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

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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 mengubahsuai 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 diubahsuai dengan menggunakan PBBTNK dan OHTNK. Campuran TNKBB yang berfungsi kovalen dan bukan kovalen kemudian telah bersama-sama mengukuhkan sifat RPTS.

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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.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

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CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 INTRODUCTION

In this research, multi walled carbon nanotube (MWCNT) was used to produce reinforced unsaturated polyester resin (UPR) nanocomposite (CNT-UPR nanocomposite). In addition non-covalent functionalized MWCNT was prepared as a means of well dispersion in matrix and to improve the property of nanocomposites as well. Different analysis including thermo-mechanical properties of nanocomposites was performed to understand the nanocomposite behavior and identifies the possible ways in which performance might be improved.

This chapter describes in brief the materials, CNT treatment methods and characterization techniques, nanocomposite processing and testing methods.

3.2 MATERIALS

Orthopthalic unsaturated polyester resin (Polymal) (UPR) was used as matrix materials. Tetra-hydro furan (THF) solvent was used as pre-dispersion media. Methyl ethyl keton peroxide (MEKP) was used as curing initiator. Multi-walled carbon nanotubes (MWCNTs) and hydroxyl functionalized MWCNT (OHCNT) was used as reinforcing nanofiller.

Hyper branched polyester (HBP)(2-2-bis (methylol) propionic acid) generation 2 was used as functional polymer to non covalent functionalization of MWCNT. In addition the natural polymer shellac (SL) was used as coating material for non covalent

functionalization of MWCNT. Figure 3.1shows the commercial grade shellac solution in THF solvent. Additionally the specification and origin of these materials are represented in Table 3.1.

Figure 3. 1: Shellac solution in THF solvent

Table 3. 1: Materials name, specification and origin of materials

Name	Properties	Manufacturer	Country of Origin
Unsaturated Polyester Resin	❖ Viscosity 700-800mPa.S at 25^0C ❖ Volatile content is 30–35%, ❖ Gel time is 8−15 min.	Luxchem Polymer Industries Snd.Bhd.	Malaysia
Multi walled Carbon nanotubes	❖ Produced by moving-bed catalysis technique ❖ Diameter <8nm, length between 10−30 μm ❖ Carbon purity of 95%	Timesnano	China
Curing agent(Peroxides)	❖ Colorless liquid	Sigma Aldrich	USA
HBP	❖ molecular weight 1749.79g/mol ❖ contained 16 hydroxyl groups	Sigma Aldrich	USA.
Shellac	❖ Solid ❖ Polish grade ❖ Light chocolate color ❖ Order less		Bangladesh
Tetrahydrofuran and Acetone		Merk	Germany
Mold releasing agent	Paste and Cream	John Burn & Co. (B'ham) Ltd	England