STUDIES ON THE BLENDS OF POLYAMIDE6/SEBS-g-MA COPOLYMER AND THEIR NANOTALC REINFORCED COMPOSITES

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STUDIES ON THE BLENDS OF POLYAMIDE6/SEBS-g-MA COPOLYMER AND THEIR NANOTALC REINFORCED COMPOSITES

by

HEMLATA

Centre for Polymer Science and Engineering

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Doctor of Philosophy

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Dedicated

To

My Husband, Prabhat

My brother, Brijesh

&

Parents

CERTIFICATE

This is to certify that the thesis entitled **“STUDIES ON THE BLENDS OF POLYAMIDE6/SEBS-g-MA COPOLYMER AND THEIR NANOTALC REINFORCED COMPOSITES”** being submitted by Ms. Hemlata to the Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** in the Centre for Polymer Science and Engineering, is a record of bonafide research work carried out by her. Ms. Hemlata has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis.

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.

Date: October 2013

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ABSTRACT

PA6 is an important semicrystalline thermoplastic which finds wide range of end uses such as in aerospace, automotive, communication and commodity products due to its attractive combination of good processability, high tensile properties and chemical resistance. PA6 is a pseudo-ductile polymer with high crack initiation energy and low crack propagation resistance in the presence of notch which limits its end use applications. In order to overcome its poor notched impact strength PA6 is blended with various elastomers. Blending with SEBS-g-MA could enhance the impact strength of PA6, but strength and stiffness characteristics decreased to a significant extent. A new approach in the field of polymer nanocomposites based on binary blends has been directed toward improving the balance level of toughness-to-stiffness that can be achieved by the addition of nanofillers.

Blends of PA6/SEBS-g-MA with 5 to 50 phr concentrations (volume fraction, Φ_d=0 to 0.38) of SEBS-g-MA were prepared by melt-compounding using co-rotating twin screw extruder. Morphology of etched surfaces of the injection molded samples were observed on a scanning electron microscope (SEM). Particle size of the dispersed phase decreased with increasing SEBS-g-MA concentrations due to reactive compatibilization. Mechanical properties of the blends were investigated by tensile and impact tests. Tensile modulus and strength gradually decreased while elongation at break and impact strength increased with SEBS-g-MA concentrations. At 20 phr impact strength increased 7.8 folds as compared to that of neat PA6. However, the samples did not break at 35 and 50 phr indicating super toughening of the blend. Various theoretical models have been used to correlate tensile modulus, tensile strength and elongation at break with experimental data. Wu’s theory has been used to correlate impact strength with matrix ligament thickness.

The effects of SEBS-g-MA on the melt rheological behaviour of PA6/SEBS-g-MA blends were investigated by means of capillary and parallel plate rheometers. Melt viscosity obtained by capillary rheometer for the blends increased with the increase in Φ_d compared to that of neat PA6 in the shear rate range investigated implying higher interfacial adhesion between the two phases which stiffens the melt systems. Shear stress-shear rate variations obeyed power law behaviour and shear thinning was exhibited by the systems. The power law coefficient decreased up to $\Phi_d = 0.30$ and slightly increased at $\Phi_d = 0.38$ while opposite trend was observed for the flow consistency index (K). The elastic modulus obtained by dynamic frequency sweep measurements increases with increasing frequency and SEBS-g-MA content implying less time available for molecular relaxation. The same relationship exists for the viscous modulus suggesting higher energy required for the viscous response with increasing test frequency and SEBS-g-MA content for all the blends. The complex viscosity increased with the Φ_d as compared to neat PA6. These results were also confirmed by lowering in $\tan \delta$ peak with increase in Φ_d implying less energy dissipated by the blend systems. Results obtained by Van Gurp plot suggested that SEBS-g-MA at $\Phi_d > 0.11$ restricts the chain mobility of PA6.

The non-isothermal crystallization kinetics of neat PA6 and binary blends of PA6/SEBS-g-MA were investigated by means of differential scanning calorimetry (DSC) at four different cooling rates. Three macro kinetic models, viz. Avrami, Jeziorny and Tobin, were used to describe the non-isothermal crystallization kinetics. Primary and secondary crystallization were analyzed by Avrami equation. The results obtained by Avrami equation suggested that under non-isothermal condition, the mechanism of primary crystallization is more complex, while secondary crystallization showed one to three dimensional crystal growths. Tobin model described the overall crystallization kinetics and results were almost similar to those of

Avrami model. The results obtained by Dobreva and Gutzowa method suggested that SEBS-g-MA did not act as a nucleating agent for PA6. Three isokinetic models (Augis-Bennet, Kissinger and Takhore) have been used for the evaluation of the activation energy of non-isothermal crystallization kinetics process. The value of activation energy ΔE slightly increases in the presence of 5, 10, 20 phr content of SEBS-g-MA and then decreases with at 35 and 50 phr contents of SEBS-g-MA. These results showed that up to 20 phr, SEBS-g-MA hinders the mobility of PA6 chain segments and at 35 and 50 phr SEBS-g-MA eases the mobility of PA6 chain segments.

PA6/SEBS-g-MA (100/20) blend was chosen for further studies on the basis of balance level of stiffness and toughness. Nanotalc was incorporated in to blend matrix to improve the tensile modulus and strength reduced by the incorporation of SEBS-g-MA in to PA6.

Ternary nanocomposites based on PA6/SEBS-g-MA (100/20) blends with varying content of nanotalc (1, 3 and 5 wt %) were prepared.The morphology of nanocomposites using wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) revealed the delamination of talc layers in the ternary nanocomposites. DSC results revealed that double melting endothermic peaks remain intact in presence of nanotalc. The mechanical properties of PA6/SEBS-g-MA nanocomposites were evaluated by tensile, flexural and impact tests. The tensile and flexural moduli and strengths continuously increased while izod impact strength and elongation-at-break decreased with increase in nanotalc content. Theoretical predictive models were used to correlate tensile modulus with the experimental data. The experimental data show positive deviation with the applied models. Bela Pukanszky model has been used to calculate the reinforcement parameter B by employing tensile strength data.

The melt rheological behaviour of PA6/SEBS-g-MA blend and PA6/SEBS-g-MA/nanotalc composites were analyzed at low and high shear rates. Shear stress of the melt system increases with the incorporation of the talc due to polymer-filler interaction. Melt viscosity of the nanocomposites also increases due to polymer-filler interaction. The power law index values, n are lower than unity and the parameter increased marginally with nanotalc content which implies a degree of flow inhibition on addition of nanotalc, the inhibition enhances with talc concentration. Flow consistent index, K increases with the addition of nanotalc content.

The storage and loss modulus of the nanocomposites significantly increased with the addition of nanotalc. The nonterminal behaviour of nanocomposites observed at low frequency region implying phase adhesion between nanotalc, PA6 and SEBS-g-MA leads to network like silicate structure which restricts the mobility of polymer chains. The complex viscosity of ternary nanocomposites increases relative to that of the blend matrix suggesting intercalated/exfoliated nanocomposite structure giving rise to confinement of polymer chains which restrict the melt flow. The tan δ of nanocomposites decreases due to enhanced elasticity in presence of nanotalc. The restriction in chain mobility of nanocomposites by the addition of nanotalc has been confirmed by the Van-Gurp plot.

The nonisothermal crystallization behaviour of PA6/SEBS-g-MA and PA6/SEBS-g-MA/ nanotalc composites were studied by differential scanning calorimetry. The classical Avrami, Tobin and Jeziorny models were employed to analyze the nonisothermal crystallization kinetics process. The Avrami model is used to describe primary, secondary and overall crystallization process. In primary crystallization the dimensions of crystal growth reduces with the addition of nanotalc, while the growth in secondary crystallization was two, three and multidimensional. The Avrami model provides a satisfactory result to describe the nonisothermal crystallization kinetics of the nanocomposites. The results obtained by Tobin model to analyze overall crystallization kinetics were almost similar to that of Avrami model. The modified rate constant and half life of crystallization obtained by Jeziorny equation showed increasing trend with nanotalc content and cooling rate. Dobreva and Gutzowa

method suggested that nanotalc acts as an effective nucleating agent for PA6/SEBS-g-MA blend. Three isokinetic methods e.g. Augis-Bennet, Kissinger and Takhore, have been used to analyze the activation energy of crystallization. The values of activation energy decreases at 1wt % of nanotalc, the parameter then increases for 3 and 5 wt % of nanotalc remaining lower than that of PA6/SEBS-g-MA blends at 1 and 3 wt % of nanotalc while the values was slightly higher at 5 wt% of nanotalc.

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HEMLATA

Table of Contents

CHAPTER 5 MECHANICAL, MORPHOLOGICAL, THERMAL AND RHEOLOGICAL PROPERTIES OF NANOTALC REINFORCED PA6/SEBS-g-MA COMPOSITES 132-166

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