# SUMMARY

Oxidation of polyolefins in the absence of any additives results in rapid chain scission, cross linking and formation of oxygen containing functional groups in the polymer. The compounds which are used to retard or arrest these processes have traditionally been referred to as stabilisers in plastics technology and antioxidants in rubber technology.

Antioxidants do not completely eliminate oxidative degradation, but they markedly retard the rate of auto-oxidation by interfering with radical propogation and provide suitable protection during the phase of the polymer's life cycle.

Isotactic Polypropylene (IPP) undergoes extensive degradation under commercial processing condition. Hydroperoxides form at a significant rate, and these reactive intermediates decompose into radicals capable of promoting either thermal or photo-oxidation. Antioxidants intend to provide protection during processing must be capable of migrating throughout the polymer mass to reach the large number of intitiation sites that are generated at elevated temperatures. For this reason a variety of antioxidants has been used to inhibit degradation at this critical stage in the life cycle of thermally-sensitive polymer.

It was found that many of the new antioxidants synthesised combine a hindered phenol group with another group containing nitrogen, sulphur, triazines, phosphates, phosphites etc. This combination would give active materials having the advantage of two or more stabilising moieties.

Antioxidants should not be coloured and should contribute as little as possible to polymer discoloration on use. For this reason, aromatic amines which are heavily staining are used only exceptionally in thermoplastics. Sterically hindered phenols usually contribute much less to the discoloration of polymers on processing and use than aromatic amines.

It had been shown that tert-butyl group in the ortho position and alkyl group at the para position result in the most effective antioxidant activity in the alkyl phenolic type of antioxidants of which 2,6-di-tert-butyl-4-methyl phenol (BHT) is one of the best known.

Although BHT is a very effective chain terminatior, it sufferes from a major drawback viz. high volatility. The 2,6-di-tert- butyl phenolics with long aliphatic groups replacing the methyl group at the para position has succeeded in reducing volatility, but at the sacrifice of reduction of active -OH on a weight / weight basis.

In the present work the structure of BHT is modified by replacing the hydrogen atom of the methyl group at the para position by different groups of high molecular weight. This was achieved by converting the methyl group into an aldehydic group by using a method reported in literature by Coppinger and Campbell. The aldehyde was converted into acid hydrazones, semicarbazone and thiosemicarbazones by reacting with appopriate reagents. Semicarbazone was cyclized to oxadiazole. The aldehyde was also converted into pyrazole derivative.

The stabilisation efficiency of some of the synthesised antioxidants with stabilised and unstabilised isotactic polypropylene (IPP) is evaluated by using the following techniques

1. Melt-mixing
2. Multiple extrusion.
3. Melt flow index.
4. Differential scanning calorimeter.
5. Mechanical properties like

(a) Izod impact strength
(b) Heat deflection temperature
(c) Tensile strength and modulus
(d) Flexural strength and modulus.

The thesis is divided into four parts. The first chapter deals with the general introduction to antioxidants, classification, types of combination, mechanism of antioxidant action with polypropylene and its applications.

In the second chapter we discuss the synthesis and characterization of some new antioxidants based upon hindered phenols. As a prelude to the present work, prior work in this field has been reviewed here. From the literature survey it is revealed that among the antioxidants based on hindered phenols, the use of combination of hindered phenol with acid hydrazones is less extensively studied, whereas the combinations of hindered phenol with thiosemicarbazones, oxadiazole, and pyrazole are apparently not reported. With these in view the following antioxidants are synthesised, starting from 2,6-di-tert-butyl-4-methyl phenol ($AO_1$) via 3,5-di-tert-butyl-4-hydroxy benzaldehyde, and the structures of the newly synthesised antioxidants are established on the basis of elemental analysis, IR and $^1$HNMR spectral studies.

1. N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine ($AO_2$).
2. N'-(3;5-di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine ($AO_3$)
3. N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-octyloxy benzohydrazine ($AO_4$)
4. N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine ($AO_5$).
5. 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carboxamide ($AO_6$).
6. 2-Amino-5-(3,5-di-tert-butyl-4-hydroxy phenyl) 1,3,4- oxadiazole($AO_7$).
7. 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide ($AO_8$)
8. 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene]-N-Phenyl hydrazine carbothioamide ($AO_9$).
9. 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene]-N-(4-methyl phenyl) hydrazine car bothioamide ($AO_{10}$).
10. 1,2-Di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} ethane ($AO_{11}$).
11. 1,4-Di {2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} benzene ($AO_{12}$).
12. 4,4'-Di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenly ($AO_{13}$).
13. 4,4'-Di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenly methane ($AO_{14}$).
14. 4,4'-Di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenly ether ($AO_{15}$).
15. 3-(4-Hydroxy phenyl)-5-(3,5-di-tert-butyl-hydroxy phenyl) 4,5-dihydro-1H-pyrazole ($AO_{16}$).

Out of the antioxidants synthesised $AO_2$, $AO_3$,$AO_5$,$AO_8$,$AO_9$ and $AO_{15}$ were selected to evaluate the stabilisation efficiency with polypropylene and they were synthesised in sufficient quantity.

Chapter 3 is divided into two sections A and B. In section A of the third chapter, we have considered the antioxidants obtained by replacing the methyl group at the para position of BHT by a long chain which is electron donating and investigated the influence of molecular weight on the efficency of these antioxidants in isotactic polypropylene, paying special attention to the changes in MFI. The MFI values of commercially available antioxidants like BHT, Ultranox and Weston also were measured. BHT was converted to 3,5-di-tert-butyl-4-hydroxy benzaldehyde by following the reported procedure. The aldehyde was then treated with 4-hydroxy benzoic acid hydrazide to get the corresponding hydrazone. The hydroxy group at the 4-position was replaced by different alkoxy groups. Each of the alkyl derivatives and each of the commercially available antioxidants were mixed with IPP and were subjected to melt mixing as well as multiple extrusion. After the multiple extrusion the melt flow index of all the extruded sample was measured and compared with the commercially available antioxidants.

The following antioxidants were selected for checking the stabilisation efficiency with stabilised IPP.

Commercially available antioxidants : (i) 2,6-di-tert-butyl-4- methyl phenol ($AO_1$) (ii) Weston 619 (iii) Ultranox 626

Synthesised antioxidants : (iv) N'-(3,5-di-tert-synthesised- butyl-4-hydroxy phenyl) methylene -4- hydroxy benzohydrazine ($AO_2$) (v) N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine ($AO_3$) (vi) N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine ($AO_4$).

Out of the four concentrations (0.015g, 0.025g, 0.035g, 0.045g) used for melt mixing torque values for synthesised antioxidants, BHT, and Ultranox were found to be maximum in case of 0.025g concentration. Based on this observation the concentration of 0.025g was selected for further studies. From the MFI values, $AO_2$ was not found to be suitable antioxidant for IPP because of its high melting point. The stabilistion efficiency of $AO_4$ was found to be more than that of $AO_3$. On comparing the structures of $AO_3$ and $AO_4$ it is observed that when the hydroxy group at the 4 position is replaced by a pentyloxy group, there is no improvement in the stabilisation of IPP against the degradation as it passes through number of extrusions. But when the hydroxyl group is replaced by decyloxy group, the stabilisation efficiency is enhanced. $AO_4$ stabilises IPP to the same extent as $AO_1$.

Section B of the third chapter deals with the synthesis of long term antioxidants by modification of the structure of 2,6-di- tert-butyl-4-methyl phenol by introducing group containing nitrogen and sulphur atoms at the para position of the -OH group of BHT. Stabilisation efficiency of the antioxidants synthesised has been checked with stabilised IPP. The influence of molecular weight of these antioxidants on the overall performance was investigated. The following antioxidants were selected as melt stabilisers for stabilised IPP.

(i) 2,6-Di-tert-butyl-4-methyl phenol ($AO_1$)

(ii) 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide ($AO_2$)

(iii) 2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene]-N-phenyl hydrazine carbothioamide ($AO_3$).

(iv) 4,4'-Di-{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} bipheny ether ($AO_4$).

These thiosemicarbazones were mixed with IPP and were subjected to melt mixing as well as multiple extrusion. After multiple extrusion the melt flow behaviour of the extruded sample was studied. The mechanical properties such as heat deflection temperature and izod impact strength of the compression moulded samples were measured.

The following concentrations were selected for each of the antioxidant for multiple extrusion, basing on the maximum torque values observed.

| Antioxidants | Concentration (with 50g of IPP) |
|---|---|
| AO | IPP with Irgonax 1010 and Calcium Stearate |
| $AO_1$ | 0.035 |
| $AO_2$ | 0.045 |
| $AO_3$ | 0.035 |
| $AO_4$ | 0.025 |

From the MFI values it has been observed that,

$AO_2$ with a higher concentration (0.45) stabilised IPP to the same extent as $AO_1$ with a lesser concentration (0.035).

In stabilisation efficiency $AO_3$ is equal to that of $AO_1$.

$AO_4$ with lesser concentration (0.025) could stabilise IPP to the same extent as $AO_1$ with a higher concentration (0.035).

Heat deflection temperature and impact strength values have been decreased as the number of extrusion increased. It is reported that as the number of extrusion increases, the polymer gets degraded and consequently, the molecular weight and melt viscosity decrease As a result MFI values increase where as the HDT values and impact strength values decrease. The same results were observed in case of $AO_1$, $AO_2$, $AO_3$ and $AO_4$.

If the activity were to depend upon relative content of hindered phenolic group, then $AO_2 > AO_3 > AO_4$, but from the present studies it was found that $AO_4 > AO_3 > AO_2$.

The last chapter of the thesis deals with the melt stabilisation of unstabilised IPP. In chapter 3A and 3B, we have discussed the performance of different antioxidants with stabilised isotactic polypropylene. Here in this chapter we discuss the degradation and stabilisation of unstabilised isotactic polypropylene in presence of synthesised antioxidants selected, depending on the performance maxima with stabilised IPP. The four antioxidants and the concentrations selected for the study are same as those selected in chapter 3B. Techniques used for the evaluation of antioxidant activity are (1) Melt Flow Index, (2) Differential Scanning Calorimeter, (3) Heat Deflection Temperature, (4) Izod impact Strength, (5) Tensile Strength and Modulus (6) Flexural Strength and Modulus. The extrusion of unstabilised IPP along with different antioxidants are carried out on Twin screw extruder. After twin screw extrusion, the MFI values of all the samples were measured. DSC of all the samples was carried out. The granules were subjected to injection moulding for getting the test speciman for mechanical properties.

It has been observed from the results of the present studies that there is an increase in MFI values as the number of extrusion proceeds. But it is quite clear from the MFI values that the degradation of unstabilised IPP could be controlled more efficiently with $AO_3$ and $AO_4$ than with $AO_1$. Thus in activity with respect to MFI values :

$AO_2$ (0.045 concentration) = $AO_1$ (0.035 concentration)
$AO_3$ (0.035 concentration) > $AO_1$ (0.035 concentration)
$AO_4$ (0.025 concentration) > $AO_1$ (0.035 concentration)

From the DSC values it can be observed that synthesised antioxidants are as good as BHT, as far as thermal properties of IPP are concerned.

From the results of the performance properties, HDT, Impact Strength, Tensile Strength and modulus and Flexural strength and modulus, it is evident that there is loss of mechanical properties in all the cases as it passes through number of extrusions It has been already reported that if the polymer gets degraded there is loss in mechanical properties and this could be observed from the increase in MFI values.

## Conclusion

With Stabilised and unstabilised IPP, the results obtained for the performance maxima have been identical. These particular antioxidants could stabilise unstabilised IPP equally well as it could stabilise stabilised IPP. Since unstabilised IPP is subjected to greater mechanical shear and consequently promotes oxidative degradation in twin screw extrusion compared to the extrusion of stabilised IPP carried out on Brabender Plasticorder, more efficient antioxidants are required. From the results of the present studies it is evident that the stabilisation efficiency of antioxidants $AO_1$, $AO_2$, $AO_3$ and $AO_4$ is encouraging and hence desirable.