Nadeem⁴

¹ Department of Chemistry, Balochistan University of Information Technology, Engineering and Management Sciences, Quetta, Pakistan

² Jinnah College for Women, University of Peshawar, Pakistan

³ National Center of Excellence in Physical Chemistry, University of Peshawar, Pakistan

⁴ Department of Chemistry, University of Zurich, Winterthurerstr, 190, 8057 Zurich, Switzerland

ARTICLE INFO

ABSTRACT

Article History:

Received: February 15, 2022

Revised: April 12, 2022

Accepted: June 28, 2022

Available Online: June 29, 2022

Keywords:

PVC

Carbon nanotubes

Nanocomposites

Ionic conductivity

AC Impedance

TGA

SEM

The goal of the current work is to bring a helpful substance to nanoscience and nanotechnology that might be a "problem solver" for ion storage. Carbon nanotubes/ PVA nanocomposites were prepared in five concentrations in aqueous medium following film formation. The resulting nanocomposites were characterized using "AC Impedance Spectroscopy, Differential Thermal Analysis, Thermal Gravimetric Analysis / (TG/DTA) and Scanning Electron Microscopy (SEM)". Ionic conductivity of the nanocomposites was determined from impedance spectroscopy. CNT/PVA nanocomposites exhibited lower conductivity as compared with CNT or PVA separately. TG/DTA graphs exhibited a regular pattern, showing an increase in the thermal stability. Morphology of the prepared samples as shown by SEM reveals a favourable polymer-filler morphological arrangement at the interphase, which is suggestive of a favourable compatibility between the polymer and the filler substance.

OPEN ACCESS

© 2022 The Authors, Published by iRASD. This is an Open Access article under the Creative Common Attribution Non-Commercial 4.0

*Corresponding Author's Email: gulfam.nasar@buitms.edu.pk, gulfamnasar@gmail.com

1. Introduction

The discovery of numerous carbon nanostructures, metal nanoparticles, and other unique structures has spurred advancements in nanoscience and nanotechnology since the second half of the twentieth century (Kakani, 2004). Metal nanoparticles and carbon nanostructures have numerous applications in a variety of sectors thanks to their distinctive thermal, electrical, magnetic, and optical properties (Masciangioli & Zhang, 2003). These materials can be used individually or as distributed media in matrices, host materials, and polymer nanocomposites (Safadi, Andrews, & Grulke, 2002). For a variety of purposes, efforts are being undertaken to find the material that is best suited. Although nanoparticles and nanocomposites have provided solutions to many contemporary challenges (Nicolais & Carotenuto, 2005), there is still unmet demand in this area, leading to the creation and development of fresh materials every day. The current study is yet another trial to add to the valuable and modern material that will serve the scientists working in the cotemporary field.

2. Experimental

2.1. Chemicals Used

Poly vinyl alcohol (PVA) 125,000 g / mol, Nitric acid, Multi Walled Carbon Nano Tubes Cetyl Trimethyl Ammonium bromide 'CTAB', De-ionized water of Millipore grade was used as solvent.

2.2. Synthesis of CNT/PVA Nanocomposites

5 w/w % stock solutions of PVA and required reagents were made. The same were used to prepare reagent solutions for synthesis of nanocomposites (Sankar, Kumar, & Rao, 2004). The CNTs were functionalized, with constant stirring with water. The contents were transferred to a glass tube and were ultra-sonicated for two hours. 5 ml solution of 5 molar nitric acid was dripped into the contents and thus subsequent mix was subjected to refluxing process 12 hours at 120 °C. The functionalized CNTs were filtered and washed until pH 7 was obtained. The CNTs were suspended in de-ionized water with the help of CTAB whose 75 mg were dissolved in water before 10 mg CNTs were introduced to it. After dilution to 100 ml, ultra-sonication was performed for 8 hours at 60 °C (Laachachi et al., 2009).

To make CNT-PVA nanocomposites, the fractions of both the solutions were mixed in appropriate ratios using dilution formula. Magnetic stirring was carried out for 24 hours and films were grown in petri dishes. Appropriate sizes and shapes were obtained from the generated films for characterizing (Rajendran & Bama, 2010).

3. Characterization

The samples were subjected to the following characterization techniques.

3.1. Electrical Properties

"AC Impedance Analyzer PGSTAT 302, manufactured by Autolab, Netherland" was used to study electrical behavior of CNT-PVA nanocomposites (Baskaran, Selvasekarapandian, Kuwata, Kawamura, & Hattori, 2007). 1 square centimeter sample piece from each composition was subjected to a three-probe measuring system of AC Impedance analyzer (Ulaganathan, Pethaiah, & Rajendran, 2011). The third electrode is used as a reference electrode in addition to two working electrodes having area of its cross section $1 \times 10^{-4} \text{ cm}^2$. The measuring frequency was set 1 Hz–30 KHz, while 10 mV amplitude was used at room temperature.

3.2. Thermal Analysis

5-8 mg sample of each composition was analyzed for thermal properties using "Diamond TG/DTA machine manufactured by Perkin Elmer Instruments, USA" (Rajendran, Kesavan, Nithya, & Ulaganathan, 2012) with a uniform heating rate of 5 °C/minute from 30-600 °C (Rimez et al., 2008).

3.3. Morphological Analysis

"Scanning Electron Microscope SEM SJ-6490LVMA manufactured by JEOL, Germany" was used to characterize morphology and dispersion of the CNT within the polymer matrix (Kim & Kim, 2006). The appropriate sizes of the samples of polymer nanocomposites were gold-coated utilizing sputter coater machine before SEM analysis. For this purpose voltage of 5-20 kV was used while the resolution was kept from 500-100000X. The most suitable voltage and resolution was used to take micrographs of the CNT-PVA nanocomposites.

4. Results and Discussion

4.1. AC Impedance of PVA/ CNT Composites

CNT-PVA nanocomposites were characterized for electrical properties. A representative Nyquist plots is shown in figure 1. Semi-circular path exhibited by the CNT-PVA nanocomposite is attributed to the conducting region of the nanocomposite. CNTs being light-weight material exhibit low density and show a commendable degree of conductivity (Zhao et al., 2008). They exhibit anisometric behavior that is quite significant in transforming a transition between non-conducting to conducting behavior by the incorporation into a polymer matrix. The individual surface properties of the components of

the nanocomposite also play a major role in characterizing the electrical properties of the nanocomposite. Detention of PVA over the interfaces of CNTs also plays a role in defining the electrical conductivity of the nanocomposite. The conductive behavior of CNT-PVA nanocomposites is depicted from figure 2 that shows the circuit diagram of the prepared sample. The obtained results comply with previous findings (Nam et al., 2012). The current study focuses more on the lower concentrations of the CNT unlike the earlier reported work, focused on higher concentrations of CNT (Khan, Shakoor, & Nisar, 2010; Wang & Qiu, 2011). This aspect marks this study significant in understanding in terms of greater compatibility and economic feasibility.

In figure 2, in order to obtain a good fit, an additional circuit component; Warburg impedances is added (Khan et al., 2010). The Warburg element can be defined as "a common diffusion circuit element that is used to model or simulate semi-infinite linear diffusion, that is, unobstructed flow to a large planar electrode." The "diffusion-limited processes" linked to the ionic conductivity of the CNT-PVA nanocomposite is simulated using this component (Zamri, Zein, Abdullah, & Basir, 2011).

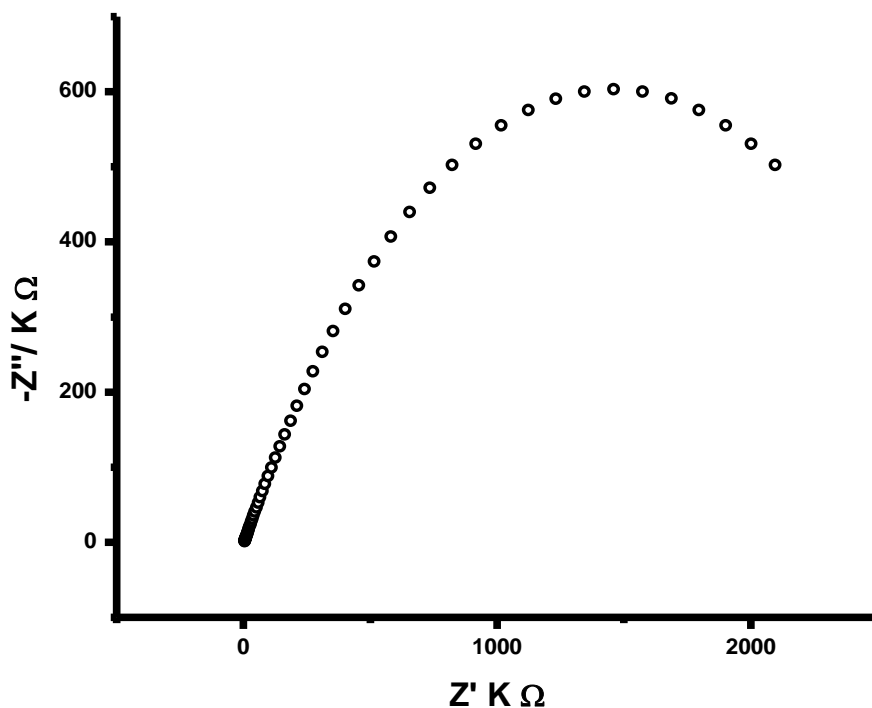


Figure 1: AC Impedance Spectrum of CNT-PVA Nanocomposite

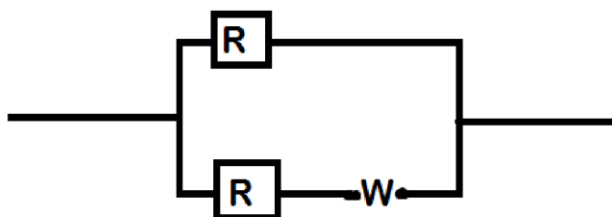


Figure 2: Circuit diagram of the CNT-PVA nanocomposite

Bulk resistance (R_b) of the nanocomposites was figured out from the frequency of a high range of Nyquist plot (Abraham, Alamgir, & Hoffman, 1995; Bhattacharyya, Salvetat, & Saboungi, 2006). One can calculate ionic conductivity (σ) of the composite from Eq. (1).

$$\sigma = l / AR_b \quad (1)$$

'A' shows the area of electrode (1 cm²) and 'l' depicts thickness of the CNT-PVA nanocomposite sample film (0.001 cm). The values calculated through Eq (1), are shown in Table 1. The same results are displayed in graphical form in figure 3, indicating that the ionic conductivity increases with an increasing amount of CNT in the nanocomposite. This increase is attributed to mobility changes and carrier concentration of the CNT in the matrix of PVA. Due to the decrease in the inter-particulate distances, this change is enhanced further in the higher concentrations of CNT. a decreased distance between the particles ensures enhanced hopping activity resulting in overall ionic conductivity augmentation (Rajendran, Bama, & Prabhu, 2010).

Table 1

Bulk Resistance and Ionic Conductivity of CNT-PVA Nanocomposites

No.	Bulk Resistance R_b/Ω	Ionic Conductivity $\sigma/S\text{ cm}^{-1}$
1	4160.10979	2.4E-06
2	4064.04392	2.46E-06
3	3760.06404	2.66E-06
4	3319.64776	3.01E-06
5	2099.26807	4.76E-06

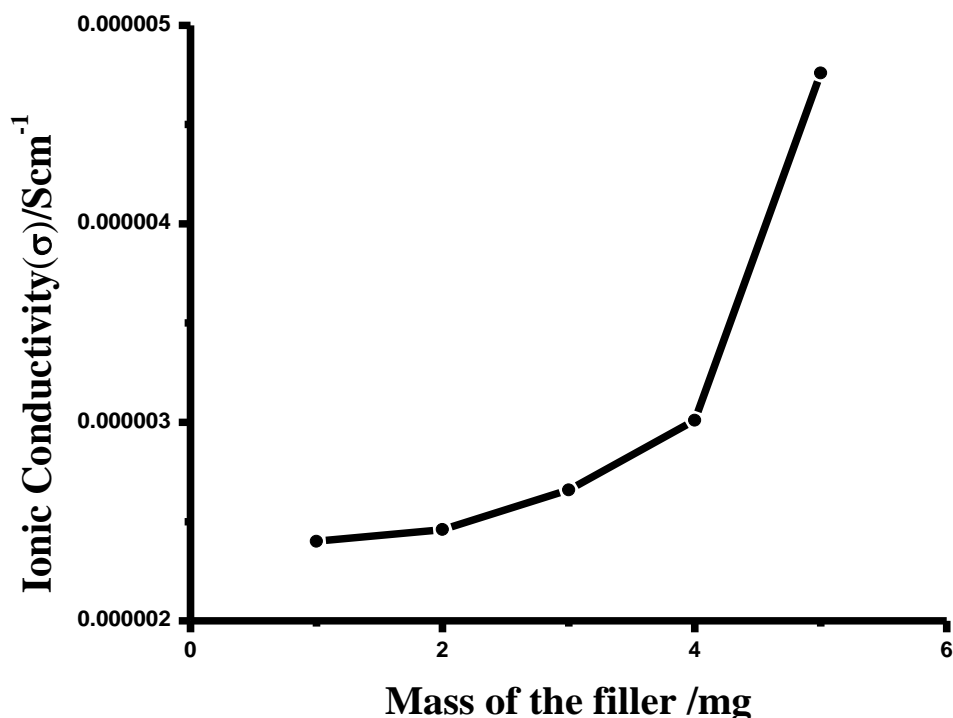


Figure 3: Ionic Conductivity of the CNT-PVA Nanocomposite

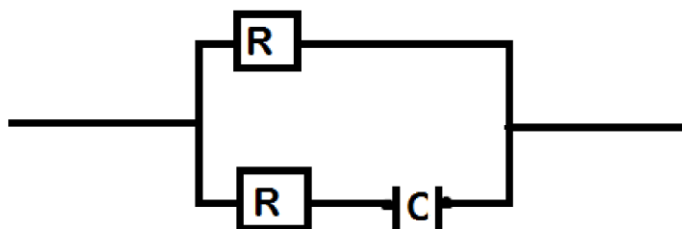


Figure 4: Circuit Diagram of the Developed Composites

4.2. Thermal Analysis of PVA /CNT Composites

Figure 5 shows a TGA thermogram of the generated samples of PVA/CNT nanocomposites showing weight loss as a temperature-function. PVA decomposes in two phases and is stable up to 265°C (Ma, Tang, & Kim, 2008). Around 350°C is the temperature at which the PVA side chain decomposes, while 450°C is the temperature at which the PVA backbone degrades (Nasar, Khan, & Khalil, 2010; Sriamornsak & Kennedy, 2006).

According to the TGA for figures 87–89, weight loss for PVA/CNT 1 mg, PVA/CNT 3 mg, and PVA/CNT 5 mg happened in three stages. First step weight loss was from 11% to 14%, attributed to vaporization of the water content. Second phase of loss in mass was 53 to 56 %, due to combustion, up to 352°C. A weight loss of around 20% occurred mainly due to decomposition of side chains and degradation of PVA to up to 600°C. DTA also supports the results shown in figures 91-96.

Figure 5 compares TGA, and Figure 6 displays DTA for various compositions. Results indicate that the thermal stability somewhat increases as CNT concentration rises from 1 mg to 5 mg. The conclusion is also supported by a comparison of the degradation temperatures for various compositions.

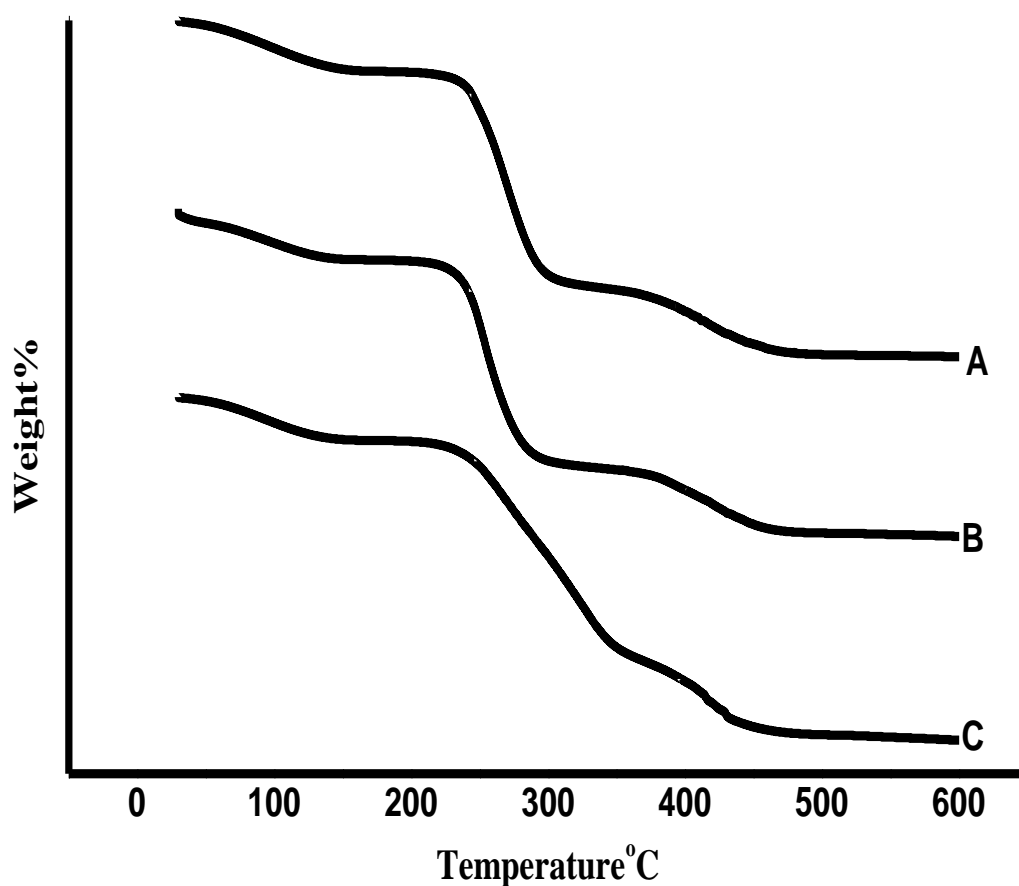


Figure 5: TGA of A: PVA/CNT 1mg, B: PVA/CNT 3mg, C: PVA/CNT 5mg

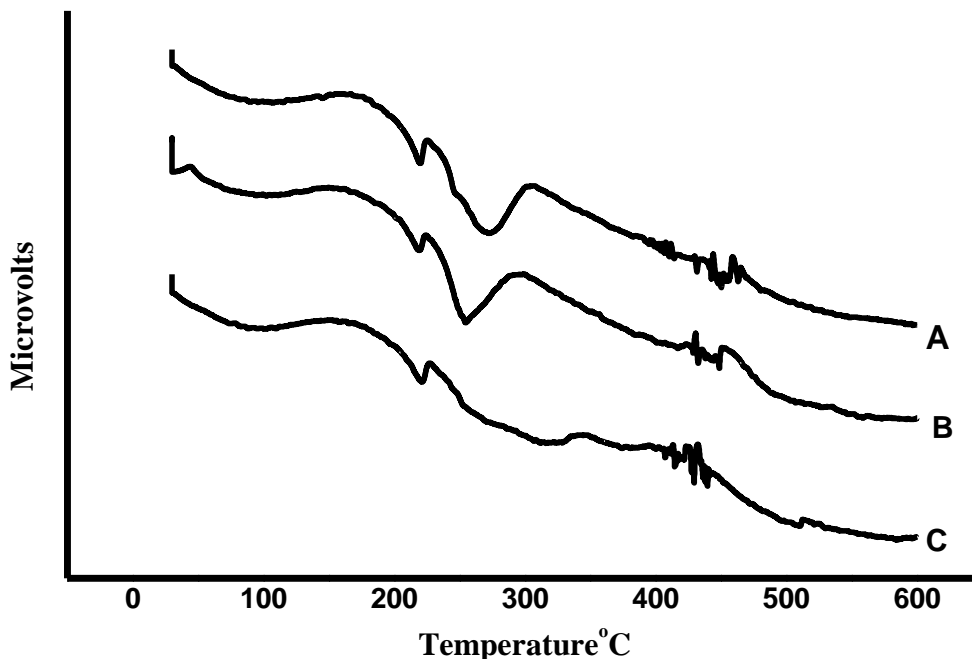


Figure 6: DTA of A: Pure PVA/CNT 1mg, B: Pure PVA/CNT 3mg, C: Pure PVA/CNT 5mg

4.3. Scanning Electron Microscopy

Samples of various compositions of CNT/ PVA nanocomposite were analyzed for assessing the morphology of nanocomposites between 5 kV and 20 kV. Figure 164 displays a network of functionalized CNTs with uniform thickness, while figure 7 shows the CNT micrograph at X37000. The particular scan of the particular conductivity. It is noteworthy that nearly all CNTs have the same diameter, which is between 30 and 45 nm.

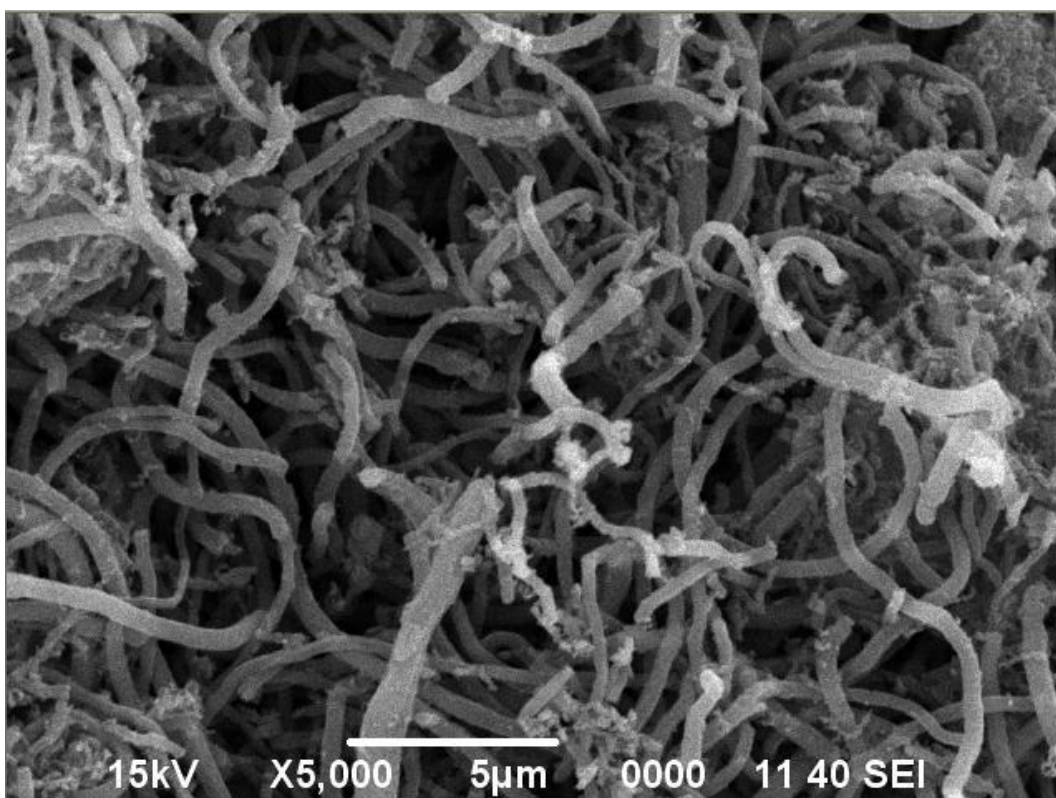


Figure 7: SEM Image of the Carbon Nanotube, Showing a Mesh/ Network of CNT

5. Conclusion

1. PVA/ CNTs nanocomposites with five different concentrations of nanocomposites were synthesized in solution form which were converted to films.
2. Thermogravimetric/Differential Thermal Analysis (TG/DTA), AC Impedance Spectroscopy, and scanning electron microscopy were used to characterise the nanoparticles in detail (SEM).
3. The fillers created homogenous nanocomposites by being evenly distributed throughout the matrix. Under the microscope, the filler is distributed uniformly throughout the matrix according to the surface morphology.
4. Using SEM, the size of the nanoparticles was examined, and it was observed that the diameter of CNT ranged from 30 to 50 nm.
5. Films displayed a highly smooth surface topography and uniform morphology. However, the matrix's embedded particles could be seen and their sizes were determined.
6. It was discovered that the ionic conductivity of all the produced nanocomposites ranged from 10^{-6} to 10^{-4} Scm⁻¹. Ionic conductivity varied in all cases depending on the filler content, from low to high. The lowest conductivity was observed to be in PVA/CNT nanocomposites.
7. According to TG/DTA, the w/w percent of the filler tends to rise with the increase in thermal stability in all produced nanocomposites.

References

- Abraham, K., Alamgir, M., & Hoffman, D. (1995). Polymer electrolytes reinforced by Celgard® membranes. *Journal of the Electrochemical Society*, 142(3), 683.
- Baskaran, R., Selvasekarapandian, S., Kuwata, N., Kawamura, J., & Hattori, T. (2007). Structure, thermal and transport properties of PVAc-LiClO₄ solid polymer electrolytes. *Journal of Physics and Chemistry of Solids*, 68(3), 407-412.
- Bhattacharyya, S., Salvétat, J.-P., & Saboungi, M.-L. (2006). Reinforcement of semicrystalline polymers with collagen-modified single walled carbon nanotubes. *Applied physics letters*, 88(23), 233119.
- Kakani, S. (2004). *Material science*: New Age International (P) Ltd., Publishers.
- Khan, M. S., Shakoor, A., & Nisar, J. (2010). Conductance study of poly (ethylene oxide)- and poly (propylene oxide)-based polyelectrolytes. *Ionics*, 16(6), 539-542.
- Kim, S., & Kim, H.-J. (2006). Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on the adhesion for engineered flooring in under heating system; ONDOL. *Thermochimica Acta*, 444(2), 134-140.
- Laachachi, A., Ruch, D., Addiego, F., Ferriol, M., Cochez, M., & Cuesta, J.-M. L. (2009). Effect of ZnO and organo-modified montmorillonite on thermal degradation of poly (methyl methacrylate) nanocomposites. *Polymer Degradation and Stability*, 94(4), 670-678.
- Ma, P. C., Tang, B. Z., & Kim, J.-K. (2008). Effect of CNT decoration with silver nanoparticles on electrical conductivity of CNT-polymer composites. *Carbon*, 46(11), 1497-1505.
- Masciangioli, T., & Zhang, W.-X. (2003). Peer reviewed: environmental technologies at the nanoscale. In: ACS Publications.
- Nam, D. H., Cha, S. I., Lim, B. K., Park, H. M., Han, D. S., & Hong, S. H. (2012). Synergistic strengthening by load transfer mechanism and grain refinement of CNT/Al-Cu composites. *Carbon*, 50(7), 2417-2423.
- Nasar, G., Khan, M. S., & Khalil, U. (2010). *A study on structural, mechanical and thermal properties of polymer composites of poly (vinyl alcohol) with inorganic material*. Paper presented at the Macromolecular symposia.
- Nicolais, L., & Carotenuto, G. (2005). *Metal-polymer nanocomposites*/edited by Luigi Nicolais, Gianfranco Carotenuto.
- Rajendran, S., & Bama, V. S. (2010). A study on the effect of various plasticizers in poly (vinyl acetate)-poly (methyl methacrylate) based gel electrolytes. *Journal of non-crystalline solids*, 356(50-51), 2764-2768.
- Rajendran, S., Bama, V. S., & Prabhu, M. R. (2010). Effect of lithium salt concentration in PVAc/PMMA-based gel polymer electrolytes. *Ionics*, 16(1), 27-32.

- Rajendran, S., Kesavan, K., Nithya, R., & Ulaganathan, M. (2012). Transport, structural and thermal studies on nanocomposite polymer blend electrolytes for Li-ion battery applications. *Current applied physics*, 12(3), 789-793.
- Rimez, B., Rahier, H., Van Assche, G., Artoos, T., Biesemans, M., & Van Mele, B. (2008). The thermal degradation of poly (vinyl acetate) and poly (ethylene-co-vinyl acetate), Part I: Experimental study of the degradation mechanism. *Polymer Degradation and Stability*, 93(4), 800-810.
- Safadi, B., Andrews, R., & Grulke, E. (2002). Multiwalled carbon nanotube polymer composites: synthesis and characterization of thin films. *Journal of applied polymer science*, 84(14), 2660-2669.
- Sankar, V., Kumar, T. S., & Rao, K. P. (2004). Preparation, characterisation and fabrication of intraocular lens from photo initiated polymerised poly (methyl methacrylate). *Trends in Biomaterials and Artificial Organs*, 17(2), 24-31.
- Sriamornsak, P., & Kennedy, R. A. (2006). A novel gel formation method, microstructure and mechanical properties of calcium polysaccharide gel films. *International journal of pharmaceutics*, 323(1-2), 72-80.
- Ulaganathan, M., Pethaiah, S. S., & Rajendran, S. (2011). Li-ion conduction in PVAc based polymer blend electrolytes for lithium battery applications. *Materials Chemistry and Physics*, 129(1-2), 471-476.
- Wang, H., & Qiu, Z. (2011). Crystallization behaviors of biodegradable poly (l-lactic acid)/graphene oxide nanocomposites from the amorphous state. *Thermochimica Acta*, 526(1-2), 229-236.
- Zamri, M., Zein, S. S., Abdullah, A. Z., & Basir, N. I. (2011). Improved electrical conductivity of polyvinyl alcohol/multiwalled carbon nanotube nanofibre composite films with MnO₂ as filler synthesised using the electrospinning process. *International Journal of Engineering & Technology IJET-IJENS*, 11(06).
- Zhao, B., Wang, J., Li, Z., Liu, P., Chen, D., & Zhang, Y. (2008). Mechanical strength improvement of polypropylene threads modified by PVA/CNT composite coatings. *Materials Letters*, 62(28), 4380-4382.