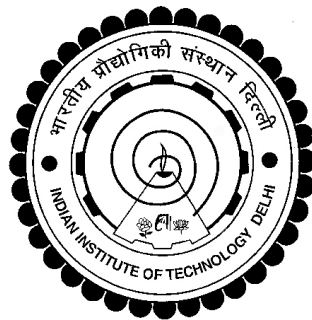


**STUDIES ON HIGH PERFORMANCE COMPOSITES BASED
ON POLY(ETHER KETONE) FOR ELECTROMAGNETIC
INTERFERENCE SHIELDING APPLICATIONS**

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ON POLY(ETHER KETONE) FOR ELECTROMAGNETIC
INTERFERENCE SHIELDING APPLICATIONS**

by

SAMPAT SINGH CHAUHAN

Department of Materials Science and Engineering

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

October 2018

Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “**Studies on high performance composites based on poly(ether ketone) for electromagnetic interference shielding applications**” being submitted by **Mr. Sampat Singh Chauhan** to Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Sampat Singh Chauhan 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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Sampat Singh Chauhan

ABSTRACT

This work is dedicated to the development of high performance EMI shields which exhibit effective shielding performance as well as other physical properties, especially in applications regarding aerospace, automobiles and next generation portable and wearable electronic devices. For this purpose, composites were prepared using poly(ether ketone) as matrix and conducting (MWCNTs, CNFs) and dielectric (BaTiO_3) materials as fillers. Multiwalled carbon nanotubes (MWCNTs, aspect ratio ~ 158), carbon nanofibers (CNFs, aspect ratio ~ 200), barium titanate (BaTiO_3 , average particle size ~ 8.6 microns) were melt-blended with poly(ether ketone) (PEK) in a twin screw extruder equipped with fractional mixing element that allow the fabrication of composites containing up to 10 wt% MWCNTs, 20 wt% of CNFs and 50 wt% of BaTiO_3 .

Morphological characterization of PEK/MWCNT composites was done using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-Ray diffraction. A uniform dispersion of MWCNTs was observed in all the samples. Thermal characterization of PEK/MWCNT composites was done using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) whereas mechanical strength was investigated by using tensile, flexural and impact testing. The percent crystallinity increased up to 1 wt% followed by slight decrease whereas thermal stability increased with increase in MWCNTs loading ($T_{\text{onset}} \sim 581$ °C at 10 wt% loading). Tensile modulus and tensile strength increased by 39% (4370 MPa to 6084 MPa) and 48% (80.4 MPa to 119 MPa) respectively relative to PEK matrix whereas flexural modulus and flexural strength increased by 27% (4163 MPa to 5304 MPa) and 19% (179 MPa to 213 MPa) respectively at 10 wt% loading. Improvement in the mechanical properties was also investigated by Raman spectroscopy. Melt and solid state rheological response of composites were investigated using parallel plate rheometer and dynamic mechanical analysis respectively. Incorporation of carbon nanotubes in the polymer matrix

resulted in an increase of storage modulus of PEK corresponding to the elastic response of composites.

Improved and efficient dispersion of nanotubes in the PEK matrix is reflected in the formation of an electrically conductive network at a very low percolation threshold value of 1.28 wt% of MWCNTs with the highest conductivity of $\sim 10^{-3}$ S/cm at 10 wt% loading. EMI shielding was measured in all the available four bands [X band-8.2-12.4 GHz, Ku band-12.4-18 GHz, K band-18-26.5 GHz and Ka-band i.e. 26.5-40 GHz]. Highest total shielding effectiveness (SE_T) of -40 dB with very high shielding effectiveness due to absorption ($SE_A \sim -36$ dB) was observed at 10 wt% loading of MWCNTs in PEK matrix in the frequency range of 26.5-40 GHz (Ka-band).

Microstructural behavior in terms of dispersion in PEK/carbon nanofibres [CNFs] was assessed by using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and wide-angle X-ray diffractometer. Reinforcement effect due to the homogenous dispersion of carbon nanofibers is responsible for enhanced thermal, mechanical and thermomechanical properties. The initial decomposition temperature of PEK increased by 27 °C i.e. from 554 °C for neat PEK to 581 °C at 20 wt% loading of CNFs. At 20 wt% loading of CNFs, tensile strength and modulus increased by 39% (80.4 MPa to 112 MPa) and 65% (4.3 GPa to 7.2 GPa) whereas flexural strength and modulus increased by 14% (179 MPa to 205 MPa) and 33% (4163 MPa to 5536 MPa) respectively. Dynamic mechanical analysis (DMA) shows that room temperature storage modulus increases from 2099 MPa for neat PEK to 2752 for PEKF-20.

Neat PEK is insulating due to the low value of electrical conductivity ($\sim 10^{-13}$ S/cm). However, incorporation of CNFs up to 20 wt% leads to a significant increase in electrical conductivity and reaches a value of 1.83×10^{-3} S/cm. Highest value of total shielding effectiveness achieved at 20 wt% loading in different bands was -14 dB (X band), -17 dB (Ku band), -30 dB (K band), -40 dB (Ka-

band). Shielding effectiveness due to absorption in Ka-band ($SE_A \sim -37$ dB) has been found to be twelve times greater than that of shielding effectiveness due to reflection ($SE_R \sim -3$ dB).

The effect of dielectric filler ($BaTiO_3$, 0-50 wt%) on thermal, mechanical, thermo-mechanical, electrical conductivity (σ), dielectric properties and EMI shielding effectiveness (SE) of PEK was also investigated. SEM studies show that $BaTiO_3$ particles were uniformly distributed in the PEK matrix up to 40 wt% loading followed by the formation of agglomerates at higher loading (50 wt%). Rockwell hardness and density increased up to 40 wt% loading followed by a decrease at 50 wt% loading. Dynamic mechanical analysis (DMA) revealed that storage modulus increases with increase in $BaTiO_3$ loading with a maximum value of 3192 MPa at 40 wt% compared to 2099 MPa for neat PEK. Dielectric constant of composites measured in the frequency range of 8.2-12.4 GHz increased ~3 times upon incorporation of 50 wt% of $BaTiO_3$. This increment in dielectric constant is reflected in improved electromagnetic shielding properties as loading of dielectric filler ($BaTiO_3$) increases. Total shielding effectiveness of -11 dB (~ 92% attenuation) at a loading of 50 wt% of $BaTiO_3$ justifies the use of these composites for suppression of EM radiations. Summary and conclusions are given at the end.

सारांश

यह काम उच्च प्रदर्शन ईएमआई ढाल के विकास के लिए समर्पित है जो प्रभावी ढाल प्रदर्शन के साथ-साथ अन्य भौतिक गुणों, विशेष रूप से एयरोस्पेस, ऑटोमोबाइल और अगली पीढ़ी पोर्टेबल और पहनने योग्य इलेक्ट्रॉनिक उपकरणों के अनुप्रयोगों में प्रदर्शित करता है। इस उद्देश्य के लिए, मैट्रिक्स के रूप में पॉली (ईथर केटोन) का उपयोग करके कंपोजिट तैयार किए गए थे और (एमडब्ल्यूसीएनटीएस, सीएनएफ) और डाइलेक्ट्रिक (BaTiO_3) सामग्री को फिल्स के रूप में संचालित किया गया था। मल्टीवाल्ड कार्बन नैनोट्यूब (एमडब्ल्यूसीएनटीएस, पहलू अनुपात ~ 158), कार्बन नैनोफाइबर (सीएनएफ, पहलू अनुपात ~ 200), बेरियम टाइटेनेट (BaTiO_3 , औसत कण आकार ~ 8.6 माइक्रोन) पॉली (ईथर केटोन) (पीईके) के साथ मिश्रित होते थे। जुड़वां पेंच एक्सड्रडर फ्रॅक्शनल मिश्रण तत्व से लैस है जो 10 wt% एमडब्ल्यूसीएनटीएस, 20 wt% सीएनएफ और BaTiO_3 50 wt% युक्त कंपोजिट्स के निर्माण की अनुमति देता है।

पीईके/एमडब्ल्यूसीएनटीएस कंपोजिट्स का मोर्फोलॉजिकल कैरेक्चरेशन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम) और एक्स-रे विवर्तन का उपयोग करके किया गया था। सभी नमूनों में एमडब्ल्यूसीएनटीएस का एक समान फैलाव पाया गया था। पीईके / एमडब्ल्यूसीएनटीएस कंपोजिट्स का थर्मल कैरेक्चरिज़ेशन डिफरेंशियल स्कैनिंग कैलोरीमेट्री (डीएससी) और थर्मोग्रामिमेंट्रिक विश्लेषण (टीजीए) का उपयोग करके किया गया था, जबकि तन्यता, लचीला और प्रभाव परीक्षण का उपयोग

करके यांत्रिक शक्ति की जांच की गई थी। प्रतिशत क्रिस्टलीटी 1 wt% तक बढ़ी है, इसके बाद मामूली कमी आई है जबकि थर्मल स्थिरता एमडब्ल्यूसीएनटीएस लोडिंग में वृद्धि के साथ बढ़ी है (Tonset~ 581 °C 10 wt% लोडिंग पर)। तन्यता मॉड्यूलस और तन्यता की शक्ति क्रमशः पीईके मैट्रिक्स के सापेक्ष 39% (4370 एमपीए से 6084 एमपीए) और 48% (80.4 एमपीए से 119 एमपीए) तक बढ़ी है जबकि लचीला मॉड्यूलस और लचीला शक्ति 27% (4163 एमपीए से 5304 एमपीए) और 19% तक बढ़ी है (179 एमपीए से 213 एमपीए) क्रमशः 10 wt% लोडिंग पर। यांत्रिक गुणों में सुधार की भी रमन स्पेक्ट्रोस्कोपी द्वारा जांच की गई थी। मिश्रित और ठोस राज्य रियोलॉजिकल प्रतिक्रिया क्रमशः समांतर प्लेट रिमोट और गतिशील यांत्रिक विश्लेषण का उपयोग करके जांच की गई। पॉलिमर मैट्रिक्स में कार्बन नैनोट्यूब के सम्मिलन के परिणामस्वरूप कंपोजिट्स की लोचदार प्रतिक्रिया के अनुरूप पीईके के स्टोरेज मॉड्यूलस में वृद्धि हुई।

पीईके मैट्रिक्स में नैनोट्यूब का बेहतर और कुशल फैलाव एक विद्युत प्रवाहकीय नेटवर्क के गठन में प्रतिबिंबित होता है जो 1.28 wt% एमडब्ल्यूसीएनटीएस के बहुत कम परिसंचरण मूल्य पर $\sim 10^{-3}$ एस / सेमी की उच्चतम चालकता 10 wt% लोडिंग पर होता है। ईएमआई शील्डिंग सभी उपलब्ध चार बैंडों [एक्स बैंड- 8.2-12.4 गीगाहर्ट्ज, क्यू बैंड -12.4-18 गीगाहर्ट्ज, के बैंड -18-26.5 गीगाहर्ट्ज और का-बैंड i.e. 26.5-40 गीगाहर्ट्ज] में मापा गया था। अवशोषण (एसईए ~ -36 डीबी) के कारण बहुत अधिक ढाल प्रभावशीलता के साथ -40 डीबी की उच्चतम कुल ढाल प्रभावशीलता (एसईटी) पीईके मैट्रिक्स में एमडब्ल्यूसीएनटी की 10 wt% लोडिंग पर 26.5-40 गीगाहर्ट्ज (का- बैंड)।

पीईके / कार्बन नैनोफिबर्स [सीएनएफ] में फैलाव के संदर्भ में सूक्ष्म संरचनात्मक व्यवहार का मूल्यांकन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम) और वाइड-एंगल एक्स-रे डिफ्रैक्टोमीटर का उपयोग करके किया गया था। कार्बन नैनोफाइबर के समरूप फैलाव के कारण सुदृढीकरण प्रभाव थर्मल, मैकेनिकल और थर्मोमैकेनिकल गुणों के लिए ज़िम्मेदार है। पीईके का प्रारंभिक अपघटन तापमान 27 °C से बढ़कर 554 °C से साफ पीईके के लिए 581 °C तक बढ़ गया, जो सीएनएफ की 20 wt% लोडिंग पर था। सीएनएफ की 20 wt% लोडिंग, तन्यता ताकत और मॉड्यूलस में 39% (80.4 एमपीए से 112 एमपीए) और 65% (4.3 जीपीए से 7.2 जीपीए) की वृद्धि हुई जबकि लचीला शक्ति और मॉड्यूलस 14% (179 एमपीए से 205 एमपीए) तक बढ़ गया और क्रमशः 33% (4163 एमपीए से 5536 एमपीए)। डायनामिक मैकेनिकल विश्लेषण (डीएमए) से पता चलता है कि पीईकेएफ-20 के लिए साफ पीईके के लिए 2052 एमपीए से कमरे का तापमान भंडारण मॉड्यूलस बढ़ता है।

स्वच्छ पीईके विद्युत चालकता ($\sim 10^{-13}$ एस / सेमी) के कम मूल्य के कारण इन्सुलेट कर रहा है। हालांकि, 20 wt% तक सीएनएफ के निगमन में विद्युत चालकता में उल्लेखनीय वृद्धि हुई है और 1.83×10^{-3} एस / सेमी के मूल्य तक पहुंच जाती है। विभिन्न बैंडों में 20 wt% लोडिंग पर प्राप्त कुल ढाल प्रभावशीलता का उच्चतम मूल्य -14 डीबी (एक्स बैंड), -17 डीबी (क्यू बैंड), -30 डीबी (के बैंड), -40 डीबी (का बैंड) था। का-बैंड (एसईए ~ -37 डीबी) में अवशोषण के कारण प्रभावशीलता को बचाने से प्रतिबिंब (एसईआर ~ -3 डीबी) के कारण ढाल प्रभावशीलता की तुलना में बारह गुना अधिक पाया गया है।

थर्मल, मैकेनिकल, थर्मो-मैकेनिकल, इलेक्ट्रिकल चालकता (σ), ढांकता हुआ गुण और पीईके की ईएमआई शील्डिंग प्रभावशीलता (एसई) पर ढांकता हुआ भराव (BaTiO_3 , 0-50 wt%) का प्रभाव भी जांच की गई। एसईएम अध्ययन से पता चलता है कि BaTiO_3 कणों को समान रूप से पीईके मैट्रिक्स में 40 wt% लोडिंग तक वितरित किया गया था, इसके बाद उच्च लोडिंग (50 wt%) पर ागग्लोमेरेट्स के गठन के बाद। रॉकवेल कठोरता और घनत्व 40 wt% लोडिंग तक बढ़ गया, इसके बाद 50 wt% लोडिंग में कमी आई। डायनेमिक मैकेनिकल विश्लेषण (डीएमए) ने खुलासा किया कि स्वच्छ पीईके के लिए 2099 एमपीए की तुलना में 40 wt% पर 3192 एमपी के अधिकतम मूल्य के साथ BaTiO_3 लोडिंग में वृद्धि के साथ भंडारण मॉड्यूलस बढ़ता है। 8.2-12.4 गीगाहर्ट्ज की फ्रीक्वेंसी रेंज में मापा गया कंपोजिट्स का डाइलेक्ट्रिक स्थिरता BaTiO_3 के 50 wt% के निगमन पर ~ 3 गुना बढ़ गया। ढांकता हुआ स्थिरता में यह वृद्धि बेहतर इलेक्ट्रोमैग्नेटिक ढाल गुणों में दिखाई देती है क्योंकि ढांकता हुआ भराव (BaTiO_3) बढ़ता है। BaTiO_3 के 50 wt% की लोडिंग पर -11 डीबी (~ 92% क्षीणन) की कुल सुरक्षा प्रभावशीलता ईएम विकिरणों के दमन के लिए इन कंपोजिट्स के उपयोग को उचित ठहराती है। अंत में सारांश और निष्कर्ष दिए गए हैं।

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List of symbols

T_g	Glass transition temperature
T_m	Melting temperature
T_c	Crystallization temperature
T	Temperature in K
ΔH_m	Melting enthalpy
ΔH_m°	Crystalline melting enthalpy of 100 % crystalline PEK
T_{max}	Temperature at which maximum degradation occurs
T_{onset}	Onset temperature of degradation
θ	Bragg diffraction angle
$Tan \delta$	Tangent delta
E	Young's modulus
E'	Storage modulus
E''	Loss modulus
G'	Melt storage modulus
G''	Melt loss modulus
η^*	complex viscosity
μ	Permeability
σ	Conductivity
δ	Skin depth
X_c	Crystallinity
R	Resistance
ε'	Real dielectric permittivity
ε''	Imaginary dielectric permittivity

List of Abbreviations

<i>PEK</i>	Poly(ether ketone)
<i>MWCNT</i>	Multi-walled carbon nanotube
<i>SWCNT</i>	Single-walled carbon nanotube
<i>CNF</i>	Carbon nanofiber
<i>CVD</i>	Chemical vapor deposition
<i>DSC</i>	Differential scanning calorimetry
<i>TGA</i>	Thermogravimetric analysis
<i>DMA</i>	Dynamical mechanical analysis
<i>WAXD</i>	Wide angle X-ray diffraction analysis
<i>SEM</i>	Scanning electron microscopy
<i>TEM</i>	Transmission electron microscopy
<i>VNA</i>	Vector network analyzer
<i>EMI</i>	Electromagnetic interference
<i>SE_R</i>	Reflection loss
<i>SE_A</i>	Absorption loss
<i>SE_M</i>	Multiple reflections
<i>SE_T</i>	Shielding effectiveness
<i>BT</i>	Barium titanate
<i>DPCs</i>	Dielectric polymer composites
<i>CPCs</i>	Conducting polymer composites
<i>HPPCs</i>	High performance polymer composites