

Characterization of Functionalized Low Density Polyethylene/Polyaniline Nano Fiber Composite

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Abstract—Nano composite based on polyaniline (PANI) nano fibers filler and chromic acid functionalized low density polyethylene (LDPE) matrix with biocompatibility and low percolation threshold value was prepared via twin screw extrusion process. Density measurement, Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray crystallography (XRD), Brunauer, Emmett and Teller analysis (BET), Thermo Gravimetric (TGA), Differential Scanning Calorimetry (DSC) and Four-Probe Conductivity measurements are reported. As low density polyethylene functionalization renders LDPE more biocompatible, it also facilitates conductivity due to carbon carbon double bonds, sulfonic, and carbonyl group moieties. PANI nano fibers also assist in charge transfer mechanism of resultant composite. Overall results indicate the formation of highly stable nanocomposite materials, with good physiochemical properties and conductivity. The resultant blend may prove beneficial as a low cost biocompatible and electrically simulated nerve tissue repair scaffolds.

Index Terms—functionalized polyethylene, polyaniline nano fibers, nano composites, characterization

I. INTRODUCTION

The earliest and most widely used conducting polymeric systems were composites in which an insulating polymer matrix was filled with particulate or fibrous conductive filler, such as a carbon or metal, to impart high conductivity, however conducting polymers such as polyaniline and polypyrrole now offer excellent electrical and mechanical properties [1]. In recent year preparation of composites polyolefin with intrinsically conducting polymers (ICP) especially polyaniline has received great attention because of their unique properties and applications in various electrical devices [2]–[4].

In this study a conducting composite of Polyaniline (PANI) nanofibres as filler and with chromic acid functionalized polyethylene as matrix was made via melt

process using twin screw extruder. Optical microscopy and measurements of thermal and physical properties of the nano composite were carried out. LDPE is a one of the largest used commodity polymer and possesses good thermal and chemical properties, except surface energy and functionality [5], [6]. Many researchers modified polyethylene (PE) by introducing functional group moieties for its extended use as specialized polymer using mineral acids [7]. The matrix of low density polyethylene (LDPE) was homogenously functionalized using mineral acid as an oxidizing agent on customized liquid phase sulfonation process [8]. Significant decrease in band gap values due to generation of π -electrons through double bonds indicates marked improvement in electret properties of chromic acid modified LDPE [9]. Polyaniline is one of the extensively studied intrinsically conducting polymers due to its ease of synthesis and low cost. Nanostructured polyaniline example rods wires and fibers due to its high interfacial area offers enhanced performance [10]. Polyaniline nano fibers were used as filler for the said nanocomposite. Nanofibres were synthesized using rapid mixing process with ammonium per sulphate (APS) and Sodium hypochlorite as oxidizing agents and hydrochloric acid (HCl) as dopant without any hard or soft templates [11]. Blending of biocompatible LDPE with enhance electret properties and PANI nanofibres as intrinsically conducting polymers resulted in conducting polymer nano composite with lower percolation threshold and immense application as bio sensors, gas sensor, moisture or humidity sensor, absorbent, catalyst, actuators, capacitors, battery, fuel cells, solar cells and electro-chromic devices [12]. Neuronal repair is one of the most important tissue engineering concepts. In tissue repairing system Mobarakeh et al demonstrated that electrical stimulation enhanced the nerve regeneration process making use of electrically conductive polymers systems [13].

II. EXPERIMENTAL

A. Materials

LDPE pellets (Petlin Malaysia Sdn. Bdh.) were used for functionalization using analytical grade sulfuric acid (96%) and Potassium di chromate (Fischer Scientific Malaysia) to make chromic acid solutions with deionized water (Millipore Elix). Cyclohexane (Merck Germany) and ethanol 95% (HmbG Chemicals) were used as non-polar and polar reagents for homogenous LDPE functionalization. Aniline (99%) from ACROS Organics, Ammonium peroxodisulfate from Merck and Hydrochloric acid (37%) from Fisher Scientific were used to make polyaniline nano fibers.

B. Functionalization of LDPE

LDPE pellets were in cyclohexane and ethanol and chromic acids were functionalized at isothermal temperature. Continuous mixing was done using an overhead variable speed motor attached with an agitator at constant speed of 200rpm. Details of functionalization reaction are stated in other communication [8].

C. Synthesis of PANI Nanofibres

The polyaniline nano fibers were synthesized using similar procedure as indicated by Rahy et al; having conductivity of about 0.5 S/cm and doped with about 15% HCl. Approximately 9.5mL of aniline was dissolved in 500 mL of 1 M hydrochloric acid while 5.7 g of ammonium peroxodisulfate (APS) was dissolved in 100 mL of 1 M hydrochloric acid. APS solution was added quickly to the aniline mixture and mixed. This gives aniline to APS molar ratio of approximate 1:1.25. The reaction vessel was maintained from 0 to 5 °C using ice bath. After starting of reaction, 10 mL of commercial sodium hypochlorite bleach was quickly added drop wise with agitation at 500 rpm. The reaction vessel was then left standing without mixing for 30 min. The thick precipitated polymer was filtered, washed with 1.0 M hydrochloric acid, deionized water and then acetone, followed by drying in an oven 75 °C overnight [11].

D. Preparation of functionalized LDPE/PANI-NF blend

Low density polyethylene based polyaniline conducting polymer nano composite was obtained. PANI nano fibers were incorporated into a thermoplastic low density polyethylene (LDPE) matrix. Both functionalized low density polyethylene and polyaniline nano fibers were dried at 60 °C prior to blending. Mixing of grinded functionalized LDPE and 5% PANI-NF was done in an electric mixer and fed into extruder with controlled feed rate. Thermo Scientific Prism, twin screw extruder was operating at temperature of 130 °C, with a speed of 20 rpm at a torques of 150Nm. The molten blend was extruded through 2mm die as a rod, cooled in and pelletized using Thermo Scientific standard granulator fixed length pelletizer.

E. Density Measurement

Density of functionalized LDPE, PANI nano fibres and resultant composite were measured using Micromeritics Accu pyc 1340 gas pycnometer. Eight cycles per samples were repeated for accurate results.

F. Elemental Analysis

Elemental analysis of functionalized LDPE, PANI nano fibers and their blend was performed via Energy-dispersive X-ray spectroscopy (EDX) using OXFORD instruments X-Max.

G. Fourier Transform Infra-Red Spectroscopy

Fourier Transform Infra-Red spectroscopy of the treated polymer was done using Perkin Elmer Spectrum 100 apparatus.

H. X-ray Diffraction

Using X-ray Diffraction (XRD) of amorphous and crystalline phases of the samples was carried out. Samples were grinded and mixed well before analysis. A RIGAKU Miniflex II X-ray diffractometer was equipped with auto-search/match software for the qualitative analysis.

I. Thermo Gravimetric Analysis

TGA measurements were carried out using thermo gravimetric analyzer (TA Instruments, TGA Q500). Each specimen was weighed around ±5mg, with scanning temperature range from 25°C to 900°C and rate of 10°C/minute.

J. Differential Scanning Calorimeter

Thermal analysis of samples were done using DSC model Q10 from TA instruments. Each sample ranged from ±2-3mg, first samples were heated from 35°C to 150°C for run 1, then cooled to 30°C using a scan rate of 10°C/minute for run 2. The samples go through last heating cycle from 35°C to 150°C for run 3.

K. Brunauer, Emmett and Teller (BET) Test

Adsorption model and total surface area of the samples were measured using BET from MICROMERITICS Model ASAP 2020.

L. Field Emission Scanning Electron Microscopy

Surface of treated functionalized LDPE, PANI nano fibers and resultant composite were observed under field emission scanning electron microscope using model JOEL JSM 7500F. Films were fixed to a metal base using double sided tape, and then coated with platinum using vacuum sputter coater to make specimen conductive prior FESEM observations.

M. Conductivity Measurements

Conductivity measurements were carried out using four probe resistivity meter model Bridge Technology Model SRM 232-2000. The conductivity of the resultant functional LDPE and PANI nano fiber composite was calculated according to formula given below using four probe resistivity meter.

$$\sigma = \frac{L}{(R \cdot x A)}$$

In above formula the conductivity is calculated from the resistance R, between two section separated by distance L having an average area A.

III. RESULTS AND DISCUSSIONS

A. Density Measurements

The density measured using fully automatic gas pycnometer of functionalized LDPE and functionalized LDPE / PANI nanofibres composite decreased from 0.9604 gm/cm^3 to 0.7608 gm/cm^3 demonstrating a light weight composite material with conducting properties. Light weight of the resulting nano composite also makes it an excellent candidate for automobile and aviation industry.

B. Elemental X-ray spectroscopy Results

The elemental percentages were measured for detection of carbon, nitrogen, oxygen and sulphur contents using elemental X-ray spectroscopy (EDX). However EDX has a drawback as X-rays are not capable to detect hydrogen so elemental weight percentage was calculated without indicating hydrogen as an element which is an integral part of both LDPE and PANI. The resultant percentage given in Table I indicates all the necessary proportion of elements for functionalized LDPE and PANI nano fibres.

TABLE I. ELEMENTAL WEIGHT PERCENTAGE MEASURED USING ELEMENTAL X-RAY SPECTROSCOPY

Element Name	Functional -LDPE	PANI-Nano Fibre	F-LDPE/ PANI NF Blend
Carbon	23.83	22.42	26.98
Oxygen	71.09	66.43	72.36
Sulphur	5.08	–	0.40
Nitrogen	–	2.35	0.12
Chlorine	–	8.81	0.14

C. Functional Group Analysis Using FTIR Spectroscopy

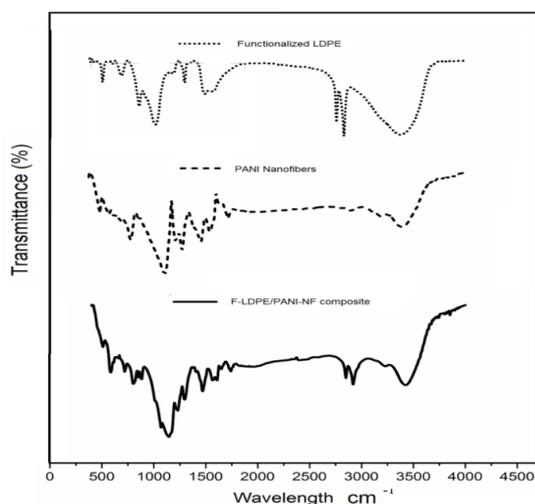


Figure 1. Fourier Transform Infrared Spectroscopy of functionalized LDPE, PANI nanofibers and their blend are compared in a graph.

A comparison of the FTIR transmittance spectra for all the samples was done to detect functional group moieties.

The comparison enables emphasizing over relative change due to blending of functionalized LDPE and PANI nano-fibres respectively. Fig. 1 relates FTIR graphs, first of functionalized LDPE, second PANI Nano fibers and last one of their composite. As for the functionalized LDPE the transmittance bands between 840 and 1250 cm^{-1} are ascribed to sulfonic groups. Other bands in region 1500 to 1800 cm^{-1} are assigned to olefinic double bonds and carbonyl groups i.e. ketones, aldehydes and carboxylic acids. Dual peaks in the region 2800-2950 cm^{-1} corresponds to alkene C-H stretch. Lastly the broad band occupying 3100-3600 cm^{-1} is referred to the presence of hydroxyl group.

For PANI Nano fibers high wavenumbers were observed that also presented strong spectrum absorption intensity peaks at 3525.01 cm^{-1} broad peak corresponds to the NH group. The main peaks at 1578 and 1479 cm^{-1} corresponds to quinone and benzene ring stretching deformations. The adsorption band at 1306 cm^{-1} corresponds to π -electron delocalization induced in polymer via protonation. Other two peaks at 1250 cm^{-1} and 1140 cm^{-1} correspond to characteristic C-N stretching vibration and imine structure formed during the protonation. Finally the spectra of functionalized LDPE and PANI nano fibers correspond to the combine spectra of both the components.

D. Crystallinity Behaviour via X-Ray Diffraction

X-ray diffraction pattern of functionalized low density polyethylene, polyaniline nanofibres and their resultant composite are given in Fig. 2 below.

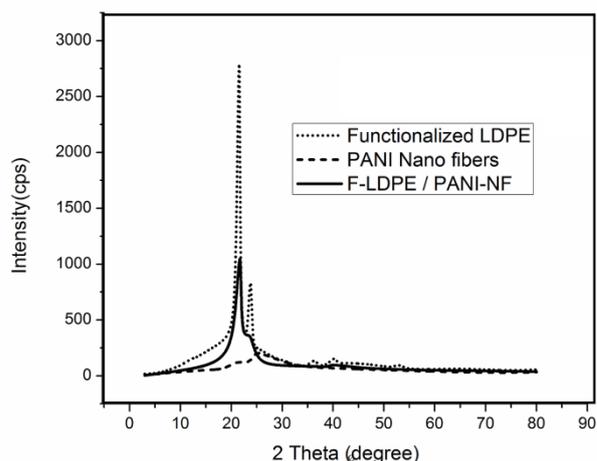


Figure 2. X-ray Diffraction of functionalized LDPE, PANI nanofibers and their blend are compared in a graph.

The functionalized LDPE matrix reveals two distinct reflections at $2\theta = 21.0$ and 23.78 degrees. PANI nanofibers exhibited two weak and broad peaks with 2θ at 21.58 and 25.21 degrees. The resultant and resulting composite also exhibit reflects functionalized LDPE at similar angles. The decrease in the peak heights of resultant composite in comparison to functionalized LDPE matrix shows that PANI nano fibres are fairly dispersed in the large amorphous portion of functionalized LDPE matrix to form a uniform nano

composite. As PANI nano fibers fillers was largely amorphous, also due to the low crystallinity of chromic acid functionalized LDPE, crystallinity of the resultant nano composites was shown to decrease.

E. Thermo Gravimetric Analysis

Specimens were weighed accurately (~5 mg) and scanned in the temperature range from 25°C to 600°C for functionalized LDPE and up to 900°C for polyaniline nanofibres and their resulting composite using a heating rate of rate of 10°C/min. The TGA curves illustrated in Fig. 3 demonstrate similar thermal behavior for the functionalized LDPE and resultant composite samples. A clear increase in the thermal stability of LDPE with increasing PANI content is proved by TGA. This enhanced thermal stability is exhibited for the resultant composite due to uniform integration of PANI nanofibres within the functionalized matrix. Resulting in optimal dispersion of the nano structure in functional groups assisted matrix system.

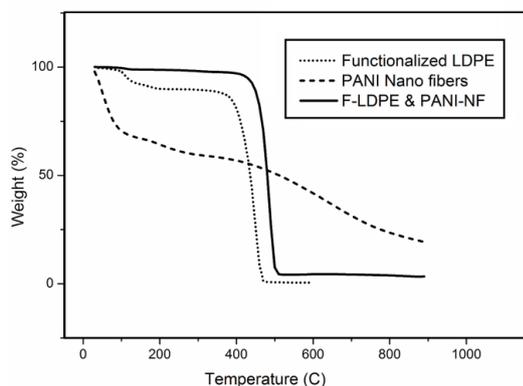


Figure 3. Thermo gravimetric analysis of functionalized LDPE, PANI nanofibres and their blend.

F. Thermal Analysis via Differential Scanning Calorimeter

Differential Scanning Calorimetry (DSC) was used to study the melting behavior, enthalpy changes and crystallinity of the functionalized low density polyethylene, polyaniline nanofibres and their resultant composite. Table II compares melt onset temperatures, peak melting temperatures, enthalpy and crystallinity of all the samples. DSC data for functionalized LDPE, PANI nanofibres and their resultant composite. Crystallinity was calculated using the following formula: $X_c = (\Delta H_f / \Delta H_f^*) \times 100$; where ΔH_f is change in enthalpy and ΔH_f^* represent enthalpy of fusion for perfect polyethylene sample having 100% crystallinity with value of 293.1 J/g [14].

Similarly the crystallinity of resulting composite was calculated using formula $X_c = (\Delta H_f / w \Delta H_f^*) \times 100$, where 'w' stands for weight percentage of functionalized LDPE in the composite [15]. As per Table II, the resultant composite exhibit a little higher onset temperature, peak melting temperature and crystallinity pointing toward ease of manufacturing as per polymer industry. The melting curves of LDPE and its composites studied by DSC indicated that PANI content did not seem

to have much influence on the melting temperature of LDPE.

TABLE I. MELTING TEMPERATURE, ENTHALPY AND CRYSTALLINITY PERCENTAGE OF FUNCTIONALIZED LDPE, PANI NANO FIBER & F-LDPE/ PANI-NF COMPOSITE

	Functionalized LDPE	PANI Nanofibres	Composite
Melt Onset Temp °C	98.2	43.53	99.41
Melt Peak Temp °C	103.4	69.95	105.84
Enthalpy (J/g)	71.6	97.78	81.41
Crystallinity (%)	24.4	-	26.39

G. Morphology Analysis

Surface analysis and morphological changes were studied by observing specimen under Field Emission Scanning Electron Microscope (FESEM). Polymer samples require high vacuum, dehydration of samples and charging was minimized by coating samples with platinum thus lowering the operating voltage requirements of the sensitive apparatus. Surface images of functionalized LDPE and PANI nano fiber composite are illustrated in Fig. 4. The SEM micrographs show that the surface of the polymer is smooth however some protuberance on submicron scale is evident.

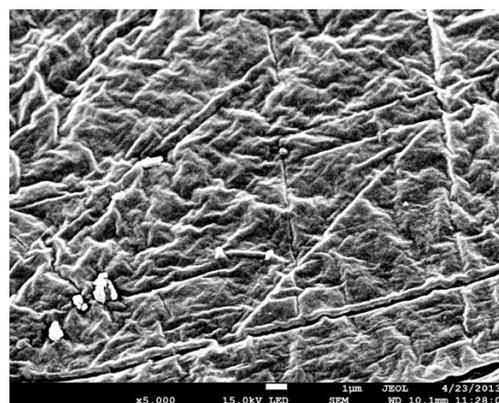


Figure 4. FESEM images of functionalized LDPE and PANI nano fibers composite with magnification of 5k times.

The above figure shows distribution of the filler particles in the polymer matrix is noticeably uniform. There are no large agglomerations of particles within the matrix. In all the orientation of PE matrix is apparent along the draw direction.

H. Brunauer, Emmett and Teller (BET) Test

Functionalized LDPE and PANI nanofibres were degassed by vacuum force or inert gas purging to remove adsorbed foreign molecules. A controlled inert gas was introduced, and the inert gas was adsorbed or, alternatively, withdrawn and desorbed. The amount of gas molecules adsorbed or desorbed was determined by

the variation in pressure due to the adsorption or desorption of the gas molecules by the material (the adsorbent). The area occupied by one adsorbate molecule and adsorption model allowed for the determination of the total surface area of the material. The BET analyzer showed that the surface area of the PANI nanofibres was 14.7535m²g, whereas the Langmuir surface area was 22.2865m²g. The single point adsorption total pore volume of pores less than 1360.863 Å diameter at P/P₀ equals 0.985570485 is 0.163343cm³g. Similarly adsorption and desorption cumulative surface areas of functionalized LDPE between 17.000 Å and 3000.000 Å diameter are 0.529 m²g and 1.7231 m²g. These porosity values obtained show that the application of PANI nano fibers into a functionalized LDPE matrix enhanced its composite properties because it created a different phase relative to the matrix materials.

I. Electrical Conductivity

The conductivity of the compounded blend of functionalized LDPE and intrinsically conducting PANI nano fibers was found in range of 10⁻⁴ S/cm. This high conducting effect can be explained in terms of the formation of a continuous network consisting of filler particles, which had a positive effect on the electrical behavior of the material.

IV. CONCLUSION

The distribution of the nano fillers in the polymer matrix was uniform as shown by SEM micrograph. The surface area measurements of the functionalized low density polyethylene, polyaniline nanofibres of the resultant blend also confirms that reinforcement of filler into matrix enhances its physical properties because it creates a different phase relative to the matrix material and conductive polymer. High conductivity of the composite is due to functionalization of LDPE and its interaction with nano scale PANI particles. Both matrix and filler triggered the connection of the conductive path. Thermal properties of functionalized LDPE /PANI nano fibers blend also improved in comparison to both individual components. In brief, the resulting composite is light weight and easy to handle with enhance morphology, crystallinity, and conductivity properties. Thus we conclude that resultant nano composite will prove suitable as low cost, biocompatible and conducting tissue repairing scaffolds.

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REFERENCES

- [1] M. Chipara, *et al.*, "On-polyethylene-polyaniline composites," *Composite PartB: Engineering*, vol. 34, pp. 637-645, March 2003.
- [2] A. Andreatta and P. Smith, "Processing of conductive polyaniline -UHMW polyethylene blends from solution in non-polar solvent," *Synthetic Metals*, vol. 55-57, pp. 1017-1022, 1993.
- [3] C. Y. Wu and A. Benatar, "Microwave welding of high density polyethylene using intrinsically conductive polyaniline," *Polymer Engineering and Science*, vol. 37, pp. 738-743, April 1997.
- [4] M. Cote, M. T. Cortes, D. Beltran, and P. Ortiz, "PANI-LDPE Composites: Effect of blending conditions," *Polymer Composites*, pp. 22-28, 2009.
- [5] J. R. Rasmussen, E. R. Stedronsky, and G. W. Whitesides, "Introduction, modification and characterization of functional groups on surface of low density polyethylene film," *Journal of American Chemical Society*, vol. 99, pp. 4737-4745, 1977.
- [6] D. Fischer and H. Eysel, "Analysis of polyethylene surface sulfonation," *Journal of Applied Polymer Science*, vol. 52, pp. 545-548, 1994.
- [7] W. Hao, J. C. Shuang, and Z. Jun, "Surface treatment of LLDPE and LDPE blends by nitric acid, sulfuric acid & chromic acid etching," *Colloid Polymer Science*, vol. 287, pp. 541-548, 2009.
- [8] M. R. Kazimi, T. Shah, S. B. Jamari, I. Ahmed, and C. K. Faizal, "Liquid-phase sulfonation of swollen low density polyethylene for in depth functionalization," Unpublished.
- [9] M. R. Kazimi, T. Shah, S. B. Jamari, I. Ahmed, and C. K. Faizal, "Functionalization of swollen low density polyethylene in liquid-phase using sulfuric and chromic acids as sulfonation agents," Unpublished.
- [10] D. Li, J. Huang, and R. B. Kaner, "Polyaniline nanofibres: A unique polymer nanostructure for versatile applications," *Accounts of chemical research*, vol. 42, pp. 135-145, January 2009.
- [11] A. Rahy *et al.*, "Polyaniline nano fiber synthesis by co-use of ammonium peroxydisulfate and sodium hypochlorite," *Chemical Matters*, vol. 20, pp. 4808-4814, 2008.
- [12] J. Wang and D. Zhang, "One dimensional nanostructured polyaniline: Syntheses, morphology, controlling, formation, mechanism, new features and applications," *Advances in Polymer Technology*, vol. 32, pp. E323-E368, 2013.
- [13] L. G. Mobarkeh, M. P. Prabhakaran, M. Morshed, M. H. N. Esfahani, *et al.*, "Application of conductive polymers, scaffolds and electrical stimulation for nerve tissue engineering," *J Tissue Eng Regen Med*, Pub Med Online, 2011.
- [14] TN 48. (n.d.), "Polymer heats of fusion," *TA Instruments*, New Castle, USA.
- [15] A. V. Nund, S. Ray, J. T. Sejdic, and P. A. Kilmartin, "Characterization of anti-oxidant low density polyethylene/polyaniline blends prepared via extrusion," *Materials Chemistry and Physics*, vol. 135, pp. 903-911, 2012.



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