Polymer Brush Carbon Nanotubes as Nanofillers in Macro and Nano Size Composites

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SUMMARY

The work outlined in this thesis covers the many aspects of carbon nanotubes and polymers by combining the two into nanocomposite materials of macro and nano size. The issues of producing and combining the two are explored and results are provided.

There are four major aspects to this work;

1. *Polymer Brushed Carbon Nanotubes:* multi-walled carbon nanotubes (MWCNT) are surface functionalized with polymer brushes produced by activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP). A "grafting from" approach was used as a higher grafting density would result and therefore it was necessary to functionalize the carbon nanotubes surface with hydroxyethyl-2-bromoisobutyrate (HEBI). This acted as the haloalkane (i.e. tertiary bromide) initiator sites in ARGET ATRP of styrene and methyl methacrylate. The successful growth of the polymer brushes were characterized for their chemical, kinetic and physical properties. In addition, polymer brushes of 2-hydroxyethyl methacrylate (HEMA) was grown by non-living means by attaching the HEMA monomer via the hydroxyl group to a carboxylic acid surface functionalized MWCNT and subsequently polymerized.
2. *Macro-sized Composites:* a composite of carbon nanotubes with homopolymers as the matrix, requires surface modification of the MWCNT to prevent nanotube aggregation. A homogeneous dispersion is necessary in order to produce improved properties for the composite. The 'macro' composite research involved the incorporation of polymer brush carbon nanotubes in concentrations of 0.1w/w% to 1w/w% (e.g. poly(methyl methacrylate) polymer brush carbon nanotubes in a poly(methyl methacrylate) matrix). The most

improved composites obtained used polystyrene brushes in a polystyrene matrix, which was due to π-π stacking interactions. The composite material possessed improved mechanical strength, increased glass transition temperature and increased processability. Furthermore, the dispersion was maintained after processing with shear forces.

3. *Pyrene as a Model System:* 1-pyrenecarboxylic acid has a very similar architecture to MWCNT and for this reason was used to model the chemical synthesis of aspects ‘1’ and ‘2’ with polystyrene. The work showed similar enhancements in terms of mechanical strength, increased glass transition temperature and increased processability. Compared to polystyrene polymer brush carbon nanotubes the improvement was not as great, however the pyrene material did not exhibit limits of dispersion like the carbon nanotubes filler.
4. *Nano-sized Composites:* This research utilized a hexagonal-packed cylindrical phase of a di-block copolymer melt, in an attempt to align the carbon nanotubes to the cylindrical phase. To ensure their affinity for the cylinder phase, polymer brushes of polystyrene were used for a 30/70 poly(styrene-b-methyl methacrylate) melt. However, the nanotubes were found to disrupt the segregation process, and the phases did not form appropriately. This ultimately did not provide strong enough forces to align the carbon nanotubes, but indicates that because of their relative massive size, greater forces are required.

Future work has been recommended with alternative polymer brush carbon nanotubes as fillers and using electric fields, as they have shown to better orientate a hexagonal-packed cylindrical phase from a parallel orientation to a perpendicular orientation. This is a suggested technique that might be able to align the carbon nanotubes.

CHAPTER SUMMARY

Chapter 1: Carbon Nanotubes and Polymers – an Introduction

What is a carbon nanotubes, what is a polymer, how are they made, and what are they used for? This first chapter is a detailed review of carbon nanotubes, polymers and combining the two.

Chapter 2: Synthesis of Homopolymers and Diblock Copolymers

Reports the findings and procedures used in this PhD research project to synthesize homopolymers of polystyrene and poly(methyl methacrylate) by activators regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP). The chapter then extends to the synthesis of di-block copolymers of poly(styrene-b-methyl methacrylate) using polystyrene as the macro-initiator.

Chapter 3: Polymer Brushes: Surface Initiated Polymerization (SIP)

In this chapter the purification of carbon nanotubes and subsequent surface functionalization with a tertiary bromide initiator is discussed. A model system is also discussed, which uses 1-pyrenecarboxylic acid, as the chemical structure is very similar to a carbon nanotube. This model system was necessary to help verify the general functionalization procedure.

The work then extends to the use of the tertiary bromide functionalized carbon nanotubes in the synthesis of ARGET ATRP polymer brushes of polystyrene and poly(methyl methacrylate). In addition, poly(2-hydroxyethyl methacrylate) brushes were produced by a different synthetic route to the above. Further work was also performed on the pyrene model system, polymerizing one polystyrene polymer brush per pyrene molecule.

Chapter 4: Polymer Brushes as Nanofillers (Macro-Sized)

The brushes produced in Chapter 3 were used as a filler in the corresponding polymer (i.e. polystyrene brushes in polystyrene). Composite concentrations as high as 1w/w% of the polymer brush carbon nanotubes were introduced and the physical characteristics were analyzed.

Chapter 5: Formation of Block Copolymer Microdomains and Hybrid Materials (Nano-Sized)

Chapter 4 discusses the formation of macro-sized composite material, whereas this chapter takes it to the nano-sized composite material. Using block copolymer melts of a 30/70 ratio, the cylindrical phase is formed and during formation the carbon nanotube polymer brushes were added. These brushes have a stronger affinity for one of the two domains and hence it was expected to align within that phase.

Chapter 6: General Conclusions, Recommendations and Future Work

This chapter summarizes the entire work of the thesis and in particular how to optimize the composite material properties. In addition, the chapter discusses future directions the research can head towards.

OTHER SUCCESSFUL OUTCOMES

Publications & Conference Proceedings

- Trout, N.; Aitchison, T.; Clarke, S. R. *The 32nd Australasian Polymer Symposium* **2011**
- Clarke, S. R.; Aitchison, T.; Trout, N. *The 32nd Australasian Polymer Symposium* **2011**
- Aitchison, T.; Clarke, S. R. *The 32nd Australasian Polymer Symposium* **2011**
- Clarke, S. R.; Trout, N.; Aitchison T.; Habibie, S.; Brown, R. J. *Chemeca* **2010** 143, ISBN 978-085-825-9713
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. *ARNAM/ARCNN 2010 Joint Workshop* (**2010**)
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S. *The Fourth Biennial Australian Colloid and Interface Symposium* (**2009**)
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G., *ARNAM Annual Workshop* (**2008**)
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G., *The 30th Australasian Polymer Symposium* (**2008**)
- Aitchison, T. J.; Ginic-Markovis, M.; Matisons, J. G., *Thinking Synergy: A Flinders Postgraduate Conference* (**2008**)
- Aitchison, T. J.; Ginic-Markovic, M.; Matisons, J. G., *Ninth International Conference on the Science and Application of Nanotubes* (**2008**)
- Aitchison, T. J.; Ginic-Markovic, M.; Matisons, J. G., *Polymer Processing Society 24th Annual Meeting Conference Proceedings* S18-925 (**2008**)
- Aitchison, T. J.; Ginic-Markovic, M.; Matisons, J. G.; Simon, G.P.; Fredericks, P. M., *J. Phys. Chem. C* **2007**, 111, 2440-2446
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- ‘Polymeric characterization of nano-filled materials,’ Prof. Henri Sautereau and Prof. Gerard Seytre, Institut National des Sciences Appliquees de Lyon (INSA-Lyon), France (**2008**)
- ‘Optical rheology of nano-filled polymeric materials,’ Dr Anson Ma, Cambridge University, England (**2008)**

Publications in Preparation

- Aitchison, T. J.; Ginic-Markovic, M.; Saunders, M.; Fredericks, P.; Valiyaveettil, S.; Matisons, J. G.; Simon, G. P. ARGET ATRP MWCNT Polymer Brushes and Their Properties, *Polymer International*
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. Kinetics of ARGET ATRP Di-Block Copolymers, *Journal of Polymer Science: Part A, Polymer Chemistry*
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. MWCNT PHEMA Polymer Brushes and Their Use *Macromolecules*
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. Polymer Brush Nanocomposites, *Chemistry of Materials*
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. Synthesis of Silicon Wafer Polymer Brushes by Using Random Tripolymers, *Chemistry of Materials*
- Aitchison, T. J.; Ginic-Markovic, M.; Clarke, S.; Matisons, J. G. Pyrene Polymer Brushes as a Nanofiller in Polymer Composites, *Chemistry of Materials*

DECLARATION

‘I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.’

Date 17/11/10

Tony Aitchison

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GLOSSARY

Abbreviations

AC	Acid Cleaved – *relating to carbon nanotubes*
AFM	Atomic Force Microscopy
AGET	Activators generated by electron transfer
AIBN	2,2’-azobis(isobutyronitrile)
AR	As Received – *relating to carbon nanotubes*
ARGET	Activators regenerated by electron transfer
ATRP	Atom-transfer radical polymerization
Conv.	Conversion
CRP	Controlled radical polymerization
CVD	Chemical vapor deposition
CNT-Br	Carbon nanotubes functionalized with HEBI
CNT-PHEMA	PHEMA polymer brushes on carbon nanotubes
CNT-PMMA	PMMA polymer brushes on carbon nanotubes
CNT-PS	PS polymer brushes on carbon nanotubes
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DTGA	Differential Thermogravimetric Analysis
EBiB	Ethyl 2-bromoisobutyrate
EDX	Energy Dispersive X-ray Spectroscopy
FRP	Free radical polymerization
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HEBI	Hydroxyethyl-2-bromoisobutyrate
HEMA	2-hydroxyethyl methacrylate
HRTEM	High Resolution Transmission Electron Microscopy
ICAR	Initiators for continuous activator regeneration
L-MWCNT	long multi-walled carbon nanotubes from NTP
MeOH	Methanol
Me_6TREN	Tris(2-dimethylamino)ethyl)amine
MMA	Methyl methacrylate

MCWNT	Multi-walled carbon nanotube
NMP	Nitroxide mediated polymerization
NMR	Nuclear Magnetic Resonance
PHEMA	Poly(2-hydroxyethyl methacrylate)
PMMA	Poly(methyl methacrylate)
ppm	parts per million
PS	Polystyrene
PS-Br	Macro-initiator of PS with an alkyl bromide functionalized end
Pyrene-HEBI	1-Pyrenecarboxylic acid functionalized with HEBI
Pyrene-PS	A PS chain covalently attached to Pyrene-HEBI
R^2	is the coefficient of determination of a linear regression. It ranges from 0 to 1 with 1 indicating the real data fits perfectly to the regression line and 0 the real data does not.
S-MWCNT	short multi-walled carbon nanotubes from NTP
SCFT	Self-consistent mean field theory
SIP	Surface initiated polymerization
$Sn(EH)_2$	Tin(II) 2-ethylhexanoate
SR & NI	Simultaneous reverse and normal initiation
SWCNT	Single-walled carbon nanotube
T_c	Crystallization temperature
T_d	Decomposition temperature
TEA	Triethylamine
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TREN	Tris(2-aminoethyl)amine
TSE	Total surface energy