

**DEVELOPMENT OF FUNCTIONAL POLYPROPYLENE RANDOM
COPOLYMER COMPOSITES FOR ELECTROMAGNETIC
INTERFERENCE SHIELDING APPLICATIONS**

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**CENTRE FOR POLYMER SCIENCE AND ENGINEERING
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COPOLYMER COMPOSITES FOR ELECTROMAGNETIC
INTERFERENCE SHIELDING APPLICATIONS**

by

PAWAN VERMA

Centre for Polymer Science and Engineering

Submitted

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

to the



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Dedicated to my parents

CERTIFICATE

This is to certify that the thesis entitled, “**Development of functional polypropylene random copolymer composites for electromagnetic interference shielding applications**” being submitted by **Mr. Pawan Verma** 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 him. **Mr. Pawan Verma** 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 rapid growth of electronic gadgets has led to electromagnetic interference (EMI) as an off-shoot. EMI is a novel kind of pollution which disturbs the normal operation of electronic appliances and adversely affects living/biological species. This work is dedicated to prepare a light weight material which can be used as shield for electromagnetic interference (EMI). For this purpose, nanocomposites were prepared using polypropylene random copolymer as matrix and combination of conducting (MWCNTs) or/and magnetic (Fe_2O_3) or/and dielectric (BaTiO_3) fillers. Two types of multi walled carbon nanotubes (MWCNTs) viz. long (l-MWCNT, aspect ratio ~1356-1937) and short (s-MWCNTs, aspect ratio ~158) were melt-blended with polypropylene random copolymer (PPCP) in a micro twin screw extruder with melt recirculation provision, that allow the formation of composites containing upto 15 wt % MWCNTs. For evaluating the effect of BaTiO_3 /or Fe_2O_3 , we chose the composite samples having an optimum combination of mechanical, electrical and EMI shielding i.e. sample s-PPCP-10 having 10 wt% short length MWCNTs in polymer matrix. Several samples were prepared by mixing s-PPCP-10 with 50 phr of BaTiO_3 /or Fe_2O_3 in varying ratio 4:1, 1:1 and 1:4.

The thesis has been divided into seven chapters. **Chapter 1** deals with the brief introduction of electromagnetic interference (EMI) and material requirements for EMI shielding followed by comprehensive literature review on various types of carbon fillers which are most commonly blended with polymer matrices for EMI shielding properties.

The detailed methods used for the preparation of MWCNTs, Fe_2O_3 , BaTiO_3 , PPCP/MWCNTs and PPCP/hybrid composites are given in **chapter 2** of thesis. The characterization techniques and evaluation of the properties of PPCP composites are also described in this chapter.

The results on morphological and thermal characterization of PPCP/MWCNTs nanocomposites are given in **chapter 3**. Morphological characterization of PPCP and its nanocomposites 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 PPCP in presence of MWCNTs was done using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Chapter 4 discuss the effect of s/l-MWCNTs on mechanical and rheological response of PPCP matrix. Melt and solid state rheological response of nanocomposites was investigated using parallel plate rheometer and dynamic mechanical analysis respectively while mechanical stability of nanocomposites was investigated by tensile test. Tensile results of composites reveal improvement in modulus and strength. PPCP samples having 15 wt% l-MWCNT or s-MWCNT loaded composites show 52% and 60% improvement in modulus respectively and 20% and 18% improvement in strength over neat PPCP. Additionally incorporation of carbon nanotubes in the polymer matrix resulted in an increases of storage modulus and loss modulus of PPCP corresponding to elastic and viscous response of nanocomposites respectively.

Chapter 5 discuss the effect of MWCNTs loading on electrical conductivity (σ), dielectric properties and EMI shielding effectiveness (SE) of PPCP. The EMI shielding properties of PPCP/MWCNT composites was measured in the frequency range of 8.2-18 GHz (X & Ku band). PPCP/MWCNTs composites display good electrical, dielectric and electromagnetic interference shielding properties and very low percolation threshold (i.e. 0.55 and 1.07 wt% for l-MWCNT and s-MWCNT respectively).

The impact of conducting (MWCNTs), magnetic (Fe_2O_3) and dielectric (BaTiO_3) fillers on the properties of PPCP are highlighted in **chapter 6**. In order to evaluate the effect of

these fillers, we kept the concentration of s-MWCNT constant i.e. 10 wt % in all the composition while iron oxide and barium titanate were blended in varying ratio (as 1:1, 1:4 & 4:1) but the total weight of iron oxide and barium titanate was kept constant as 50 phr. The dc conductivity of hybrid composites reveals that at fixed MWCNT content (i.e. 10 wt%), no significant change was observed in conductivity with iron oxide and barium titanate loading and typical attainment of dc conductivity value of $\sim 10^{-3}$ S/cm along with electromagnetic interference (EMI) shielding effectiveness (SE) value of -38 dB (>99.99% attenuation) in the composite having barium titanate and iron oxide in the ratio 1:4.

Chapter 7 summarises all the results and includes conclusions. Exciting results obtained during the course of this work especially EMI shielding properties at higher loading could be addressed in the future studies. There is a need to demonstrate the practical utility and commercial viability of such light weight as EMI shielding materials.

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List of symbols

T_g	Glass transition temperature
T_m	Melting temperature
T_c	Crystallization temperature
T	Temperature in K
R	Cooling rate.
ΔH_m	Melting enthalpy
ΔH_m°	Crystalline melting enthalpy of 100 % crystalline PP
ΔT	Super cooled temperature
T_{onset}	Onset temperature of crystallization
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
n	Avrami exponent
k	Avrami rate constant
X_t	Relative crystallinity
$t_{1/2}$	Half time
G	Linear growth rate
T_m°	Equilibrium melting temperature
R_v	Resistance
e	Dielectric permittivity

List of Abbreviations

<i>PPCP</i>	Polypropylene random copolymer
<i>SWCNT</i>	Single walled carbon nanotubes
<i>MWCNT</i>	Multi walled carbon nanotubes
<i>CVD</i>	Chemical vapor deposition
<i>DSC</i>	Differential scanning calorimetry
<i>TGA</i>	Thermogravimetric analysis
<i>PLM</i>	Polarized light microscopy
<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>BA</i>	Barium titanate
<i>FA</i>	Iron oxide