University of Southampton

Faculty of Engineering, Science and Mathematics
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POLYETHYLENE-MONTMORILLONITE NANOCOMPOSITES

by

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Thesis for Doctor of Philosophy

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ABSTRACT

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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^{TM} 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.

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Declaration of authorship

I, ...

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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.

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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