CHAPTER - 4

INTRODUCTION

The important role of antioxidants in stabilisation of polymers is already discussed in chapter 1. Here we highlight some of the aspects of stabilisation of unstabilised Isotactic Polypropylene (IPP) with the aid of antioxidants. The demand for higher stability during processing as well as in end products of polyolefins has been on the increase over the last two decades. The reason for this increase is due to technical, commercial and environmental factors.

Higher production output involving higher conversion temperatures as well as the development of new grades of polyolefins requiring more stringent processing conditions has brought about the need for improved processing stability During processing of polyolefins in extruders, injection moulding equipment or in rotational moulding machines, exposure of the polymer to oxygen and heat is prevalent These induce degradation through radical chain reactions, resulting in change in polymer molecular weight and consequent changes in viscosity and flow behaviour. It also leads to undesirable changes of physical properties in the final article.[1] The high temperatures associated with compounding, fabrication and regrind processes promote thermal oxidative degradation of polypropylene. Degradations generally begins when reactive impurities contained in IPP thermally decompose to radical species These radical species continue the polymer degradation through a number of sequential reactions including abstraction of hydrogen from IPP, formation of thermally unstable hydroperoxides and additional occurrence of radical species. As thermal oxidative degradation proceeds, chain scission occurs along the polymer backbone, causing reduction in molecular weight and loss of physical properties In order to counteract such degradation processes, stabilisers are incorporated into the polymer.

Even though different types of antioxidants are available, all are not suitable as processing stabilisers for polypropylene Selection is based on several factors like the ability of antioxidants to inhibit degradation and its cost The types of antioxidants that tend to meet these requirements and which are therefore most frequently used as processing stabilisers for polypropylene are hindered phenolic antioxidants.

Hindered phenolic antioxidants contain labile hydrogens and inhibit degradation by donating these hydrogens to the radical species generated during thermal oxidative degradation The resulting phenolic radical is relatively stable and does not abstract additional hydrogen from the polymer chain.[2] Radical scavangers like sterically hindered phenols are widely used to retard processing degradation. Some of the important publications on degradation and stabilisation are given in references[3-11]

Present Work :

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

To demonstrate processing stabilitation of polypropylene, four antioxidants (one commercially available and three synthesised) are selected for the study Their chemical structures and abbreviations used are given in Figure 4.1 The following techniques were used for the evaluation of antioxidant activity :

(i) Melt Flow Index,
(ii) Differential Scanning Calorimetry,
(iii) Heat Deflection Temperature,
(iv) Izod Impact Strength,
(v) Tensile Strength and Modulus, and
(vi) Flexural Strength and Modulus.

EXPERIMENTAL

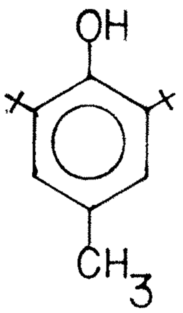
Material :

Polypropylene .

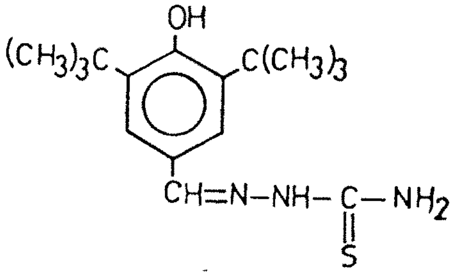
An unstabilised general purpose moulding grade polypropylene with an initial melt flow index of 11.05 g/10 min (ASTM D -1238 condition) supplied by Indian Petrochemical Corporation Ltd. was used for the studies

Conditioning of Material .

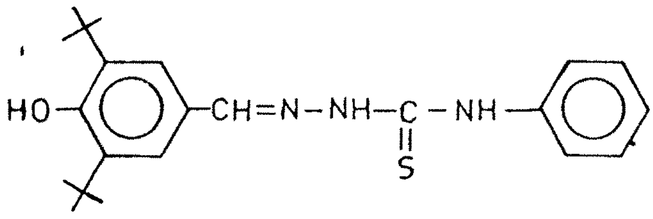
Unstabilised isotactic polypropylene was used as a matrix material This gets degraded in contact with air and creates problem in processing. So, to avoid degradation, it should be preserved under nitrogen blanket till it is mixed with antioxidants. After each extrusion the granules are dried in oven at 80°C before going for another extrusion



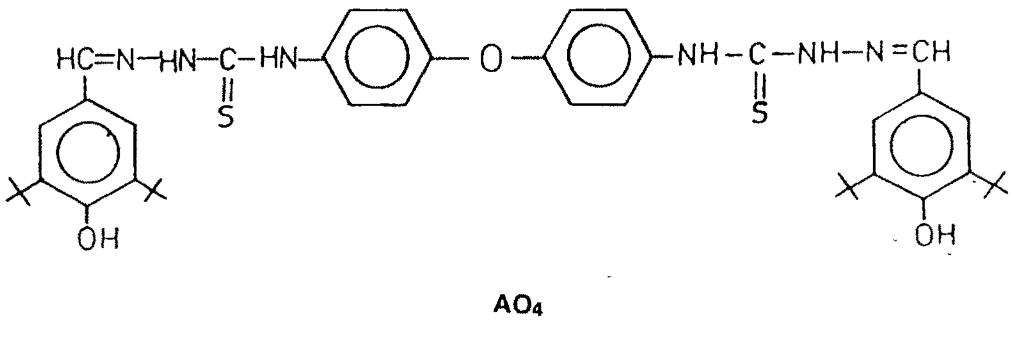
AO₁



AO₂



AO₃,



AO₄

Figure 4.1

Mixing of Isotactic Polypropylene with BHT or Synthesised Antioxidants :

Here the mixing of BHT or synthesised antioxidant with IPP was carried out in rotating spring mill, by rotating the mixture in the mixing jar for five minutes

Twin Screw Extrusion :

The twin screw extruder ZSK 30 (Warner p-fleider, West Germany) was used for carrying out the extrusion of IPP with BHT or synthesised antioxidants. It has two co-rotating screws having deeper screw flights which result in a greater free volume per unit length and a lower average shear rate.

Process for twin-screw extrusion :

Commercially available antioxidants like 2,6-di-tert-butyl-4-methyl phenol BHT (AO_1) or each of the 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) and 4,4'-di- {2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamido} biphenyl ether (AO_4) along with calcium sterate, Irgonax 1010, were mixed with unstabilised isotactic polypropylene and then extruded on twin-screw extruder with a given temperature profile. The condition for extrusion and temperature profiles of different zones maintained during the five multiple extrusions are given in Table 4.1. The resultant mixture was extruded in thread form and cooled in the water bath maintained at 20-25°C and then granulated on conair model : 206 (Michigan) to an average size of 8 to 10 mm The granules were dried in oven at 80°C and re-extruded in twin-screw extruder The same process was followed upto five extrusions

The concentrations selected as discussed in chapter 3B for twin- screw extrusion of IPP with BHT as well as each of the synthesised antioxidants are given below

Antioxidants	Code No.	Concentration (for 50 gms of IPP)
2,6-di-tert-butyl-4-methyl phenol	AO_1	0 035
2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene] hydrazine carbothioamide	AO_2	0.045

Table 4.1

Various formulations of unstabilised IPP with BHT or synthesised antioxidants prepared in Twin-Screw extruder, at screw speed of 100 r.p.m.

Sr. No.	Antioxidant	Mixing termperature of different zones.				
		1	2	3	4	5
1	AO_1	160	210	260	250	210
2	AO_2	160	210	260	250	210
3	AO_3	160	210	260	250	210
4	AO_4	160	210	260	250	210

2-[(3,5-Di-tert-butyl-4-hydroxy phenyl) methylene]-N- phenyl-hydrazine carbothioamide	AO_3	0.035
4;4'-Di{2-[(3,5-di-tert-butyl-4-hydroxy phenyl) methylene]-hydrazine carbothioamido} biphenyl ether	AO_4	0 025

Preparation of specimen :

Prior to moulding, the pellets of all the samples were dried in oven at 100°C to avoid any moisture. The pellets were then subjected to injection moulding to obtain the samples for measurements of their Heat deflection temperature, Izod impact strength, Tensile strength, tensile modulus and Flexural strength and Flexural modulus. All the samples were annealed at room temperature for 72 hours prior to the measurements.

Process of Injection Moulding :

The extruded granules of different samples were injection moulded (Windsor Model SP-3) to get standard ASTM test specimens. The injection moulding machine has a shot capacity of 75 gms. All formulations were moulded under identical conditions as given in Table 4.2.

CHARACTERISATION :

Melt Flow Index (MFI) :

MFI was determined according to ASTM standard (D 1238-57) test method. The test procedure is already discussed in chapter 3A. The relevant data are given in Table 4.3

Differential Scanning Calorimetry (DSC) :

Thermoanalytical techniques are being extensively used to characterise a polymer The principle behind these techniques is to measure the temperature dependence of some mechanical or physical properties and to correlate it to the structure.[12] Thermoanalytical techniques involve a group of techniques in which properties are measured as a function of temperature or time, by keeping every other variable constant Out of these, the two important techniques are Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

Here in this chapter DSC of the extruded sample after 1st, 3rd and 5th extrusions was carried out. Perkin-Elemer (DSC-2C) scanning calorimetry with (TADS) was used to study the melting

Table 4.2

Injection Moulding conditions for all the formulators.

Sr. No.					
1.	Temperature profile for different zones				
	Zone	1	2	3	4
	Temp(O °C)	210	200	165	220
2.	Injection pressure (Kg/Sq.cm)			70	
3	Locking mould (Tons)			60	
4.	Injection period (Sec)			20	
5.	Cooling period (Sec)			20	
6.	Back pressure (Kg/cm^2)			35	
7.	Screw Division			6	
8.	Screw Speed (r.p.m)			100	

Table 4.3

Processing stability of unstabilised IPP; multiple extrusion at a melt temperature of 260°C and a screw speed of 100 r.p.m; IPP with 0.1% calcium stearate and different antioxidants. Concentration of each of the antioxidants are given in parenthesis.

Antioxidants	Melt flow index MFI,(g/10 min) 230°C/2.16kg. Extrusion cycles		
	1	2	3
AO_1 (0.035)	10.78	12.84	16.96
AO_2 (0.045)	10.21	11.38	16 99
AO_3 (0.035)	9.30	12.77	16.89
AO_4 (0 025)	8.90	11 14	14.05
MFI of unstabilised IPP = 11.05 g/10 min			

behaviour of isotactic polypropylene with different antioxidants. In this test, the sample of definite weight 10 mg was taken and heated from 25°C to 327°C at a heating rate of 10°C/min in presence of inert nitrogen atmosphere (20 psi, N_2 purge pressure) and the melting curves were recorded. The area enclosed by the DSC curve is proportionality constant which is independent of temperature. The percent crystallinity of various samples was obtained by using the following expression.[13]

$$\%\ \text{crystallinity} = \frac{\Delta Hf^*}{\Delta Hf^0} \times 100$$

Where, ΔHf^0 is heat of fusion of 100% crystalline polypropylene and ΔHf^* heat of fusion of polypropylene with different antioxidants after repeated extrusions The Melting temperature, heat of fusion ΔHf^* and % crystallinity values of unstabilised IPP with different antioxidants are given in Table 4.4 and 4.5 respectively

Performance Properties :

The specimens were tested in laboratory environment of temperature 25°C and relative humidity of 40-45% to determine the various mechanical properties like Heat deflection temperature, Izod impact strength, Tensile strength, Tensile modulus, Flexural strength and Flexural modulus.

Heat Deflection Temperature (HDT) :

HDT was carried out according to ASTM standard (D 648-56) test method using injection moulded samples. The test procedure is discussed in chapter 3B and the relevant data is given in Table 4.6.

Izod Impact Strength (IS) :

Impact strength was measured using injection moulded samples according to ASTM standard (D 256-56) test method. The relevant data is given in Table 4 7.

Test method for Tensile Strength and Tensile Modulus :

Tensile properties of polypropylene containing antioxidants (AO_1, AO_2, AO_3 and AO_4) were tested by using injection moulded bars according to ASTM standard (D 638-82) The test method was carried out on a Universal Testing Machine (Instron-1195) which has a constant rate of cross head movement The self-aligning mechanical grips were used in such a manner

Table 4.4

Melting Temperature values of unstabilised IPP with different antioxidants.

Antioxidants	Melting Temperature (°C) Extrusion cycles 1	 3	 5
AO_1	167.16	168.64	168.98
AO_2	168.15	166.03	167.69
AO_3	172.02	168.04	167.75
AO_4	167.72	165.42	168.36

Table 4.5

% Crystallinity index values of unstabilised IPP with various antioxidants.

Antioxidants	Extrusion cycles 1		3		5	
	Crystallinity index(%)	Heat of fusion(ΔHf^*)	Crystallinity index(%)	Heat of fusion(ΔHf^*)	Crystallinity index(%)	Heat of fusion(ΔHf^*)
AO_1	40.48	20.24	38.30	19.99	36.22	18.11
AO_2	40.01	20.05	38.44	19.22	36.96	18.42
AO_3	42.50	21.25	37.04	18.52	31.96	15.93
AO_4	45.96	22.98	42.94	21.47	30.38	15.19

Table 4.6

Heat Deflection Temperature of Injection moulded samples of unstabilised IPP stabilised with different antioxidants.

Antioxidants	Heat Deflection Temperature HDT (°C) Extrusion cycles		
	1	3	5
AO_1	72.5	68 0	67.0
AO_2	68 0	66 0	65 0
AO_3	65 0	64.0	63 0
AO_4	64.5	64 0	63 0

Table 4.7

Izod Impact Strength of injection moulded samples (notched) of unstabilised IPP stabilised with different antioxidants.

Antioxidants	Izod Impact Strength IS (kg-cm/cm) Extrusion cycles		
	1	3	5
AO_1	1.628	1.627	1.620
AO_2	1.636	1.628	1.624
AO_3	1.634	1 631	1 624
AO_4	1.638	1 628	1 627

that they would move freely into alignment as soon as the load is applied, so that the axis of the test specimens coincides with the direction of applied pull through the centre line of the grips Five specimens of each sample were tested under following conditions, and the load displacement curves recorded.

Cross head speed	=	50 mm/min
Chart speed	=	10 mm/min
Full scale loading	=	500 kgs
Gauge seperation	=	115 mm

Tensile strength and tensile modulus of the samples were determined as follows

$$\text{Tensile Strain} = \frac{(\text{Chart Displacement})}{(\text{Gauge Separation})\ (\text{Chart Speed})}$$

$$\text{Tensile Stress} = \frac{(\text{Load})}{(\text{Original cross sectional area})}$$

$$\begin{array}{l}\text{Tensile Strength} \\ \text{at yield } (\text{Kg/cm}^2)\end{array} = \frac{(\text{Maximum load at yield})}{(\text{Original cross sectional area})}$$

$$\text{Tensile Modulus } (\text{kg/cm}^2) = \frac{\text{Tensile Stress}}{\text{Tensile Strain}}$$

The relevent data is given in Table 4.8 and 4.9.

Test Method for Flexural Strength and Flexural Modulus :

Flexural properties of different samples were tested using injection moulded bars according to ASTM standard (D790) test method on a Universal Testing Machine (Instron-1195) which has constant rate of cross head movement.

Testing was carried out under the following conditions

Cross head speed	=	2.8 mm/min
Span length	=	10 cm
Chart speed	=	5 1
Full scale load	=	50 kg.

Table 4.8

Tensile Strength of injection moulded samples of unstabilised IPP stabilised with different antioxidants.

Antioxidants	Tensile Strength Kg/cm^2 Extrusion cycles 1	3	5
AO_1	381	380	374
AO_2	386	382	377
AO_3	387	384	380
AO_4	389	385	380

Table 4.9

Tensile Modulus of injection moulded samples of unstabilised IPP stabilised with different antioxidants.

Antioxidants	Tensile modulus Kg/cm^2 Extrusion cycles 1	3	5
AO_1	14578	14474	14360
AO_2	14335	14269	14084
AO_3	14335	14295	14206
AO_4	14326	14301	14208

The test specimens were conditioned according to ASTM standard prior to their testing Testing conditions were kept constant for all the samples. The following expression has been used to calculate flexural strength and flexural modulus

$$\text{Flexural Strength}(\text{kg/cm}^2) = \frac{2\,wl}{2\,bd^2}$$

Where
w = load at fracture
l = span length
b = width of the sample
d = thickness of the sample.

Flexural modulus has been calculated as the ratio of stress and strain for Hooken behaviour

$$\text{Flexural Modulus}(\text{kg/cm}^2) = \frac{wl^2}{4\,bd^3e}$$

Where w is the value of load in kgs and e is deflection corresponding to the load The relevant data is given in Table 4.10 and 4.11.

RESULTS AND DISCUSSION:

Since the results obtained for thiosemicarbazones with stabilised IPP were encouraging with respect to antioxidant activity, we decided to proceed with the detailed study of these antioxidants with unstabilised IPP. The structure, abbreviations and concentrations for the antioxidants considered are given in experimental section.

Melt Flow Index (MFI) :

The degradation of IPP in the presence of the antioxidants was studied by measuring the melt flow index of all the extruded samples after 1st, 3rd and 5th extrusions The MFI of each of the extruded sample was plotted against the number of extrusion as shown in Figure 4.2.

From the Table 4.3 and Figure, 4.2 it has been observed that as the number of extrusion increases, the MFI values of the extruded samples with both BHT and synthesised antioxidants increase from 1st to 5th Now in case of AO_1 with 0.035 concentration, the MFI values continue to increase as we pass from first extrusion to third and then to the fifth. This is due to the degradation of IPP and consequent decrease in the molecular weight and melt viscosity.

Table 4.10

Flexural Strength of injection moulded samples of unstabilised IPP stabilised with various antioxidants.

Antioxidants	Flexural Strength Kg/cm^2 Extrusion cycles		
	1	3	5
AO_1	440	422	406
AO_2	469	434	421
AO_3	457	421	407
AO_4	453	425	422

Table 4.11

Flexural Modulus of injection moulded samples of unstabilised IPP stabilised with different antioxidants.

Antioxidants	Flexural Modulus Kg/cm^2 Extrusion cycles		
	1	3	5
AO_1	13007	12395	12209
AO_2	13108	11914	11824
AO_3	12774	12230	11695
AO_4	13194	12821	12103

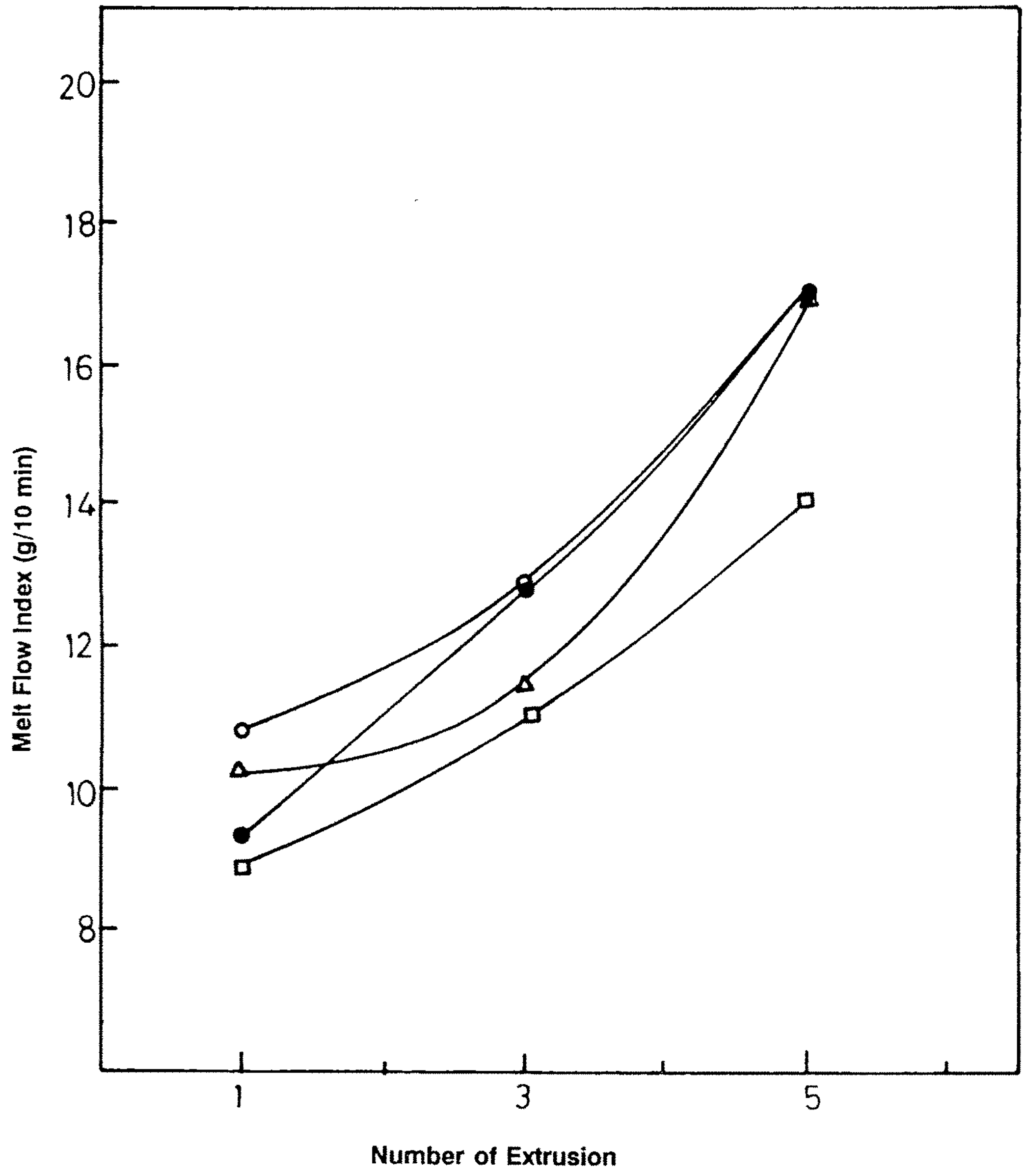


Fig. 4.2 Melt flow index (MFI) plotted against the number of extrusions for unstabilised IPP stabilised with antioxidants; (O) AO$_1$, (Δ) AO$_2$, (●) AO$_3$, (□) AO$_4$.

In case of AO_2, the concentration of this antioxidant is higher (0.045) than that of BHT (AO_1) (0.035). Here the MFI values of AO_2 after 1st and 5th extrusions are 10.21 and 16.99 respectively and those of AO_1 are 10.78 and 16.96 respectively. From the Table and the graph, it can be observed that as the number of extrusion increases, the MFI values increase indicating the degradation of IPP. The MFI values of AO_2 are quite similar to those of AO_1 However, in case of AO_1, the concentration is less as compared to that of AO_2. Thus, the stabilisation performance of AO_1 with 0.035 concentration can be considered to be equal to that of AO_2 (0.045 gm)

In case of AO_3, the concentration selected is 0.035 which is same as that for AO_1 From the table and graph it can be observed that the MFI values in case of AO_3 after 1st and 5th extrusions are 9.3 and 16.89 respectively. These values are less compared to those of AO_1 after 1st and 5th extrusion which are 10.78 and 16.96 respectively. AO_3 could stabilise IPP to a better extent than AO_1. Here the concentrations of both the antioxidants have been same (0.035)

With the synthesised antioxidant AO_4, the concentration of AO_4 is less (0.025) compared to that of AO_1 (0.035). From the table and graph, it can be observed that the MFI values after 1st and 5th extrusions are 8.9 and 14.05 respectively which are less compared to those of AO_1. So AO_4 could work more efficiently with a lesser concentration (0.025) compared to that of AO_1.

Klemchuk and Lihorng[14] showed that, hindered phenols provided significant protection against the chain scission which took place in unstablise polypropylene. As a result of this there is a reduction in the melt flow values of IPP from its original value and as the number of extrusion increases the MFI increases. In the present studies, similar results were obtained with synthesised antioxidants AO_3 and AO_4. This could be seen from the Table 4.4. that after 1st extrusion the MFI values are 9.3 and 8.9 in case of AO_3 and AO_4 and the MFI values after 5th extrusion are 16.89 and 14.05 respectively. So from the above studies it can be concluded that unstabilised polypropylene can be stabilised with synthesised antioxidant like AO_3 and AO_4 better than with BHT, also AO_3 and AO_4 can be effectively used as melt stabiliser for unstabilised polypropylene.

Chucta [2] reported that as unstabilised IPP passes through number of extrusions through the twin screw extruder, the chain scission occurs along the polymer backbone causing a reduction in molecular weight and loss of physical properties. Paolino[15] has also reported that the degradation takes place via chain scission and this results in decrease in molecular weight and melt viscosity and at the same time an increase in melt flow values. According to Gugumus [16] as the degradation of IPP proceeds, the MFI values increase, whereas the molecular weight and melt viscosity decrease.

The results of the present studies also showed the increase in MFI values as the extrusion proceeds. But it is quite clear from the MFI values that the degradation of unstabilised IPP could be controlled more effectively with AO$_4$ and AO$_3$ than 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)

Differential Scanning Calorimetry (DSC) :

Temperature changes in the sample are due to endothermic or exothermic transitions caused by reactions such as phase changes, fusion, boiling, sublimation, vaporization, dehydration reactions, dissociation or decomposition, oxidation or reduction, destruction of crystalline lattice structure and many others.[17] Generally speaking, phase transitions, dehydration and some decomposition reactions (chain scission) produce endothermic effects, whereas crystallisation, crosslinking or polymerisation, oxidation and other decomposition reactions produce exothermic effect.[18]

Calorimetric studies have proved to be of immense value in probing the morphology of polymers. [19] The earlier calorimetric studies of IPP sought to establish a relationship between the polymer melting point and isotacticity[20-22] The physical properties of IPP are essentially determined by its degree of tacticity or crystallinity and molecular weight Isotactic polypropylene is a semicrystalline polymer capable of producing multiple peaks in its melting endotherm. [23] Literature values of heat of fusion of hypothetical 100% crystalline IPP show wide discrepancies ranging from 15.4 to 62 cal/g The most reliable value seems to be 59 8 cal/g as obtained by calorimetric measurements in connection with data on crystallinity derived from X-ray diffraction. The experimental heats of fusion for polyolefins are ofcourse considerably lower than the values cited in literature because of their partially crystalline character.[24] The typical DSC thermograms (Figure 4.3 - 4.14) agree very well with those reported in literature. Values of heat of fusion (ΔHf^*) are listed in Table 4.5. It is clear from the thermograms and the values from the table that the synthesised antioxidants are as good as BHT. The enthalpy of fusion of the synthesised antioxidants AO_2, AO_3 and AO_4 was found to be equal to that of BHT. Thus we can say that synthesised antioxidants are as good as BHT, as far as thermal properties of IPP are concerned. The unstabilised polypropylene is expected to show decomposition at a much lower temperature. But when it is stabilised with BHT or AO_2, AO_3, AO_4, it showed decomposition at higher temperature. Moreover repeated extrusions in presence of BHT or AO_2, AO_3, AO_4 do not affect the thermal stability The percent crystallinity was calculated on the assumption that heat of fusion ΔHf^0 of 100% crystalline IPP is 50 Kcal/gm.[25] The heat of fusion is directly proportional to the amount of crystalline IPP in the sample. From the values it has been observed that the % crystallinity decreases as the extrusions increase from 1st to 5th both with the standard and synthesised antioxidants. The % crystallinity values of IPP with synthesised antioxidants AO_2, AO_3, AO_4 are quite comparable with those values of commercially available antioxidant BHT. From the above study it can be concluded that as the % crystallinity decreases the molecular weight also decreases and as a result there is increase in the MFI values.

Performance Properties :

Heat Deflection Temperature (HDT) :

The heat deflection temperature values were plotted against the number of extrusions (Figure 4.15). From the Figure 4.15 and Table 4 7 it can be observed that as the number of extrusions increase, the HDT values decrease and as a result the polymer gets degraded and consequently, the molecular weight and melt viscosity decrease, at the same time MFI values increase. The same pattern of graph was observed with AO_1, AO_2, AO_3, and AO_4 From the graph and table it has been observed that unstabilised polypropylene gets degraded faster in presence of BHT as compared to IPP in presence of AO_2, AO_3 and AO_4 The HDT values of IPP in presence of BHT is high compared to that of synthesised antioxidants. Among the synthesised antioxidants AO_2, AO_3 and AO_4, AO_4 could stabilise IPP more efficiently than AO_2 and AO_3.

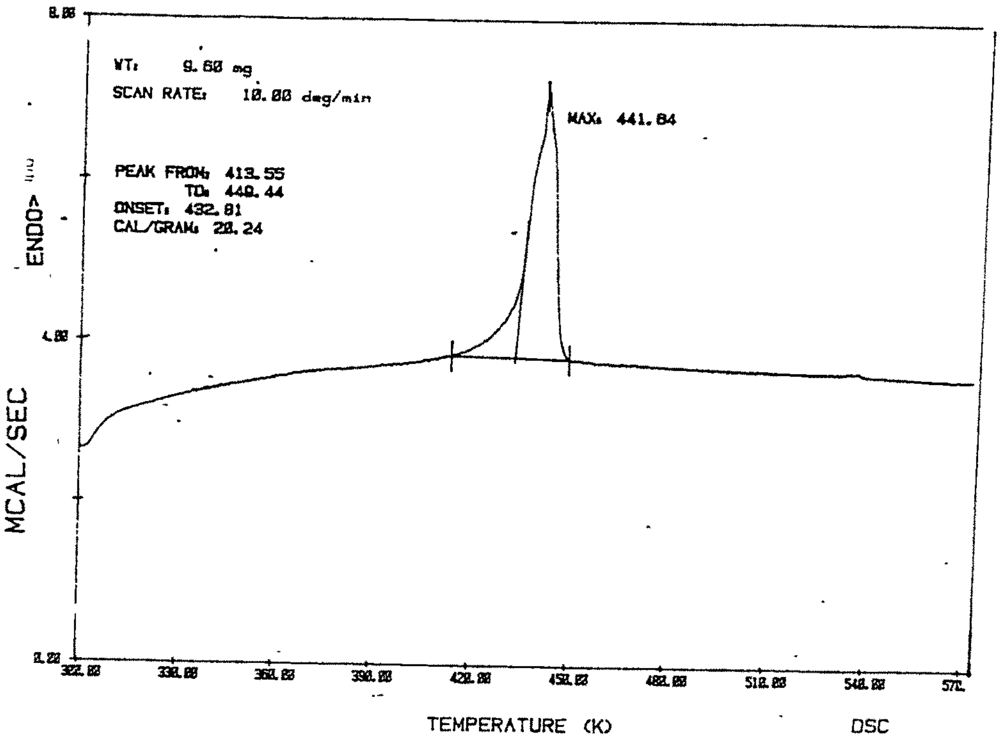


Fig. 4.3 DSC thermogram of unstabilised IPP with AO1 after 1st extrusion.

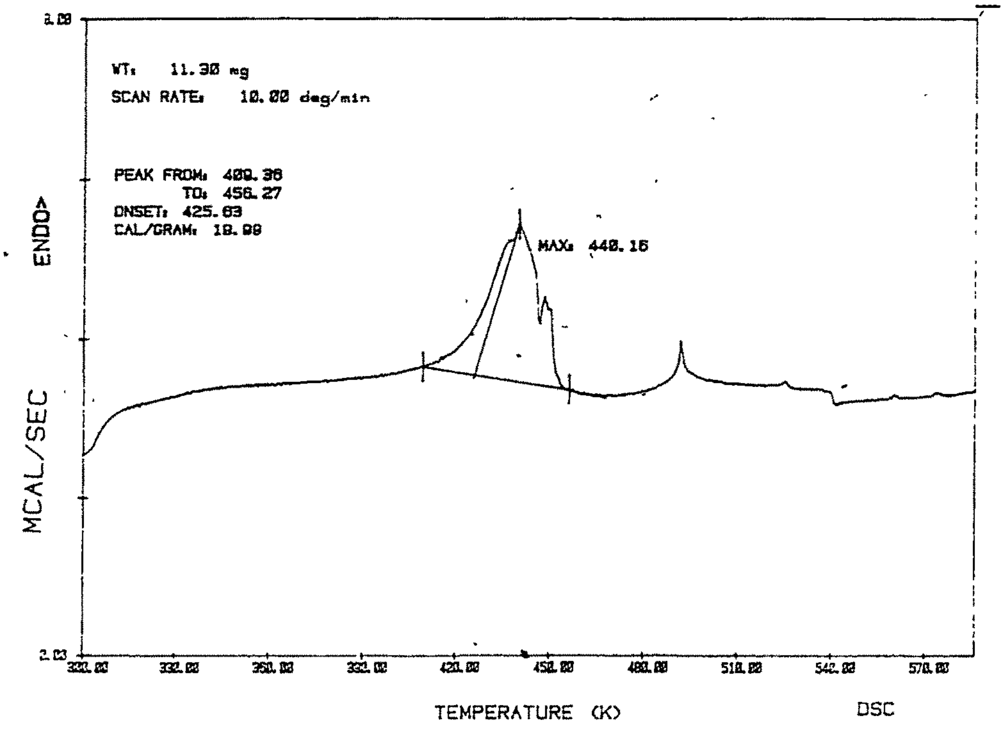


Fig. 4.4 DSC thermogram of unstabilised IPP with AO1 after 3rd extrusion.

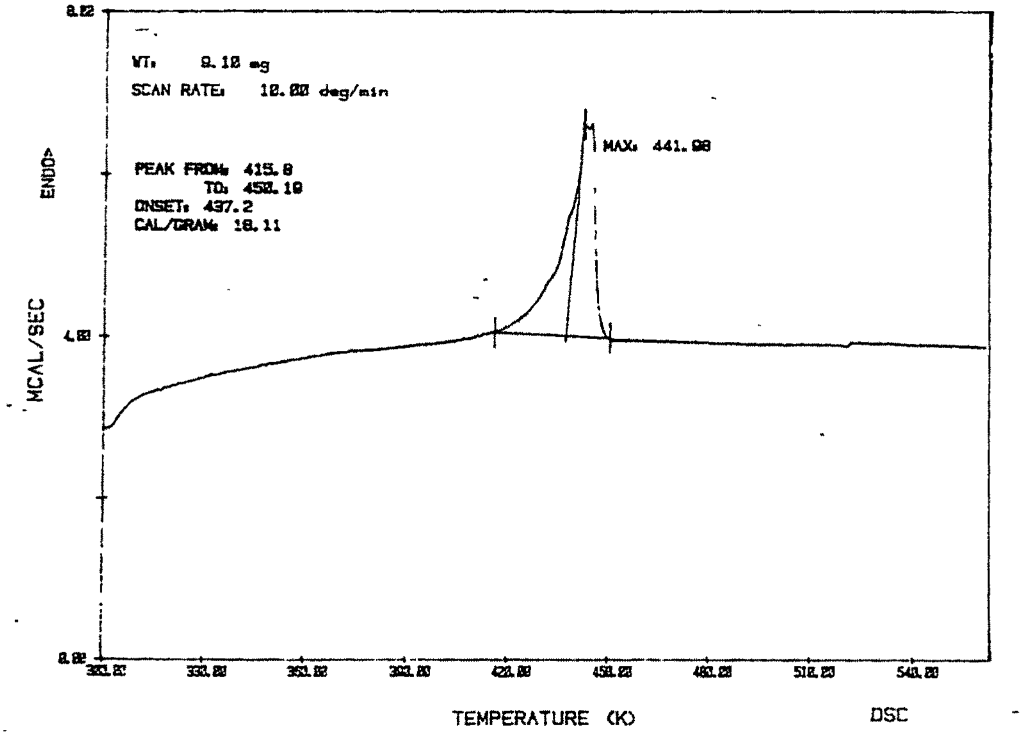


Fig. 4.5 DSC thermogram of unstabilised IPP with AO_1 after 5th extrusion.

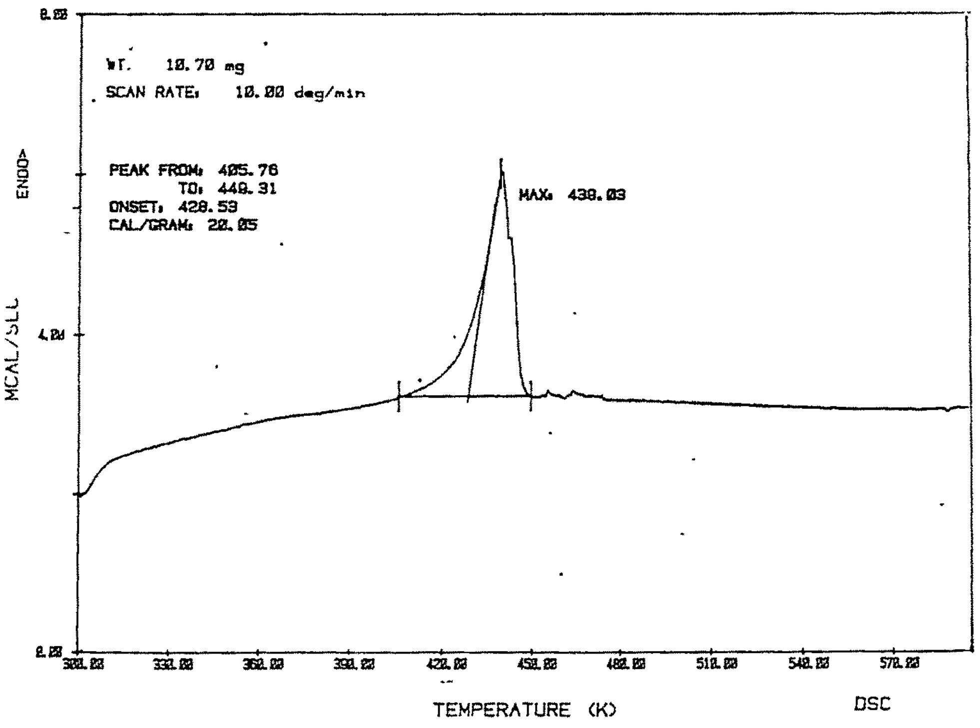


Fig. 4.6 DSC thermogram of unstabilised IPP with AO_2 after 1st extrusion.

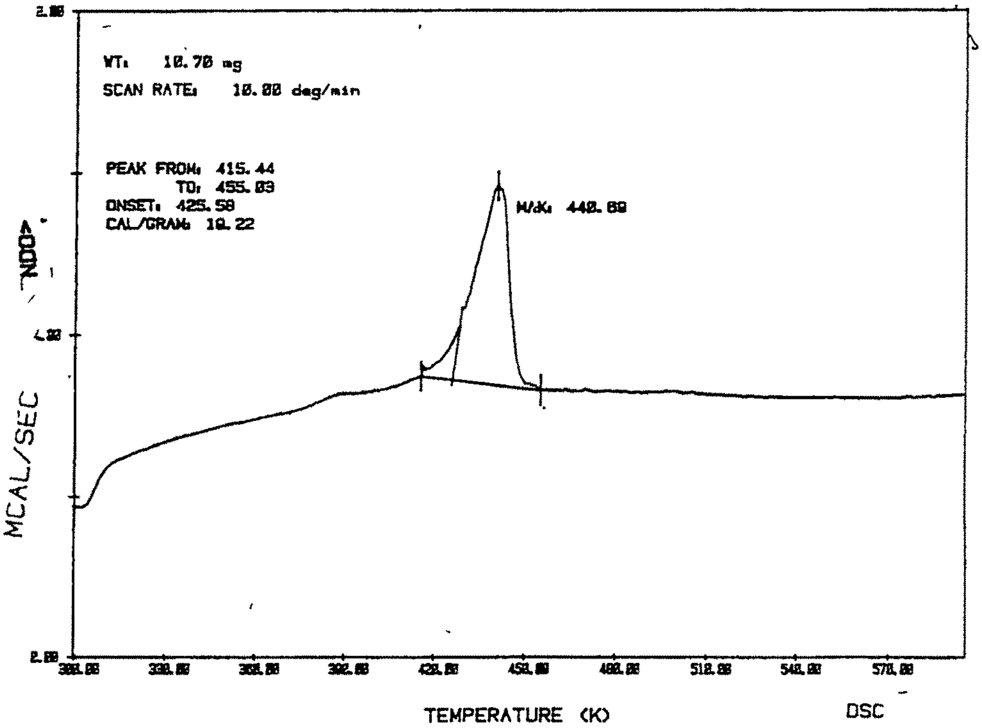


Fig. 4.7 DSC thermogram of unstabilised IPP with AO_2 after 3rd extrusion.

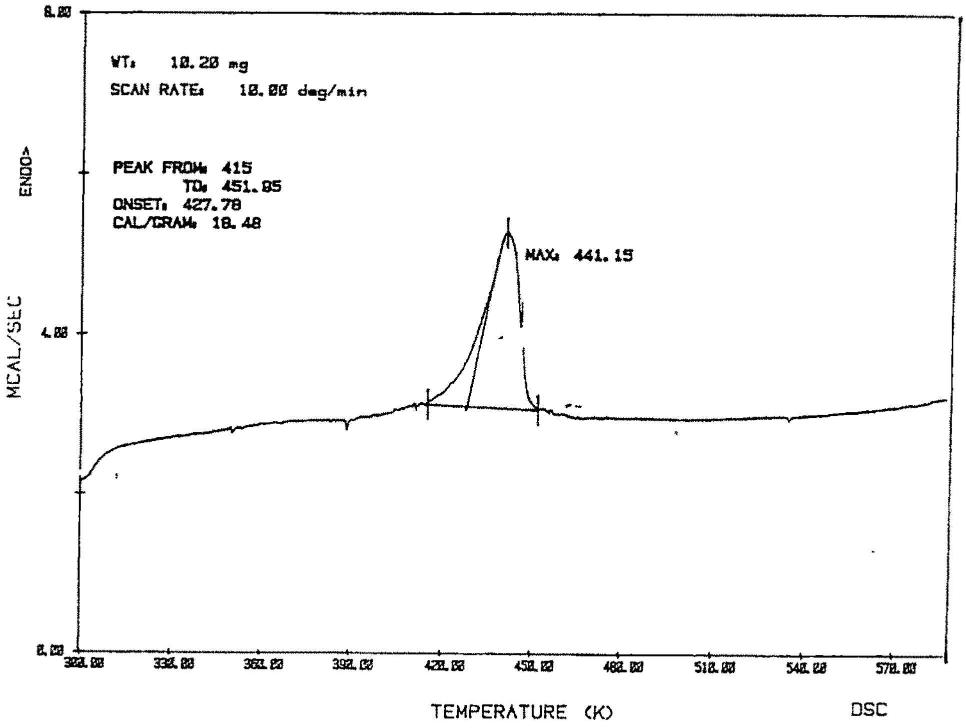


Fig. 4.8 DSC thermogram of unstabilised IPP with AO_2 after 5th extrusion.

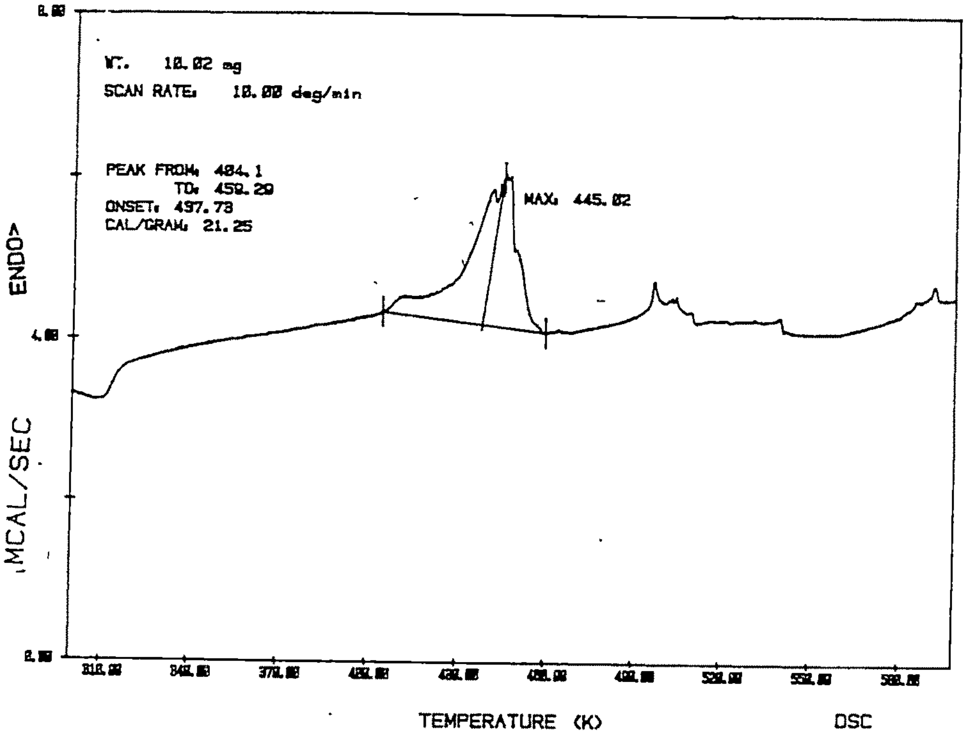


Fig. 4.9 DSC thermogram of unstabilised IPP with AO_3 after 1st extrusion.

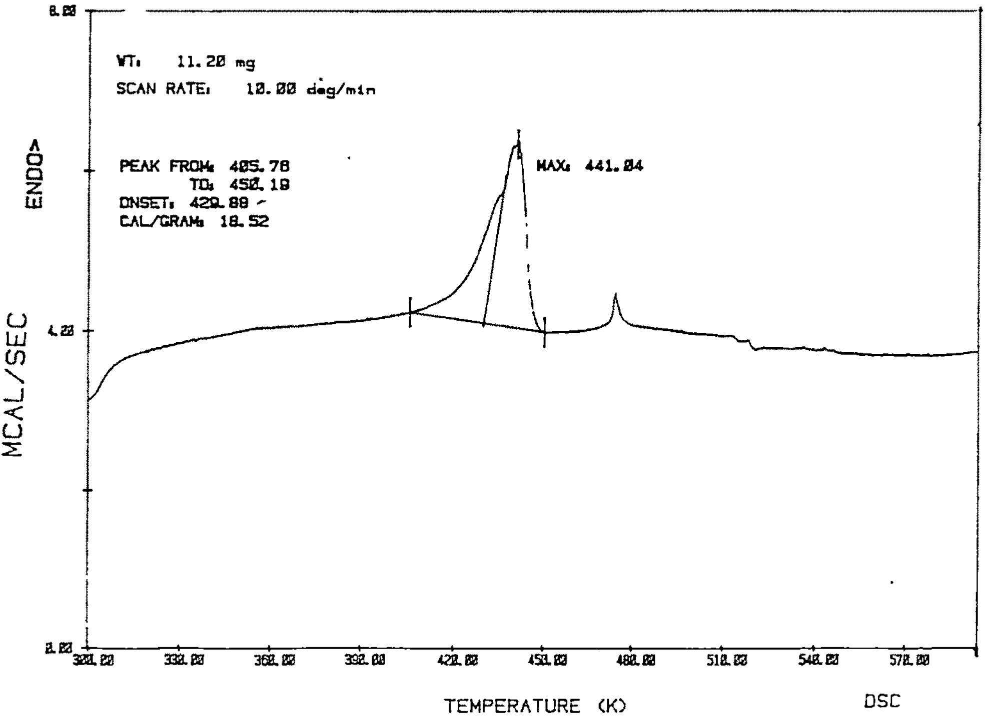


Fig. 4.10 DSC thermogram of unstabilised IPP with AO_3 after 3rd extrusion.

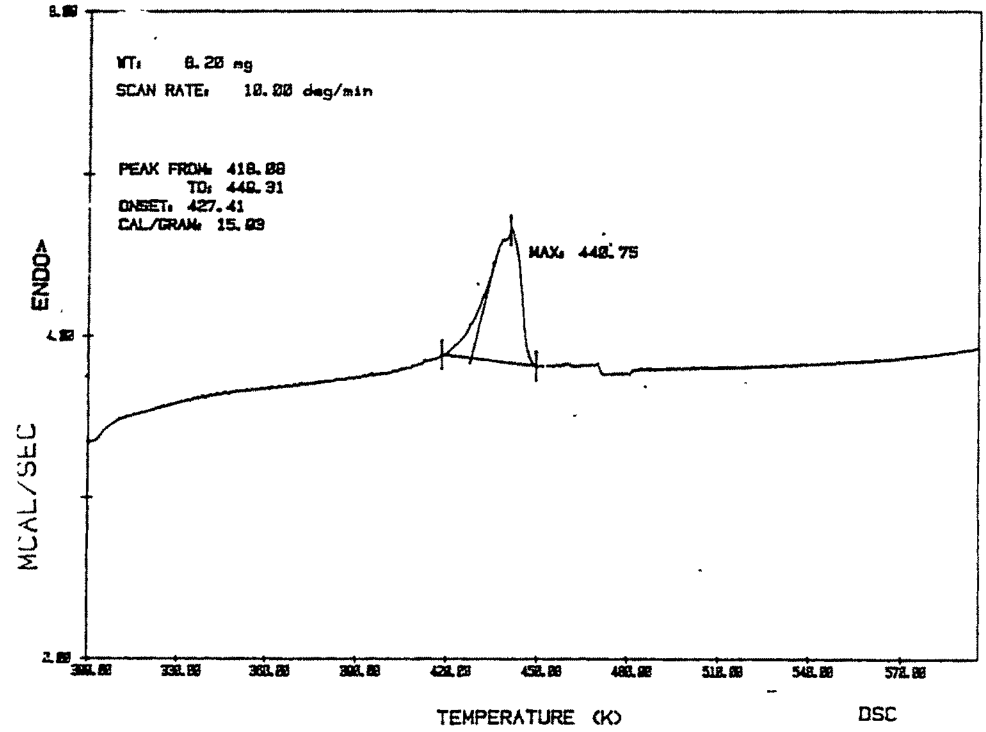


Fig. 4.11 DSC thermogram of unstabilised IPP with AO3 after 5th extrusion.

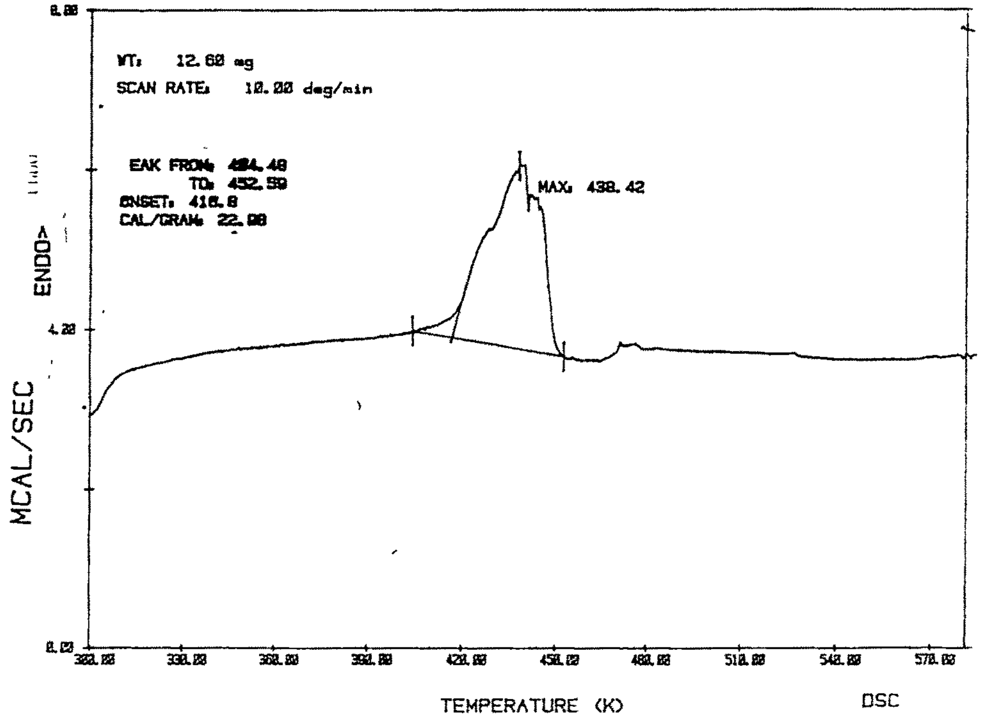


Fig. 4.12 DSC thermogram of unstabilised IPP with AO4 after 1st extrusion.

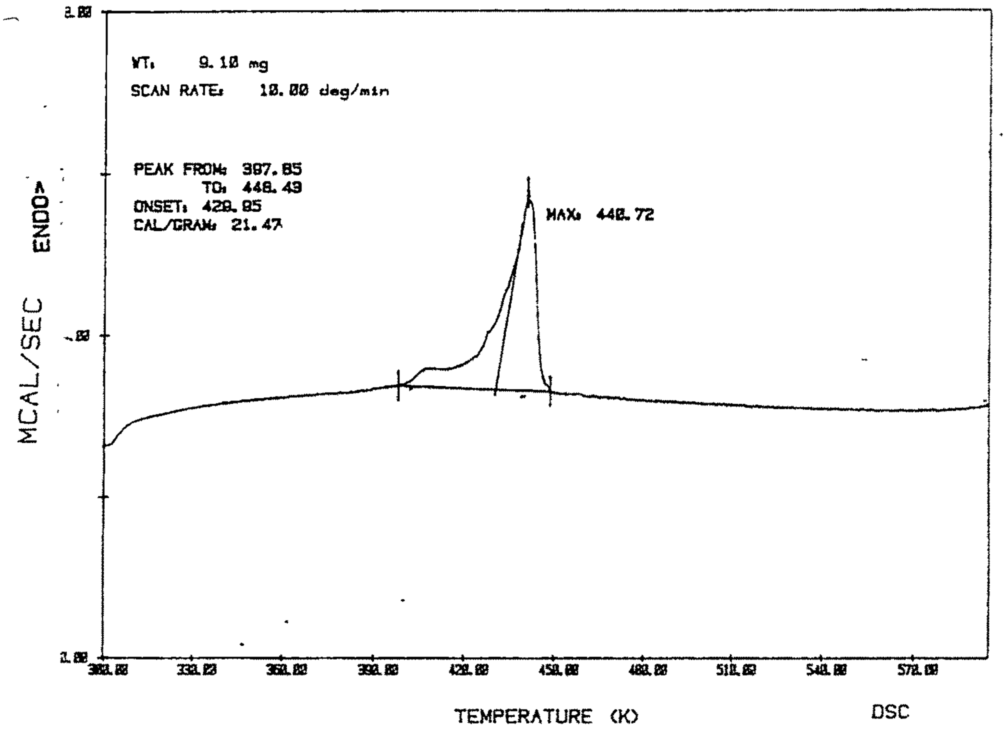


Fig. 4.13 DSC thermogram of unstabilised IPP with AO4 after 3rd extrusion.

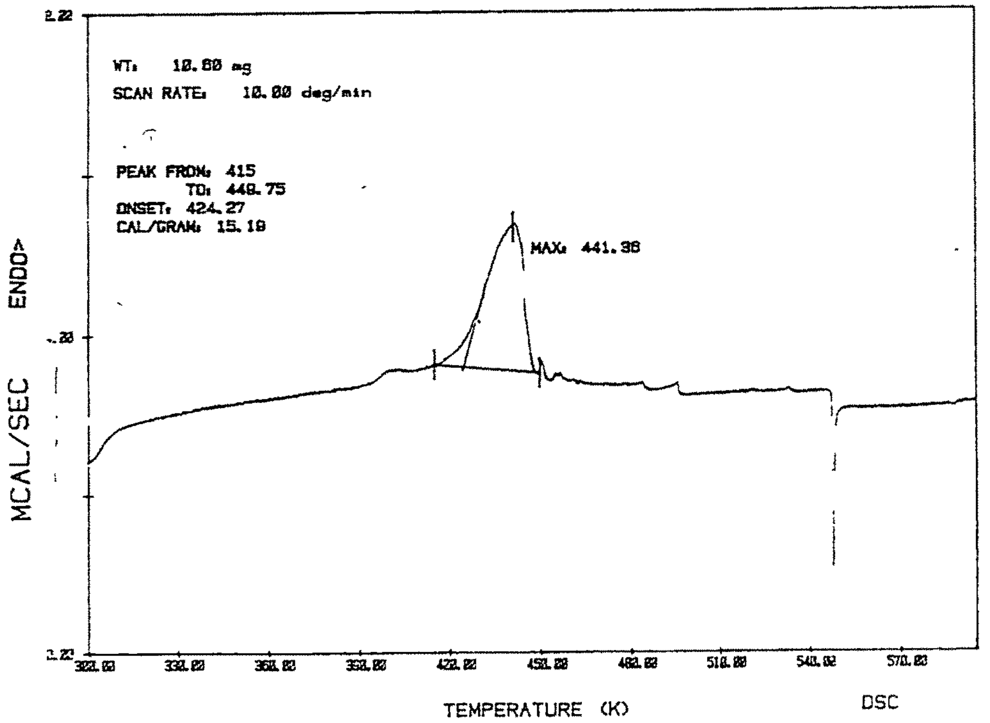


Fig. 4.14 DSC thermogram of unstabilised IPP with AO4 after 5th extrusion.

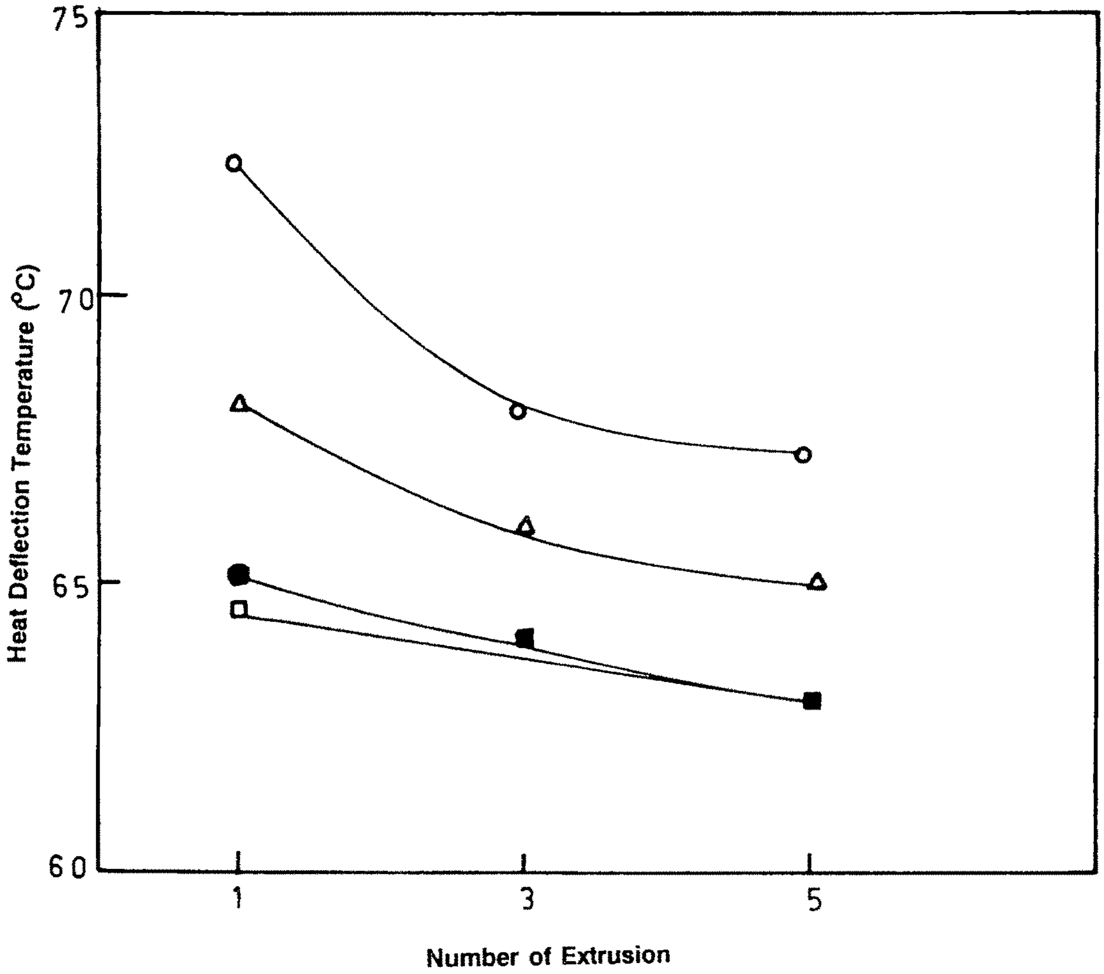


Fig. 4.15 Heat Deflection Temperature (HDT) plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO_1, (△) AO_2, (●) AO_3, (☐) AO_4.

Izod Impact Strength (IS) :

The Izod impact strength was plotted against the number of extrusion as shown in Figure 4.16. In this case too as the number of extrusion increases, the impact strength decreases 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.[16]

Unstabilised polypropylene in presence of AO_1 showed same pattern of decrease in impact strength value as in case of synthesised antioxidants. So from the above results it can be concluded that synthesised antioxidants are comparable with commercially available antioxidant BHT (AO_1).

Tensile Strength and Tensile Modulus :

The tensile strength and tensile modulus values were plotted against the number of extrusions as shown in Figure 4.17 and 4.18 respectively. From the table and the graph, it has been observed that as the number of extrusions increase, the tensile strength and tensile modulus decrease both with BHT as well as with the synthesised antioxidants. Unstabilised polypropylene, when subjected to multiple extrusion without antioxidant got degraded very rapidly, at the same time tensile strength and tensile modulus also decrease very fast But here, IPP gets stabilised with BHT or with the synthesised antioxidants AO_2, AO_3 and AO_4. When IPP gets degraded, then it requires very less energy for elongation but as it gets stabilised it requires more energy for elongation. From the table and graph it could be seen that there is not much change in the tensile strength and modulus values after 1st, 3rd and 5th extrusions, both with the BHT and synthesised antioxidants. The values of tensile strength and tensile modulus after 1st and 5th extrusion in case of BHT is comparable with that of synthesised antioxidants AO_2, AO_3, AO_4 So BHT can be replaced by AO_2, AO_3 or AO_4

Flexural Strength and Flexural Modulus :

The flexural strength and flexural modulus were plotted against the number of extrusion as shown in Figure 4.19 and 4.20. From the table and graph it has been shown that as the number of extrusion increases, flexural strength and modulus also decrease. As the number of extrusion increases polymer gets degraded via chain scission and as a result of this mechanical properties, flexural strength and modulus decrease and this manifests as an increase in melt flow index. Such observations have also been reported by Gugumus.[15] Here

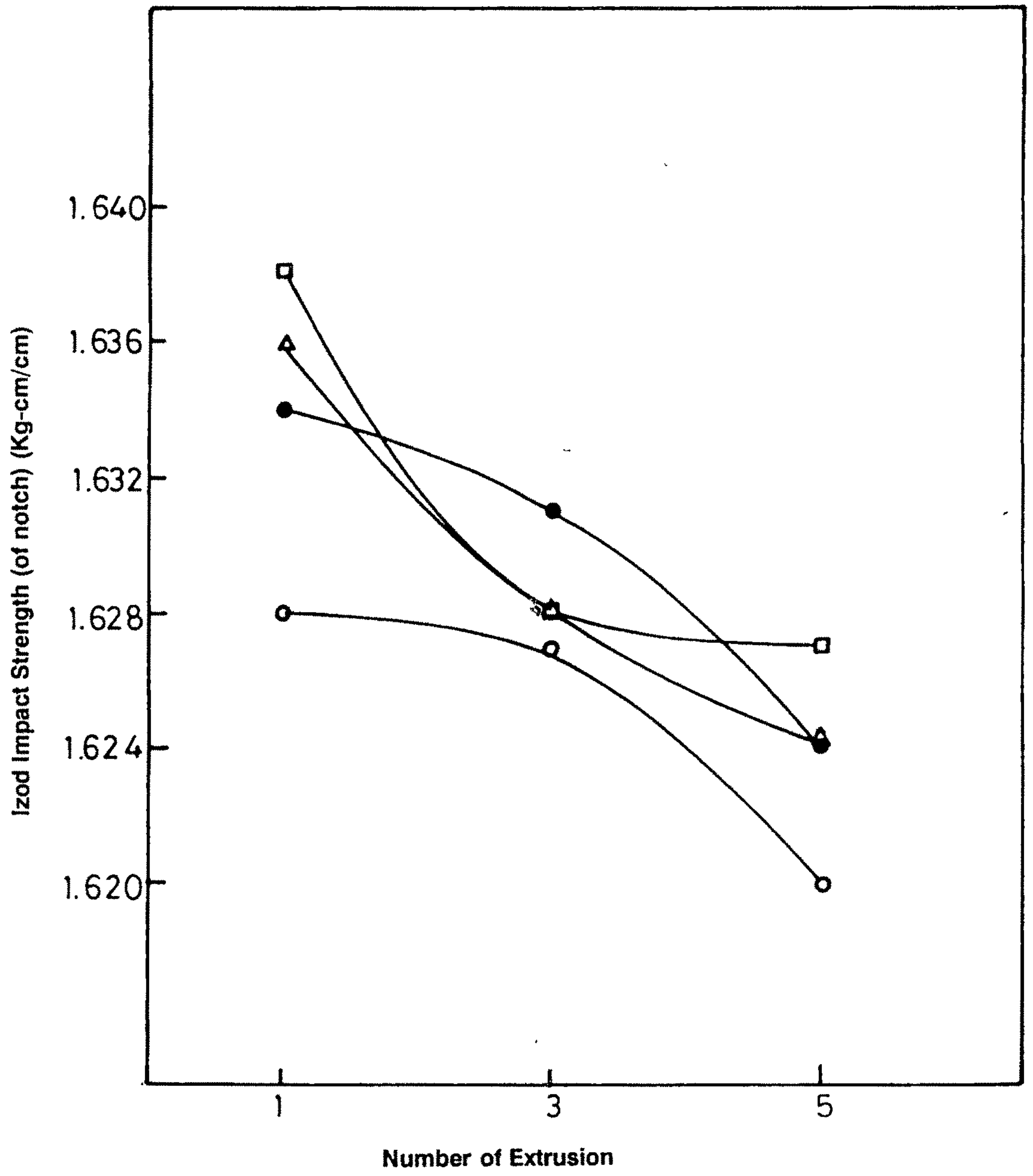


Fig. 4.16 Izod Impact Strength plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO_1, (△) AO_2, (●) AO_3, (□) AO_4.

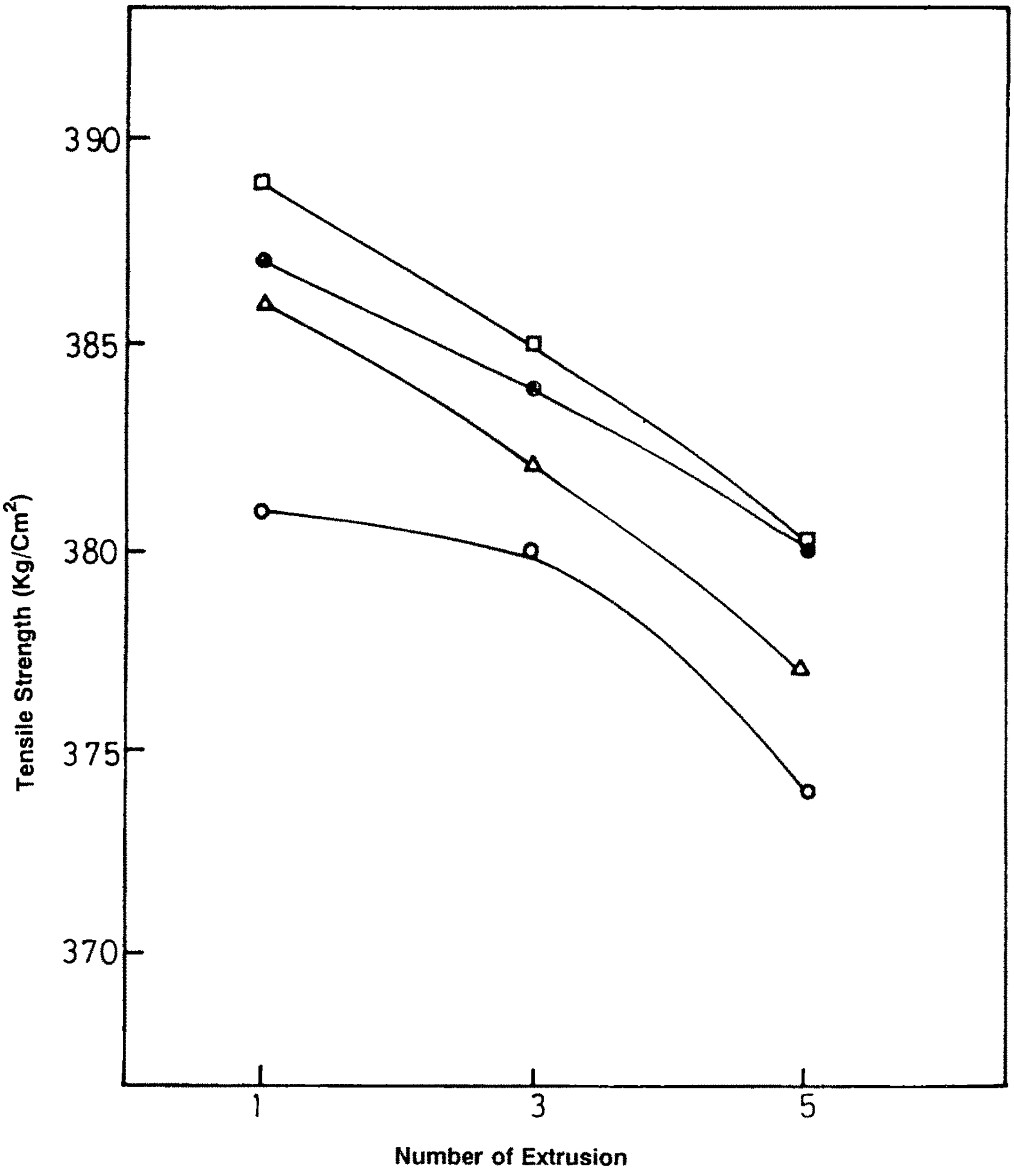


Fig. 4.17 Tensile Strength plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO$_1$, (△) AO$_2$, (●) AO$_3$, (□) AO$_4$.

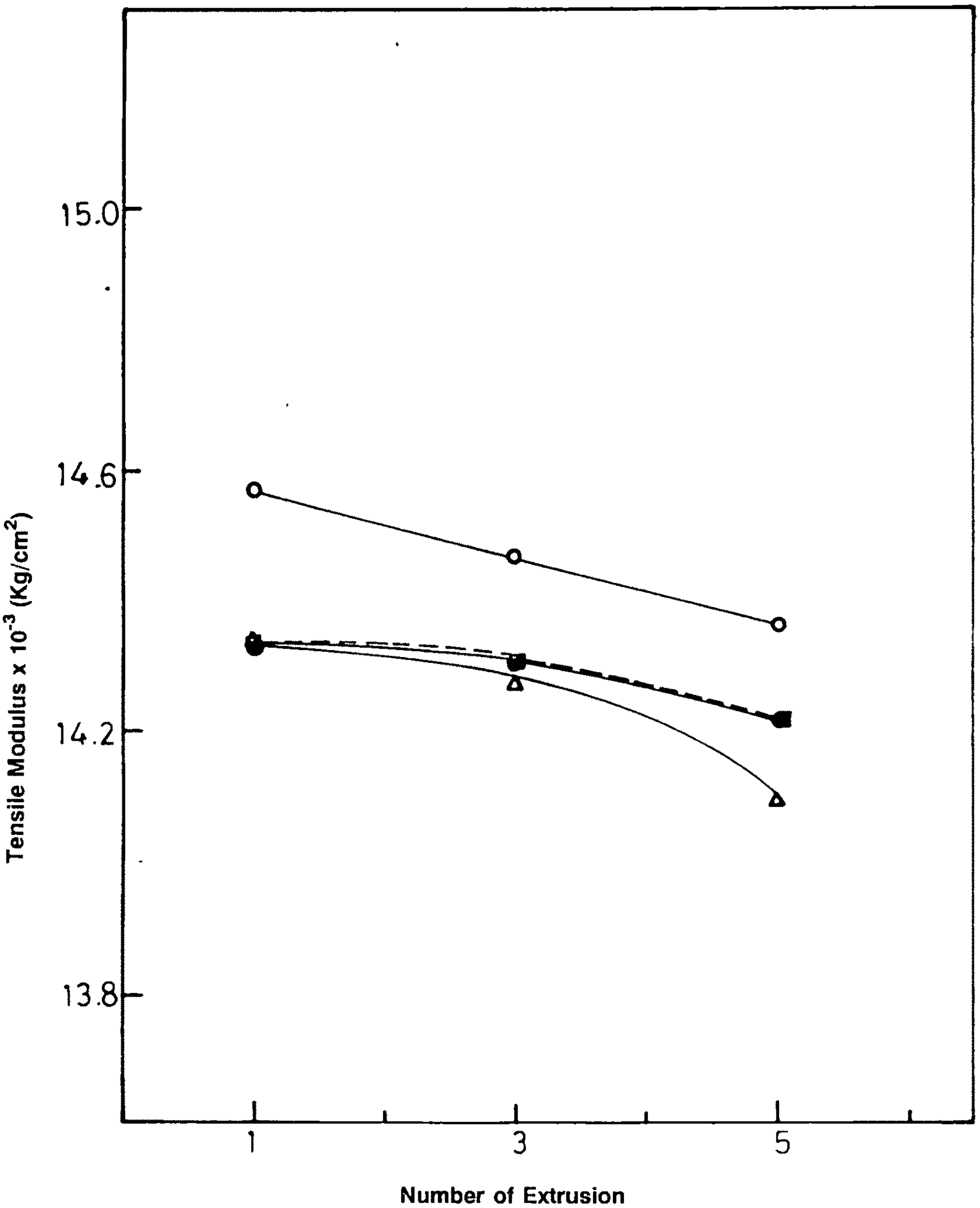


Fig. 4.18 Tensile Modulus plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO1, (△) AO2, (●) AO3, (■) AO4.

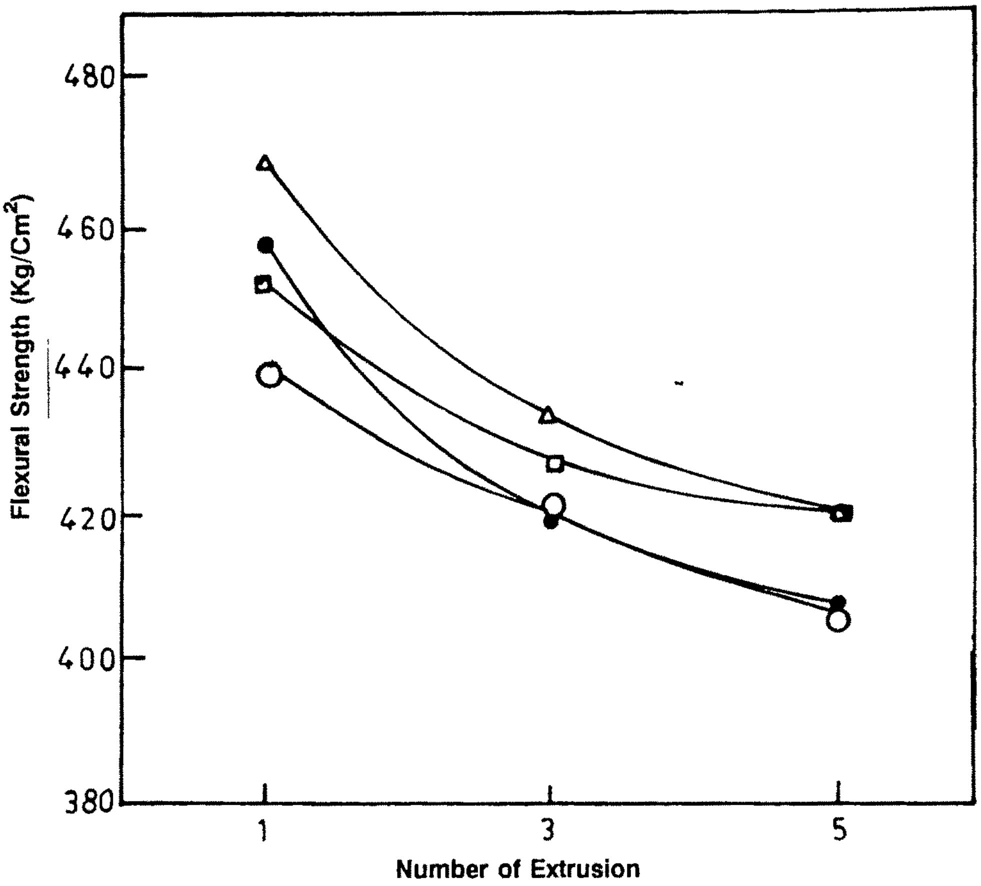


Fig.4.19 Flexural Strength plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO_1, (△) AO_2, (●) AO_3, (☐) AO_4.

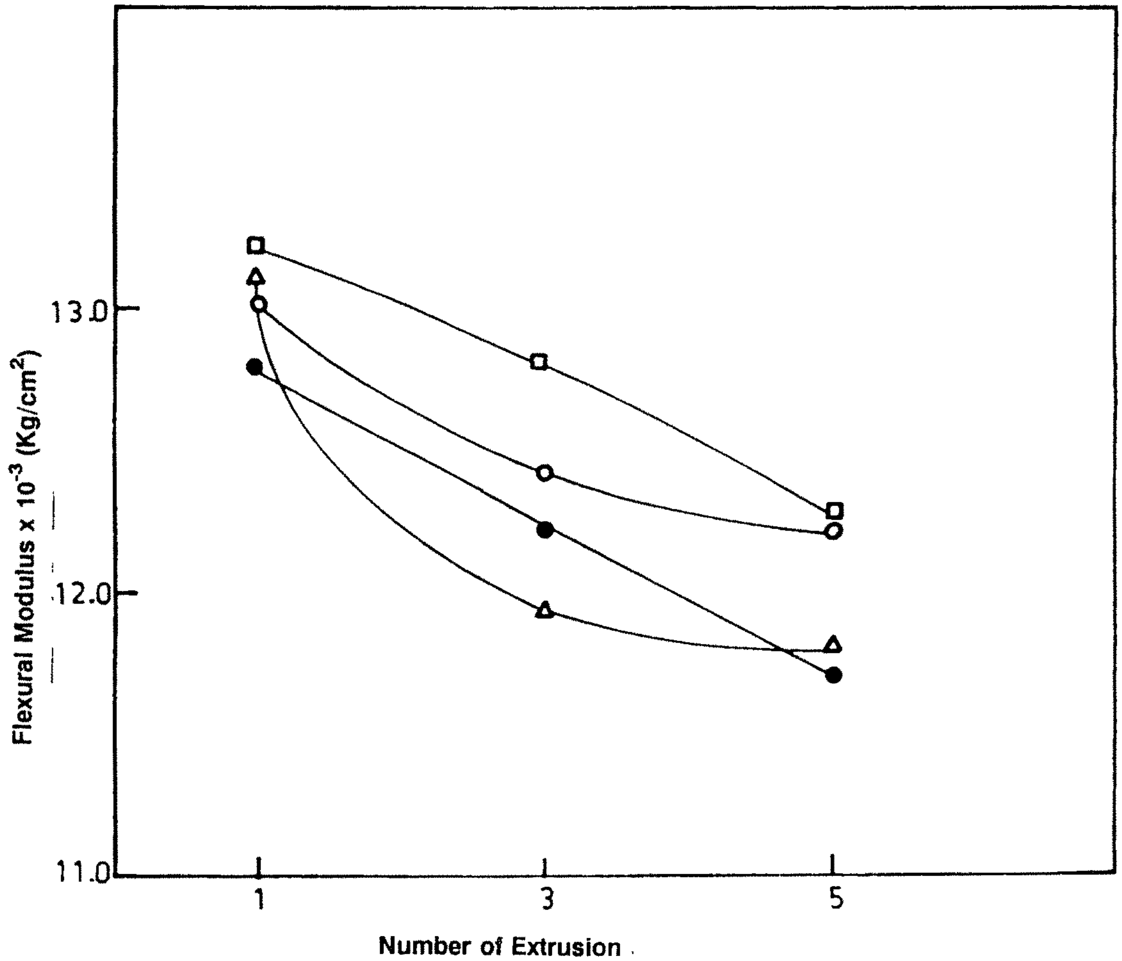


Fig. 4. 20 Flexural Modulus plotted against the number of extrusion for unstabilised IPP stabilised with antioxidants; (O) AO_1, (△) AO_2, (●) AO_3, (□) AO_4.

IPP could be stabilised either with BHT or with synthesised antioxidants so there is no considerable degradation and it requires more energy to break the samples, but as the number of extrusion increases the degradation takes place, so energy required to break the sample after 1st extrusion is more compared to the energy required to break the sample after 5th extrusion. The IPP in presence of BHT or synthesisded antioxidants showed same pattern of graph. The values of flexural strength and modulus in case of BHT were comparable with that of synthesised antioxidants. So from above studies it can be concluded that BHT can be replaced by synthesised antioxidants

From the results of the performance properties HDT, Impact strength, Tensile strength, and Modulus 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[14] that if the polymer gets degraded there is loss in mechanical properties and this could be observed from the increase in MFI valuies.

From above studies, we can explain the performance maxima of antioxidants on the basis of :

(i) Molecular weight of the antioxidant,
(ii) Relative content of hindered phenolic group, and
(iii) Individual chemical structure

The molecular weights of AO_2, AO_3 and AO_4 are 307, 341, and 780 respectively. From our studies we observed that the activity of these antioxidants increased according to the increase in molecular weight and they are in the range of 300-800.

The molecular weights of commercially available antioxidants are almost always in the range of 200-2000. The existence of such optimum molecular weight is explained by Minagawa [26] as follows. Antioxidants with smaller molecular weights may escape from the resin during processing and end use, thus imparing their performance. Antioxidants with excessively high molecular weight on the other hand may have lower compatibility with resin thus, causing decrease in effective concentration. A high molecular weight leads to low mobility, which may cause a decrease in the ratio of stabilisation. Moreover in a stabilised with high molecular weight, each molecule contains a large number of functional groups which may contribute towards stabilisation, and this may also have same effect on mobility and/or compatibility

Tochacek and Sedlar [27] have reported that values of induction period for antioxidants with hindered phenolic moiety in isotactic polypropylene is maximum in the molecular weight range 500-550. Thus there is an optimum antioxidant molecular weight, the stabilising moiety being other wise the same. According to them low efficiency at low molecular weight could be attributed to high volatility, while the reason for the loss of performance at molecular weights higher than the optimum could be likely due to the lower mobility of the stabilised molecule.

A similar phenomenon was described by Gugumus[28] for oligomeric hindred amine light stabilisers, where a maximum stabilisation efficiency was also observed although its position was shifted to a value of 2700.

Moisan [29] reported that the solubility and the ability to migrate within the polymer matrix are very important factors in determining the effectiveness of stabilisation. Maximum values of diffusion coefficient D and solubilities S in the molecular range 500-600 and 600-650 respectively are observed by Tochacek and Sedlar.[27] When they measured the effectiveness of stabilisation in a HORO they showed a some what different molecular weight dependence. The maximum induction period is shifted to higher value of molecular weight of about 850-950. This shift is believed to be caused by the volatility of the compounds.

The relationship between performance and molecular weight of hindered phenol was reported by Minagawa.[26] The data indicate the existence of an optimum molecular weight under each test condition. These molecular weights may change with test conditions, applications and types of stabilisers used in combination.

From the results of the present studies, it has been observed that out of three antioxidants compared, AO_4 is more effective in stabilising IPP compared to AO_2 and AO_3. Out of AO_2 & AO_3, AO_3 is more effective than AO_2. Here the molecular weight of AO_4 is 780 and it is in the range of 550 to 950. This is in line with the observations reported by Tochacek and Sedlar. [27]

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 active than AO_2 and AO_3, again AO_3 more effective than AO_2.

Here we presume that the reason for such performance maxima can be attributed to the influence of the individual chemical structure of the antioxidants The role of molecular weight seems to represent just a complimentary factor out of many. We suppose that more than molecular weight itself, the influence of the individual structure is responsible for the maxima of performance. Each structure is characterised by its physical properties and its behaviour in polymer. The presence of performance maxima reported by different authors at different molecular weights support this idea.[26-28]

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 promoted 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.

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