

FABRICATION AND CHARACTERIZATION OF MODIFIED MULTI WALLED
CARBON NANOTUBE REINFORCED UNSATURATED POLYESTER
NANOCOMPOSITES

ABU KASHEM MOHAMMAD MOSHIUL ALAM

Thesis submitted in fulfillment of the requirements
For the award of the degree of
Doctor of Philosophy (PhD) (Chemical Engineering)

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

MARCH 2016

ABSTRACT

This research presents a non-destructive modification of multi-walled carbon nanotube (MWCNT) and fabrication of MWCNT reinforced unsaturated polyester resin (UPR) nanocomposite. In this work, pre-dispersion of MWCNTs was performed in the tetra hydro furan (THF) solvent. In addition, pre-dispersion and post- dispersion time was optimized as 1.5 hour and 2 hour, respectively. The pre-dispersed MWCNT reinforced UPR (THF-MWCNT-UPR) nanocomposite exhibited better properties as compared to directly dispersed MWCNT reinforced UPR (MWCNT-UPR) nanocomposite. The optimum amount of MWCNT was evaluated through mechanical properties of nanocomposites contained 0.05 to 0.5 wt% MWCNT. The experimental tensile modulus (TM) of 0.3 wt% MWCNT reinforced 0.3CNT-UPR nanocomposite linearly fitted with Halpin –Tsai equation. Therefore, 0.3 wt% MWCNT was suggested as the optimum quantity. The nondefect modification of MWCNT was carried out with hyper branched polyester (HBP) and shellac (SL) functional polymers. The structural and thermal properties of 10 wt% HBP and SL coated HBCNT and SLCNT was noticeably improved as compared to pristine MWCNT. Moreover, 10 wt% HBP and SL coated HBCNT and SLCNT nanotubes remarkably reduced the curing temperature of nanosuspensions. Therefore, 10 wt% was considered as the optimum amount of HBP and SL to modify MWCNT. Optimum HBP coated MWCNT incorporated (OHBPCNT-UPR) nanocomposite became stiff. Conversely, optimum SL coated MWCNT incorporated (OSLCNT-UPR) nanocomposite became tough as compared to MWCNT reinforced nanocomposite. Different ratios of HBCNT and hydroxyl (OH) functionalized MWCNT (OHCNT) were incorporated in UPR to fabricate hybrid (HBOHCNT-UPR) nanocomposites. The ratio of HBCNT and OHCNT was optimized as 2:1 through the curing behavior of hybrid nanosuspensions. The comparative study was carried out among non-covalent and covalent functionalized as well as hybrid MWCNT reinforced UPR nanocomposites. Hybrid MWCNT incorporated nanosuspension exhibited the lowest curing temperature as compared to non-covalent and covalent functionalized MWCNT incorporated nanosuspensions. The hybrid nanocomposite exhibited the highest stiffness among nanocomposites which was individually fabricated with HBCNT and OHCNT. The mixture of non-covalent functionalized and covalent functionalized MWCNT jointly reinforced the properties of UPR.

ABSTRAK

Kajian ini menunjukkan kaedah pengubahsuaian tidak musnah Tiub Nano Karbon Berdinding Banyak (TNKBB) dan pembikinan TNKBB yang dikuatkan dengan komposit nano resin poliester tidak tepu (RPTS). Dalam kajian ini, penghancuran TNKBB telah dilakukan terlebih dahulu menggunakan cecair pelarut tetra hidro furan (THF). Di samping itu, masa yang diambil semasa proses sebelum penghancuran dan selepas penghancuran telah dioptimumkan masing-masing selama 1.5 jam dan 2 jam. Komposit nano TNKBB dengan kekuatan RPTS (THF-TNKBB-RPTS) yang telah dihancurkan terlebih dahulu menunjukkan sifat yang lebih baik berbanding komposit nano TNKBB dengan kekuatan RPTS (TNKBB-RPTS) yang tidak dihancurkan terlebih dahulu menggunakan cecair pelarut THF. Jumlah kuantiti optimum TNKBB telah dinilai melalui sifat mekanikal komposit nano yang mengandungi kira-kira 0.05-0.5% berat TNKBB. Modul eksperimen yang dapat diregangkan (MK) serta mengandungi 0.3% TNKBB yang dikuatkan dengan 0.3 komposit nano TNK RPTS telah berpadanan secara selari dengan persamaan Halpin-Tsai. Oleh yang demikian, 0.3% TNKBB telah dicadangkan sebagai jumlah kuantiti optimum. Proses pengubahsuaian TNKBB tanpa kerosakan telah dijalankan dengan menggunakan poliester bercabang banyak (PBB) dan juga syelek (SL) polimer berfungsi. Sifat struktur dan haba 10% PBB dan SL yang disaluti dengan PBBTNK dan SLTNK telah dapat dilihat. Tambahan itu, 10% PBB dan SL yang disaluti dengan tiub nano PBBTNK dan SLTNK telah mengurangkan suhu pemulihan tapisan nano. Oleh itu, 10% wt telah dikira sebagai kuantiti PBB dan SL optimum yang diperlukan untuk mengubahsuaikan TNKBB. PBB optimum yang telah disaluti TNKBB digabungkan dengan komposit nano (OPBBTNK-RPTS) telah menjadi keras. Sebaliknya, komposit nano gabungan SL optimum yang disaluti TNKBB (OSLTNK-RPTS) telah menjadi kuat dan tahan lasak berbanding komposit nano yang digabungkan dengan TNKBB. Nisbah yang berbeza antara PBBTNK dan hidroksil (OH) dengan fungsi TNKBB (OHTNK) telah digabungkan di dalam RPTS untuk menghasilkan kacukan komposit nano (PBBOHTNK-RPTS). Nisbah PBBTNK and OHTNK telah dioptimumkan kepada 2:1 melalui sifat penyembuhan tapisan nano kacukan tersebut. Kajian perbandingan telah dijalankan menggunakan gabungan komposit nano RPTS berfungsi kovalen dan bukan kovalen dan kacukan. Hasilnya, komposit nano yang digabungkan dengan kacukan TNKBB telah menunjukkan pengawalan suhu yang terendah berbanding tapisan nano komposit nano RPTS yang digabungkan dengan fungsi kovalen dan bukan kovalen dan kacukan TNKBB. Komposit nano kacukan tersebut telah menunjukkan sifat kekerasan yang tertinggi antara komposit nano lain yang telah diubahsuaikan dengan menggunakan PBBTNK dan OHTNK. Campuran TNKBB yang berfungsi kovalen dan bukan kovalen kemudian telah bersama-sama mengukuhkan sifat RPTS.

TABLE OF CONTENT

	Page
STATEMENT OF AWARD FOR DEGREE	ii
SUPERVISOR’S DECLARATION	iii
STUDENT’S DECLARATION	iv
ACKNOWLEDGEMENT	vi
ABSTRACT	vii
ABSTRAK	viii
TABLE OF CONTENTS	ix
LIST OF TABLE	xv
LIST OF FIGURES	xvi
LIST OF SYMBOLS	xx
LIST OF ABBREVIATIONS	xxi
CHAPTER 1 INTRODUCTION	
1.1 Background	1
1.2 Problem Statement	5
1.3 Objectives	6
1.4 Scope of Study	7
1.5 Significance of Study	8
CHAPTER 2 LITERATURE REVIEW	
2.1 Introduction	9
2.2 Unsaturated Polyester Resin	9
2.2.1 Types of Polyesters	11
2.2.2 Curing Process of UPR	12
2.2.3 Filler Effect on Curing Process	14
2.3 Unsaturated Polyester Nano Composites	16
2.4 Carbon Nanotube As Reinforcing Agent	17
2.4.1 Features of Carbon Nanotubes	21
2.4.2 Scavenging Nature of CNT	22
2.4.3 Dispersion Techniques of CNT	24

2.4.4	Physical Dispersion Methods	25
2.4.5	Chemical Dispersion Methods	28
	(i) Solvent Dispersion	28
	(ii) Covalent Functionalization	31
	(iii) Non-covalent Functionalization	37
2.5	Thermal Analysis of Polymer Nanocomposites	40
2.6	Dendritic Polymers and Carbon Nanotubes	42
2.7	Shellac as Polymer Coating Materials	44
	2.7.1 Shellac	45
	2.7.2 Extraction of Shellac	46
	2.7.3 Components in Shellac	47
	2.7.4 Characteristics of Shellac	49
	2.7.5 Application of Shellac	50
2.8	MWCNT Reinforced Polymer Nanocomposites	51
2.9	Hybrid Composite	55

CHAPTER 3 MATERIALS AND EXPERIMENTAL METHODS

3.1	Introduction	59
3.1	Materials	59
3.3	Methods	62
	3.3.1 Pre-Dispersion and Post Dispersion Time Optimization	62
	3.3.2 MWCNT Quantity Optimization	64
	3.3.3 MWCNT Coating Process	65
	(i) Hyper Branched Polyester (HBP) Coating on MWCNT	65
	(ii) Shellac Coating on MWCNT	66
	3.3.4 Fabrication of Coated MWCNT Reinforced UPR nanocomposites	67
	3.3.5 Fabrication of Hybrid CNT Nanocomposite	67
3.4	Characterization	67
	3.4.1 Evaluation of Anti -Scavenging behavior of Modified MWCNT	67
	3.4.2 Viscosity	68
	3.4.3 Fourier-Transform Infrared Spectroscopy	68
	3.4.4 X-ray Diffractometry	68
	3.4.5 Field Emission Scanning Electron Microscopy (FESEM)	69
	3.4.6 Tensile Testing of Composites	69

3.4.7	Impact Testing	70
3.4.8	Differential Scanning Calorimetry	70
3.4.9	Thermogravimetric Analysis	70

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Introduction	72
4.2	Optimization of Pre-Dispersion and Post Dispersion Time of MWCNT in Solvent and Matrix	72
4.2.1	Evaluation of Sonication Time for MWCNT Pre-dispersion	72
4.2.2	Evaluation of Sonication Time for Post dispersion of THF-MWCNT in UPR matrix: Effect of Pre-dispersion Technique on Nanocomposites Properties	74
	(i) Physical observation of MWCNT sediment	74
	(ii) Rheology of Nano suspensions at different sonication times	75
	(iii) Plain surface morphology of nanocomposites	77
	(iv) Mechanical properties of nanocomposites	79
	(v) Fracture morphology of nanocomposites	82
4.3	Evaluation of Optimum MWCNT Quantity	85
4.3.1	Physical Observation of MWCNT Sediment in UPR with Different Concentration of MWCNT	85
4.3.2	Rheology of CNT-UPR Nanosuspensions at Different Content of MWCNT	86
4.3.3	Mechanical Properties	88
	(i) Tensile modulus	88
	(ii) Tensile strength and Elongation at break of nanocomposites	91
4.3.4	Surface Morphology of Nanocomposites at Different Content of MWCNT	92
	(i) Plain surface morphology	92
	(ii) Fracture surface morphology	93
4.3.5	Structural Analysis of Nanocomposites as a Function of MWCNT Concentration	95
	(i) X-ray Diffraction at different content of MWCNT	95
	(ii) Correlation between the full width at half maximum and MWCNT content	96
	(iii) Lattice parameters as a function of MWCNT content	97
4.3.6	Thermal Analysis of Nanocomposites as Function of MWCNT Concentration	98
	(i) Effect of CNT concentration on curing temperature of nanosuspensions	98
	(ii) Thermal transitions of neat UPR and CNT-UPR	101

	nanocomposites	
	(iii) Thermogravimetric analysis of nanocomposites	102
4.4	Characterization of HBP Coated MWCNT and Nanocomposites	105
4.4.1	Optimization of HBP Concentration	105
	(i) Structural analysis of HBCNT as a function of HBP concentration	105
	(ii) DSC Analysis of HBCNT as a function of HBP concentration	106
	(iii) Thermogravimetric Analysis of HBCNT as a function of HBP Concentration	108
	(iv) Curing Behavior of HBCNT-UPR nanosuspensions	109
4.4.2	Comparative Characterization of UPR, CNT-UPR and HBCNT-UPR Nanocomposite	112
	(i) Chemical interaction of HBP /MWCNT and between HBP coated MWCNT and UPR	112
	(ii) Plain surface morphology of OPCNT-UPR and OPHBCNT-UPR nanocomposites	115
	(iii) Mechanical properties of neat UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	116
	(iv) Fracture morphology of OPHBCNT-UPR nanocomposite	118
	(v) Comparative XRD Analysis of neat resin, OPCNT-UPR and OPHBCNT-UPR Nanocomposites	120
	(vi) Thermal transition of OPHBCNT-UPR Nanocomposites	121
	(vii) Thermogravimetric Analysis of OPHBCNT-UPR nanocomposite	123
4.5	Characterization of Shellac Coated MWCNT and Shellac Coated MWCNT Reinforced Nanocomposites	127
4.5.1	Optimization of Shellac Concentration	127
	(i) Structural analysis of shellac coated MWCNT	127
	(ii) DSC analysis of shellac coated MWCNT	128
	(iii) Thermogravimetric analysis of SLCNT	130
	(iv) Curing behavior of SLCNT-UPR nanosuspensions	133
	(v) Interaction of Shellac and MWCNT	134
4.5.2	Comparative Characterization of UPR, CNT-UPR and SLCNT-UPR Nanocomposites	138
	(i) Interaction SLCNT and UPR in SLCNT-UPR nanocomposite	138
	(ii) Plain surface morphology of OPCNT-UPR and OPSLCNT-UPR nanocomposites	141
	(iii) Mechanical properties of SLCNT-UPR nanocomposite	142
	(iv) Fracture morphology of SLCNT-UPR nanocomposites	144
	(v) X-ray diffraction of SLCNT-UPR nanocomposite	145
	(vi) Differential scanning calorimetry of SLCNT-UPR nanocomposite	147
	(vii) Thermogravimetric analysis of SLCNT-UPR	148

	nanocomposite	
4.6	Characterization of Hybrid MWCNT Reinforced Nanocomposites	151
4.6.1	Assessment of Non-covalent and Covalent Functionalized MWCNT Ratio in HBOHCNT-UPR Hybrid Nanocomposite	151
	(i) Curing behavior of HBOHCNT-UPR hybrid nanocomposites	151
	(ii) Plain surface morphology of HBOH-CNT-UPR nanocomposites	152
	(iii) Structural analysis of HBOH-CNT-UPR nanocomposites	153
	(iv) Mechanical properties of HBOH-CNT-UPR nanocomposites	155
	(v) Fracture morphology of HBOH-CNT-UPR nanocomposites	156
4.6.2	Comparative study of covalent, non covalent functionalized and hybrid MWCNT reinforced UPR nanocomposites	158
	(i) Comparative curing behavior of HBCNT-UPR, OHCNT-UPR and HBOH-CNT-UPR nanosuspensions	158
	(ii) Comparative structural analysis of HBCNT-UPR, OHCNT-UPR and HBOH-CNT-UPR nanocomposites	159
	(iii) Comparative mechanical properties of OPHBCNT-UPR, OHCNT-UPR and OPHBOH-CNT-UPR nanocomposites	161
	(iv) Comparative fracture morphology OPHBCNT-UPR, OHCNT-UPR and OPHBOH-CNT-UPR nanocomposites	163

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1	Conclusions	165
5.2	Recommendations	167

REFERENCES		168
-------------------	--	-----

APPENDIX

A	LIST OF PUBLICATIONS	202
----------	-----------------------------	-----

LIST OF TABLES

Table No.	Title	Page
3.1	Materials name, specification and origin of materials	61
4. 1	Parameters for Halpin Tsai Equations (4.1) and (4.2)	90
4.2	FWHM, percentage of crystallinity, lattice spacing and crystal size as a function of MWCNT content	97
4.3	Curing temperature and activation energy of neat resin and CNT-UPR nanosuspension at different concentrations of MWCNT	100
4.4	The T _g , and T _m values obtained from DSC thermograms of UPR and CNT-UPR nanocomposites together with their T _d , as evaluated from 50% weight loss from TGA thermograms	103
4.5	Curing temperatures and activation energies of HBCNT-UPR nanosuspensions	110
4.6	The characteristic FTIR peaks of MWCNT, OPHBCNT, OPCNT-UPR and OPHBCNT-UPR nanocomposites	112
4.7	Comparative FWHM, lattice spacing and crystal size, percentage of crystallinity of OPHBCNT-UPR nanocomposite	121
4.8	Characteristic transition temperature OPHBCNT-UPR nanocomposite in DSC and TGA thermograms	123
4.9	T _g , T _c and residue content of SLCNT at different concentration of shellac	131
4.10	Comparative curing temperatures and activation energies of UPR, CNT-UPR and SLCNT-UPR nanosuspensions	133
4.11	Characteristic FTIR peaks of MWCNT, shellac and shellac coated MWCNT (OPSLCNT)	136
4.12	FTIR characteristic peaks of UPR, OPCNT-UPR and OPSLCNT-UPR	139
4.13	Comparative FWHM, lattice spacing and crystal size, percentage of crystallinity of OPSLCNT-UPR nanocomposite	146
4.14	Characteristic transition temperatures of UPR, OPCNT-UPR and OPSLCNT-UPR nanocomposites in DSC and TGA thermograms	147
4.15	Curing temperatures and activation energies of HBOH-CNT-UPR hybrid nanosuspensions at different ratio of HBCNT and OHCNT	151
4.16	Crystallite parameters of HBOH-CNT-UPR hybrid nanocomposites as function of HBCNT and OHCNT ratio	154
4.17	Comparative curing temperatures and activation energies of HBCNT, OHCNT and hybrid HBOHCNT reinforced UPR nanosuspension	159
4.18	Comparative lattice parameters of OPHBCNT-UPR, OHCNT-UPR and OPHBOH-CNT-UPR nanocomposites	160

LIST OF FIGURES

Figure No.	Title	Page
2.1	Chemical Reaction scheme of UPR	12
2.2	Chemical structure of crosslinked UPR	13
2.3	Graphene Sheet (a), Single Walled Carbon Nanotube (b), Double Walled Carbon Nano Tube (c), Multi Walled Carbon Nano Tube (d)	19
2.4	Carbon nanotube as scavenger	24
2.5	Chemical structure of hyperbranched polymer (HBP)	43
2.6	Melt filtration process (a) and Melt filtrated commercial shellac (b)	47
2.7	Chemical structure of characteristic components (a, b,c, d) and Shellac (e)	48
3.1	Shellac solution in THF solvent	60
3.2	Overall methodology flow chart	62
3.3	Pre-Dispersion (A) and Post Dispersion (B) Sonication Process Flow Chart	63
3.4	Composite Fabrication Process Flow Chart	65
3.5	MWCNT Coating process flow chart	66
4.1	Photographs of (a) 0.5hr, (b) 1hr and (c) 1.5hr sonicated THF- MWCNT pre-dispersed suspensions	73
4.2	FESEM of MWCNT and THF-MWCNT	73
4.3	Photographs of (a) 1hr, (b) 1.5hr, and (c) 2hr sonicated MWCNT sediment in THF- MWCNT-UPR nanosuspension and (d) 2hr sonicated MWCNT-UPR nano suspensions	74
4.4	Shear thinning behavior of (a) THF-MWCNT-UPR nanosuspensions dispersed at different sonication time (b) UPR, MWCNT-UPR and THF-MWCNT-UPR nanosuspension	76
4.5	Plain surface of (a) 1hr, (b) 1.5hr, and (c) 2hr sonicated THF-MWCNT-UPR nanocomposites and (d) 2hr sonicated MWCNT-UPR nanocomposite	78
4.6	Tensile strength and tensile modulus (a), Elongation at break and impact strength (b) of THF-MWCNT-UPR nanocomposites as a function of sonication time	80
4.7	(a) Tensile strength and tensile modulus (b) Elongation at break and impact strength of UPR, MWCNT-UPR and THF-MWCNT-UPR nanocomposites	82
4.8	Fracture Micrographs of (a) 1hr, (b) 1.5hr, and (c) 2hr sonicated THF-MWCNT-UPR nanocomposites and (d) MWCNT-UPR nanocomposite	83

4.9	Photographs of MWCNT Sediment in CNT-UPR nanosuspensions contained 0.1, 0.3 and 0.5 wt% MWCNT	86
4.10	Viscosity of CNT-UPR nano suspensions as a function of shear rate	87
4.11	Tensile modulus of composites as a function of MWCNT content fitted with modified Halpin -Tsai equation	88
4.12	Tensile strength and Elongation at break of nanocomposites as a function of MWCNT content	92
4.13	Plain surface micrographs of UPR (a), 0.1CNT-UPR (b), 0.3CNT-UPR (c), and 0.5CNT-UPR (d) nanocomposites	93
4.14	Fracture surfaces of neat UPR (a), 0.1CNT-UPR (b), 0.3CNT-UPR (c) and 0.5CNT-UPR (d) nanocomposites	94
4.15	X-Ray scattering peaks of UPR and CNT-UPR nanocomposites	96
4.16	Curing exotherm of UPR and CNT-UPR nanosuspensions	100
4.17	DSC thermograms of neat UPR, 0.1CNT-UPR, 0.3CNT-UPR and 0.5CNT-UPR nanocomposites	101
4.18	TGA thermograms of UPR and CNT-UPR nanocomposites	103
4.19	DTG thermograms of UPR and CNT-UPR nanocomposites	105
4.20	XRD profiles of MWCNT, HBCNT1, HBCNT2 and HBCNT3	106
4.21	DSC thermograms of MWCNT, HBPCNT1, HBPCNT2 and HBPCNT3	107
4.22	TGA thermograms of MWCNT and HBCNT	108
4.23	DTG thermograms of MWCNT and HBCNT	109
4.24	Curing thermograms of HBCNT-UPR1, HBCNT-UPR2 and HBCNT-UPR3	110
4.25	Schematic HBP coated MWCNT Anti scavenger	111
4.26	FTIR spectra of MWCNT, HBCNT, OPCNT-UPR, OPHBCNT-UPR	113
4.27	Schematic interaction of HBP, MWCNT and UPR	115
4.28	Plain surface morphology of (A) OPCNT-UPR and (B) OPHBCNT-UPR nanocomposites	116
4.29	TS and TM of UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	117
4.30	IS and EB of UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	118
4.31	Fracture surface of OPCNT-UPR (A) and OPHBCNT-UPR (B) nanocomposites	119
4.32	XRD profiles of UPR, OPCNT-UPR and OPHBCNT-UPR	121

4.33	DSC thermograms of UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	122
4.34	TGA thermograms of UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	124
4.35	DTG thermograms of UPR, OPCNT-UPR and OPHBCNT-UPR nanocomposites	125
4.36	XRD profiles of MWCNT and Shellac coated MWCNT (SLCNT)	128
4.37	DSC Thermograms of MWCNT and Shellac coated MWCNT	129
4.38	TGA thermograms of MWCNT and Shellac coated MWCNT (SLCNT)	130
4.39	DTG Thermograms of MWCNT and Shellac coated MWCNT (SLCNT)	132
4.40	Curing exotherms of UPR and SLCNT-UPR nanosuspensions	134
4.41	FTIR spectra of MWCNT, Shellac and OPSLCNT	135
4.42	Schematic interactions between Shellac and MWCNT in SLCNT	137
4.43	FTIR spectra of (i) neat resin, (ii) OPCNT-UPR and (iii) OPSLCNT-UPR Nanocomposites	138
4.44	Schematic interaction between SLCNT and UPR	140
4.45	FESEM Plain surface of OPCNT-UPR (A) and OPSLCNT-UPR (B) nanocomposites	141
4.46	Tensile strength and Tensile Modulus of UPR, OPCNT-UPR and OPSLCNT-UPR Nanocomposites	142
4.47	Elongation at break and Impact strength of UPR, OPCNT-UPR and OPSLCNT-UPR nanocomposite	143
4.48	Fracture surfaces of OPCNT-UPR (a) and OPSLCNT-UPR (b) Nanocomposites	144
4.49	X-ray Diffraction of neat UPR, OPCNT-UPR and OPSLCNT-UPR nanocomposites	146
4.50	DSC thermograms of neat resin, OPCNT-UPR and OPSLCNT-UPR nanocomposites	148
4.51	TGA Thermograms of UPR, OPCNT-UPR and OPSLCNT-UPR nanocomposites	149
4.52	DTG Thermograms of UPR, OPCNT-UPR and OPSLCNT-UPR Nanocomposites	150
4.53	Curing thermogram of HBOH-CNT-UPR nanocomposites	152
4.54	Plain surface micrographs of HBOH-CNT-UPR1 (A), HBOH-CNT-UPR2 (B), HBOH-CNT-UPR3 (C) hybrid nanocomposites	153
4.55	X-ray diffraction of HBOH-CNT-UPR Nanocomposites	154
4.56	TS and TM of HBOH-CNT-UPR Nanocomposites as a function HBCNT and OHCNT ratio	155

4.57	IS and EB of HBOH-CNT-UPR Nanocomposites as a function HBCNT and OHCNT ratio	156
4.58	Fracture micrographs of HBOH-CNT-UPR1 (a), HBOH-CNT-UPR2 (b) and HBOH-CNT-UPR3(c) hybrid nanocomposites	157
4.59	Curing exotherms of OPHBCNT-UPR, OHCNT-UPR and OPHBOH-CNT-UPR Nanocomposites	158
4.60	X-ray diffraction of OPHBCNT-UPR, OHCNT-UPR and OPHBOH-CNT-UPR Nanocomposites	160
4.61	TS and TM of HBCNT-UPR, OHCNT-UPR and HBOH-CNT-UPR nanocomposites	161
4.62	IS and EB of HBCNT-UPR, OHCNT-UPR and HBOH-CNT-UPR nanocomposites	162
4.63	Fracture surface micrographs of (i) OPHB-CNT-UPR (ii) OHCNT-UPR and (iii) OPHBOH-CNT-UPR nanocomposites	163

LIST OF SYMBOLS

D	Crystal size
d	Outer diameter of nanotube
E_a	Activation Energy
E	Tensile modulus
GPa	Gigapascals
I	X-ray intensities
l	Length of MWCNTs
MPa	Megapascals
R	Gas constant
T	Peak temperature
T_d	Decomposition temperature
T_c	Crystallization Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
v	Volume fraction
θ	Scattering angle
λ	Wavelength
β	Heating rate
δ	Full width at half maximum
χ_c	Degree of crystallinity

LIST OF ABBREVIATIONS

ASTM	American Standard Testing Method
CNT	Carbon nanotube
DMF	Dimethyl Formamide
DSC	Differential Scanning Calorimetry
DTG	Differential thermo Gravimetric
EB	Elongation At Break
FESEM	Field Emission Scanning Electron Microscope
FTIR	Furrier Transform Infra Red Spectroscopy
FWHM	Full width at Half Maximum
GF	Glass fiber
GFC	GF reinforced Composite
HBP	Hyper Branched Polyester
HBCNT	HBP coated MWCNT
HBOHCNT	Hybrid of HBCNT and OHCNT
IS	Impact strength
MEKP	Methyl Ethyl keton Peroxide
MWCNT	Multiwalled Carbon Nanotube
OHCNT	Hydroxyl (OH) functionalized MWCNT
OPHBCNT	Optimum amount of HBP coated MWCNT
OPSLCNT	Optimum amount of SL coated MWCNT
PEs	Polyesters
SL	Shellac
SLCNT	Shellac coated MWCNT
TGA	Thermo Gravimetric Analysis
THF	Tetra Hydro Furan
TM	Tensile Modulus
TS	Tensile Strength
UP	Unsaturated Polyester
UPR	Unsaturated Polyester Resin
UV	Ultra-violet

XRD X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Polyesters (PEs) are one of the most versatile synthetic copolymers. They are hetero chain macromolecules that possess carboxylate ester groups as an integral component of their polymer backbones. PEs are extensively used as fibres, plastics, composites and for coatings applications as well (Goodman and Rhys, 1965; Goodman, 1968; Morgan, 1965; Wen et al., 2011; Albdiry and Yousif, 2013).

Unsaturated polyester resins (UPRs) are more readily processable than metals and ceramics. They are widely used as thermosetting resins in various sectors. Usually, UPRs are solidified with cross-linking agents to produce cross-linked UPRs, which have limited structural reliability for engineering applications. Therefore, they are frequently reinforced with macro, micro and nanofillers to boost up their desired properties. Successful incorporation of fillers in UPR composite has enabled new combinations of mechanical, electrical, magnetic, optical, chemical and surface properties. As a result, they are found in wide applications in the arena of construction, marine, automotive, aerospace, packaging, electronics, information, pharmaceuticals, biomedical, energy, sports goods and personal care sectors (Genhua et al., 2004; Gojny et al., 2005; Marco et al. 2011; Wen et al., 2011; Albdiry and Yousif, 2013).

At the beginning, blending of different polymers was conducted to fabricate composite materials for unique properties. However, blending lead to marginal improvement in properties which were not suitable as engineering materials. Therefore to improve the strength and stiffness of polymer materials different kinds of organic and

inorganic silicate, carbon and metal compound were blended as filler with polymer matrix (Barrau et al. 2003). Moreover to achieve desired mechanical and other properties, it was necessary to load high amount of filler which increase cost and processing become difficult. Therefore, currently nanofillers are very popular to get high mechanical as well as other properties at lower concentration of filler. The nanofiller reinforced polymer matrix is known as polymer nanocomposite (Bellayer et al., 2005).

Polymer nanocomposite is a new arena of composite materials, which is receiving significant attention both in academia and industry. The nano filler can provide ultra-large interfacial area per volume between the nano-element and polymer matrix. As a result, the reinforced composites exhibited superior toughness without giving up stiffness or optical clarity. It also possesses greater thermal and oxidative stability, better barrier, mechanical properties and self-extinguishing behavior as unique properties. Carbon nanotubes (CNTs) are emerged as the most promising nanofiller for polymer nanocomposites because of their outstanding properties compared to other fillers. The fantastic properties of individual CNT make an ideal reinforcing agent in the arena of polymer nanocomposites (Iijima, 1991; Kayatin and Davis, 2009; Spitalsky et al., 2010).

Besides, CNT is geometrically distinctive due to its structure as well as surface area which provides vast opportunity for interaction with any continuous phase (Gojny et al., 2004). Moreover, a small amount of CNTs with sound dispersion in polymer matrix exhibits abundant enhancement of different properties (Kota et al., 2007). Therefore, incorporation of carbon nanotubes (CNTs) is an attractive alternative filler to reinforce polymer matrix.

However, CNT reinforced nanocomposite properties are dependent on the degree of dispersion, interfacial adhesion with matrix in the composite system (Singh et al. 2013). The curing process of filler incorporated UPR is delayed due to free radical scavenging nature of carbon nano materials (Monti et al., 20011). Additionally several phenomena limit the promising application of CNT in nano composite technology. For instance, the main drawbacks of CNT are dispersion and compatibility with polymer

matrices, their morphology and Van der Waal's forces are aggregated them into bundles as like as ropes which are stabilized by numerous π - π interactions (Gryshchuk et al., 2006). Moreover, not only potential energy but also the aspect ratio and flexibilities of CNTs are responsible for their entanglements as a consequence difficult to separate into individual nanotube (Breton et al., 2004; Quanxiang et al., 2014). Therefore they are restricted to homogeneous dispersion in polymer matrix.

Extensive effort has been applied to break the nanotube bundles for using individual nanotube as potential reinforcing filler. For this reason, destructive and nondestructive modification techniques are employed to overcome these drawbacks. Nondestructive technique such as non-covalent functionalization attracts attention to modify the nanotube side wall without any defect which can be carried out by physical and chemical methods (Chen et al., 2001; Britz and Khlobystov, 2006; Nanda Gopal Sahoo et al., 2010). Physical method involves shear mixing of CNTs in matrix. These have been carried out at room temperature with different non hydrogen bonding Lewis base solvents to take away the nanotube surface interaction (Ausman et al. 2000; Lau et al., 2005; Liu and Choi, 2012).

Chemical methods are carried out by action of surfactants, surface modification and polymer wrapping technology (Barber et al. 2003; Myung et al. 2012, Kim et al., 2012). This modification can be carried out with synthetic and natural polymers which contain functional end groups (Xu et al., 2004; Singh et al., 2004; Pan et al., 2009; Soradech et al., 2013).

Multi functional hyper branched polyesters are emerged as incredible Dendron for functionalization of CNT. Hyper branched polymers are highly branched macromolecules with three-dimensional dendritic architecture. Because of their high solubility, and abundance of functional groups, hyper branched polymers have potential applications in wide range of fields from drug delivery to material coatings (Bifeng Pan et al., 2009; Caminade and Majoral, 2010; Siqueira Jr et al., 2012;). Besides the large number of reactive end-groups of hyperbranched polymer capable for rapid cross-linking, therefore, they are potential to design thermosetting network (Gao and Yan 2004; Voit 2005; Carlmark et al., 2009).

Wide ranges of naturally occurring polymers derived from renewable resources are available for various material applications. They are potentially used in coatings, gels, foams, films, thermoplastics and thermoset resins (Long Yu et al., 2006). Shellac is one of the thermosetting resin of animal origin secreted by the lac insect *Kerria lacca*. The resin is secreted as a covering for the insect larvae. It is a hard, tough, amorphous resin, which is nontoxic and produces films of good water resistance and exceptional gloss. Shellac is generally believed to be a physical mixture of two resins secreted simultaneously by the lac insect (*Kerria lacca*). These resins are composed of a number of aliphatic polyhydroxy acids present in the form of lactones, lactides and inter-esters. The major components of shellac include aleuritic acid, shellolic acid and jalaric acid. Besides, it contains waxiness, pigments and other water-soluble substances. Nonetheless, it has macromolecular like properties due to its extreme hydrogen bonding (Hagenmaier and Baker, 1993). It has been used as thermoplastics, adhesives, sealants, insulating materials, and coating materials in various fields such as industrial materials, medicine, and food ingredients due to its various unique properties such as thermoplasticity, oil resistibility, cohesiveness, and insulating ability along with its nonpoisonous nature. Shellac has been extensively used for water, gas, lipid and microbial spoilage protection to extend the shelf-life of products in food and agro industries (Hagenmaier and Baker, 1993; McGuire and Hagenmaier, 1996; Phan The et al., 2008; Valencia-Chamorro et al., 2009). It has also been used for the moisture protection of drugs, controlled drug delivery system and enteric coating for drugs and probiotics in the pharmaceutical industry (Limmatvapirat et al., 2004; Stummer et al., 2010; Soradech et al., 2013).

These studies reveal that shellac is a potential functional coating material. Researchers have used shellac to coat nanoparticles. In the case of coating application it serves desired purposes due to availability and easy processability, from this point of view it has been considering to coat MWCNT.

Among various CNTs, multi-walled carbon nanotubes (MWCNTs) are frequently incorporated with varieties of polymers as an important reinforcement to find superior properties of the resulting materials (Logakis et al., 2011; Hemmati et al.,

2008; Ritter et al., 2010; Mina et al., 2010; Mina et al., 2014). However, there have been limited investigations on MWCNT reinforced UPR composites because of stated drawbacks (Battisti et al., 2009; Seyhan et al., 2007).

1.2 PROBLEM STATEMENT

The background study reveals that UPR is a popular thermosetting resin. Several types of research have done to overcome the drawbacks of UPR. Numerous researchers incorporated different types of filler to reinforce this matrix. To date, nanofillers are more attractive as compared to macro and micro fillers. Among nanofillers CNT attract attention to reinforce polymer matrix. However, in the case of CNT there are some limitations which discourage for fabrication of CNT- reinforced polymer nanocomposites. The specific problems are stated below:

- ❖ The mechanical properties of commercially available unsaturated polyester resin (UPR) are relatively weak. Due to these poor properties, UPR cannot be fully exploited in industrial applications. Therefore, carbon nanotubes are used as nanofillers to reinforce the UPR matrix for fabrication of nanocomposites. However, the potential reinforcing efficiency of these nanofillers is not achieved due to their inhomogeneous dispersion in the matrix if they are directly incorporated without modification. Generally, better dispersion of CNTs in polymer matrix reportedly results in improved mechanical and thermal properties of the polymer nanocomposites.
- ❖ There are no controls on the concentration of carbon nanotubes (CNT) and dispersion time for fabrication of CNT- reinforced polymer nanocomposites. Usually, lower content of CNT is dispersed more easily than higher concentration. However, the addition of lower content of CNT which does not provide desired mechanical properties in one hand and the addition of higher content gives rise to aggregate formation on the other, enabling poor dispersibility and hence resulting in the poor mechanical performance of the nanocomposites. As a result, optimization of CNT concentration and dispersion time in UPR is essential for the enhancement of mechanical properties.

- ❖ Shellac used as a coating material which contains carboxylic and hydroxyl functional groups. These functional groups can functionalize the nanomaterials through adhering to the surface. However there are no attempts have been found to functionalize multi-walled carbon nanotube with shellac.
- ❖ Carbon based nanofillers delay the curing process of the unsaturated polyester resin due to scavenging behavior. This delay involves energy loss for fabrication of nanocomposites. To overcome this problem, modification of CNTs is necessary to investigate the effect of CNT modification on curing process.
- ❖ CNT dispersion is affected by van der Waals force which exists among CNTs and helps them to form CNT bundles. Different techniques are followed to reduce the van der Waals force and to improve sound dispersion in the matrix. The defect functionalization, as well as covalent functionalization of CNT is very common to improve the dispersion quality. However, defective CNT is not appropriate to improve mechanical and other properties of CNT- based UPR nanocomposites.

1.3 OBJECTIVES

In the light of the aforesaid problems, this work has been undertaken to improve the dispersion of Multi-walled CNTs (MWCNTs) in UPR matrix by means of a method of solvent pre-dispersion. In this case, noncovalent functionalization of MWCNT has been performed with synthetic and natural functional polymers. The specific objectives of this work are:

- (i) To improve dispersion of MWCNT in UPR matrix by using tetrahydrofuran (THF) as low-boiling point Lewis base solvent as a pre-dispersing agent.
- (ii) To evaluate optimum sonication time and concentration of MWCNT for fabrication of MWCNT reinforced UPR nanocomposite.
- (iii) To perform non-covalent functionalization of MWCNT with synthetic hyperbranched polyester (HBP) and natural shellac (SL) functional polymers and to evaluate the optimum concentration of those functional polymers.

(iv) To reduce the scavenging behavior of MWCNT as well as to reduce cross linking time

(v) To compare the reinforcing efficiency of non-covalent functionalized CNT, covalent functionalized CNT and hybrid CNT in nanocomposites.

1.4 SCOPE OF STUDY

(i) Dispersion of MWCNT at 0.5–1.5 hr sonication in Tetrahydrofuran (THF) as low-boiling point Lewis base solvent. Dispersion of MWCNT in UPR with mechanical stirring and ultra sonication technique at time 1–2 hr.

(ii) Optimization of different loaded MWCNTs (0.05–0.5 wt%). The optimum amount of MWCNT was evaluated by the application Halpin–Tsai model in observed mechanical properties of nanofiller loaded nanocomposites.

(iii) Non defect as well as Non covalent functionalization of MWCNT is performed with hyper branched polyester (HBP) and shellac (SL) functional polymers. Different amount (5–15 wt %) of these polymers were coated on the surface of MWCNT and then optimization of these polymers are performed.

(iv) Fabrication of hybrid nanocomposite with the different ratio (1:1, 2:1, 1:2) of HBCNT and covalent hydroxyl (OH) functionalized MWCNT (OHCNT) and optimization of CNT ratio.

(v) Characterization of non-covalent functionalized MWCNTs and nanocomposites is done using Fourier transform infra-red spectroscopy, X-ray diffraction studies, field emission scanning electron microscopy, thermogravimetric analysis and differential scanning calorimetry.

(vi) Comparative study of non-covalent functionalized CNT, covalent functionalized CNT and hybrid CNT incorporated nanocomposites.

1.5 SIGNIFICANCE OF STUDY

Solvent pre-dispersion method produces well dispersed MWCNT reinforced UPR nanocomposites. The properties of pre-dispersed MWCNT reinforced nanocomposites are greater compared to direct dispersed MWCNT reinforced nanocomposites. The thermal properties of noncovalent functionalized MWCNT are significantly improved as compared to pristine MWCNT. The curing performance, as well as structural properties of modified MWCNT incorporated nanocomposites, is also remarkably improved as compared to pristine MWCNT reinforced nanocomposite. HBP coated MWCNT increases the stiffness of nanocomposite whereas shellac coated MWCNT enhances the toughness of nanocomposite. Hybrid nanocomposite which contained a higher amount of HBPCNT increases the stiffness of the resulting nanocomposite.