

**INTERRELATIONSHIP OF MORPHOLOGICAL,
RHEOLOGICAL, THERMOMECHANICAL AND
ELECTRICAL BEHAVIOURS IN POLYAMIDE 12/
POLYPROPYLENE–MWCNT NANOCOMPOSITES**

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**MATERIALS SCIENCE AND ENGINEERING
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ELECTRICAL BEHAVIOURS IN POLYAMIDE 12/
POLYPROPYLENE–MWCNT NANOCOMPOSITES**

by

Sucharita Sethy

Materials Science and Engineering

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CERTIFICATE

This is to certify that the thesis entitled “**Interrelationship of Morphological, Rheological, Thermomechanical and Electrical Behaviors in Polyamide 12/ Polypropylene–MWCNT Nanocomposites**” submitted to the Indian Institute of Technology Delhi by **Ms Sucharita Sethy**, for the award of the degree of **Doctor of Philosophy** in the Department of Materials Science and Engineering (formerly known as Centre for Polymer Science and Engineering), is a bonafide record of original research work carried out by the candidate. The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree.

I further certify that Ms Sethy has fulfilled all the requirements for the submission of the thesis.

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ABSTRACT

Ternary nanocomposites of polyamide 12 (PA-12) and multi-walled carbon nanotubes-embedded-polypropylene (as PP-MWCNT masterbatch) were fabricated at different in composition ratios of PA-12:PP-MWCNT (100:0, 70:30, 60:40, 50:50, 40:60, 30:70 and 0:100) by melt-mixing route. The polymer nanocomposites fabricated by masterbatch dilution technique were characterized for their structural, thermal, morphological, rheological, dynamic mechanical, mechanical and electrical conductivity behaviours. The structural characteristics of the nanocomposites were obtained from wide angle X-ray diffraction (WAXD) which showed a decrease in the overall crystallinity of the PA-12 phase followed by a nominal increase upon the incorporation of PP-MWCNT above 50 wt.% though crystallite size remained in the range of 8-9 nm (Scherrer's equation). The morphological attributes of the ternary nanocomposites were characterized for their dispersion-nanomorphology (by transmission electron microscopy (TEM)) and phase-selective micromorphology (by scanning electron microscopy (SEM)). SEM studies revealed the existence of a quasi-co-continuous phase-distribution wherein the conducting PP-MWCNT phase formed elongated continuous channels dispersed in the PA-12 matrix with localized-MWCNT in the PP phase as theoretically confirmed by wetting coefficient analysis. The partial migration of MWCNT from PP phase to PA-12 phase was evident from the spreading coefficient estimations based on interfacial dynamics and transmission electron microscopy (TEM) analysis.

The melt rheological properties (storage and loss modulus) of the nanocomposites were investigated to understand the dissipation in polymer networks and network rigidity. Melt rheology measurements based on scaling parameters associated with various viscosity models such as, Cross model, Carreau-Yasuda model and Berzin model indicated systematic variation in network rigidity that was in tune with dispersion-selective nano-morphology of the nanocomposites. The phase inversion was attained in the composition range of 50-60 wt. % of PP-MWCNT as indicated by Cole-Cole plot and van-Gurp Palmen plots. The phase inversion has a direct correspondence to dispersed-phase-volume-fraction range of ~0.3-0.35. Critical analysis of the solid-state mechanical behaviour showed broadening and shifting of the $\tan \delta$ peaks (characterizing solid state relaxation) towards higher temperatures with increase in MWCNT. Estimations from modified Kerner composite equation revealed that the chain segments of PA-12 matrix are effectively immobilized due to the infiltration of MWCNT into the PA-12 phase (TEM). Broadening of loss-peaks vis-a-vis enhanced storage moduli signified

the reduced mobility (of polyamide chains) causing an enhanced stiffness. The trend of tensile properties of the nanocomposites demonstrated a switch over in the composition range of PA-12/PP-MWCNT (60:40) to PA-12/PP-MWCNT (40:60). Such switch over in tensile properties remained in tune with not only the entanglement density but also to a composition-dependent phase distribution micro-morphology.

The non-isothermal crystallization behaviour of the nanocomposites were analyzed at various cooling rates of 2.5-20 °C/min. Several kinetic models such as Jeziorny, Ozawa, Mo and Tobin models were employed to analyse the crystallisation behavioural trend with respect to time and temperature of the nanocomposites. The activation energy for crystallization was evaluated by several established models as Takhor, Kissinger Augis-Bennett methods and Friedman. The nucleation activity (MWCNT induced crystallization) values close to zero irrespective of MWCNT loading reiterated the enhanced crystallization (rate) of PA-12 in the nanocomposites. A comprehensive approach was attempted to discuss the sensitivity of electrical conductivity with temperature for conducting polymer composites (CPCs) focussing on the correlation of morphology, temperature dependent electrical conductivity, solid state relaxation dynamics and melt endothermic transitions. A negative temperature coefficient behaviour similar to semiconductor based electrical components was observed for the CPCs. The correlation between solid state mechanical behaviour and surface electrical conductivity was confirmed by the close proximity between the respective glass transition values of PA-12 and the corresponding temperature at which change of slope in electrical conductivity was observed. The reproducibility of such temperature sensitivity of the nanocomposites has also been explored. The outcomes of the experiments concluded that the PA-12 based conducting nanocomposites to be potentially a promising material for functional electrical applications over a wide temperature range.

सार

पॉलियामाइड १२ (पीए-१२) के टर्नरी नैनोकम्पोजिट और बहु-दीवार वाले कार्बन नैनोट्यूब-एम्बेडेड-पॉलीप्रोपाइलीन (पीपी-एमडब्ल्यूसीएनटी मास्टरबैच के रूप में) को पीए-12:पीपी-एमडब्ल्यूसीएनटी (१००:0, ७०:३०, ६०:४०, ५०:५०, ४०:६०, ३०:७० और ०:१००) के संरचना अनुपात में अलग-अलग गढ़े गए थे। पिघल-मिश्रण मार्ग द्वारा मास्टरबैच तनुकरण तकनीक द्वारा निर्मित पॉलीमर नैनोकम्पोजिट्स को उनके संरचनात्मक, तापीय, रूपात्मक, रियोलॉजिकल, गतिशील यांत्रिक, यांत्रिक और विद्युत चालकता व्यवहारों के लिए चित्रित किया गया था। नैनोकम्पोजिट्स की संरचनात्मक विशेषताओं को वाइड एंगल एक्स-रे विवर्तन (डब्ल्यू ए ऐक्स डी) से प्राप्त किया गया था, जिसमें पीए-१२ चरण की समग्र स्फटिकता में कमी देखी गई थी, इसके बाद पीपी-एमडब्ल्यूसीएनटी को ५० वजन % से ऊपर शामिल करने पर मामूली वृद्धि हुई थी। क्रिस्टलीय आकार ८- ९ एनएम (शेरेर समीकरण) की सीमा में रहा। टर्नरी नैनोकम्पोजिट्स की रूपात्मक विशेषताओं को उनके फैलाव-नैनोमोर्फोलॉजी (ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम) द्वारा) और चरण-चयनात्मक माइक्रोमॉर्फोलॉजी (शेरेर इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) द्वारा) की विशेषता थी। एसईएम अध्ययनों से एक अर्ध-सह-निरंतर चरण-वितरण के अस्तित्व का पता चला, जिसमें पीपी-एमडब्ल्यूसीएनटी चरण ने पीपी चरण में स्थानीय- एमडब्ल्यूसीएनटी के साथ पीए-१२ मैट्रिक्स में फैले हुए निरंतर चैनल बनाए, जो सैद्धांतिक रूप से गीला गुणांक विश्लेषण द्वारा पुष्टि की गई थी। एमडब्ल्यूसीएनटी का पीपी चरण से पीए-१२ चरण में आंशिक प्रवास, इंटरफेसियल डायनामिक्स और ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (टीईएम) विश्लेषण के आधार पर प्रसार गुणांक अनुमानों से स्पष्ट था।

बहुलक नेटवर्क और नेटवर्क कठोरता में अपव्यय को समझने के लिए नैनोकम्पोजिट्स के पिघले हुए रियोलॉजिकल गुणों (भंडारण और हानि मापांक) की जांच की गई। विभिन्न चिपचिपापन मॉडल जैसे क्रॉस मॉडल, कैरेउ-यसुदा मॉडल और बर्ज़िन मॉडल से जुड़े स्केलिंग मापदंडों के आधार पर पिघल रियोलॉजी माप ने नेटवर्क कठोरता में व्यवस्थित भिन्नता का संकेत दिया जो कि नैनोकम्पोजिट्स के फैलाव-चयनात्मक नैनो-आकृति विज्ञान के अनुरूप था। चरण उलटा ५० - ६० वजन % की संरचना रेंज में प्राप्त किया गया था। पीपी-एमडब्ल्यूसीएनटी का जैसा कि कोल-कोल प्लॉट और वैन-गुरप पाल्मेन प्लॉट्स द्वारा दर्शाया गया है। चरण उलटा $\sim 0.3-0.35$ के फैलाव-चरण-वॉल्यूम-अंश सीमा के लिए सीधा पत्राचार है। सॉलिड-स्टेट मैकेनिकल व्यवहार के महत्वपूर्ण विश्लेषण ने एमडब्ल्यूसीएनटी में वृद्धि के साथ उच्च तापमान की ओर टैन ४ चोटियों (ठोस अवस्था छूट की विशेषता) को चौड़ा और स्थानांतरित करना दिखाया। संशोधित कर्नेर समग्र समीकरण के अनुमानों से पता चला है कि पीए-१२ मैट्रिक्स के श्रृंखला खंड पीए-१२ चरण (टीईएम) में एमडब्ल्यूसीएनटी की घुसपैठ के कारण प्रभावी रूप से स्थिर हो गए हैं। बढ़े हुए भंडारण मोडुली की तुलना में हानि-शिखरों के चौड़ीकरण ने कम गतिशीलता (पॉलियामाइड श्रृंखलाओं की) को बढ़ाया जिससे कठोरता बढ़ गई। नैनोकम्पोजिट्स के तन्य गुणों की प्रवृत्ति ने पीए-१२/पीपी-एमडब्ल्यूसीएनटी (६०:४०) से पीए-१२/पीपी-एमडब्ल्यूसीएनटी (४०:६०) की संरचना रेंज में एक स्विच ओवर का प्रदर्शन किया। तन्यता गुणों में इस तरह का स्विच न केवल उलझाव घनत्व के साथ-साथ एक संरचना-निर्भर चरण वितरण सूक्ष्म-आकृति विज्ञान के अनुरूप रहा।

नैनोकम्पोजिट्स के गैर- समतापी क्रिस्टलीकरण व्यवहार का विश्लेषण २.५-२० डिग्री सेल्सियस / मिनट की विभिन्न शीतलन दरों पर किया गया था। नैनोकम्पोजिट्स के समय और तापमान के संबंध में क्रिस्टलीकरण व्यवहार की प्रवृत्ति का विश्लेषण करने के लिए कई गतिज मॉडल जैसे कि जेज़ियोर्नी, ओज़ावा, मो और टोबिन मॉडल को नियोजित किया गया था। क्रिस्टलीकरण के लिए सक्रियण ऊर्जा ताखोर, किसिंगर ऑगिस-बेनेट बेनेट तरीकों और फ्राइडमैन के रूप में कई स्थापित मॉडलों द्वारा

मूल्यांकन किया गया था। न्यूक्लियेशन गतिविधि (एमडब्ल्यूसीएनटी प्रेरित क्रिस्टलीकरण) मान शून्य के करीब एमडब्ल्यूसीएनटी लोडिंग के बावजूद नैनोकम्पोजिट्स में पीए-१२ के बढ़े हुए क्रिस्टलीकरण (दर) को दोहराया। आकारिकी के सहसंबंध, तापमान पर निर्भर विद्युत चालकता, ठोस अवस्था छूट गतिकी और पिघले एंडोथर्मिक संक्रमणों पर ध्यान केंद्रित करते हुए बहुलक कंपोजिट (सीपीसी) के संचालन के लिए तापमान के साथ विद्युत चालकता की संवेदनशीलता पर चर्चा करने के लिए एक व्यापक दृष्टिकोण का प्रयास किया गया था। सीपीसी के लिए अर्धचालक आधारित विद्युत घटकों के समान एक नकारात्मक तापमान गुणांक व्यवहार देखा गया। ठोस अवस्था यांत्रिक व्यवहार और सतह विद्युत चालकता के बीच सहसंबंध की पुष्टि पीए-१२ के संबंधित ग्लास संक्रमण मूल्यों और संबंधित तापमान के बीच निकटता से हुई थी, जिस पर विद्युत चालकता में ढलान का परिवर्तन देखा गया था। नैनोकम्पोजिट्स की ऐसी तापमान संवेदनशीलता की पुनरुत्पादकता का भी पता लगाया गया है। प्रयोगों के परिणामों ने निष्कर्ष निकाला कि पीए-१२ आधारित नैनोकंपोजिट्स एक विस्तृत तापमान सीमा पर कार्यात्मक विद्युत अनुप्रयोगों के लिए संभावित रूप से एक आशाजनक सामग्री है।

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Abbreviations

Abbreviations	Full form
PA 12	polyamide 12
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 (ϵ -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 ₃	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
ρ	density
χ_c	relative crystallinity
ΔH_c	heat of fusion of nanocomposites
ΔH_m	heat of fusion of 100 % crystalline PA 12
ϕ_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
σ	conductivity
ρ	resistivity
I	constant current applied to the sample
V	voltage measured across the sample
I	intensity
2θ	diffraction angle
L	crystallite size
λ	wavelength of the radiation
B	full width half maxima
K	proportionality constant (~ 0.9)
ω_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_{g1}	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
ϕ_T	immobilized volume fraction
E_m	elastic moduli of matrix
E_c	elastic moduli of composites
ν_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
ρ	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
ϕ_f	volume fraction of filler
β	square root of $\sqrt{\phi_f}$
ν_m	Poisson's ratio of matrix
λ_{ijk}	spreading coefficient of dissimilar components (i, j , and k)
γ	surface energy
p	polar component
d	dispersion component
G'	storage modulus (rheological)
G''	loss modulus (rheological)
ω	angular frequency
η^*	complex viscosity
G^*	shear modulus
Φ_d or $\phi_{PP-MWCNT}$	volume fraction of the dispersed phase (PP-MWCNT)

η_{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
η_0	zero shear viscosity
λ	cross-over time or the characteristic time
a	power law exponent
I	intensity
2θ	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
ϕ	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
ΔE	activation energy

dX/dt	instantaneous crystallization rate at a given relative crystallinity X
ΔE_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
σ_c	DC electrical conductivity of the composite
σ_f	DC electrical conductivity of the PP-MWCNT composite filler
C^2	geometrical factor
ϕ_p	volume fraction of polymer
λ	structural factor
I	current
V	voltage
α, β	constants
E_a	activation energy for thermally activated hopping mechanism
σ	electrical conductivity
T	absolute temperature
σ_o	constant
K	boltzmann constant (1.308×10^{-23} J/K)