International Journal of Engineering &Technology, 7 (3.12) (2018) 1025 -1029

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Development of Conductive Nanocomposite for Sensing Application

Brijesh Prasad[1], Varij Panwar[2*], Mayank Chaturvedi[3], Vikash Rathi[4], F.S. Gill[5], Kapil Sharma[6], Pravin.P.Patil[7]

Graphic Era (Deemed to be University), Dehradun-248002, Uttarakhand, INDIA
**Corresponding author E-mail: [1]prasasdbrijesh10@gmail.com , [2]varijpanwarcertain@gmail.com*

Abstract

Carbonaceous compounds being conductive in nature have proved themselves as the best conductive network assembly material with Poly (vinylidene fluoride) (PVDF) polymer matrix which forms dielectric medium. Carbon based compounds are conductive in nature and are being used to form conductive channels for the flow of charge for the application of health as soft electronic devices and smart flexible conducting thin films in the form of sensors and actuators. Carbon nano fibers (CNF) play role of conductive filler to form conductive networks for the flow of charge in the polymer matrix. The interesting thing about CNF is its tailorable concentration. It influences the mechanical and electrical properties with different weight percent. In the present study solvent casting technique is used for the development of composite membrane, which is easy to fabricate and less costly. An increase in CNF content leads to deterioration of young's modulus in comparison with pure PVDF, while with the infiltration of CNF in different quantities increases toughness and overall mechanical strength of the polymer composite of PVDF-CNF. CNF helped in increasing the electrical conductivity of the samples by entrapping in between the matrix and helping in bridge formation for the charge flow. The obtained conductive membrane showed low resistance, good electrical properties and high conductivity. The conductive film can be utilized as a conductive medium as it was able to glow the LED bulb at very low voltage of 2 V with drop of 1.8 V.

Keywords- *conductive membrane; dielectric medium; conductive fillers; flexible conductive film*

1. Introduction

Smart materials with insulator as polymer and carbon based nano composites as conductive materials are vastly being studied by the researchers. There is a huge demand of Polymer matrix with conductive filler to be applied in the field of electronic devices and smart materials. This has been attributed due to the high mechanical properties, chemical resistant, enhanced thermal resistance to flammability with dimensional ability and durability of the smart materials [1]. PVDF is a promising polymer material for the transduction application as it shows piezoelectric behavior to transform the mechanical energy to electrical and vice versa [2]. PVDF shows very good mechanical strength, chemical resistant, thermal stability and durability properties, and easily binding ability with different organic and inorganic compounds [2, 3, 4].
It is a semi-crystalline polymer material having five crystalline phases among which alpha phase and beta phase are highly active for electrical transformation. Material Carbon has been used in different forms such as graphene and its oxides [5,6], single-walled carbon nanohorns (SWCNH), single wall carbon nano tubes (SWCNT), multi wall carbon nano tubes MWCNT, carbon black and different carbon nano forms [7-14]. Among all carbon nano fibers have been in high demand because of their high aspect ratio to weight, ease of mixing with any polymer, ease of fabrication and most effectively low cost [15]. Different studies have been done on the effect of addition of conductive filler to the dielectric medium.
In which the drawback was not able to define the threshold point till where the maximum concentration of the filler show change and after that there is no change in the conductivity by adding more of it [16]. Among all electromechanical behavior shown by the PVDF-CNF composite have been high in demand for the application of sensors and actuators in various electronic devices. But the main focus has been kept on the intrinsic behavioral properties of the carbonaceous nanofillers having high aspect ratio and good electrical properties. CNF shows very good mechanical properties in case of load distribution at the time of deformation to a certain limit. Aiding of CNF in PVDF matrix help to increase the toughness of the composite but there is decrease in the young's modulus in comparison to pure PVDF. CNF is being used to increase the mechanical properties but with that it enhances the ion conductivity or electrical property of the composite matrix with low percolation threshold [17, 18]. The major property of the composite matrix depend on the polymer, conductive filler, processing method to get uniform distribution and aggregation of compounds and the alignment of the conductive network to get the desired output [19]. Carbon nanofibers show large variations in resistance on the deformation and show large strain resistivity due to the change in the conducting channel path till the point of separation causing the hopping and tunneling effect sensed by the nearby fillers particles [20, 21]. Different strategies have been implemented by researchers to study the behavior of CNF in the polymer matrix to detect sensing signals of pressure sensor, strain sensor [22], resistive sensor, gas sensor, thermal sensor, light sensor and many others [23].
Metal strain gauges show interesting properties but limits in the flexibility and cost [24]. Whereas the polymer sensors show high

flexibility with good mechanical strength and low cost with ease of fabrication. All these qualities make polymer as a promising material for the application for different types of sensors [25] for the human health applications [26]. Previous researchers have used different carbon fillers with the PVDF, such as carbon nano tubes and graphene but very less work has been done with CNF to the best of our knowledge to enhance the mechanical properties of the carbon based polymer composite.

In the present manuscript we have tried infiltrate the CNF in the PVDF matrix to increase the mechanical strength and the electron conductivity of the material by the percentage of carbon nano fiber in the PVDF polymer matrix. Solvent casting technique has been used in the study as its simple with ease of fabrication and low cost method. The obtained composite membrane with the CNF showed improved mechanical strength in comparison to pure PVDF and PVDF-CNF composite with high electron conductivity.

2. Materials and Synthesis of Polymer Membrane

The materials used for the development of polymer membrane were purchased from the Merck's USA. PVDF with density of 1.74 g ml-1 was purchased by the trade name of 182702 having molecular weight of 534,000.00. CNF having density of 1.90 g ml-1 with average diameter of 130 nm, having fiber length 20µm - 200µm was used to increase the electron conductivity. N, N dimethylformmamide (DMF) as a solvent with trade name 57457 having molecular weight of 236.29 was purchased from sigma Aldrich USA.

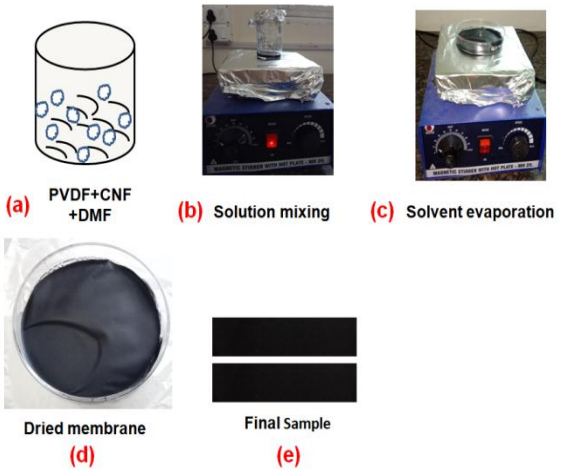

Fig. 1: Development of PVDF-CNF-IL polymer nanocompositemembrane

The polymer flexible thin membrane was synthesized with the solution mixing and casting technique. For that firstly the solute PVDF and CNF was weighed with the help of digital weighing machine purchased from conetech India Pvt. Ltd. Total 10 wt% solution was made by adding 1 wt % of solute in 9 wt % of solvent DMF to form the final mixture shown in figure 1 (a). This mixture was allowed to heat at the temperature of 50°C for 4 hours with continuous stirring with the help of magnetic bead on the magnetic stirrer with hot plate shown in figure 1(b) supplied by Glassco India Pvt. Ltd. After mixing, the transparent PVDF transformed to homogeneous black dense colour mixture because of the CNF content. The obtained mixture was poured in the glass Petridis as shown in figure 1 (c) having 80 mm diameter and was dried for next 3 hours at a constant temperature of 80°C to evaporate the solvent (DMF) completely from the solution. After the solvent evaporation the film was completely dry with no solvent percentage. The dried film in the petridish was allowed to cool as shown in figure 1(d) at room temperature for 30 minutes. Finally the dried membrane was peeled off from the glass petridish with the help of surgical knife. The final membrane was cut into different shapes Shown in figure 1(e) for characterization.

3. Results and Discussion

MIRA3b TESCAN, USA Field emission scanning electron microscopy was used to characterize the microstructure of the membrane. To do that the samples were first dipped in the liquid nitrogen for 5 min and fractured to obtain the abrupt surfaces on the corners of the breaking point. The Obtained corners were gold sputter with the sputtering machine for clear visibility. After that the SEM micrographs were taken at different resolutions. SEM images were obtained at different resolution and the best configuration are reported and shown in figure 2. Where figure 2(a) shows the SEM images of the pure PVDF/CNF (95/5) (b) shows the composite membrane of PVDF/CNF (85/15) and 2(c) shows the composite membrane of PVDF/CNF (80/20). It can be clearly observed from the SEM images that the CNF is clearly visible in the PVDF polymer matrix in the form of cylindrical tubes coming out from the fractured surface after the samples were dipped in the liquid nitrogen followed by fracturing. When IL was added to the PVDF-CNF matrix empty spaces was generated in the form of holes shown in figure 2(c), (d).

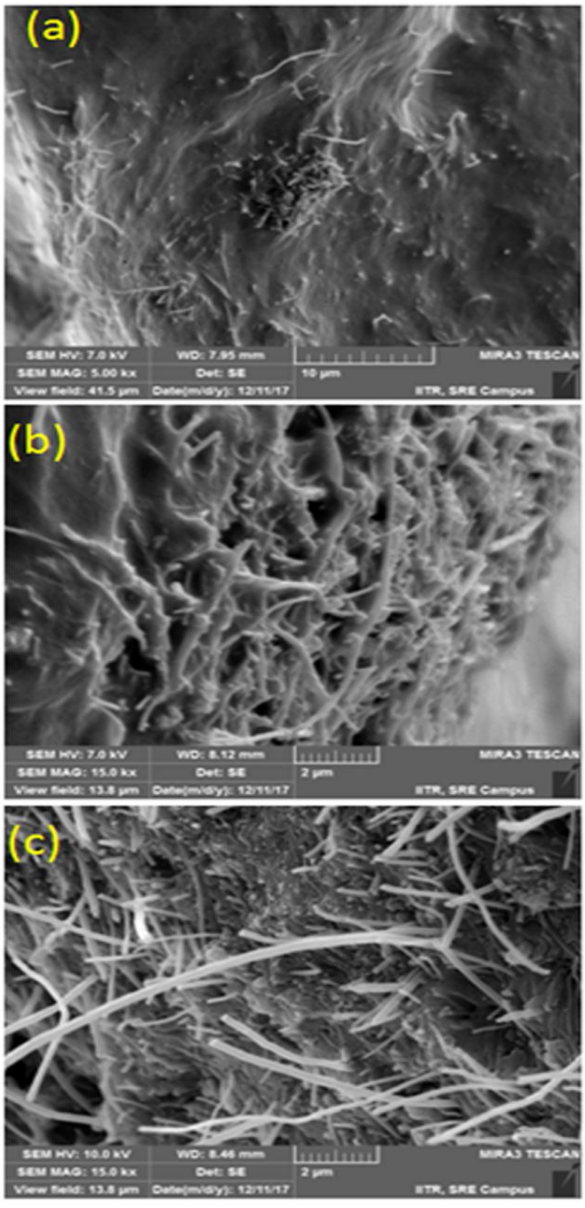

Fig. 2: SEM images of PVDF-CNF polymer composite

The electrical properties of the samples were measured with the help of impedance spectroscopy. For that E4900A impedance analyzer supplied by the Keysight technologies made in Germany was used working under the frequency range of 20Hz to 1MHz. The analysis was done using the stainless steel two probe parallel plate 16451B models. The sample membranes were sandwiched in between the parallel plates having the diameter of 2 mm. The samples were made in circular shape of 2 mm diameter to calculate the pure resistance of the membrane. The resistance of the samples was calculated by plotting Nyquist plots in between the real and imaginary parts of the impedance with respect to frequency.

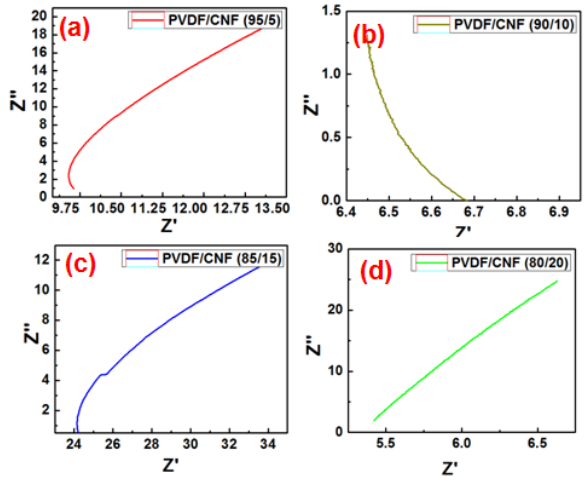

Fig. 3: Pure resistance of the polymer nano-composites

Figure 3 show the graph obtained by the impedance analyzer showing the pure resistance of the polymer nano-composites. The obtained resistance was used in the equation 1 to calculate the electron conductivity of the newly developed polymer composite.

$$\sigma = \frac{L}{A \times R} \quad (1)$$

The mechanical properties of the samples were carried using Instron 3300 Series universal test machine. Three samples of each PVDF-CNF compositions were taken for the tensile test. The sample sizes were prepared according to ASTM code D790. The samples were made in rectangular shape where the size was kept 30 mm x 0.5 mm length having support span length of 10 mm with 10 mm gauge length. The testing speed of the sample was set at 10 mm/min. The samples with best results are reported in the present work. It was observed during the study that the PVDF-CNF (80/20) samples showed very good young's modulus and high toughness in comparison to PVDF-CNF (95/5) samples.

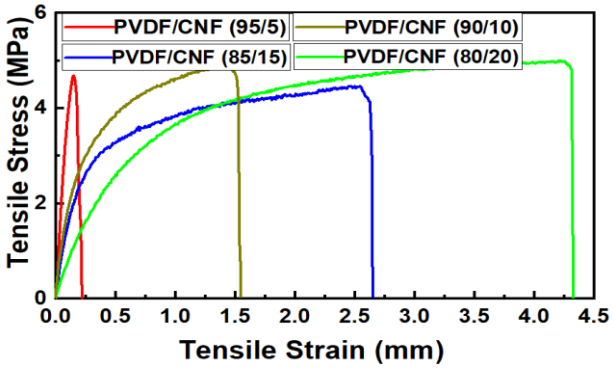

Fig. 4: Tensile stress strain curve for PVDF-CNF samples

It was seen that the holes generated by the infiltration of CNF shown in the SEM images in figure 2(c) played a crucial role in increasing the mechanical strength of the polymer composite. The holes allowed space for the molecules to stretch along the direction of force applied. Even the CNF was very much helpful in load distribution from PVDF matrix to CNF fibers which helped in the streaching of the polymer membrane and made it more flexible. It is clear from the figure 4that the aid of CNF helped in increasing the yield strain of the samples in comparison to pure PVDF–CNF. There was increase in the elongation before brake point for the samples. Figure 3 clearly shows that the samples infiltrated with CNF showed very good yield strength in respect to the PVDF samples. Other major thing showed the high elongation of the PVDF-CNF (90/10), (85/5), (80/20) samples which increased from 1.5 mm to 4.4 mm which was higher to the 0.4 of the PVDF-CNF (95/5) sample. Obtained values for tensile strength and young's modulus are shown in table 1. There was large increase in the area under the curve for the PVDF-CNF-IL which proved of increase in toughness with the aid of CNF in respect of PVDF. This also improves the flexibility of the membrane. There was large change in the yield platue as it was sharp in case of PVDF-CNF while the upper yield platue was seen broadened as more energy could be stored before breaking.

Table 1: mechanical properties of the PVDF- CNF samples

Composition	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at brake point (mm)
PVDF/CNF (95/5)	4.3 ± 0.2	40 ± 0.5	0.43327 ± 2
PVDF-CNF (90/10)	4.45 ± 0.2	10 ± 0.5	2.94526 ± 2
PVDF-CNF (85/15)	3.85 ± 0.2	6.9 ± 0.5	4.8309 ± 2
PVDF-CNF (80/20)	4.98 ± 0.2	7.85 ± 0.5	6.39141 ± 2

The samples of PVDF-CNF with different compositions were bent to form semicircle and the change in values of resistance and voltage noted with the help of digital multimeter and obtained values are shown in table 2. The resistance for electron conductivity was obtained from impedance analyzer and further after calculating by equation 1 the obtained results are shown in table 1 where T defines the thickness obtained by Yokohama digital micrometer, A defines the area of cross-section, R defines the initial resistance before bending, R0 defines the resistance obtained after bending, DR shows the change in resistance, RI shows the change in resistance obtained by impedance analyzer obtained from the Nyquist plots, s define the electron conductivity of the sample, V defines the resistance before bending, Vo defines the resistance after bending, D V shows the change in voltage of the samples. It is clear from the table that there is change in resistance on bending the membrane therefore there is lot of possibility of making the samples in use of for resistive sensor. The sensing voltage is very much helpful for the application of different sensors.

Table 2: Parameters obtained on bending of samples to without bending

Sample name	T (cm)	A $(cm)^2$	Δ R (Ω)	R_I (Ω)	σ (S/cm)	ΔV (V)
PVDF/CNF (95/5)	0.0026	3.14	334.4	6.25	2E-05	0.197
PVDF-CNF (90/10)	0.0022	3.14	419.8	21.03	3E-05	0.045
PVDF-CNF (85/15)	0.0028	3.14	620	9.59	9E-05	0.0049
PVDF-CNF (80/20)	0.0015	3.14	892	9.6	5E-05	0.112

The sensing performance of the PVDF/CNF/IL conductive membrane was investigated with the help of relative resistance change delta Ro/R with respect to the uniaxial strain. With the increase in relative resistance there is increase in strain. Therefore the sensitivity which is defined as the ratio of relative resistance to the strain and shown below by the formula in equation 2. The change in resistance of samples was measured with the help of digital multimeter while performing the test simultaneously. The

values for Δ R/R of the samples were measured to obtain the graph with the error bar. For the sensitivity change of the relative resistance, the evaluation of gauge factor was done by gauge factor equation shown by equation 2.

$$G_f = \frac{\Delta R}{\varepsilon \times R} \quad (2)$$

Where Gf is the gauge factor, ΔR is the change in resistance, ε is the applied strain and R is the original resistance before loading. The test was performed with the loading time 120 s and unloading or relaxation time of 120 s. CNF played a crucial role in increasing the tensile strength with increase in toughness of the sample but there was decrease in the young's modulus of PVDF-CNF (80/20) samples in comparison to other PVDF-CNF samples. It showed that the deformation of CNF polymers also contributed in enhancing the resistive sensitivity of the composite polymers with the aid of CNF. The yield strain for PVDF-CNF (95/5) sample was near by 2.5% while with the PVDF-CNF (80/20) it increased to 53%. It is remarkably very high in comparison to base samples for the cyclic loading conditions. The gauge factor also increased with the increase in change of relative resistance. It revealed that the higher the value of gauge factor higher will be the piezo-resistive sensitivity. This increase in piezo sensitivity occurred due increase of tunneling effect till the separation point by streaching of the composite membrane as a result the distance in between the fillers increased. Evaluating the mechanical strain with the change in resistance showed that there is increase in the value of ΔR/R with the increase of strain till the yield point. The composite filled with CNF in the PVDF matrix showed high sensitivity and high strain ranges. All these results show that CNF can play a major role in enhancing the piezoresistive properties and the mechanical strength by the increase of toughness. The durability and stability of the samples can be achieved by controlling the structure of the composite. It can be achieved by uniform homogeneous dispersion of the conductive fillers in the polymer matrix so proper channels can obtained for the charge flow.

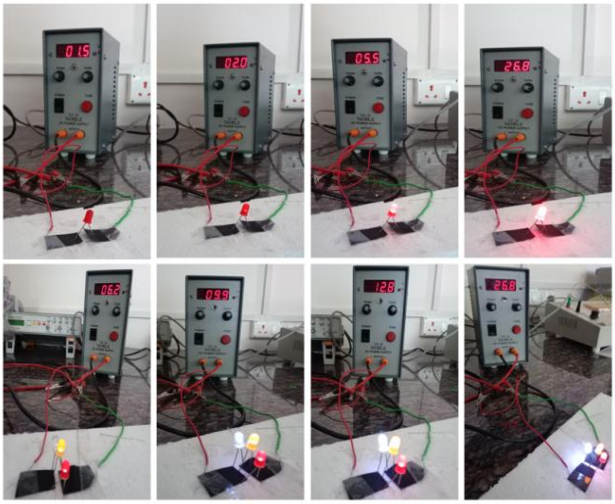

Fig. 5: Glowing of led with the composite membrane as conductive channel

For the accessing of conductive electrical properties of the PVDF/CNF composite a rectangular shape circuit with the LED bulbs as indicator, conductive film as the connecting channel in series was fabricated and is shown in figure 5. The circuit shown is connected to an external voltage source of 12 V. It can clearly be seen from the figure that with the application of external voltage to the circuit the LED starts glowing and with the change in voltage there is variation in the intensity of glowing of the LED in without any mechanical deformation of the conductive film. The supplied voltage was changed regularly at different volts as shown in figure 5. It was seen during the study that with an increase in the voltage, the glow of LED also increased without any LED failure.

4. Conclusion

In the present manuscript we developed a new carbon based conductive polymer composite with the help of CNF as conductive fillers, PVDF as the binding insulated matrix as the interface linker. Infiltration of CNF showed increased electrical properties and enhanced the mechanical properties significantly by increasing the toughness of the newly developed polymer composite material. The mechanical strength can be tailored with the change in weight percentage of the CNF and similarly there is change in the electrical properties with the variation of the conductive filler element. The developed polymer composite membrane also worked as strain sensor, as the change in resistance on the application of bending force can be clearly observed. The conductive polymer composite membrane can be further used as replacement of metal wire for the conduction purpose or can be used in device for light weight with complex shapes. This could be very much helpful in developing human health related electronic devices such as artificial arm movement device where the force brings change in the resistance of the material. The newly developed membrane also exhibited considerable flexibility and durability.

5. Acknowledgments

This work was supported by the Science and Engineering Research Board, File No.-ECR/2016/001113 and Graphic Era deemed to be University, Dehradun.

References

[1] Zulfli, N. M., Bakar, A. A., & Chow, W. S. (2013). Mechanical and water absorption behaviors of carbon nanotube reinforced epoxy/glass fiber laminates. Journal of Reinforced Plastics and Composites, 32(22), 1715-1721.

[2] Zhai, T., Lu, X., Wang, F., Xia, H., & Tong, Y. (2016). MnO 2 nanomaterials for flexible supercapacitors: performance enhancement via intrinsic and extrinsic modification. Nanoscale Horizons, 1(2), 109-124.

[3] Li, N., Yang, G., Sun, Y., Song, H., Cui, H., Yang, G., & Wang, C. (2015). Free-standing and transparent graphene membrane of polyhedron box-shaped basic building units directly grown using a nacl template for flexible transparent and stretchable solid-state supercapacitors. Nano letters, 15(5), 3195-3203.

[4] Eswaraiah, V., Balasubramaniam, K., & Ramaprabhu, S. (2011). Functionalized graphene reinforced thermoplastic nanocomposites as strain sensors in structural health monitoring. Journal of Materials Chemistry, 21(34), 12626-12628.

[5] Jiménez, P., Maser, W. K., Castell, P., Martínez, M. T., & Benito, A. M. (2009). Nanofibrilar polyaniline: Direct route to carbon nanotube water dispersions of high concentration. Macromolecular rapid communications, 30(6), 418-422.

[6] Spain, Ian L. "The electronic properties of graphite." Chemistry and Physics of Carbon 8 (1973): 87-94.

[7] Mikhaylova, A. A., Tusseeva, E. K., Mayorova, N. A., Rychagov, A. Y., Volfkovich, Y. M., Krestinin, A. V., & Khazova, O. A. (2011). Single-walled carbon nanotubes and their composites with polyaniline. Structure, catalytic and capacitive properties as applied to fuel cells and supercapacitors. Electrochimica Acta, 56(10), 3656-3665.

[8] Zhou, Y., Qin, Z. Y., Li, L., Zhang, Y., Wei, Y. L., Wang, L. F., & Zhu, M. F. (2010). Polyaniline/multi-walled carbon nanotube composites with core–shell structures as supercapacitor electrode materials. Electrochimica Acta, 55(12), 3904-3908.

[9] Li, L., Qin, Z. Y., Liang, X., Fan, Q. Q., Lu, Y. Q., Wu, W. H., & Zhu, M. F. (2009). Facile fabrication of uniform core− shell structured carbon nanotube− polyaniline nanocomposites. The Journal of Physical Chemistry C, 113(14), 5502-5507.

[10] Ginic-Markovic, M., Matisons, J. G., Cervini, R., Simon, G. P., & Fredericks, P. M. (2006). Synthesis of new polyaniline/nanotube composites using ultrasonically initiated emulsion polymerization. Chemistry of Materials, 18(26), 6258-6265.
[11] Jiménez, P., Maser, W. K., Castell, P., Martínez, M. T., & Benito, A. M. (2009). Nanofibrilar polyaniline: Direct route to carbon nanotube water dispersions of high concentration. Macromolecular rapid communications, 30(6), 418-422.
[12] Gao, B., Fu, Q., Su, L., Yuan, C., & Zhang, X. (2010). Preparation and electrochemical properties of polyaniline doped with benzenesulfonic functionalized multi-walled carbon nanotubes. Electrochimica Acta, 55(7), 2311-2318.
[13] Jiménez, P., Castell, P., Sainz, R., Ansón, A., Martínez, M. T., Benito, A. M., & Maser, W. K. (2010). Carbon nanotube effect on polyaniline morphology in water dispersible composites. The Journal of Physical Chemistry B, 114(4), 1579-1585.
[14] Kudo, H., Sawada, T., Kazawa, E., Yoshida, H., Iwasaki, Y., & Mitsubayashi, K. (2006). A flexible and wearable glucose sensor based on functional polymers with Soft-MEMS techniques. Biosensors and Bioelectronics, 22(4), 558-562.
[15] Fidelus, J. D., Wiesel, E., Gojny, F. H., Schulte, K., & Wagner, H. D. (2005). Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites. Composites Part A: Applied Science and Manufacturing, 36(11), 1555-1561.
[16] Wang, P., Geng, S., & Ding, T. (2010). Effects of carboxyl radical on electrical resistance of multi-walled carbon nanotube filled silicone rubber composite under pressure. Composites Science and Technology, 70(10), 1571-1573.
[17] Costa, P., Silva, J., Sencadas, V., Costa, C. M., Van Hattum, F. W. J., Rocha, J. G., & Lanceros-Méndez, S. (2009). The effect of fibre concentration on the α to β-phase transformation, degree of crystallinity and electrical properties of vapour grown carbon nanofibre/poly (vinylidene fluoride) composites. Carbon, 47(11), 2590-2599.
[18] Pang, H., Xu, L., Yan, D. X., & Li, Z. M. (2014). Conductive polymer composites with segregated structures. Progress in Polymer Science, 39(11), 1908-1933.
[19] Spitalsky, Z., Tasis, D., Papagelis, K., & Galiotis, C. (2010). Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. Progress in polymer science, 35(3), 357-401.
[20] Ra, E. J., An, K. H., Kim, K. K., Jeong, S. Y., & Lee, Y. H. (2005). Anisotropic electrical conductivity of MWCNT/PAN nanofiber paper. Chemical Physics Letters, 413(1-3), 188-193
[21] Nigro, B., Grimaldi, C., Miller, M. A., Ryser, P., & Schilling, T. (2012). Tunneling conductivity in composites of attractive colloids. The Journal of chemical physics, 136(16), 164903.
[22] Georgousis, G., Pandis, C., Kalamiotis, A., Georgiopoulos, P., Kyritsis, A., Kontou, E., ... & Omastova, M. (2015). Strain sensing in polymer/carbon nanotube composites by electrical resistance measurement. Composites Part B: Engineering, 68, 162-169.
[23] Zhu, H., Wang, X., Liang, J., Lv, H., Tong, H., Ma, L., ... & Liu, Z. (2017). Versatile Electronic Skins for Motion Detection of Joints Enabled by Aligned Few- Walled Carbon Nanotubes in Flexible Polymer Composites. Advanced Functional Materials, 27(21).
[24] Gonçalves, B. F., Costa, P., Oliveira, J., Ribeiro, S., Correia, V., Botelho, G., & Lanceros- Mendez, S. (2016). Green solvent approach for printable large deformation thermoplastic elastomer based piezoresistive sensors and their suitability for biomedical applications. Journal of Polymer Science Part B: Polymer Physics, 54(20), 2092-2103.
[25] Spitalsky, Z., Tasis, D., Papagelis, K., & Galiotis, C. (2010). Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. Progress in polymer science, 35(3), 357-401.
[26] Eswaraiah, V., Balasubramaniam, K., & Ramaprabhu, S. (2011). Functionalized graphene reinforced thermoplastic nanocomposites as strain sensors in structural health monitoring. Journal of Materials Chemistry, 21(34), 12626-12628.