CHAPTER - 3

SECTION A

INTRODUCTION

Polypropylene undergoes extensive degradation under commercial processing conditions[1] Hydroperoxides are formed at a significant rate and these reactive intermediates decompose into radicals capable of promoting either thermal or photo-oxidation. A variety of antioxidants have been used to inhibit degradation at this critical stage in the life cycle of thermally sensitive polymers.[2]

Wasser and Smith[3] reported that tert-butyl groups at the ortho position and alkyl group at the para position resulted 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. Among the 2,6- di-tert-butyl-4-alkyl phenols, a variation of alkyl chain from a methyl to n-butyl did not cause any significant modification in the antioxidant activity.[4] It was reported by Miller[5] that an electron donating group at the para position of the alkyl phenols would enhance the antioxidant activity. On the other hand, an electron withdrawing group at the same position has been reported to retard or completely eliminate the antioxidant activity.[5,6] Furthermore, it has been observed that the removal of such an electron withdrawing group at the para position of 3,5-di-tert-butyl-4-hydroxy benzaldehyde resulted in the recovery of antioxidant activity. 3,5-Di-tert-butyl-4-hydroxy benzaldehyde regained antioxidant activity when it was converted into 3,5-di-tert-butyl-4-hydroxy benzaldehyde isonicotinoyl hydrazone[6] (BHB-INH).

The antioxidant activity of BHT and BHB-INH was compared towards the oxidation of lard and found that BHB-INH prevented oxidation of lard more efficiently than BHT This indicates that an isonicotinoyl hydrazino methyl group potentiates the phenol better than the methyl group.

Antioxidants intended to provide protection during processing must be capable of migrating freely throughout the polymer mass to reach the large number of initiation sites that are generated at elevated temperatures.[7] For this reason, low- molecular weight antioxidants like 2,6-di-tert-butyl-4-methyl phenol are preferred. However BHT suffers from a major drawback viz. high volatility. The 2,6-di-tert-butyl-phenol 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[8]

This probably is the reason why the molecular weights (MW) of commercial stabilisers are almost always in the range of 200-2000, although there are some exceptions. However, Minagawa [9] reported that the current tendency is towards an increase in the molecular weight of stabilisers to prevent loss from the polymer in increasingly severe conditions of applications

Present Work* :

Here we have considered the antioxidants obtained by replacing the methyl group at para position of BHT by a long chain which is electron donating and investigated the influence of molecular weight on the efficiency of these antioxidants in isotactic polypropylene paying special attention to the changes in Melt Flow Index(MFI). This was achieved by converting the methyl group into an aldehydic group by using a method reported in the literature by Coppinger and Campbell.[11] The aldehyde was then treated with parahydroxy-benzoic acid hydrazide to get the corresponding hydrazone. The hydroxy group at the 4-position of the phenyl group was replaced by different alkoxy groups. Each of these alkyl derivatives and each of the commercially available antioxidants e.g BHT, Ultranox and Weston were mixed with Isotactic Polypropylene (IPP) and were subjected to melt-mixing as well as multiple extrusion.

After multiple extrusion, the melt-flow index of the extruded sample was measured and compared with the MFI values of commercially available antioxidants

EXPERIMENTAL :

Materials :

The commercially available antioxidants 2,6-di-tert-butyl-4-methyl phenol (AO_1) was supplied by Hicu Bombay, Ultranox 626 and weston 619 were supplied by Borg Warner Chemicals, USA. The antioxidants AO_2, AO_3 and AO_4 used were synthesised in this laboratory. The procedure for synthesis of these antioxidants is discussed in chapter-2.

Polypropylene .

Stabilised isotactic polypropylene (Indian Petrochemical Corporation Ltd , Baroda, India) with MFI grade 10 (g/10 min) was used for the experiments.

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* Accepted for publication[10]

Calcium Stearate :

Commonly, polypropylene is stabilised with calcium stearate for interface lubrication and for catalyst deactivation. In all cases 0.1% calcium stearate was added to neutralise acids resulting from residual catalysts. The chemical structures and abbreviations for the antioxidants used for processing stabilisation of isotactic polypropylene are given in Figure 3A 1

Processing and Testing of Polypropylene with Antioxidants AO_1-AO_4 .

The performance of antioxidants in polymer processing was tested in the polymer melt and assessed by multiple extrusion. The multiple extrusion of isotactic polypropylene was carried out with the suitable concentration of the commercially available antioxidants as well as with synthesised antioxidants. To find out the suitable concentration of the antioxidants, initially melt mixing of isotactic polypropylene was carried out by using commercially available antioxidant and synthesised antioxidants. The stability of a polymer melt viscosity was controlled through measurement of torque as a function of time and temperature in a Brabender Plastograph.

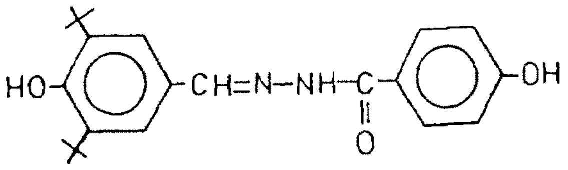
Procedure for Melt-Mixing :

To 50g of stabilised IPP in powder form (MFI 9.6g/10 min.) was added, 0.05g(0.1 wt%) of calcium stearate, 0.025g (0.05 wt%) of Irgonax 1010 and 0.015 to 0.045g (0.03 to 0.09 wt%) of synthesised antioxidant (AO_2) in various proportions. This mixture was melt-mixed at 230 °C at screw speed of 15 r.p.m. for one minute and then at screw speed of 60 r.p m for five minutes. The melt material was taken out, cooled and the mixing process was repeated five times under similar conditions and torque values were recorded for all the five mixing cycles. Similarly, melt-mixing was carried out with commercially available antioxidants like Ultranox, Weston 2,6-di-tert-butyl-4-methyl phenol (BHT). Torque values were recorded for $T_{maximum}$ and the values are given in Table 3A.1

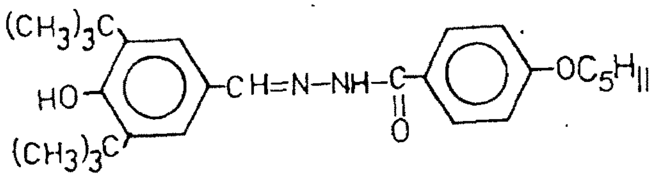
Process for Multiple Extrusion :

Different antioxidants, commercially available like BHT, Ultranox, and newly synthesised antioxidants (i) N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-hydroxy benzohydrazine (AO_2) (ii) N'-(3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-pentyloxy benzohydrazine (AO_3). (iii) N'- (3,5-di-tert-butyl-4-hydroxy phenyl) methylene-4-decyloxy benzohydrazine

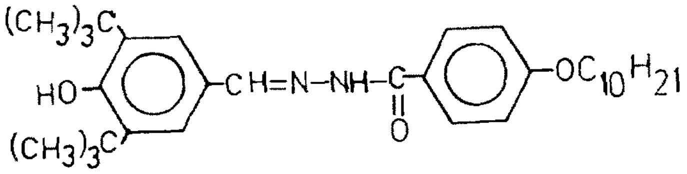
Synthesised Antioxidants



AO_2



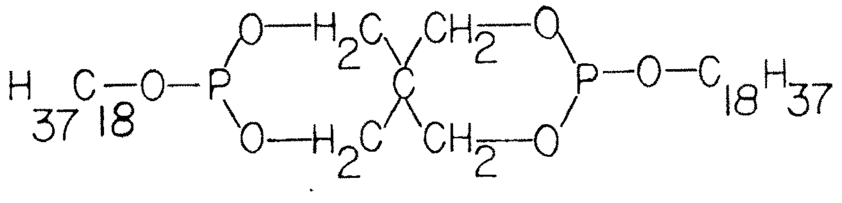
AO_3



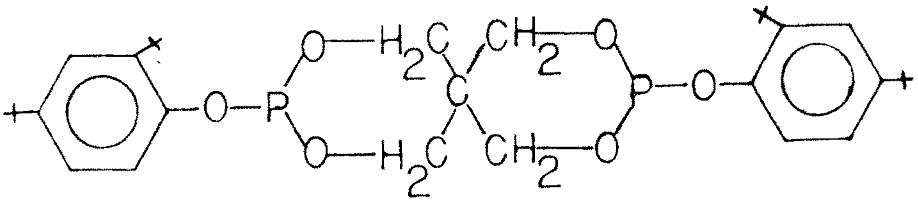
AO_4

Figure 3A.1

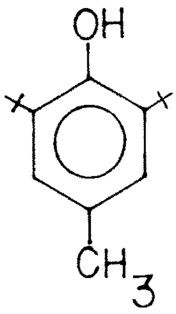
Commercially available antioxidant



WESTON 619



ULTRANOX 626,



BHT AO1

Table 3A.1

Torque values of IPP stabilised with different antioxidant, recorded at T maximum (Nm) for all the five mixing cycles.

Antioxidants	Concentration	Torque values (Nm) Melt mixing cycles.				
		1	2	3	4	5
Weston	0.015	20.58	41.65	27.44	24.50	26.46
	0.025	21.07	30.87	20.58	30.87	18.62
	0.035	21.07	44.10	21.07	34.30	22.54
	0.045	21.31	29.40	27.93	14.45	11.02
Ultranox	0.015	18.62	29.15	35.05	27.44	10.78
	0.025	14.21	22.05	24.50	11.76	3.92
	0.035	18.13	25.50	10.78	16.66	6.61
	0.045	18.13	17.15	41.65	12.25	15.68
AO_1	0.015	13.72	32.34	9.80	6.86	4.90
	0.025	15.66	23.52	18.62	17.64	3.92
	0.035	18.62	20.09	25.54	11.76	4.90
	0.045	16.66	25.97	16.66	19.11	10.78
AO_2	0.015	16.66	27.44	23.52	22.54	6.86
	0.025	16.06	45.08	45.57	17.93	32.34
	0.035	18.13	13.23	19.60	13.72	11.76
	0.045	14.70	11.76	23.52	13.72	30.38

(AO_4) were used for stabilised IPP and simple IPP (without antioxidant) Using each antioxidant together with calcium stearate and Irgonax 1010, the IPP was extruded on Brabender Plasticorder at 210°C. With each antioxidant the extrusion was repeated six times in order to see the stability of the basic polymer. Simple IPP along with calcium stearate and Irgonax 1010 was also extruded six times under similar conditions

Process for Melt Flow Index (MFI) :

MFI is the weight of polymer extruded through a standard orifice in a given time and is inversely related to molecular weight. MFI gives an idea about melt viscosity and thus the ease of processing.

MFI of isotactic polypropylene with different antioxidants was determined by using a rheometer (Devenport, England). It has capillary die of length 8mm, diameter 2mm and the driving weight of 2.16 kg.

MFI was taken at a temperature of 230°C. The melt through the die was cut at an interval of 10 seconds and five such samples were taken and weighed. For each of the antioxidant Ultranox, AO, AO_1, AO_2, AO_3 and AO_4, the experiment was repeated twice and the average values of MFI measured. The experiment was carried out according to ASTM (D 1238-57) Test method. The relevant data is given in Table 3A-2.

RESULTS AND DISCUSSION :

Melt-Mixing :

Torque values for Tmax were plotted against the number of melt-mixing for different antioxidants as shown in Figures 3A.2 to 3A.5. Here the torque values were recorded in meter grams which were then converted to newton meter

From the figures it has been observed that the synthesised as well as commercially available antioxidants have shown reasonable activity against the degradation of IPP which is indicated by the reasonable retention of the torque values Now, the suitable concentration with torque maxima and steady torque values have been identified from among the antioxidants considered. Such concentrations are selected for further studies like multiple extrusion Among the four concentrations studied, the torque value was found to be maximum in case of 0 025g

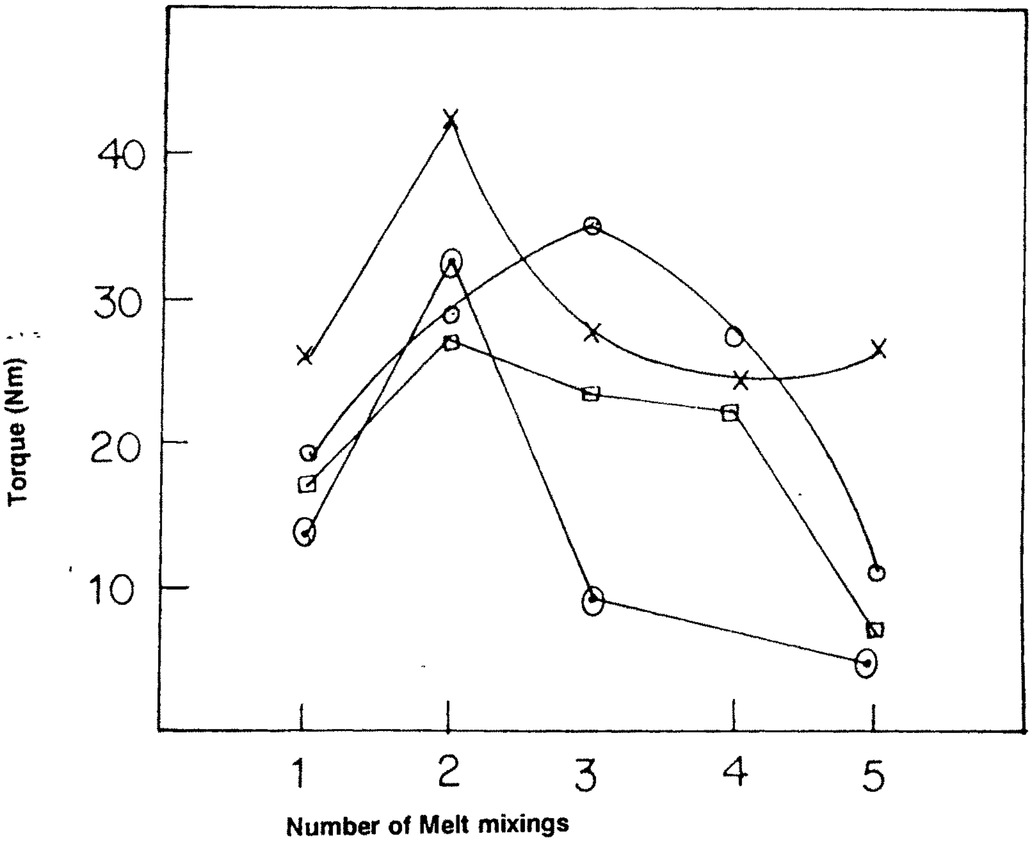


Fig. 3A.2 Torque values plotted against the number of melt mixings for IPP stabilised with 0.015g concentration of (X) Weston, (O) Ultranox, (⊙) BHT (AO_1) and (☐) AO_2.

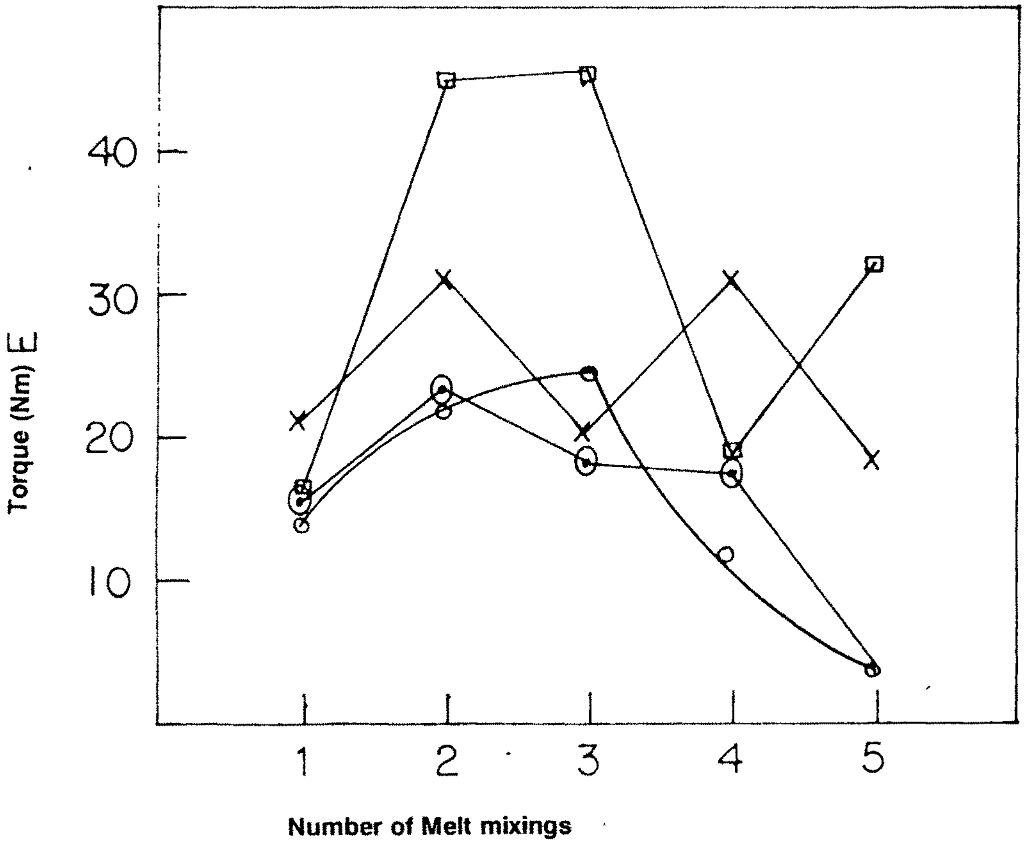


Fig. 3A.3 Torque values plotted against the number of melt mixings for IPP stabilised with 0.025g concentration of (X) Weston, (O) Ultranox, (⊙) BHT (AO_1) and (☐) AO_2.

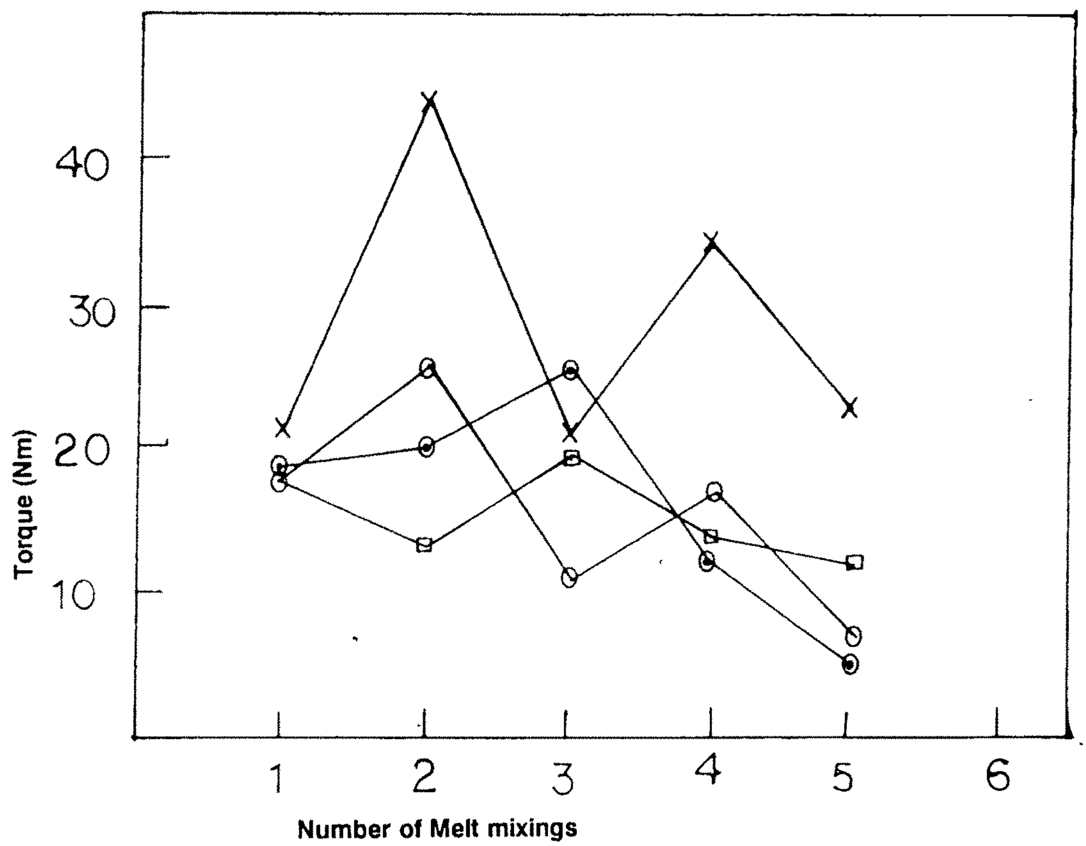


Fig. 3A.4 Torque values plotted against the number of melt mixings for IPP stabilised with 0.035 g concentration of (X) Weston, (O) Ultranox, (⊙) BHT (AO_1) and (☐) AO_2.

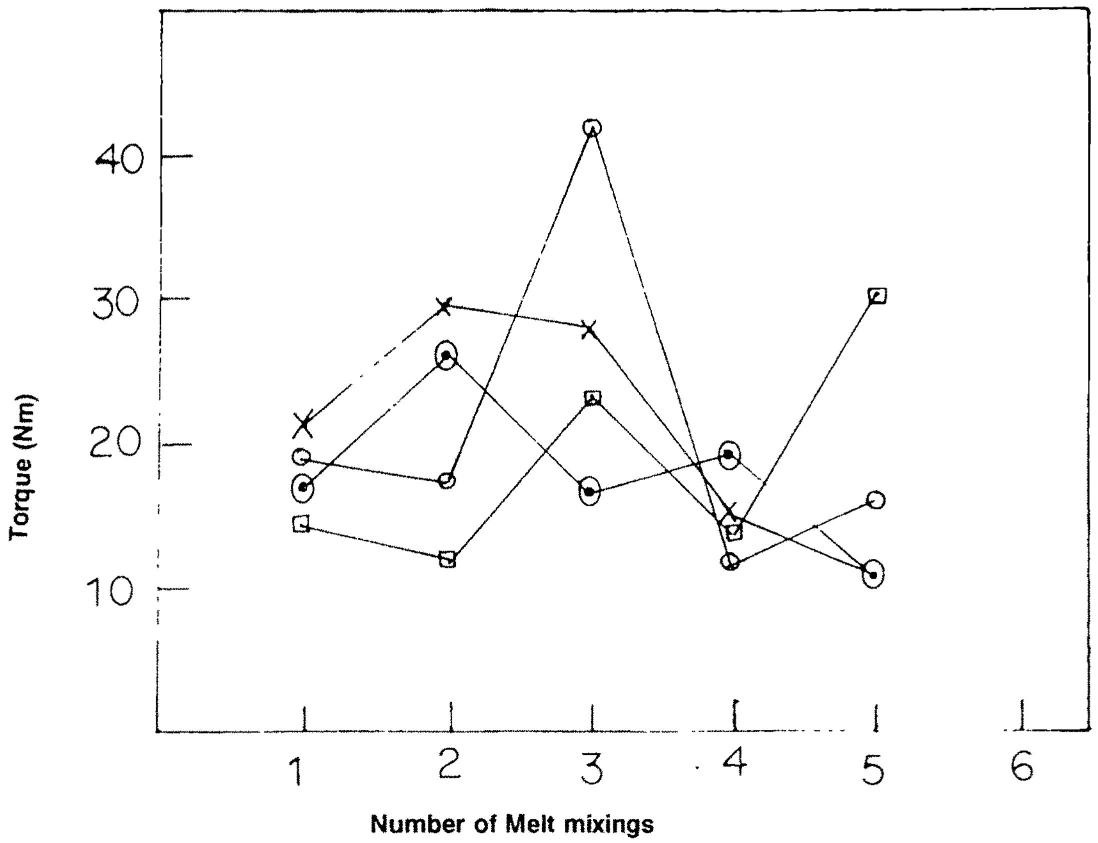


Fig. 3A.5 Torque values plotted against the number of melt mixings for IPP stabilised with 0.045 g concentration of (X) Weston, (O) Ultranox, (⊙) BHT (AO_1) and (☐) AO_2.

concentration of synthesised antioxidant as well as in case of BHT and Ultranox Based on this observation, the concentration 0.025g was selected for further studies.

Melt Flow Index:

The MFI of the extruded sample was plotted against the number of extrusions as shown in Figure 3A.6. From Table 3A.2 and Figure 3A.6, it is observed that MFI of the extruded sample (IPP) increases as the number of extrusions increase from 1 to 6 i.e., melt viscosity decreases both with the commercially available antioxidant and synthesised antioxidants. When simple IPP (AO) without any antioxidant was subjected to multiple extrusion, the MFI values increased rapidaly from 1st to 6th i.e., 10.21 to 18.57. This showed that without any antioxidant, the degradation of IPP is very fast, this probably is because of the formation of free radicals. So in this case the degradation takes place via chain scission. It is reported that if the polymer (IPP) gets degraded via chain scission, it results in a decrease in molecular weight, leading to increased melt flow and reduced tensile strength[8]

However, with commercially available antioxidant like BHT (AO_1), the MFI values do not increase rapidly. The MFI values are quite stable upto the 4th extrusion, after that it increase very fast. This is because after 4th extrusion the polypropylene gets degraded and as a result, molecular weight decreases.

With Ultranox, the MFI values remain constant which means that the melt viscosity as well as the molecular weight of the IPP remain intact, i.e., the IPP is not getting degraded fast. So it is an effective antioxidant.

In case of AO_2, it can be observed from Table 3A.2 and Figure 3A.6 that it is not a suitable antioxidant for IPP. This is due to its high melting point (273°C). Since, the extrusion of IPP was carried out at 210°C, at this temperature, the antioxidant AO_2 could not intrude into the polymer matrix of IPP, as it melts only at 273°C. So in the molten state of IPP, AO_2 remained solid, it did not go into the viscous form so as to mix uniformly with the IPP. It could be observed from its MFI values that degradation started after 2nd extrusion. So AO_2 is not an effective antioxidant due to its high melting point

Table 3B.2

Processing stability of IPP; multiple extrusion at a melt temperature of 210°C and a screw speed of 25 r.p.m.; IPP with 0.1 wt% of calcium stearate and 0.025g of antioxidant.

Antioxidants	**Melt flow index MFI (g/10min) 230°C/2.16kg Extrusion cycle**					
	1	**2**	**3**	**4**	**5**	**6**
Ultranox	6.45	6.65	6.69	6.92	6.92	7.38
AO*	10.21	13.72	15.04	16.35	17.46	18.57
AO 1	7.06	7.85	8.01	10.14	11.01	11.82
AO 2	9.01	9.34	---a	----a	-----a	----a
AO 3	10.01	11.75	13.06	14.91	16.67	18.93
AO 4	8.43	9.32	10.62	11.91	13.63	14.35
MFI of only IPP powder = 10 g/10 min						

* IPP without antioxidant

a M.p. of the antioxidant being higher than the experimental temperature, no uniform mixing occurs and MFI is found to be higher after second extrusion. So MFI of 3,4,5, and 6 is not measured

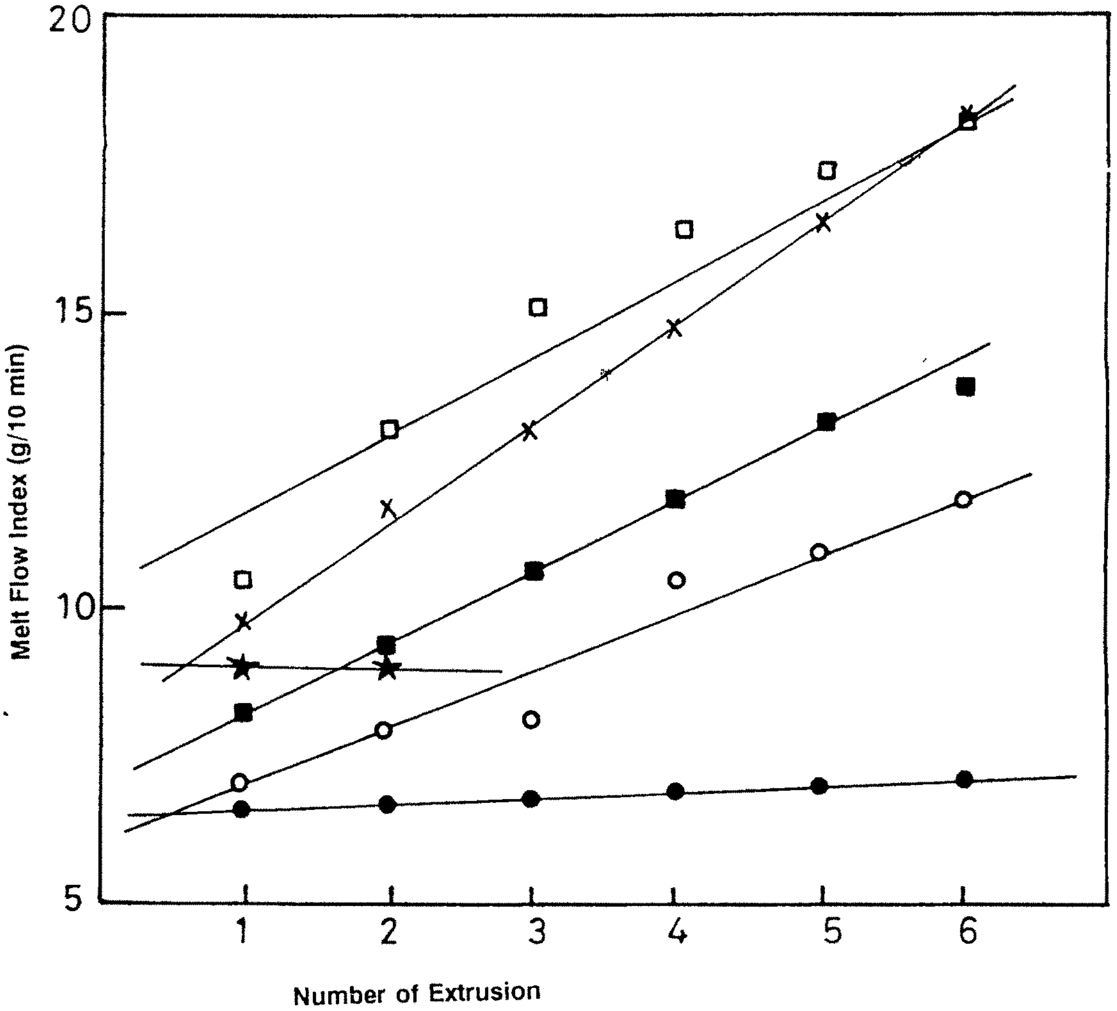


Fig. 3A.6 Melt flow index (MFI) plotted against the number of extrusion : for IPP stabilised with antioxidant; (●) Ultranox, (□) AO, (O) BHT (AO1), (★) AO2, (X) AO3 and (■) AO4.

The MFI values of AO_3, indicate that the degradation of IPP in presence of AO_3 is equal to isotactic polypropylene without any antioxidant. So it is not a suitable antioxidant for IPP, too.

With synthesised antioxidant AO_4, the molecular weight of the antioxidant is high compared to that of BHT. From Figure 3A.6, it has been observed that MFI values increase slowly, compared to AO. The MFI values are quite comparable with that of IPP with BHT (AO_1). The MFI values are quite stable upto 3rd extrusion. This implies that in IPP as it passes through the number of extrusions, the degradation is less as compared to AO. So it is an effective antioxidant.

In case of antioxidants AO_3 and AO_4, the melting points are 186°C and 80°C respectively and since the extrusion of IPP was carried out at 210°C, at this temperature AO_3 and AO_4 could go into the polymer matrix.

On comparing the structures of AO_3 and AO_4 it is observed that when the hydroxy group at the para position is replaced by a pentyloxy group, there is no improvement in the stabilisation of IPP against the degradation as it passes through extrusion. But when this hydroxyl group is replaced by decyloxy group, there is considerable improvement in the stabilisation of IPP. AO_4 stabilises IPP to the same extent as the commercially available antioxidant AO_1 Here the molecular weight of AO_4 is higher than that of AO_1.

The molecular weights of antioxidants AO_3 and AO_4 are 438 and 508 respectivley. The influence of molecular weight on the efficiency of antioxidants is discussed by different authors. [9,12,13]

Minagawa [9] reported that in the case of hindered phenols, the performance maxima was found to be at the molecular weight of 600. Tochacek and Sedlar[12] reported that, in case of series of phenolic antioxidants, the maximum performance was observed for the molecular weight of 500-550 This is in good accord with that observed for the stabilisation efficiency of antioxidant AO_4.

The role of molecular weight seems to represent a complementary factor out of many. More than the molecular weight itself. The influence of the individual chemical structure is responsible for the maxima of performance. Each structure is characterised by its physical properties and its behaviour in polymer.

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CHAPTER - 3

SECTION - B

INTRODUCTION

The adequate resistance to thermooxidation is one of the most important factors directly determining the commercial success of any polymeric material. The exposure to the deteriorative impacts, both during the processing and the actual service life, may cause irreversible changes in the polymer backbone, which are consequently reflected in the change or total loss of the physico-chemical properties.[1] The use of an efficient stabilisation system in the matrix, especially in the case of polyolefins, is therefore mandatory. The choice of a particular antioxidant or a formulation is always to be done with respect to the kind of polymer, the way of its processing and the kind of its intended application.

In order to attempt good stabilising systems, hindered phenols came into the picture. Hindered phenols function as labile hydrogen donors in protecting hydrocarbon polymers and elastomers against auto– oxidation. Low molecular weight phenols such as 2,6-di-tert-butyl-4-methyl phenol (BHT) are effective short-term antioxidants.[2] BHT is, however, highly volatile because of its low molecular weight, and high loss can occur during extrusion, particularly when high surface area extrudates (e.g. film), are used. Consequently, although it protects polymers during processing, further stabilisers are used to impart long-term ageing stability.[3] Stabilisers designed for long-term protection are usually large complex molecules which have high mobility through the polymer but are also less volatile and so have superior retention.[2]

Synthesis and evaluation of antioxidant activity of sulphur and nitrogen containing phenolic antioxidants are summarised in chapter 2.

The mechanism of antioxidant action of 3,5-di-tert-butyl-4-hydroxy benzyl mercaptan and bis (3,5-di-tert-butyl-4-hydroxy benzyl) sulphonic acid is reported by Scott and Suharto.[5]

Compounds containing phenolic antioxidant and semicarbazide have been used as stabilisers for polyolefin compositions as reported by Ozeki et al.[5]

Recently, Asakura et al.[6] synthesised some phenolic compounds containing both phenolic hydroxyl groups and sulphide groups and examined the antioxidant effect of those compounds.

Although the use of several phenolic compounds containing sulphur and nitrogen is recorded in the literature, the use of thiosemicarbazones as antioxidants is not apparently reported. So it was thought worthwhile to explore the possibility of the use of thiosemicarbazones with 2,6-di-tert-butyl phenolic moiety as antioxidants.

Present Work[*] :

Present study 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 efficiencies of the antioxidants synthesised have been checked in IPP. The influence of molecular weight of these antioxidants on the overall performance was investigated.

The synthesis of thiosemicarbazones of 3,5-di-tert-butyl-4-hydroxy benzal-dehyde is reported in chapter 2. First the methyl group of BHT was converted into aldehydic group by using a method reported in the literature by Coppinger and Campbell[8] The aldehyde was then treated with thiosemicarbazides to get the corresponding thiosemicarbazones These thiosemicarbazones were mixed with isotactic polypropylene (IPP) and were subjected to meltmixing 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 impact strength of the compression moulded samples were measured.

EXPERIMENTAL

Materials :

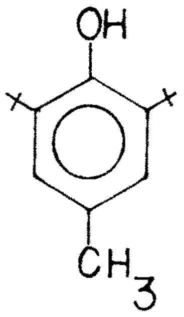
The commercially available antioxidants 2,6-di-tert-butyl-4-methyl phenol (AO_1) was supplied by HICU, Bombay. The antioxidants AO_2, AO_3 and AO_4 used were synthesised in this laboratory. The synthesis of these antioxidants is discussed in chapter 2

Polypropylene :

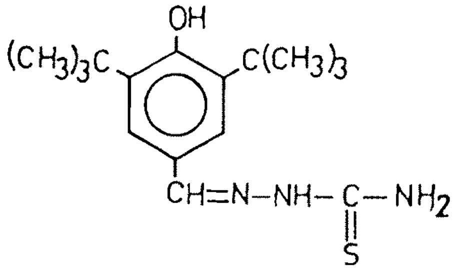
Stabilised isotactic polypropylene (Indian Petrochemical Corporation Ltd., Baroda, India) with MFI grade 13 56 (g/10 min) was used for the experiments

The chemical structures and abbreviations for the antioxidant used for processing stabilisation of IPP are given in Figure 3B.1

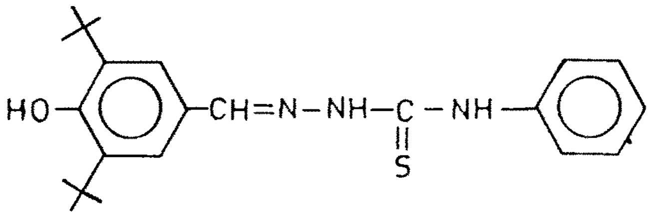
* This work has been accepted for publication[7]



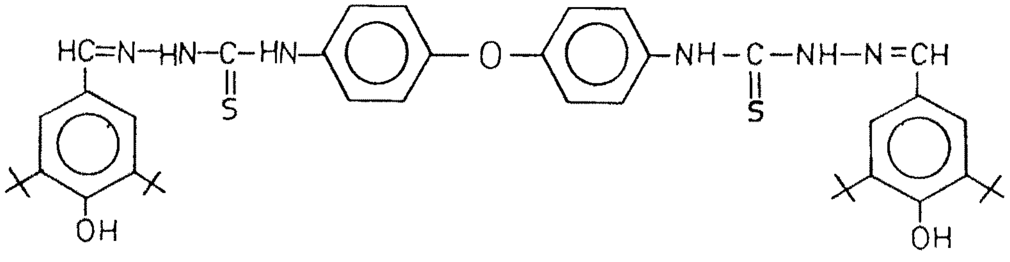
AO₁



AO₂



AO₃



AO₄

Figure 3B.1

Processing and Testing :

The performance of antioxidants in polymer (isotactic polypropylene) processing is tested in the polymer melt and is assessed by multiple extrusion The multiple extrusion of isotactic polypropylene was carried out with the suitable concentration of the commercially available antioxidants like 2,6-di-tert-butyl-4-methyl phenol (BHT) as well as with synthesised antioxidants. In order to find out the suitable concentration of BHT and synthesised antioxidants, the melt mixing was done on Brabender Plastograph with different concentration of BHT as well as with synthesised antioxidants. The stability of polymer melt viscosity was controlled through measurement of torque as a function of time and temperature.

Procedure for Melt-Mixing :

To 50g of stabilised IPP in powder form (MFI 13 56g/10 min) was added, 0.05g (0.1 wt. %) of calcium stearate, 0.025g (0.05 wt. %) Irgonax 1010 and 0.015 to 0 045g (0 03 to 0.09 wt %) of BHT or synthesised antioxidants 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide (AO_2), 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]-N-Phenyl hydrazine carbothioamide (AO_3), 4,4'-di-{ 2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]- hydrazine carbothioamido} biphenyl ether (AO_4), in various proportions. This mixture was melt-mixed at 230°C at Screw speed of 15 r.p m for one minute and then at screw speed of 60 r.p m for five minutes. The melt material was taken out, cooled and the mixing process was repeated five times under similar conditions. The torque values were recorded in meter-grams for all the five mixing cycles. These torque values were converted from meter-grams to Newton meter (Nm) as per SI units So the values reported in table and graph are given in Nm The torque values for T maximum are given in Table 3B.1

Process for Multiple Extrusion :

Commercially available antioxidants like BHT (AO_1), or each of the synthesised antioxidants AO_2, AO_3, and AO_4 along with calcium stearate and Irgonax 1010, was mixed with IPP and extruded on Brabender Plasticorder at 210°C.

The extrusion process was repeated six times with each of the antioxidant in order to see the stability of the basic polymer. The isotactic polypropylene along with calcium stearate and Irgonax 1010 was also extruded in the similar fashion

Table 3B.1

Torque values of IPP stabilised with different antioxidants, recorded at T maximum (Nm) for all the five mixing cycles.

Antioxidants	Concentration	Torque(Nm) after number of Melt-Mixing				
		1	2	3	4	5
AO_1	0.015	13.23	15.68	24.50	16.66	23.03
	0.025	16.66	18.13	19.11	15.68	9.31
	0.035	21.07	41.16	21.07	18.62	8.82
	0.045	15.19	16.66	28.91	19.11	12.25
AO_2	0.015	22.05	45.08	15.68	19.11	10.29
	0.025	15.68	38.22	21.07	17.15	13.72
	0.035	18.13	28.42	29.40	34.30	14.70
	0.045	19.60	19.60	20.58	13.72	9.80
AO_3	0.015	16.17	15.19	17.64	11.76	20.58
	0.025	22.54	14.21	18.13	13.13	12.74
	0.035	20.58	17.64	19.60	14.70	10.78
	0.045	12.74	15.68	18.13	13.23	12.25
AO_4	0.015	20.58	27.44	16.66	11.76	11.27
	0.025	17.64	48.02	32.34	23.52	20.58
	0.035	17.64	27.93	15.68	30.38	7.84
	0.045	14.70	12.74	19.60	13.23	12.74

Process for Melt Flow Index (MFI) :

The Melt flow index was carried out according to the ASTM standard test method (D 1238-57) as is given in chapter 3A The relevant data is given in Table 3B.2.

Process for Compression Moulding :

The small granules were stacked in between two thin polished stainless steel plates (1mm thickness) and moulded at 200°C + 2°C. The whole system containing granules were inserted in between the preheated upper and lower platen of hydraulic press. The press has temperature control system. After insertion of the material, the upper and lower platen of press were brought near each other and kept for 2 minutes. Then the material was compressed at 10 Kg/cm^2 for two minutes and thereafter at 100 Kg/cm^2 for 1 minute. The granules have thus been moulded into a sheet. The sheet was immediately removed from the press and was allowed to cool in air and subsequently in cold water.

In brief the condition of preparing compression moulded sheet is given in Table 3B 3 The specimens for various testing were cut from the prepared sheet prior to testing and were annealed at 60°C for 48 hours.

Process for Heat Deflection Temperature (HDT) :

Heat deflection temperature of the IPP along with different antioxidants under flexural load was determined in accordance with ASTM (D 648-82).

The test sample was tested as a beam with the applied load at its centre to give maximum stress of 18.20 kpa. The specimen was immersed in a heat transfer medium (silicon oil) and was well strirred during the test so as to provide a means of raising the temperature at the rate of 2°C/min. The metal supports for the specimen were 100 mm apart and the load was applied on the top of the specimens vertically and midway between the supports The temperature of the medium was measured when the test bar showed a deflection of 0.25 mm which is the deflection temperature under flexural load of the test specimen

Depending upon the geometry of the specimen, the load required for a maximum stress of 18.20 kpa was calculated as follows ·

Table 3B.2

Processing stability of IPP; multiple extrusion at a melt temperature of 210°C and a screw speed of 25 r.p.m.; IPP with 0.1% calcium stearate and different antioxidants. Concentrationsof each of the antioxidant are given in paranthesis.

Antioxidants	Melt flow index MFI (g/10 min) 230°C,2.16kg Extrusion cycles					
	1	2	3	4	5	6
AO (without AO)	10.75	11.79	12.92	13.64	15.43	16.56
AO_1 (0.035)	9.71	9.80	11.26	12.12	12.88	14.01
AO_2 (0.045)	8.93	9.29	9.98	10.67	11.08	12.06
AO_3 (0.035)	9.98	10.20	11.23	12.25	12.95	14.04
AO_4 (0.025)	8.77	9.41	10.30	10.66	11.24	12.24
Only IPP Powder =13.56 g/10 min.						

TABLE 3B.3

Compression Moulding of IPP with different antioxidants.

Sr. No.	Operations °C.	Temp. Kg/Cm^2	Pressure min.	Time
1.	Contact of upper and lower platen of hydraulic press	200	Atmospheric	2
2.	Contact under pressure	200	10	2
3.	Moulding operations	200	100	1

$$p = \frac{(2.s.b.d^2)}{(3.L.)}$$

In this formula :

p = Load
s = Maximum fibre stress in the specimen
=18.20 kpa
b = Width of specimen
d = Depth of specimen
L = Length of span between supports

Before starting the experiment, the temperature of the heating bath was maintained at about 25 °C. Then the load was applied to the test specimen and the heating bath was stirred for five minutes. After five minutes the deflection was adjusted at zero.

Three specimens of each of the IPP with different antioxidants were tested and an average value was taken as a heat deflection temperature of the sample. The relevent data is given in Table 3B.4.

Izod Impact Strength Measurement :

Izod impact strength of samples were tested by using compression moulded specimen according to (D 258-81).

The notch was carefully milled into the specimen to concentrate the stress and direct the fracture. Notched specimens were clamped in a vice with the notch facing the direction of the impact. A pendulum was raised to a fixed height and then released to break the sample

Five samples of each of the antioxidant were tested with the pendulum of 30 kgs load. The relevent data is given in Table 3B. 5.

RESULTS AND DISCUSSION :

Melt-Mixing :

Torque values for Tmax were plotted against the number of mix-ups for each of the antioxidants as shown in Figures 3B.2. to 3B.5

TABLE : 3B.4

Heat Deflection Temperature of compression moulding samples of IPP stabilised with different antioxidants

Antioxidants	**Heat Deflection Temperature HDT(°C) Extrusion cycles.**					
	1	**2**	**3**	**4**	**5**	**6**
AO^*	66.0	65.5	64.0	63.0	62.0	59.0
AO_1	68.0	67.0	66.0	65.0	64.0	63 5
AO_2	66.0	65.0	64.0	64.0	63.0	62.5
AO_3	68.5	68.0	68.0	67.5	67.0	65.0
AO_4	70.0	66.0	64.0	64.0	62.0	61.0

* IPP without antioxidant

TABLE : 3B.5

Impact strength of compression moulding samples of IPP incorporated with various antioxidants

Antioxidants	**Impact Strength IS. (Kg.cm/cm.) Extrusion cycles**					
	1	**2**	**3**	**4**	**5**	**6**
AO^*	1.295	1.124	1 191	1.082	1.069	0.946
AO_1	1.319	1.304	1.302	1.282	1.165	1.125
AO_2	1.382	1.372	1 354	1 346	1.058	1.060
AO_3	1.366	1.368	1.320	1 253	1.043	1.037
AO_4	1 361	1.347	1.332	1.210	1.186	1 147

* IPP without antioxidant

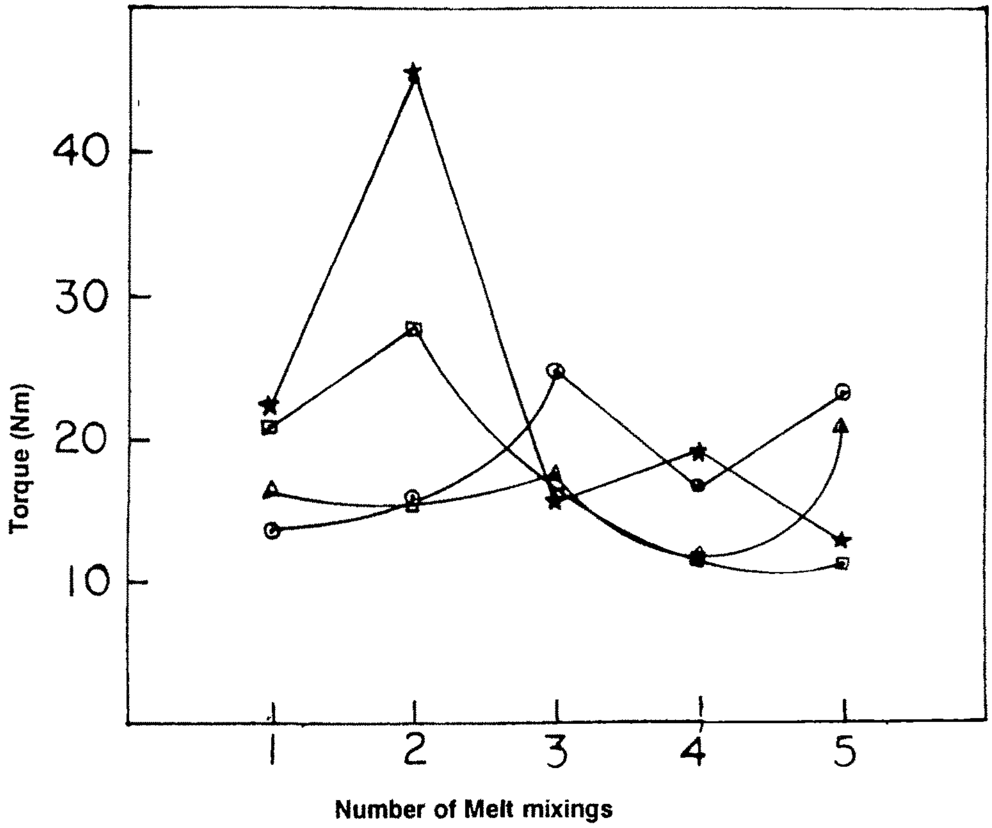


Fig. 3B.2 Torque values plotted against the number of melt mixings for IPP stabilised with 0.015 g concentration of (⊙) BHT (AO_1), (*) AO_2, (Δ) AO_3 and (⊡) AO_4.

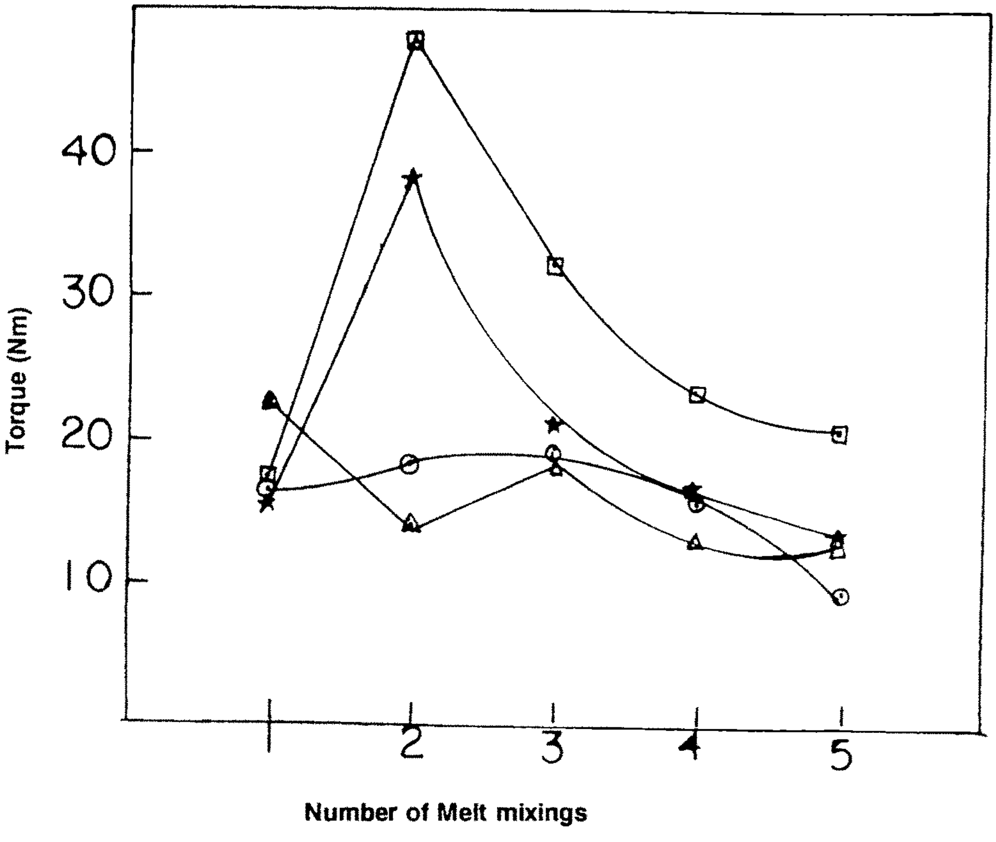


Fig. 3B.3 Torque values plotted against the number of melt mixings for IPP stabilised with 0.025 g concentration of (O) BHT (AO_1), (*) AO_2, (Δ) AO_3 and (⊡) AO_4 (AO_4)

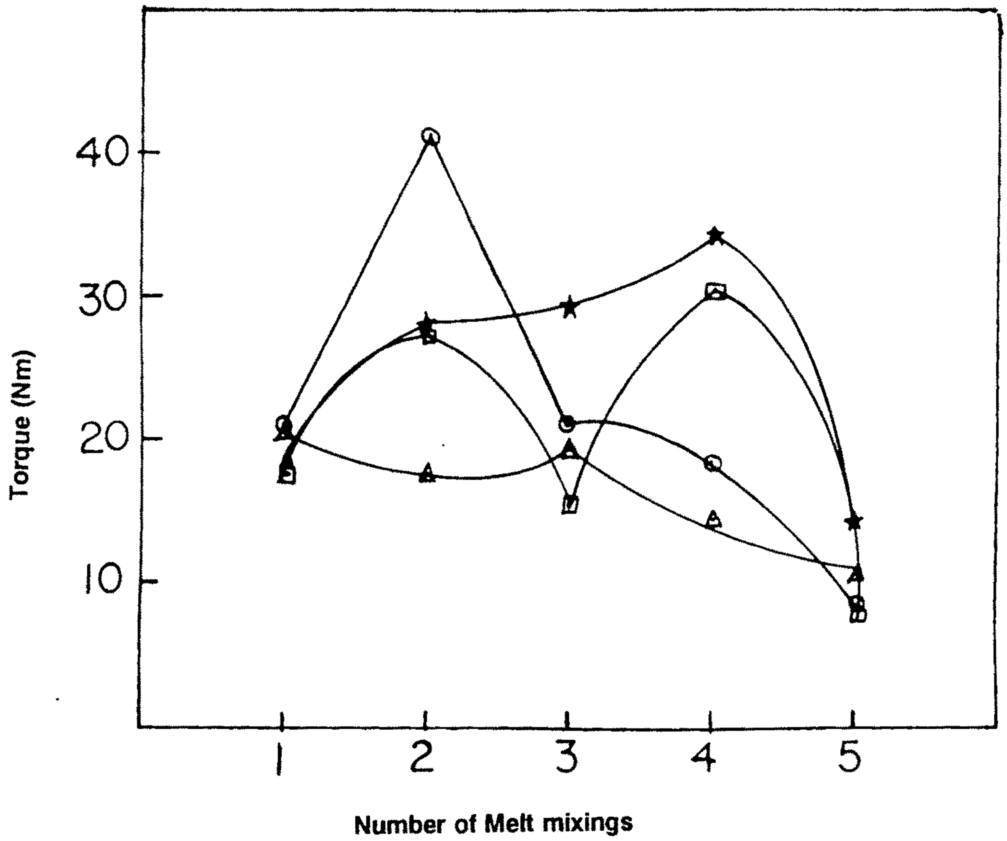


Fig. 3B.4 Torque values plotted against the number of melt mixings for IPP stabilised with 0.035 g concentration of (O) BHT (AO_1), (*) AO_2, (△) AO_3 and (⊡) AO_4.

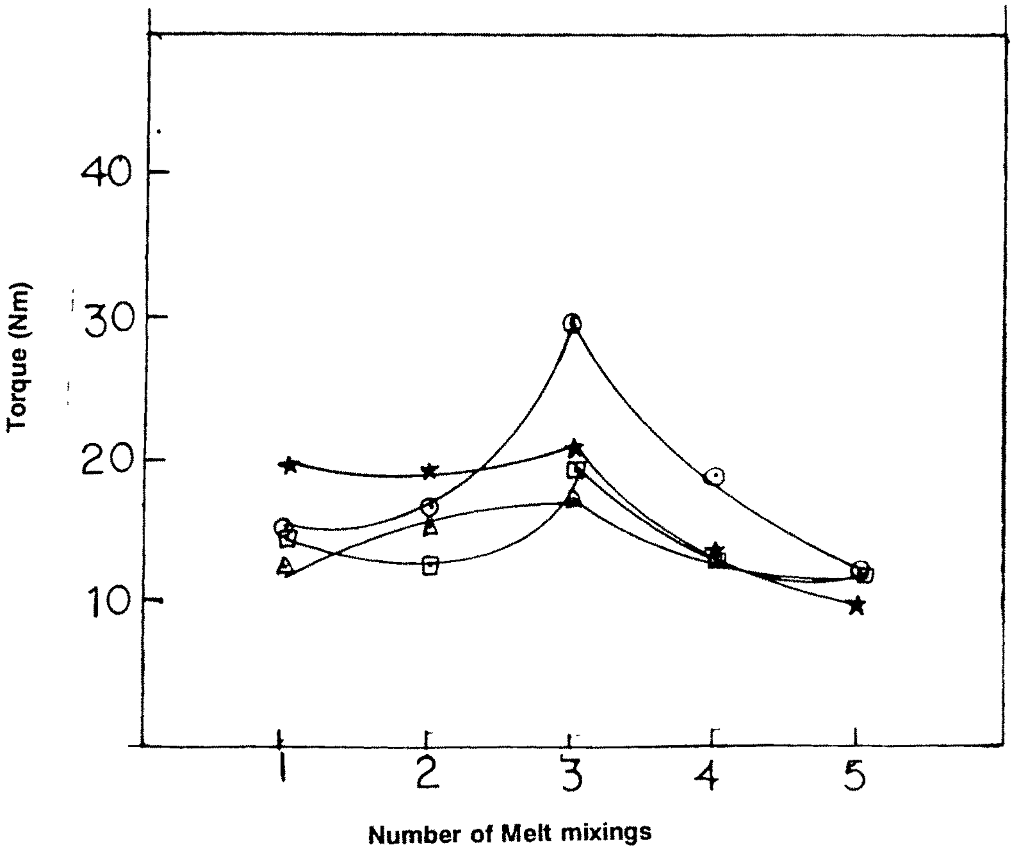


Fig.3B.5 Torque values plotted against number of melt mixings for IPP stabilised with 0.045 g concentration of (O) BHT (AO_1), (*) AO_2, (△)AO_3 and (⊡) AO_4.

From the figures and table, it has been observed that BHT and synthesised antioxidants have shown reasonable activity against the degradation of IPP. This is indicated by the reasonable retention of the torque values. In order to carry out the multiple extrusion, the definite concentration of each of the antioxidant would be important. So selection of the particular concentration depends upon the torque values. Hence the following concentrations were selected for each of the antioxidant for multiple extrusion, basing on the maximum torque values observed.

Antioxidant	**Concentration (for 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

Melt-Flow Index :

The degradation studies of IPP along with each of the antioxidants were carried out by measuring the melt behaviour of the extruded samples, according to process discussed in chapter-3A.

The MFI of each of the extruded sample was plotted against the number of extrusion as shown in Figure 3B.6.

From Table 3B.3 and Figure 3B.6 it is observed that as the number of extrusion increases, the MFI values of the extruded sample increase from 1 to 6 in case of both BHT and synthesised antioxidants.

When simple IPP (AO) without any antioxidant was subjected to multiple extrusion, the MFI values were found to increase rapidly from 1st to 6th i e., 10 75 to 16.56. This indicates that degradation of IPP is very fast in absence of antioxidants This may be because of the formation of free radicals. As it does not contain any antioxidant for the stabilisation against the degradation, the MFI shows great deal of difference in values

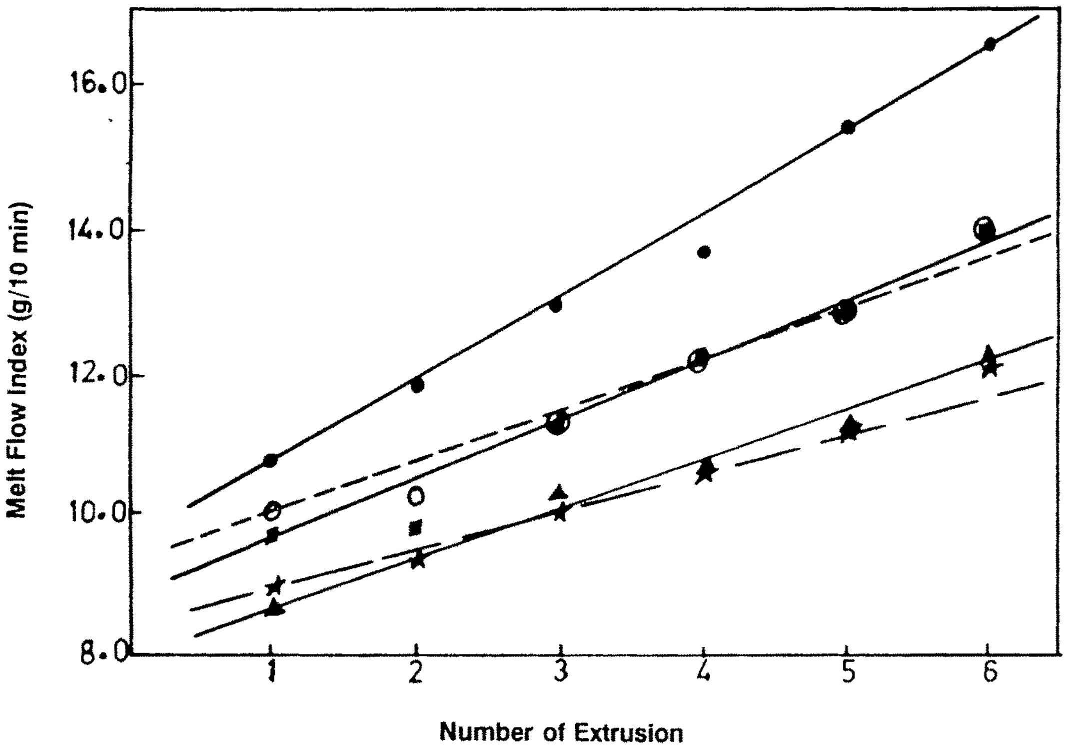


Fig. 3B.6 Melt flow index (MFI) plotted against the number of extrusions; for IPP stabilised with antioxidants; (●) AO, (■) AO1, (★) AO2 (O) AO3, (▲) AO4.

However when the extrusion was carried out with commercially available antoxidants like BHT, the MFI values did not increase rapidly In case of AO_1, the maximum torque value was observed with 0.035 (figure 3B.4) concentration. Hence that particular concentration was selected for multiple extrusion. From Table 3B.2 it can be observed that the MFI values after 6th extrusion is 14.01 which implies that IPP can be extruded upto 5th extrusion in presence of BHT. From the above observation, it is observed that IPP gets stabilised in presence of BHT upto the 5th extrusion. Here no degradation of IPP takes place upto the 4th extrusion. So BHT is an effective antioxidant.

It is reported in literature[9] that as the number of extrusion increases, polymer gets degraded and at the same time molecular weight and melt viscosity of the polymer decreases. As a result of this MFI increases. The results of the present studies are identical to those reported. In case of AO_2, from Figure 3B.5 maximum torque value for AO_2 was found to be with concentration of 0.045. In presence of AO_2, the MFI values increase gradually upto 6th extrusion. After 6th extrusion, the value is only 12.06, this implies that after the 6th extrusion the molecular weight and melt viscosity of the parent polymer is intact. There is no degradation of IPP. Here the concentration of AO_2 is 0.045, which is higher than that of AO_1 but at this higher concentration it stabilises IPP to the same extent as BHT (AO_1) with 0.035 concentration. So AO_2 is a good antioxidant to stabilise IPP during the multiple extrusion at this particular concentration.

From figure 3B.4, it was observed that the maximum torque values for AO_3 was with 0 035 concentration. With the synthesised antioxidant AO_3, the MFI values were very much similar to those of AO_1 (BHT). Here the concentration of BHT is same as that of synthesised antioxidant. AO_3 has high molecular weight compared to that of BHT and AO_2, it stabilises IPP to a greater extent than AO_2 with lesser concentration So here both the antioxidants show the same pattern of stabilisation of IPP. Hence AO_3 is an effective antioxidant this particular concentration and can replace BHT.

In case of AO_4, the torque value was found to be maximum for 0 025 concentration (Figure 3B.3) and this was therefore, selected for multiple extrusion This concentration is less compared to that selected for AO_1 (0.035).

From Table 3B.3 and Figure 3B.6, it has been observed that AO_4 with a lesser concentration could stabilise IPP to a greater extent than $A0_1$ with higher concentration i.e. MFI values in case of AO_4 after 1st and 6th extrusion are 8.77 and 12.24 respectively and MFI values in case of AO_1 after 1st and 6th extrusion are 9.71 and 14.01 respectively So, from the MFI values, AO_4 is found to be an effective antioxidant at this particular concentraion i.e. 0.025. From above data it has been observed that the synthesised antioxidant with lesser concentration stabilised IPP to a greater extent than that of BHT

So it can be concluded from the above MFI values that AO_1 is effective only upto 5th extrusion where as AO_4 is effective upto 6 extrusions

Heat Deflection Temperature (HDT) :

The heat deflection temperature values were plotted against the number of extrusion From the Figure 3B.7 it has been observed that as the number of extrusion increased, the HDT values decreased. In case of AO (IPP without antioxidant), as the number of extrusion increases, the IPP gets degraded and the HDT values decrease rapidly.

The HDT values decrease very fast in case of AO compared to that of IPP stabilised with antioxidants like AO_1, AO_2, AO_3 and AO_4.

The HDT values of AO_1, AO_2, AO_3 and AO_4 decrease slowly compared to that of AO. As the number of extrusion increases, the polymer gets degraded and consequently, the molecular weight and melt viscosity decrease. As a result MFI value increases, where as the HDT value decreases. The same pattern of graph was observed with AO_1, AO_2, AO_3 and AO_4

Impact Strength :

The izod impact strength of all the notched samples after each extrusion was noted. The impact strength values were plotted against the number of extrusions as shown in Figure 3B.8. In case of AO, the decrease in impact strength clearly indicates that the polymer gets degraded as it requires less amount of energy to break the samples as compared to that of stabilised IPP. In case of IPP stabilised with commercially available antioxidants or synthesised antioxidant, the impact strength values are high compared to that of IPP without any antioxidants, this may be due to the presence of antioxidant and that could stop the

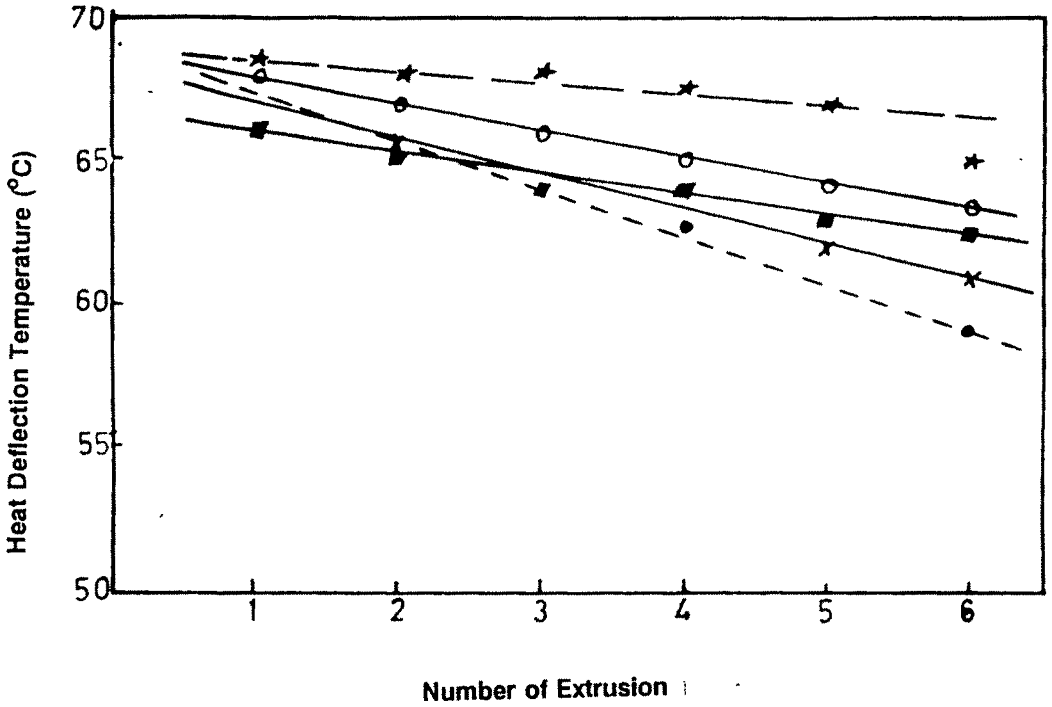


Fig.3B.7 Heat Deflection Temperature plotted against the number of extrusion for IPP stabilised with antioxidants; (●) AO, (O)AO1, (■) AO2, (⋆) AO3, (X) AO4.

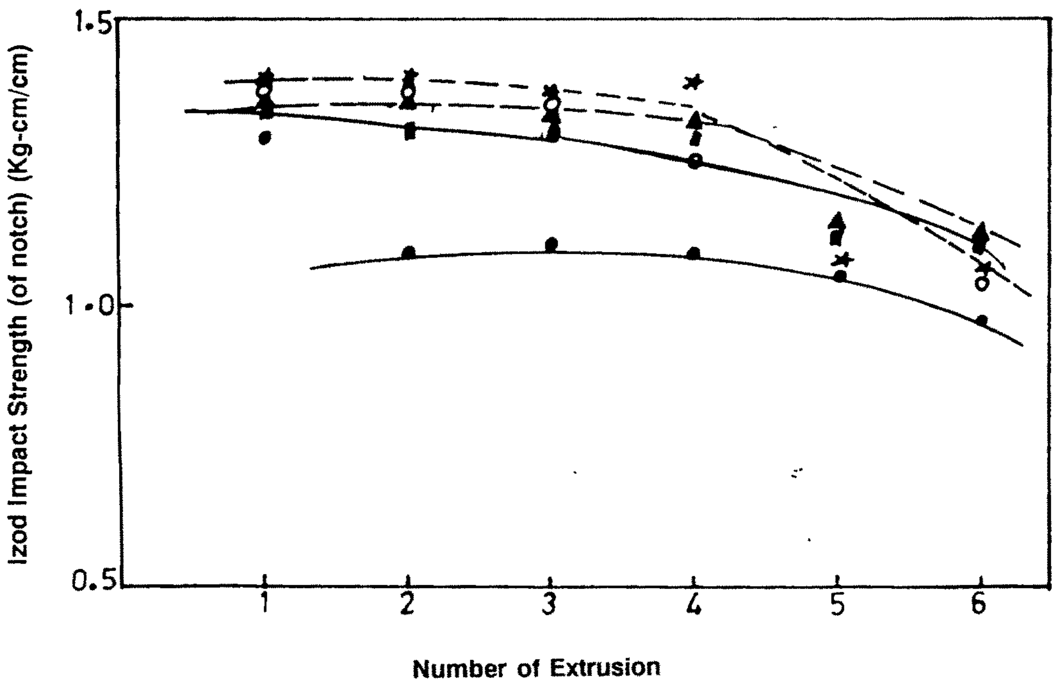


Fig. 3B.8 Impact strength plotted against the number of extrusion, for IPP stabilised with antioxidants; (●) AO, (■) AO1, (⋆) AO2, (O) AO3, (▲) AO4.

degradation of IPP as it passes through the multiple extrusion. But once it gets degraded it requires lesser amount of energy to break the sample

The decrease in impact strength implies that as the number of extrusion increases, the polymer gets degraded and as a result the molecular weight and melt viscosity decrease as against an increase in MFI values. In case of AO (without antioxidant), izod impact strength is less compared to that 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 should be more active as compared to AO_3 and AO_4, also AO_3 more active than AO_4. But as per the present study AO_4 is found to be more effective than AO_2 and AO_3, again AO_3 more effective than AO_2.

Thus, in activity, $AO_4 > AO_3 > AO_2$.

Here we presume that reason for such performance maxima can be attributed to the influence of the individual chemical structure of the antioxidants. The presumption is in line with the observation reported by different authors.[10,11,12] Each structure is characterised by its physical properties and its behaviour in polymer

In the present study, the influence of molecular weight in the performance maxima of different antioxidants could be explained as follows.

The molecular weight, of AO_2, AO_3 and AO_4 are 307, 341 and 780 respectively. From present studies it is observed that AO_4 is more effective compared to AO_2 and AO_3. Out of AO_2 and AO_3, AO_3 is more effectives. This shows that the activity is enhanced as the molecular weight increases

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