STUDIES ON PBT/SEBS AND PBT/SEBS/SEBS-g-MA BLENDS AND PBT/SEBS/SEBS-g-MA/CLAY NANOCOMPOSITES

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by

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Submitted

In fulfillment of the requirements of the degree of

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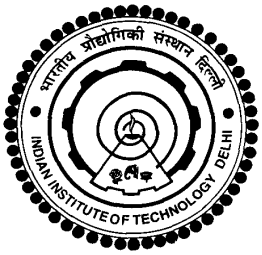

INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2015

Dedicated
To

My Parents,

My Husband, Manuj
&
My Lovely Daughters

CERTIFICATE

This is to certify that the thesis entitle "**Studies On PBT/SEBS And PBT/SEBS/SEBS-g-MA Blends And PBT/SEBS/SEBS-g-MA/CLAY Nanocomposites**" being submitted by **Ms. Rajul Sharma** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of the original and bonafide research work carried out by her under my guidance and supervision. Ms. Rajul Sharma has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

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

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Abstract

Poly (butylene terephthalate) (PBT), a fast crystallizable engineering polymer is used in various automotive, electrical and other engineering applications due to a combination of excellent dimensional stability, low moisture absorption, powerful insulation resistance and good frictional and wear properties, good oil and solvent resistance which hardly get affected by chemicals. PBT's main drawbacks are its notch sensitivity and low impact strength which are very common to pseudo ductile materials. To overcome these drawbacks it is necessary to blend PBT with various types of impact modifiers. Melt compounding is an economic and attractive route to prepare impact modified PBT blends due to lower development cost, faster development and attainment of tailored properties.

Blending with SEBS could enhance the impact strength of PBT but strength and stiffness characteristics decrease to a significant extent. A new approach in the field of polymer nanocomposites based on ternary blends has been directed toward improving the balance of toughness-to-stiffness properties that can be achieved by the addition of nanofillers.

The details of characterization such as mechanical, crystallization, morphological, melt rheological and thermal properties performed are described. Tensile properties were determined according to the ASTM D638 test procedure and the Izod impact strength of notched specimens was measured on a falling hammer type Ceast Impactometer following ASTM D256 test method. Thermal stability studies have been made by thermogravimetric analysis (TGA) whereas crystallization parameters have been evaluated from DSC and wide-angle X-ray diffraction (WAXD) measurements. Morphological studies have been made by scanning electron microscope (SEM) and transmission electron microscope (TEM). A piston-type capillary rheometer was used to generate the rheological parameters such as shear stress, shear rate, apparent melt viscosity, and the melt elasticity at SEBS concentrations from 0 to 30 phr (volume fraction, Φ_d = 0 to 0.38). Dynamic shear rheological properties of all the

PBT/SEBS blends and PBT/SEBS/SEBS-g-MA blends are also carried out using parallel plate rheometer. Viscoelastic properties were determined by dynamic mechanical analyzer (DMA). The details of analysis procedures employed for the blends and nanocomposites are also elucidated.

Above studies on PBT/SEBS and PBT/SEBS/SEBS-g-MA blends were carried out to characterize and analyze the blend systems. Blends of PBT/SEBS and PBT/SEBS/SEBS-g-MA were prepared by varying SEBS concentration from 0 to 30 phr concentrations (volume fraction, Φ_d = 0 to 0.38) using co-rotating twin screw extruder. The effect of SEBS and SEBS-g-MA on mechanical and morphological properties of PBT/SEBS and PBT/SEBS/SEBS-g-MA blends has been determined as a function of SEBS concentration. Tensile properties were compared with simple predictive models. Attempts have been made to correlate the tensile properties of the blends with crystallinity of the matrix PBT, morphology and interphase adhesion. The normalized notched izod impact strength increased with SEBS content, up to Φ_d = 0.38 the parameter enhanced 5 folds for PBT/SEBS blends. In the presence of maleic anhydride-grafted SEBS (SEBS-g-MA), the tensile modulus and strength decreased significantly while normalized relative notched Izod impact strength data were higher than PBT/SEBS blend systems because of enhanced interphase adhesion, the parameter enhanced by 7.5 times at Φ_d = 0.38.

The dispersion of the blending polymer SEBS in PBT has been examined by the SEM studies of cryogenically fractured samples after etching out the SEBS phase. Concentration and interparticle distance of the dispersed phase influenced impact toughening. Melt rheological properties of PBT/SEBS and PBT/SEBS/SEBS-g-MA blends at SEBS volume fraction (Φ_d) = 0.00-0.38 were studied at 240^{o}C, 250^{o}C and 260^{o}C using a capillary rheometer. Variations of first normal stress coefficient function (ψ_1), recoverable shear strain (γ_R), relaxation time (λ) and shear compliance (J_c) values vs. shear rate were also analyzed for both the blend systems.

Dynamic shear rheological properties of all the PBT/SEBS blends and PBT/SEBS/SEBS-g-MA blends are also carried out using parallel plate rheometer. The compression molded samples (~1mm thickness) were investigated at 250^{o}C. The test performed is dynamic frequency sweep over an angular frequency range starting from 0.1 rad/s to 100 rad/s.

A systematic study has been undertaken to investigate the effect of SEBS on the crystallization and the melting behaviour of PBT in PBT/SEBS and PBT/SEBS/SEBS-g-MA blends. Various crystallization and melting parameters were evaluated from the exothermic and endothermic peaks respectively. The degree of crystallinity was evaluated from wide angle X-ray diffraction and DSC.

The viscoelastic behaviour of the PBT/SEBS blends and also the effect of compatibilizer SEBS-g-MA on the PBT/SEBS blends are also studied and analyzed at the temperature range -70^{o}C to 200^{o}C on a single cantilever bending mode. Storage modulus and loss modulus decrease and Tan δ values increase with increasing volume fraction for both the blend systems implying that presence of SEBS reduced the stiffness of the blends.

PBT/SEBS/SEBS-g-MA (20phr) blend was chosen for further studies on the basis of its optimum impact strength and modulus. Nanoclay was melt mixed in the above blend at Φ_f varying from 0.005 to 0.02. Analysis of the tensile properties and their comparison with the theoretical predictions after eliminating the effect of crystallinity indicates phase interaction between the filler and matrix up to critical filler concentration 0.01 volume fraction. Theoretical predictive models were used to correlate tensile modulus with the experimental data.

The effect of nanoclay on the crystallization and the melting behaviour of PBT in PBT/SEBS/SEBS-g-MA/Clay nanocomposites were studied. the increase in crystallinity of PBT in presence of nanoclay and its enhanced concentration may be attributed to the nucleating effect of the nanoparticles for the crystallization of the polymer.

The distribution of nanoclay particles throughout the matrix was studied by transmission electron microscopy (TEM). XRD and TEM studies showed intercalation and exfoliation of nanoclay. The effect of nanoclay on the viscoelastic properties of matrix blend was evaluated and analyzed on dynamic mechanical analyzer at the temperature range -70^{o}C to 200^{o}C on a single cantilever bending mode. The storage modulus, loss modulus and the damping parameter (Tan δ) were measured and analyzed. Storage and loss modulus increased with Φ_f indicating reinforcing effect of nanoclay.

Melt rheological properties at the range of 100-5000 s^{-1}shear rates were evaluated. The study includes shear stress-shear rate variation, evaluation of melt viscosity and extrudate swell of PBT/SEBS/SEBS-g-MA/Clay nanocomposites. Dynamic shear rheological properties of PBT/SEBS/SEBS-g-MA/clay nanocomposites are also carried out using parallel plate rheometer. PBT/SEBS/SEBS-g-MA/Clay nanocomposites have higher elastic modulus, loss modulus and complex viscosities compared with PBT/SEBS/SEBS-g-MA matrix blend, the parameters show a monotonic increase with nanoclay content. The reason for the increase of elastic modulus, loss modulus and complex viscosities might arise from the confinement of polymer chains within the clay layers. The complex viscosity of nanocomposites showed shear thinning behaviour at all frequencies. The restriction in chain mobility of nanocomposites by the addition of nanoclay has been confirmed by the Van-Gurp plot.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABS	- Poly (acrylonitrile-co-butadiene-co-styrene)
ABS-g-MA	- Maleic anhydride functionalized acrylonitrile-butadiene- styrene
AFM	- Atomic Force Microscopy
ASTM	- American Society for Testing and Materials
CaCO3	- Calcium carbonate
CEC	- Cation exchange capacity
CNT	- Carbon nanotube
CMNC	- Ceramic matrix nanocomposite
DMA	- Dynamic mechanical analysis
DSC	- Differential scanning calorimeter
D_n	- Number average domain size
D_w	- Weight average domain size
EAA	- Ethylene-acrylic acid copolymer
EBA	- Poly (ethylene-co-butyl acrylate)
EBR	- Ethylene-butene rubber
E_m	- Tensile modulus of matrix
ENR	- Epoxidized natural rubber

EPDM	- Ethylene propylene diene mono rubber
EPDM-g-MA	- Ethylene propylene grafted maleic anhydride
EPR	- Ethylene propylene rubber
EVA	- Ethylene Vinyl Acetate
FTIR	- Fourier transform infrared spectroscopy
GMA	- Glycidyl methacrylate
G*	- Complex modulus
G’	- Elastic modulus
G”	- Viscous modulus
ID	- Inter particle distance
MA	- Maleic anhydride
MFI	- Melt flow index
MMT	- Montmorillonite
MWCNT	- Multi walled carbon nanotube
OMMT	- Organically modified montmorillonite
PA6	- Polyamide 6
PBT	- Poly (butylene terphthalate)
PNC	- Polymer nanoclay
PEEKK	- Polyether ether ketones
PET	- Poly (ethylene terphthalate)

Phr	- Parts per hundred of resin
POE	- Poly (octane-ethylene)
POM	- Polyethylene octane
POSS	- Polyhedral Silsesquioxanes
PS	- Polystyrene
R	- Universal gas constant
R & D	- Research and development
SAN	- Styrene-acrylonitrile copolymer
SBS	- Styrene-butadiene-styrene block copolymer
SEBS	- Styrene-ethylene-butylene-styrene block copolymer
SEBS-g-MA	- Styrene-ethylene-butylene-styrene grafted with maleic anhydride
SEM	- Scanning electron microscopy
T_o	- Crystallization initiation temperature
$T_{½}$	- Half time of crystallization
TBT	- Tough brittle transition
TEM	- Transmission electron microscopy
TGA	- Thermogravimetric analysis
TPE	- Thermoplastic elastomer
T_m	- Melting temperature

T_{onset}	- Onset of degradation temperature
T_g	- Glass transition temperature
T_p	- Peak temperature
WAXD	- 2D Wide Angle X-ray Diffraction
X_e	- Degree of crystallinity
X_t	- Relative crystallinity
ΔT_c	- Cooling temperature
ΔE	- Activation energy
ΔH_m	- Heat of melting
ϕ_f	- Filler volume fraction
ϕ_d	- Volume fraction of blend
σ_{ye}	- shape factor parameter
τ_{ym}	- Composites yield stress
	- Matrix yield stress
	- Shear stress
η^*	- Complex Viscosity
δ	- Phase angle
v	- Poisson's ratio