Effect of Oven Aging on Polypropylene

M. G. WYZGOSKI, *Polymers Department, General Motors Research Laboratories, Warren, Michigan 48090*

Synopsis

Injection-molded tensile bars of unstabilized polypropylene were oven aged at 90°C. After an induction period, tensile elongation decreased catastrophically. During the induction period no evidence of oxidation was observed by infrared reflectance; however, a definite surface etching was noted by electron microscopy. Differential scanning calorimetry measurements indicated that, for samples aged beyond the induction time, oxidative degradation caused a decrease in the melting temperature of polypropylene. Toluene immersion was used to remove selectively material from the surface of tensile bars aged for various times. Using this technique, changes in melting behavior were observed for partially aged polypropylene even prior to the catastrophic decrease in tensile elongation. Similarly, oxidation products and a reduction in molecular weight were detected for the dissolved surface layer during the apparent induction time. Results indicate that molecular weight measurement is the most sensitive indicator of oxidative degradation during the induction period.

INTRODUCTION

Oven aging is a commonly used technique to accelerate the oxidative degradation of polyolefins. It is well known that during an apparent induction period of oven aging, the bulk mechanical properties may remain relatively constant and then decrease catastrophically.[1] The chemical basis for this type of behavior has been presented by numerous authors.[2-4] Moreover, the relation between the induction period for the loss of mechanical properties and the chemical induction period observed, for example, by oxygen absorption measurements has been discussed by Oswald and Turi.[5] They note that a general correlation exists; however, the loss of mechanical properties begins prior to the autocatalytic stage of oxygen absorption. The sudden loss of properties obviously complicates attempts to predict the useful life of plastic parts, particularly if no effects of aging are detectable during the induction period. The purpose of the present investigation was to determine to what extent surface oxidation was occurring during the induction period for injection molded polypropylene.

EXPERIMENTAL

Materials

Hercules Profax 6501 unstabilized polypropylene was used in this study. The unstabilized resin was employed during this initial phase of the investigation to obtain severely oxidized samples in relatively short time intervals at a moderate aging temperature of 90°C. ASTM D638 type-I tensile bars were injection molded using standard molding conditions. These dumbbell-shaped bars are 3 mm thick, 216 mm long, and 12.7 mm wide in the gauge section.

CCC 0021-8995/81/051689-16$01.60

Procedure

Samples were aged at 90°C in a forced air oven. Tensile properties were measured at 5 mm/min in accordance with ASTM D638-72, except that an extensometer was not used. A gauge length of 63.5 mm was employed for calculating elongation.

Differential scanning calorimetry (DSC) measurements were made at 10°C/min using a DuPont 990 thermal analyzer. Samples were razor cut from the surface of the tensile bar or dissolved off the surface by immersion for 60 sec in boiling toluene. A 25-mm length of the tensile bar was used for immersion in 100 ml of toluene which was constantly agitated with a magnetic stirrer. The dissolved surface material was subsequently concentrated by removal of toluene in a rotary evaporator, cast into petri dishes, air dried for 24 hr at room temperature, and vacuum dried at 75°C for 1 hr. Reagent-grade toluene was used after distillation. This procedure resulted in the removal of approximately 25 mg of polypropylene from the as-molded bar. The amount of dissolved polypropylene generally increased for the oven aged samples under the same immersion conditions.

The surface morphology of the injection molded tensile bars was examined by use of a Siemens Elmiskop-I transmission electron microscope. For this purpose platinum–carbon replicas were prepared by evaporation using standard procedures.

Infrared spectra of the tensile bars were obtained in two ways. First, the bars were examined directly using a frustrated multiple internal reflectance attachment with a Perkin–Elmer model 621 grating spectrophotometer. A 45° KRS-5 internal reflecting crystal was employed. Secondly, the transmission infrared spectra of the dissolved polypropylene from aged tensile bars were examined. The latter samples were prepared by compacting the polypropylene with potassium bromide (KBr) powder in an evacuated die at room temperature.

Molecular weight was determined by high-temperature gel permeation chromatography by Waters Associates, Inc. Samples were run at 135°C in 1,2,4-trichlorobenzene. Numerical values of number- and weight-average molecular weight are based upon polyethylene standards.

RESULTS

Tensile Properties

The effect of oven aging at 90°C on the tensile elongation of unstabilized polypropylene is shown in Figure 1. After an induction time, t_I, of 400 hr, a catastrophic loss of elongation is observed for samples aged in air. Prior to tensile testing, the samples aged for 400 hr exhibited numerous microcracks or crazes along the edges of the tensile bar. These surface crazes appear to initiate the catastrophic brittle failure of the entire sample during tensile testing. Aging in dry nitrogen does not produce crazing or a loss of elongation. The sudden drop in elongation is, therefore, attributed to oxidative attack. The apparent induction time during which elongation does not change is typical for oxidation of polyolefins.[1,5] In the course of this study, it was noted that the value of t_I varied from 300 to 800 hr. This depended on the batch of polypropylene, the storage time at room temperature, the processing conditions, and the type of oven
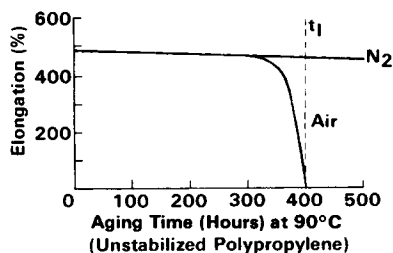
Fig. 1. Effect of oven aging at 90°C on tensile elongation of injection-molded unstabilized poly-propylene. Induction time (t_I) is indicated.

used for aging. Thus, for comparative purposes t_I was measured for each set of tensile bars used. The onset of crazing always coincided with the observed t_I.

Microscopy

The surface morphology of injection molded polypropylene was observed by examination of replicas in the transmission electron microscope. Numerous bars were examined to obtain representative micrographs of the surface before and after aging. It was found that the initial unaged surface generally evidenced a striated appearance as shown in Figure 2(a). The striations are assumed to represent crystaline lamellae viewed edge on. In general, the lamellae are 100–200Å thick and are oriented perpendicular to the melt flow direction (long axis of the tensile bar). Figure 2(b) shows another typical feature found on the injection molded surface. Here, long narrow ridges are observed which probably result from the high shearing action and rapid quenching characteristic of injection molding. The lamellar texture is less apparent in Figure 2(b) and there is some indication of a cross-hatched structure of interwoven lamellae.

Oven aging in air was found to produce a very definite etching effect on the polypropylene surface. This results in a more grainy lamellar texture as shown in Figures 3(a) and 3(b). A general orientation perpendicular to the melt flow direction is still observed. The grainy structure is also oriented perpendicular to the long dimension of the surface ridges shown in Figure 3(b). Moreover, if the ridges are considered to be lying on the surface, then the lamellae in the ridges are shallow in depth and the grainy structure may be more aptly described as ropelike rather than lamellar.

For the purposes of the present study, the important point is that the etched surface of aged tensile bars can be distinguished from that of unaged polypropylene. Examination of samples aged for various times indicates that the surface etching effect is observable before the loss of tensile elongation. For example, after aging for 50% of the induction time, a grainy texture is clearly observed. Samples aged in nitrogen do not show a change in surface texture. Thus, the etching effect is not due to crystallization. On the other hand, slight weight losses are observed for samples aged in air. Thus, volatilization of low-molecular-weight oxidation products may be responsible for the observed surface etching.

Figure 4(a) shows the surface structure at the interface of one of the crazes which initiates at the edge of the tensile bar after 400 hr aging. The grainy
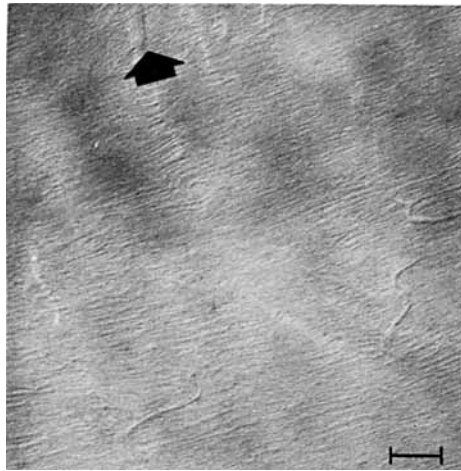
(a)
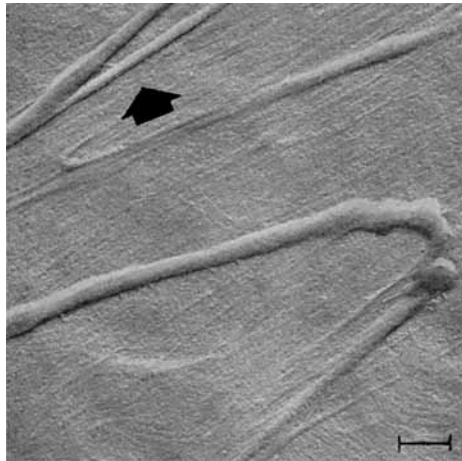
(b)

Fig. 2. (a) Lamellar structure on surface of unaged injection molded polypropylene. Bar represents 0.25 μm, arrow indicates melt flow direction. (b) Ridge structures on surface of unaged injection-molded polypropylene.

texture is not as predominant in this region. The craze is composed of fibrils which are parallel to the long axis of the tensile bar (melt flow direction). Blocks of surface material are seen to be broken off and pulled into the fibrillar network. The extensive fibrillation of the core of the tensile bar suggests that the underlying ductile regions may be relatively unoxidized. The surface layer, on the other hand, develops fissures and breaks apart in a more brittle manner presumably as a result of the oxidative degradation.

Figure 4(b) shows a different crazed region where the growth proceeds by a shearing or peeling off of large blocks of the oxidized surface layer. Again, extensive ductility of the underlying material is suggested by the drawing of large fibrils parallel to the melt flow direction and the presence of smaller fibrils in a perpendicular direction. The extent of deformation within the crazes is perhaps surprising in view of the fact that no external mechanical stress is imposed
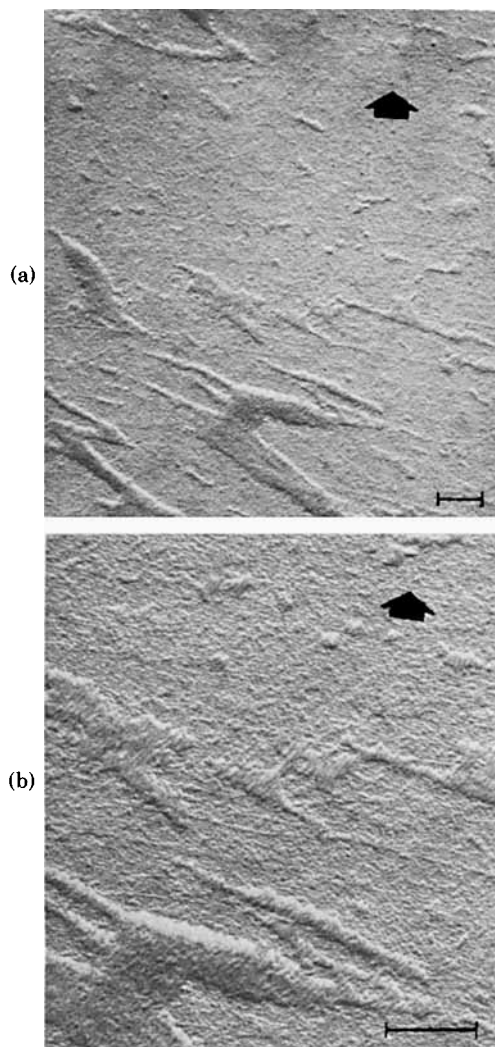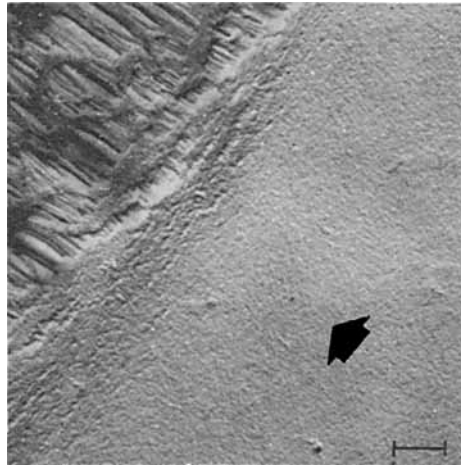
Fig. 3. (a) Surface of injection-molded polypropylene after aging at 90°C for 400 hr. Bar represents 0.25 μm. (b) Same as (a) but higher magnification. Arrow indicates melt flow direction.

on the polypropylene tensile bars. This suggests that the internal stresses from molding are large and/or the oxidative attack significantly lowers the stresses required for this localized deformation.

Thermal Analysis

Differential scanning calorimetry traces for aged and unaged polypropylene are shown in Figure 5. Samples were cut from the edges of the tensile bar. The bar, aged for 600 hr at 90°C, is extensively oxidized and the edges consist of yellow crumbly powder. The location of the melting endotherms in Figure 5 indicates that, with extensive oxidation, the polypropylene crystalline phase melts at a reduced temperature. The measured reduction in melting temperature as a

(a)
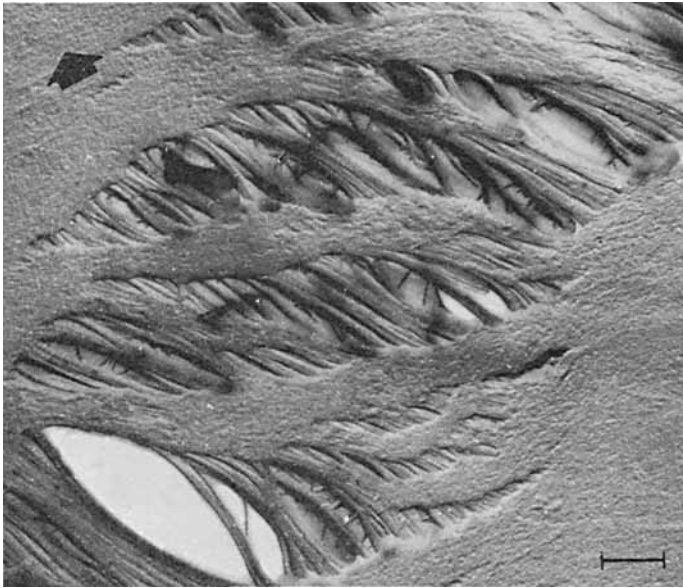
(b)

Fig. 4. Crazes in injection-molded polypropylene aged at 90°C for 400 hr. (a) Craze-matrix interface; (b) peeled craze structure. Arrows indicate melt flow direction, bars represent 0.25 μm.

function of aging time is shown in Figure 6. As mentioned previously, the first visible sign of oxidative degradation occurs after 400 hr, when crazing or microcracking initiates along the sample edges. For lesser aging times, samples cut from the tensile bars did not evidence a reduction in melting temperature.

As an alternative to mechanical cutting, the technique of dissolving the surface in a proper solvent was investigated. Preliminary results using boiling tetrahydrofuran (66°C) as a solvent were not reproducible, although surface dissolution occurred for some oven-aged samples. For the latter, relatively long immersion times (24 hr) were required and oxidation of the tetrahydrofuran com-
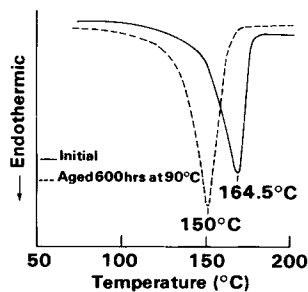
Fig. 5. Melting endotherms of injection molded polypropylene before (—) and after (- - -) aging 600 hr at 90°C.

plicated the subsequent infrared analysis. To overcome these problems, toluene immersion was employed. An immersion time of only 60 sec was sufficient to dissolve enough of the polypropylene surface for subsequent analysis. While measuring the melting temperature of these samples, it was noted that the shape and temperature of the melting endotherm depend strongly on the thermal history of the sample. Figure 7 shows two differential scanning calorimetry traces for the same partially oxidized polypropylene sample.

The initial heating at 10°C/min results in an endothermic peak at 166°C with evidence of a slight shoulder on the low temperature side of the peak. After cooling the sample at 5°C/min and rerunning the DSC trace, the temperature location of the endotherm melting peak is decreased to 159.5°C. There is also a slight indication of a shoulder on the high temperature side of this endotherm. By comparison, an unaged polypropylene evidences an initial endotherm at 167°C, which shifts to 163.5°C after cooling at 5°C/min.
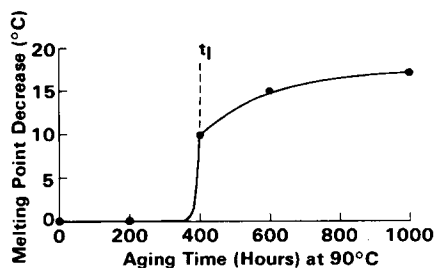

Fig. 6. Melting point decrease vs. aging time at 90°C for injection-molded polypropylene. t_I is induction time for loss of tensile elongation.
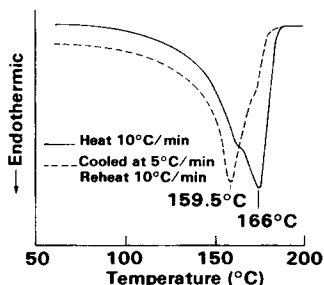

Fig. 7. Melting endotherms of toluene dissolved surface material from polypropylene aged 336 hr at 90°C. Initial heating (—) and reheating after cooling at 5°C/min (- - -).
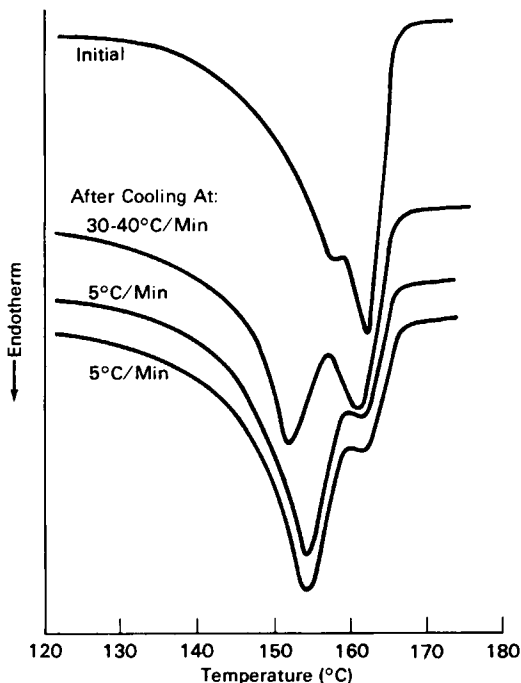
Fig. 8. Effect of cooling rate on melting endotherms of polypropylene aged 503 hr at 90°C.

Figure 8 shows an example where controlled cooling more clearly reveals two endotherms. The slower cooling rate is observed to increase the size of the lower temperature peak. This also suggests that the initial cast sample is highly quenched. The twice repeated measurement, after cooling at 5°C/min, demonstrates that the observed change is due to cooling rate and is not a function of the residence time in the DSC. This shows that the change in melting behavior is not due to further oxidation of the sample during the course of the DSC measurement.

Figure 9 shows the measured reduction in melting temperature of samples dissolved from the surface as a function of oven aging time. The melting temperature was measured after heating at 10°C/min, cooling at 5°C/min, and reheating at 10°C/min to enhance the lower temperature endotherm. Also shown in Figure 9 is the induction time, t_I, for the loss in tensile elongation. It is clear
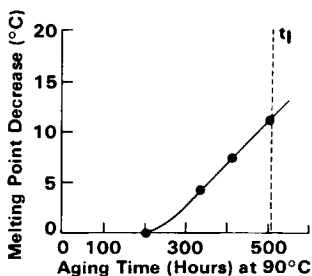

Fig. 9. Changes in melting point of dissolved surface layer of polypropylene as function of aging time at 90°C. t_I is induction time for loss of tensile elongation.

that significant changes in melting behavior are detected prior to the catastrophic decrease in tensile elongation. Also there is an apparent induction time during which changes in melting temperature are not observed. The magnitude of the induction time is independent of whether the onset or peak of the melting endotherm is taken as the melting temperature. Available data indicates that the onset is a more reproducible measurement.

To determine whether the higher temperature melting peak was due to recrystallization in the DSC, samples of highly oxidized polypropylene were run at various heating rates. Results are shown in Figure 10 for heating rates of 2 and 50°C/min. It is clear that the second peak is eliminated by use of an increased DSC heating rate, thus this peak can be attributed to recrystallization. These results also indicate that the magnitude of the first melting peak alone reflects the initial crystalline content of the sample. Thus, the enhancement of the first melting peak by slower cooling rates (Fig. 8) can be understood. For rapidly quenched samples, on the other hand, the melting of material crystallized in the DSC tends to completely mask the presence of a lower temperature melting endotherm.

Infrared

For tensile bars aged for 400 hr or less, oxidation products were not detected by direct examination using infrared reflectance. Transmission infrared spectra were, therefore, recorded for the polypropylene dissolved off the surface of the aged tensile bars. For these samples, oxidation products were detected. Figure 11 shows the increase in absorbance at 1708 cm^{-1} with aging time at 90°C. This absorption band is due to C=O vibration and is commonly associated with hydrocarbon oxidation products such as acids, aldehydes, and ketones. The absorbance values are normalized using the absorption band at 974 cm^{-1} to account for variations in the amount of polypropylene exposed to the infrared beam. By comparing Figures 11 and 9, it is seen that oxidation is occurring on the surface of the polypropylene tensile bars prior to the loss of tensile elongation. Also, there is a close parallel between the decrease in melting temperature and the increase in oxidation products.

Changes in the degree of crystallinity of the polypropylene samples can also be determined from the infrared spectra. The crystallinity index of the material
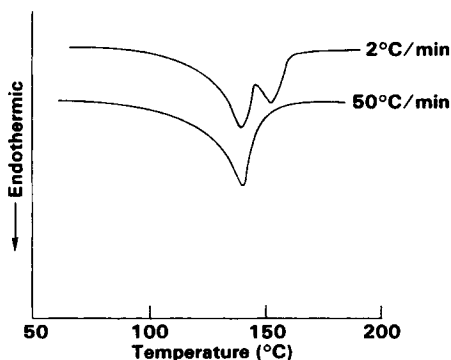

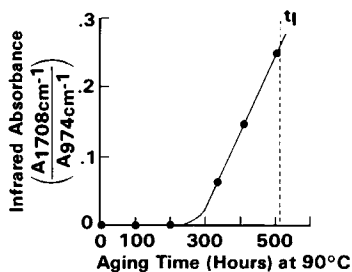Fig. 10. Effect of heating rate on melting endotherms of polypropylene aged 570 hr at 90°C.

Fig. 11. Increase in infrared absorbance at 1708 cm^{-1} as function of oven aging time at 90°C. t_I is infuction time for loss of tensile elongation.

dissolved off the surface of the polypropylene tensile bars is shown in Figure 12. For comparison, the crystallinity index measured directly on the surface (before dissolution) by reflectance infrared (IR) is also shown. The results indicate that, although oven aging increase the crystalline content of the polypropylene surface, the material removed by toluene immersion has a relatively constant crystalline content. Therefore, the observed decreases in melting temperature are not influenced by the changes in crystalline content which occur during aging. The IR results also indicate that oxidative degradation does not necessarily make polypropylene more crystallizable. This observation is compatible with the suggestion by previous investigators that oxidation allows recrystallization of tie molecules which have undergone chain scission.[5,7] These chain segments may also crystallize after casting from the toluene solution; however, other segments can form new tie molecules during solidification, thereby keeping a constant degree of crystallinity.

To determine whether the oxidative degradation was limited to the outer surface of the tensile bars the surface was dissolved sequentially to remove several layers. A sample aged for 503 hr at 90°C was reimmersed in five separate containers of toluene for 60 sec each. The resultant material was analyzed both by transmission IR and DSC. Figure 13(a) shows the IR spectra in the region of the 1708-cm^{-1} absorption band. There is a clear trend from extensive oxidation on the outer surface to lesser evidence of oxidation for the underlying regions. Similarly, the DSC analysis [Fig. 13(b)] shows the progression of the melting endotherm for the various layers. The melting temperature of all layers of polypropylene is decreased. However, the trend suggests even for this exten-
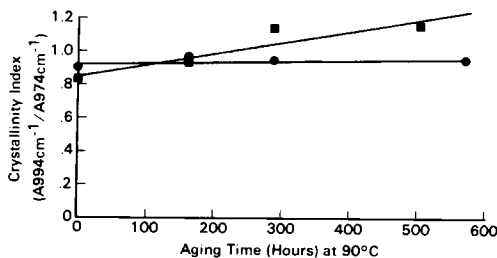

Fig. 12. Infrared crystallinity index as function of aging time for polypropylene before and after surface dissolution. ■, reflectance IR, as aged; ●, transmission IR, dissolved surface layer.
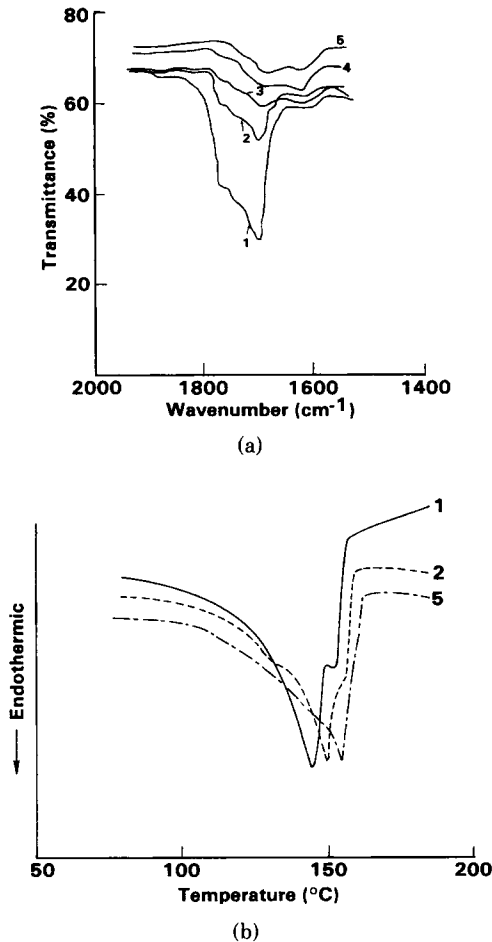
Fig. 13. (a) Transmission IR spectra of successive layers removed from injection-molded polypropylene aged at 90°C for 503 hr. (b) Melting endotherms of layers.

sively oxidized sample the bulk of the inner core may be relatively unoxidized.

For example, an estimate of the surface layer thickness can be obtained from the weight of the dissolved polypropylene from each successive immersion (~50 mg), the initial surface area (1500 mm²), and the density of polypropylene (0.9 g/cm³). The calculated layer thickness is 37 μm. From the infrared results it appears that only the outer 75 μm is severely oxidized. Similarly, extrapolation of the melting temperature data suggests only the outer 300 μm will evidence a reduced melting temperature. These figures are only approximate since the surface dissolution was observed to occur preferentially at the edges of the tensile bar. However, they do serve to emphasize that a large core (perhaps 2500 μm thick) of relatively unoxidized material exists within the aged tensile bar, even for samples whose tensile elongation has been reduced to zero.
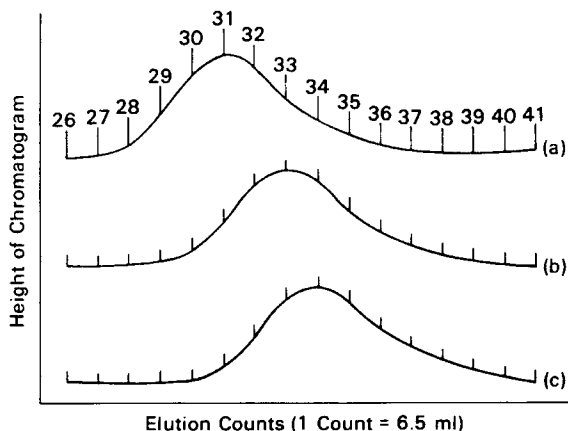
Fig. 14. Gel permeation chromatographs of polypropylene. (a) molding powder; (b) surface layer from unaged injection-molded tensile bar; (c) surface layer from injection-molded tensile bar aged 164 hr at 90°C.

Gel Permeation Chromatography

Decreases in molecular weight as a result of oven aging were found by gel permeation chromatography to be very significant. Figure 14 shows the chromatograms obtained from polypropylene samples dissolved from the surface of injection-molded tensile bars and also a sample of the as-received molding powder. Table I lists the calculated values of $\overline{M}_w$, weight-average molecular weight, and $\overline{M}n$, number-average molecular weight. The molecular weight dispersity is given by the ratio $\overline{M}_w/\overline{M}_n$.

Even prior to aging, the molecular weight distribution on the surface of the injection molded bar is significantly changed from the as-received polypropylene powder. There is an increase in both the high- and low-molecular-weight tails of the distribution while the peak is shifted to lower molecular weight. At the present time, it is not known whether these changes are related to oxidation, shear effects during injection molding,[8] or whether they are due to a molecular weight fractionation peculiar to the surface dissolution technique.[9] In view of the magnitude of the changes observed, this effect warrants further study.

The gel permeation chromatography data clearly demonstrates that oven aging causes a decrease in molecular weight. This is shown in Figure 15 along with concurrent changes in tensile elongation and melting temperature. The latter data was taken on the same tensile bars used for molecular weight determina-

TABLE I
Molecular Weight of Polypropylene 6501

| | Molecular wt. | | |
Sample	number aver.	weight aver.	dispersity
PP6501 "as received"	48,900	340,000	7.0
Tensile bar surface at 90°C			
Unaged	9,200	601,200	65.3
Aged 164 hr	4,700	31,700	6.7
Aged 288 hr	2,100	11,200	5.3
Aged 570 hr	1,300	3,700	2.8
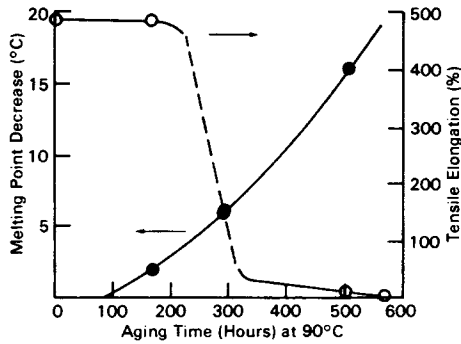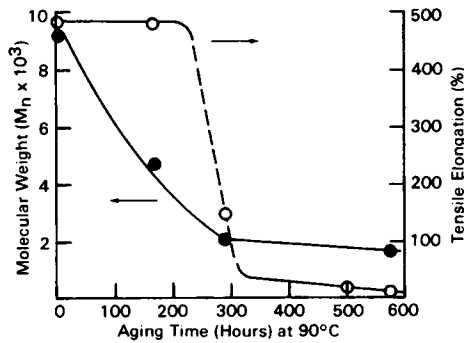
Fig. 15. Comparison of changes in (a) tensile elongation and melting point, (b) tensile elongation and number-average molecular weight of polypropylene as function of aging time at 90°C.

tions. The induction time for loss of elongation in Figure 15 differs from the value presented in Figure 3 because of differences in processing and storage conditions for the tensile bars. From Figure 15 it is seen that there is no apparent induction time in the molecular weight decrease with aging time. In fact, while tensile elongation is unchanged after 164 hr aging at 90°C, the number-average molecular weight of the polypropylene on the surface has decreased by 50% of its initial value. Although a melting point decrease is observed during this same time interval, it is apparent that the molecular weight measurements provide the most sensitive indicator of changes due to oven aging.

DISCUSSION

Aging of Polypropylene

The results of this investigation demonstrate conclusively that during oven aging of unstabilized polypropylene, extensive oxidative degradation occurs on the surface of molded parts even prior to the loss of tensile elongation. The surface oxidation results in a large decrease in molecular weight which is easily detected by gel permeation chromatography. The appearance of oxidation products on the surface was also verified by infrared spectroscopy. Moreover, thermal analysis revealed that the melting point of the oxidized polypropylene

is decreased. It is important to recognize that all of these changes occur during the induction period when no visible degradation is apparent (crazing or yellowing). Although indications of oxidative attack are obtained by electron microscopy, infrared, and DSC, it appears that molecular weight analysis is the most sensitive indicator.

Surface Dissolution

The technique of dissolving the outer surface of the relatively thick tensile bars was shown to be a viable approach for studying aging. For example, neither the DSC analysis of surface shavings nor the reflectance IR technique could detect oxidation during the induction time. Dissolution not only allows a separation and concentration of the outer surface material but also permits the study of successive layers. In the present study, it was noted that the extent of oxidation decreases rapidly toward the center of the molded bar. The craze structure shown in Figure 4(a) also exhibits features suggesting a brittle surface layer and a more ductile core. This surface oxidation is an expected result based on previous reports and can be attributed to limitations on diffusion of oxygen into the thick tensile bar.[10]

Although dissolution of the surface may appear straightforward there are several complicating factors. First, even for completely homogeneous samples, the dissolution process will be dependent on variables such as solvent diffusion, stirring rate, crystallinity, and immersion time as discussed by Blackadder and Lepoidevin.[9] The extent of aging also influences the dissolution rate as it was noted that aged polypropylene dissolves more readily. Also, the injection-molded samples used in this investigation exhibit a skin-core morphology similar to that reported by Kantz, Newman, and Stigale.[11] The dissolved surface material examined in this study is estimated to be taken entirely from the highly oriented surface skin which was determined by optical microscopy to be over 100 μm thick. Further complication arises from the possible segregation of polypropylene molecules according to molecular weight owing to the high rate of shearing during processing. For example, Heuke, Smith, and Abbott[8] have noted that a higher molecular weight is measured from the surface region of an injection-molded polypropylene copolymer. Obviously, much further work is needed in order to optimize conditions for dissolving surface layers for analysis and to sort out the effects of oxidation, processing, and dissolution.

Molecular Weight Changes

The reason for the changes in molecular weight distribution before and after processing by injection molding (Table I) is not presently known. The effect of subsequent oven aging on the molecular weight of the dissolved surface material is more easily understood. The systematic decrease in molecular weight (either number average or weight average) with aging time indicates the predominance of chain scission reactions as discussed by previous investigators.[2-4] It is also interesting to note that the molecular weight dispersity approaches a value of 2.0 as shown in Figure 16. Scott has discussed the criteria of a limiting value of dispersity of 2.0 for random chain scission.[12] This is based upon the molecular weight distribution approaching the most probable one with large
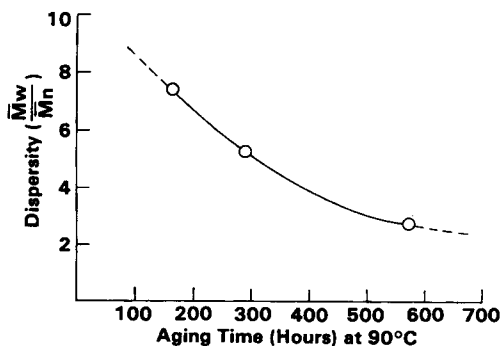
Fig. 16. Molecular weight dispersity ($\overline{M}w:\overline{M}n$) of unstabilized polypropylene vs. aging time at 90°C.

amounts of scission. The data presented here are, therefore, compatible with a random chain scission process. However, as Scott pointed out, the dispersity is a consequence of all reactions of polymeric species and does not necessarily reflect only the initial chain scission reactions. A rigorous analysis of molecular weight changes during aging cannot be performed until one resolves the effect of processing and sample preparation. At present, it is not clear which initial molecular weight in Table I should be used in Scott's analysis scheme—the as-received powder or the as-molded bar.

Melting Temperature Decrease

The effect of oxidation in reducing the melting temperature of polypropylene has been reported only recently.[13] Based on the results of this study, the melting point decrease is attributed to the reduction in molecular weight of polypropylene with aging. It is well known that long chain polymers exhibit higher melting points than their low-molecular-weight homologs.[14] Unfortunately, specific data for polypropylene are not available. Oxidation is also modifying the chemical structure of the polypropylene and this heterogeneity in structure may be contributing to the melting behavior. Cooling rate was also observed to affect the melting behavior. Rapid quenching reduced the degree of crystallinity as shown by the decreased magnitude of the lower temperature melting endotherm and also affected the peak location. For a given molecular weight distribution and thermal history, available data indicates that a unique melting temperature exists, though it may be strongly masked by crystallization phenomena in the DSC.

It is important to note that the melting temperature decrease is not dependent on the surface dissolution technique. For example, polypropylene which has been aged beyond the apparent induction time exhibits similar melting behavior both by use of surface shavings or by use of the dissolved surface material.

X-ray diffraction patterns of the extensively aged polypropylene revealed no change in crystal structure from the usually observed α form. Similarly, no gross change in surface morphology was observed by electron microscopy. Morphological dependence is also unlikely in view of the similar melting behavior of surface shavings and dissolved material. It was noted by IR as well as by DSC that aging did increase the degree of crystallinity. However, there is at present

no evidence to indicate that the melting of this recrystallized material can be distinguished from that of the initial crystalline phase. In summary, although a variety of physical and chemical changes are occurring during the aging of polypropylene, it is believed that the decrease in melting temperature is primarily caused by molecular weight reduction.

CONCLUSIONS

(1) Surface oxidation is readily detected during the apparent induction period for aging of unstabilized polypropylene.

(2) Oxidative chain scission decreases the molecular weight of polypropylene with a consequent reduction in melting temperature.

(3) Surface dissolution provides a convenient technique for analyzing the extent of aging and demonstrates that oxidation is largely confined to the outer surface of thick injection molded polypropylene tensile bars.

References

1 J. W. Tamblyn and G. C. Newland, *J. Appl. Polym. Sci.*, **9**, 2251 (1965).

2. L. Reich and S. S. Stivala, *Autoxidation of Hydrocarbons and Polyolefins*, Marcel Dekker, New York, 1969.

3. M. B. Neiman, *Aging and Stabilization of Polymers*, Consultants Bureau, New York, 1965.

4. A. S. Kuzminskii, *The Ageing and Stabilisation of Polymers*, Elsevier, New York, 1971.

5. H. J. Oswald and E. Turi, *Polym. Eng. Sci.*, **5**, 152 (1965).

6. J. P. Luongo, *J. Appl. Polym. Sci.*, **3**(9), 302 (1960).

7. I. A. Abu-Isa, *J. Polym. Sci. Part A-1*, 8(4), 961 (1970).

8. S. J. Heuke, C. E. Smith, and R. F. Abbott, *Polym. Engr. Sci.*, **15**(2), 72 (1975).

9. D. A. Blackadder and G. J. Lepoidevin, *Polymer*, **17**, 387 (1976).

10. C. R. Boss and J. C. W. Chien, *J. Polym. Sci. Part A-1*, 4 1543 (1966).

11. M. R. Kantz, H. D. Newman, Jr., and F. H. Stigale, *J. Appl. Polym. Sci.*, **16**, 1249 (1972).

12. K. W. Scott, *J. Polym. Sci. Polym. Symp.* **46**, 321 (1974).

13. N Ya. Rapaport and Yv. A. Shlyapnikov, *Polym. Sci. (USSR)*, 17(4), 847 (1975).

14. M. G. Broadhurst, *J. Chem. Phys.*, **36**(10), 2578 (1962).