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Enhancing Carbon Nanotubes Dispersion in Thermoplastics for the Development of Multi-functional Composites

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of the Karlsruhe Institute of Technology
for the award of Ph.D. (Dr.-Ing.)

Dissertation

by
M.Sc., Diplôme d'Ingénieur. **Shyam Sundar Sathyanarayana**

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Co-supervisor:	Prof. Dr.-Ing. Christian Bonten
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DECLARATION

The work presented in this project is to the best of my knowledge and belief, original and my own piece of work, except as otherwise acknowledged in the text. I have not submitted this material, either as a whole or in part for a degree elsewhere.

- Shyam Sundar Sathyanarayana

Dedicated to my dear wife & parents

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Abstract

This work aims to develop a polypropylene-based multifunctional composite with excellent electrical, thermal, and mechanical characteristics; taking advantage of the excellent electrical conductivity of carbon nanotubes as conductive fillers and to overcome their major drawback to substantially enhance the mechanical properties by the use of glass fibers as structural reinforcement.

The extremely high electrical conductivity of carbon nanotubes makes them an attractive choice as conductive filler. However, the intrinsic tendency of carbon nanotubes to exist as agglomerates due to van der Waals forces of attraction limits their theoretical potential. Achieving good nanotube dispersion in polypropylene is a pre-requisite for good electrical properties prior to the addition of glass fibers. This however is a significant challenge owing to the non-polar nature of polypropylene, high interfacial energy difference with commercially available carbon nanotubes, and the intrinsically inert chemical nature of the nanotubes.

The mechanism of carbon nanotube dispersion in a thermoplastic and the lack of relevant literature on large scale processing of polyolefins with carbon nanotubes mandate proper understanding of the process factors contributing towards improved filler dispersion. Hence, for a start the influence of twin-screw compounding parameters on the quality of carbon nanotube dispersion was investigated with the Design of Experiments approach. Excellent electrical characteristics were achieved on a composite containing 2 wt.% carbon nanotubes at higher screw speeds and lower material throughputs owing to better filler dispersion at these conditions, facilitated by higher specific mechanical energy of processing. Variation in screw configuration had an influence on lowering the resistivity of the composites processed at increased throughputs at lower nanotube loadings. Feeding of carbon nanotubes in the polymer melt resulted in improved electrical and mechanical properties compared to feeding them along with the polymer in the main feed of the extruder.

Peroxides were incorporated as a processing additive to reduce the melt viscosity to facilitate better melt infiltration into the nanotube agglomerates and improve hydrophilicity of polypropylene for better wetting of the agglomerates. Substantially enhanced carbon nanotube dispersion in polypropylene was possible at 50% lower processing energy by using peroxides. In situ functionalization of carbon nanotubes by peroxides confirmed by a novel approach of online Raman spectroscopy observations could have contributed positively in enhancing the dispersion, but also led to structural defects on the carbon nanotubes.

Electrical percolation occurred around 0.4 wt.% carbon nanotube loading on the composites with peroxides. Compression molding parameters had a strong influence on the magnitude of observed resistivities of the composites. Higher melt temperatures and longer holding times were found to be beneficial for improved electrical conductivity. Though carbon nanotube addition slightly enhanced the mechanical properties of polypropylene, the addition of peroxides had a negative effect on the modulus and impact properties of the composites. The structural defects created on the nanotube on functionalization by peroxides could have been a reason for the aforementioned. The composites presented enhanced thermal stability due to the excellent free radical accepting capacities of nanotubes.

The addition of short glass fibers as secondary fillers resulted in substantially enhanced tensile and impact properties of the composites accompanied by a loss in ductility. The combined reinforcing effect of carbon nanotubes and glass in the bi-filler composite outperforms the mechanical properties achieved with the additive effect of their individual counterparts. The electrical resistivity of the composites resulting from the formation of the conductive percolative pathway by the carbon nanotubes was only minimally altered by the addition of glass fibers. The thermal stability of the bi-filler composite was also considerably high. The bi-filler composite thus shows all the traits of an excellent multi-functional composite.

Optimization of process parameters for achieving good carbon nanotube dispersion in a polypropylene resin, significant savings in both raw-material and energy costs by employing peroxide as a reactive functional additive, and the addition of economic short glass fibers as secondary fillers augurs well for the development of a multi-functional composite with excellent electrical, mechanical and thermal properties, and also tremendous potential for product development.

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List of Abbreviations

CNT	Carbon nanotube
SWCNT	Single-walled carbon nanotube
MWCNT	Multi-walled carbon nanotube
DWCNT	Double-walled carbon nanotube
vdW	van der Waals
CVD	Chemical vapour deposition
DC	Direct current
CEFIC	European chemical industrial council
CKNMT	Centre for knowledge management of nanoscience and technology
CAGR	Compounded annual growth rate
CFRP	Carbon fiber reinforced plastic
EMI	Electromagnetic interference
ESD	Electrostatic dissipation
SEM	Scanning electron microscopy
MFR	Melt flow rate
PP	Polypropylene
PP-Px	Peroxide modified polypropylene
PS	Polystyrene
PMMA	Poly(methyl methacrylate)
PE	Polyethylene
PC	Polycarbonate
PA	Polyamide
PVC	Polyvinyl chloride
SBR	Styrene-butadiene rubber
HIPS	High impact polystyrene

DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
L/D	Aspect ratio of the twin-screw compounder
MF	Mainfeed position for filler (position of polymer feed)
SF	Sidefeed position for filler (located at the L/D = 16 of the extruder)
DoE	Design of experiments
SE	Screening experiment
ME	Mainstream experiment
Sxy	Sample nomenclature for SE (where: xy are numerals)
Eab	Sample nomenclature for ME (where: ab are numerals)
R2	Measure of how well the DoE model fits data
Q2	Measure of how well the DoE model predicts new data
D peak	CNT peak in the Raman spectra activated by the presence of disorders
G peak	Graphitic peak in the Raman spectra resulting from in-plane C-C vibration
G* peak	Secondary overtone of D peak in the Raman spectra
δ-CH_2 peak	Bending vibration peak of PP in the Raman spectra
FWHM	Full width at half maximum
I_D/I_G	Intensity ratio of the CNT D peak to the CNT G peak (Measure of CNT defect concentration)

E	Elastic Modulus	MPa (or) GPa
I_{notch}	Notched impact strength	kJ/m^2
σ_{max}	Maximum tensile strength	MPa
ε_{break}	Failure strain	%
Strain at σ_{max}	Elongation at maximum tensile strength	%

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