STUDIES ON NEEM BARK FLOUR AND TEAK WOOD FLOUR FILLED HIGH DENSITY POLYETHYLENE COMPOSITES

KAMINI SEWDA

CENTRE FOR POLYMER SCIENCE AND ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2008

STUDIES ON NEEM BARK FLOUR AND TEAK WOOD FLOUR FILLED HIGH DENSITY POLYETHYLENE COMPOSITES

by

KAMINI SEWDA

Centre for Polymer Science and Engineering

Submitted

in fulfillment of the requirements for the degree of
Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

DECEMBER 2008

Dedicated toMy Parents

and Family

CERTIFICATE

This is to certify that the thesis entitled **"STUDIES ON NEEM BARK FLOUR AND TEAK WOOD FLOUR FILLED HIGH DENSITY POLYETHYLENE COMPOSITES"** being submitted by **Kamini Sewda** 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. Kamini Sewda 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

Acknowledgement

*The opportunity to pursue my Ph.D. at IIT provided me a platform to interact with exceptionally distinguished faculty and state-of-the-art facilities. I am highly pleased to express my best regards, profound gratitude, indebtedness and deep appreciation to my honorable academic supervisor Dr. S. N. Maiti, Professor, Centre for Polymer Science & Engineering, Indian Institute of Delhi for his constant supervision, inspiring guidance, enthusiastic encouragement, and sagacious advice throughout the entire period of my research work. I feel very fortunate to have had the opportunity to study with such a wonderful personality. He not only taught me planning and execution of experiments but also devoted hours to inspire me to achieve higher heights. I would like to quote these lines for him "**Dhyanamulam gurur-murti; pujamulam gurur-padam; mantramulam gurur-vakyam; mokshmulam gurur-kripa**".*

I would also like to sincerely thank my committee members, Prof. Mangala Joshi, Prof. A. K. Gupta and Prof. A. K. Ghosh for their knowledge and valuable suggestions throughout the experimental work and writing up this thesis.

I am pleased to express my thanks to Prof. V. Choudhary and Dr. Jacob and Dr. .Bhabani for their constant encouragement and advice

I thank my colleagues G. Bala, Neetu, Senthil and Prakashan, for providing a congenial and super-friendly environment to work with. I wish them good luck in their endeavors. Thanks to Mr. A. Kapoor, Mr. S. Sharma, Mr. Shivkant, Mr. Devendra and Mr. D.C. Sharma of SEM lab for their technical support and Mrs. Rama for her official support and inspiration. I would like to thank all members of the CPSE for their support.

I would like to thank the Council of Scientific and Industrial Research (CSIR), New Delhi, for junior research fellowship and senior research fellowship for the research work. I also acknowledge the travel fellowship provided by CSIR, Department of Science and Technology (DST), Delhi, Indian institute of Technology, Delhi and Forest Product Society, Wisconsin, USA to attend and presenting the part of the study at 9th International Conference on Wood and Biofiber Plastic Composites, 2007, Madison, Wisconsin, USA.

The most important part of my life is my family. I dedicate this entire work to my Grandma and parents for their blessings, love and encouragement. They have been example of sincerity and hard work which always inspires me. I would never have been able to accomplish any of my goals without the support of my family members. My parents instilled in me the value and many rewards of

perseverance and responsibility. I owe so much to my mother, who spent her whole life of taking care of everyone in family, whether in daily life or in my scientific endeavors. Although she is not a scientist herself, she is no doubt responsible for helping to produce three scientists in one small family! My father, a teacher, has always demonstrated great enthusiasm, perseverance and diligence in his devotion to science, and as such, has been an exemplary role model for me. My two younger brothers were always a source of love and help. I am grateful for the blessings and inexorable support of my in-laws.

My husband, Virendra, is behind the successful completion of this work who stood by me with great love, guidance, encouragement, patience and understanding during the research work. Without his steadfast love, support and help, I doubt if I would have been able to complete this thesis successfully. He has always been there to help me face and overcome any challenge that I have confronted. I am also so proud of his excellent research. He compromised on his own research studies so that this thesis can see the light of day. I love you and thank you.

Thanks to my little angel Dakshaja who is my inspiration. I will never be able to express all of my love. Our lovely daughter is the reason the world exists, her single hug is more than anything in the world.

I thank the ALMIGHTY for giving me ample strength and right path to attain this cherished moment in my life.

(Kamini Sewda)

ABSTRACT

In the recent years development of wood based plastics have interested the researchers and scientists for enduses such as in the structural, interiors and automotive applications due to their ecofriendliness and economic advantages. In this work wood plastic composites have been developed by incorporation of bark flour (BF) and teak wood flour (TWF) into high density polyethylene (HDPE). The composites have been characterized for their melt rheological, thermal, crystallization and mechanical properties such as tensile and flexural properties and impact behaviours. Morphology of the systems have been studied by scanning electron microscopy (SEM). The effect of a coupling agent, maleic anhydride grafted HDPE, HDPE-g-MAH, on the above properties has also been examined.

The melt rheological studies on HDPE/BF composites were carried out at 180°C, 190°C and 200°C using the extruded pellets. The melt viscosity of the HDPE increases with the increase volume fraction, Φ_f because the BF particles obstruct the flow of the HDPE. With the incorporation of HDPE-g-MAH, there was decrease in the viscosity than the corresponding compositions in the HDPE/BF/HDPE-g-MAH systems. HDPE-g-MAH acted as a plasticizing agent in the HDPE/BF composites. The activation energy (E_a) for the viscous flow was calculated following the Arrhenius equation which showed that E_a increases with increase in the filler concentration. For the HDPE/BF/HDPE-g-MAH composite systems less energy was required compared to the corresponding HDPE/BF systems. HDPE-g-MAH provides the plasticizing effect which was also evidenced by the E_a data. The power law coefficient and the consistency index analyzed for both the systems also support the above findings. The power law coefficient decreases with increase in the filler content but it increases with temperature for the

corresponding systems while the consistency index follows the opposite trend.

A systematic study was undertaken to investigate the effects of BF on the crystallization and melting behaviour of HDPE/BF composites at BF $\Phi_f = 0.00 - 0.26$. The crystallinity evaluated by two techniques: wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) were in good agreement and comparable, with correlation coefficients $R^2 = 0.91$ and 0.86, for the HDPE/ BF and the HDPE/BF/HDPE-g-MAH systems, respectively. The melting and crystallization range of HDPE is broad and the filler inclusions may also have influence on the crystallization characteristics. The crystallization behaviour of the composites were studied for the evaluation of the crystallization parameters from the DSC exothermic peak. The BF particles act as nucleating agent in the HDPE/BF composites, the efficiency increases in presence of the coupling agent. Crystallinity studied by DSC decreases from 65 to 56% linearly with Φ_f with $R^2 = 0.81$ and 0.90 for the HDPE/BF and the HDPE/BF/HDPE-g-MAH systems, respectively.

The effects of BF on the mechanical and morphological properties of HDPE are explained. The BF concentration in the HDPE/BF composites varied from 0.00-0.26 Φ_f. Tensile strength and tensile modulus showed a decreasing trend with increase in Φ_f. In order to understand the behaviour of HDPE/BF composite structure the modulus data were analyzed and compared with theoretical predictions of Cohen and Ishai and Einstein's equations. The data were normalized by dividing the moduli with the crystallinity of HDPE. The data showed an extent of good phase interaction in the HDPE/BF/HDPE-g-MAH composite. The percentage elongation data were compared with Nielsen' model, the data showed disagreement. The weakness in the composite structure was analyzed by comparing the tensile strength data of the HDPE/BF composite with "Nicolias-Narkis model" and "Porosity model" while the reinforcement

in the HDPE/BF/HDPE-g-MAH composite was evaluated using Bela-Pukanszky model. The data agreed well with Nicolias-Narkis model with weightage factor, K = 0.39, which implies good extent of phase adhesion. Porosity model showed a value of stress concentration factor, $\alpha = 0.84$, indicating an extent of stress concentration. The impact strength decreases significantly with increases in Φ_f.

Morphological studies were carried out on cryogenically fractured samples to analyze the phase morphology by SEM. Impact fractured samples were examined by SEM to analyze the fracture mechanisms.

The viscoelastic behaviour of the HDPE/BF composites and also the effect of the coupling agent on the HDPE/BF composites are described. The neat HDPE shows only two peaks due to γ and α-relaxation. At low concentration ($\Phi_f = 0.03$ and 0.07) the BF acts as pseudolubricant which induced the ball bearing effect on HDPE chains due to which storage modulus data show lower values through the studied temperature range. High damping composite can be obtained by using BF particle for the engineering structural applications to reduce the vibration level in the structural components. β-relaxation peak magnitude increases as the amorphous region in the composites increases with increase in the filler content and also it increases in the presence of HDPE-g-MAH. In the α-relaxation region the transition slightly shifts towards the higher temperature side showing that the BF particles decrease the crystallinity and provide mechanical restraint to HDPE. This shifting was higher in HDPE/BF/HDPE-g-MAH composites indicating bonding at the interface due to HDPE-g-MAH.

The thermal stability of HDPE/BF composite decrease with the increase in the BF content, as the BF comprises of cellulose, hemicellulose, lignin and extraneous substances which pyrolyzed at low temperature when exposed to the programmed heating in the inert atmosphere. The degradation of the HDPE/BF systems was two steps

leading to the increased char yield with increase in the BF concentration. The thermal stability of the HDPE/BF composites slightly increases in the presence of HDPE-g-MAH for the lower BF concentration (Φ_f = 0.03 and 0.07) only. The initial, maximum and final temperature of decomposition for both the steps and the char were evaluated and analyzed.

The properties of the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH composites are described below:

The melt rheological studies on HDPE/TWF composites were carried out at Φ_f = 0.00-0.32 and at 180 °C, 190°C and 200°C. The melt viscosity of HDPE/TWF composites increases with the filler concentration while it decreases with increase in the temperature. Addition of HDPE-g-MAH to the HDPE/TWF composites enhances the viscosity as compared to the corresponding HDPE/TWF systems. This was attributed to the increase in the interaction between the TWF and HDPE by HDPE-g-MAH which in turn stiffens the system. The power law coefficient, n, decreases with increase in the Φ_f and increase in the temperature. Values of n were found to be lower for the HDPE/TWF/HDPE-g-MAH composites as compared to the HDPE/TWF composites. The consistency index increases with increase in Φ_f and were higher for the HDPE/TWF/HDPE-g-MAH systems. The activation energy increases with increase in the Φ_f for both the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH systems.

The non-isothermal crystallization behaviour and melting characteristics of HDPE in the HDPE/TWF composites have been studied by DSC. Various crystallization parameters evaluated from the DSC exotherms were employed to study the non-isothermal crystallization behaviour. The melting temperature (T_m) and crystallization temperature (T_p) of the composites were slightly higher than those of the neat HDPE. Since the hydrocarbon polymer HDPE and polar TWF are incompatible, to enhance the

phase interaction HDPE-g-MAH was used as a coupling agent. A shift in the crystallization and melting peak temperatures towards the higher temperature side and broadening of the crystallization peak (increased crystallite size distribution) were observed while crystallinity of HDPE declines with increase in Φ_f. The degree of crystallinity (%) calculated for the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH systems from the ΔH_{fusion} followed the linear decreasing trend. The crystallinity data obtained from the WAXD and the DSC measurements are in good agreement with the correlation coefficient, R^2 = 0.84 and 0.86, for the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH systems, respectively.

The study on the HDPE/TWF composites to evaluate the effect of TWF content from Φ_f = 0.05 to 0.32 on the mechanical and morphological properties of HDPE is described. The normalized relative tensile moduli (ratio of the normalized moduli of the composites to that of the matrix), enhanced to ~ 1.3 at Φ_f = 0.09, the value then decreased to 1 to 0.7, depending on the Φ_f. The data were compared with the predictive models for two phase compositions namely, Einstein equation with and without adhesion. HDPE/TWF showed disagreement with the models. In presence of the coupling agent, HDPE-g-MAH, the normalized relative moduli increase with Φ_f. The data agree well with Einstein equation with adhesion, which implies a good degree of phase adhesion. Percentage elongation data were compared with Nielsen's model with perfect adhesion. The elongation data were far below the theoretical model. The tensile strength data were compared with Bela-Pukanszky model. The reinforcement factor, B_a was 4.2 for the HDPE/TWF/HDPE-g-MAH composites, indicating good phase interaction. The impact strength decreases quite drastically to ~ 0.4 at Φ_f =0.16, the data then level off at $\Phi_f > 0.16$. Morphological studies were carried out on cryogenically fractured surfaces. The unmodified TWF particles were non-adherent with HDPE.

Surface of separation of the particles are easily observed in the SEM photomicrographs. In the HDPE/TWF/HDPE-g-MAH composites the particle boundaries are to an extent not distinct and the fracture surfaces are relatively smoother implying increased phase interaction.

The viscoelastic behaviours of the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH composites are describes here. In the HDPE/TWF composites storage modulus values first decrease, then the data increase with TWF content. The loss modulus and the damping parameter increase with the TWF concentration. In the HDPE/TWF/HDPE-g-MAH composites storage modulus decreases while loss modulus and damping parameter increase with TWF content. The peak corresponding to the β- transition also increases with the TWF concentration, and also the peak intensity was higher for the HDPE/TWF/HDPE-g-MAH composite systems. There was shifting of α-relaxation peak towards the higher temperature side in both the systems.

The thermal stability of HDPE with varying Φ_f (0.00 to 0.32) is described in this section. The thermograms show two steps degradation for both the HDPE/TWF and the HDPE/TWF/HDPE-g-MAH composites. The initial temperature for decomposition decreases with increase in the Φ_f. The char yield increase with increase in the filler concentration. HDPE-g-MAH has not much influence on the thermal degradation of the HDPE/TWF composites. The initial, maximum and final temperature of decomposition for both the steps and the char were evaluated and analyzed.

Chapter 5 summarizes how two bio based fillers had modified the properties of HDPE and also the conclusions were drawn on the basis of these results.

TABLE OF CONTENTS