

University of Southampton Research Repository ePrints Soton

Copyright © and Moral Rights for this thesis are retained by the author and/or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder/s. The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given e.g.

AUTHOR (year of submission) "Full thesis title", University of Southampton, name of the University School or Department, PhD Thesis, pagination

University of Southampton

Faculty of Engineering, Science and
Mathematics
School of Electronics and Computer Science

**POLYETHYLENE-MONTMORILLONITE
NANOCOMPOSITES**

by

Christopher Duncan Green

Thesis for Doctor of Philosophy

September 2008

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

Faculty of Engineering, Science and Mathematics
School of Electronics and Computer Science

Doctor of Philosophy

Polyethylene-montmorillonite nanocomposites

by Christopher Duncan Green

Nanocomposite materials are currently attracting much interest due to their possibility of global property improvement – mechanical strength, toughness, electrical breakdown strength, electrical erosion resistance and flame retardancy. In order to disperse montmorillonite clay (MMT) into polyethylene (PE), the clay sheets need to be rendered organophilic. Masterbatches with a high level (~40 %wt) of organomodified clay can then be dispersed into a host by a simple mechanical process. Two chemically different masterbatches were purchased: Nanoblend 2101 from PolyOne Corp. and C30PE from Nanocor Inc. These were let down using a Randcastle™ single screw extruder with a patented mixing device to provide elongational flow. Wide angle X-ray diffraction was used together with transmission electron microscopy to evaluate the particle dispersion, which consisted of intercalated clay organised in clusters up to one micron in diameter.

The performance of these materials was assessed in terms of AC ramp breakdown statistics, dielectric spectroscopy, dynamic and tensile mechanical properties. Nanoblend masterbatch consistently improved the breakdown statistics, more than overcoming the inherent demerit of extrusion, which mildly aged the unfilled material (as confirmed by Raman spectroscopy.) On the other hand, even low loading levels of Nanocor could result in reduced breakdown strength and increased scatter. Furthermore, both sets of materials demonstrated large dielectric losses at power frequencies and poorer performance under mechanical tension. These materials would therefore require considerable development before they could confidently be used commercially.

The nature of the PE-MMT interactions was examined by investigating the crystallisation kinetics and resulting morphologies with differential scanning calorimetry and scanning electron microscopy. By varying the masterbatch type, loading level and crystallisation temperature, it was possible to study a wide range of supercrystalline morphologies using a permanganic etching technique. This is a useful contribution to the field of nanocomposites research. It is known that the morphologies of polymers can affect their mechanical properties and electrical treeing behaviour, and so it is possible that controlled crystallisation could provide a route toward designer materials with optimised behaviour.

Table of contents

1. Introduction

1.1 The concept of nanocomposites	1
1.2 The filler: montmorillonite clay	5
1.3 The matrix: polyethylene	9
1.4 Dielectric breakdown of polymers	11
1.5 Aims and objectives	16
1.6 Contents of this thesis	17

2. Materials preparation

2.1 Materials selection	18
2.2 Extrusion	20
2.3 Wide angle X-ray scattering (WAXS)	25
2.4 Transmission electron microscopy (TEM)	32
2.5 Assessment of degradation	37
2.6 Conclusion	42

3. Thermal analysis

3.1 Introduction	43
3.2 Avrami analysis	44
3.3 Melting behaviour	54
3.4 Analysis of crystallisation and melting enthalpies	56
3.5 Discussion	60
3.6 Conclusions	67

4. Morphological characterisation

4.1 Introduction	68
4.2 Small angle X-ray scattering (SAXS)	68
4.3 Scanning electron microscopy	70
4.4 Establishment of sample preparation protocol	71

4.5 Initial investigation of unfilled and 10 parts-filled materials	77
4.6 Influence of loading level on morphology	84
4.7 Discussion	94
4.8 Conclusions	96
5. Dielectric and mechanical properties	
5.1 Introduction	98
5.2 Dielectric spectroscopy	101
5.3 Discussion of dielectric properties	105
5.4 Dynamic mechanical thermal analysis	109
5.5 Large strain behaviour	113
5.6 Discussion of mechanical properties	122
5.7 Conclusions	123
6. AC ramp breakdown testing and analysis	
6.1. Experimental procedure	125
6.2. Statistical background: Selecting the best distribution	128
6.3. Statistical background: optimal parameter estimation	135
6.4 Non-parametric estimation	143
6.5 Methodology: summary	144
6.6 Results	144
6.7 Discussion	154
6.8 Conclusion	160
7. Conclusions and Future Work	
7.1 Discussion of original aims and objectives	162
7.2 Other issues arising	164
7.3 Conclusions	166
7.4 Future work	167
8. References	165

List of figures and tables

1.1: Comparative laser ablation resistance of nano- and micro-filled silicone rubber	4
Table 1.1: Summary of properties of MMT/polymer nanocomposites compared to virgin polymer	5
1.2: Crystal structure of two thirds of a phyllosilicate layer	7
1.3: MMT platelets in various degrees of dispersion	8
1.4: (A) A stack of two lamellae with interconnecting polymer chains. (B) Schematic of a spherulite.	10
2.1: Chemical structure of the organomodifying surfactants used in Nanoblend 2101 (upper right) and Nanocor C30PE (lower left) masterbatches	18
Table 2.1: Extruded blend composition and nomenclature	20
2.2: Schematic of a Randcastle single-screw extruder with Recirculator TM mixing section	21
2.3: Dependence of circulating currents on back pressure	21
2.4: Photograph of extrudate samples from initial trials	24
2.5: Schematic of WAXS optics	26
2.6: X-ray diffractograms of the poorly dispersed sample (upper) and NC10 (lower.)	29
2.7: X-ray Intensity cross-sections for a xylene blended sample containing 90 : 10 : 5 w/w/w LDPE : HDPE : I30P powder	30
2.8: X-ray Intensity cross-sections for extrudates	31
2.9: TEM micrograph of material NC20	36
2.10: TEM micrograph of NB20	37
2.11: Comparison of Infra-red absorbance spectra from the extrudates	39
2.12: Raman assessment of degradation	41
2.13: Optical micrograph of material NB0=NC0	41
Table 3.1: Theoretical Avrami parameters	45
3.1: Integration of the power flow curve associated with isothermal crystallisation	46

3.2: Comparison of K_3 obtained for NB0=NC0 and NC10 using variable onset and variable shape methods for a crystallisation temperature of 120 °C	47
3.3: As Figure 3.1, but for crystallisation temperatures of 118 °C and 116 °C	48
3.4: As Figure 3.2, but for crystallisation temperatures of 114 °C and 110 °C	49
3.5: K_3 data for Nanoblend-filled systems	51
3.6: K_3 data from Figure 3.4, normalised to NB0=NC0	51
3.7: Dependence of K_3 on loading level for Nanocor-based systems	52
3.8: Structure of a maleic anhydride graft	53
3.9: K_3 parameters for NB10 (MA) and NB0 (MA)	53
3.10: Melting endotherms for materials crystallised at 113 °C	54
3.11: Melting endotherms for all materials	55
3.12: Crystallisation enthalpies for all materials as a function of temperature	57
3.13: Amount of crystallisable material in masterbatches estimated through comparison of data in Figure 3.8	58
3.14: Enthalpies of crystallisation and melting for Nanoblend masterbatch	59
3.15: As Figure 3.12 but for enthalpies of melting in the Nanoblend-based systems	59
3.16: Melting enthalpies for NC5, NC10 and NC20 together with predictions obtained by scaling response of NB0=NC0 using Equation 3.3 with $f = 0$	60
3.17: Schematic of hypothetical lamella growing between two parallel clay sheets	62
3.18: Linearised Avrami plots associated with variable shape method	63
4.1: SAXS plot for Nanocor-based blends	69
4.2: SAXS plot for Nanoblend-based blends	70
4.3: NB0=NC0, crystallised at 117 °C	74
4.4: Poorly dispersed reference sample, crystallised at 119 °C	75

4.5: Space between sheaves of NB10 (MA), crystallised at 119 °C	76
4.6: As Figure 4.5, but for MA-NB0	76
4.7: NB0=NC0, crystallised at 124 °C	77
4.8: NB10, crystallised at 120 °C	78
4.9: NC10, crystallised at 120 °C	78
4.10: NB0=NC0, crystallised at 124 °C	79
4.11: Schematic of idealised sheaf to aid discussion in text	80
4.12: NB10, crystallised at 124 °C	81
4.13: NC10, crystallised at 124 °C	81
4.14: NB0=NC0, crystallised at 120 °C	82
4.15: NC10, crystallised at 120 °C	82
4.16: NB0=NC0, crystallised at 117 °C	83
4.17: NB10, crystallised at 117 °C	83
4.18: NC10, crystallised at 117 °C	84
4.19: NC5, crystallised at 124 °C	86
4.20: NC20, crystallised at 124 °C	87
4.21: NC5, crystallised at 120 °C	87
4.22: NC5, crystallised at 117 °C	88
4.23: NC20, crystallised at 117 °C	88
4.24: NB5, crystallised at 117 °C	89
4.25: NB20, crystallised at 117 °C	89
4.26: NB5, crystallised at 120 °C	90
4.27a: NB20, crystallised at 120 °C	91
4.27b: As Figure 4.27a, but etched with one tenth the concentration of KMnO_4	91
4.28: NB5, crystallised at 124 °C	92
4.29: NB20, crystallised at 124 °C	92
4.30: Very high magnification images of NB20 crystallised at 124 °C	93
5.1: Comparison of real, imaginary and tan-delta Debye responses for various values of high frequency permittivity	99
5.2: Room temperature loss data for various masterbatch compositions and loading levels	103

5.3: Loss characteristics as a function of frequency	104
5.4: Real permittivity of the materials as a function of clay content	105
5.5: Effect of included phase shape parameter on percentage increase in composite permittivity	108
5.6: Real and imaginary modulus data for unfilled and highly filled materials	111
5.7: Real and imaginary compliance data for unfilled and highly filled materials	112
5.8: Tensile behaviour as a function of loading level and masterbatch composition	114
5.9: Two halves of a tensile fracture belonging to material NB20	115
5.10: Post-failure fibrillar deformation observed in NC20	116
5.11: SEM micrograph showing tip of failure zone for NC20	117
5.12: Post-failure image of NC5	118
5.13: Polarised optical micrograph (POM) of material NC20, following squashing at 200 °C	119
5.14: Post-failure image of material NB5	120
5.15 POM images of pellets squashed on a glass slide at 200 °C	121
6.1 Schematic diagram for electrical breakdown rig	126
6.2: CDF of Weibull function under $\alpha=1$ and various values of β	130
6.3: PDF of Weibull function under $\alpha=1$ and various values of β	131
Table 6.1: Chi-squared goodness-of-fit rankings for most of the datasets of between 15 and 25 datapoints obtained in this study	132
6.4: Likelihood function surface for quenched NB20	134
6.5: MLE estimation on 1000 Monte Carlo datasets with $n=20$ and $\beta=6$, 90% 2-sided confidence intervals	136
6.6: As Figure 6.5 but with RRY estimation	137
6.7: As Figures 6.5 and 6.6 above but with RRX estimation	137
6.8: Predicted bias in MLE-estimated $\langle\beta\rangle$ from Monte Carlo data	139
6.9: Predicted bias in RRX-calculated β from Monte Carlo data	140
6.10 Predicted bias in MLE-calculated $\langle\alpha\rangle$ from Monte Carlo data	141
6.11: Predicted bias in RRX-calculated $\langle\alpha\rangle$	142
Table 6.2: Estimated Weibull parameters from RRX and MLE	

for all data in Figures 6.16-6.19	145
6.12: Influence of Nanoblend loading level on breakdown statistics relative to a non-extruded LDPE reference sample	147
6.13: Kaplan-Meier plots with 90% confidence bounds for Nanoblend and Nanocor systems	148
6.14: Comparison of the LDPE reference samples used in this study	149
6.15: Effect of crystallising samples at 117 °C on breakdown strength	152
6.16: Weibull plots for material 2/NC0=NB0 with differing thermal histories	153
6.17: Weibull plots for 2/NC10	154
6.18: Weibull probability plots for material NB10 (MA) and NB0 (MA) following quenching	155
6.19: SEM images of ablated hole in material NB5	159

Declaration of authorship

I,

declare that the thesis entitled

POLYETHYLENE-MONTMORILLONITE NANOCOMPOSITES

and the work presented in this thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly while in candidature for a research degree at this University;
- no part of this theses has previously been submitted for a degree or any other qualification at this University or any other institution;
- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help;
- where the thesis is based on work done by myself jointly with others, I have made clear what exactly was done by others and what I contributed myself;
- parts of this work have been published as:

Green CD, Vaughan AS, IEEE Electr. Insul. Mag., 2008, 24, 6.

Green CD, Vaughan AS, IEEE Trans. Dielectr. Electr. Insul., 15, 134, 2008.

CD Green, AS Vaughan, IEEE-CEIDP, Oct 2007, 635.

AS Vaughan, CD Green, Y Zhang, G Chen, IEEE-CEIDP, Oct 2004, 732.

AS Vaughan, SG Swingler, Y Zhang, IEEJ Trans. Fund. Mater., 126, 1057.

CD Green, AS Vaughan, IEEE-ICSD, Jul 2007, 364.

CD Green, AS Vaughan, IEEE-ICSD, Jul 2007, 368.

Acknowledgements

Naturally, I would like to thank my supervisor, Professor Alun Vaughan, for his enthusiasm and encouragement, and his patience with me throughout the last four years. I also owe a debt of gratitude towards all of my colleagues in the Tony Davies High Voltage Lab as a whole for their support and cooperation. In particular, Dr Ian Hosier for his expertise in setting up the electrical breakdown rig, Messrs Niel Palmer, Mike Smith, Brian Rogers and Melvyn Kelly for their technical support and Messrs Gabriele Gherbaz, Toby Matheson and Martin Reading for their friendship. Many thanks to Dr Barbara Lessing in the Southampton University Department of Chemistry for obtaining Figure 2.10 on a Jeol 3010 TEM microscope.

Much of the work was performed at Reading University, and I thank the following people for this: Professor Geoffrey Mitchell, for spending hours training me up on his X-ray diffraction equipment, and for collecting small-angle diffractograms at the Daresbury Synchrotron Radiation Source; Dr Peter Harris, Mr Chris Stain and Miss Tracey Finn for their technical support in the Centre for Advanced Microscopy; Mr Robert Olley, for his stimulating discussion.

I would like to thank my wife Laura for being wonderful in every way, for my parents, both by nature and in law, for their faithful support. This thesis is dedicated to my yet-to-be-conceived daughter Polly Ethel Green, who is destined to be as lovely as her mother and as interested in electrical insulation as her father.

Lord Jesus, this is for you. Eight years ago I was lying in a psychiatric hospital somewhere between Reading and Oxford, tired of searching for meaning. And, though I rejected you as irrelevant or even nonexistent, after 21 years of patience you sent your Holy Spirit to give me new birth. You are with me always, through my disobedience and faithlessness – because you have taken the infinite wrath of the Father against my sin.....as your body was hung on nails by wicked men just like me, so that it may be the Father's pleasure to accept me as yours.

Abbreviations

AEV	asymptotic extreme value
xAEV	x'th asymptotic extreme value distribution
AFM	atomic force microscopy
BPE	branched polyethylene
CCD	charge coupled device
CDF	cumulative distribution function
DMTA	dynamic mechanical thermal analysis
DFT	density functional theory
DSC	differential scanning calorimetry
EVA	ethylene vinyl acetate
FTIR	Fourier transform infrared spectroscopy
HDPE	high density polyethylene
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
LLPS	liquid-liquid phase separation
LN ₂	liquid nitrogen
LPE	linear polyethylene
MMT	montmorillonite clay
MWS	Maxwell-Wagner-Sillars relaxation
ODA	octadecylammonium
o-MMT	organomodified montmorillonite clay
PCL	polycaprolactone
PDF	probability density function
PE	polyethylene
PET	polyethylene terephthalate
PMMA	poly(methyl methacrylate)
PP	polypropylene
POM	polarised light optical microscopy
PSD	particle size distribution
PVC	poly(vinyl chloride)
PVF ₂	poly(vinylidene fluoride)

rms	root mean square
SAXS	small angle X-ray scattering
SEM	scanning electron microscopy
SLPS	solid-liquid phase separation
SPM	scanning probe microscopy
TEM	transmission electron microscopy
WAXS	side angle X-ray scattering