SYNTHESIS OF HYBRID POLYMER/GRAPHENE MATERIALS USING MINIEMULSION POLYMERIZATION

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Abstract

The goal of this research has been to exploit the amphiphilic properties of graphene oxide (GO) for the preparation of well-dispersed polymer-graphene nanocomposites. In order to achieve this aim, the synthesis of nano-dimensional GO was conducted according to a recent method for the preparation of small and uniform GO. The ability of GO to function as surfactant was demonstrated in miniemulsion polymerization of styrene and other vinyl monomers of different polarities, in the absence of conventional surfactant. Miniemulsion polymerization was chosen due to its unique characteristic which enables the initial entrapment of GO on the surface of monomer droplets. The formation of 'armoured' particles indicated the presence of GO at the surface of particles, consistent with its surface active properties. Polymer particles with diameters ranging from ~500 nm to a few microns, with relatively broad particle size distributions were observed.

The polarity of the monomers was found to strongly influence the emulsion stability; monomers with a relatively small polar component (based on Hansen solubility parameters) such as styrene, lauryl methacrylate and benzyl methacrylate, generate stable emulsions that can be effectively polymerized. The differences in pH of the emulsion investigated in this research exerted a relatively minor influence on the polymerization, whereas the ionic strength on the other hand had a more significant effect – the presence of a suitable concentration of NaCl resulted in increased colloidal stability and narrower particle size distribution. Poly(styrene-*co*-butyl acrylate)/GO film resulting from miniemulsion polymerization was visually homogeneous with evidence of preserved 'armoured' particles, hence presenting an efficient method for the preparation of polymer/graphene nanocomposites.

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Key to Symbols and Constants

cm	Centimetre
d_n	Number average diameter
d_v	Volume average diameter
d_z	Zeta average diameter
D	The diffusion coefficient of GO sheet from the aqueous phase to the newly generated oil-water interface
Đ	Dispersity
g	Gram
GPa	Gigapascal
h	Hour
k_{act}	Rate constant of activation
k_{deact}	Rate constant of deactivation
k_d	Rate constant of initiator decomposition
k_i	Rate constant of initiation
k_t	Rate constant of termination
L	Litre
M	Mol litre^{-1}
mA	Milli ampere
mg ml^{-1}	Milligram per millilitre
min	Minute
mL	Millilitre
µm	Micrometre
M_n	Number average molecular weight
M_w	Weight average molecular weight
mV	Milli volt
nm	Nanometre
pH	Measure of the acidity or basicity of an aqueous solution
π	pi
rpm	Revolutions per minute
S m^{-1}	Siemens per metre
T_g	Glass transition temperature

v/v	Volume by volume
W m^{-1} K^{-1}	Watt per meter Kelvin

Key to Abbreviations and Acronyms

AIBN	Azobisisobutyronitrile
AOT	Sodium bis-2-ethylhexylsulfosuccinate
ATR	Attenuated Total Reflectance
ATRP	Atom transfer radical polymerization
BAM	Brewster angle microscopy
BMA	Benzyl methacrylate
BPO	Benzoyl peroxide
$CDCl_3$	Deuterated chloroform
CLRP	Controlled living radical polymerization
CMC	Critical micelle concentration
CNT	Carbon nanotubes
CTAB	Cetyltrimetyl ammonium bromide
CVD	Chemical vapour deposition
DLS	Dynamic light scattering
DCM	Dichloromethane
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DTAB	Dodecyl trimethylammonium bromide
DVB	Divinyl benzene
EIP	Emulsion inversion point
FTIR	Fourier-Transform Infra-Red Spectroscopoy
GO	Graphene oxide
HCl	Hydrochloride acid
HD	Hexadecane
HLB	hydrophilic-lipophilic balance
H_2SO_4	Sulphuric acid
ITO	Indium tin oxide
$KCIO_3$	Potassium chlorate
KPS	Potassium persulphate

LED	Light emitting diodes
LMA	Lauryl methacrylate
MA	Methyl acrylate
MgSO4	Magnesium sulphate
MMA	Methyl methacrylate
NaCl	Sodium chloride
NaOH	Sodium hydroxide
n-BA	Normal butyl acrylate
NMP	1-methyl-2-pyrrolidinone
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance
OLED	Organic light emitting diodes
PGNs	Polymer/graphene nanocomposites
PhD	Doctor of Philosophy
PHEMA	Poly(2-hydroxyethyl methacrylate)
PIT	Phase inversion temperature
PMMA	Polymethyl methacrylate
PNIPAM	Poly(*N*-isopropylacrylamide)
PS	Polystyrene
PS-GO	Polystyrene-graphite oxide
P_2O_5	Phosphorus pentoxide
RAFT	Reversible addition-fragmentation chain transfer
RGO	Reduced graphene oxide
SDBS	Sodium dodecylbenzene sulfonate
SDS	Sodium dodecyl sulphate
SEM	Scanning Electron Microscopy
SFC	Supercritical fluid
SiC	Silicon carbide
St	Styrene
t-BA	Tertiary butyl acrylate
TEM	Transmission Electron Microscopy
TCE	Transparent conducting electrodes
THF	Tetrahydrofuran

TGA	Thermogravimetric Analysis
XPS	X-Ray Photoelectron Spectroscopy

Table of Contents

CHAPTER 1: Introduction

1.1 Introduction

The discovery of single layer graphene in 2004[1] has been one of the most significant achievements due to the promising applications of this novel material in various fields. Graphene possesses a unique combination of excellent electrical, thermal, optical and mechanical properties.[2,3] One of the most promising applications of this material is in polymer nanocomposites.[4,5] Polymeric nanocomposite materials, *i.e.* materials comprising polymer and "filler" (*e.g.* carbon black, clay), are attractive because their properties can be significantly enhanced relative to the pure polymer. The infusion of graphene into polymer matrices has resulted in a significant property enhancement of the nanocomposites at much lower percolation threshold in comparison to other fillers.[6] Nevertheless, the long standing desire in polymer nanocomposites is to achieve enhanced filler dispersion with good compatibility within the polymer host in order to fully utilise the great properties of the filler. To date, much effort with regard to physical and chemical modifications to increase the compatibility between graphene and polymer matrices has been reported due to the hydrophobic nature of this novel material.[7,8]

Graphene oxide (GO), the oxidized form of exfoliated graphene, has generated significant interest due to the extensive array of functional groups that permit further functionalization and is considered as a promising precursor for the production of graphene-based materials. A recent report in 2010 revealed the ability of GO to stabilize mixtures of hydrophobic liquids and water due to its amphiphilic properties with the unique combination of hydrophilic edges (carboxylic acid groups) and more hydrophobic basal plane.[9] Thus, it is possible to use GO sheets to prepare polymer nanocomposites through the self assembly of material/particles at the droplets interface, which is known as Pickering emulsions.[10,11]

In-situ polymerization involving the presence of graphene/GO *via* heterogenous system, in particular, miniemulsion polymerization has been widely reported in order to achieve high filler dispersion in polymer matrices.[12-14] Miniemulsion polymerization is particularly important for synthesis of organic/inorganic hybrid particles by encapsulation of inorganic material,[15] preparation of hollow particles[16,17] and for implementation of controlled/living radical polymerization (CLRP) in dispersed systems.[18] Typically, relatively large amounts of surfactants are required to maintain colloidal stability and avoid large scale coagulation in such systems. The idea of employing GO as sole surfactant, which eliminates the use of conventional surfactant, in miniemulsion polymerization, presents another promising pathway for the production of graphene-based materials. Earlier reports on the synthesis of polymer nanocomposites *via* miniemulsion polymerization in the presence of GO as sole surfactant resulted in ill-defined systems, due to large and non-uniform GO sheets.[19,20] Therefore, much effort is still needed to establish the implementation of this promising method. In addition, the behaviour of GO as surfactant, and the factors affecting its efficiency *e.g.* GO sheet size, pH, ionic strength, in particular, in miniemulsion polymerization are generally not well understood.

1.2 Objective of the Research

The main objective of this thesis is to deliver a method for the preparation of novel hybrid graphene-based nanocomposite materials *via* aqueous miniemulsion polymerization by employing nano-dimensional GO as sole surfactant (in the absence of conventional surfactant). In order to achieve the objective, the detailed descriptions of the milestones are as below:

1. Nano-dimensional graphene oxide sheets is prepared according to a new method which entails synthesis of small and uniform GO sheets (~100 nm) from graphite nanofibers using a modified Hummers method.[9] Subsequently, the ability of GO sheets to stabilize oil-in-water miniemulsions is investigated by varying the parameters; GO sheet size (“large”, “medium” and “small”) and GO loading (1, 3 and 5 wt%). The best condition that could give good colloidal stability is determined.

2. Aqueous miniemulsion polymerization of styrene using nano-dimensional GO as sole surfactant is conducted according to the findings in Milestones 1. The

morphology of the latex is characterized in terms of particle size and particle size distributions.

3. The ability of nano-dimensional GO sheets to serve as sole surfactant in miniemulsion polymerization based on various vinyl monomers (acrylate and methacrylate) is investigated.

4. The efficiency of GO as surfactant in miniemulsion polymerization of styrene is investigated at different pH and ionic strength solution. The optimum pH/sodium chloride concentration (NaCl) that gives the most stable miniemulsion with good particle size distribution is determined.

5. Poly(styrene-*co*-butyl acrylate)/GO (*via* miniemulsion polymerization) film is prepared to investigate the dispersion of GO in the polymer matrix. The physical properties of the prepared nanocomposite film is tested using a range of experimental techniques *e.g.* differential scanning calorimeter (DSC) and thermal gravimetry analysis (TGA).

1.3 Layout of Thesis

This thesis consists of seven chapters where in Chapter 1, a general introduction and the aims of the studies are presented. Chapter 2 describes the introduction to graphene and GO, the current review on GO as surfactant and general preparation of polymer/graphene nanocomposites. This chapter also briefly explains radical polymerization and its implementation in dispersed systems with emphasis on miniemulsion polymerization. The experimental procedures for the preparation of nano-sized GO and the miniemulsion polymerization are described in Chapter 3. In this chapter, a brief outline of the analytical instrument used throughout the studies is also given. Chapter 4 describes the preparation of polystyrene ‘armoured particles’ with nano-sized GO sheets *via* aqueous miniemulsion polymerization in the absence of conventional surfactant.

The ability of nano-size GO sheets to stabilize oil-in-water miniemulsions based on various vinyl monomers is demonstrated in Chapter 5. The effect of monomer polarity (evaluated *via* the Hansen solubility parameters) on the stability of miniemulsion is explained. In Chapter 6, the effect of pH and ionic strength of the solution on the aqueous miniemulsion polymerization of styrene using nano-sized GO as sole surfactant is described. Chapter 7 describes the preparation of poly(styrene-*co*-butyl acrylate)/GO *via* miniemulsion polymerization for highly dispersed GO in the nanocomposite. Chapter 8 concludes the preceding chapters with recommendation provided for future studies.

1.4 List of Publications

1. S. H. Che Man, Stuart C. Thickett, Michael R. Whittaker, and Per B. Zetterlund. **Synthesis of Polystyrene Nanoparticles "Armoured" with Nanodimensional Graphene Oxide Sheets by Miniemulsion Polymerization.** *J. Polym. Sci.: Part A: Polym. Chem.* **2013**, 51 (1), 47-58.

2. S. H. Che Man, N. Y. Mohd Yusof, Michael R. Whittaker, Stuart C. Thickett, and Per B. Zetterlund. **Influence of Monomer Type on Miniemulsion Polymerization Systems Stabilized by Graphene Oxide as Sole Surfactant.** *J. Polym. Sci.: Part A: Polym. Chem.* **2013**, 51 (23), 5153-5162.

3. S. H. Che Man, David Ly, Michael R. Whittaker, Stuart C. Thickett, and Per B. Zetterlund. **Nano-sized graphene oxide as sole surfactant in miniemulsion polymerization for nanocomposite synthesis: Effect of pH and ionic strength.** *Polymer*. **2014**, 55 (16), 3490-3497.

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