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ПОЛИМЕРНИ КОМПОЗИТНИ ЕЛЕКТРОПРЕДЕНИ НАНОВЛАКНА С НАНО ПЪЛНИТЕЛИ

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POLYMERIC COMPOSITE ELECTROSPUN NANOFIBERS WITH NANO FILLERS

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Abstract

CNT- and Fe-based nanofillers were applied to optimize the properties of polymer matrices in fiber form and investigate their effects in a comparative way. Electrospinning was successfully used to fabricate nanofibers of iron oxide/poly(m-anthranilic acid)/poly(ε-caprolactone) and CNT/poly(styrene–butadiene–styrene) (SBS) composite elastomers, which were then thermomechanically, morphologically, and spectroscopically characterized.

Keywords: Electrospun nanofibers, carbon nanotube, poly(styrene–butadiene–styrene),iron oxide, poly(ε-caprolactone)

Introduction

Electrospinning is one of the processing methods for deriving micro- and nanofibers from polymer solutions and melts by the presence of electrical forces[1]. Electrospun fibrous polymer–matrix composite membranes with a high surface area due to high pore density serve a broad range of applications,i.e., medical and tissue engineering, electromagnetic interference shielding, and batteries and catalytic applications as smart textile products. Smart textile products have a crucial role in their development such as medical textiles, protective clothing, touch screen displays, flexible fabric keyboards, and sensors.

CNTs are a unique class of nanomaterials with exceptional mechanical, electrical, and thermal properties. When embedded into a polymer matrix, they can significantly improve the composite's overall performance, including its strength, stiffness, toughness, conductivity, and heat resistance. CNT-embedded polymer composites have a wide range of potential applications, i.e., aerospace, automotive, electronics, and energy, due to lightweight and heat resistance.

CNT-containing polymeric composite fiber mats can contribute especially to health and medical applications i.e., bone reconstruction, where sensing and soft surface are required, and for the development of fiber and textile structures with enhanced breathability as a delivery tool for drugs and biomolecules to enhance cell recovery. CNTs feature a unique one-dimensional structure and high aspect ratio, lightweight, and good electrical conductivities. The mechanical properties of CNTs-filled fibers are improved compared to the conventional fibers, produced by electrospinning [2,3].

Iron-based polymeric composites are also used in a wide variety of applications, including, electromagnetic shielding, magnetic resonance imaging (MRI) as contrast agents, drug delivery, sensors, and energy storage.

This study compares the effects of separately applied CNT- and iron-based nanofillers in fiber form on the optimized properties of polymer matrices.

Experimental

Details of fabrication by electrospinning, and material properties are given in our recent publications[2-5]. Advanced characterization techniques such as X-ray photoelectron spectroscopy(XPS), high-resolution scanning electron microscopy(HRSEM), high-resolution differential scanning calorimetry, Dynamic mechanical analyses(DMA), Fourier-transform infrared spectroscopy(FTIR), Raman spectroscopy, and X-ray diffractometry(XRD) are employed to investigate the mechanism of interaction between nanofiller and polymer matrices.

In the case of CNT filler poly(styrene–butadiene–styrene) (SBS) (Mw ~ 140 000 g mol^{-1})-, polystyrene (PStyr, Mw ~ 192 000 g mol−1) and polybutadiene(PBu Tg = 95 °C, Mw ~ 200 000 g mol^{-1})-polyethylene oxide (PEO, Tg =-67°C, Mw of ~100,000 g.mol^{-1}) matrices are used .

Fe_2O_3 (NP; Sigma Aldrich) nanoparticles embedded in polyanthranilic acid(P3ANA) and poly(ε-caprolactone) (PCL, Mw: 80 000 g mol−1) matrices.

Results & Discussion

The results indicate that the inclusion of CNTs into SBS decreases the fiber thickness by an order of magnitude, from micro to nanoscale, while a transition from a porous to non-porous and rough morphology is attained[4].HRSEM and energy-dispersive X-ray (EDX) supported the findings of the thermomechanical analysis by examining the influence of composition and CNT inclusion.

Polymer blends, nanofillers, and processing parameters affect the fiber

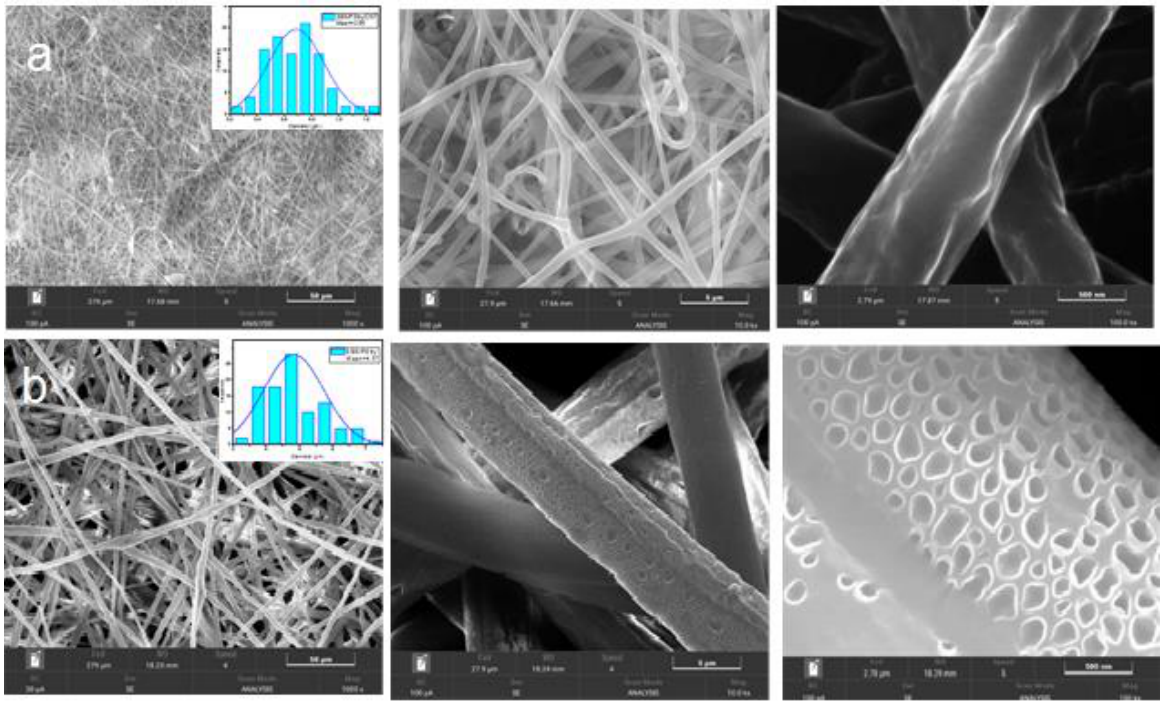

Fig.1. SEM images of the SBS/PStyr (a), CNTincluded SBS/PStyr (b) composite fibers with different magnifications (Insets: diameter distributions) (Reproduced with permission from Royal Society of Chemistry, Sarac B., Gürbüz R., Micusik M., Omastova M., Rezvan A., Yüce E., Xi L., Eckert J., Ozcan A., Sarac A.S., Styrene–butadiene–styrene-based stretchable electrospun nanofibers by carbon nanotube inclusion, *Mol. Syst. Des. Eng*., 2023,8, 911-921)

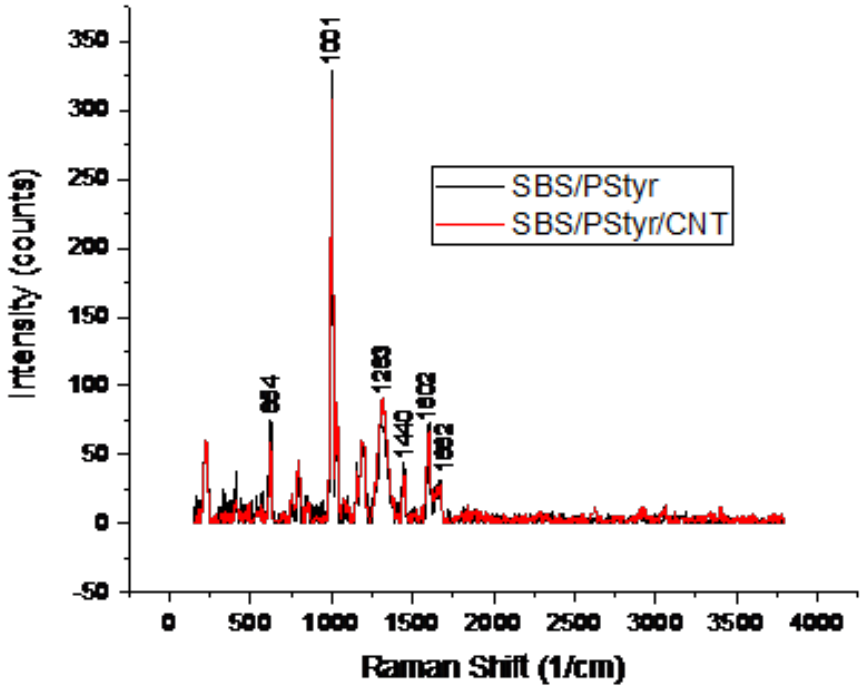

Fig.2 . Comparison of the Raman plots for SBS/PStyr and SBS/PStyr/CNT samples. (Reproduced with permission from Royal Society of Chemistry, Sarac B., Gürbüz R., Micusik M., Omastova M., Rezvan A., Yüce E., Xi L., Eckert J., Ozcan A., Sarac A.S., Styrene–butadiene–styrene-based stretchable electrospun nanofibers by carbon nanotube inclusion, *Mol. Syst. Des. Eng.*, 2023,8, 911-921)

morphology,i.e., CNTs are included in the blends to enhance electrical conductivity and interfacial reinforcement and for better micro-crack control and higher friction and thermal conductivity.

Homogeneous fibers and distribution are obtained for the SBS/PStyr case compared to the PStyr/PBu and in the presence of CNT, fiber diameters are drastically decreased by the presence of CNT in the case of SBS/PStyr (Fig.1)

The CNT inclusion into PStyr/PBu changes the thermal properties by shifting the glass transition of the PBu peak to much lower temperatures. The drop in the absorbance in FTIR and the intensity drop in Raman spectroscopy account for the inclusion of CNTs even in small quantities(Fig.2). Furthermore, the Raman spectroscopy results indicate that intramolecular interactions between additional PStyr and PBu in SBS limited the interaction of CNTs compared to the PStyr/PBu blend.

The XPS results concluded that the major structural, thermal, and morphological changes happen with the addition of CNTs to the SBS/PStyr sample. The inclusion of 1.25 wt% CNTs eliminates the semi-crystallinity of SBS/PStyr, indicating that even small quantities of CNTs can retard the

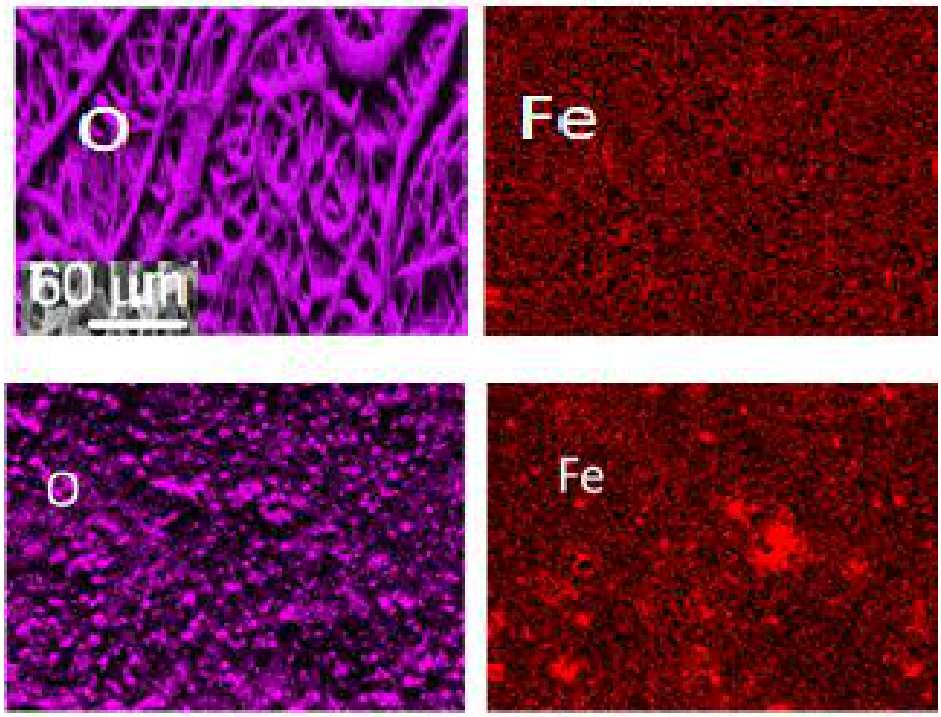

Fig.3. EDX of 5% Fe_2O_3 in PCL (above) and, 5% Fe_2O_3 /10% P3ANA in PCL (bottom Fig.) (Reproduced with permission from Royal Society of Chemistry, Iron oxide – poly (m-anthranilic acid)–poly(ε-caprolactone) electrospun composite nanofibers: fabrication and properties, Huner K., Sarac B., Yüce E., Rezvan A., Micusik M.,Omastova M., Eckert J., Sarac A.S., *Mol. Syst. Des. Eng.*, 2023,8, 394-406)

crystallization process. In FTIR, the decreased absorbance of both SBS/PStyr and PStyr/PBu reveals the presence of CNTs.

Employed advanced characterization techniques,i.e., XPS, XRD, and Raman spectroscopic results(Fig.2) enlighten the mechanism of interaction between CNTs and the SBS tri-block copolymer matrix through the determination of the morphology, pi–pi* interactions, and the crystallinity of the synthesized fibers with the presence of CNT fillers.

The glass transition (Tg) of the PBu peak is determined to be changing between −96 and −72 °C, whereas the Tg of polystyrene is not majorly influenced by copolymerization nor by CNT addition.

The inclusion of iron and carboxylic acid-functionalized polyaniline into polymeric polycaprolactone structures enhanced the electron-donating ability which in turn increases the compound conductivity and may induce reversible redox chemistry, allowing them to be used in electrochemical immunosensors[5].

Hence, this study presents a new composite structure, Fe_2O_3 /P3ANA/PCL composite nanofibers, and the assessment of their intrinsic properties enables the discovery of possible application fields in biomedical and sensor applications.

The characterization results of iron

oxide-containing poly(m-anthranilic acid) (P3ANA)–polycaprolactone (PCL) composite nanofibers confirm that blending polymers with different characteristics improves morphological homogeneity and electrical (impedimetric) properties. SEM & EDX-mapping indicates NPs well dispersed in PCL composite nanofibers without bead formation. (Fig.3) Fe2O3 nanoparticles embedded in the polymer matrix hinder cross-linking throughout the network and enhance inter-chain interactions.

Frequency-dependent electrochemical impedance spectroscopy reveals remarkable changes in the percentage of polymer content, particularly in the presence of Fe_2O_3.The modifications in the chemical state of the samples confirmed by the C−O and C=O peaks are analyzed by means of XPS.

The presence of Fe_2O_3 and P3ANA renders an increase in crystallinity in the polymer matrix and brittle-to-ductile transition at the macro-scale. SEM and EDX-mapping indicate that nanoparticles were well dispersed in PCL composite nanofibers without any bead formation.

Conclusions

The incorporation of CNTs into SBS reduces the fiber thickness from a microscale to a nanoscale by an order of magnitude, while simultaneously achieving a transition from a porous to a non-porous and rough morphology. High-resolution scanning electron microscopy (HRSEM) and energy-dispersive X-ray spectroscopy (EDS) support the findings of the thermomechanical analysis, and the mechanism of interaction between CNTs and the SBS tri-block copolymer matrix is elucidated through the determination of the morphology, pi–pi interactions, and the crystallinity of the composite fibers. Even small quantities of CNTs can hinder the crystallization process and improve the mechanical properties of electrospun fibers. This is because CNTs act as nucleation sites for polymer crystallization, resulting in smaller and more uniform crystal sizes. The disappearance of the semi-crystallinity of SBS/PStyr with the inclusion of CNTs (1.25 wt%) further corroborates the retarding effect of CNTs on crystallization. It is hypothesized that CNTs may interfere with the formation of polymer crystals.

The incorporation of iron and carboxylic acid-functionalized polyaniline into PCL enhances the electron-donating ability of the composite material, which in turn increases its conductivity and may induce reversible redox chemistry, enabling its use in electrochemical immunosensors and drug delivery. Homogeneous Fe_2O_3/P3ANA/PCL electrospun composite nanofiber meshes have the potential to be used as skin patches due to the growing interest in magnetic nanocomposites in biomaterials science.

This study demonstrates that the incorporation of Fe_2O_3 and P3ANA allows for the tuning of the morphology and electrical conductivity of the composite nanofibers, which promises their use in a variety of applications. Additionally, as the incorporation of Fe_2O_3 nanoparticles into PCL fibers makes them more prone to cell attachment, PCL nanofibers enriched with iron oxide-P3ANA could be introduced as a scaffold to improve the performance of liver tissue engineering.

References

[1] Sarac, A.S.(2016), Nanofibers of Conjugated Polymers, Pan Stanford

[2] Gurbuz R., Sarac,B.,Soprunyuk V.,Yuece E.,J.Eckert,Ozcan A.,Sarac A.S.,Polym.Adv.Tech. 32,1,248-261(2021)

[3] Gürbüz R., Sarac B.,Soprunyuk V.,Rezvan A.,Yüce E.,Schranz W.,Eckert J.,Ozcan A. , Sarac A.S.,Polym. Adv.Tech.33(12) 3966-3976(2022)

[4] Sarac B., Gürbüz R., Micusik M., Omastova M., Rezvan A.,Yüce E.,Xi L.,Eckert J., Ozcan A.,Sarac A.S., ,Mol. Syst. Des. Eng.8, 911-921(2023)

[5] Huner K.,Sarac B.,Yüce E.,Rezvan A.,Micusik M., Omastova M., Eckert J.,Sarac A.S., Mol. Syst. Des. Eng.,8,394-406(2023)