

**SYNTHESIS, CHARACTERIZATION AND EVALUATION OF
POLYPYRROLE BASED NANOCOMPOSITES FOR
ELECTROMAGNETIC SHIELDING APPLICATION**

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ELECTROMAGNETIC SHIELDING APPLICATION**

by

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Submitted

in fulfilment of the requirements of degree of Doctor of Philosophy

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Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “**Synthesis, Characterization and Evaluation of Polypyrrole Based Nanocomposites for Electromagnetic Shielding Application**” being submitted by **Mrs. Pragati Gahlout** to the Indian Institute of Technology Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Mrs. Pragati Gahlout** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

The objective of the present thesis is to design and develop processable conducting polymer i.e. polypyrrole and its composites filled with conducting fillers such as multi walled carbon nanotubes/or graphene for EMI shielding application. In addition polypyrrole impregnated conducting fabrics and polypyrrole filled thermoplastic polyurethane composites were also prepared for microwave shielding application. These conducting polymers and their composites were characterized thoroughly for structural (XRD, FTIR, Raman), thermal (TGA), morphological (SEM, HR-TEM), electrical (two probe and four probe conductivity) properties. Evaluation of EMI shielding was carried out in the frequency range of 8.2-12.4 GHz (X-band) and 12.4-18.0 GHz (Ku or P-band).

The thesis is divided in seven chapters. Chapter 1, gives an idea about the increasing threat of electromagnetic interference. It throws light on the basic concept of shielding, suppression of electromagnetic interference (EMI), need of material for shielding, methods to measure EMI shielding properties and electromagnetic attributes of shielding effectiveness. This chapter also thoroughly describes the concept of π -conjugated polymers (intrinsically conducting polymers), with a special focus on polypyrrole (PPy). This chapter gives an idea about different synthesis routes for preparing doped conducting polymers and their composites and blends.

Chapter 2, describe the method used for the synthesis of conducting polymer, composites, blends, fabrics. This chapter also describes the characterization techniques and their working principles. Chapter 3, describe optimization parameters for the synthesis of highly conducting polypyrrole for efficient EMI shielding application. The effect of reaction parameters i.e. oxidant concentration (ferric chloride), dopant concentration and nature of dopant (sodium lauryl sulphate [SLS], sodium dodecyl benzene sulphonate [SDBS], lithiosulphoisophthalic acid [LiSiPA] and naphthalene disulphonic acid [NDSA]) on the conductivity and electromagnetic shielding

properties of polypyrrole (PPy) was investigated. The conductivity and shielding effectiveness of PPy obtained was found to be dependent on the concentration of oxidant and nature of dopant and it was highest when the molar ratio of pyrrole: oxidant: dopant was 1:2:1. Polypyrrole synthesized using optimized conditions and SLS as dopant had highest conductivity (42 S/cm) and electromagnetic shielding effectiveness i.e. an average of -110 dB in the X-band [8.2-12.4 GHz] which is the highest value ever reported for the PPy synthesized by chemical oxidative polymerization. Absorption dominant shielding mechanism makes PPy a suitable candidate for radar absorbing materials. The shielding properties are very close to the conventional metals with an additional advantage that the primary mechanism of shielding is absorption dominant.

Chapter 4, describes the synthesis of highly conducting composites of polypyrrole using conducting fillers [Multiwalled carbon nanotubes (MWCNT) and graphene]. Although polypyrrole prepared in presence of SLS as a dopant and MWCNT as a filler did not show much difference in EMI shielding due to higher limiting value of VNA but PPy prepared in presence of LiSiPA and MWCNT show a great increase in conductivity (25 S/cm to 52 S/cm) as well as EMI shielding properties (-75 dB to -108 dB) upon incorporation of 0-5 weight percent of MWCNTs. PPy prepared in the presence of graphene as a filler also exhibit an increase in conductivity and EMI shielding effectiveness.

In chapter 5, synthesis methods of conducting blends of thermoplastic polyurethane with PPy/MWCNT has been discussed. Composite of polyurethane filled with polypyrrole/MWCNT (PPy) were prepared by solution blending using DMF as solvent. The composites were characterized by XRD and Raman spectroscopy. The effect PPy/MWCNTs on electrical conductivity and microwave shielding efficiency of TPU was investigated to evaluate their potential as an effective EMI shield. These composites show absorption dominated total shielding effectiveness (SE_T) up to -46 dB in 8.2-12.4 GHz range suggesting their utility for microwave absorbers.

In chapter 6, an attempt was made to prepare wearable conducting fabrics by impregnation of PPy over the surface of different fabrics by in-situ polymerization of pyrrole using optimized conditions. The idea of impregnation of PPy over fabrics was adopted to combine conducting properties of PPy with good mechanical strength, flexibility and stitch-ability of fabrics. For this purpose four different fabrics (cotton, cotton lycra, nylon, polyester) were selected. Cotton lycra impregnated with polypyrrole showed EMI shielding efficiency of -18.7 dB in X- band at a thickness of 0.3mm. Summary of the thesis and main conclusions are given in chapter 7. Suggestions and future scope is also included. The effect of dielectric or magnetic particles on EMI shielding of PPy is included in Appendix.

एब्स्ट्रैक्ट

वर्तमान थीसिस का उद्देश्य प्रक्रियात्मक संचालन बहुलक डिजाइन और विकसित करना है यानी पाली पाइरोल और कंपोजिट फिलर से भरे इसके चालित जैसे कि ईएमआई शील्डिंग एप्लिकेशन के लिए बहु दीवार वाले कार्बन नैनोट्यूब / या ग्राफेन । इसके अलावा पाली पाइरोल इम्प्रेग्नेटेड संचालन फैब्रिक और पाली पाइरोल भरे थर्मोप्लास्टिक polyurethane कंपोजिट भी माइक्रोवेव शील्ड एप्लिकेशन के लिए तैयार किए गए थे। ये संचालन पॉलिमर और उनके कंपोजिट्स संरचनात्मक (एक्सआरडी, एफटीआईआर, रमन), थर्मल (टीजीए), मॉर्फोलॉजिकल (एसईएम, एचआर-टीईएम), विद्युत (दो प्रोब और चार प्रोब चालकता) गुणों के लिए पूरी तरह से चित्रित किए गए थे। ईएमआई शील्ड का मूल्यांकन 8.2-12.4 गीगाहर्ट्ज (एक्स-बैंड) और 12.4-18.0 गीगाहर्ट्ज (के यू या पी-बैंड) की आवृत्ति रेंज में किया गया था।

थीसिस सात अध्यायों में बांटा गया है। अध्याय 1, विद्युत चुम्बकीय हस्तक्षेप के बढ़ते खतरे के बारे में एक विचार देता है। यह सील्डिंग की बुनियादी अवधारणा, विद्युत चुम्बकीय व्यतीकरण (ईएमआई) के दमन, सील्डिंग के लिए सामग्री की आवश्यकता, ईएमआई सील्डिंग गुणों को मापने के तरीके और सील्डिंग प्रभावशीलता के विद्युत चुम्बकीय गुणों पर प्रकाश डालता है। यह अध्याय पाली पाइरोल (PPy) पर विशेष ध्यान देने के साथ, π -संयुग्मित बहुलक (आंतरिक रूप से बहुलक संचालन) की अवधारणा का भी वर्णन करता है। यह अध्याय विभिन्न प्रकार के संश्लेषण मार्गों के बारे में एक विचार देता है जो डोपड कंडक्टिंग पॉलिमर और उनके कंपोजिट्स और मिश्रणों की तैयारी के लिए करते हैं।

अध्याय 2, बहुलक, कंपोजिट्स, मिश्रण, फैब्रिक आयोजित करने के संश्लेषण के लिए इस्तेमाल विधि का वर्णन करें। यह अध्याय विशेषता तकनीकों और उनके कार्य सिद्धांतों का भी वर्णन करता है। अध्याय 3, कुशल ईएमआई शील्डिंग अनुप्रयोग के लिए अत्यधिक संचालन पाली पाइरोल के संश्लेषण के लिए अनुकूलन पैरामीटर का वर्णन करें। प्रतिक्रिया पैरामीटर यानी ऑक्सीडेंट concentration (फेरिक क्लोराइड), डोपेंट एकाग्रता और डोपेंट की प्रकृति (सोडियम लॉरिल सल्फेट [एसएलएस], सोडियम डोडसील बेंजीन सल्फोनेट [एसडीबीएस], लिथियोसुलफोइसोफथैलिक एसिड [लीएसआईपीए] और नेफथालेन डिसल्फोनिक एसिड [एनडीएसए]) पर प्रभाव पाली पाइरोल (पीपीआई) की चालकता और विद्युत चुम्बकीय शील्ड गुणों की जांच की गई थी। प्राप्त पीपीआई की चालकता और शील्ड प्रभावशीलता ऑक्सीडेंट और डोपेंट की प्रकृति की एकाग्रता पर निर्भर थी और यह सबसे अधिक था जब पायरोल के दाढ़ अनुपात: ऑक्सीडेंट: डोपेंट 1: 2: 1 था। पॉलीपीरोल ऑप्टिमाइज्ड स्थितियों और एसएलएस के रूप में संश्लेषित किया गया है क्योंकि डोपेंट में उच्चतम चालकता (42 एस / सेमी) और विद्युत चुम्बकीय शील्ड प्रभावशीलता यानी एक्स-बैंड [8.2-12.4 गीगाहर्ट्ज] में -110 डीबी का औसत होता है जो कि पीपीआई के लिए सबसे ज्यादा मूल्य है रासायनिक ऑक्सीडेंटिव बहुलकरण द्वारा संश्लेषित। अवशोषण प्रभावशाली शील्ड तंत्र पीपी को रडार अवशोषक सामग्री के लिए एक उपयुक्त उम्मीदवार बनाता है। शील्ड गुण पारंपरिक धातुओं के बहुत करीब हैं जो अतिरिक्त लाभ के साथ हैं कि शील्ड का प्राथमिक तंत्र अवशोषण प्रभावी है।

अध्याय 4, fillers आयोजित करने का उपयोग कर पाली पाइरोल के अत्यधिक संचालन कंपोजिट्स के संश्लेषण का वर्णन करता है [Multiwalled कार्बन नैनोट्यूब (MWCNT) और graphene]। हालांकि एक भराव के रूप में एसएलएस की उपस्थिति में तैयार पॉलीपीरोल और एफपीए के उच्च सीमित मूल्य के कारण ईएमआई शील्ड में बहुत अंतर नहीं दिखता है, लेकिन लीएसआईपीए और एमडब्ल्यूसीएनटी की उपस्थिति में तैयार पीपीआई चालकता में बड़ी वृद्धि दिखाती है (25 एस / सेमी 52 एस / सेमी तक) साथ ही ईएमआई शील्ड गुण (-75 डीबी से -108 डीबी) MWCNTs के 0-5 वजन प्रतिशत

को शामिल करने पर। एक भराव के रूप में graphene की उपस्थिति में तैयार पीपीआई भी चालकता और ईएमआई संरक्षण प्रभावशीलता में वृद्धि प्रदर्शित करता है।

अध्याय 5 में, पीपी / MWCNT के साथ थर्मोप्लास्टिक पॉलीयूरेथेन के मिश्रणों के संचालन के संश्लेषण विधियों पर चर्चा की गई है। पॉलीपीरॉल / MWCNT (पीपीआई) से भरे पॉलीयूरेथेन के समग्र को डीएलएफ का उपयोग विलायक के रूप में समाधान मिश्रण द्वारा तैयार किया गया था। कंपोजिट्स को एक्सआरडी और रमन स्पेक्ट्रोस्कोपी द्वारा विशेषता थी। टीपीयू की विद्युत चालकता और माइक्रोवेव शील्डिंग दक्षता पर प्रभाव पीपी / MWCNT की जांच प्रभावी ईएमआई शील्ड के रूप में उनकी क्षमता का मूल्यांकन करने के लिए की गई थी। ये कंपोजिट्स शोषण को कुल शील्ड प्रभावशीलता (एसईटी) पर निर्भर करते हैं -46 डीबी तक 8.2-12.4 गीगाहर्ट्ज रेंज में माइक्रोवेव अवशोषक के लिए उनकी उपयोगिता का सुझाव देते हैं।

अध्याय 6 में, अनुकूल परिस्थितियों का उपयोग करते हुए पायरोल के इन-सीटू पॉलीमराइजेशन द्वारा विभिन्न कपड़ों की सतह पर पीपीवाई के प्रजनन द्वारा पहनने योग्य घटाने वाले फैब्रिक तैयार करने का प्रयास किया गया था। अच्छी यांत्रिक शक्ति, लचीलापन और फैब्रिक की स्थिरता के साथ पीपीआई के गुणों को संयोजित करने के लिए कपड़ों पर पीपीआई के प्रजनन का विचार अपनाया गया था। इस उद्देश्य के लिए चार अलग-अलग फैब्रिक (कपास, सूती लाइक्रा, नायलॉन, पॉलिएस्टर) का चयन किया गया था। पॉलीपीरॉल के साथ लगाए गए कपास लाइक्रा ने 0.3 मिमी की मोटाई पर एक्स-बैंड में -18.7 डीबी की ईएमआई शील्डिंग दक्षता दिखायी। थीसिस और मुख्य निष्कर्षों का सारांश अध्याय 7 में दिया गया है। सुझाव और भविष्य के दायरे भी शामिल हैं। पीपीआई की ईएमआई शील्ड पर ढांकता हुआ या चुंबकीय कणों का प्रभाव परिशिष्ट में शामिल है।

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LIST OF ABBREVIATION AND SYMBOLS

EMI	Electromagnetic interference
SE	Shielding effectiveness
SE _T	Total shielding effectiveness
SE _A	Shielding effectiveness due to absorption
SE _R	Shielding effectiveness due to reflection
SE _M	Shielding effectiveness due to multiple internal reflection
dB	Decible
EM	Electromagnetic
MIRs	Multiple internal reflections
SNA	Scalar network analyser
VNA	Vector network analyser
R	Reflectance
T	Transmittance
A	Absorbance
CPs	Conducting polymers
ICPs	Intrinsically conducting polymers
PPy	Polypyrrole
PTH	Polythiophene
PANI	Polyaniline

PPV	Poly(p-phenylene vinylene)
CNTs	Carbon nanotubes
MWCNTs	Multi wall carbon nanotubes
SWCNTs	Single wall carbon nanotube
SLS	Sodium lauryl sulphate
SDBS	Sodium dodecyl benzene sulphonate
NDSA	Naphthalene disulphonic acid
LiSiPA	Lithiosulphoisophthalic acid
DMF	Dimethyl formamide
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
HR-TEM	High Resolution Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
μ	Magnetic permeability
σ	Electrical conductivity
ε	Dielectric permittivity
λ	Wavelength
δ	Skin depth

2θ	Diffraction angle
V	Voltage
I	Current