

DEVELOPMENT OF POLYMERIC ALLOYS BASED ON PP  
AND SELECTED ENGINEERING PLASTICS

SUMMARY OF THE  
THESIS SUBMITTED TO

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

FOR THE AWARD OF DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

BY

RAGESH B. BRAHMBHATT

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

VADODARA - 390 002

INDIA

NOVEMBER 2002

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Development of newer polymers with desirable properties is not always economically viable route and is also a time consuming process. Whereas polymers with desirable properties can be easily prepared by solution or melt blending process. Resulting blends or alloys are miscible or immiscible depending on the polarity and molecular interaction parameter of polymers involved. Compatibility in immiscible polymer can be improved by using block or graft copolymers as compatibilizers. The most interesting factor of polymer blends/alloys is that the major component retains most of its properties, while the dispersed phase imparts certain specific properties. Hence, it is an effective technique for achieving tailor made material with balanced combination of processing conditions and characteristic properties. As a result polymer blends/alloys have gained important position in the field of polymer technology.

Polypropylene is an inexpensive commodity thermoplastic with balance of heat and chemical properties. ABS is typically styrenic engineering thermoplastic blend with good mechanical properties. PP and ABS both are extensively, used in automobiles and household applications. Various types of blends such as PP/nylon, ABS/PC, ABS/PVC, iPP/PE have been studied in past. We have undertaken a study of iPP/ABS blends, using graft copolymer as a compatibilizer. Both polymers are immiscible with each other, due to their chemical nature. Polypropylene is hydrophobic while ABS is hydrophilic, hence for achieving compatibility between the two polymers a third component is required (i.e., compatibilizer or interfacial agent). This compatibilizer can be a graft or block copolymer. Here, we have used iPP-based graft copolymer as a compatibilizer. The graft copolymers were synthesized in our laboratory by using different grafting techniques, such as solid-phase and solution grafting and grafting on hydroperoxidised-PP. The compatibilizers have been used in iPP/ABS binary blends. The mechanical, morphological and rheological properties of these blends have been tested.

## Synthesis of compatibilizer

Grafting onto iPP with various monomers was carried out at 110 °C temperature. The reaction conditions such as polymer to monomer ratio, types and concentration of initiator, reaction time, temperature, reaction atmosphere and reaction medium were optimized to achieve maximum % of grafting for all the monomers. Some important results are given in Table 4.1.

**Table 4.1 : Grafting onto iPP with various monomers**

| Monomer    | 4-vinyl pyridine | Glycidyl methacrylate | Methacrylic acid | Styrene-methylmethacrylate copolymer* |
|------------|------------------|-----------------------|------------------|---------------------------------------|
| % grafting | 12.7             | 2.8                   | 6 – 7            | 5 - 6                                 |

\* indicates grafting onto hydroperoxidized-PP

### Solid phase grafting (iPP-g-4-VP)

4-vinyl pyridine monomer was grafted onto iPP using solid-phase grafting technique. Compared to other techniques this technique has many advantages such as low cost, lower solvent requirement, low temperature and environmentally friendly process and also leads to higher percent of grafting. iPP-g-4-VP synthesized using this grafting technique resulted into 12.7% of grafting at optimized conditions. Solution grafting of 4-VP onto iPP resulted into 6% of grafting. The products were characterized by FTIR, TGA and DSC analysis. Graft copolymers were observed to be thermally stable.

### Solution grafting (iPP-g-GMA and iPP-g-MAA)

It is an oldest technique for the modification of polyolefins. Number of monomers have been grafted onto iPP and/or PE using this technique, though it is not an industrially viable due to its two major disadvantages.

- requirement of large amount of solvent and
- lower percent of grafting

The advantage of this technique is no degradation and crosslinking of polymers takes place.

Methacrylic acid was also grafted onto iPP and the copolymers were characterized by FTIR, TGA and DSC analysis. 2.8 and 5.0 - 6.0 % grafting was observed for glycidyl methacrylate(GMA) and methacrylic acid(MAA) respectively.

### **Grafting onto hydroperoxidized-PP**

Styrene-methylmethacrylate copolymer was grafted onto hydroperoxidized-PP through thermolytic cleavages of peroxide linkage. Extent of graft increased with temperature, time and monomer concentration. Grafted copolymers were observed to be thermally more stable.

### **Development of iPP/ABS blends**

iPP/ABS binary blends of different composition and ternary blends containing 2.5, 5.0 to 7.5 phr (parts per hundred of resin) compatibilizer were prepared by using 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 analysis. Attempts were made to find out suitable model for the prediction of tensile modulus of the blends. Rheology of the blends was studied on Rheometer and melt flow index was measured on Melt Flow Machine.

**Table 4.2 : Mechanical properties of iPP/ABS binary blends**

| Composition of iPP/ABS (%) | Impact strength (kgcm/ cm) | Tensile strength (MPa X 10 <sup>-2</sup> ) | Modulus (MPa X 10 <sup>-3</sup> ) | Elongation at break (%) | Flexural modulus (MPa X 10 <sup>-3</sup> ) |
|----------------------------|----------------------------|--|-----------------------------------|-------------------------|--|
| 100/0                      | 2.23                       | 28.64                                      | 1.202                             | 16.22                   | 1.288                                      |
| 90/10                      | 2.2                        | 28.11                                      | 1.22                              | 10.47                   | 1.353                                      |
| 85/15                      | 2.45                       | 29.06                                      | 1.249                             | 9.5                     | 1.344                                      |
| 75/25                      | 4.5                        | 31.19                                      | 1.355                             | 5.65                    | 1.393                                      |
| 0/100                      | 24.7                       | 38.34                                      | 1.575                             | 5.17                    | 1.901                                      |

**Table 4.3 : Mechanical properties of iPP/ABS blends compatibilized with HPP-g-STY-MMA system**

| Composition of iPP/ABS/HPP-g-STY-MMA* (%) | Impact strength (kgcm/cm) | Tensile strength (MPa X 10 <sup>-2</sup> ) | Modulus (MPa X 10 <sup>-3</sup> ) | Elongation at break (%) | Flexural modulus (MPa X 10 <sup>-3</sup> ) |
|---|---------------------------|--|-----------------------------------|-------------------------|--|
| 90/10/2.5                                 | 5.60                      | 32.82                                      | 1.487                             | 13.65                   | 1.482                                      |
| 85/15/2.5                                 | 4.58                      | 32.36                                      | 1.499                             | 11.23                   | 1.54                                       |
| 75/25/2.5                                 | 4.48                      | 31.68                                      | 1.552                             | 6.85                    | 1.538                                      |
| 90/10/5.0                                 | 3.56                      | 31.48                                      | 1.464                             | 13.07                   | 1.413                                      |
| 85/15/5.0                                 | 4.92                      | 31.87                                      | 1.479                             | 11.12                   | 1.495                                      |
| 75/25/5.0                                 | 4.11                      | 31.77                                      | 1.54                              | 7.0                     | 1.553                                      |
| 90/10/7.5                                 | 2.60                      | 30.69                                      | 1.415                             | 11.52                   | 1.435                                      |
| 85/15/7.5                                 | 4.60                      | 31.19                                      | 1.454                             | 10.23                   | 1.503                                      |
| 75/25/7.5                                 | 4.60                      | 31.38                                      | 1.489                             | 6.48                    | 1.592                                      |

\* HPP-g-STY-MMA was added as a compatibilizer in parts per hundred of resin (phr)

**Table 4.4 : Rheological and Morphological properties of iPP/ABS blends compatibilized with HPP-g-STY-MMA system**

| Composition of iPP/ABS/HPP-g-STY-MMA* (%) | Size of dispersed particle ( $\mu\text{M}$ ) | MFI (g/10 min.) | Shear viscosity (Pa.s) 220 °C at 500 shear rate (1/s) | Shear viscosity (Pa.s) 220 °C at 2000 shear rate (1/s) | Shear viscosity (Pa.s) 220 °C at 5000 shear rate (1/s) |
|---|--|-----------------|---|--|--|
| 100/0/0                                   | -  | 10.5            | 113   | 50   | 28   |
| 90/10/0                                   | 2.80   | 9.9             | 111   | 51   | 29   |
| 85/15/0                                   | 4.54   | 9.1             | 113   | 53   | 30   |
| 75/25/0                                   | 5.0  | 8.7             | 117   | 55   | 31   |
| 0/100/0                                   | -  | 10.0            | 374   | 157  | 83   |
| 90/10/2.5                                 | 1.49   | 9.87            | 73  | 49   | 28   |
| 90/10/5.0                                 | 1.82   | 9.35            | 112   | 51   | 28   |
| 90/10/7.5                                 | 2.23   | 10.8            | 117   | 52   | 29   |
| 75/25/2.5                                 | 2.7  | 8.6             | 120   | 55   | 31   |
| 75/25/5.0                                 | 3.05   | 8.8             | 120   | 54   | 31   |
| 75/25/7.5                                 | 3.10   | 8.9             | 123   | 55   | 31   |

\* HPP-g-STY-MMA was added as a compatibilizer in parts per hundred of resin (phr)

**Table 4.5 : Mechanical properties of iPP/ABS blends compatibilized with iPP-g-MAA system**

| Composition of iPP/ABS/iPP-g-MMA* (%) | Impact strength (kgcm/cm) | Tensile strength (MPa X 10 <sup>-2</sup> ) | Modulus (MPa X 10 <sup>-3</sup> ) | Elongation at break (%) | Flexural modulus (MPa X 10 <sup>-3</sup> ) |
|---------------------------------------|---------------------------|--|-----------------------------------|-------------------------|--|
| 91/10/2.5                             | 5.86                      | 31.46                                      | 1.47                              | 10.96                   | 1.602                                      |
| 85/15/2.5                             | 5.50                      | 31.19                                      | 1.43                              | 10.21                   | 1.645                                      |
| 75/25/2.5                             | 4.87                      | 30.40                                      | 1.43                              | 7.34                    | 1.553                                      |
| 90/10/5.0                             | 5.03                      | 31.68                                      | 1.46                              | 10.21                   | 1.632                                      |
| 85/15/5.0                             | 4.81                      | 30.7                                       | 1.45                              | 9.97                    | 1.680                                      |
| 75/25/5.0                             | 5.39                      | 30.69                                      | 1.46                              | 7.48                    | 1.778                                      |
| 90/10/7.5                             | 4.67                      | 30.2                                       | 1.42                              | 9.87                    | 1.500                                      |
| 85/15/7.5                             | 4.79                      | 31.38                                      | 1.48                              | 9.04                    | 1.540                                      |
| 75/25/7.5                             | 4.15                      | 30.30                                      | 1.42                              | 6.67                    | 1.624                                      |

\* iPP-g-MAA was added as a compatibilizer in parts per hundred of resin (phr)

**Table 4.6 : Rheological and Morphological properties of iPP/ABS blends compatibilized with iPP-g-MAA system**

| Composition of iPP/ABS/iPP-g-MAA* (%) | Size of dispersed particle ( $\mu\text{M}$ ) | MFI (g/10 min.) | Shear viscosity (Pa.s) 220 °C at 500 shear rate (1/s) | Shear viscosity (Pa.s) 220 °C at 2000 shear rate (1/s) | Shear viscosity (Pa.s) 220 °C at 5000 shear rate (1/s) |
|---------------------------------------|--|-----------------|---|--|--|
| 100/0/0                               | -  | 10.5            | 113   | 50   | 28   |
| 90/10/0                               | 2.80   | 9.9             | 111   | 51   | 29   |
| 85/15/0                               | 4.54   | 9.7             | 113   | 53   | 30   |
| 75/25/0                               | 5.0  | 8.7             | 117   | 55   | 31   |
| 0/100/0                               | -  | 10.0            | 374   | 157  | 83   |
| 90/10/2.5                             | 1.93   | 12.4            | 102   | 47   | 26   |
| 90/10/5.0                             | 2.18   | 14.5            | 96  | 45   | 25   |
| 90/10/7.5                             | 2.63   | 17.4            | 96  | 45   | 25   |
| 75/25/2.5                             | 3.28   | 9.7             | 112   | 51   | 29   |
| 75/25/5.0                             | 4.19   | 10.5            | 109   | 50   | 28   |
| 75/25/7.5                             | 4.65   | 13.7            | 100   | 46   | 26   |

\* iPP-g-MAA was added as a compatibilizer in parts per hundred of resin (phr)

Application of various models to binary and ternary iPP/ABS blends show that blends show positive deviation from Kerner's model for perfect adhesion between two phases indicating adhesion between iPP and ABS on the addition of compatibilizers. Smaller  $\phi_{\max}$  values obtained through Nielsen's model for iPP rich blends after compatibilization also indicate increased blend interface area of dispersed phase due to the possible smaller particle size. Better adhesion between the phases is supported by SEM and rheological studies.

The blends showed considerable changes in mechanical, morphological and rheological properties, particularly in iPP-rich region upon addition of 2.5 to 7.5 phr level of the compatibilizer. From the results it was observed that 2.5 phr level of HPP-g-STY-MMA and same level of iPP-g-MAA as a compatibilizer gave higher impact strength and modulus as compared to other concentration of the compatibilizer (Table 4.2, 4.3 and 4.5) which is also supported by rheological data (Table 4.4 and 4.6).

The blends exhibited good tensile behavior for both the systems at 10 to 15 % ABS content due to good enough adhesion at interface between two phases. The blends showed the ductile nature upon 15% ABS incorporation and further increase lead to brittle nature even after compatibilization. The ABS rich blends showed poor mechanical properties and also poor morphology and are not of commercial importance.

#### **Following are the major observations**

- Grafting onto iPP using solid-phase and hydroperoxidation technique leads to higher % of grafting.
- Solvents play an important role in governing the graft level in solid phase grafting. Higher level of solvent decreases the % of grafting, due to its chain transferring effect.

- Maximum 12.7 and 6.0 % of grafting was achieved for 4-vinyl pyridine onto iPP using solid-phase and solution grafting technique respectively.
- Maximum 2.8, 6.0 to 7.0 and 5.0 to 6.0 % of grafting was achieved for glycidyl methacrylate(GMA), methacrylic acid(MAA) and styrene-methyl methacrylate (STY-MMA) onto iPP using solution and hydroperoxidization technique.
- Grafted polymers were observed to be thermally more stable than virgin iPP.
- Grafted polymers can give good compatibilizing effect on iPP/ABS blends.
- iPP-rich iPP/ABS blends showed better mechanical performance as compared to ABS-rich iPP/ABS blends.
- 2.5 phr level of concentration of compatibilizer (i.e., iPP-g-MAA and HPP-g-STY-MMA) is good enough for better mechanical properties such as impact strength, modulus, % elongation at break.
- Rheological and MFI values showed homogeneous dispersion and distribution of ABS as an inclusion. Inclusion in iPP matrix with 2.5 phr level of concentration of compatibilizer can produce very good adhesion between two phases.
- iPP-rich ternary blend system shows positive deviation from Kerner's model for perfect bound inclusion, which is due to the complex structural features of ABS, whereas adjusted  $\phi_{max}$  values obtained from Neilsen's model showed increased interface volume of blends on compatibilization.