

#### chapter 4

Polymer blending a recent technology is considered to be a convenient route for the development of new polymeric materials, which can combine the excellent properties of more than one existing polymers. The blending technology is usually cheaper and less time consuming than the development of new monomers and/or new polymerization route, as the basis for entirely new polymeric materials. Additional advantage of polymer blends is that a wide range of material properties is within reach by merely changing the blend composition.

Polymer blends are either homogeneous or heterogeneous. In homogeneous blends, components lose part of their identity. Whereas in heterogeneous blends, the properties of all blend components are present and weaknesses of one polymer can to a certain extent be camouflaged by strength of other.

Heterogeneous or immiscible blends show no adhesion between the two phases and hence exhibit poor properties. They can be made miscible by using third component called as compatibiliser, which decreases the interfacial tension between the two phases. The compatibilisers are macromolecular species which ore usually block or graft copolymers. The one constitutive part of it is miscible with one blend component and the other part is miscible with other polymer.

Various types of blends such as Nylon-6/ABS, Nylon-6/PC, PP/PE, PP/Nylon-6 PVC/ABS have been studied in past. We have undertaken a study of PP/ABS

198

blends. PP as well as ABS is widely used in automobile industry. However, PP/ABS being incompatible requires compatibiliser to achieve desirable properties.

PP modified through grafting has been used in the development of various blends such as PP/ Nylon-6, PP/ Nitrile rubber, PP/PS etc. However, not much work is done in PP/ABS blends. The reported compatibilisers are SEBS block copolymers and PE as a third component for PP/ABS blends. But no report claims improvement in mechanical properties may be due to lack of proper compatibilisation. Hence we have developed a series of PP grafted copolymers and used them in the PP/ABS blends for compatibilisation.

# Synthesis of compatibilisers

Grafting of PP with various monomers was carried out at 110<sup>o</sup>C using various initiators and monomer / polymer ratios. The time and temperature of the reaction was optimized. Some important results are given in **Table 1**.

Table 1 Grafting of PP with various monomers

Monomer	acrylic acid	2-HEMA	2-HEMA*	St-AN <sup>†</sup>	EMA <sup>†</sup>	MMA⁺	EMA-AN <sup>†</sup>
% grafting	7.2	3.6	8.6	6.7	8.03	9.0	24.6

\*On insitu chlorinated PP; <sup>+</sup>On Hydroperoxidized PP

۰.

### **Grafting onto PP**

Grafting of 2-HEMA was carried out on PP through free radical solution method. Various reaction conditions optimised were, 1:2 polymer to monomer ratio,  $110^{\circ}$  C temperature, 8.6 mM BPO concentration, toluene as reaction medium and three hour reaction time. The % grafting obtained was 3.2 %. The graft copolymers were characterized by FTIR, contact angle measurement, DSC and TG analysis. The appearance of stretching vibrations due to >C=O group at 1714-1727 cm<sup>-1</sup> in FTIR spectrum of PP-g-2-HEMA confirmed the incorporation of 2-HEMA in PP. The TGA showed the graft copolymers are thermally more stable compared to virgin PP. Decrease in contact angle with increased % grafting indicated increased surface polarity of the graft copolymers.

2-HEMA was also grafted on insitu chlorinated PP, the optimised reaction conditions were 8.6 mM BPO concentration, at 110<sup>o</sup> C temperature and at 5 h reaction time. The maximum % grafting was observed to be 8.6.

Acrylic acid was also grafted on PP and it was characterized by FTIR and acid titration method for estimation of % grafting. The 7.2 % grafting was obtained for PP-g-acrylic acid.

Summary

# **Grafting onto HPP**

Various monomers were grafted on hydroperoxidized PP through thermolytic cleavages of peroxide linkage. Percentage grafting decreased with increased polarity of monomers and followed a sequence : styrene > MMA > EMA > St-MMA > St-AN > EMA-AN > MMA-AN. Grafting efficiency was observed to be more than 90% in all the cases. Extent of grafting increased with temperature, time and monomer concentration. Gelling was observed to be more in the hydrophobic monomers where swelling of HPP surface is more. In the case of HPP-g-styrene maximum gelling was observed to be 7.2%. Grafting extent was also confirmed through <sup>13</sup>C NMR analysis and SEM. Graft copolymers were observed to be thermally stable. The % grafting calculated from <sup>13</sup>C NMR analysis is in good agreement with that obtained gravimetrically.

# **Development of PP / ABS Blends**

PP/ABS binary blends of different compositions and ternary blends containing 2.5, 5 and 7.5 % compatibiliser were prepared by single screw extruder melt blending process. The mechanical properties of the blends were measured as per ASTM standards. Morphology of impact fractured blend specimens was determined through SEM studies. Particle size of dispersed phase was determined. Attempts were made to find out suitable models for the prediction of tensile modulus of the blends.

	.,				
Composition of PP/ABS	Izod Imact strength kg.cm/cm	Tensile Strength Kg/cm2	Modulus kg	Elongation at yield %	Size of dispersed phase µm
100/0	2.3	195	12256	1701.3	-
90/10	2.2	203.1	12440	1605.0	7.5
85/15	2.4	209.4	11506	1425.6	-
75/25	2.5	307.2	13816	613.2	6.9
0/100	24.7	345.5	16063	454.6	_

# Table 2 Mechanical and morphplogical properties of PP/ABSbinary blends

# Table 3 Mechanical and morphological properties PP/ABS blends compatibilized through PP-g-acrylic acid

Composition PP/ABS/ Compatibiliser	Izod Imact strength kg.cm/cm	Tensile strength Kg/cm2	Modulus Kg	Elongation at break %	Size of dispersed phase µm
90/10/2.5	3.4	307.9	14380	807.8	5.6
85/15/2.5	2.8	305.9	14485	749.3	
75/25/2.5	2.9	295.4	14716	619.0	6.4
90/10/5	4.2	279.6	14136	787.5	5.4
85/15/5	3.9	268.9	14186	889.5	-
75/25/5	3.1	250.3	13823	589.2	6.3
90/10/7.5	3.2	289.2	14183	606.0	6.1
85/15/7.5	3.3	262.9	13656	740.2	-
75/25/7.5	2.2	256.5	14350	512.1	6.8

ł

Composition PP/ABS/Comp atibiliser	Izod Imact strength Kg cm / cm	Tensile strength Kg / cm <sup>2</sup>	Modulus kg	Elongation at yield %	Size of dispersed phase µm
90/10/2.5	7.5	286.0	15673	1347	4.2
85/15/2.5	6.7	289.8	15236	1230	-
75/25/2.5	4.9	299.8	15526	705.3	5.1
90/10/5	6.1	279.2	15580	1351	4.1
85/15/5	<b>5.2</b> <sup>°</sup>	286.0	15527	1090.2	-
75/25/5	4.3	308.4	16043	623.2	5.4
90/10/7.5	6.1	297.0	15290	1240	5.1
85/15/7.5	5.9	289.7	15480	1163.6	
75/25/7.5	5.0	310.1	16096	695.1	6.1

Table4 PP/ ABS blends compatibilized through PP-g-2-HEMA

Application of various models (Kerners' and Nielsens') to binary and ternary PP / ABS blends shows that blends follow Kerners' model for perfect adhesion between two phases indicating a good adhesion between PP and ABS on the addition of compatibilisers. Whereas in Nielsen model the small  $\emptyset_{max}$  values were obtained for PP rich blends after compatibilisation, which also indicates increased bends interface of dispersed phase due to the possible smaller particle size and better adhesion which is supported by SEM analysis.

Composition PP/ABS/ Compatibiliser	Izod Imact strength Kg cm / cm	Tensile Strength Kg /cm2	Modulus Kg	Elongation at break %
90/10/2.5	5.2	262.2	16496	1400
85/15/2.5	4.5	298.2	16143	987.5
75/25/2.5	4.1	327.8	16440	629.5
90/10/5	4.4	306.8	16243	1090
85/15/5	4.2	304.1	15687	906.9
75/25/5	3.9	308.3	15500	62 <u>1</u> .9
90/10/7.5	4.4	283.5	15416	1200.6
85/15/7.5	4.5	294.2	16150	87.8
75/25/7.5	4.2	312.5	15893	581.3

# Table 5 PP/ ABS blends compatibilized through PP-g-St-AN

The blends shows considerable changes in mechanical properties, particularly in PP rich blend upon addition of 2.5% to 7.5% PP-g-acrylic acid as a compatibiliser. It was observed that 5 % PP-g-acrylic acid gives the higher impact strength and Youngs' modulus as compared to 2.5% and 7.5% compatibiliser concentration. The blend exhibits good tensile behavior at 10-15% ABS content due to good enough adhesion at interface between two phases. The blends show the ductility upto 15 % ABS and after that they become brittle in nature even after compatibilisation. The ABS rich blends show poor mechanical properties and also poor morphology and are not of commercial importance.

#### chapter 4

The another compatibiliser PP-g-2-HEMA was also used to compatibilise PP/ ABS blends. The compatibilised blends showed improvement in izod impact strength, tensile strength and tensile modulus properties of PP / ABS bends. The 2.5% concentration of compatibiliser was observed to be critical for the improvement in the properties. Kerner's model for perfect adhesion was observed to be applicable only for PP rich blends, whereas the  $\emptyset_{max}$  values obtained through Neilsens' model indicated increased interface volume when blends were compatibilised particularly in PP rich region.

The third compatibiliser used was PP-g-St-AN. The compatibilised blends showed improvement in izod impact strength, tensile strength and tensile modulus properties of PP/ABS bends. The 2.5% concentration of compatibiliser was observed to be critical for the improvement in the properties. Compatibilisation of blends resulted into smaller size of dispersed phase (ABS) in PP rich blends. The particles were observed to be finely and homogeneously distributed and extraction of the ABS dispersed phase by MEK from PP rich blends was not possible. Though the impact strength was observed to be less as compared to the blends compatibilised with PP-g-2-HEMA (7.5 kg-cm/cm) the Youngs' modulus was observed to be very high (16500 kgcm<sup>2</sup>) even higher than ABS (16000 kgcm<sup>2</sup>).

### chapter 4

## Thus it can be concluded that

- PP rich PP/ABS blends show better mechanical performance as compared to ABS rich PP/ABS blends
- 2.5 % concentration of PP-g-2-HEMA and PP-g-St-AN and 5% PP-g-acrylic acid is good enough for better mechanical properties, particularly impact strength and Youngs' modulus.
- Kerners' model for perfectly bound inclusions was applicable for PP rich compatibilised blends, whereas adjusted Ø<sub>max</sub> values obtained from Nielsens' model show incresed interface volume of blends when compatibilised.

## References

- 1. C. Markin and H. C.Williams, J. Appl. Polym. Sci., 25,2451,1980.
- 2. A. K. Gupta; A.K. Jain and S.N. Maiti , J .Appl. Polym. Sci., 38, 1699, 1989.
- 3. M. Frounchi and R. P. Burford, Iran. J. Polym. Sci. and Technol., 2, 59,1993.
- 4. H. Aibe Jap.Pat., 04,110,335 (1992)
- 5. A. Kawai, Jap.Pat., 06,248,154, (1995)
- 6. D.R. Paul In Paul D.R. and NewMan S., Editor, 'Polymer Blends', NewYork, Academic Press, 1978.
- L. A. Utracki, 'Polymer Alloys and Blends, Thermodynamics and Rheology' Hanser Publishers, Munich, Vienna, New York, 1989.