Studies on Antioxidants. III. 2[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)methylene]hydrazine Carbothioamide as a Melt Stabilizer for Unstabilized Polypropylene

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SYNOPSIS

Polypropylene's high processing temperatures initiate thermal oxidative degradation and loss of physical properties. Antioxidants protect polymers through the severe conditions of processing and fabrication and also through end use. Small amounts of antioxidants like 2,6-di-*tert*-butyl-4-methylphenol and 2[(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylene]-hydrazine carbothioamide are shown to be effective in protecting isotactic polypropylene (IPP) against thermooxidative degradation. 2[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-methylene]hydrazine carbothioamide was melt compounded with IPP using a twin screw extruder. The melt flow index of the extruded sample was measured. The extruded granules were injection molded to get specimens suitable for testing mechanical properties, such as heat deflection temperature, Izod impact strength, tensile strength, tensile modulus, flexural strength, and flexural modulus. 2[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)methylene]hydrazine carbothioamide was found to be an effective melt stabilizer for unstabilized polypropylene.

INTRODUCTION

Virtually all polymeric materials, both of synthetic or natural origin, undergo reactions with oxygen. Technically it is important to distinguish whether such oxidation reactions are taking place as purely thermal processes at usually elevated temperatures or with the assistance of light. The high temperatures associated with the compounding, fabrication, and regrind processes promote thermal oxidative degradation of polypropylene. Degradation generally begins when reactive impurities contained in polypropylene thermally decompose to radical species. These radical species continue the polymer decomposition through a number of sequential reactions, including abstraction of hydrogens from polypropylene, formation of thermally unstable hydroperoxides, and additional formation of radical species. As thermal oxidative degradation proceeds, chain scission occurs along the polymer backbone, causing a reduction in molecular weight and loss of physical properties.

Antioxidants are added to inhibit degradation and its deleterious effects. Numerous types of antioxidants are available, but not all are suitable as processing stabilizers for polypropylene. The types of antioxidants that tend to meet these requirements and that are therefore most frequently used as processing stabilizers 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.[1]

It has been reported that the *tert*-butyl group in the *ortho* position and the alkyl group in the *para*

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position result in the most effective antioxidant activity in the alkylphenolic type of antioxidants, of which 2,6-di-*tert*-butyl-4-methylphenol (BHT) is one of the best known.[2] However, BHT suffers from a major drawback: high volatility. It is reported that high volatility could be minimized by increasing the length of the side chain at the para position of the —OH group of BHT.[3]

We have reported the synthesis and characterization of antioxidants by modification of the structure of 2,6-di-*tert*-butyl-4-methylphenol (BHT) by introducing a group containing nitrogen or nitrogen and sulphur atoms at the position para to the —OH group of BHT. The performance of the synthesized antioxidants with stabilized isotactic polypropylene is also reported.[4,5] Since the results obtained for thiosemicarbazone with stabilized IPP were encouraging with respect to antioxidant activity, we decided to proceed with the detailed study of these antioxidants with unstabilized IPP. This article is devoted to studying the degradation and stabilization of unstabilized isotactic polypropylene in the presence of 2[(3,5-di-*tert*-butyl-4-hydroxyphenyl)-methylene]hydrazine carbothioamide.

To demonstrate processing stabilization of polypropylene, two antioxidants (one commercially available and one synthesized) were selected for the study. Their chemical structures and abbreviations are given in Figure 1. The following techniques were used for the evaluation of antioxidant activity:

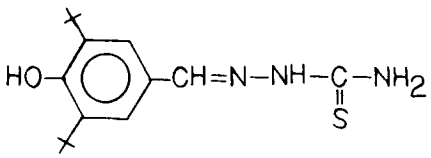
1. Melt flow index
2. Heat deflection temperature
3. Izod impact strength
4. Tensile strength and tensile modulus
5. Flexural strength and flexural modulus.

EXPERIMENTAL

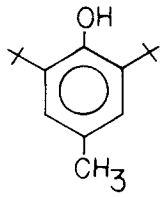
2[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)methylene] hydrazine carbothioamide was synthesized by the reported procedure.[5]

Material

An unstabilized general-purpose molding-grade polypropylene with an initial melt flow index of 11.05 [10^{-3} kg/10 min (ASTM D 1238) condition] supplied by Indian Petrochemicals Corporation Ltd. was used for the studies. Unstabilized IPP was used as a matrix material. It becomes degraded in contact with air and creates a problem in processing. To avoid degradation, prior to mixing with antioxidants the IPP should be preserved under a nitrogen blanket. The twin screw extruder ZSR 30 (Warner P-fledier, Germany) was used for carrying out the extrusion of IPP with BHT or synthesized antioxidant.



AO_2



AO_1

Figure 1 Structure (AO_1): 2,6-di-*tert*-butyl-4-methylphenol. Structure (AO_2): 2, [(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylene]hydrazine carbothioamide.

Process for Twin Screw Extrusion

Commercially available antioxidants like 2,6-di-*tert*-butyl-4-methylphenol BHT (AO_1) or synthesized antioxidant 2-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)-methylene]hydrazine carbothioamide (AO_2) along with calcium stearate and Irgonaz 1010 were mixed with unstabilized IPP and then extruded on a twin screw extruder with a given temperature profile. The temperature profile of five different zones for five multiple extrusions was 160°, 210°, 260°, 250°, and 210°, respectively. The resultant mixture was extruded in thread form and cooled in the water bath maintained at 20 to 25°C and then granulated on a Conair model 206 to an average size of 8 to 10 mm. The granules were dried in an oven at 80°C and reextruded in a twin screw extruder. The same process was followed for up to five extrusions.

Preparation of Specimen

Prior to molding, the pellets of all the samples were dried in oven at 100°C to avoid moisture. The pellets

were then subjected to injection molding to obtain the samples for measurement of heat deflection temperature, Izod impact strength, tensile strength, tensile modulus, flexural strength, and flexural modulus. All the samples were annealed at room temperature for 72 h prior to the measurements.

Process for Injection Molding

The extruded granules of different samples were injection molded (Windsor model SP-3) to get standard ASTM test specimens. The injection molding machine has a shot capacity of 75 g. All formulations were molded under identical conditions, as given in Table I.

Melt Flow Index

The melt flow index (MFI) was determined according to the ASTM standard (D 1238-1257) test method. The relevant data are given in Table II.

Heat Deflection Temperature

Heat deflection temperature (HDT) was carried out according to the ASTM standard (D 648-656) test method using injection molded samples.

Izod Impact Strength

Impact strength (IS) was measured using injection molded (notched) samples according to the ASTM standard (D 256) test method.

Tensile Strength and Tensile Modulus

Tensile properties of IPP containing antioxidants AO_1 and AO_2 were tested by using injection molded bars according to the 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.

Flexural Strength and Flexural Modulus

Flexural properties of different samples were tested using injection molded bars according to the ASTM standard (D 790) test method on a Universal Testing Machine (Instrone 1195), which has a constant rate of cross-head movement.

RESULTS AND DISCUSSION

Melt Flow Index

The degradation of IPP in the presence of the antioxidants was studied by measuring the melt flow index of all the extruded samples after the first, third, and fifth extrusions. The MFI of each of the extruded samples was plotted against the number of extrusions, as shown in Figure 2.

From Table II and Figure 2, it has been observed that as the number of extrusions increases, the MFI values of the extruded samples with both BHT and synthesized antioxidants increases from the first to fifth. In the case of AO_1 with 0.035 concentration, the MFI values continue to increase as we pass from the first extrusion to the third and then to the fifth. This is due to the degradation of IPP and consequent decrease in the molecular weight and melt viscosity. In the case of AO_2, the concentration of synthesized antioxidant AO_2 (0.045) is higher than that of BHT (AO_1) (0.035). Here the MFI values after the first and fifth extrusions are 10.21 and 16.99, respectively, and those of AO_1 are 10.78 and 16.96, respectively. From Table II and Figure 2, it can be observed that as the number of extrusions increases, the MFI values increase, indicating the degradation of IPP. The MFI values of AO_2 are similar to those of AO_1. However, in the case of AO_1, the concentration is less as

Table I Injection Molding Conditions for All the Formulations

1.	Temperature profile for different zones				
	Zone	1	2	3	4
	Temp (0°C)	210	200	165	220
2.	Injection pressure (kg/sq cm)			70	
3.	Locking mold (tons)			60	
4.	Injection period (s)			20	
5.	Cooling period (s)			20	
6.	Back pressure (kg/cm^2)			35	
7.	Screw division			6	
8.	Screw speed (rpm)			100	

Table II Processing Stability of Unstablized IPP; Multiple Extrusions at a Melt Temperature of 260°C and a Screw Speed of 100 rpm; IPP with 0.1% Calcium Stearate and Different Antioxidants

	Melt Flow Index (MFI) (kg/10 min), 230°C/2.16 kg Extrusion Cycles		
Antioxidants	1	3	5
AO_1 (0.035)	10.78×10^{-3}	12.84×10^{-3}	16.96×10^{-3}
AO_2 (0.045)	10.21×10^{-3}	11.38×10^{-3}	16.99×10^{-3}
MFI of unstabilized IPP = 11.05×10^{-3} kg/10 min			

Concentrations of each of the antioxidants for 50 g of IPP are given in parentheses.

compared to that of AO_1. Thus the stabilization performance of AO_1 with 0.035 concentration can be considered to be equal to that of AO_2 (0.045 g).

Klemchuk and LiHorng[6] showed that hindered phenols provided significant protection against the chain scission which took place in unstabilized IPP. As a result, there is a reduction in the melt flow values of IPP from its original value, and as the number of extrusions increases, the MFI increases. In the present study, similar results were obtained with antioxidants AO_1 and AO_2. As shown in Table II, after the first extrusion the MFI values are 10.21 and 10.78 in the case of AO_1 and AO_2, respectively, and the MFI values after the fifth extrusion are 16.99 and 16.96, respectively, as compared to that of IPP powder (11.05 kg/10 min).

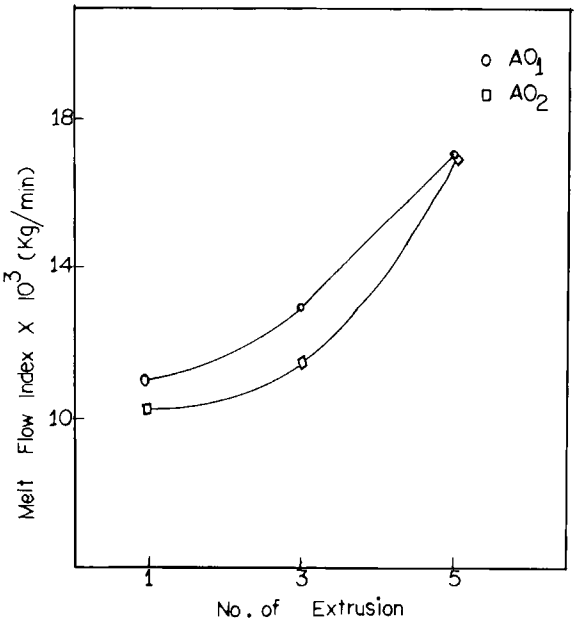


Figure 2 Melt flow index (MFI) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (○) AO_1, (□) AO_2.

Chucta[1] reported that as unstabilized IPP passes through a number of extrusions using a twin screw extruder, chain scission occurs along the polymer backbone, causing a reduction in molecular weight and loss of physical properties. Paolino[3] has also reported that the degradation takes place via chain scission, and this results in a decrease in molecular weight and melt viscosity and, at the same time, an increase in melt flow values. The results of the present study also showed an increase in MFI values as the extrusion proceeds. So it is clear from the MFI values that the degradation of unstabilized IPP could be controlled effectively with AO_1 and AO_2. Thus, with respect to MFI values,

AO_2 (0.045 concentration)

$= AO_1$ (0.035 concentration)

Performance Properties

Heat Deflection Temperature

The heat deflection temperature values were plotted against the number of extrusions (Fig. 3). From Figure 3, it can be observed that as the number of extrusions increases, the HDT values decrease. As a result, the polymer becomes degraded and, consequently, the molecular weight and melt viscosity decrease at the same time that MFI values increase. The same pattern was observed with AO_1 and AO_2. Based on Figure 3, unstabilized polypropylene becomes degraded faster in presence of BHT (AO_1) as compared to IPP in the presence of AO_2. The HDT values of IPP in the presence of BHT are high compared to those of synthesized antioxidants.

Izod Impact Strength

The Izod impact strength was plotted against the number of extrusions, as shown in Figure 4. In this

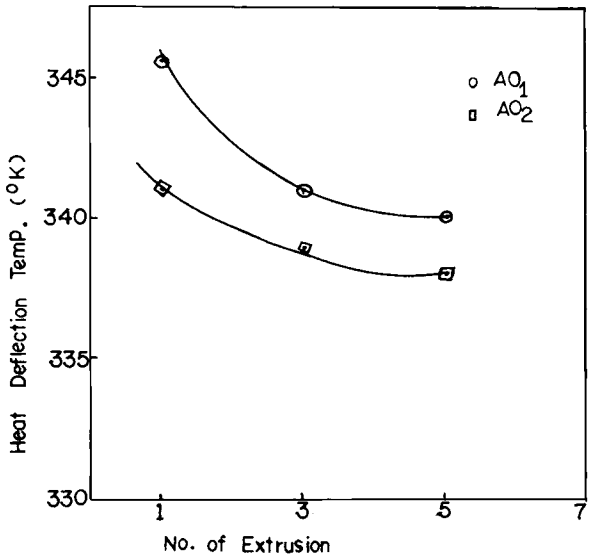


Figure 3 Heat deflection temperature (HDT) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (O) AO_1, (□) AO_2.

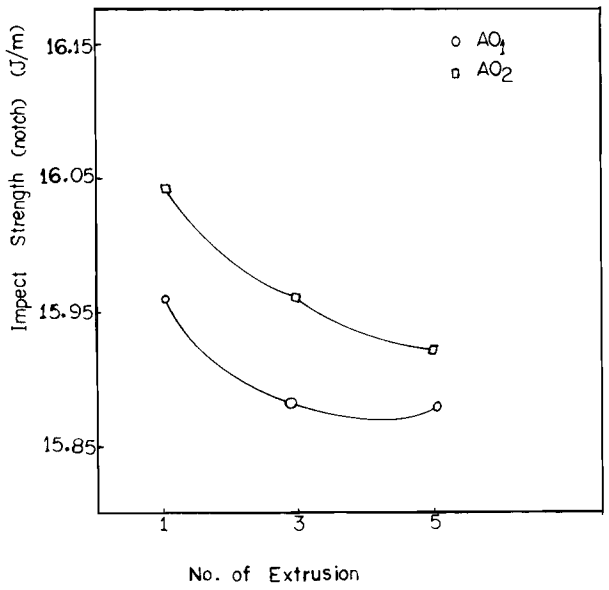


Figure 4 Izod impact strength (IS) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (O) AO_1, (□) AO_2.

case, as the number of extrusions increases, the impact strength decreases. The decrease in impact strength implies that as the number of extrusions increases, the polymer becomes degraded and, as a result, the molecular weight and melt viscosity decrease in contrast to an increase in MFI values. Unstabilized polypropylene in the presence of AO_1 showed the same pattern of decrease in impact strength values, as in the case of synthesized antioxidants. Thus it can be concluded that synthesized antioxidant is comparable to commercially available antioxidant BHT (AO_1).

Tensile Strength and Tensile Modulus

The tensile strength and tensile modulus were plotted against the number of extrusions, as shown in Figures 5 and 6, respectively. Based on these figures, as the number of extrusions increases, the tensile strength and tensile modulus decrease, as with BHT and AO_2. Unstabilized IPP, when subjected to multiple extrusion without antioxidant, became degraded very fast. However, IPP became stabilized with BHT or with AO_2. When IPP becomes degraded, it requires less energy for elongation. As it becomes stabilized, it requires more energy for elongation. Based on Figures 5 and 6, there is not much change in the values of tensile strength and modulus after the first, third, and fifth extrusions, both with AO_1 and AO_2. The values of tensile strength and tensile modulus after the first and fifth extrusions in the case of AO_1 are comparable to those of AO_2.

Flexural Strength and Flexural Modulus

The flexural strength and flexural modulus were plotted against the number of extrusions, as shown in Figures 7 and 8, respectively. Based on these figures, as the number of extrusions increases, flexural strength and modulus also decrease. As the number of extrusions increases, the polymer

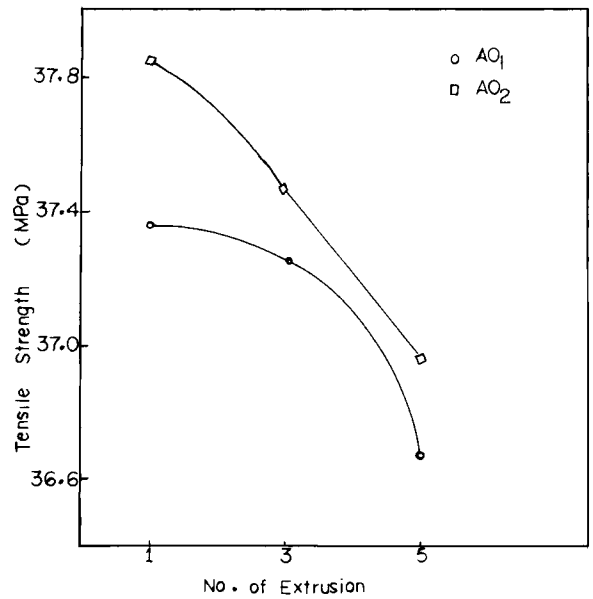


Figure 5 Tensile strength (TS) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (O) AO_1, (□) AO_2.

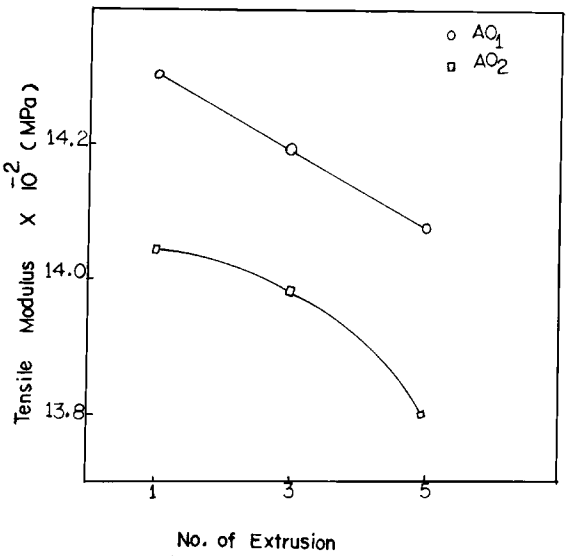


Figure 6 Tensile modulus (TM) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (○) AO_1, (□) AO_2.

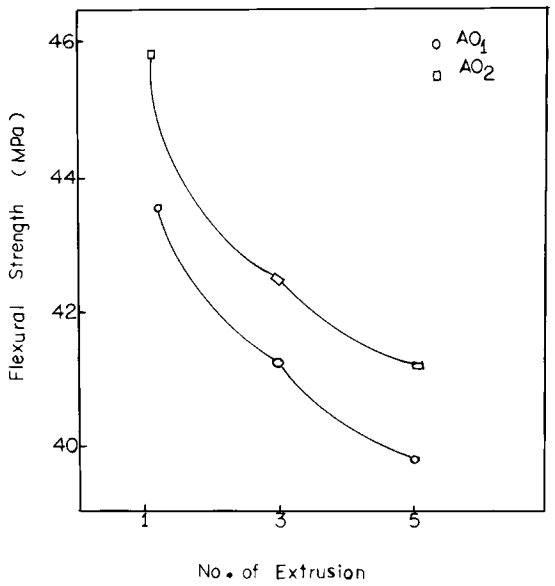


Figure 7 Flexural strength (FS) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (○) AO_1, (□) AO_2.

becomes degraded via chain scission. As a result of this mechanical property, flexural strength and flexural modulus decrease, and this is evident by an increase in the melt flow index. Such observations have also been reported by Gugumus.[7] In our study, IPP could be stabilized either with BHT or with AO_2, so there is no considerable degradation and more energy is required to break the samples. However, as the number of extrusions increases, the degradation takes place, so the energy required to break the samples after the first extrusion is greater compared to the energy required to break the sample after the fifth extrusion. The IPP in the presence of AO_1 or AO_2 showed the same pattern. The values of flexural strength and modulus in the case of BHT (AO_1) were comparable to those of synthesized antioxidant AO_2.

CONCLUSION

Based on the performance properties HDT, impact strength, tensile strength and modulus, and flexural strength and modulus, it is evident that there is a loss of mechanical properties in all the cases relative to the number of extrusions. Since in the present study unstabilized IPP was subjected to greater mechanical shear and consequently promoted oxidative degradation in twin screw extrusion (compared to the extrusion of stabilized IPP carried out on a Brabender Plasticorder), more efficient antioxidants are required. It is evident that the stabilization efficiency of synthesized antioxidant AO_2 is encouraging and hence desirable.

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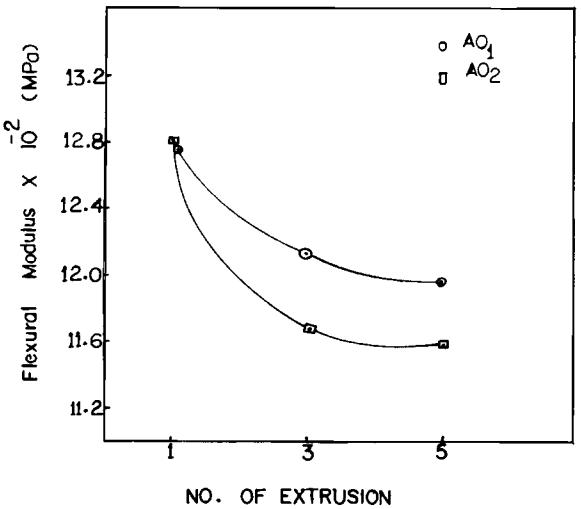

Figure 8 Flexural modulus (FM) plotted against the number of extrusions for unstabilized IPP stabilized with antioxidants; (○) AO_1, (□) AO_2.

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