STUDIES ON POLYMER COMPOSITES USING PARTICULATE FILLERS

By

PRATAP KUMAR MAHAPATRO

THESIS SUBMITTED
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

CENTRE FOR MATERIALS SCIENCE AND TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

November, 1988

DEDICATED

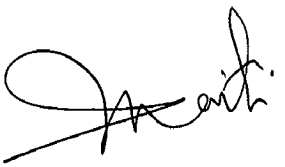
TO MY

PARENTS

CERTIFICATE

This is to certify that the thesis entitled "Studies on Polymer Composites Using Particulate Fillers" being submitted by Sri Pratap Kumar Mahapatro to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Sri Pratap Kumar Mahapatro has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis which to my knowledge has requisite standard.

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



(S.N. Maiti)
Asst. Professor
Centre for Materials Science & Technology
Indian Institute of Technology
New Delhi - 110016.

ACKNOWLEDGEMENTS

I wish to express my thanks to Dr. S.N. Maiti, Assistant Professor, Centre for Materials Science & Technology Indian Institute of Technology, Delhi for his dynamic guidance, constant encouragement and kind help which motivated me in doing this work.

I am thankful to Prof. V. Raghavan, Prof. (Mrs.) I.K. Varma, who in their capacity as Head Centre for Materials Science & Technology, extended all the facilities during the course of this work. I also thank Prof. M.L. Gulrajani and Prof. (Miss) P. Bajaj, who in their capacity as Head Textile Technology Department extended to me the necessary facilities.

I also sincerely wish to thank Prof. A. Misra and Dr. A.K. Gupta for the fruitful discussions and suggestions during the progress of the work.

Thanks are due to Dr. Dabholkar and Dr. Saroop for extending experimental facilities at Sri Ram Institute for Industrial Research, Delhi.

The help rendered by Mr. H.S. Varma, Mr. S.P. Gupta, Mrs. Sneh Saxena, S.R. Anantha Krishnan Mr. M.R. Patri, Mr. Anand Kumar, Mr. S.K. Mishra, Mr. A.K. Mitra, Mr. M.M. Sinha and Mr. Rakesh Koul, is gratefully acknowledged. Finally, I thank all my friends of Centre for Materials Science & Technology and Textile Technology Department for their help and co-operation. The assistance from the technical staff to carry out this work is also sincerely acknowledged.

(Pratap Kumar Mahapatro)

ABSTRACT

Filled Polymer composites have been developed, by incorporation of metallic and mineral fillers into polypropylene, with a view to estimate the performance characteristics of the same to suit various end use applications. A number of composites, both metal particle filled and mineral filled, have been prepared taking PP as the polymer matrix. The fillers chosen for the composites were metallic aluminium (Al), nickel (Ni) and calcium carbonate ($CaCO_3$). As the interaction between the filler and the polymer matrix is often poor, resulting lower strength and unfavourable processing conditions, a titanate coupling agent (LICA 12) was used in the case of $CaCo_3$ filled composites to enhance interfacial bonding between the filler and the matrix.

Various studies have been performed on these composites thus developed and their results and probable applications are reported in this work. These include the mechanical properties by tensile, impact and flexural studies; the tensile results were compared with different theoretical models of two phase systems; crystallization characteristics by DSC and x-ray measurements and these are correlated with the tensile properties; melt rheological properties; thermal conductivity, thermogravimetric analysis

and vicat softening measurements; and morphological studies by scanning electron mycroscopy. In the case of $CaCo_3$ filled composites the untreated samples were compared to the treated samples for most of these properties.

The tensile strength and elastic modulus of the metallic Al, and Ni filled composites decreased with the filler, the decrease is very rapid at lower filler content and then the decrease is marginal. However, the incorporation of $CaCO_3$ increased the modulus. Elongation-at-yield decreased with the increase of the filler content. There is an increase in the notched impact strength upto a critical filler content i.e. about 10 wt. % in all the cases. Rigidity of the composites is enhanced through an increase in flexural properties. Treatment of CaC_3 either retain most of the properties of PP or slightly enhance the same. Analysis of the tensile properties and their comparison with the theoretical prediction indicates that fillers act as stress concentration sites and the structure changes from with no stress concentration effect to a significant stress concentration effect with the increase in the filler concentration.

The overall crystallinity of the composites determined by x-ray and DSC measurements have shown good agreement and the degree of crystallinity was found to

decrease with the filler concentration. The treatment of $CaCO_3$ further decreases the crystallinity values. A good correlation was obtained between the crystallization parameters and tensile strength, tensile modulus and strain at yield of all the composites.

The results of melt rheological properties of all the composites show that all the composites are pseudoplastic in nature and follow the power law relation. The melt viscosity of PP/Al and PP/Ni composite increases upto a certain level of the filler, while that of PP/$CaCO_3$ increases throughout the filler content. The decrease in viscosity at higher metallic Al or Ni is due to better thermal conductivity of the composites, which facilitates the flow. The viscosity of the treated $CaCO_3$ filled composites are slightly less than that of untreated samples. The melt elasticity parameters were found to decrease in all the cases excepting PP/$CaCO_3$ (treated) samples. The linearity in the recoverable shear strain throughout the filler range studied and the decrease in melt elasticity parameters revealed that these fillers make the processing safer without any melt fracture in the extrudates. However, in PP/$CaCO_3$ (treated) samples this safety margin is lowered.

The thermal conductivity, in the case of PP/Al and PP/Ni composites, was shown to be increasing with increase

in the filler content and the experimental data were in good agreement with the theoretical results predicted by Cheng-Vachon. The deviation percentage between the theoretical results and the experimental values for other predicted models are significant. The thermal stability increases upto a critical volume percent of the filler through an increase in the activation energy for thermal degradation. The vicat softening temperature increases very rapidly at low percent of filler and then the increase is marginal.

The results of dynamic mechanical analysis revealed that incorporation of metallic fillers increased damping while with $CaCO_3$ it decreased. α-relaxation peak temperature increased in all the cases. At lower filler content there exists a β-relaxation peak at a temperature lower than the α-relaxation peak. With further increase in the filler content the α-relaxation peak broadens and the β-relaxation peak shifts to higher temperature region. After the treatment of $CaCO_3$ the damping further decreases and this decrease is attributed to the plasticizing action of coupling agent and good dispersion of the filler. Similar trend of peaks shifting and broadening also occur in the treated CaC_3 filled composites.

Scanning electron microscopy was used to visualize the dispersion of the filler in the composites. It shows that fillers are randomly dispersed through out the matrix, however, there are some agglomeration at low filler content. The conductivity property indicates that Al and Ni are randomly distributed in the polymer matrix. The ductility of PP decreases at higher filler content and upon the treatment of the filler the agglomeration is further reduced giving better dispersion.

CONTENTS