بسم الله الرحمن الرحيم

MONA MAGHRABY

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

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جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

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Novel Multifunctional Graphene Based Nanocomposites for Technological Applications

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Title: Novel Multifunctional Graphene Based Nanocomposites for Technological Applications

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In the present work, two main applications for graphene composites are targeted which are active packaging material and supercapacitors. So, graphene / hyperbranched polyester is prepared for the first application and Ag @ graphene / CuO @ graphene were prepared. For both cases, reduced graphene oxide was obtained from Hummer method as a precursor. Then, the former type of graphene nanocomposite was synthesized using in-situ and ex-situ techniques and the produced modified graphene hybrids were included in the polycaprolactone films (PCL) with different ratios via casting and melting processes.

X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscope (TEM) confirmed the amorphous structure of few layers with the sharp edges of reduced graphene oxide, respectively. Meanwhile, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) emphasized the formation of graphene/ hyperbranched polyester nanocomposites through non-covalent interaction. The prepared casting PCL nanocomposite films showed improvement in the thermal, mechanical, and barrier properties in terms of degradation and crystallization temperatures, elasticity, and water permeability rate, respectively. On contrast, the nanocomposite films fabricated under the melt process displayed further upgrade of the matrix properties. The decomposition and glass transition temperatures increased along with stiffness, mechanical strength, tensile strength, and elongation at break.

The rate of water permeability decreased to about one third and the reduction up to 20 % against the permeability of CO_2 and H_2O was also observed. Moreover, hybrid graphene nanocomposites impart hydrophilic and antibacterial characters to the PCL films thanks to the modification of graphene with hyperbranched polyester. Also, the biodegradation test indicated the successful decay of the casted PCL and its nanocomposite films in the soil. However, exposure of the films obtained by melt process to specific type of fungus showed a weight loss three-fold higher than the neat matrix.

Additionally, for the second application, the nanocomposites were accomplished via in-situ reduction of graphene oxide in presence of metallic precursors. TEM and XRD proved anchoring of silver and copper oxide nanoparticles at the graphene' surface. The electrochemical evaluation of these hybrids showed that the specific capacitance of RGO was duplicated in presence of CuO nanoparticles which promotes this composite as a promising electrode material for supercapacitor applications.

K E Y W O R D S

Graphene Nanosheets; Hyperbranched Polymers; Graphene Nanocomposites; Polycaprolactone; Active Packaging; Metal/Metal Oxide Nanoparticles; Supercapacitor Electrodes

This work aims at exploring modified reduced graphene oxide (RGO) for active packaging or energy storage applications. To fulfill this aim, surface modification of RGO with two types of modifiers, hyperbranched polyester (PES) for the first application and silver/copper oxide nanoparticles, has been carried out. The purpose of surface functionalization of RGO with PES, is not only to improve the dispersion of graphene nanosheets and hence their properties but also to impart new characteristics to a hosting biodegradable matrix (we choose polycaprolactone (PCL)). Meanwhile, the surface decoration of RGO with metal/metal oxide nanoparticles goes to enhance the electrochemical properties of supercapacitor electrodes.

In more details, RGO was firstly prepared by Hummer method and then functionalized with PES using in-situ and ex-situ approaches, in order to determine the best technique that provides improved properties. The successful preparation of graphene and its modified forms was confirmed with different characterization techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, infrared spectroscopy, Raman spectroscopy, transmission electron microscope, and atomic force microscope. The biological activity against deleterious pathogens was also discussed and the results showed improved biocidal activity in presence of PES. Moreover, the impact of RGO during the in-situ polymerization step was investigated using proton magnetic resonance and gel permeation chromatography for structural analysis of unattached PES obtained in presence of RGO compared with pure PES that prepared in absence of RGO. The results confirmed that, in presence of RGO, the polymerization was occurred and the PES was formed with its well-known chemical structure. Nevertheless,

the degree of branching was found lower than in case of pure PES. Finally, the prepared RGO and its in-situ and ex-situ modified forms were added with different ratios to the PCL films utilizing two comparable techniques; casting and melting. In the latter process, the filler or its modified form was blended with the commercial PCL under thermal conditions in the Barbender and then thermal pressing to obtain free standing films. Moreover, these nanocomposite films were also obtained using casting technique. The thermal and mechanical properties were studied for all produced films. The results obtained were different and depending on the method of film fabrication. Particularly, the films prepared with casting technique exhibited improvement in the degradation and crystallization temperatures of PCL film, with the incorporation of fillers, without significant changing in the T_g. On contrast, inclusion of such fillers under melting conditions showed increasing in the decomposition and glass transition temperatures without changing in the crystallinity of the PCL matrix. Mechanically, addition of the prepared fillers to melt PCL matrix led to enhancement of stiffness, mechanical strength, tensile strength, and elongation at break. Nevertheless, the surface modification of RGO with PES could be an effective approach to fine tune the stiffness and elasticity of the PCL matrix prepared with casting method. The improvement of surface wettability was checked with contact angle measurements. The results emphasized that the inclusion of modified fillers decreased the values of contact angle whatever the method of film fabrication. The rate of water permeability decreased to ~ one third of PCL film after the reinforcement with modified filler either with casting or with melting process. However, further improvement ~ 20 % against the permeability of CO_2 and H_2O was

observed for the nanocomposite blends prepared with melting process. Meanwhile, the casted films did not exhibit a significant enhancement either in water or gas permeability. The antimicrobial performance against Gram-positive and Gram-negative bacteria was debated in details. Specifically, the PCL films incorporated with the prepared fillers are selective to Gram-positive bacteria regardless the way of film preparation. Lastly, the biodegradation test indicated to the successful decay of the PCL and its nanocomposite films in soil. However, utilizing fungal based method, blends reinforced with modified graphene showed a weight loss three-fold higher than the neat matrix. Generally, the results indicate the strong workability of the modified RGO incorporated in the PCL matrix particularly under melting process which simulates the industrial conditions.

On the other hand, surface decoration of RGO with silver and copper oxide nanoparticles was achieved via in-situ reduction process of graphene oxide in presence of metallic precursors in order to improve the electrochemical properties of RGO. The successful preparation of metal/metal oxide doped RGO was confirmed with transmission and scanning electron microscopes, X-ray diffraction, and Energy-dispersive X-ray spectroscopy. Particularly, TEM images confirmed that the obtained copper oxide nanoparticles have a lower particle size than silver nanoparticles. The prepared electrodes based RGO and RGO hybrid materials were check in different electrolyte medium. The effect of nanoparticle loading percentages, scan rates, and cycling were also intensively investigated in order to determine the optimized conditions at which the modified electrode exhibit superior performance. The results showed that the specific capacitance of RGO was found two fold greater

(200 F g^{-1}) in presence of 5 Wt. % CuO nanoparticles at 50 mVs^{-1} in the acidic medium. Interestingly, these results emphasize that the copper oxide nanoparticles doped RGO is a promising electrode material for supercapacitor applications.

Finally, it could be claimed that the findings presented in this thesis have provided not only fundamental understanding of graphene nanocomposites impacts in the polymeric matrix but also applications in different potential fields.