

**STUDIES ON TOUGHENING OF BIOBASED POLYAMIDE  
410 AND ITS MWCNT FILLED NANOCOMPOSITES**

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410 AND ITS MWCNT FILLED NANOCOMPOSITES**

*by*

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*Submitted*

*in fulfilment of the requirements of the degree of Doctor of Philosophy*

*to the*



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**October 2022**

# CERTIFICATE

This is to certify that the thesis entitled, “**Studies on Toughening of Biobased Polyamide 410 and Its MWCNT Filled Nanocomposites**” being submitted by Mr. Saroj Kumar Samantaray 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. Samantaray 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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*Saroj Kumar Samantaray*

# Abstract

The microstructural, thermomechanical, and quasistatic mechanical properties of biobased polyamide 410 (PA410)/poly(octane-co-ethylene)-g-maleic anhydride (POE-g-MA) blends with the impact toughener in the composition range of 0–20 wt. % have been investigated, with an aim to overcome the poor notch and strain sensitivity of PA410. A remarkably substantial increase, i.e., ~15-fold enhancement, in the impact strength of the PA410/POE-g-MA blends leading to ultra-toughening of PA410 accompanied by a significant increase in tensile strain at breaking is achieved though the elastic modulus ( $E$ ) and yield strength ( $\sigma$ ) decreased with impact modifier content. The interdependence of impact toughness, ductility ratio, and domain size of the dispersed rubber phase in the PA 410/POE-g-MA blends could successfully be established vis-à-vis the mechanistic role of interparticle distance. Scanning electron microscopy showing domain coalescence of the soft elastomeric POE phase thus reiterated the pivotal role of interdomain distance and domain size in influencing the toughening mechanism of PA 410/POE-g-MA blends.

The sol-gel or viscous-elastic transitions of the toughened blends have been systematically discussed in the framework of melt rheology as assessed on a parallel plate rheometer set-up in small amplitude oscillatory shear mode and solid state dynamic mechanical relaxation measurements. A direct correlation between the gel point (estimated from the cross-over of frequency-independent loss tangent curves) and the ultra-toughness could be established vis-a-vis its corroboration from the morphology of the impact-failed surfaces. The study establishes a qualitative correlation between ultra-toughening of polyamide 410 to that parameter based on relaxation dynamics measurements using melt rheology and solid-state dynamic responses conforming to the principles of gelation rheology.

The influence of elastomeric poly (octene-co-ethylene) on the crystallization of polyamide 410 in PA-410/POE-g-MA blends was systematically analysed using a non-isothermal crystallization kinetics approach. A novel power-law criterion was employed to characterize the crystallization regimes (primary and secondary) as a function of cooling rate to understand the nature of crystal arrangement vis-a-vis various kinetic models proposed by Avrami, Jeziorny (modified Avrami method), Ozawa and Liu-Mo. The POE phase acted as a weak nucleating agent for PA 410. The effect of elastomer on crystallization rate constant remained almost unchanged regardless of the blend composition. This insensitivity is attributed to (1) the nucleating effect of POE-g-MA (because of resemblance in the molecular scheme) and (2) the hindrance effect through the formation of an interfacial network; these two effects nearly offset one another.

The equivalence in strain-rate dependent fracture toughness of toughened biobased polyamide 410 blends under high-strain conditions as in Izod impact toughness and low strain conditions as in essential work of fracture (EWF) assessment is discussed in this work. An escalation of ~57% in resistance to crack initiation ( $w_e$ ) (EWF parameter) and an increase of ~356% Izod impact strength confirms the semi-ductile to ductile transition in the range of 10-15 wt.% of elastomer loading. The isotropic responses, i.e., strain-rate independent fracture-toughness of the blends, have indicated three factors (a) toughness originating from shear yielding/banding or craze bridging of dispersed elastomer domain, (b) gradual reduction in matrix stiffness and strength with greater extent of plastic deformation and (c) crack tip-blunting based fracture work to be responsible behind toughening of the blends.

The blends with 15 wt.% POE-g-MA loading showed optimized toughness-to-stiffness ratio. To address the challenges like embrittlement (reduction in ductility) in conducting polymer nanocomposite, polypropylene-multi wall carbon nanotube (PP-MWCNT) masterbatch was reinforced to the toughened blend system while keeping constant elastomeric

content. The polymer nanocomposites fabricated by the masterbatch dilution technique were characterized for their structural, thermal, morphological, rheological, dynamic mechanical, mechanical and electrical conductivity behaviours. The localization and migration of MWCNT induced rheological percolated network and its influence on solid state relaxation dynamics, electrical conductivity and EMI shielding performances was established.

This work conceptually demonstrates the interdependence of morphological, rheological and fracture behaviour of toughened bio-based polyamide 410 that would not only ensure reduction in the strain rate and notch sensitivity but also pave the way to design a fracture-resistant and durable class of polyamide compounds with much less dependency on fossil fuels. The outcomes of developed interfacial compatibilized flexible conducting nanocomposite may be potentially a promising material for functional EMI shielding applications where flexibility and light weigh aspects are critically sought.

## सार

बायोबेड पॉलियामाइड 410 (पीए410)/पॉली (ऑक्टेन-को-एथिलीन)-जी-मैलिक एनहाइड्राइड (पीओई-जी-एमए) के माइक्रोस्ट्रक्चरल, थर्मोमेकेनिकल और कासिस्टेटिक मैकेनिकल गुण 0-20 की संरचना रेंज में इम्पैक्ट टफनर के साथ मिश्रित होते हैं। डब्ल्यूटी PA410 की खराब पायदान और तनाव संवेदनशीलता को दूर करने के उद्देश्य से % की जांच की गई है। उल्लेखनीय रूप से पर्याप्त वृद्धि, यानी, PA410 / POE-g-MA मिश्रणों की प्रभाव शक्ति में 15-गुना वृद्धि, PA410 के अति-सख्त की ओर ले जाती है, साथ ही टूटने पर तन्यता तनाव में उल्लेखनीय वृद्धि प्राप्त होती है, हालांकि लोचदार मापांक प्राप्त होता है (ई) और उपज शक्ति (σ) प्रभाव संशोधक सामग्री के साथ घट गई। पीए 410/पीओई-जी-एमए मिश्रणों में प्रभाव की कठोरता, लचीलापन अनुपात, और फैले हुए रबर चरण के डोमेन आकार की अन्योन्याश्रयता को इंटरपार्टिकल दूरी की यंत्रवत भूमिका की तुलना में सफलतापूर्वक स्थापित किया जा सकता है। सॉफ्ट इलास्टोमेरिक पीओई चरण के डोमेन सहसंयोजन दिखाते हुए स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी ने पीए 410/पीओई-जी-एमए मिश्रणों के सख्त तंत्र को प्रभावित करने में इंटरडोमेन दूरी और डोमेन आकार की महत्वपूर्ण भूमिका को दोहराया।

कड़े मिश्रणों के सोल-जेल या चिपचिपा-लोचदार संक्रमणों को पिघले हुए रियोलॉजी के ढांचे में व्यवस्थित रूप से चर्चा की गई है, जैसा कि छोटे आयाम थरथरानवाला कतरनी मोड और ठोस राज्य गतिशील यांत्रिक विश्राम माप में समानांतर प्लेट रियोमीटर सेट-अप पर मूल्यांकन किया गया है। जेल बिंदु (आवृत्ति-स्वतंत्र हानि स्पशरिखा वक्रों के क्रॉस-ओवर से अनुमानित) और अल्ट्रा-कूरता के बीच एक सीधा संबंध प्रभाव-विफल सतहों के आकारिकी से इसकी पुष्टि के साथ स्थापित किया जा सकता है। अध्ययन में पॉलीमाइड 410 के अल्ट्रा-टफनिंग के बीच उस पैरामीटर के बीच गुणात्मक सहसंबंध स्थापित किया गया है, जो पिघले रियोलॉजी और सॉलिड-स्टेट डायनेमिक रिस्पॉन्स का उपयोग करके रिलैक्सेशन डायनेमिक्स मापन पर आधारित है, जो जेलेशन रियोलॉजी के सिद्धांतों के अनुरूप है।

PA-410/POE-g-MA मिश्रणों में पॉलियामाइड 410 के क्रिस्टलीकरण पर इलास्टोमेरिक पॉली (ऑक्टीन-को-एथिलीन) के प्रभाव का गैर-इज़ोटेर्मल क्रिस्टलीकरण कैनेटीक्स दृष्टिकोण का उपयोग करके व्यवस्थित रूप से विश्लेषण किया गया था। अवरामी, जेज़ियोर्नी (संशोधित अवरामी विधि) द्वारा प्रस्तावित विभिन्न गतिज मॉडलों की तुलना में क्रिस्टल व्यवस्था की प्रकृति को समझने के लिए शीतलन दर के एक कार्य के रूप में क्रिस्टलीकरण व्यवस्थाओं (प्राथमिक और माध्यमिक) को चिह्नित करने के लिए एक उपन्यास शक्ति-कानून मानदंड को नियोजित किया गया था। ओज़ावा और लियू-मो। पीओई चरण ने पीए 410 के लिए एक कमजोर न्यूक्लियेटिंग एजेंट के रूप में काम किया। क्रिस्टलीकरण दर स्थिर पर इलास्टोमेर का प्रभाव मिश्रण संरचना की परवाह किए बिना लगभग अपरिवर्तित रहा। इस असंवेदनशीलता को (1) POE-g-MA (आणविक योजना में समानता के कारण) के न्यूक्लियेटिंग प्रभाव और (2) एक इंटरफेसियल नेटवर्क के गठन के माध्यम से बाधा प्रभाव के लिए जिम्मेदार ठहराया जाता है; ये दो प्रभाव लगभग एक दूसरे को ऑफसेट करते हैं।

इस काम में फ्रैक्चर (ईडब्ल्यूएफ) मूल्यांकन के आवश्यक कार्य के रूप में इज़ोड प्रभाव क्रूरता और कम तनाव की स्थिति के रूप में उच्च तनाव स्थितियों के तहत कठोर बायोबेड पॉलियामाइड 410 मिश्रणों की तनाव-दर निर्भर फ्रैक्चर कठोरता में समानता पर चर्चा की गई है। क्रैक दीक्षा (हम) (ईडब्ल्यूएफ पैरामीटर) के प्रतिरोध में 57% की वृद्धि और 356% इज़ोड प्रभाव शक्ति की वृद्धि, इलास्टोमेर लोडिंग के 10-15 wt.% की सीमा में अर्ध-नमनीय से नमनीय संक्रमण की पुष्टि करती है। आइसोट्रोपिक प्रतिक्रियाएं, यानी, मिश्रणों की तनाव-दर स्वतंत्र फ्रैक्चर-क्रूरता, ने तीन कारकों का संकेत दिया है (ए) कतरनी उपज / बैडिंग या बिखरे हुए इलास्टोमेर डोमेन के क्रेज ब्रिजिंग से उत्पन्न होने वाली कठोरता, (बी) मैट्रिक्स कठोरता और ताकत में क्रमिक कमी के साथ प्लास्टिक विरूपण की अधिक सीमा और (सी) मिश्रणों के सख्त होने के पीछे जिम्मेदार होने के लिए क्रैक टिप-ब्लॉटिंग आधारित फ्रैक्चर कार्य।

15 wt.% POE-g-MA लोडिंग के साथ मिश्रणों ने अनुकूलित कठोरता-से-कठोरता अनुपात दिखाया। पॉलिमर नैनोकम्पोजिट के संचालन में एम्ब्रिटलमेंट (लचीलापन में कमी) जैसी चुनौतियों का समाधान करने के लिए, पॉलीप्रोपाइलीन-मल्टी वॉल कार्बन नैनोट्यूब (पीपी-एमडब्ल्यूसीएनटी) मास्टरबैच को निरंतर इलास्टोमेरिक सामग्री रखते हुए कड़े मिश्रण प्रणाली के लिए प्रबलित किया गया था। मास्टरबैच तनुकरण तकनीक द्वारा निर्मित बहुलक नैनोकंपोजिट्स को उनके संरचनात्मक, तापीय, रूपात्मक, रियोलॉजिकल, गतिशील यांत्रिक, यांत्रिक और विद्युत चालकता व्यवहार के लिए विशेषता थी। MWCNT प्रेरित रियोलॉजिकल परकोलेटेड नेटवर्क का स्थानीयकरण और माइग्रेशन और सॉलिड स्टेट रिलैक्सेशन डायनेमिक्स, इलेक्ट्रिकल कंडक्टिविटी और ईएमआई परिरक्षण प्रदर्शन पर इसका प्रभाव स्थापित किया गया था।

यह कार्य अवधारणात्मक रूप से कठोर जैव-आधारित पॉलियामाइड 410 के रूपात्मक, रियोलॉजिकल और फ्रैक्चर व्यवहार की अन्योन्याश्रयता को प्रदर्शित करता है जो न केवल तनाव दर और पायदान संवेदनशीलता में कमी सुनिश्चित करेगा बल्कि पॉलीमाइड यौगिकों के फ्रैक्चर-प्रतिरोधी और टिकाऊ वर्ग को डिजाइन करने का मार्ग प्रशस्त करेगा। जीवाश्म ईंधन पर बहुत कम निर्भरता के साथ। विकसित इंटरफेसियल कंपैटिबिलाइज्ड फ्लेक्सिबल कंडक्टिंग नैनोकम्पोजिट के परिणाम संभावित रूप से कार्यात्मक ईएमआई परिरक्षण अनुप्रयोगों के लिए एक आशाजनक सामग्री हो सकते हैं जहां लचीलेपन और हल्के वजन के पहलुओं की गंभीर रूप से मांग की जाती है।

# Contents

<b>Certificate</b>	i
<b>Acknowledgements</b>	ii-iii
<b>Abstract</b>	iv-ix
<b>Contents</b>	x-xiv
<b>List of Figures</b>	xv-xx
<b>List of Tables</b>	xxi-xxii
<b>List of Abbreviations and symbols</b>	xxiii-xxx
<b>1. Introduction and literature survey</b>	<b>1-34</b>
1.1. Introduction	1
1.2. Elastomer induced toughening mechanism	6
1.2.1. Elastomer domain size and its influence on toughening	8
1.2.2. Toughening mechanism	11
1.2.3. Elastomer influence on melt rheology and crystallization behavior	13
1.2.3.1. Melt rheology of toughened polyamide blends	13
1.2.3.2. Crystallization behavior of blends	15
1.2.4. Fracture behavior of the toughened blends	17
1.2.4.1. Essential work of fracture theory	19
1.3. Multiwall carbon nanotube filled polyamide composites	23
1.4. Motivation	29
1.5. Objective of the thesis	31
1.6. Format of thesis	32
<b>2. Experimental: materials and methods</b>	<b>35-43</b>
2.1. Raw materials	35
2.2. Preparation of PA 410/POE-g-MA blends	35

2.3.Fabrication of nanocomposites	37
2.4.Thermal characterisation	37
2.4.1. Differential scanning calorimetry (DSC) measurements	37
2.4.2. Thermogravimetric analysis (TGA)	38
2.5.Morphological characterisation	38
2.5.1. Scanning electron microscopy (SEM)	38
2.5.2. Lateral force mode atomic force microscopy (AFM)	39
2.5.3. Transmission electron microscopy (TEM)	39
2.6. Structural characterization	39
2.7.Rheological characterization	40
2.8.Mechanical (Quasistatic) and Thermomechanical (Dynamic) Properties	40
2.9.Fracture behavior of blends	41
2.9.1. Essential work of fracture	41
2.9.2. Crack opening displacement (COD)	42
2.10. Electrical conductivity measurements	43
2.11. EMI Shielding performance	43
<b>3. Studies on PA 410/POE-g-MA blends: morphology, mechanical properties, rheological and thermo-mechanical analysis</b>	<b>44-76</b>
3.1.Thermal characterization	44
3.2.Morphological characteristics	46
3.3.Mechanical response of the blends	48
3.4.Domain size–ductility–toughness interdependence	53
3.5.Failure surface morphology	56
3.6.Rheological behaviour of the blends	59
3.6.1. Complex viscosity	59

3.6.2.	Storage and loss modulus	61
3.6.3.	Damping behavior and Phase angle transition (van Gorp–Palmen plot)	65
3.6.4.	Phase compatibility (Han Plot)	66
3.6.5.	Gel point	67
3.6.6.	Gel point and ultra-toughening relationship	69
3.7.	Dynamic mechanical analysis (DMA) of the blends	72
3.8.	Summary	75
<b>4.</b>	<b>Dynamic crystallization kinetics of PA 410/POE-g-MA blends</b>	<b>77-104</b>
4.1.	FT-IR analysis of blends	77
4.2.	Exothermic Crystalline Curves at Different Cooling Rates	78
4.3.	Nucleation Activity and Activation Energy	89
4.4.	Modified Avrami equation (Jeziorny method)	93
4.5.	Ozawa Analysis	98
4.6.	Liu and Mo Analysis	99
4.7.	Summary	103
<b>5.</b>	<b>Assessment of fracture toughness of the blends and relaxation behavior in cyclic Tensile mode</b>	<b>105-130</b>
5.1.	Essential work of fracture	105
5.1.1.	Load –Displacement curve	105
5.1.2.	Specific work of fracture	108
5.2.	Crack opening displacement (COD)	112
5.3.	Uniaxial cyclic tensile responses	116
5.4.	Thermo-mechanical relaxation	125
5.5.	Summary	129

<b>6. Melt and solid-state viscoelasticity, conductivity and EMI shielding</b>	<b>131-165</b>
<b>performances of toughened PA 410/PP-MWCNT nanocomposites</b>	
6.1. Thermal properties of the nanocomposites	131
6.2. Structural characterization	133
6.2.1. 2D wide angle X-ray diffraction (WAXD)	133
6.2.2. Raman spectroscopy	136
6.3. Morphology of the nanocomposites	137
6.3.1. Field Emission Scanning Electron Microscope (FESEM) micrographs	137
6.3.2. High resolution transmission electron microscopy (HR-TEM) images	140
6.4. Melt rheology of the nanocomposites	141
6.4.1. Amplitude sweep	141
6.4.2. Small amplitude oscillatory sweep (SAOS)	143
6.4.2.1. Storage and loss modulus	143
6.4.2.2. Loss tangent and phase angle	146
6.4.2.3. Complex viscosity and Cole-Cole plot	147
6.4.2.4. Gel point	148
6.5. Solid state relaxation of nanocomposites	150
6.6. Electrical conductivity and EMI shielding performance of nanocomposites	154
6.6.1. DC conductivity	154
6.6.2. EMI Shielding performance of nanocomposites	156
6.7. Mechanical properties of nanocomposites	161
6.8. Summary	164
<b>7. Conclusion and future Scope</b>	<b>166-169</b>
7.1. Conclusions of the thesis	166
7.2. Future scope	169

**Reference**

**170-188**

**8. Publications and biography**

## List of Figures

<i>Figure No.</i>	<i>Description</i>	<i>Page No.</i>
<b>Fig. 1.1</b>	Structure of polyamide 66 [5]	2
<b>Fig. 1.2</b>	Structure of polyamide 410 [9]	4
<b>Fig. 1.3</b>	Synthesis route of PA 410 and PA 66 [9]	4
<b>Fig. 1.4</b>	(a) Glass transition and melting temperature of polyamides and (b) moisture uptake of different polymers [9]	5
<b>Fig. 1.5</b>	Interfacial reaction between the compatibilized elastomer and polyamide	7
<b>Fig. 1.6</b>	(a) Schematic of interparticle distance and domain diameter [5], and (b) notched impact strength as function of weight average domain diameter [38]	10
<b>Fig. 1.7</b>	Morphology–impact–toughness correlations as a function of POE-g-GMA content [42]	11
<b>Fig. 1.8</b>	Toughening mechanism during impact loading [45]	13
<b>Fig. 1.9</b>	Schematic of DENT specimen and fracture process in EWF [34]	20
<b>Fig. 1.10</b>	Impact strength and EWF parameter variation with domain size in PA 56/POE-g-GMA blends [42]	22
<b>Fig. 1.11</b>	Comparison of pristine and masterbatch dilution in PA 410 matrix [7]	24
<b>Fig. 1.12</b>	Tensile failure in PA 12/PP-MWCNT nanocomposites (through masterbatch dilution route) [115]	24
<b>Fig. 1.13</b>	Possible morphology of CPNs for electrical applications	26
<b>Fig. 1.14</b>	(a) Schematic of EMI shielding process [157] and (b) shielding efficiency variation with material thickness [155]	29

<b>Fig. 2.1</b>	Extrusion Temperature Profile (in °C)	36
<b>Fig. 2.2</b>	Temperature Profile (in °C) Injection Moulding Machine	36
<b>Fig. 2.3</b>	Schematic of lateral force mode AFM	39
<b>Fig. 2.4</b>	Schematic representation of double-edge-notch-tension (DENT) specimen	42
<b>Fig. 3.1</b>	DSC (a) melting endotherms on second heating, (b) crystalline exotherms, and (c) degradation temperature profile (TGA) of PA410/POE-g-MA	45
<b>Fig. 3.2</b>	Etched (cryo-fractured) scanning electron microscopy (SEM) micrographs of PA410/POE-g-MA blends	47
<b>Fig. 3.3</b>	Lateral force mode AFM images of PA410/POE-g-MA blends	48
<b>Fig. 3.4</b>	(a) Stress (s) versus strain (%) of blends, (b) tensile modulus and ultimate tensile strength, (c) flexural modulus and strength, and (d) impact energy and impact strength to the Young's modulus ratio as a function of POE-g-MA content (wt. %).	49
<b>Fig. 3.5</b>	Theoretical model for (a) elastic modulus and (b) yield stress as a function of the POE-g-MA volume fraction.	52
<b>Fig. 3.6</b>	Domain size–ductility–toughness interdependence	55
<b>Fig. 3.7</b>	Impact-failed xylene-etched SEM micrographs of PA410/POE-g-MA blends	57
<b>Fig. 3.8</b>	Schematic representation of the toughening mechanism	58
<b>Fig. 3.9</b>	(a) complex viscosity of PA 410 and POE-g-MA and (b) complex viscosities of PA 410/POE-g-MA blends	60
<b>Fig. 3.10</b>	Storage and loss modulus variation with angular frequency, and relaxation time	62

<b>Fig. 3.11</b>	(a) Storage and (b) loss modulus of PA 410/POE-g-MA blends	64
<b>Fig. 3.12</b>	(a) Loss tangent vs. angular frequency and (b) variation of phase angle with complex modulus	66
<b>Fig. 3.13</b>	Modified Cole-Cole plot (Han plot)	67
<b>Fig. 3.14</b>	Variation frequency independent loss tangent with elastomer content	69
<b>Fig. 3.15</b>	Gel point and ultra-toughening relationship	70
<b>Fig. 3.16</b>	Variation of (a) storage moduli decay and (b) damping behavior of PA410/POE-g-MA blends with temperature	73
<b>Fig. 3.17</b>	Comparison of experimental (solid line) and theoretical (dotted line) loss tangent in solid state	74
<b>Fig. 3.18</b>	Normalized loss tangent in solid-state with temperature	75
<b>Fig. 4.1</b>	(a) Schematic presentation of reaction between PA 410 and POE-g-MA and, FT-IR analysis of (b) PA 410/POE-g-MA blends and (c) magnified FT-IR region for comparison	78
<b>Fig. 4.2</b>	DSC exotherms of PA 410/POE-g-MA blends	79
<b>Fig. 4.3</b>	Variation of relative crystallinity with crystalline temperature	81
<b>Fig. 4.4</b>	Variation of relative crystallinity with crystallization time	82
<b>Fig. 4.5</b>	Variation crystallization time with cooling rate	86
<b>Fig. 4.6</b>	(a) Acceleration of cooling with relative crystallinity and POE-g-MA loading (wt.%) and (b) Y-intercept of crystallization time versus cooling rate curve as function of relative crystallinity	87
<b>Fig. 4.7</b>	Schematic presentation of interfacial network build-up	89
<b>Fig. 4.8</b>	Friedman plot for activation energy pattern	90
<b>Fig. 4.9</b>	Nucleation activity of PA 410/POE-g-MA blends	91

<b>Fig. 4.10</b>	Modified Avrami/Jeziorny analysis	94
<b>Fig. 4.11</b>	Ozawa analysis of PA 410/POE-g-MA blends	98
<b>Fig. 4.12</b>	Liu & Mo analysis of PA 410/POE-g-MA blends	101
<b>Fig. 4.13</b>	Variation F(T) with POE-g-MA for different degree of crystallinity	102
<b>Fig. 5.1</b>	Self –similarity of the load-displacement curves for the various PA410/POE-g-MA blend compositions	106
<b>Fig. 5.2</b>	Failure stages of PA 410/POE - g -MA blends	107
<b>Fig. 5.3</b>	(a) Hill's analysis for plane stress criterion and (b) variation of specific work of fracture with ligament length	107
<b>Fig. 5.4</b>	Variation of EWF parameters and notched Izod impact energy with ligament length of POE-g-MA	109
<b>Fig. 5.5</b>	(a) Variation of (a) onset to failure displacement with ligament length and (b) COD parameter with POE-g-MA loading	113
<b>Fig. 5.6</b>	Schematic of fracture process	115
<b>Fig. 5.7</b>	SEM micrographs of fracture surface	116
<b>Fig. 5.8</b>	(a) Cyclic tensile test protocol and (b) schematic representation of a typical loading-unloading cycle	118
<b>Fig. 5.9</b>	Strain rate dependent tensile cyclic curves	120
<b>Fig. 5.10</b>	(a) Cyclic hysteresis and (b)Plastic strain as function of number of cycles for PA 410/POE-g-MA blends	124
<b>Fig. 5.11</b>	Variation of storage modulus against loss modulus (Cole-Cole plot)	126
<b>Fig. 5.12</b>	(a) Temperature dependent $\tan \delta$ and (b) variation of entanglement density variation $\tan \delta$	127

<b>Fig. 5.13</b>	Matrix loss-tangent ( $\tan \delta_m$ ) normalized loss tangent ( $\tan \delta_b$ ) of the blends ( $\tan \delta_b / \tan \delta_m$ )	129
<b>Fig. 6.1</b>	(A) Endothermic melting peak and (B) exothermic crystalline peaks of the nanocomposites	132
<b>Fig. 6.2</b>	Degradation profile (TGA curves) of nanocomposites	133
<b>Fig. 6.3</b>	WAXD diffractogram of nanocomposites	134
<b>Fig. 6.4</b>	Raman spectra nanocomposites	136
<b>Fig. 6.5</b>	FESEM micrographs of xylene etched cryo-fractured surfaces of nanocomposites	138
<b>Fig. 6.6</b>	Apparent viscosities of PA 410, POE-g-MA and PP-MWCNT	139
<b>Fig. 6.7</b>	HR-TEM images of cryo-microtomed nanocomposite surfaces	141
<b>Fig. 6.8</b>	Schematic of phase compatibility and MWCNT migration	141
<b>Fig. 6.9</b>	Amplitude sweep of nanocomposites at 270 °C and 1 Hz frequency	142
<b>Fig. 6.10</b>	Storage and loss modulus variation	143
<b>Fig. 6.11</b>	(a) Storage and (b) loss modulus variation with PP-MWCNT loading	144
<b>Fig. 6.12</b>	(A) Loss tangent (B) van-Grup Palman plot	146
<b>Fig. 6.13</b>	(A) Complex viscosity (B) modified Han plot	148
<b>Fig. 6.14</b>	Estimation of gel point	149
<b>Fig. 6.15</b>	(A) Storage modulus variation, (B) derivative of storage modulus, (C) solid-state loss tangent, and (D) Immobilized volume fraction with temperature	152
<b>Fig. 6.16</b>	(A) Matrix normalized loss tangent (B) Cole-Cole plot	154

<b>Fig. 6.17</b>	(A) Current-voltage plot (B) electrical conductivity with MWCNT wt.%	155
<b>Fig. 6.18</b>	Magnified xylene etched surfaces (a) 10, (b) 20, (c) 30 wt.% of PP-MWCNT loading	155
<b>Fig. 6.19</b>	(A) Dielectric constant and (B) dielectric loss of the nanocomposites	157
<b>Fig. 6.20</b>	(A) Total shielding effectiveness (B) $SE_A/SE_R$ ratio	159
<b>Fig. 6.21</b>	Influencing parameters on shielding process	161
<b>Fig. 6.12</b>	(A) Stress-strain curve, (B) matrix normalized tensile properties and (C) impact strength and ductility ratio with composition	162

## List of Tables

<i>Table No.</i>	<i>Description</i>	<i>Page No.</i>
<b>Table 2.1</b>	Details and specifications of selected raw materials	35
<b>Table 2.2</b>	Composition of PA 410/POE-g-MA blends	36
<b>Table 2.3</b>	Process parameter values maintained in an injection moulding machine	36
<b>Table 2.4</b>	Sample designation and composition of nanocomposites	37
<b>Table 3.1</b>	Crystallization and Melting temperature of PA410/POE-g-MA wt. % melt-mixed Blends	45
<b>Table 3.2</b>	Morphological Parameters of PA410/POE-g-MA Blends	47
<b>Table 3.3</b>	Melt Flow Index (MFI) of the PA410/POE-g-MA Blends	60
<b>Table 3.4</b>	Power law indices <i>a</i> and <i>b</i>	64
<b>Table 4.1</b>	DSC parameters of crystalline exotherms of PA 410/POE-g-MA blend	79
<b>Table 4.2</b>	Crystallization time for primary, secondary, and overall crystallization	83
<b>Table 4.3</b>	Power-law fitting parameters	85
<b>Table 4.4</b>	Nucleation activity	92
<b>Table 4.5</b>	Modified Avrami (Jeziorny) analysis	97
<b>Table 4.6</b>	Ozawa analysis	99
<b>Table 4.7</b>	Liu and Mo analysis	102
<b>Table 5.1</b>	Radius of plastic zone	112
<b>Table 5.2</b>	Comparison of $w_e$ estimated from COD and EWF	113
<b>Table 5.3</b>	Observation from cyclic tensile test	121
<b>Table 6.1</b>	Crystallinity (%) and average crystallite size of nanocomposites	135

<b>Table 6.2</b>	Scaling law coefficients	145
<b>Table 6.3</b>	AC conductivity of nanocomposites at mid band frequency	158

## Abbreviations

<b>Abbreviations</b>	<b>Full form</b>
PA 410	polyamide 410
PP	polypropylene
MWCNT	multi-walled carbon nanotubes
WAXD	wide angle x-ray diffraction
TEM	transmission electron microscopy
SEM	scanning electron microscopy
DSC	differential scanning calorimetry
PA 6	polyamide 6
ABS	acrylonitrile butadiene styrene
HDPE	high density polyethylene
PU	polyurethane
CPPC	chlorinated poly(propylene carbonate)
PTC	positive temperature coefficient
NTC	negative temperature coefficient
PET	polyethylene terephthalate
PA 66	polyamide 66
CNT	carbon nanotubes
PS	polystyrene
PPE	poly(phenylene ether)
PA 6/12	polyamide 6,12
EMA	ethylene-acrylate copolymer
PVDF	poly(vinylidene fluoride)
EMAA	poly(ethylene-co-methacrylic acid) copolymer
m-EMMA	modified-poly(ethylene-co-methacrylic acid) copolymer
PMMA	polymethyl methacrylate
PB-1	polybutene-1
HIPS	high impact polystyrene
cPA	copolyamide
SEBS	styrene-ethylene-butylene-styrene
PA 6T	polyphthalamide
m-SEBS	modified-styrene-ethylene-butylene-ethylene

POE-g-MA	polyethylene octene copolymer grafted with maleic anhydride
Na-AHA modified	sodium salt of amino-hexanoic acid modified mwcnt
MWCNT	
Hytrel	thermoplastic elastomer of co-polyester by dupont
PC	polycarbonate
PLA	polylactic acid
PCL	poly ( $\epsilon$ -caprolactone)
SANMA	styrene-acrylonitrile-maleic anhydride
MPP	maleated polypropylene
LDPE	low density polyethylene
PE-g-MA	polyethylene-grafted-maleic anhydride
SAN	poly(styrene-acrylonitrile)
DMA	dynamic mechanical analysis
PP-g-MAH	polypropylene grafted maleic anhydride
AlN	aluminium nitride
ECO	(poly(epichlorohydrin-co-ethylene oxide))
EVA	ethylene-vinyl acetate
PVC	polyvinyl chloride
SWCNT	single walled carbon nanotubes
PLLA	poly l-lactide
SWCNTs-COOH	carboxylic acid functionalized single walled carbon nanotubes
PA 11	polyamide 11
GO	graphite oxide
POM	polyoxometalate
WO <sub>3</sub>	tungsten trioxide
PA 56	polyamide 56
PEGMA	poly (ethylene-co-glycidyl methacrylate)
isotactic polypropylene	ipp
KB	ketjenblack
EMI	electro-magnetic interference
A-MWCNT	acid-oxidized multi wall carbon nanotubes
EVA-g-MA	maleic-anhydride-graft-ethylene-vinyl acetate
TRG	thermally reduced graphene oxide

CPCs	conducting polymer composites
Ag	silver
UHMWPE	ultrahigh molecular weight polyethylene
NBR	acrylonitrile butadiene rubber
LMWPE	low molecular weight polyethylene
TGA	thermogravimetric analysis
TEM	transmission electron microscope
HRTEM	high-resolution transmission electron microscope
SEM	scanning electron microscope
LVR	linear viscoelastic range
FWHM	full width half maxima
EA	ethylene-acrylate copolymer
IROM	inverse rule of mixture model
NR	natural rubber

## List of symbols

Symbol	Meaning
$T_g$	glass transition temperature
$T_m$	melting temperature or melting point
$\rho$	density
$\chi_c$	relative crystallinity
$\Delta H_c$	heat of fusion of nanocomposites
$\Delta H_m$	heat of fusion of 100 % crystalline PA 12
$\phi_f$	volume fraction of the composite-filler masterbatch
$A_c$	crystalline area
$A_a$	amorphous area
$E'$	storage modulus (from DMA)
$E''$	loss modulus (from DMA)
$\tan \delta$	damping parameter
$s$	distant between probes
$t$	thickness of sample
$\sigma$	conductivity
$\rho$	resistivity
$I$	constant current applied to the sample
$V$	voltage measured across the sample
$I$	intensity
$2\theta$	diffraction angle
$L$	crystallite size
$\lambda$	wavelength of the radiation
$B$	full width half maxima
$K$	proportionality constant ( $\sim 0.9$ )
$\omega_a$	wetting coefficients
$\gamma_{MWCNT-PP}$	interfacial energy between MWCNT and PP
$\gamma_{MWCNT-PA-12}$	interfacial energy between MWCNT and PA 12
$\gamma_{PA-12-PP}$	interfacial energy between PA 12 and PP
$T_g$	glass transition temperatures corresponding to nanocomposites obtained from $\tan \delta$ peak
$T_{gl}$	glass transition temperature of PA 12 matrix

$T_{g2}$	extent of temperature rise (equivalent) due to incorporation of PP-MWCNT
$w_1$	weight fraction of PA 12 matrix
$w_2$	weight fraction of PP-MWCNT masterbatch as the composite filler
$\phi_T$	immobilized volume fraction
$E_m$	elastic moduli of matrix
$E_c$	elastic moduli of composites
$\nu_m$	Poisson's ratio of the matrix (~0.3)
$T$	temperature from DMA
$R_g$	radius of gyration
$M_w$	molecular weight
$M_e$	physical entanglements
$\rho$	density of the polymer composites
$R$	universal gas constant
$T$	reference temperature
$G'$	storage modulus at temperature t
$N_a$	Avogadro's number
$E_c$	elastic modulus of composites
$E_f$	elastic modulus of reinforcement
$E_m$	elastic modulus of matrix
$\phi_f$	volume fraction of filler
$\beta$	square root of $\sqrt{\phi_f}$
$\nu_m$	Poisson's ratio of matrix
$\lambda_{ijk}$	spreading coefficient of dissimilar components ( $i, j$ , and $k$ )
$\gamma$	surface energy
$p$	polar component
$d$	dispersion component
$G'$	storage modulus (rheological)
$G''$	loss modulus (rheological)
$\omega$	angular frequency
$\eta^*$	complex viscosity
$G^*$	shear modulus
$\Phi_d$ or $\phi_{PP-MWCNT}$	volume fraction of the dispersed phase (PP-MWCNT)

$\eta_{PA-12}$	viscosity of PA 12
$\eta_{PP-MWCNT}$	viscosity of PP-MWCNT
$[\eta]$	intrinsic viscosity
$K$	intrinsic nature of the material in the absence of shear stress
$\eta_0$	zero shear viscosity
$\lambda$	cross-over time or the characteristic time
$a$	power law exponent
$I$	intensity
$2\theta$	diffraction angle
$T_c$	crystallization temperature
$X(t)$	relative crystallinity
$dH_c/dT$	heat released
$T_0$	crystallization onset temperatures
$T_e$	crystallization end temperatures
$\phi$	cooling rate
$T$	temperature
$t$	time
$n$	avrami exponent
$Z_t$	crystallization rate constant
$R^2$	regression coefficient
$t_{1/2}$	half time of non-isothermal crystallization
$Z_c$	corrected crystallization rate constant
$K(T)$	cooling crystallization function
$m$	Ozawa exponent
$\log(t)$	crystallization time
$F(T)$	kinetics parameter
$b$	ratio of Avrami exponent to Ozawa exponent ( $n/m$ )
$K_T$	Tobin crystallization rate constant
$n_T$	Tobin exponent
$f$	nucleation activity
$A$	constant
$B, B^*$	parameters for homogeneous and heterogeneous nucleation
$\Delta E$	activation energy

$dX/dt$	instantaneous crystallization rate at a given relative crystallinity X
$\Delta E_X$	effective activation energy at given relative crystallinity X
$f(X,i)$	function for conversion depending on the reaction mechanism
$T_{X,i}$	set of temperatures at a given crystallinity at different cooling rates
$i$	individual cooling rate (used)
$A$	pre-exponential factor
$\sigma_c$	DC electrical conductivity of the composite
$\sigma_f$	DC electrical conductivity of the PP-MWCNT composite filler
$C^2$	geometrical factor
$\phi_p$	volume fraction of polymer
$\lambda$	structural factor
$I$	current
$V$	voltage
$\alpha, \beta$	constants
$E_a$	activation energy for thermally activated hopping mechanism
$\sigma$	electrical conductivity
$T$	absolute temperature
$\sigma_o$	constant
$K$	boltzmann constant ( $1.308 \times 10^{-23}$ J/K)