POLY(PYRROLE) NANOSTRUCTURES BASED ELECTRICALLY CONDUCTING COMPOSITE FIBERS

KIRAN RANA

DEPARTMENT OF TEXTILE AND FIBRE ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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POLY(PYRROLE) NANOSTRUCTURES-BASED ELECTRICALLY CONDUCTING COMPOSITE FIBERS

by

Kiran Rana

Department of Textile and Fibre Engineering

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Dedicated to my Teachers, my Parents

and

Especially to my Supervisors

Prof. Ashwini K. Agrawal and Prof. Manjeet Jassal

CERTIFICATE

This is to certify that the thesis titled "**Poly(pyrrole) nanostructure based electrically conducting composite fibers,"** being submitted by **Ms. Kiran Rana** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis, which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

Dr. Manjeet Jassal
Professor
Department of Textile and Fibre Engineering
Indian Institute of Technology Delhi

Dr. Ashwini K. Agrawal
Professor
Department of Textile and Fibre Engineering
Indian Institute of Technology Delhi

Date:
New Delhi

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Kiran Rana

Department of Textile and Fiber Engineering

Indian Institute of Technology Delhi

ABSTRACT

The advancement of smart and wearable electronic textiles has significantly impacted various industries, including healthcare, sports, defense, and consumer technology. These innovative fabrics integrate electronic functionalities into traditional textiles, enabling applications like real-time health monitoring, adaptive clothing, and interactive fashion. A key challenge in developing smart textiles is achieving flexibility, durability, and efficient electrical conductivity while maintaining the comfort and mechanical properties of conventional fabrics. This study explores the development of electrically conductive fibers by incorporating different morphologies of conducting polymeric nanostructures as fillers into traditional textile fibers. Various fabrication methods, including wet spinning, are examined to enhance fiber performance in terms of conductivity, mechanical strength, and flexibility. The findings highlight the importance of material selection, processing techniques, and structural design in optimizing the electrical and mechanical properties of these fibers. By advancing the integration of conductive materials in textiles, this research contributes to the evolution of next-generation wearable electronics, offering new possibilities for functional, durable, and adaptable smart fabrics.

In the first part of the study, the chemical oxidative method was used for the synthesis of poly(pyrrole) (PPy) nanostructures, i.e., poly(pyrrole) nanoparticles (PPyNPs) and poly(pyrrole) nanotubes (PPyNTs). The PPyNTs showed a 60-90 nm diameter and average length of 8-10 microns. Meanwhile, PPyNPs were formed in clusters. To make them

usable, sonication was carried out. After sonication, the clusters could be broken down, and the size of the NPs was observed to be approximately 100-200 nm in diameter using DLS. The bulk electrical conductivity of PPyNPs and PPyNTs compressed in a pellet form was 17 ± 0.2 and 90.9 ± 0.6 S/cm, respectively.

Electrically conductive composite fibers of nylon 6 (Ny)-poly(pyrrole) nanotubes (PPyNTs) by solution spinning were successfully fabricated. The incorporation of PPyNTs in nylon 6 was found to increase the electrical conductivity of the composite fibres significantly. The high aspect ratio of PPyNTs could provide a good electrically conductive network and show a percolation threshold at a low concentration of ~2 wt% of PPyNTs in the nylon matrix compared to that of PPyNPs. The composite fibers exhibited good DC electrical conductivity of ~0.002 S/cm at only 6 wt% of PPyNTs. The influence of PPyNT concentration on the morphology and physical, chemical, and electrical properties of the fibers have been investigated.

In the next part of the thesis, with the aim of preparing stretchable conducting composite fibres, nylon-6 was replaced with polyurethane. The rheological behavior of polymer solutions plays a crucial role in fabricating composite fibers via solution spinning. This study investigates the influence of poly(pyrrole) (PPy) nanostructures, including PPyNPs and PPyNTs, on the viscoelastic and shear-thinning properties of polyurethane (PU)-based dopes. The dispersion stability of PPy nanostructures in N, N-dimethylformamide (DMF) was optimized using controlled sonication, followed by rheological characterization through steady-state and oscillatory shear measurements. The viscosity of PU solutions

increased significantly with PPyNT incorporation, exhibiting strong shear-thinning behavior due to polymer-filler interactions and the formation of percolated networks at higher concentrations. Frequency sweep experiments demonstrated a transition from liquid-like to solid-like behavior as PPyNT content increased, with crossover points in storage (G′) and loss (G″) moduli shifting towards higher frequencies. In contrast, PPyNP-filled solutions exhibited lower viscosities and minimal shear-thinning, indicating reduced filler interaction and weaker percolation effects. These results provide valuable insights into the processing parameters necessary for optimizing fiber spinnability and structural integrity. The enhanced rheological response of PPyNT-based solutions highlights their potential for developing stretchable, conductive composite fibers suitable for wearable electronic textiles and advanced functional materials.

Polyurethane (PU) and poly(pyrrole) nanostructures were used to fabricate stretchable and flexible composite fibers. Two nanostructures- poly(pyrrole) nanoparticles (PPyNPs) and nanotubes (PPyNTs) were compared as additives in the range of 2 to 12 wt%. The aspect ratio of nanostructures profoundly affected the rheology, spinning behavior, and properties of the resulting fibers. With the same amounts as PPyNPs, the PPyNTs exhibited better spinnability, higher mechanical properties, and significantly greater electrical conductivities. The composite fibers with 12 wt% of PPyNTs showed a high conductivity of 0.21 S/cm compared to 8.6E-8 S/cm with 12 wt% of PPyNPs. Further, the fibers showed high stability in repeated deformations. The fibers may find applications as connecting wires in wearable e-textiles.Thus, using poly(pyrrole) nanotubes, flexible and stretchable composite fibers could be developed by solution spinning.

सारांश

स्मार्ट और पहनने योग्य इलेक्ट्रॉनिक वस्त्रों का विकास कई उद्योगों, जैसे कि स्वास्थ्य देखभाल, खेल, रक्षा और उपभोक्ता प्रौद्योगिकी पर महत्वपूर्ण प्रभाव डाल चुका है। ये नवाचारक वस्त्र पारंपरिक वस्त्रों में इलेक्ट्रॉनिक कार्यक्षमताएँ एकीकृत करते हैं, जो वास्तविक समय में स्वास्थ्य निगरानी, अनुकूलनीय वस्त्रों और इंटरएक्टिव फैशन जैसी अनुप्रयोगों को सक्षम बनाते हैं। स्मार्ट वस्त्रों के विकास में एक प्रमुख चुनौती लचीलापन, स्थायित्व और कुशल विद्युत चालकता प्राप्त करना है, जबकि पारंपरिक वस्त्रों की आरामदायकता और यांत्रिक गुणों को बनाए रखना। इस अध्ययन में पारंपरिक वस्त्रों के रेशों में भराव के रूप में विभिन्न रूपरेखाओं वाले कंडक्टिंग पॉलिमरिक नैनोसंरचनाओं को शामिल करके विद्युत् चालक रेशों का विकास किया गया है। विभिन्न निर्माण विधियों, जिनमें wet spinning शामिल है, का परीक्षण किया गया ताकि रेशों के प्रदर्शन को चालकता, यांत्रिक ताकत और लचीलापन के मामले में सुधारा जा सके। निष्कर्ष यह बताते हैं कि इन रेशों की विद्युत और यांत्रिक गुणों को अनुकूलित करने में सामग्री चयन, प्रसंस्करण तकनीकों और संरचनात्मक डिजाइन का महत्वपूर्ण योगदान है। कंडक्टिव सामग्री के वस्त्रों में एकीकरण को बढ़ावा देते हुए, यह शोध पहनने योग्य इलेक्ट्रॉनिक्स की अगली पीढ़ी के विकास में योगदान करता है, जो कार्यात्मक, टिकाऊ और अनुकूलनीय स्मार्ट वस्त्रों के लिए नई संभावनाएँ प्रस्तुत करता है।

अध्ययन के पहले भाग में, पॉली(पाइरोल) (PPy) नैनोसंरचनाओं, अर्थात् पॉली(पाइरोल) नैनोकण (PPyNPs) और पॉली(पाइरोल) नैनोट्यूब्स (PPyNTs), के संश्लेषण के लिए रासायनिक आक्सीकरण विधि का उपयोग किया गया। PPyNTs का व्यास 60-90 नैनोमीटर था और औसत लंबाई 8-10

माइक्रोन थी। जबकि, PPyNPs गुच्छों के रूप में बने थे। इन्हें उपयोगी बनाने के लिए सोनिकेशन किया गया। सोनिकेशन के बाद, गुच्छों को तोड़ा जा सका, और नैनोकणों का आकार डीएलएस द्वारा लगभग 100-200 नैनोमीटर व्यास के रूप में देखा गया। PPyNPs और PPyNTs की बल्क विद्युत चालकता, जो पैलेट रूप में संकुचित की गई थीं, क्रमशः 17 ± 0.2 और 90.9 ± 0.6 S/cm थी।

नायलॉन 6 (Ny)-पॉली(पाइरोल) नैनोट्यूब्स (PPyNTs) के इलेक्ट्रिकली कंडक्टिव कम्पोजिट रेशों को समाधान स्पिनिंग द्वारा सफलतापूर्वक तैयार किया गया। नायलॉन 6 में PPyNTs के समावेश से कम्पोजिट रेशों की विद्युत चालकता में महत्वपूर्ण वृद्धि देखी गई। PPyNTs का उच्च आयाम अनुपात एक अच्छा विद्युत् चालक नेटवर्क प्रदान कर सकता है और नायलॉन मैट्रिक्स में ~2 wt% PPyNTs की कम सांद्रता पर पर्कोलेशन थ्रेशोल्ड दिखा सकता है, जो PPyNPs की तुलना में है। कम्पोजिट रेशों ने केवल 6 wt% PPyNTs पर ~0.002 S/cm की अच्छी डीसी विद्युत चालकता दिखाई। रेशों की संरचना और भौतिक, रासायनिक और विद्युत गुणों पर PPyNTs सांद्रता का प्रभाव जांचा गया।

अगले भाग में, स्ट्रेचेबल कंडक्टिव कम्पोजिट रेशों को तैयार करने के उद्देश्य से, नायलॉन-6 को पॉलीयुरेथेन (PU) से प्रतिस्थापित किया गया। पॉलिमर समाधानों का रियोलॉजिकल व्यवहार कम्पोजिट रेशों को समाधान स्पिनिंग के माध्यम से तैयार करने में महत्वपूर्ण भूमिका निभाता है। इस अध्ययन में, पॉली(पाइरोल) (PPy) नैनोसंरचनाओं, जिनमें PPyNPs और PPyNTs शामिल हैं, के प्रभाव का विश्लेषण पॉलीयुरेथेन (PU)-आधारित डोप्स के विस्कोएलास्टिक और शीयर-थिनिंग गुणों पर किया गया। N, N-डाइमेथिलफॉर्माइड (DMF) में PPy नैनोसंरचनाओं के डिस्पर्शन स्थिरता को नियंत्रित सोनिकेशन द्वारा अनुकूलित किया गया, इसके बाद स्थिर-राज्य और आक्षेपक शीयर माप द्वारा रियोलॉजिकल गुणांक का विश्लेषण किया गया। PU समाधानों की विस्कोसिटी में PPyNTs

के समावेश से महत्वपूर्ण वृद्धि देखी गई, जो पॉलिमर-फिलर इंटरैक्शन और उच्च सांद्रताओं पर पर्कोलेटेड नेटवर्क के निर्माण के कारण शीयर-थिनिंग व्यवहार का प्रदर्शन करते हैं। आवृत्ति स्वीप प्रयोगों ने दिखाया कि जैसे-जैसे PPyNTs की सांद्रता बढ़ी, समाधान में तरल जैसे से ठोस जैसे व्यवहार में बदलाव आया, जिसमें भंडारण (G′) और हानि (G″) मापांक के क्रॉसओवर पॉइंट उच्च आवृत्तियों की ओर स्थानांतरित हो गए। इसके विपरीत, PPyNPs-आधारित समाधानों में कम विस्कोसिटी और न्यूनतम शीयर-थिनिंग था, जो कम फिलर इंटरैक्शन और कमजोर पर्कोलेशन प्रभाव को दर्शाता है। ये परिणाम महत्वपूर्ण हैं क्योंकि ये रेशा स्पिनबिलिटी और संरचनात्मक अखंडता को अनुकूलित करने के लिए प्रसंस्करण पैरामीटर पर महत्वपूर्ण दृष्टिकोण प्रदान करते हैं। PPyNT-आधारित समाधानों का बढ़ा हुआ रियोलॉजिकल प्रतिक्रिया पहनने योग्य इलेक्ट्रॉनिक वस्त्रों और उन्नत कार्यात्मक सामग्रियों के लिए स्ट्रेचेबल, कंडक्टिव कम्पोजिट रेशों के विकास में उनके संभावित उपयोग को उजागर करता है।

पॉलीयुरेथेन (PU) और पॉली(पाइरोल) नैनोसंरचनाओं का उपयोग करके स्ट्रेचेबल और लचीले कम्पोजिट रेशों को तैयार किया गया। दो नैनोसंरचनाओं - पॉली(पाइरोल) नैनोकण (PPyNPs) और नैनोट्यूब्स (PPyNTs) को 2 से 12 wt% के अनुपात में ऐडिटिव्स के रूप में तुलना की गई। नैनोसंरचनाओं का आयाम अनुपात रियोलॉजी, स्पिनिंग व्यवहार और परिणामी रेशों के गुणों पर गहरा प्रभाव डालता है। समान मात्रा में PPyNPs के साथ, PPyNTs ने बेहतर स्पिनबिलिटी, उच्च यांत्रिक गुण और महत्वपूर्ण रूप से उच्च विद्युत चालकता दिखाई। 12 wt% PPyNTs वाले कम्पोजिट रेशों में 0.21 S/cm की उच्च चालकता दिखी, जबकि 12 wt% PPyNPs के साथ 8.6E-8 S/cm थी। इसके

अतिरिक्त, रेशों ने बार-बार विकृति में उच्च स्थिरता दिखाई। इन रेशों का उपयोग पहनने योग्य ई-टेक्सटाइल्स में कनेक्टिंग वायर के रूप में किया जा सकता है।

इस प्रकार, PPyNTs का उपयोग करके लचीले और स्ट्रेचेबल कम्पोजिट रेशों को समाधान स्पिनिंग द्वारा तैयार किया जा सकता है।

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Symbols/Abbreviations	Expanded form/Term
R	Resistance
V	Voltage
I	Current
ρ	Resistivity
L	Length
σ	Conductivity
R_s	Sheet resistance
T	thickness
R_v	Volume resistance
$\sigma(p)$	electrical conductivity at (p) filler concentration
σ_0	proportionality constant
p	Filler concentration
p_c	Percolation threshold
t	exponent depends upon filler properties and system dimensionality for 2D systems; the critical exponent varied from 1.1 to 1.3, and for 3D systems, it varied from 1.6 to 2.0
fi	volume fraction of polymer matrix and conductive filler

σi	conductivity of matrix and filler
σeff	effective conductivity of the composite
A	geometric factor (depends upon filler shape and system's dimensionality)
s	critical exponent depends upon filler shape and system dimensionality
EMT	effective medium theory
CNT	Carbon nanotubes
S/cm	Siemens/cm
wt%	Weight %
MWCNT	Multiwall carbon nanotubes
SWCNT	Single-wall carbon nanotubes
PVA	Polyvinyl acetate
PVDF	Polyvinylidene fluoride
PU	Polyurethane
MDI	4,4-methylene bis(phenyl isocyanate)
PANI	Polyaniline
CNF	Carbon nanofibers
PAN	Polyacrylonitrile
CB	Carbon black
BZCB	benzoxazine-modified carbon black
ABCB	4-Aminobenzoyl-Functionalized Carbon Black
LC	Liquid crystals

rGO	Reduced graphene oxide
GNPs	graphene nanoplatelets
TPU	Thermoplastic polyurethane
AgNPs	Silver nanoparticles
PEG	Polyethylene glycol
PPy	Poly(pyrrole)
PPyNPs	Poly(pyrrole) nanoparticles
PPyNTs	Poly(pyrrole) nanotubes
MO	Methyl orange
NTs	Nanotubes
NWs	Nanowires
V_2O_5	Vanadium pentoxide
PEDOT: PSS	Poly(3,4-ethylene-dioxythiophene) polystyrene sulfonate
FE-SEM	Field emission scanning electron microscopy
EDX	Energy-dispersive X-ray spectroscopy
TEM	Transmission electron microscope
FTIR	Fourier transform infrared spectroscopy
XPS	X-ray photoelectron spectroscopy
VDP	Van der Pauw's method
SMU	Source measurement unit
TGA	Thermogravimetric analyzer
MFI	Melt flow index

Ny	Nylon 6
IV	Current-voltage
DMF	N N’-dimethylformamide
N6	Nylon 6