Modification of Atactic Polypropylene to Prepare Emulsions by Oxidation in Melt

ÖZDEN YAYKIN and Ö.TUNÇ SAVAŞÇI, *Research and Development Center, PETKİM Petrochemicals Corporation, P. K. 46 İzmit,* BAHATTİN M. BAYSAL, *Department of Chemistry, İstanbul Technical University, İstanbul, Turkey*

Synopsis

Oxidation of atactic polypropylene (APP) obtained as by product from polypropylene production is studied in melt to obtain polymers which are easily emulsified by commercial emulsifiers. The experiments are done using a stirred, jacketed glass reactor and the relevant heating, air-feeding, and sampling attachments. Oxidation is followed by the change of carbonyl absorbance, iodine number, acid number, molecular weight, and melt flow index (MFI) by time. The relevant tests are done by infrared (IR) spectroscopy and gel permeation chromatography (GPC) and standard tests with minor modifications are applied. It is found that as temperature, air flow rate, and mixing speed are increased, higher oxidation rates are obtained. It is also found that initiator types and concentrations used are not as effective as the above parameters. By oxidation as molecular weight reduces, molecular weight distribution narrows. Correlation between MFI, iodine number, and molecular weight of the oxidized APP is also made for easy follow-up of oxidations. In addition, it is found that for easy and stable emulsions, APP must be modified by oxidation to iodine number and MFI higher than 30 mg/g and 3.5, respectively.

INTRODUCTION

Polypropylene (PP) is one of the major thermoplastics produced in large quantities throughout the world. Propylene molecules are polymerized with Ziegler-Natta catalysts to produce PP in which is a mixture of different molecular structures. One is isotactic PP which methyl groups are oriented regularly the other is atactic polypropylene (APP) in which methyl groups are oriented irregularly.

During the commercial production of PP, isotactic structure is the goal. APP is produced as a byproduct, usually in amounts of 3–5% of the total propylene consumed. This figure of 3–5% is closer to zero when recently developed, more selective catalysts are used.[1]

Atactic polypropylene is obtained as a waxy, odorless, semitransparent, noncrystalline material. Its molecular weight ($\overline{M}_w$), as obtained from intrinsic viscosity measurements from solutions in tetraline[2], decaline[3], and benzene[4] is about 30,000.

APP can be used directly or usually in modified form such as chlorinated APP, in adhesives, plastic, rubber, paint, and printing ink formulations. It can also be used as a binder for limited applications.[5–19] In the literature APP is said to be used as a fuel after thermal cracking[20] and sometimes it is claimed that large portions of APP was disposed of as landfill.[21]

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TABLE I

Properties of Atactic Polypropylene

Volatile matters (wt %)[a]	0.5
Specific gravity (g/cm^3)[b]	0.8
Viscosity (cp)[c]	10^3–2×10^6
Ash content (%)	Trace
Isotacticity (%)[d]	17 – 22
Molecular weight, ($\overline{M}_w$)	20,000 – 40,000
MFI[e]	3.8–5.1
Iodine number	

[a] In 2 h at 160°C.
[b] At 23°C.
[c] At 240°C.
[d] By IR spectroscopy.
[e] At 75°C.

To use APP as a binder, emulsions of the polymer are sometimes required for special techniques. However, APP itself is very difficult or impossible to emulsify. In this work, we have attempted to modify APP by limited oxidation to a point where the products can be emulsified easily with commercial emulsifiers and retain useful binder properties.

As an experimental approach to this procedure, partial oxidation of APP in melt is preferred. In the literature oxidation of polyolefins in solution has been studied extensively,[22–27] which brings about the problem of separating the modified polymer from the solvent. Therefore, for practical reasons and to obtain data lacking in the literature, melt oxidation is preferred.

EXPERIMENTAL

Materials

The APP used in the experiments is obtained from the Petrochemical Complex of Petkim A. Ş. İzmir, Turkey, typical values for the specification of which are given in Table I. Compressed air is used for oxidation. Partially oxidized polyethylene (OPE) obtained from Türk-Henkel and dicumyl peroxide obtained from Concord Chem. Ind., Taiwan are used as radical initiators. From time to time partially oxidized APP (OAPP) obtained from the experiments was also used as an initiator. Reagent-grade chemicals are used for the tests and other analytical procedures.

Oxidation Procedure

Oxidation experiments of APP are carried out as shown in Figure 1. The set-up consists of a glass, three-liter-jacket reactor, 82 mm ID, with a magnetic-type variable-speed stirrer, obtained as a set from Buchi AG Switzerland. The relevant air supply and venting connections involve a rotameter to measure air flow, a sparger for fine distribution of air in the molten polymer, and a venting tube.
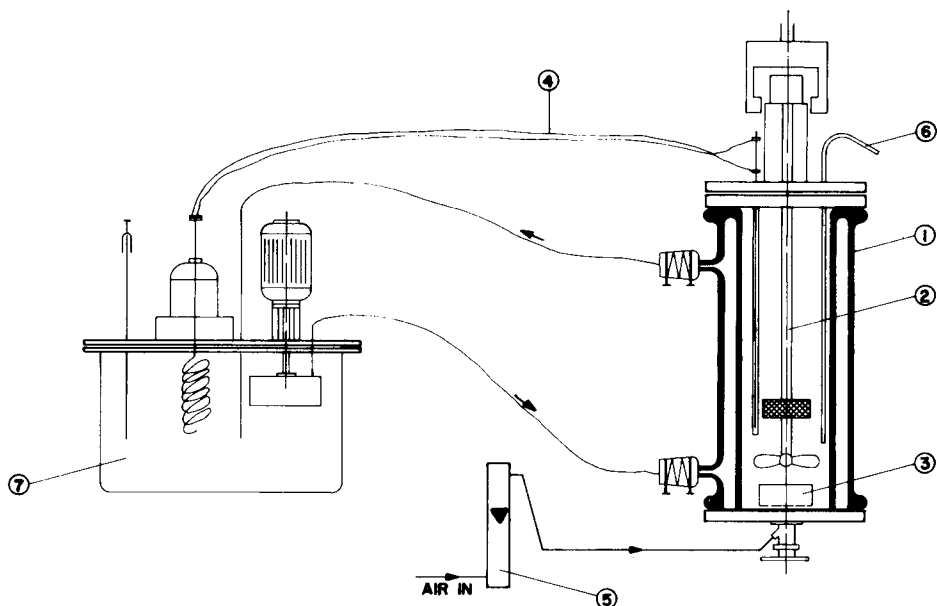
Fig. 1.   Set up for oxidation of APP in molten state (1) reactor, (2) stirrer shaft, (3) sparger, (4) thermocouple, (5) air flowmeter, (6) sample suction outlet, (7) circulating thermostat.

Temperature of the reactor is controlled by a thermocouple immersed in the molten polymer. The thermocouple is connected to a control unit which controls the temperature of the oil which is circulated in the jacket of the reactor through a thermostat.

For oxidation experiments, APP samples obtained as pellets are cut into small pieces of about 1 cm^3, then a 1 kg sample is placed in the reactor and heating is started. In the interim, air is supplied to the reactor in very small amounts to prevent plugging of the sparger by the molten polymer. The melting of the polymer is observed through the glass reactor. When melting occurs the stirrer at the desired speed and the air flow at the desired rate are started together with the addition of the desired amount of the radical initiator. Oxidation is followed by the extracting samples which are periodically sucked out of the reactor to a sample cup connected to vacuum.

Tests and Analytical Procedures

Carbonyl Absorbance (CA). Carbonly absorbance of the samples of the same film thicknesses prepared on KBr windows are determined by IR spectroscopy using the band at 1710 cm^{-1}. For this purpose 2.5% solutions of samples in benzene are prepared. A few drops of the solution are placed on KBr windows and the solvent is evaporated at room temperature and further dried in vacuum oven. To obtain the same film thicknesses each time, the number of drops is kept approximately constant. The film thickness is checked for the same IR absorbances at 1458 cm^{-1}.[28,29] Absorbance value of 0.40 $\pm$ 0.04 is retained throughout the experiments.

Acid Number. Acid number is determined in accordance with ASTM D-1980-67 with the exception that the solvent is changed from isopropyl alcohol to carbon tetrachloride.

Iodine number. Iodine number is determined by Wijs' method.

Molecular Weight and Distribution. The change in molecular weight distribution is followed by gel permeation chromatography (GPC), using a Waters Model 150 C GPS system. Four ultrastyragel column combinations $(10^5, 10^4, 10^3, 500$ Å) are employed at 135°C. o-Dichlorobenzene with the addition of 0.25% (w/vol) 2,6-ditertiary butyl paracresol as antioxidant is used as a carrier liquid at a speed of 1.5 mL/min. The samples used in this work contain 17–22% high molecular weight isotactic PP. These samples are not soluble in common solvents at ambient temperatures. Therefore, we used o-dichlorobenzene as a solvent at high temperatures. A refractive index detector at the same temperature with the columns is used.

The molecular weights calculated are based on a calibration curve generated with polystyrene standards obtained from Waters Associates (Milford, MA U.S.A.)

Melt Flow Index. Melt flow index of the samples is determined in accordance with ASTM D 1238-65 T except that the temperature involved is reduced from 230°C to 30°C.

RESULTS

Effect of Air Flow Rate and Temperature

Polypropylene is one of the major polymers used commercially and is quite susceptible to oxidation by molecular oxygen since it has alternate tertiary hydrogens in the main chain. Therefore much work has been performed to understand the mechanism and the kinetics of oxidation.[27,30–41]

The bulk of thermooxidation of PP has been performed at temperatures in the range of 120–170°C and usually in solution, and significant findings have been obtained.

Among others it is concluded that the concentration of the volatile products formed depends on the amount of oxygen absorbed rather than on the temperature of oxygen absorption,[35] the ratio of the volatile products (water, acetone, acetaldehyde, and formaldehyde) formed in the temperature range 120–140°C is only slightly dependent on the temperature[38] and the main volatile organic products observed are acetone, acetaldehyde, formaldehyde, acetic acid, and α-methylacrolein.[35,38] Other products such as methanol, 2-butanone, 2,4-dimethylfuran, propanal, butanal, and 2-pentanone were also identified.[35]

In this work, air flow rates corresponding to 1.25, 2.50, and 10 L/min oxygen are used to study the effect of oxygen flow rate. These figures are chosen after gas hold-up tests carried out before the experiments to determine the amount of oxygen to be consumed for oxidation. Figure 2 shows gas hold-up test results at 155°C as an example. As seen from the figure, flow rates correspondingly higher than 10 L/min oxygen do not change the gas hold up, which means that the amount of oxygen above 10 L/min will not be used for oxidation purposes.
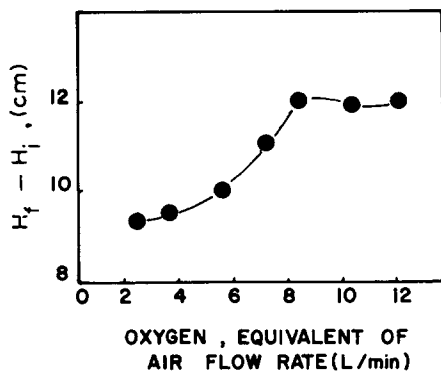
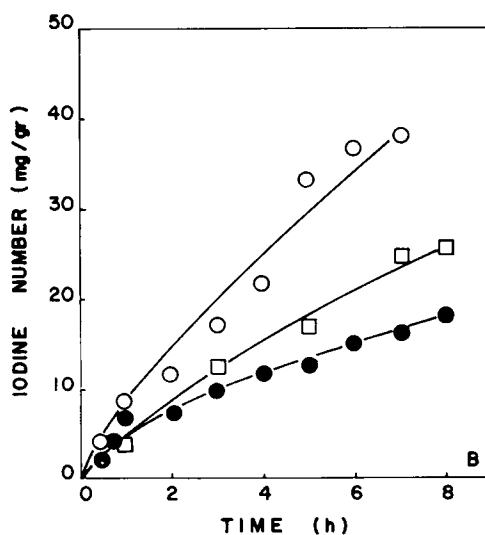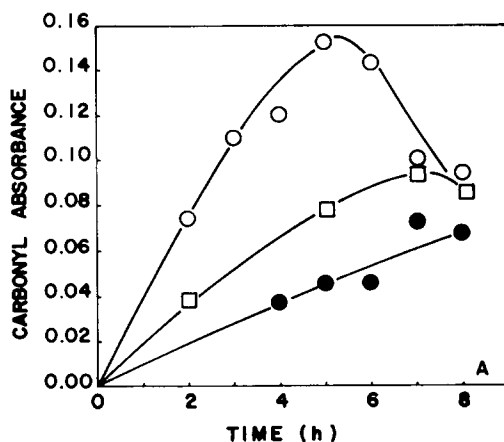Fig. 2.   Gas hold up test results at 155°C. H_f = Final level (cm), H_i = Initial level (cm).

Fig. 3.   Change of carbonyl absorbance (A) and iodine number (B) by air flow rate at 160°C, 250 rpm. Initiator content, 2% OPE. (●) 1.25 L/min; (□) 2.50L/min; (○) 10 L/min oxygen equivalent air flow rates.

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The changes of carbonyl absorbance and iodine number, over time at three different flow rates are given in Figure 3.

As seen from this figure, as the increased oxygen flow rates obtain faster oxidations. Furthermore, stripping of the volatile oxidation products occurs at all the flow rates studied, as observed by the decrease of the carbonyl absorbance occurring at earlier stages as the flow rate increases. However, since double-bond formations do not always give volatile products, as oxidation proceeds, iodine number keeps increasing flow rates.

At the second stage of our work effect of temperature is studied. Change of carbonyl absorbance as well as iodine and acid number by time are given in Figures 4 and 5, respectively. The data presented in Figures 3 to 5 clearly
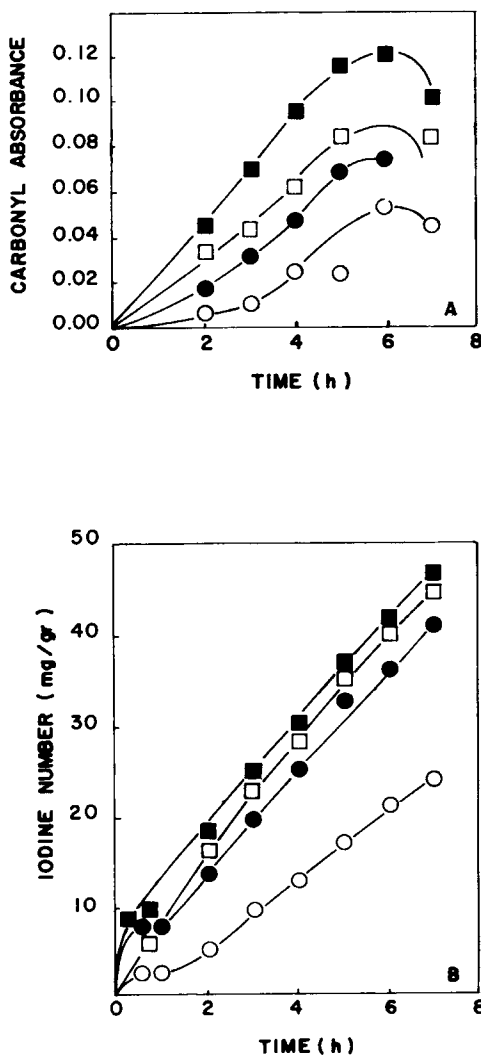

Fig. 4.   Change of carbonyl absorbance (A) and iodine number (B) by temperature at 500 rpm, 10 L/min oxygen equivalent of air flow rate. Initiator content, 2% OPE. (O) 140°C, (●) 150°C, (□) 155°C, (■) 160°C.
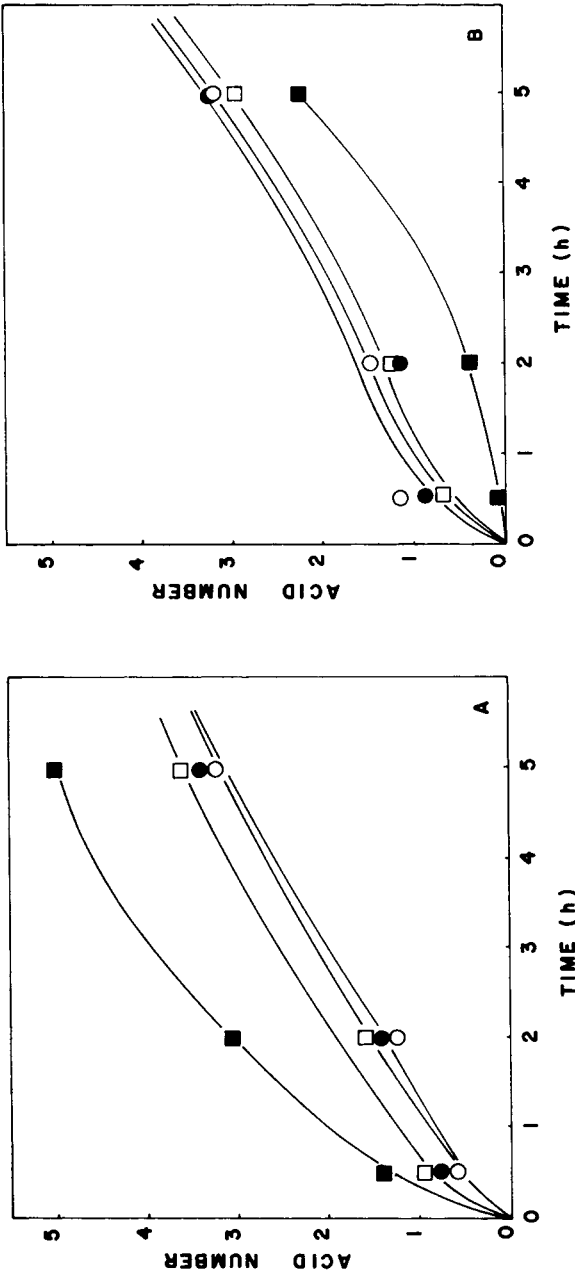
Fig. 5.   Change of acid number by temperature and time at 500 rpm, 10 L/min oxygen equivalent of air flow rate. (A) initiator content, 2% OPE, (B) initiator content, none. (■) 140°C, (●) 150°C, (○) 155°C, (□) 160°C.

indicate that flow rate of air equivalent to 10 L/min oxygen and temperature of 160°C are most effective oxidation conditions for the setup used. Therefore, the effect of the subsequent parameters on the melt oxidation of APP are all studied at 160°C and 10 L/min oxygen equivalent of air flow rate.

Effect of Distribution of Air in the Polymer Melt and the Radical Initiator Concentrations Used

As seen from Figure 1, a sparger is used to distribute the air in the molten polymer. For a finer distribution of air a mixer with two types of propellers
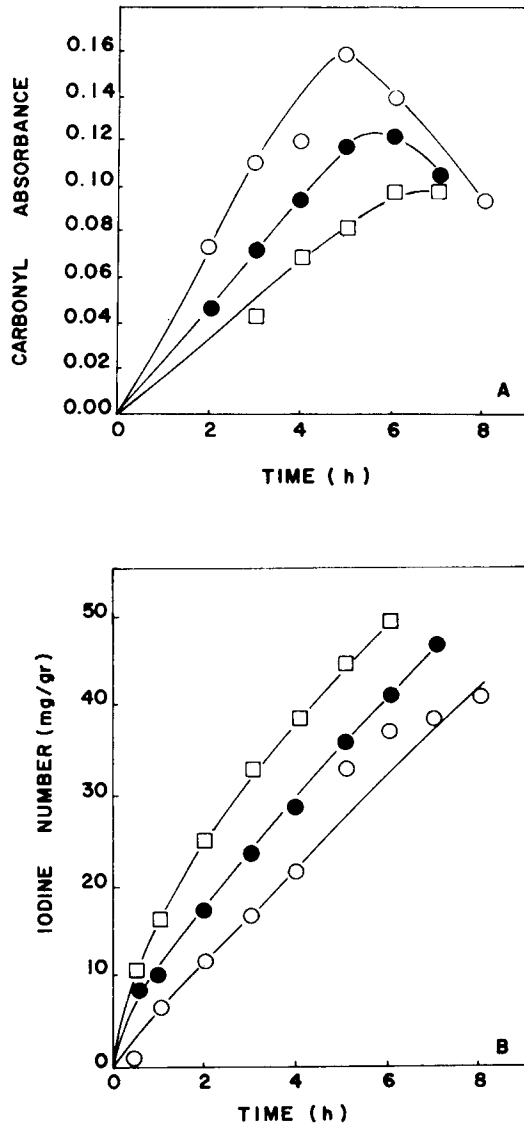

Fig. 6. Change of carbonyl absorbance (A) and iodine number (B) by mixing speed at 160°C, 10 L/min oxygen equivalent of air flow rate. Initiator content, 2% OPE. (O) 250 rpm, (●) 500 rpm, (□) 750 rpm.

mounted on the shaft are used. The turbine type is located at the tip, with the blade 10 cm above it.

The observed changes of carbonyl absorbance and iodine number by time with the mixing speed are given in Figure 6. Figure 6(A) shows that carbonly absorbances decreases with increasing mixing speed. This may seem inconsistent with the results obtained from oxygen flow rate studies. However, it will be seen from Figure 6(B) that a more efficient distribution of air in the molten polymer yields higher degrees of oxidation and higher amounts of volatiles, which are better stripped at higher mixing speeds. In fact, higher iodine numbers indicating higher degrees of oxidation as the mixing speed increases [shown in Fig. 6(B)] support this explanation.

As a radical initiator, oxidized PE (OPE) is mainly used because of its similar commercial applications. Effect of the concentrations of the initiator
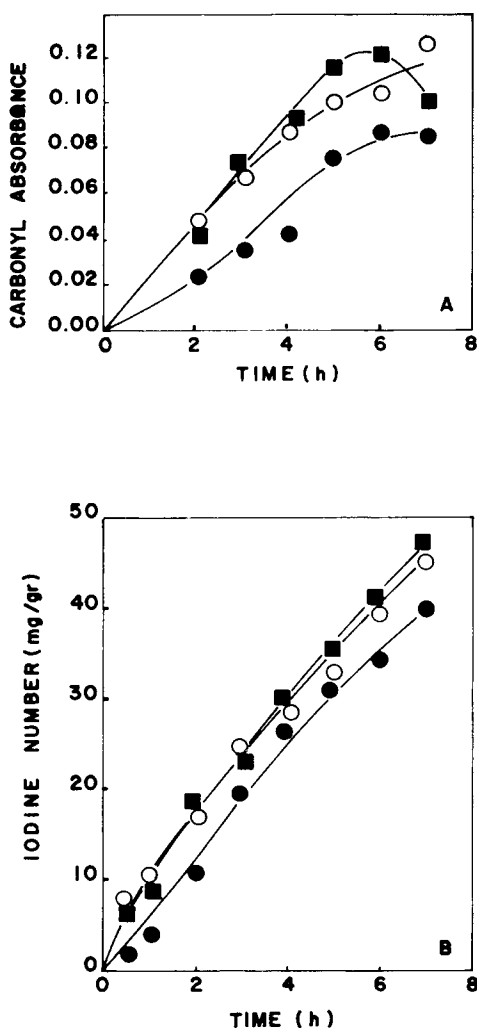

Fig. 7.   Change of carbonyl absorbance (A) and iodine number (B) by initiator concentration at 160°C, 500 rpm, 10 L/min oxygen equivalent of air flow rate. (●) none, (○) 1% (■) 2% OPE.
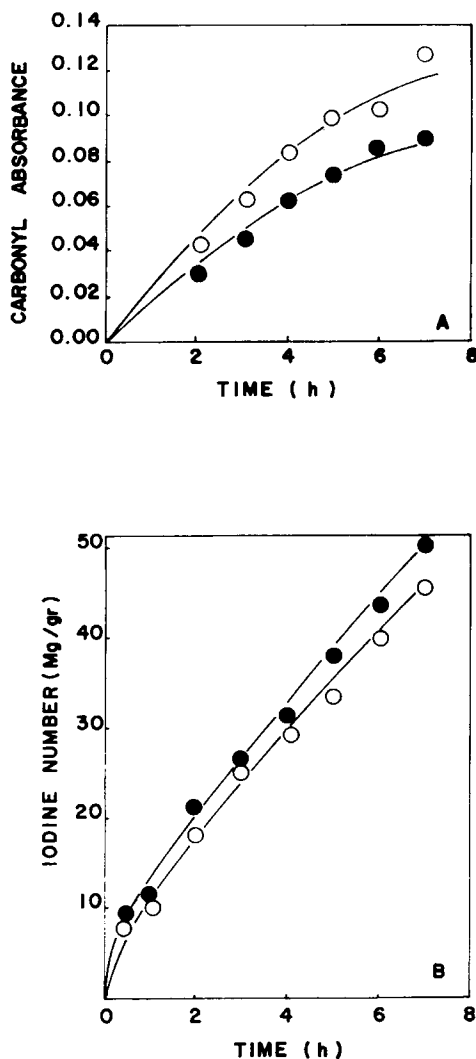
Fig. 8. Change of carbonyl absorbance (A) and iodine number (B) by initiator type at 160°C, 500 rpm and 10 L/min oxygen equivalent of air flow rate. (○) 1% OPE, (●) 1% dicumyl peroxide.

used during the oxidations are given in Figure 7. From this figure it is seen that radical initiator concentration is not as effective on the iodine number as it is on carbonyl absorbance. For comparison reasons, dicumyl peroxide and oxidized APP obtained from previous runs are also used as initiators. The results of these oxidations involving dicumyl peroxide are given in Figure 8 as an example.

Change of Molecular Weight

Molecular weights of the samples obtained from oxidations at 10 L/min oxygen equivalent of air flow, 500 rpm stirring speed, and 2% OPE as a radical initiator at various temperatures are determined by GPC. The change of
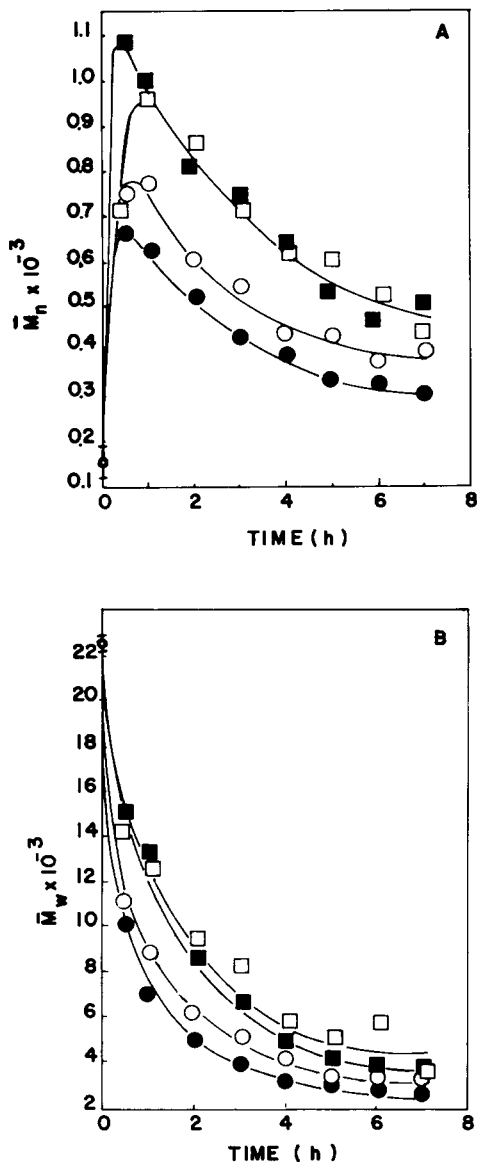
Fig. 9.   Change of $\overline{M}_n$ (A) and $\overline{M}_w$ (B) by temperature at 500 rpm, 10 L/min oxygen equivalent of air flow rate. Initiator content, 2% OPE. (□) 140°C, (■) 150°C, (○) 155°C, (●) 160°C.

molecular weights, $\overline{M}_n$ and $\overline{M}_w$, of oxidation products by time at 140, 150, 155, and 160°C are shown in Figure 9.

Polydispersity $(\overline{M}_w/\overline{M}_n)$ of the initial APP occurs at about 155°C. After oxidation of 30 min and 6 h, dispersities of the oxidized APP are diminished to 20.0 and 8.0, respectively. The effect of initiators used on the molecular weight distribution is studied at 160°C with other parameters as given above. The results obtained are shown in Figure 10. These results show that molecular weight of APP is more effected by temperature than the type of initiators used during oxidation.We can also conclude that OPE is more effective on
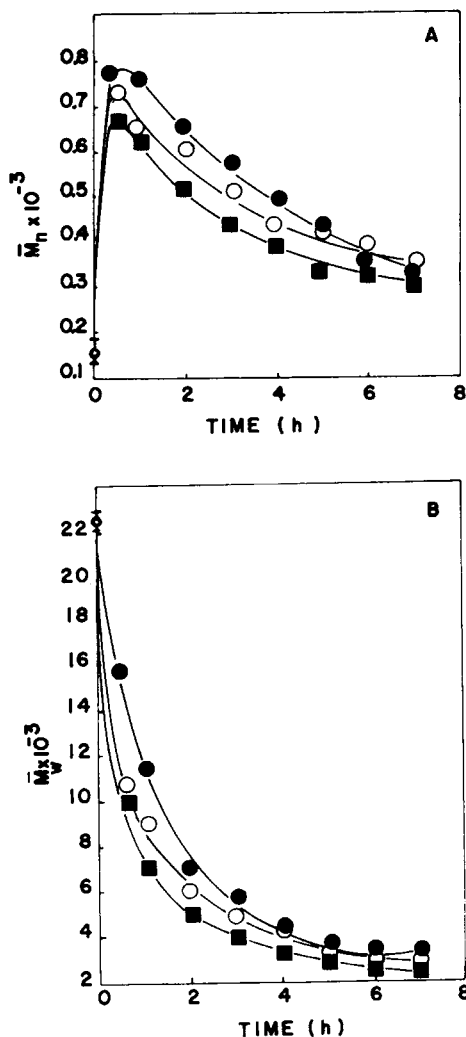
Fig. 10.   Change of $\overline{M}_n$ (A) and $\overline{M}_w$ (B) by initiator concentration (OPE) at 160°C, 500 rpm, 10 L/min oxygen equivalent of air flow rate. (●) none, (○) 1%, (■) 2%OPE.

molecular weight reduction than OAPP. It is also obvious that molecular weight distribution of the polymer is narrowed by oxidation which is also easily seen from GPC chromatograms. Representative gel permeation chromatograms of the samples obtained at 160°C oxidations are given in Figure 11.

These chromatograms show that reduction of molecular weight begins mostly with the high molecular weight fractions. This is most probably because scission of a long chain causes a significant change in molecular weight; scission of a short chain produces a proportionally smaller effect. As the reaction time increases, a shift of the molecular weight distribution peaks toward the lower end is observed. Therefore, during melt oxidation molecular weight is reduced and polydispersity is narrowed.

Fig. 11.   Gel permeation chromatograms of oxidized atactic polypropylene oxidation time: (—) 30 min, (– –) 1 h, (–●–) 2 h, (– + –) 4 h, (- - - -) 5 h, (+ + +) 6 h.

Change of Melt Flow Index (MFI) and its Relation to Molecular Weight and Iodine Number

In this work, APP is oxidized to prepare easily emulsifiable oxidized polymers. Therefore, emulsions are prepared with the oxidized samples. During emulsification the ease of this process and the stability of the emulsions prepared are observed to collect preliminary information for the in-depth emulsification studies which followed this work. Emulsions of at least 40% solid contents are prepared by using industrial nonionic and nonionic-anionic emulsifier combinations suitable for OAPP-type materials. Emulsifiers are obtained from Henkel AG and ICI Petrochemicals and Plastics Division and Gunther and Co. Model T45 DPX Ultraturax system is used for emulsifications. These emulsification studies indicated that for ease of emulsification
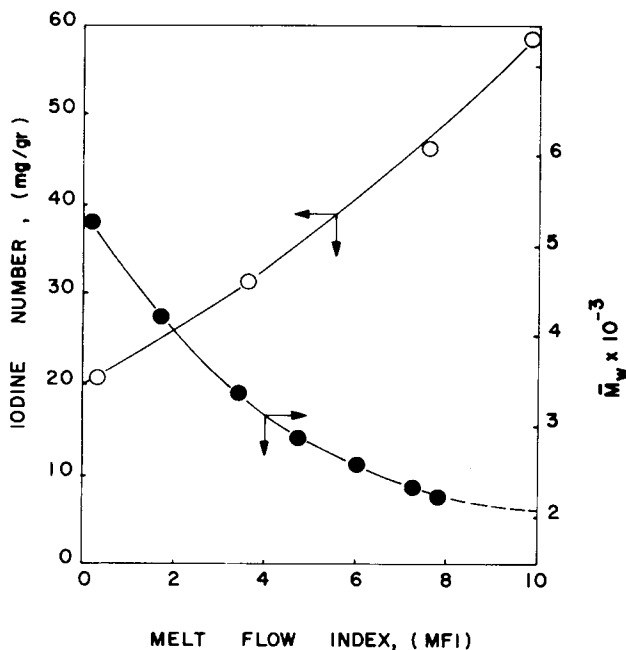

Fig. 12.   Correlation between melt flow index (MFI), weight-average molecular weight and iodine number in atactic polypropylene oxidation. Experimental parameters for iodine number test samples: $\overline{M}_w$ = 2,100: 160°C, 10 L/min oxygen equivalent of air flow rate, 750 rpm, 2% OPE. $\overline{M}_w$ = 2,250: 160°C, 10 L/min oxygen equivalent of air flow rate, 500 rpm, 2/OPE. $\overline{M}_w$ = 3,350: 150°C, 10 L/min oxygen equivalent of air flow rate, 500 rpm, 1% OPE. $\overline{M}_w$ = 5,000: 155°C, 1.25 L/min oxygen equivalent of air flow rate, 250 rpm, 2% OPE.

and good stability of the emulsions obtained, molecular weights lower than about 3500 ($\overline{M}_w$) and iodine number of higher than 30 mg/g are required.

Both iodine number and molecular weight determinations are rather time-consuming determinations to follow up oxidation experiments. To establish a more practical test procedure an attempt is made to correlate iodine numbers and molecular weights of the oxidized samples to their melt flow index (MFI) values.

MFI is a very common and widespread test used in the plastics industry, and standard procedures have been established for it. In our work, ASTM D 1238-65 T is used with modified temperature. When the test is performed as described, both APP and OAPP gave very short flow times due to their low molecular weights. To cope with this problem, the temperature of the test is reduced. After scanning various temperatures, 30°C is chosen as the temperature which gives the most suitable flow times. Melt flow index values of the oxidized samples are shown in Figure 12 together with their iodine number and molecular weight, $\overline{M}_w$, test results. It is evident that by performing a simple test like MFI, molecular weights and iodine numbers of the oxidized samples can easily be followed up by using this figure.

CONCLUSIONS

Oxidation studies of APP in molten state gave results similar to other studies in the literature which covers oxidation of APP in solution.

Air flow rate, fine air distribution in the molten polymer, temperature, initiator type and concentration are effective parameters.

Air flow rate which gives the maximum gas hold up in the reactor is the maximum flow rate to be used.

Temperature seems to be the most effective parameter, while initiator type and concentration is the least effective.

There is a quite good correlation between MFI, iodine number, and molecular weights of oxidized APP. Therefore, by determining MFI values of oxidized APP samples both molecular weight and iodine number can easily be estimated by using Figure 12.

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