MORPHOLOGICAL, THERMO-MECHANICAL AND FRACTURE PERFORMANCE OF POLYAMIDE-612/POLY(ETHYLENE-CO-OCTENE) ELASTOMER BLENDS AND THEIR HALLOYSITE NANOTUBE FILLED TERNARY NANOCOMPOSITES

SUNIL KUMAR

CENTRE FOR POLYMER SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

OCTOBER 2015

MORPHOLOGICAL, THERMO-MECHANICAL AND FRACTURE PERFORMANCE OF POLYAMIDE-612/POLY(ETHYLENE-CO-OCTENE) ELASTOMER BLENDS AND THEIR HALLOYSITE NANOTUBE FILLED TERNARY NANOCOMPOSITES

by

SUNIL KUMAR

Centre for Polymer Science and Engineering

Submitted

In fulfillment of the requirements of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology Delhi

October 2015

CERTIFICATE

This is to certify that the thesis entitled "**Morphological, thermo-mechanical and fracture performance of polyamide-612/poly(ethylene-co-octene) elastomer blends and their halloysite nanotube filled ternary nanocomposites**" being submitted by **Mr. Sunil Kumar,** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Centre for Polymer Science and Engineering, is a record of bonafide research work carried out by him. Mr. Sunil Kumar has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

Prof. S. N. Maiti
Professor
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi

Dr. B. K. Satapathy
Associate Professor
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi

ACKNOWLEDGEMENTS

With deep sense of gratitude and sincere regards, I would like to acknowledge the guidance and encouragement given by my supervisors, Prof. S. N. Maiti and Associate Prof. B. K. Satapathy for this research work. They have always been a source of inspiration and have been extremely generous in providing advice, guidance and inputs despite their busy schedules and multiple pre-occupations. Every interaction with them has been an opportunity to learn and bring in clarity of concepts.

I express my sincere thanks to my SRC members, Prof. A. K. Ghosh, Associate Prof. J. Jacob and Associate Prof. A. Rawal for their constructive criticism and valuable suggestions.

I gratefully acknowledge the help and suggestions by Prof. Veena Choudhary as and when required.

I gratefully acknowledge the scholarship (Senior Research Fellowship) supported by Indian Institute of Technology Delhi, India, to carry out this work.

I am thankful to the staff members Mr. Surender Sharma, Mr. Ashok Kapoor, Mr. Shiv Kant of the Centre for Polymer Science and Engineering, for extending a helping hand whenever needed. Also, I thank the staff members of the laboratories of Textile Department and Department of Physics for providing me the facilities to carry out the SEM and XRD testing.

I gratefully acknowledge the help and cooperation given by all my friends and colleagues for their direct and indirect help. I am especially thankful to my friends Mr. Harjeet S. Jaggi, Mr. Rakesh K. Kachhap, and Mr. D. Das.

I express my heartiest thanks to my parents and my wife Yashi for their encouragement and understanding, which enabled me to devote sufficient time to the research work.

Last but not the least, this research study and preparation of this report has been contributed by several persons whose names have not been mentioned above. I express my sincere thanks to all of them.

Sunil Kumar

ABSTRACT

Blends of polyamide-612 (PA-612)/poly(ethylene-co-octene)-grafted-maleic anhydride elastomer (POE-g-MA) were prepared in a twin screw extruder in the composition range of 0-35 wt% of POE-g-MA and were characterized for their morphological, thermo-kinetics, rheological, mechanical properties and fracture performance using SEM, DSC, TGA, tensile, flexural, Izod impact testing and essential work of fracture (EWF). The micro-structural changes due to POE-g-MA incorporation in the PA-612 matrix have been analyzed and their microstructural attributes-mechanical performance correlations have been explored for PA-612/POE-g-MA model system. Micromechanical aspects were analyzed using conventional theoretical models for low strain mechanical response such as rule of mixtures and foam model and high strain mechanical response such as Nicolais-Narkis model and porosity model.

The blend with 10 wt% of POE-g-MA showed optimum tensile, impact properties and fracture resistance and hence was selected as the (impact modified PA-612) base matrix for the preparation of halloysite nanotube (HNT) filled composites. Ternary nanocomposites of PA-612/POE-g-MA/HNT based on optimized blends of PA-612/POE-g-MA were prepared and characterized for their structural, rheological, thermal, mechanical and fracture behavior. The morphological attributes such as state of dispersion as a function of HNT content and *soft* elastomer phase domain sizes dispersed in PA-612 matrix were characterized by TEM and SEM, whereas microstructural attributes such as crystalline organization/chemical interaction and fractured surface topography of the optimized blends and their nanocomposites were characterized by WAXD, SEM and other supporting techniques. Non-isothermal crystallization kinetics behaviors of neat PA-612, PA-612/POE-g-MA blends and their nanocomposites were investigated by DSC vis-à-vis the determination of various crystallization parameters using

Avrami kinetics and Mo theory based models. The activation energies responsible for crystallization process have been estimated for the blends and their nanocomposites using Takhor equation. The thermo-mechanical response of the blends and nanocomposites were studied using dynamic mechanical analysis.

The melt rheology of blends and nanocomposites were studied by using parallel plate rheometry and capillary rheometry to assess the frequency dependence of moduli and complex viscosities.

Comparative assessment of the crack toughness behavior of the blends and nanocomposites were carried out following the essential work of fracture (EWF) approach based on post yield fracture mechanics (PYFM) concept. The kinetic and energy related fracture parameters like crack extension, crack tip opening displacements (CTOD) and crack velocity (CTOD rate) were used to evaluate the rate sensitivity of the blends and nanocomposites, while real-time visualization of strain field attributes responsible for toughness variations (as obtained by essential work of fracture approach) were computed based on surface displacement measurement techniques.

Firstly, our study establishes the material design ideology of toughness-enhancement via POE-g-MA incorporation into PA-612 matrix by manipulating the compositional ratio and hence the *soft*-phase domain size. Secondly, the study demonstrates the quantification of the stress wave dissipation modes via strain field analysis and strain mapping via multi-stage section diagrams, which is fundamentally a new approach not only to understand fracture mechanics for designing materials for specific applications but also to elucidate the validity regime of the post yield fracture mechanics principles for such model systems.

Contents

List of figures

List of abbreviations and symbols

ABS	-	Poly(acrylonitrle-co-butadiene-co-styrene)
ASTM	-	American Society for Testing and Materials
AFM	-	Atomic Force Microscopy
BI	-	Brittleness index
$CaCO_3$	-	Calcium carbonate
CNT	-	Carbon nanotubes
CTOD	-	Crack-tip opening displacement
D_n	-	Number average dispersed domains size
D_w		Weight average dispersed domains size
DENT	-	Double-edge-notched-tension
DIC	-	Digital image correlation
DMA	-	Dynamic mechanical analysis
DSC	-	Differencial scanning calorimeter
E	-	Young's modulus
E'	-	Storage modulus
E"	-	Loss modulus
EBR	-	Ethylene-butene rubber
EPDM	-	Ethylene propylene diene monomer rubber
EPDM-g-MA	-	Ethylene propylene diene grafted maleic anhydride
EPFM	-	Elastic-plastic fracture mechanics
EPR	-	Ethylene propylene rubber

EPR-g-MA	-	Ethylene propylene rubber grafted maleic anhydride
EVA	-	Ethylene Vinyl Acetate
EWF	-	Essential work of fracture
FPZ	-	Frontal process zone
G	-	Strain-energy release rate
G’	-	Melt storage modulus
G’’	-	Melt loss modulus
G_c	-	Critical strain-energy release rate
HDPE	-	High density polyethylene
HIPS	-	High impact polystyrene
IFPZ	-	Inner fracture process zone
J_c	-	Critical J-integral value
K	-	Stress-intensity factor
KCP	-	Kinetics of crack propagation
K_c	-	Critical stress-intensity factor
K_{IC}	-	Fracture toughness
l	-	Ligament length
LEFM	-	Linear elastic fracture mechanics
LDPE	-	Low density polyethylene
LDPE-g-MA	-	Low density polyethylene grafted maleic anhydride
MFI	-	Melt flow index
MMT	-	Montmorillonite
NBR	-	Butadiene-acrylonitrile rubber

NE	-	PA-612/POE-g-MA
NEH	-	PA-612/POE-g-MA/halloysite
N-EWF	-	Non-essential work of fracture
OPDZ	-	Outer plastic deformation zone
PA	-	Polyamide
PBT	-	Polybutylene terephthalate
PC	-	Polycarbonate
PET	-	Polyethylene terephtalate
PEEK	-	Polyether ether ether ketones
PEGMA	-	Poly(ethylene-co-glycidyl methacrylate)
POE	-	Poly(ethylene -co-octene)
POE-g-MA	-	Poly(ethylene-co-octene) grafted maleic anhydride
PP	-	Polypropylene
PP-g-MA	-	Polypropylene grafted maleic anhydride
PPO	-	Poly(phenylene oxide)
PS	-	Polystyrene
PVC	-	Poly(vinyl chloride)
PVDF	-	Poly(vinylidene fluoride)
PYFM	-	Post-yield fracture mechanics
SAN	-	Styrene-acrylonitrile copolymer
SBR	-	Styrene-butadiene rubber
SEBS	-	Styrene-ethylene-butylene styrene block copolymer
SEBS-g-MA	-	Maleated styrene-ethylene-butylene-styrene

SEM	-	Scanning Electron Microscopy
tanδ	-	Tangent delta
TEM	-	Transmission electron microscopy
TGA	-	Thermogravimetric analysis
WAXD	-	2D Wide Angle X-ray Diffraction
XRD	-	X-ray diffraction
T_c	-	Crystallization temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperatures
T_p	-	Crystallization peak temperature
$t_{1/2}$	-	Half time of crystallization
δ	-	Crack-tip opening displacement
$d\delta/dt$	-	Crack-tip opening displacement rate
J_c	-	Critical *J*-integral value
X_c	-	Degree of crystallinity
W_f	-	Total fracture work
w_f	-	Specific total fracture work
w_e	-	Essential work of fracture
βw_p	-	Nonessential work of fracture
W_s	-	Specific wear rate
w_{pp}	-	Weight fraction of PP
β	-	Plastic zone shape factor
σ_y	-	Yield stress

ΔH_f	-	Measured enthalpy of melting
ΔH	-	Ideal enthalpy of melting a perfect crystal
Δa	-	Crack-extension
δ	-	Crack-tip opening displacement
ε_b	-	Elongation-at-break
ρ	-	Density
σ_s	-	Tensile strength
σ_s	-	Yield stress
η^*	-	Complex viscosity