SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17107
STSM title: Carbon Nanotube /Polybutadiene based stretchable electrospun fibrous composite membranes for advanced textile applications
STSM start and end date: 20/09/2021 to 29/09/2021
Grantee name: Prof.Dr.Abdülkadir Sezai SARAC

PURPOSE OF THE STSM:

Electrospinning is an electrostatic fiber fabrication method that has attracted much attention recently due to its potential for applications in diverse research areas, including smart textiles for health and medical applications. Electrospun polymer composites have obtained widespread attention as biomaterials for designing antimicrobial nanofibrous membranes as a delivery tool for drugs and biomolecules to enhance cell recovery. Electrospinning is used to produce electrocatalysts for hydrogen evolution reactions, enhance thermal conductivity, treat dye-polluted waters, etc.
In terms of production, the specific polymer types, that is, spinnable polymers, as well as solution and processing parameters, significantly affect the fiber morphology. Carbon nanotubes and nanofibers could be added to blends to enhance electrical conductivity, interfacial reinforcement, better micro-crack behavior, friction, and better thermal conductivity. Polybutadiene (PBu) has some critical and potential applications in some biomedical fields showing appealing mechanical properties and chemical stability; this material has no breathability, limiting its biomedical application as a single product. Production of conductive Fibers as carbon nanotube(CNT) containing polymeric composite fiber mats, including PBu, opens the possibility of applications in Smart textiles for health and medical applications.CNT containing polymeric composite fiber mats can contribute to health and medical applications of smart textiles,i.e., produced and characterized fibers can be utilized for surgical implants by coating, where sensing and soft surface is required and development of fiber and textile structures with enhanced breathability and electro-active properties, and in automotive and aeronautic applications i.e., as electro active and interactive nanofibrous sensors in the context of CONTEXT WG1 & WG2. In this STSM, detailed characterization of carbon nanotube /polybutadiene based stretchable electrospun fibrous composite membranes is aimed and planned by X-ray diffraction, FESEM measurements, and frequency-dependent thermomechanical measurements via dynamic mechanical analysis in the presence and absence of cryogenic conditions

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

Controlled polymer content with the components allows to generate homogenous, thermally stable and stretchable bio-composite scaffold, and fibrous membrane scaffolds out of PBu/PEG/CNT composite. We have combined the different properties of PEG with high pore density with the rubber elasticity of PBu and produced electrospun woven fibers with different PEG (PEO)/PBu ratios. In this STSM, the following characterization techniques, i.e., thermomechanical (DMA) measurements, are performed under cryogenic conditions, and XRD, FESEM, EDX measurements are used for the determination of morphology and the crystallinity of the fibers, which is created by the blending of SWCNTfiller in a polymer matrix.

Funded by the Horizon 2020 Framework Programme of the European Union

Frequency-dependent thermomechanical characterization via dynamic mechanical analysis is realized under cryogenic conditions, indicating the pronounced changes in the onset and extent of failure point, and the storage and loss modulus values at the onset are improved. Homogeneously dispersed CNTs in electrospun polybutadiene (PBu) composite elastomeric fibers exhibit distinct physical features such as uniform fiber diameter and improved thermomechanical properties.

Compared to polyethylene and polypropylene i.e., PEG is more sensitive to thermal oxidation. Moreover, the scission of chains during fabrication induces morphological changes reflected in the overall degree of crystallinity. It is an essential biocompatible polymer because of its non-toxicity, nonantigenic activity, and convenience for engineering bio-related nanomaterials by structurally- and temporally-controlled peptide self-assembly.

Polybutadiene (PBu) was one of the first elastomers to be invented and the second-largest volume elastomer currently used in industrial products. Due to its very low vinyl content, it has a shallow glass transition temperature (Tg ~ −90 ^{0}C) and a very high resilience conferring superior performance such as wear resistance, cold resistance, high elasticity, and low friction wet surfaces. PBu has some critical and potential applications in some biomedical fields, particularly in the form of Styrene Butadiene Styrene (SBS) produced via UV polymerization, as well as by electrospinning. Although showing appealing mechanical properties and chemical stability, this material has no breathability, which limits its biomedical application as a single product. During this STSM in Erich Schmid Institute of Materials Science (ESI), Carbon Nanotube Polybutadiene based stretchable electrospun fibrous composite membrane characterizations were successfully accomplished. In addition to X-ray diffraction, FESEM measurements, frequency-dependent thermomechanical characterization via dynamic mechanical analysis under cryogenic conditions are performed, and these results indicated pronounced changes in the onset and failure point, as well as the storage and loss modulus values, are improved, in particular in the presence of of CNTs.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

As a solution for obtaining fiber forms of PBu, rubbery polymer fibers are produced as a blend with poly(ethylene glycol) and polybutadiene. The good solubility of PEG in water and organic solvents, and hydrophilic character, balance the hydrophobic character of PBu, whereas the mechanical flexibility of PBu contributed to the overall mechanical performance of the blend material(Fig.2). The frequency-dependent thermomechanical characterization via dynamic mechanical analysis under cryogenic conditions indicates crystallinity increase, and the storage and loss modulus values are improved, especially in the presence of high amounts of PEO.

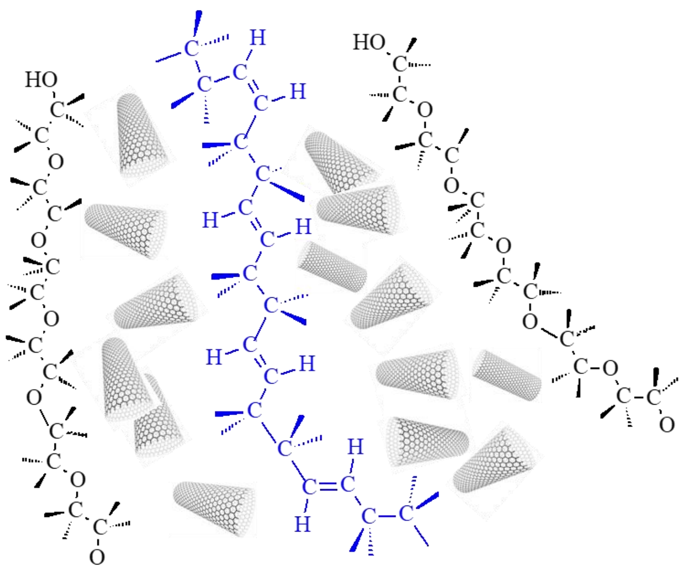


Fig 1 . Scheme of possible structure of PEO/PBu/CNT .

The frequency-dependent thermomechanical analysis showed the notable changes under cryogenic conditions , with the storage and loss modulus values of the onset of melting, in particular when carbon nanotube (CNT) in small amounts (1.25% by wt.%) is present. The dynamic-mechanical behavior of fiber of polybutadiene blend (Fig.1), and the crystallization behaviour was investigated especially at low

temperatures. We report the detailed dynamic mechanical analyses of unvulcanized elastomeric polybutadiene composite fiber obtained by the electrospinning technique under cryogenic conditions . The results indicate that the treatment improves the poor interfacial contact between the CNTs and polymer, which is one of the obstacles for achieving stronger CNT composites.
CNTs is one of the most interesting nanofiller for applications due to their extraordinary properties and large aspect ratio, very small amount of CNTs can have an unusual large influence on the properties of a composite .The Young's modulus and strength of polymer-nantoubes composites should increase with nanotube loading, with a well dispersion and alignment in the matrix, but this assumes that the interfacial contact is sufficient so if there could be a failure might not be due to CNTs pull out.

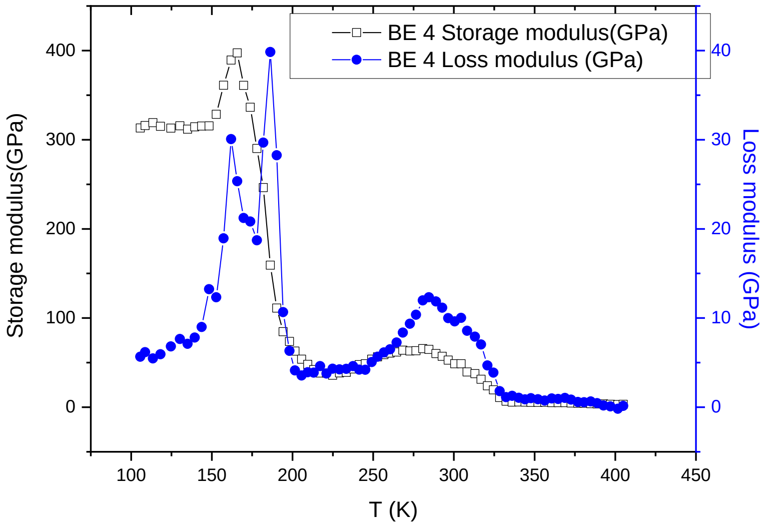
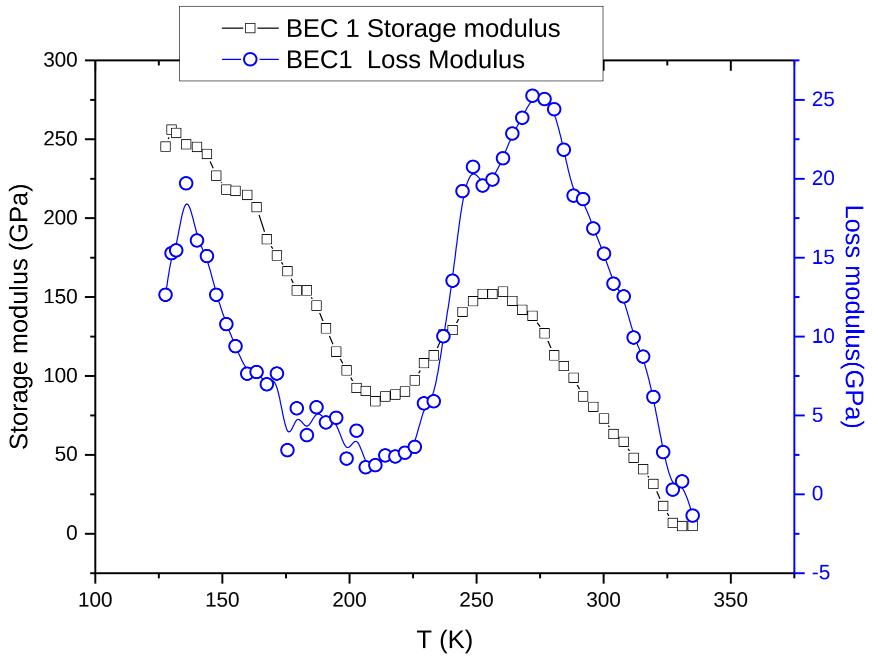
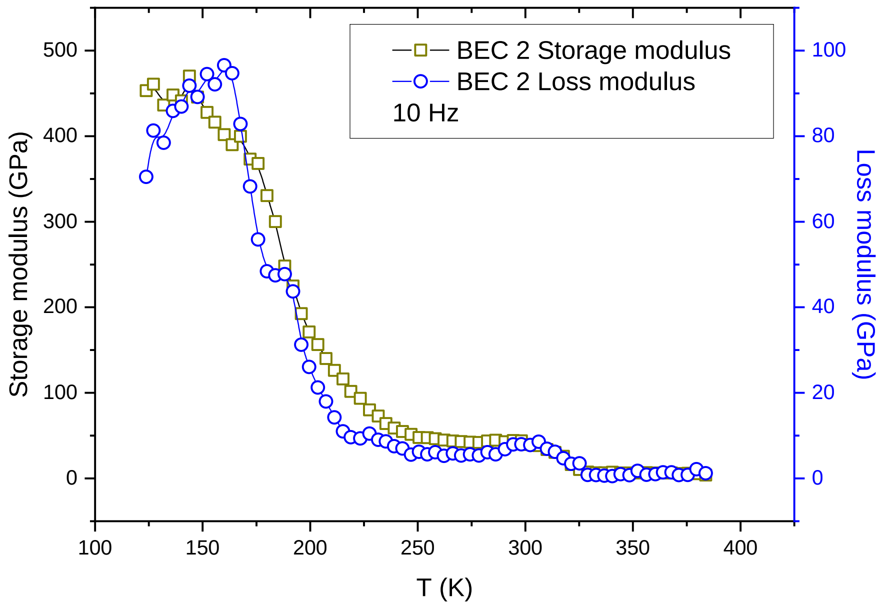


Fig.2. Comparative exemplary graph of storage and loss modulus for BE4 sample

The storage modulus changes with the frequencies is not generally effective in this range of temperature .But in the case of BEC1 where PEO content is lowest the polymer chains in nanocomposites significantly resist against the short-range deformation (high frequencies),but they cannot tolerate the long-time distortion (low frequencies). The storage modulus correlates to the PEO /PBu ratio with low CNT contents,at low temperatures BEC 2 has higher storage modulus compared to BEC 2 but at high temperatures BEC 1 exhibited higher storage modulus indicating the effect of PEO content in the matrix (Fig.3)
Data shows the storage modulus value of PEO/PBu/CNT fiber was increased with the presence of low CNT content at about 270K peak, followed by a tendency to decrease with the increasing of PEO content at low temperatures. Consequently, the storage modulus of CNT/PBu PEO fiber will be increased as similar behaviour was also reported for the multiwalled CNT/ polypropylene composites.
In this study we have used the optimum concentration of CNT and changed PEO/ PBu ratio.It is also observed that the storage modulus was decreased by blending with high PEO (and low PBu) content at about 270K, due to the the interfacial bonding between CNT and polyethyleneoxide might become weaker at higher temperatures.



a



b

Fig.3. Storage and loss modulus values change vs time for different samples at 10Hz (for BEC 1 PEO/PBu ratio is 6.99 (**a**) ,and for BEC 2 this ratio is 3.0(**b**) with the inclusion of CNT)

XRD pattern of pure PEO has two sharp Bragg peaks indicating the semicrystalline nature of polymer . The XRD pattern of a broad hump, according to the literature, indicates an amorphous phase connection with the the intermolecular structure of PBu .
These results demonstrate that the PEO polymer blend fibers shows two-phase morphology, i.e., crystalline and amorphous states(supported by SEM results). To estimate the crystallinity for all samples and resolve the crystalline peaks, a combination of the scattered intensities can be used. In this method, the percentage of the degree of crystallinity (Xc) was obtained from the ratios of the area under the crystalline peak and the corresponding amorphous halos. In order to separate the crystalline and

amorphous peaks, the XRD pattern for all polymer blend compositions are deconvoluted and calculated according to the following equation.

$$X_c = \frac{A_c}{A_c + A_a} \times 100\%$$

where *A*c and *A*a are, respectively, the area under crystalline peaks and amorphous halos. Table 1 shows the center and the full width at half maximum (FWHM) for deconvoluted XRD patterns into Gaussian components for PEO:PBu:CNT polymer blend films.

Comparison of the data and the morphology of fibers (Fig.4) (one representative figure is given) supports the results obtained by other results of characterizations .

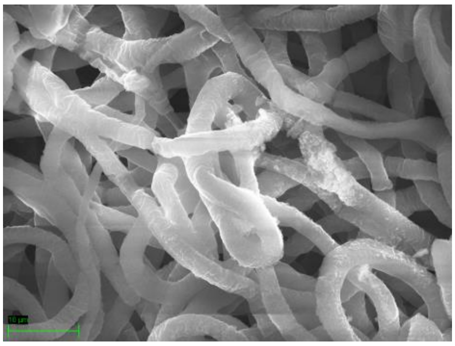


Fig .4 HRSEM picture of BEC 1 as-electrospun(after cryogenic applications) fibers

FUTURE COLLABORATIONS

Carbon nanotubes (CNTs) have impressive mechanical properties by the addition of CNTs helps transform fibers into highly sophisticated, integrated technical textiles, and so the conversion of the textile into a value-added, in the high-tech industry. In this study, we combined the knowledge and experience of ITU and ESI on these specific fibers, which can be an initiation to build up a typical R&D project, specifically developing advanced textile fiber prototypes by producing composite fibers and nanofibers.
We have also realized a meeting with the attendance of research collaborators related to STSM project subject.
Both laboratory groups will continue on the investigation of CNT –Polymer Composite Nanofibers using different combinations and copolymers, including terpolymers. During this period, we collected and obtained prominent data on our results and evaluated them together. The findings led us to develop CNT-Polybutadiene-based composite membrane fibers to be used for smart textile applications. The application of the mentioned techniques certainly improved our knowledge and cooperation. We started to prepare publications on our results as articles in international peer-reviewed journals resulting from this STSM and planning future project preparation. Enhancing our collaborative research activities through the COST CONTEXT action is very much acknowledged.