STUDIES ON POLYAMIDE12/ SEBS-g-MA BLENDS AND COMPOSITES WITH ORGANOCLAY AND ZINC BORATE FILLERS

KHUSHBOO RINAWA

CENTRE FOR POLYMER SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
FEBRUARY 2015

STUDIES ON COMPOSITES BASED ON POLYAMIDE12/ SEBS-g-MA BLENDS WITH ORGANOCLAY AND ZINC BORATE FILLERS

by

KHUSHBOO RINAWA

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
February 2015

DEDICATED

TO MY

PARENTS, FAMILY

&

DAUGHTER

CERTIFICATE

This is to certify that the thesis entitled **“Studies on Polyamide12/ SEBS-g-MA Blends and Composites with Organoclay and Zinc Borate Fillers”** being submitted by **Ms. Khushboo Rinawa** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy**, in Polymer Science and Technology, is a record of bonafide research work carried out by her. Ms. Khushboo Rinawa has worked 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,
Hauz Khas, New Delhi 110016, India

Dr. José-Marie LOPEZ-CUESTA
Professor
Centre des Matériaux de Grande Diffusion,
Ecole des Mines d’Alès,
6, Avenue de Clavières,
30318 Alès Cedex, France

Acknowledgements

It is a pleasant aspect to express my deep sense of gratitude to all who have helped me along my way through the doctoral studies and a memorable stay at IIT Delhi and Ecole de mines, d'Ales France. There are, of course, very few words to properly thank all of them.

First and foremost, I would like to thank my supervisor ***Prof. S. N. Maiti****. I am deeply indebted to him for his mentoring, able guidance, stimulating suggestions and inspiring thoughts, which have been of tremendous help for me throughout my doctoral studies. He has always been there, through every thick and thin and encouraged me to move forward in life. He gave me the opportunity to work in France at CMGD, Ecole de mines, d'Ales. The period abroad enriched me scientifically and personally. I express my profound sense of gratitude and veneration to my supervisor,* ***Prof. José-Marie LOPEZ-CUESTA*** *, for guiding me all the way during my stay in CMGD. His constant inspiration and encouragement has been a great motivation for me behind all the work I have conducted.*

I express my deep sense of gratitude to my senior research committee members, Prof. B. L. Deopura, Prof. A. K Ghosh, and Prof. Manjeet Jassal for monitored my work and provided me the valuable suggestions. I would like to offer my gracious thanks to Prof. A K Gupta, Prof. Veena Choudary, Dr. J. Jacob and Dr. B. Satapathi 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.

I would like to express my sincere gratitude to my research engineer ***Dr. Rodolphe Sonnier*** *for supportive and providing me guidance to use the laboratory facilities at CMGD which helps me in improving the quality of this research work. I have learnt from him that failures in all doing should motivate one to work harder. He has always boosted me to put in extra efforts and I am indebted to him what I am today. His wide experience in the field of nanocomposites and flame retardancy helps in explaining the experimental data and supported me to present all my work in a systematic way.*

My special thanks to Belkacem Otazaghine and Aurélie Taguet who continuously provided guidance and support during my stay in CMGD laboratory in France. I am indebted to Claire Loguet, Didier Perrin, Marc Longerey, Benjamin, Sylvain, Jean-Marie , Sylvie Cruvellier, for helpful assistance and discussions. My heartiest thanks to Mr. Robert Lorquet, Dr. Hossein Vahabi , Annie and all the members of AIMA for their love and care.

My thanks to Mr. Surender Sharma, Mr. Ashok Kapoor, Mr. Shivkant and all official staffs of CPSE for their immediate help whenever needed.

This work would not be possible without the support and encouragement from my friends, seniors and juniors. My special thanks go to P. Balamurugan, Satpal Singh, Saiket banerjee, Anju gupta, Sneh Bharti, Manisha Tomar, Sanjeev Kumar, Manash Jyoti Kashyap, Hemlata Jaiswal, Rajul Sharma, Shikha Jain, Jutika Goswami, Priyanka Singh, Tahir Zafar, Priya Sonkar, Aastha Garhwal, Garima Agarwal, Rishi, Rajendra for their cooperation and moral support during my work at CPSE. I would like to thank my friends Carmen, Andrea, Thao, Diego,Mirko, Siska, Lucie, Yen, Nico Concha, Juliea and others for their friendly support and care which has encouraged me immensely during my stay in France. I would also like to thank Chainika, Deeplata, Punam, Naveet, Vanessa, Vikas Garhwal, Kalpana, Shilpi, Pushpendra, Neha, Rajneesh,

Anisha, Shiv, Major Rohit, Vivek, Rahul, Sunita, Gaurav Kumar and others, for their love and never ending support through the years. I had the pleasure to be close.

*I am deeply indebted to my beloved parents (**Mr. N. K.Rinawa and Mrs. Uma Rinawa)** who are at the back of my each and every movement. I wish to record my sincere appreciation and thanks to them for their invaluable blessings, support, patience and encouragement throughout my study years. I am also thankful to my brothers (Abhishek and Amit) and bhabhi (Shilpa and Swati), for their eternal love and supportive hand. Thanks to my nephews (Arnav and Amay) for making me smile in every situation.*

*A very special thanks to my parents-in-laws (**Mr. C.P.Sharma and Mrs. Hemlata Sharma**) , brother-in-law (Pawan Sharma), bhabhi (Abhilasha Sharma) and little angel "Pahee" for bringing happiness in our life. It's a joy and pride to be their daughter-in-law. They ceaselessly and tirelessly encouraged me with all their love and support and let me freely do whatever I wanted to. Without them, there is no way in which I could possibly have accomplished this stupendous task. Their understanding of the value of education is truly beyond my comprehension.*

*I cannot forget to mention the name of my little daughter '**Eashta**' who had been a constant source of enthusiasm and ecstasy by her sweet smile.*

*Lastly I'm left with lack of words to acknowledge my strength, motivation and stable force, my better half **'Kashyap'**. He has an deep influence on my ability to see and understand my path of self-awareness, for all the pains he bore to make me smile, helped me to take the pressure for the completion of this thesis and more of this, always stood by me with a smile during the storms of life.*

I would also like to thank CSIR, Indo-French Sandwich programme from French embassy and Ecole des Mines d'Ales for providing funding and fellowship for carrying out this research work. Finally, thanks to GOD for HIS impeccable guidance and support, this helped me to remain focused even in many obstacles that came during the course of this journey.

Khushboo Rinawa

ABSTRACT

Polyamides have been the subject of intense research over the past two decades in academia and industry. Polyamide 12 [PA12] is a semi-crystalline polymer with wide variety of applications such as aerospace, communication, engineering, automobile and commodity industries. To meet the satisfactory performance PA12 needs to be modified by blending with rubber and other reinforcing fillers. Blending with rubber has been chosen 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 for by incorporating reinforcement, thereby concurrent improvements in strength and toughness could be achieved.

The present study deals with the mechanical and morphological properties of polyamide 12/maleic anhydride grafted styrene-b-(ethylene-co-butylene)-b-styrene rubber (PA12/SEBS-g-MA) binary blends at varying dispersed phase (SEBS-g-MA) concentrations. Tensile behaviour, impact strength and crystallinity of these blend systems were evaluated. Influences of microstructure, dispersed phase particle size, and ligament thickness on the impact toughness of the blend were studied. DSC data indicated an increase in crystallinity of PA12 in the blends. Tensile modulus and strength decreased while impact strength and elongation-at-break increased with the elastomer concentration. The macro-mechanical and micro-structural property evaluation studies revealed that 20 wt% of SEBS-g-MA content was the optimum level to achieve a reasonably good balance in strength and toughness in PA12/SEBS-g-MA blends. The enhanced properties were supported by interphase adhesion between the grafted maleic anhydride groups of rubber with polar moiety of PA12. Analysis of the tensile data employing

simple theoretical models showed the variation of stress concentration effect with blend composition.

The thermal degradation kinetics and crystallization kinetics of PA12/SEBS-g-MA blends were investigated under non-isothermal and isothermal conditions using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. The activation energy of thermal degradation from Kissinger method was found to be less in case of SEBS-g-MA than that of PA12 but the blends show comparatively high activation energy. The macrokinetic model given by Avrami was used to analyze both the non-isothermal and isothermal crystallization kinetics of the blends. The value of Avrami exponent during non-isothermal crystallization for pure PA12 and PA12/SEBS-g-MA blends predicted spherulitic growth with random nucleation of crystal structures as the n values lie between 3 to 4. The dependence of crystallization rate constant (k) and half life of crystallization ($t_{1/2}$) on cooling rate by Jeziorny model also predicted almost similar values. The slight nucleating effect of SEBS-g-MA was showed by nucleating activity calculated by the Dobreva and Gutzowa method. The evaluated activation energy values according to Kissinger, Augis-Bennet, and Takhore methods were higher in case of blends supporting the mechanism of weak nucleating effect of SEBS-g-MA copolymer and the hindrance to PA12 chain mobility. The Avrami exponent, rate constant and time to half crystallization under isothermal condition show similar crystal growth and heterogeneous nucleation for both PA12 and the blends.

The viscoelastic behaviour of PA12/SEBS-g-MA blends was studied. Time sweep, amplitude sweep, and frequency sweep tests were analyzed by the use of parallel plate rheometer. Time sweep test shows time-independent viscoelastic behaviour of the polymer and blends during the entire duration of test. The critical shear strain was higher for PA12 as

compared to that of SEBS-g-MA and the blends in amplitude sweep test. However the plateau modulus was higher for SEBS-g-MA as compared to PA12. The complex viscosity, dynamic storage and loss moduli of PA12 increased with the addition of SEBS-g-MA as a consequence of phase interaction between them. The influence of phase morphology of the blends on their rheological properties was also examined. A transition from liquid-like to solid like behaviour in blends was observed. The decrease in viscosity for PA12 and blends was observed with increasing temperature. The van Gurp plots were successfully used to validate Time-Temperature Superposition principle (TTS) for PA12, SEBS-g-MA and blend compositions. PA12 holds TTS with a horizontal shift factor that fits Arrhenius equation. Whereas TTS fails for SEBS-g-MA and the blends because of different temperature-sensitive response and microstructural changes of melt during shear application.

Addition of 1 to 5 wt% of organoclay to an optimized PA12/SEBS-g-MA blend (20wt % of SEBS-g-MA) led to ternary nanocomposites where the rigidifying effect of clay and toughening effect of the rubber came together. The dispersion of organoclay, phase morphology and orientation in impact modified PA12 blend with its static and dynamic mechanical properties were characterized by XRD, HRTEM, SEM, tensile test, impact test and DMTA, respectively. Interfacial tension between components of the nanocomposites was evaluated by contact angle measurement. Theoretical prediction of selective localization of organoclay in elastomeric phase was used to characterize morphological and mechanical property modifications. Tensile moduli of PA12/SEBS-g-MA based nanocomposites enhanced significantly with the incorporation of higher organoclay content. Microstructural changes to the PA12/SEBS-g-MA blend resulted in an extended ellipsoidal shape of the rubber particles. Furthermore, elongation at break (ϵ_b) increased from 127% for optimized PA12/SEBS-g-MA blend to 416% for PA12/SEBS-g-

MA/organoclay (5 wt%) nanocomposite with respect to that of neat PA12. Efficient energy-dissipation mechanisms during deformation were attributed to microvoid formation, sliding and their alignment in the melt flow direction. FTIR and DMTA results were used to propose reaction between organically modified nanoclay and maleic anhydride of SEBS-g-MA copolymer considered responsible for improved dispersion of nanoplatelets.

The melt rheological analysis of the PA12/SEBS-g-MA/organoclay nanocomposites was also performed in a parallel plate rheometer at 220 °C temperatures and a frequency range of 0.01 to 100 Hz. The influence of frequency and organoclay content on complex viscosity, storage and loss moduli and damping behavior was investigated. A shear thinning behavior at high frequencies was observed for all the compositions. Incorporation of 5wt% of organoclay increased the viscosity of the system whereas there was slight decrease in viscosity with the incorporation of 1wt% of organoclay in NS20 matrix. At 5wt% of clay the pseudo solid-like behavior was observed which delayed the relaxation time as a consequence of jammed network structure formation which acts as a barrier to the polymer chain mobility. The sliding and orientation effect of clay was responsible for slight decrease in viscosity with 1wt% of clay.

The fire performance of impact modified PA12 polymer was studied in presence of 5-25wt% of conventional flame retardant zinc borate. The influence of zinc borate on decomposition pathway of elastomer modified PA12 blend was characterized using thermogravimetric analysis (TGA), pyrolysis combustion flow calorimeter (PCFC), and cone calorimeter. Interfacial tension measurements are used to predict the localization of zinc borate in PA12/SEBS-g-MA blend. Although, ESEM and HRTEM micrographs are not able to predict such selective localization, contact angle is supposed to be a primary test to predict such type of selective localization with some limitation. TGA and micro calorimeter are used to analyze the thermal behavior of the composites. Cone-calorimeter is used to evaluate the exact fire behavior of zinc borate composites. The cone calorimeter brings quantitative analysis to materials flammability research by investigating parameters such as heat release rate (HRR), time to ignition (TTI), total heat release (THR) and mass loss rate (MLR). It was seen that there was no significant change in onset and peak decomposition temperature of the composites. It was concluded that alone zinc borate could not create the desired flame retardant effect other than providing an inorganic residue as seen in the TGA residue. So, it is necessary to combine zinc borate with other fillers.

The thermal and fire behavior of impact modified PA12 blend in presence of nanoparticle (organoclay) was also studied. TGA and microcalorimeter are used to analyze the thermal behavior of the nanocomposites. The parameters investigated from cone calorimeter test showed improved fire performance of the nanocomposites. There was no change in decomposition temperature but the residue content confirm the presence of char which is responsible for improved fire properties of the nanocomposites. Significant decrease in HRR in cone calorimeter test also establishes the flame retardancy of intercalated/exfoliated organoclay which acts as physical barrier to external heat flux and protects the underlying substance from burning. The formation of stable char reinforced by organoclay layers at the nanoscale provided significant reduction in peak heat release rate and mass loss rate in the cone calorimeter. The effect of different external heat flux (35, 50, 65 kW/m^2) on fire properties of the system was also studied to systematically analyze the flammability in different fire scenario.

The combining effect of micro sized conventional flame retardant additive (zinc borate) with nanosized filler (organoclay) was also studied. Interfacial tension measurements, HRTEM, and XRD are used to explain the morphology of quaternary nanocomposites. TGA and

microcalorimeter were used to analyze degradation of the system at lab scale. Cone calorimeter data were used to analyze the effect of combination of zinc borate and organoclay on flammability of PA12/SEBS-g-MA/organoclay/zinc borate system. Residues characterization by SEM and XRD ascribed the improved flame retardancy of the nanocomposites due to the presence of physically strong and consolidated barriers owing to the action of residual zinc and boron along with clay layers, providing tortuous pathway or barriers to the heat and mass transfer during fire. Rheological properties were correlated with the flammability of the system. Finally, dynamic mechanical properties and mechanical properties of selected compositions were presented to see overall performance of the system produced in this research.

TABLE OF CONTENT

Chapter 2: Materials and experimental........37-52

Chapter 4: INFLUENCE OF ORGANOCLAY INCLUSION ON MORPHOLOGICAL, MECHANICAL, CRYSTALLIZATION AND RHEOLOGICAL BEHAVIOUR OF IMPACT MODIFIED PA12……………………………………………………………..148-190