

**STUDIES ON POLYPROPYLENE BASED BLENDS AND  
COMPOSITES**

by

**D.PURNIMA**

**Centre for Polymer Science and Engineering**

**Submitted**

**In fulfillment of the Requirements  
of the degree of**

**DOCTOR OF PHILOSOPHY**

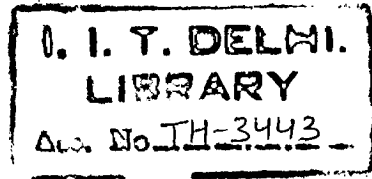
to the



**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

**MARCH 2007**

Polypropylene  
Polypropylene - fibers



TH  
678-742.3  
PUR-S

*Dedicated*  
to  
*My Parents,*  
*Husband, Brother and Son*

# CERTIFICATE

This is to certify that the thesis entitled **“Studies on Polypropylene Based Blends and Composites”** being submitted by Mrs. D.Purnima to Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Polymer Science and Technology, is a record of bonafide research work carried out by her. Mrs. D.Purnima has worked under our guidance and supervision and fulfilled the requirement for the submission of this thesis which to our knowledge has reached the requisite standard. The results contained in the thesis have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.



Prof. A.K.Gupta  
Thesis Supervisor  
Professor



Prof. S.N.Maiti  
Thesis Co-Supervisor  
Professor

## ACKNOWLEDGEMENT

*I find, words falling short in expressing the multitude of overflowing gratitude for my guides Prof. A.K.Gupta and Prof. S.N.Maiti for whose impetus, sustained efforts and able and persistent guidance, the project could be undertaken and fostered me with the strength and spirit to see to its culmination. I must not forget less, their timely catering to my otherwise tough needs posed by times past, which enabled me to garner enough strength to persuade the uphill task in the face of turmoil.*

*My heartfelt thanks are due to Prof. A.K.Ghosh, Head of the Centre, for extending the necessary infrastructure necessary for the work, valuable suggestions, support, both moral and technical during the tenure of the work, I would also like to thank the ex-Head of the Department, Prof Veena Chaudhary for her valuable suggestions and extending the necessary facilities required for the work, I also thank Dr.Josmen Jacob for his suggestions during the work, My sincere thanks to Prof.B.L.Deupora for his fruitful technical advices during the period of the work.*

*I am thankful to technical staff of CPSE Mr.Surinder Kapoor, Mr.Ashok Kapoor, Mr.Devinder Singh and Mr.Shivkant for their cordial association and timely help rendered during the period of this work, I thank Mr.Sharma of Textile Department for the SEM studies carried out for the work as when required.*

*I accord my thanks to thank the staff of CIPET, Dr.Palanivelu, and Mr.Vishal for extending their support during the work done at CIPET.*

*I extend my very personal thanks to Mr.Ranga Rao of Centre for Energy studies for his unconditional and selfless cooperation and help as and when required by me.*

*My special thanks to my friends Dipti Singh, Pooja Chabra, Sujata Misra, Neetu Tomar, Sangita Nandi, Geeta Saini, Shveta, Prasath Bala Murugan, Dilip Kolluri, Senthil Kumar, Prakshan, Praveen, Dr.Rashmi Chauhan, Dr.Nimisha Agarwal, Dr.Muthulakshmi R.T.S., Dr.Jaykishor Pal, Dr.Anantha Padmanabha and Dr.Rakesh Kumar for their all time cooperation during the entire period.*

*I cannot, at this moment fail to remember with utmost love, encouragement of my parents and brother who have tolerated and bore me with patience all through. The incessant love, cooperation and perseverance put forth by my husband, has made the accomplishment of the work a spirited affair, to be remembered forever. Lastly but not the least I would like to thank my son for bearing my absence at time when he really needed me and allowing me to consummate this work.*

*D. Purnima  
D.Purnima*

## ABSTRACT

Blends of polypropylene (PP) with ethylene propylene diene monomer (EPDM) rubber were prepared to improve the impact properties. However PP/EPDM blends are immiscible and have inferior mechanical properties. Maleic anhydride (MAH) grafted EPDM was used as the dispersed phase in the blend to improve the interfacial adhesion in the blend. Incorporation of elastomer results in improved impact properties but decrease of modulus. Talc filler was added to the PP/EPDM and PP/EPDM-g-MAH blends to improve the modulus. PP/talc composites were also prepared to be used as reference system. PP-g-MAH was used as coupling agent in PP/talc composites to improve the filler adhesion to the PP matrix.

Various studies have been performed on the composites and blends and the results are reported. The studies include mechanical properties by tensile, impact and flexural studies; tensile results were compared with simple theoretical models; crystallization properties by Differential Scanning Calorimetry (DSC) and X-ray diffraction measurements and these are correlated with tensile properties: melt rheological properties and morphological properties by scanning electron microscopy (SEM) also have been studied.

In PP/talc composites the effect of talc concentration on the above properties was studied. Yield stress, breaking stress and modulus increased with talc concentration, while yield strain and breaking strain decreased. Impact strength increased up to 0.02 volume fraction of the filler and then decreased marginally than that of unmodified PP. Flexural modulus and strength enhanced with talc contents. The increase in yield stress and

modulus of the composites indicated that talc reinforced the PP matrix. In presence of coupling agent PP/talc composites also showed similar trends of yield stress, breaking stress, modulus, yield strain and flexural properties with increase in talc content. Talc reinforced the PP matrix in the presence of coupling agent also, however the values of these properties decreased slightly in the presence of coupling agent. The tensile modulus however was higher in the presence of coupling agent. Impact strength values of the composites were higher in the presence of coupling agent. Analysis of tensile strength indicated better phase interaction in the absence of the coupling agent.

DSC crystallization exotherms show decrease in nucleation rate and increase in overall crystallization rate resulting in increase in crystallinity with talc content in PP/talc composites. Similar results were obtained in the presence of coupling agent. Tensile parameters showed good correlation with crystallization parameters in PP/talc composites both in the presence and absence of the coupling agent.

Rheological properties of the composites show that all the composites are pseudoplastic and show the power law relation. The viscosity of the composites increases with increase in talc content. The viscosity of the composites was slightly lower in the presence of coupling agent.

SEM studies were carried out to visualize the dispersion of the filler and mode of fracture of the composites. The talc particles were dispersed distinctly in the system. PP/talc systems showed brittle fracture. However in presence of the coupling agent the system showed some extent of plastic deformation.

PP/EPDM blends showed decrease in yield stress, breaking stress and modulus with incorporation of the EPDM. These parameters decreased with further

increase in EPDM concentration. Yield strain, breaking strain and impact strength increased with EPDM content. Flexural properties showed a decrease with incorporation of rubber indicating a decrease in the rigidity. Similar trends in tensile properties, impact and flexural properties were observed with incorporation of EPDM-g-MAH as dispersed phase in PP. However, the values were higher in comparison to the PP/EPDM systems at all volume fractions of the dispersed phase indicating better interfacial adhesion in presence of grafting on EPDM in the blend. Analysis of tensile data using theoretical models also predicted better interfacial adhesion in PP/EPDM-g-MAH blends in comparison to PP/EPDM blends.

The DSC exotherms showed decrease in nucleation rate and overall crystallization rate resulting in decrease in overall crystallinity in PP/EDPM blends with increase in EPDM content. X-ray crystallinity also showed a similar decrease. Similar trend was observed in the case of PP/EPDM-g-MAH blends in nucleation, overall crystallization rate, and crystallinity with increase in EPDM-g-MAH content. However the crystallinity was lower than that of PP/EPDM blends due to hindrance to chain mobility due to increased interfacial adhesion in the presence of grafting on EPDM. Tensile properties showed good correlation with the crystallization parameters in both cases.

Results of the rheological properties of PP/EPDM blends show that the blends are pseudoplastic in nature and follow power law. The melt viscosity of the blends increased with the EPDM content. PP/EPDM-g-MAH blends also showed pseudoplastic behaviour and followed power law. The viscosity of PP/EPDM-g-MAH blends was higher than the PP/EPDM blends.

Morphology of the PP/EPDM blends showed EPDM as the dispersed phase in the PP matrix. The weight average diameter increased and the interparticle distance decreased with increase in EPDM content. The critical ligament thickness for brittle to ductile transition in the blends was found to be  $0.6\mu\text{m}$ . Similar trend for weight average diameter and interparticle distance was observed with increase in EPDM-g-MAH content in PP/EDPM-g-MAH blends. However the values of these parameters were lower than in PP/EPDM blends indicating better interfacial adhesion. The critical ligament thickness was  $0.3\mu\text{m}$ .

Fracture surface morphology of the blends indicates stress whitening of the matrix. The stress whitening increased with the increase of rubber content in PP/EPDM blends.

PP/EPDM-g-MAH blends also showed stress whitening.

PP/EPDM / talc composites showed increase in yield stress, breaking stress and modulus with increase in talc content. Yield strain and breaking strain decreased. Flexural properties increased with talc content. Talc reinforced the PP/EPDM matrix. Impact strength of the composites increased with increase in filler concentration with a maximum at 0.06 volume fraction of talc. PP/EPDM-g-MAH/talc composites showed a decrease in tensile strength up to 0.06 and the value then showed increase. The values were lower than PP. The values were however lower than PP/EPDM-g-MAH blend. Tensile modulus also showed similar trend. The breaking strength however showed increasing trend. Yield strain showed an increase. Breaking strain showed slight increase and then decreased. Flexural properties increased with increase in talc content indicating increase in rigidity of the PP/EPDM-g-MAH matrix. However the values of yield stress, modulus, breaking strain and flexural properties were higher than the PP/EPDM/talc

composites at similar composition of talc Impact strength value remained similar to the value of PP/EPDM-g-MAH blend up to 0.06 volume fraction of talc and then decreased. Impact strength was however lower than in PP/EPDM/talc composites.

Crystallization exotherms of the PP/EPDM/talc composites showed decrease in nucleation rate and increase in overall rate of crystallinity with increase in talc content. DSC crystallinity increased with talc content. X-ray crystallinity increased with increase in talc content. The rate of nucleation and rate of crystallization increases with increase in talc content in PP/EPDM-g-MAH/talc composites. The overall crystallinity of the composites both by DSC and X-ray crystallinity methods increased with talc content in PP/EPDM-g-MAH/talc composites. Mechanical properties correlated well with crystallization parameters in both PP/EPDM/talc and PP/EPDM-g-MAH/talc composites.

Melt rheological properties of PP/EPDM/talc composites showed pseudoplastic behaviour and followed power law. The melt viscosity of the composites increased with increase in talc content. Similar trend of pseudoplastic behaviour is seen in PP/EPDM-g-MAH/talc composites. The melt viscosity increased with increase in talc content. The melt viscosity of the PP/EPDM-g-MAH/talc composites was higher than PP/EPDM/talc composites.

The fracture surface morphology of the PP/EPDM/talc and PP/EPDM-g-MAH/talc composites showed stress whitening.

# Table of Contents

Topic	Page No
<b>Chapter 1 Introduction</b>	<b>1</b>
<b>1.1 Polypropylene</b>	<b>1</b>
<b>1.2 Mineral Filled PP</b>	<b>1</b>
1.2.1 Talc Filled PP	2
1.2.2 Coupling Agents	3
1.2.3 PP-g-MAH as Coupling Agent	4
<b>1.3 Impact Modification of PP</b>	<b>6</b>
1.3.1 PP/EPDM Blends	6
<b>1.4 PP/Elastomer/filler Composites</b>	<b>9</b>
<b>1.5 Theoretical Models to Predict the Interface Properties</b>	<b>10</b>
1.5.1 Models Applicable to Tensile Strength	10
1.5.2 Models Applicable to Tensile Modulus	13
<b>1.6 Objective of the work</b>	<b>16</b>
<b>Chapter 2 Experimental Details</b>	<b>16</b>
<b>2.1 Materials used</b>	<b>16</b>
<b>2.2 Preparation of Blends and Composites</b>	<b>17</b>
<b>2.3 Preparation of the samples</b>	<b>18</b>
2.3.1 Extrusion	18
2.3.2 Injection Molding	18
<b>2.4 Measurement and Analysis Procedure</b>	<b>19</b>
2.4.1 Mechanical Properties	19

2.4.1.1 Tensile Properties	19
2.4.1.2 Impact Behaviour	20
2.4.1.3 Flexural Properties	21
2.4.2 Crystallization Properties	22
2.4.2.1 Differential Scanning Calorimetry (DSC)	22
2.4.2.2 X-ray Diffraction	24
2.4.3 Rheological Studies	25
2.4.4 Morphological Studies	25
<b>Chapter 3 Studies on PP/Talc composites in absence and presence of coupling agent</b>	
3.1 Introduction	26
3.2 Mechanical Properties	26
3.2.1 Tensile Properties	27
3.2.2 Analysis of Composite Dependence of Tensile Properties and Comparison with Theoretical Predictions	34
3.2.2.1 Yield Stress	34
3.2.2.2 Tensile Modulus	36
3.2.2.3 Yield Strain	38
3.2.3 Impact Strength	40
3.2.4 Flexural properties	41
3.3 Crystallization Behaviour and its Correlation with Tensile Properties	44
3.3.1 Differential Scanning Calorimetry	44
3.3.2 X-Ray Diffraction	49
3.3.3 Correlation of Tensile Properties with Crystallization Parameters	57

<b>3.4 Rheological Properties</b>	<b>61</b>
3.4.1 Shear stress ( $\tau_w$ )-Shear rate ( $\dot{\gamma}_w$ ) (Flow) Curves	61
3.4.2 Melt Viscosity	67
3.4.3 Melt Elasticity	70
	72
<b>3.5 Fracture Surface Morphology</b>	
<b>Chapter 4 Effect of interfacial adhesion on PP/EPDM through maleic anhydride grafting on EPDM</b>	<b>76</b>
4.1 Introduction	76
4.2 Mechanical Properties	76
4.2.1 Tensile Properties	77
4.2.2 Analysis of Composition Dependence of Tensile Properties and Comparison with Theoretical Predictions.	84
4.2.2.1 Yield stress	84
4.2.2.2 Tensile Modulus	87
4.2.3 Impact Strength	90
4.2.4 Flexural Properties	92
4.3 Crystallization Behaviour and its Correlation with the Tensile Properties	94
4.3.1 Differential Scanning Calorimetry	94
4.3.2 X-Ray Diffraction	99
4.3.3 Correlation of Tensile Properties with Crystallization Parameters	104
4.4 Rheological Properties	108
4.4.1 Shear stress ( $\tau_w$ )-Shear rate ( $\dot{\gamma}_w$ ) (Flow) Curves	108
4.4.2. Melt viscosity	114

4.4.3 Melt Elasticity	117
4.5 Morphology	119
4.5.1 State of dispersion	120
4.5.2 Mode of fracture	131
<b>Chapter 5 Studies on PP/EPDM/talc composites in absence and presence of MAH grafting on EPDM</b>	
	135
5.1 Introduction	
5.2.1 Tensile Properties	136
5.2.2 Impact Strength	142
5.2.3 Flexural Properties	143
5.3 Crystallization Behaviour and its Correlation with Tensile Properties	147
5.3.1 Differential Scanning Calorimetry	147
5.3.2 X-ray diffraction	153
5.3.3 Correlation of Tensile Properties with Crystallization Parameters	158
5.4 Rheological Properties	161
5.4.1 Shear stress ( $\tau_w$ )-Shear rate ( $\dot{\gamma}_w$ ) (Flow) Curves	161
5.4.2. Melt Viscosity	167
5.4.3 Melt Elasticity	170
5.5 Morphology	174
5.5.1 State of dispersion	174
5.5.2 Impact fracture	176
<b>Chapter 6 Summary and Conclusions</b>	179