INVESTIGATIONS ON THE BLENDS OF POLYAMIDE 6 AND POLY (ETHYLENE-CO-BUTYL ACRYLATE) AND THEIR NANOTALC REINFORCED COMPOSITES

by

G. PRASATH BALAMURUGAN

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 2008

Dedicated to
My Parents and Sisters

CERTIFICATE

This is to certify that the thesis entitled **"Investigations on the Blends of Polyamide 6 and Poly(ethylene-co-butyl acrylate) and their Nanotalc Reinforced Composites"** being submitted by **Mr. G. Prasath Balamurugan** to Centre for Polymer Science and Engineering (CPSE), Indian Institute of Technology, Delhi is worthy of consideration for the award of degree of **Doctor of Philosophy** and is a record of the original bonafide research work carried out by him, under my guidance and supervision and 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.

Dr. S.N. Maiti
Professor
Centre for Polymer Science and Engineering
Indian Institute of Technology Delhi
New Delhi, India.

ACKNOWLEDGEMENTS

Many peoples have accompanied me during this adventure and provided their support and encouragement. First and foremost, I would like to thank my supervisor Prof. S.N.Maiti, who provided me guidance, knowledge, insight and direction for my research work. It is hard to describe the immeasurable impact that he has on my career and professional development. It has been a great pleasure discussing my ideas with him and receiving his encouragement and excellent advice at every step of the way, often-long distance and always promptly right on the point. I owe him so much.

I thank my research committee members Prof. Veena choudhary, Prof. Deopura and Prof. AK Singh for their invaluable suggestions and directions, especially during the early stages of my research work.

I am deeply indebted to Prof. A K Ghosh for providing me invaluable advice and friendly support during my PhD and on my future plans. I would also like to thank him for giving me opportunities to work for some international conferences, lecture series and workshops, as a participant and volunteer during my research period.

I would like to offer my gracious thanks to Prof. S.N. Maiti, Prof. A K Gupta, Prof. A K Ghosh, Prof. I.K Verma and Prof. Veena Choudary, for teaching me courses like Polymer testing and technology, polymer blends and alloys, polymer rheology and processing, polymer composites and engineering plastics during the early stages of my research career. It helped me a lot in understanding the fundamentals to the core and to apply them later on in my dissertation work.

My special thanks to Prof. Pitchumani, Department of Chemical Engineering IIT Delhi for providing me nanotalc material for preparing the nanocomposites. I would like to offer my special thanks to Dr. Josemon Jacob and Dr. Bhabani, who are always my well wishers and are very much concerned about me.

I would like to express my sincere gratitude to Mr.Surrender and Mr.Ashok Kapoor, who always helped me in characterizing the materials for my research, from the very beginning. I also thank Mr. Devendar singh and Mr. Shivkant for assisting me during my experimental work. My rich thanks to Mr.Sharma for his friendly introduction to the Scanning electron microscope, and his effective help in scanning the samples.

I thank my friends K.Senthil kumar, M.Senthil Kumar, Dilip Kumar kolluri Prakashan, Ravi, Anand, Hari, Selvaganapathy, Arun, Elavarasan, Sakthivel, Prathap and Srinivasan. With them all, I shared substantial part my life. I always had longtime discussions, shared all my thoughts, joy, sorrows and whatever that happened through the way with my friends. I would also like to thank my senior research fellows Anantha Padmanaba, Jay Kishore Pal, Muthulakshi, Purnima, Neetu tomar for giving me brotherly support and advices during my stay in Delhi.

I would also like to thank Mr. UP singh, Mr.Pragalathan of CIPET Ahmedabad and their colleagues, for providing the compounding facilities and assisting me while processing the materials for my research work.

Last but not least, I am very grateful to my Parents (Mr. S. Ganesan, Mrs. Padmavathy Ganesan) and my Sisters (Ms. Bramiyadhevi, Ms. Praveena and Ms. Prem Kumari). Without their love, constant support, encouragement and motivation, it would have been impossible for me to complete this task.

I wish to acknowledge Centre for Polymer Science and Engineering and Indian Institute of Technology Delhi, for providing funding and fellowship for carrying out this research work. Furthermore, I also would like to thank the researchers all over the world, those who contributed and published their manuscripts in international journals in the area of Polymer Blends and Composites, which actually stimulated and motivated me to carry out research in this wonderful area.

G. PRASATH BALAMURUGAN

ABSTRACT

Polyamide 6 [PA6] is a semi-crystalline polymer utilized in wide variety of applications such as aerospace, communication, engineering, and commodity industries. Most of these applications demand materials of high strength, stiffness, dimensional stability and toughness. The growing current commercial interest and the performance demands for polyamide 6 can only be satisfied by the dual advantages offered by blending and reinforcement of polyamide 6 with the existing materials that can give distinctive properties superior than either material. Polyamide-6 is pseudo ductile in nature with relatively low impact strength under notched conditions, which has to be given considerable attention to meet a satisfactory performance. Rubber toughening of polyamide 6 is one of the most effective ways to achieve a distinctive improvement in the toughness. However, rubber toughening may lead to considerable reduction in the strength and stiffness related properties, which can be compensated only by incorporating reinforcement, thereby concurrent improvements in strength and toughness could be achieved.

In the present investigation an attempt has been made to improve the impact properties of polyamide 6 [PA6] by blending with an ethylene based copolymer elastomer, poly (ethylene-co-butyl acrylate) [EBA]. PA6/EBA blends are expected to be incompatible owing to their varying chemical nature and very low entropy change that could be achieved by melt-mixing. Hence a maleic anhydride (MAH) grafted EBA has been prepared by reactive extrusion technique and used as a reactive compatibilizer for the immiscible PA6/EBA blends. EBA grafted MAH (EBA-g-MAH) with two different MAH graft percentages 0.49 wt% (EBA-g-MAH$^{0.49}$) and 0.96 wt% (EBA-g-MAH$^{0.96}$)

were prepared. The binary PA6/EBA blends were prepared in a twin screw extruder (TSE), by varying the EBA content from 0 to 50 phr [PA6/EBA binary blends ratio in pbw: 100/05; 100/10; 100/20; 100/35; 100/50]. The macro-mechanical and micro structural property evaluation studies revealed that 10 phr of EBA content was the optimum level to achieve a reasonably good balance in strength and toughness in PA6/EBA blends. Two series of compatibilized blends of PA6/EBA were prepared by replacing 1, 2, 3, and 4 phr of EBA in 100/10 blend (PA6/EBA) by EBA-g-$MAH^{0.49}$ and EBA-g-$MAH^{0.96}$, reactive compatibilizers respectively. The two series of compatibilized blends were denoted as PA6/EBA-g-$MAH^{0.49}$/EBA [PA6/EBA-g-$MAH^{0.49}$/EBA ratio in pbw: 100/1/9,100/2/8,100/3/7,100/4/6] and PA6/EBA-g-$MAH^{0.96}$/EBA [PA6/EBA-g-$MAH^{0.49}$/EBA ratio in pbw: 100/1/9,100/2/8,100/3/7,100/4/6]. The reactively compatibilized toughened blend, PA6/EBA-g-$MAH^{0.49}$/EBA with 2wt% compatibilizer (100/2/8) was chosen to prepare nanotalc reinforced composites. PA6/nanotalc and (PA6/EBA-g-$MAH^{0.49}$/EBA)/nanotalc composites were prepared in TSE by varying the nanotalc content as 1, 2 and 4 wt %, respectively in both the composites. The melt compounded blends and the nanocomposites were injected moulded to prepare the test specimens.

Various studies have been performed to understand the influence of reactive compatibilization on the morphology, melt rheology, crystallization and mechanical properties of PA6/EBA blends, and the effect of nanotalc inclusion in the PA6 and PA6/EBA based nanocomposites. The characterization techniques employed for the blends and composites prepared include scanning electron microscopy (SEM), capillary melt rheometry for high shear and extensional behaviour, differential scanning

calorimetry (DSC), wide angle X-ray diffraction (WAXD), static contact angle measurements by transmission electron microscopy (TEM) and mechanical testing such as tensile, impact, essential work of fracture (EWF).

PA6/EBA blends exhibited two phase droplet-matrix morphology owing to the incompatibility while examining their morphology under scanning electron microscope. Fine dispersion of EBA particles as spherical domains with a relatively good distribution in the PA6 matrix was observed at low EBA contents (5 and 10 phr). The reactively compatibilized blends exhibited finer dispersion and even distribution of elastomeric EBA particles in the PA6 matrix and the presence of EBA-g-MAH resulted in considerable reduction of interfacial tension between the component polymers. The interfacial adhesion between the PA6 and EBA phase in the compatibilized blends was enhanced by the interfacial reaction between the amide end-groups of PA6 and maleic anhydride group of EBA-g-MAH compared to uncompatibilized blends. The matrix ligament thickness and particle diameter values were lower than the predicted critical values and were responsible for the ductile behavior of the compatibilized blends during impact fracture. Impact loading could only bend the compatibilized samples and was unable to break them completely. *Stress whitening* around the notch (the major energy dissipation zone) was observed in all the compatibilized blends after impact testing. Matrix *shear yielding* or plastic flow without crazing was the dominant deformation mechanism in the tough compatibilized PA6/EBA-g-MAH$^{0.49}$/EBA and PA6/EBA-g-MAH$^{0.96}$/EBA blends. As a result the compatibilized PA6/EBA blends showed very enhancements in the impact strength. There was no sign of shear yielding during impact

fracture of the uncompatibilized PA6/EBA blends where the elastomeric particles were completely dislodged from the matrix.

The effect of phase interaction induced by reactive compatibilization during high shear and extensional flow in polyamide (PA6) and ethylene-co-butyl acrylate (EBA) blends was clear when the melt rheological behaviour was studied using advanced dual bore capillary rheometer. The viscosity-composition behavior of the uncompatibilized PA6/EBA blends exhibited negative deviation behavior from the log-additivity rule. The interfacial slip mechanism, operative between the matrix PA6 and dispersed EBA in the uncompatibilized blends was responsible for the negative deviation behaviour during shear flow and was further confirmed by Lin's and Bousmina-Palierne-Utracki (BPU) model for viscosity for the blends. On the other hand, the viscosities of the compatibilized PA6/EBA-g-MAH$^{0.49}$/EBA and PA6/EBA-g-MAH$^{0.96}$/EBA blends with varying dispersed phase volume fraction showed positive deviation behavior. The reactive compatibilizers EBA-g-MAH $^{0.49}$ and EBA-g-MAH$^{0.96}$ increased the phase interaction with adequate reduction in the dynamic interfacial tension, which favored the particle break-up and stabilized the morphology in the compatibilized blends. The extensional viscosity of the blends enhanced due to the inclusion of EBA in all the uncompatibilized and compatibilized blends. The melt elasticity and the elasticity function systematically evaluated from first normal stress coefficient functions (ψ_1) confirmed that the melt elastic parameters were improved with the addition of EBA. The variation in the recoverable shear strain (γ_R), shear rate dependent relaxation time (λ) and shear compliance (J_c) under various shear rates also confirmed the same.

The uniaxial tensile deformation studies revealed that the deformation mechanism during

tensile loading is quite different for the uncompatibilized PA6/EBA blends when compared to the compatibilized PA6/EBA-g-$MAH^{0.49}$/EBA and PA6/EBA-g-$MAH^{0.96}$/EBA blends. The uncompatibilized blends showed an extensive interface delamination during tensile deformation especially at higher EBA concentrations. The deformed samples examined by high resolution scanning electron microscopy along the stretching direction reveal that at lower EBA concentrations, the interface cavitation resistance is relatively good with higher work of yield in these samples. This interface cavitation has generated extensive matrix shear yielding in these samples during cold drawing after localized necking. While at higher EBA concentrations, beyond 20phr level of EBA, cavitation resistance was relatively poor, leading to macro-voiding around the elastomer domains, and the stress-strain behavior of the samples showed rubber like deformation. In the compatibilized blends, the high interfacial adhesion achieved by reactive compatibilization prevented interface cavitation and arrested cold drawing of the samples at higher compatibilizer concentration. The essential work of fracture (EWF) studies revealed that the compatibilized PA6/EBA blends show much better fracture resistance than the uncompatibilized blends. High interfacial adhesion with finer dispersion of EBA domains induced extensive shear yielding with the formation of thin ligaments during EWF testing in compatibilized blends, and was responsible for the higher crack resistance behavior of these blends.

The non-isothermal melt-crystallization and melting behavior of uncompatibilized PA6/EBA blends at different blend compositions were investigated using differential scanning calorimetry at different scanning rates. Several macro-kinetic models such as Avrami, Jeziorny, Ozawa, Liu, Ziabicki, and Tobin, were applied to analyze the

crystallization behavior thoroughly under non isothermal conditions. Among the models used Ozawa and Liu models for nonisothermal crystallization described the course of the transformation process in the uncompatibilized PA6/EBA blends. The analysis by these macro kinetic models suggests that there is an increasing rate of transformation throughout the crystallization process and all the forms of nylon 6 crystals grow simultaneously in the PA6/EBA binary blends. The kinetic crystallizability of PA6 in the uncompatibilized PA6/EBA blends calculated using Ziabicki's approach suggests that the inclusion of EBA molecules slightly altered the crystallization ability of PA6 in the presence of EBA. Nucleation activity of EBA in the uncompatibilized PA6/EBA blends estimated by Dobreva and Gutzowa method revealed that the EBA particles are inert in nature and do not act as nucleating agent, however it favored the growth of γ-crystalline phase, when compared to the α-crystalline phase of PA6 in the blends. The energy barrier of non-isothermal crystallization, activation energy calculated using Augis-Bennett, Kissinger and Takhor method indicated that activation energy is slightly lower for the blends when compared to the neat PA6.

In the compatibilized PA6/EBA-g-$MAH^{0.49}$/EBA blend the macro-kinetic models such as Avrami, Tobin and also the isothermal approach confirm that the crystallization process was very slow in the presence of compatibilizer. The interfacial reaction delayed the macromolecular diffusion process during crystallization. In the compatibilized blends also the growth of γ-crystalline phase is favoured when compared to the α-crystalline phase. However the degree of crystallinity in both the uncompatibilized and the compatibilized blends does not vary with the inclusion of EBA and also the compatibilizer.

Reinforcing effects of nanotalc on PA6/talc and (PA6/EBA-g-MAH$^{0.49}$/EBA)/nanotalc nanocomposites were revealed by the significant improvements in strength and the stiffness. The PA6/nanotalc registered a very high improvement in the strength/stiffness related properties with decreased strain related properties such as elongation and toughness of the composites. Systematic study of the phase morphology by SEM, TEM and XRD revealed the formation of extended brane-like and network-like structures alongwith delaminated talc layers due to stack-sliding effect of talc, while processing. The preferential retention of nanotalc in the polyamide phase of the ternary composites has resulted in remarkable improvements in the mechanical properties with moderately improved toughness. The modulus predicted by micromechanical models such as Halpin-Tsai and Mooney equation suggests that the nano-phase in the composites retained a very good aspect ratio after melt-mixing. The presence of EBA elastomer domains has induced matrix crazing during impact fracture but could not induce shear yielding due to the blocking effect of the talc in the PA6 phase during stress percolation, resulting in moderate improvement in the toughness. The presence of nanotalc has improved the shear flow behavior in the binary and ternary nano composites by their capability of orientation during flow.

TABLE OF CONTENTS