Chapter 5

Hindered phenols as stabilisers for Polypropylene-copolymer

The performance of polyolefin based antifacts is adversely affected through various stages of life cycle involving polymer manufacture, storage, processing and the environment. They are highly susceptible to attack by molecular oxygen and the auto-oxidation process is the major cause of irreversible deterioration leading to loss of useful properties and ultimate mechanical failure of the polymer antifacts [1].

Polypropylene-copolymer (PPCP) is the most oxidisable polymer amongst the major commercial polyolefins. The oxidative degradation processes of PPCP, however, are normally accelerated under the influence of temperature, UV light, mechanical stress, atmospheric pollutant and metal ion contamination.

The adverse effect of oxidation, however, can be minimised by the use of oxidation inhibitor referred to as antioxidants. The effectiveness of melt processing antioxidants is normally assessed by subjecting the polymer containing antioxidant to the processing conditions similar to those used in practice, e.g. multiple extrusion, and measuring the change in melt flow rate of the polymer and comparing this value with control sample processed similarly but in the absence of the antioxidant. Sterically hindered phenols (chain breaking) are the most important processing antioxidant for PPCP. Important commercial examples based on alkylated hindered phenols are 2,6-di-tert-butyl-4-methyl phenol (BHT), Irganox 1010. and Irganox1076. Hindered phenols impart various degree of colour to polymer due to the formation of quinonoid transformation product. However polymer discoloration can be minimised by incorporating peroxidolytic antioxidants e.g. phosphites.

Under normal condition of thermal oxidation, the ratio of peroxyl radical to alkyl radical is high. The most effective antioxidants for the above condition of high temperature aging are hindered phenols. Antioxidant with higher molar mass and lower volatility are potentially more effective than those which have same antioxidant function but with lower molar mass and high volatility[1].

Wasson and Smith[2] reported that tert-butyl group at the ortho positions and alkyl group at the para position resulted in the most effective antioxidant activity in the alkyl phenolic type of antioxidants of which BHT is well known. *Miller and Quackenbush*[3] reported that electron donating group at para position of the alkyl phenol 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. Further more, it has been observed that the removal of such an electron withdrawing group at the para position of hydroxyl group in 3,5-di-tert-butyl-4-hydroxybenzaldehyde resulted in the recovery of antioxidant activity.

Antioxidants are intended to provide protection to polymers during processing. They must be capable of migrating freely throughout the polymer mass to reach the large number of initiation sites that are generated at elevated temperature[4]. For this reason, low molecular weight antioxidants like BHT are preferred. However BHT suffers from a major drawback of high volatility. The 2,6-di-tert-butyl phenol with long aliphatic group 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[5]. This probably is the reason why the molecular weights of commercial stabilisers are almost always in the range of 200-2000, although there are some exceptions. *Minagawa*[6] reported that current tendency is towards an increase in the molecular weight of stabilisers to prevent loss from the polymer in increasingly severe conditions of applications.

PPCP because of its high heat deflection temperature is subjected to higher processing temperature and more severe service conditions. So the stabilisation of PPCP is achieved through the use of high molecular weight antioxidants. BHT was initially used as an antioxidant for PPCP but because of its high volatility it was replaced by the additive package of Irganox 1010 (hindered phenolics) and Irgafos 168 (phosphite stabilisers). A serious drawback of phosphite stabilisers is their sensitivity towards hydrolysis, which leads to the formation of phosphorus acid. This can cause corrosion to processing equipments. Thus efforts are being made for improving the additive package for PPCP.[5]

A co-operative interaction between more than one antioxidant (or antioxidant functions) which leads to a greater overall antioxidant effect than the sum of separate individual antioxidants is referred to as synergism. Synergism can arise from the combined action of two chemically similar antioxidants, e.g. two hindered phenols known as homosynergism. When two different antioxidant functions are present in the same molecule, the effect is known as autosynergism. The co-operative effect between mechanistically different class of antioxidants, e.g. the combined effect of chain breaking antioxidant and peroxide decomposer is referred to as heterosynergism[7].

Present Work

The present work was started with a view to modify the structure of BHT by introducing a bulky group at the position para to hydroxyl group and to check the stabilisation efficiency of the synthesised antioxidants in PPCP by paying special attention to the change in melt flow rate (MFR) and oxidative induction time (OIT).

In this chapter the antioxidant activity of six different antioxidants [AO1-AO6] is discussed. Commercial antioxidant and all the synthesised antioxidants were separately mixed with PPCP and were subjected to melt mixing and multiple extrusion. After melt mixing and multiple extrusion, melt flow behaviour of the extruded samples was studied and oxidative induction time of extruded samples was measured by using differential scanning calorimeter.

EXPERIMENTAL

Materials

The commercially available antioxidant 2,6-di-tert-butyl-4-methyl phenol was supplied by HICU, Bombay. The following antioxidants

1) 3,5-di-tert-butyl-4-hydroxylbenzyl triphenyl phosphonium chloride **(AO1)**
2) 4-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-5-carbethoxy-6-methyl pyrimidin-2-one **(AO2)**
3) 1-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-2-(4'-methyl phenoxy) ethanone **(AO3)**
4) N-(4'-ethylphenyl)-3,5-di-tert-butyl-4-hydroxy benzyl amine **(AO4)**
5) 1-(3',5'-di-tert-butyl-4'-hydroxybenzyl)-4- phenyl piperazine **(AO5)** and
6) 1-(3',5'-di-tert-butyl-4-hydroxybenzyl) piperidine **(AO6)**

employed in this work were synthesised in this laboratory and are discussed in earlier chapters. Unstabilised polypropylene-copolymer, grade MI 3530 having melt flow rate 4.3 g/10min at 230^0C/2.16kg load measured according to ASTM test method D1238-95, produced by M/S. Indian Petrochemicals Corporation Ltd., Baroda, India, was used for all the experiments.

Instruments

The Oxidative Induction Time tests were performed on DSC 2910 of TA instrument, USA. Melt flow behaviour of the samples was studied using Melt Flow

Indexer, (Davenport, England). Multiple extrusions were carried out using Brabender plasticorder PLV-151 (Duisburg, Germany).

The performance of antioxidant in polymer processing was assessed by multiple extrusions. The multiple extrusions of PPCP were carried out with a suitable concentration of BHT as well as the synthesised antioxidants. In order to find out the suitable concentration of BHT and synthesised antioxidants, the melt mixing was done on a Brabender plasticorder with different concentrations of BHT as well as synthesised antioxidants. The stability of polymer melt was assessed through measurement of MFR values as a function of time and temperature.

Procedure for Melt-Mixing

To 100 gm of unstabilised PPCP in powder form, 500 ppm of calcium stearate, 600 ppm of glycerine mono stearate (GMS) and 300 ppm of synthetic hydro talsite (SHT) were added. BHT and synthesised antioxidants were added individually in the concentration range of 700-900 ppm. The mixture was extruded in Brabender Plasticorder with temperature profile 180-210-230-205^{0}C with screw speed of 50 rpm. The extrudate was granulated, dried at 80^{0}C $\pm$ 2^{0}C for 1.5 hr. MFR values were recorded at 230^{0}C using 1.00, 2.16 and 3.16 kg loads in order to identify the appropriate concentration of each antioxidant which impart stability to PPCP. The MFR values recorded are given in Table 1.

Process for Multiple Extrusions

To 1000 gm of unstabilised PPCP in powder form, calcium stearate 500 ppm, GMS 600 ppm and SHT 300 ppm were added. Suitable concentration of commercial antioxidant (BHT) and synthesised antioxidants were added individually to PPCP. The mixture was extruded on Brabender plasticorder with temperature profile 180-210-230-205^{0}C at a screw speed of 50 rpm. The extrudate was granulated, dried at 80^0C ± 2^0C for 1.5 hr and subjected to second extrusion. Thus the extrusions were carried out six times with each antioxidant. Unstabilised PPCP with calcium stearate, GMS and SHT without any antioxidant was also extruded under similar conditions as a reference material.

Procedure for measuring Oxidative Induction Time

The thermo-oxidative stability of a polymeric formulation may be assessed by using differential scanning calorimeter to measure its oxidative induction time (OIT) which is the time when the onset of thermal oxidation occurs in the melt (ASTM test method D3895-95).

The instrument was temperature calibrated at 1^0C min^{-1} using tin and indium standards. Each sample was placed in an oxidised copper pan. An oxidised copper pan was used as a reference. Each sample and reference pan was heated to 200^0C at 20^0 C/min with 50 ml/min nitrogen flow rate. After attaining equilibrium, the environment is changed from nitrogen to oxygen at same flow rate and kept in isothermal mode till the sample degraded. The OIT was taken as the time corresponding to the point at which the extrapolated exotherm intersects the extended base line. The measurement of OIT is one of the most practical and commonly used methods for obtaining information on polymer stability, antioxidant effectiveness and the degree of degradation incurred during polymer processing[8]. The thermo-oxidative stability of the first extruded samples was measured.

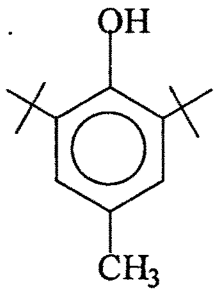
Process for measuring Melt Flow Rate.

MFR is the weight of polymer extruded through a standard orifice in a given time and is inversely related to molecular weight. MFR gives idea about melt viscosity and thus the ease of processing. MFR of the polypropylene-copolymer with different antioxidant was determined by using a rheometer (ASTM test method

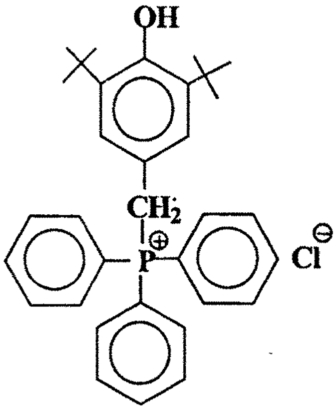
D1238-95). It has capillary die of length 8mm, diameter 2mm with driving weights of 1.00, 2.16 and 3.16 kg. MFR was taken at a temperature of 230^{0}C. The melt through the die was cut at an interval of 10 seconds and five such samples were taken and weighed. For each of the antioxidant AO1, AO2, AO3, AO4, AO5 and AO6, the experiment was repeated twice and the average value of MFR was measured.

Part 1

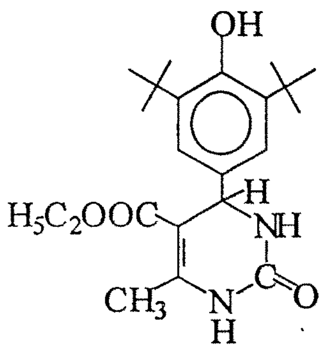
In this part the following antioxidants were selected for evaluation of antioxidant activity



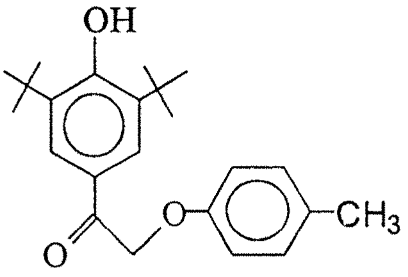
BHT



AO1



AO2



AO3

Results and Discussion

Melt mixing

The influence of different concentrations of antioxidants on MFR values of PPCP measured under three different loads is illustrated in Figures 1 to 3 and in Table 1. It is observed that the synthesised antioxidants have shown similar behaviour compared to conventional BHT towards PPCP. This is indicated by retention of the MFR values that at three different tested loads. From the MFR values for all the three concentrations at all three tested loads, the concentration at which the minimum MFR values obtained at all three tested loads was selected for multiple extrusions. Amongst the three concentrations studied, the lowest MFR values were found to be in case of 700 ppm concentration of the synthesised antioxidants as well as in case of BHT. Based on this observation the concentration of 700 ppm was selected for further studies.

Melt Flow Rate

Figure 4 shows the variation of MFR after each extrusion.

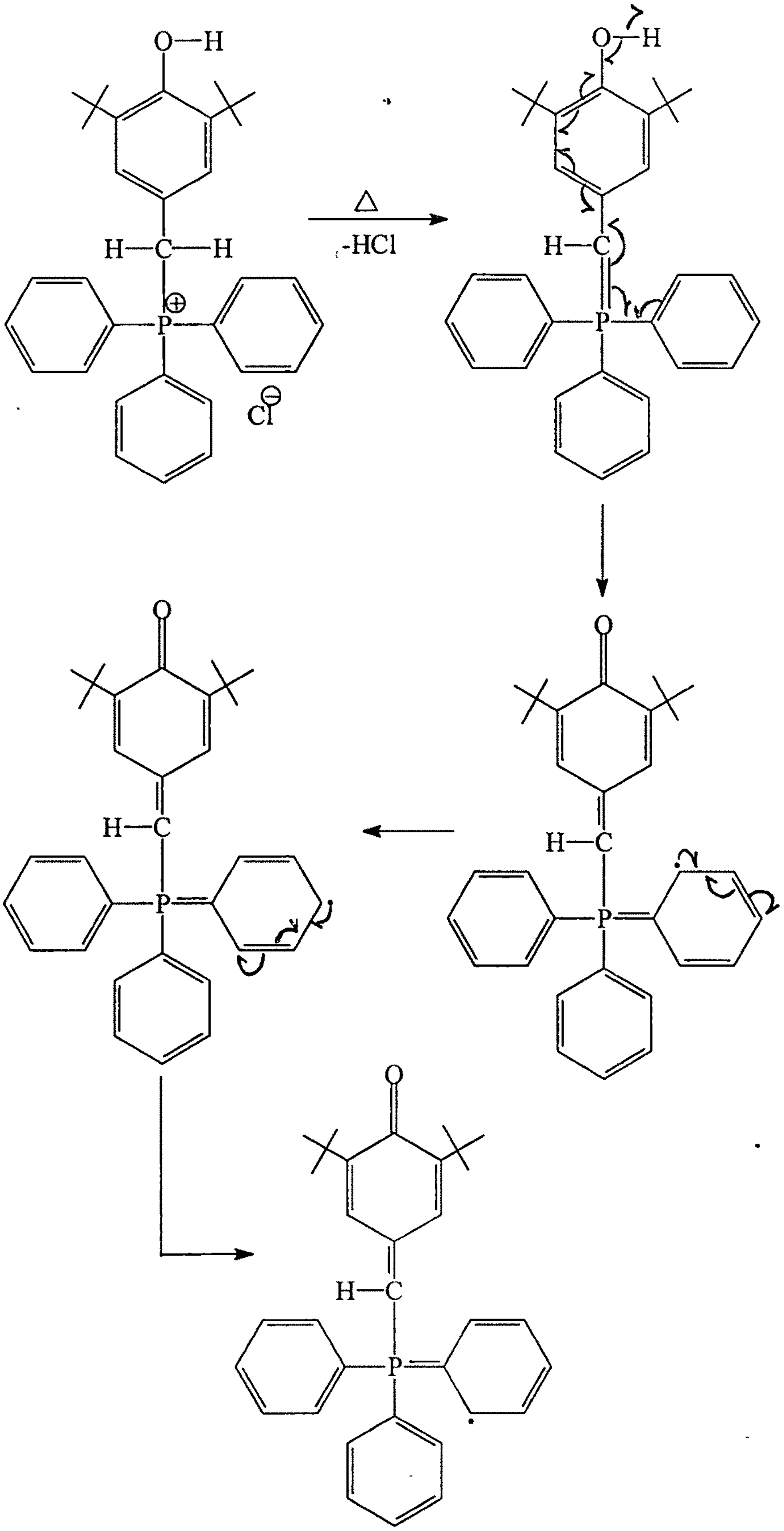
From the Table 2 and Figure 4, it is observed that the MFR values of the extruded sample increase with the number of extrusions for PPCP stabilised with BHT as well as with the synthesised antioxidants. PPCP without any antioxidant, when subjected to multiple extrusions at temperature profile 180-210-230-205^{0}C, the MFR values were found to increase from 4.60 to 16.58 g/10min. The difference in MFR values between sixth and first extrusion (ΔMFR) is 11.98 g/10 min indicating rapid degradation of PPCP, 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 gets degraded via chain scission it results in a decrease in molecular weight leading to increase in melt flow rate.[9]

It is also reported in the literature[10] that as the number of extrusions increases, the polymer undergoes degradation with reduction in molecular weight and melt viscosity which is manifested as increase in MFR.

From Table 2 and Figure 4, it is also observed that **AO1** offers higher degree of stabilisation to PPCP. The MFR values, at equal concentration of 700 ppm varied from 2.76 to 5.79 g/10 min during multiple extrusions, with ΔMFR equal to 3.03. From the ΔMFR value it can be concluded that **AO1** offers higher degree of stabilisation towards PPCP and hence it is an effective antioxidant.

The molecular weight of antioxidant **AO1** is 516.5. *Tochacek and Selder*[11] 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 **AO1**.

The antioxidant activity of **AO1** can be explained by considering the following plausible mechanism. In the Antioxidant **AO1** three phenyl rings are attached to phosphorus atom. At the extrusion temperature (230^{0}C) HCl is first removed. Hydroxy group donates hydrogen radical to peroxide radical and get converted itself into phenoxide radical. This phenoxide radical is stabilised by the three phenyl rings through resonance stabilisation. Each phenyl ring contributes three resonance stabilised structure. Stabilisation by resonance through one phenyl ring is shown in Figure 1.


Δ
-HCl

In the presence of **AO2** at 700 ppm, the MFR values increase from 2.70 to 5.09 g/10 min with 2.39 as ΔMFR value. This value suggests that stabilisation efficiency of **AO2** is more than that of BHT towards PPCP.

With the synthesised antioxidant **AO3**, the MFR values and Δ MFR values are similar to those of BHT. Here the concentration of BHT is same as that of synthesised antioxidant. Both the antioxidants show approximately equal antioxidant activity towards PPCP.

Here we presume that the individual chemical structure is responsible for the performance maxima. Each structure is characterised by its physical properties and its behaviour in polymer. The presumption is in line with the observation reported by other authors.[6,11,12]

From Table 3 and Figure 5, it is observed that the OIT value for BHT is 0.53min, which means that BHT can prevent the degradation of PPCP for 0.53min in the presence of oxygen atmosphere at 200°C under the given experimental conditions. OIT value for **AO1** is 1.90 min, which indicates that stabilisation efficiency of **AO1** is more in comparison with that of BHT. The OIT values for **AO2** and **AO3** are 2.26 and 0.60 min respectively. The OIT values for BHT and **AO3** are close indicating comparable stabilisation efficiency towards PPCP. From these values it is observed that **AO2** offers highest degree of stabilisation towards PPCP among all studied.

The degree of stabilisation and hence antioxidant activity towards PPCP for the above antioxidants under study is as follows

AO2>AO1>BHT~ AO3

Table 1 : MFR values of PPCP extruded with various antioxidants at three different concentrations measured using three different loads

Additive	**Conc. (ppm)**	**Melt Flow Rate (g/10min) at 230^{0}C using loads**		
		1.00 Kg	***2.16 Kg***	***3.16 Kg***
BHT	**700**	1.34	3.04	6.13
	800	1.42	3.22	6.49
	900	1.50	3.52	6.76
AO1	**700**	1.05	2.65	4.90
	800	1.09	2.68	5.04
	900	1.17	2.93	5.44
AO2	**700**	1.59	2.80	6.50
	800	1.81	3.25	6.82
	900	1.75	3.20	6.86
AO3	**700**	1.60	2.89	6.41
	800	1.62	3.04	6.46
	900	1.58	3.06	6.44
PPCP without Antioxidant		3.41	7.68	14.2

Table 2. MFR values of PPCP after multiple extrusions carried out at a melt temperature of 230^{0}C and screw speed of 50 rpm.

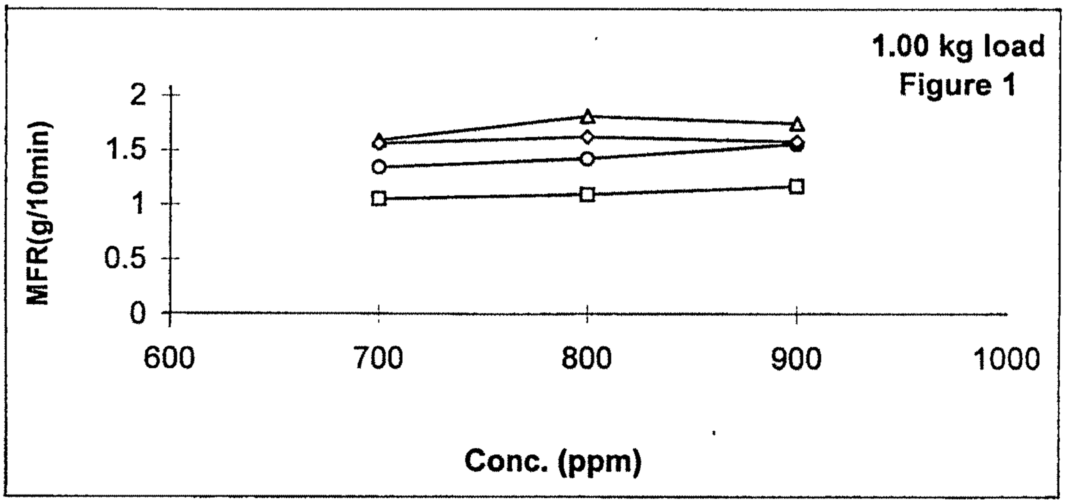
Additives	Melt Flow Rate (g/10min) at 230^{0}C/2.16kg load after Extrusion cycle						
	First	Second	Third	Fourth	Fifth	Sixth	ΔMFR[b]
---[a]	4.60	5.20	6.03	8.90	11.53	16.58	11.98
BHT	2.94	3.10	3.38	4.16	4.71	6.09	3.29
AO1	2.76	3.16	3.61	4.39	4.72	5.79	3.03
AO2	2.70	3.10	3.52	4.15	4.60	5.10	2.40
AO3	2.79	3.17	3.40	4.14	4.68	5.98	3.19

a. MFR values of PPCP extruded without antioxidant

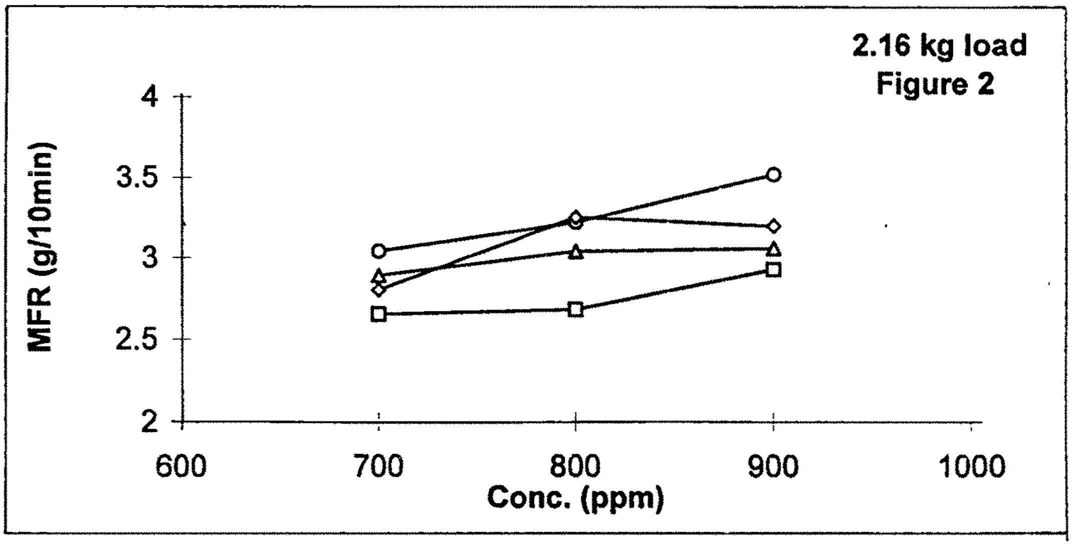
b. Difference in MFR values between sixth and first extrusion.

Table 3. Oxidative induction time values for PPCP stabilised with various antioxidants after first extrusion

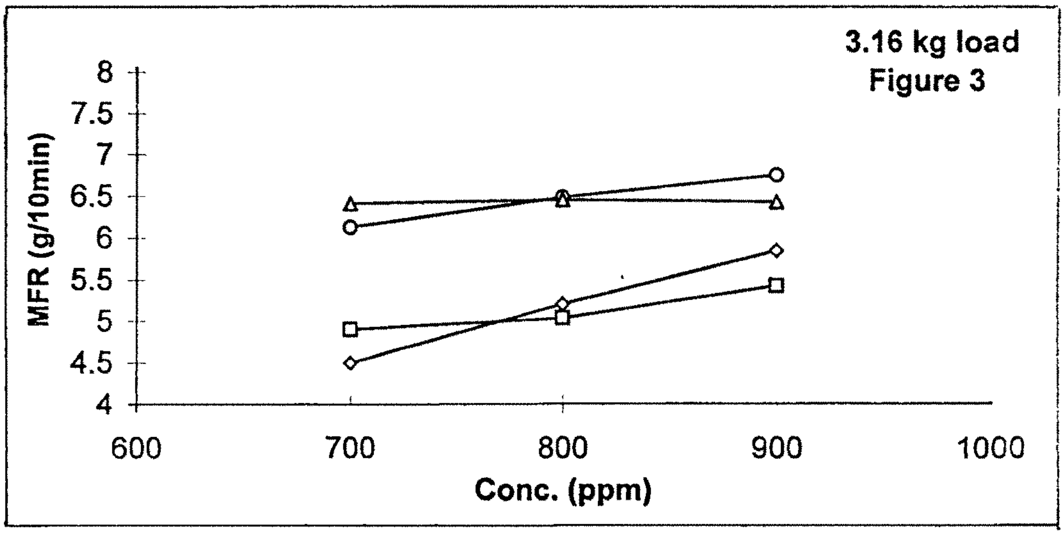
Additives	OIT (min)
BHT	0.54
AO1	1.90
AO2	2.26
AO3	0.60



1.00 kg load
Figure 1



2.16 kg load
Figure 2



3.16 kg load
Figure 3

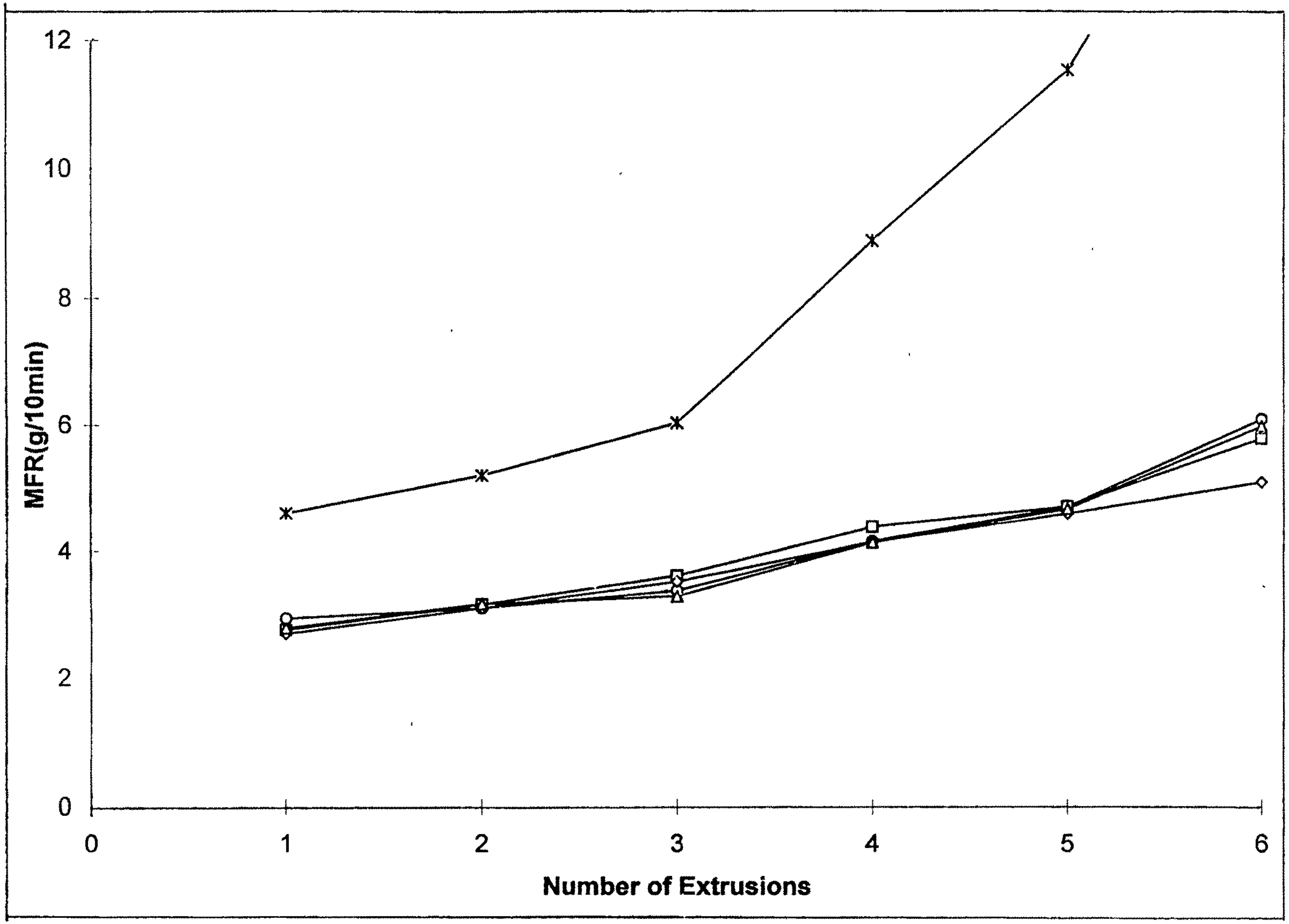


Figure 4

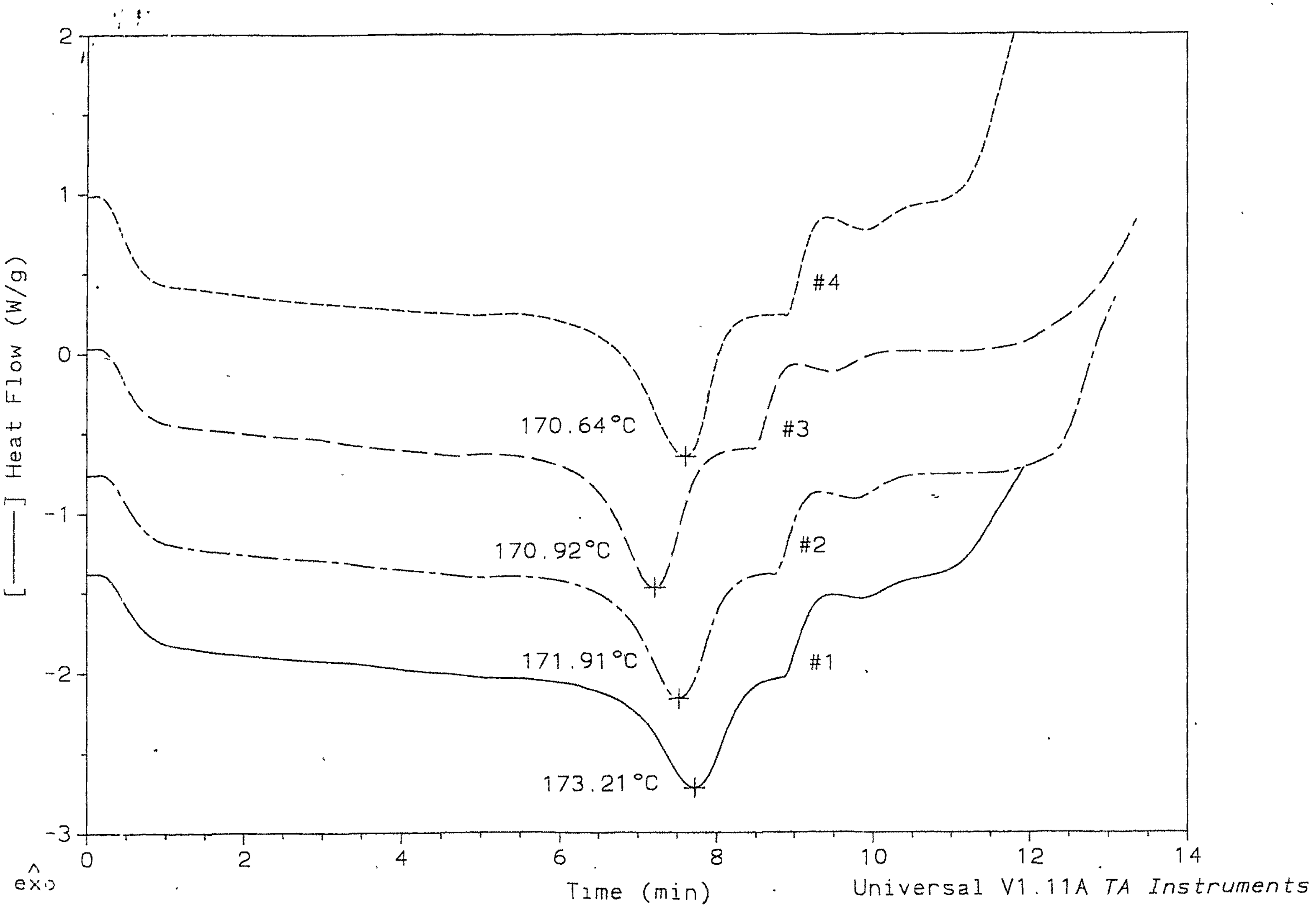
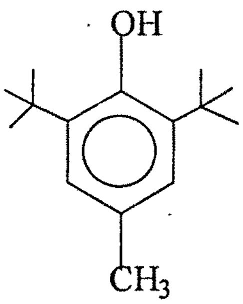

[——] Heat Flow (W/g)
2
1
0
-1
-2
-3
exo
0
2
4
6
8
10
12
14
Time (min)
Universal V1.11A *TA Instruments*
170.64°C
170.92°C
171.91°C
173.21°C
#4
#3
#2
#1

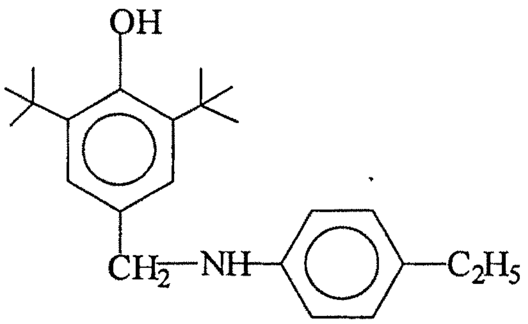
Figure 5

Part 2

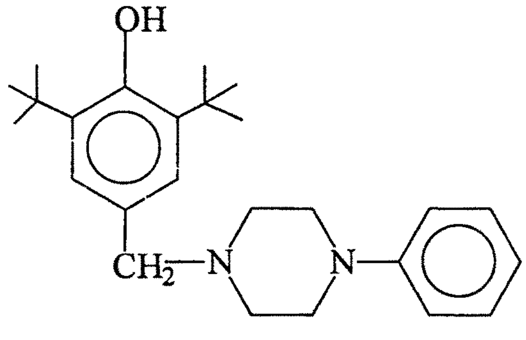
Following antioxidants were selected for activity evaluation based on hindered phenol and hindered amines and BHT served as standard.



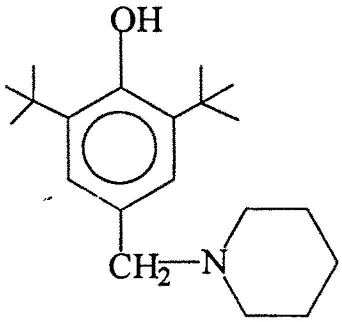
BHT



AO4



AO5



AO6

The influence of different concentrations of antioxidants on MFR values of PPCP measured under different loads is illustrated in Figures 6 to 8 and in Table 4. It has been observed that the synthesised antioxidants have shown similar behaviour as BHT towards PPCP. This is indicated by retention of the MFR values that at three different tested loads. The concentration, at which minimum melt flow rates at different loads, was identified as suitable and multiple extrusions were carried out with the identified concentration of antioxidant. It is observed that different synthesised antioxidants exhibited optimum performance at different concentrations.

Antioxidants	For 1000g of PPCP
BHT	700 ppm
AO4	800 ppm
AO5	900 ppm
AO6	700 ppm

Table 5 shows the variation of MFR values after each extrusion. From the Table 5, it is observed that MFR values of the extruded sample increase with the number of extrusions for PPCP stabilised with BHT as well as with the synthesised antioxidants.

PPCP without any antioxidant, when subjected to multiple extrusions, the MFR values were found to increase from first to sixth extrusions, i.e. from 4.60 to 16.58. The difference in MFR values between sixth and first extrusion ΔMFR=11.98 indicating rapid degradation of PPCP in the absence of antioxidant.

Table 4 shows that the minimum MFR values for BHT at all three tested loads were observed with 700 ppm concentration. Hence that particular concentration was selected for multiple extrusions. When extrusion was carried out with BHT, the MFR values do not increase rapidly. From the Table 5, it is observed that the MFR values after the first and sixth extrusions are 2.80 and 6.09 respectively. The ΔMFR value is 3.29, which implies that BHT protects the degradation of PPCP.

As mentioned earlier[10], with the increase in number of extrusions, the polymer is degraded and its molecular weight and melt viscosity decrease, which is manifested as increase in MFR values.

From Table 4, polymer exhibited stability in its melt flow rate when the antioxidants **AO4** was present at 800 ppm and this concentration was identified as optimum for multiple extrusions. The MFR values in the case of **AO4** after first and sixth extrusions are 2.91 and 5.60 respectively and ΔMFR for **AO4** is 2.69, which implies that degradation of PPCP in the presence of **AO4** is less. This indicates that **AO4** offers enhanced antioxidant activity for the stabilisation of PPCP.

From Table 4, the minimum MFR values for **AO5** was found to be at 900 ppm concentration. In the presence of **AO5**, the MFR values increase gradually from 2.83 to 5.50 from first to sixth extrusion with ΔMFR of 2.57, which is lower than that of **AO4**. These values indicate that stabilisation efficiency of **AO5** is higher than that of BHT and **AO4** towards PPCP.

It is observed from Table 4 that the minimum MFR values for **AO6** was found to be at 700 ppm concentration at all three loads. With the synthesised antioxidant **AO6**, the MFR value increases from 3.06 to 5.94 between first to sixth extrusion and so ΔMFR value is 2.88. This indicates that **AO6** offers antioxidant activity less than **AO5** and **AO6** and higher than BHT.

The oxidative induction time data from Table 6 and Figure 10 suggests that hindered phenolic group containing antioxidant BHT prevents the oxidation of PPCP for 0.54 min, where as antioxidants with combination of hindered phenol and hindered amine prevent the oxidation of PPCP for more time. The OIT value for **AO4** is 2.03min indicating that **AO4** is more effective antioxidant than BHT for PPCP stabilisation. OIT value for **AO5** is 2.91 min and that of **AO6** is 1.23 min. It is observed that AO5 showed higher antioxidant activity than other antioxidants.

The above observations support the effect of autosynergism i.e., two different antioxidant functionalities present in a single molecule. In case of **AO4, AO5** and **AO6,** hindered phenol is present in combination with hindered amine so the stabilisation efficiency of these antioxidants towards PPCP is higher than that of BHT having only phenolic stabilisation moiety.

The degree of stabilisation, and hence antioxidant activity towards PPCP for the above antioxidants under study is as follows

AO5>AO4>AO6>BHT.

The molecular weight of **AO5, AO4, AO6** and BHT are 380.95, 339.52, 303 and 220. Literature data revealed that the high molecular weight of an antioxidant ensures lower volatility[5]. From this a conclusion can be drawn that by increasing the molecular weight of an antioxidant, volatility can be decreased and hence the loss of antioxidant from the surface during processing and enduse can also be reduced.

Table 4 : MFR values of PPCP extruded with various antioxidants at three different concentrations and measured using three different loads

Additive	Conc. (ppm)	Melt Flow Rate (g/10min) at 230^0C using loads		
		1.00 Kg	*2.16 Kg*	*3.16 Kg*
BHT	**700**	1.34	3.04	6.13
	800	1.42	3.22	6.49
	900	1.50	3.52	6.76
AO4	**700**	1.09	2.82	5.41
	800	1.08	2.78	5.20
	900	1.12	2.81	5.26
AO5	**700**	1.33	3.05	5.81
	800	1.38	3.30	6.42
	900	1.21	2.90	5.71
AO6	**700**	1.22	3.05	5.67
	800	1.66	3.44	6.20
	900	1.33	3.24	5.90
PPCP without Antioxidants		3.41	7.68	14.2

Table 5. MFR values of PPCP after multiple extrusions carried out at a melt temperature profile 180-210-230-205^{0}C and screw speed of 50 rpm.

Additives	Melt flow rate(g/10min) at 230^{0}C/2.16kg load after Extrusion cycle						
	First	**Second**	**Third**	**Fourth**	**Fifth**	**Sixth**	**ΔMFR**[b]
--[a]	4.60	5.20	6.03	8.90	11.53	16.58	11.98
BHT	2.94	3.10	3.38	4.16	4.71	6.09	3.29
AO4	2.91	3.24	3.53	4.00	4.79	5.60	2.69
AO5	2.83	3.13	3.35	4.00	4.46	5.50	2.57
AO6	3.06	3.39	3.82	4.27	4.96	5.94	2.88

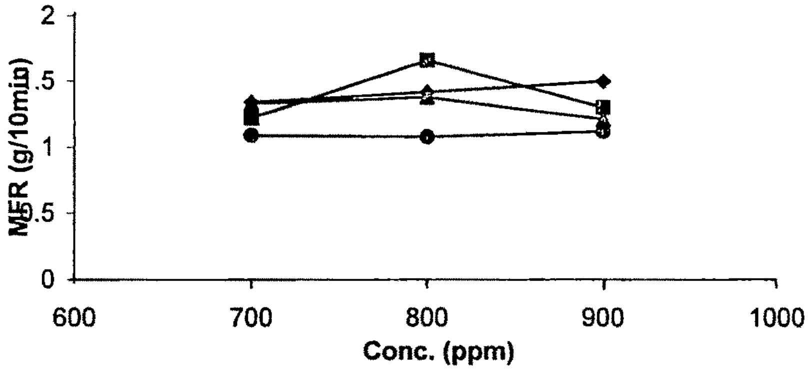
--a. PPCP extruded without antioxidant

b. Difference in MFR values between sixth and first extrusion

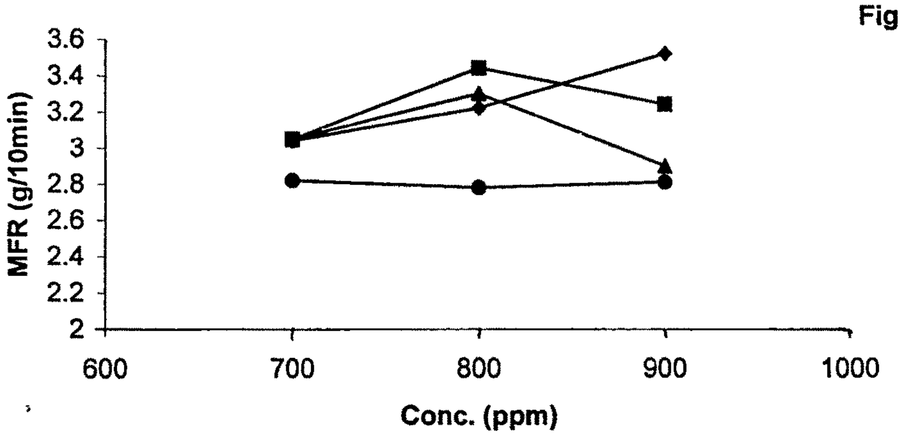
Table 6. Oxidative induction time values for PPCP stabilised with various antioxidants

Additives	OIT (min)
BHT	0.54
AO4	2.03
AO5	2.91
AO6	1.28

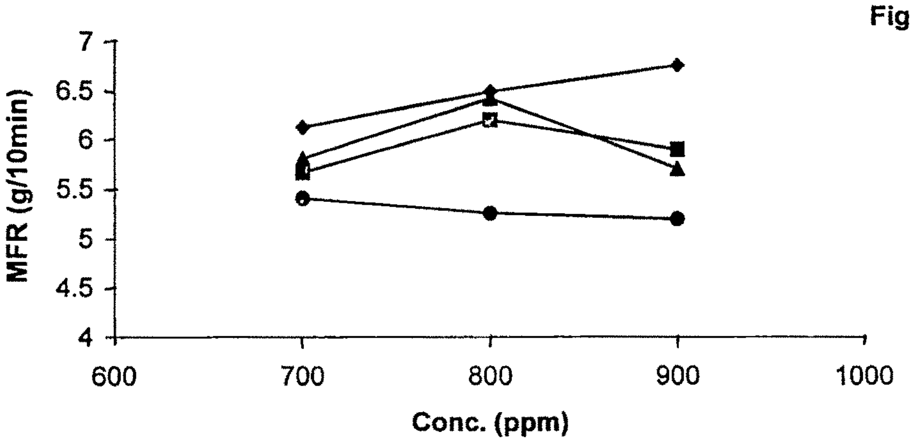
1.00 Kg load
Figure 6



2.16 Kg load
Figure 7



3.16 kg load
Figure 8



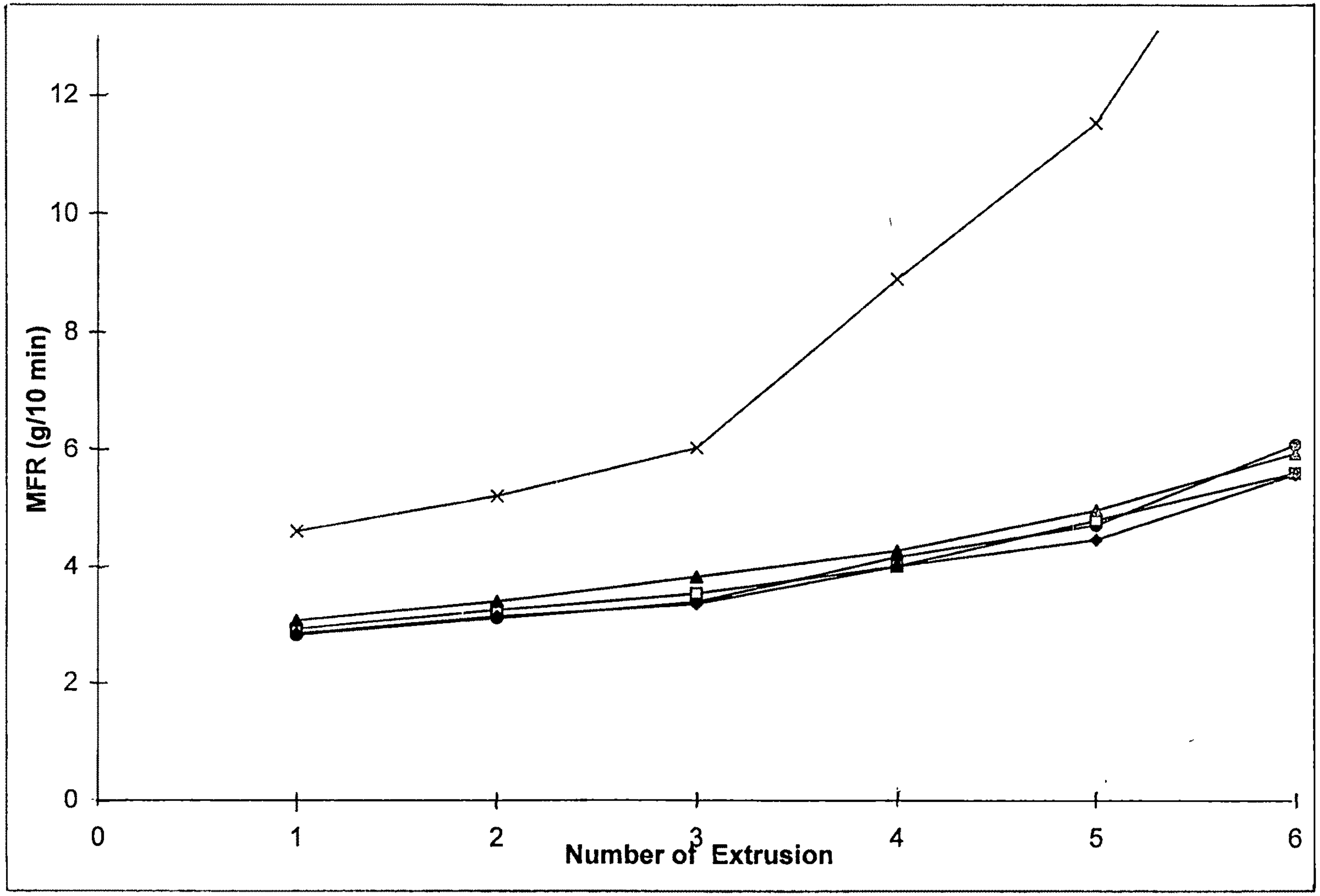


Figure 9

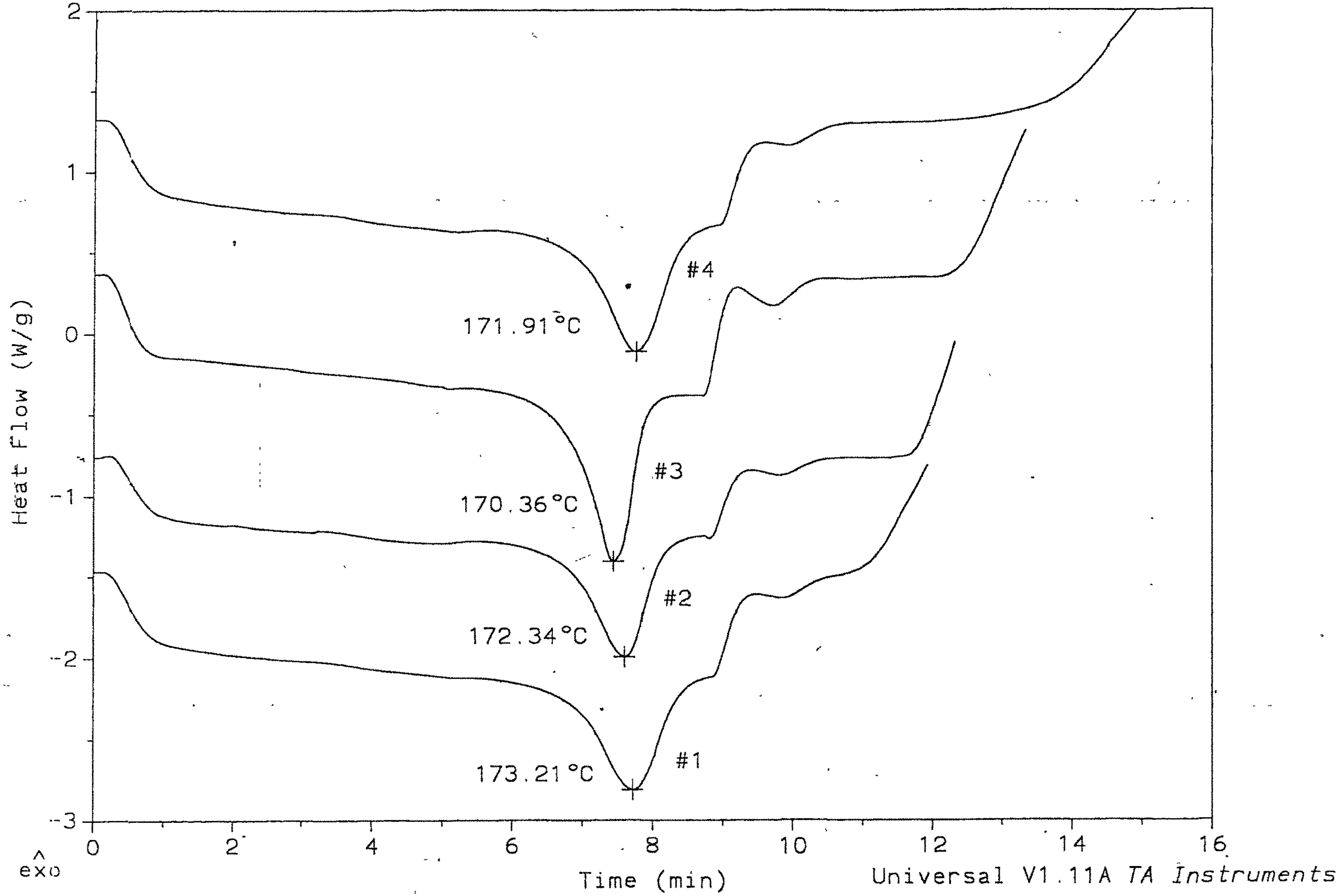

2
1
0
-1
-2
-3
Heat Flow (W/g)
exo
0
2
4
6
8
10
12
14
16
Time (min)
Universal V1.11A TA Instruments
#4
171.91°C
#3
170.36°C
#2
172.34°C
#1
173.21°C

Figure 10

Legends to the Figures

Fig. 1: MFR values at 1kg load plotted against different concentrations of antioxidants added to PPCP. (0)BHT, (□) AO1, (◊)AO2, (Δ)AO3. MFR value for unstabilised PPCP at load 1kg= 3.41g/10min

Fig. 2: MFR values measured at 2.16 kg load, plotted against the concentration of antioxidants added to PPCP. (0)BHT, (□)AO1, (◊)AO2, (Δ)AO3. MFR value for unstabilised PPCP at load 2.16kg=7.68g/10min.

Fig.3: MFR values measured at 3.16 kg load, plotted against the concentration of antioxidants added to PPCP (0) BHT, (□)AO1, (◊)AO2, (Δ)AO3. MFR value for unstabilised PPCP at load 3.16Kg= 14.2g/10min.

Fig. 4: MFR values plotted against the number of extrusions; (0) BHT, (□)AO1, (◊)AO2, (Δ)AO3. MFR value for unstabilised PPCP (x) after sixth extrusion is 16.58.

Fig.5: Oxidative Induction Time (OIT) thermogram of PPCP stabilised with various antioxidants #1/BHT = 0.54min; #2/AO1 = 1.90min; #3/AO2 = 2.26min; #4/AO3= 0.60min.

Fig. 6: MFR values at 1kg load plotted against different concentrations of antioxidants added to PPCP. (♦)BHT, (•)AO4, (▲)AO5, (▣)AO6. MFR value for unstabilised PPCP at load 1kg= 3.41g/10min

Fig. 7: MFR values measured at 2.16 kg load, plotted against the concentration of antioxidants added to PPCP. (♦)BHT, (•)AO4, (▲)AO5, (■)AO6. MFR value for unstabilised PPCP at load 2.16kg=7.68g/10min.

Fig.8: MFR values measured at 3.16 kg load, plotted against the concentration of antioxidants added to PPCP. (♦)BHT, (•)AO4, (▲)AO5, (■)AO6. MFR value for unstabilised PPCP at load 3.16Kg= 14.2g/10min.

Fig. 9: MFR values plotted against the number of extrusions; (♦)BHT, (•)AO4, (▲)AO5, (■)AO6. MFR value for unstabilised PPCP (x) after sixth extrusion is 16.58.

Fig.10: Oxidative Induction Time (OIT) thermogram of PPCP stabilised with various antioxidants #1/BHT = 0.54min; #2/AO6 = 2.03min; #3/AO4 = 2.91min; #4/AO5= 1.28min.

REFERENCES

1. S. Al Malakia, *Thermal Antioxidants, Polypropylene, An A-Z reference*, Karger-Kosis, Ed., Kluwer Acamedic Publisher, London, (1999), 821.
2. J. I. Wasson, W. M. Smith, *Industrial Engineering Chemistry*, (1953), **45**, 197.
3. G. J. Miller, F. W. Quackenbush, *J. Am. Oil Chem. Soc.*, (1953), **34**, 304.
4. W. L. Hawkins, in *Polymer Degradation and Stabilisation*, W. L. Hawkins, Ed., Springer- Verlag, Berlin, (1984), p.1.
5. R. P.; Paula, *Thermoplastic Polymer Additive, Theory and Practice*, John. T. Lutz, Ed., Marcel Dekker Inc., Pennsylvania, (1983), 3.
6. M. Minagawa, *Polym. Degrad. Stab.*, (1989), **25**, 121.
7. G. Scott, Ed., *Synergism and Antagonism in Atmospheric Oxidation and Antioxidants*, Elsevier applied science, London, (1993), **2**, 431.
8. N. C. Billingham, D. C. Bott, A. S. Manke, *Development in polymer degradation –3 .In,* N. Grassie, Ed., Applied science publisher, London, (1988), 63.
9. R. P. Paolino "*Thermoplastic Polymer Additive and Practice*, T. T. Lutz, Ed., Marcel Dekker Inc., Pennsylvania (1989), 3.
10. F. Gugumus, *Plastic Additive*, G. Muller, Ed., Henser Publisher, New York, 1990, p. 49.
11. J. Tochacek, J. Selder, *Polym. Degrad. Stab.*, (1989), **24**,1.
12. F. Gugumus, *Res. Discl*, (1981), **209**, 257.