

# Molecular Weight Measurement in Weathered Polymers

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## SYNOPSIS

Gel permeation chromatography has been used to monitor the molecular weight changes that occur when polymers are degraded by photooxidation. Methods of sample preparation and procedures for conducting the chromatography measurements and for analyzing the results are discussed. Examples are given of applications to studies of polystyrene (PS), polypropylene (PP), and glass fiber-reinforced polypropylene (GFPP) exposed to ultraviolet (UV) irradiation in the laboratory. The results show that the degradation rate is fastest near the exposed surface, but in PS and PP, degradation is much faster at the unexposed surface than in the center of the molding, where the UV intensity is greater than at the unexposed surface. It is deduced that degradation at the center is slowed by a shortage of oxygen. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Photooxidation causes chain scission in polymers under natural conditions outdoors, particularly in hot sunny climates.<sup>1,2</sup> This is the main cause of property deterioration, and molecular weight reduction is one of the most important characteristics in the study of weathering of polymers. The most severe chemical degradation occurs at the exposed surface of the polymer, and in most studies of molecular weight reduction, samples are taken from the surface or exposures are conducted on thin samples that are then analyzed complete. Degradation in the interior of a thick molding will depend on the local ultraviolet (UV) level (and therefore on the absorption characteristics of the polymer and any additives that are present) and on the concentration of the reactants, principally oxygen. In a thick molding in which oxygen diffusion is slow, degradation in the interior will be much slower than near to the surface. Nevertheless, from studies of the mechanisms of failure of weathered polymer moldings, it is evident that degradation of material deep inside the wall may sometimes have a strong influ-

ence over behavior,<sup>3</sup> especially after extended periods of exposure. It is therefore of great interest to determine the extent of molecular weight degradation as a function of depth through the molding wall.

In the studies reported here, molded bars made from polystyrene (PS), polypropylene (PP), and glass fiber-reinforced polypropylene (GFPP) were subjected to controlled UV exposures in the laboratory using fluorescent tubes; then, samples were taken from different depths and analyzed by gel permeation chromatography (GPC). Samples were prepared using high-speed milling, a technique used extensively for the layer removal analysis of residual stress distribution.<sup>4,5</sup> The significance of the molecular weight measurements made by GPC has been investigated and is reviewed critically.

## EXPERIMENTAL

### Sample Preparation

The study of GPC reported here was conducted as part of a larger investigation on the weathering of injection moldings in the form of tensile test bars measuring approximately  $190 \times 12.7 \times 3$  mm. After a weathering treatment, samples for GPC analysis were prepared using high-speed milling using a sin-

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gle-point cutter and fly-cutting action. This method has been tested thoroughly in studies of residual stress measurement by layer removal analysis. It does not produce a significant temperature rise at the machined surface (though this was not true in trials conducted with a four-fluted end mill) and no indication of serious damage can be seen in the scanning electron microscope.

Two methods of mounting the bar for milling have been used. In the first, the bar is fastened to a steel block using double-sided adhesive tape, then placed on the bed of the milling machine. In the second, the bar is held flat on a hollow steel block using a vacuum drawn through a porous ceramic block that provides support for the bar<sup>6</sup>; this is important when the bar remainder is thin. The latter method facilitates detachment of the remainder of the bar from the mounting block after a layer has been removed. This is particularly useful in the case of residual stress distribution analysis because the bar curvature has to be measured after each layer removal,<sup>4,5</sup> though if the need is only to produce samples for molecular weight analysis, the double-sided adhesive tape method is perfectly satisfactory. The machined chippings are collected after each layer removal. It is essential that the machine bed is cleaned thoroughly before the machining operation begins and that chippings are collected only from the clean surface. The final remainder of the bar is in the form of a thin tape and a sample was cut from this for GPC analysis. The material in the remainder has a very different form and a very different mechanical history to the machined chippings and provides a useful comparator.

When layers are removed, the residual stresses become imbalanced, causing the bar to bend if released from external tractions. This is why it is necessary to fasten the bar flat using a continuously distributed force as supplied by adhesive tape or a vacuum. When tape is used to secure the bar onto the block, removal of the bar after machining away a layer must be performed with great care so that no distortion is introduced at this stage.

**Table I** Column Operating Conditions

Polymer	Solvent	Concentration (kg dm <sup>-3</sup> )	Injection Volume (mL)	Flow Rate (mL min <sup>-1</sup> )	Temp (°C)
PS	Tetrahydrofuran	2.0	0.2	1.0	≤ 30
PP	1,2-Dichlorobenzene	1.0 or 1.5	0.2	1.0	140
GFPP	1,2-Dichlorobenzene	1.5	0.2	1.0	140

### Gel Permeation Chromatography (GPC)

The molecular weight analysis of the samples was carried out using the standard systems and procedures of the Polymer Supply and Characterization Centre at Rapra Technology Ltd. (Shawbury, Shrewsbury, UK). The columns used for all the materials for which results are reported here were Polymer Laboratories PL gel 2 × mixed gel-B, with column length of 300 mm and particle size of 10 microns. The solvents used all contained the antioxidant 2,6-*tert*-butyl-*p*-cresol. Details of the column operating conditions are given in Table I.

The concentration of the solution eluted from the column was measured using a refractive index detector in the case of PS and by an infrared detector monitoring at a wavelength of 3.4 microns in the case of PP and GFPP. The system was calibrated with narrow molecular weight distribution PS calibrants (Polymer Laboratories Ltd., Church Stretton, Shropshire, UK) and the data were processed using GPC-PRO software (Viscotek Corp., Porter, TX). With both PP and GFPP, the "Universal Calibration Procedure" was applied to allow for the difference in the chemical type between the samples and the calibrants using the following Mark-Houwink parameters:

	Samples	Calibrants
$\alpha$	0.780	0.700
$\log K$	-3.987	-3.860

where the Mark-Houwink equation for the limiting viscosity  $[\eta]$  for a monodisperse polymer of molar mass  $M$  is

$$[\eta] = KM^\alpha$$

Sample solutions of PS were prepared the day before the chromatography. A small amount of 1,2-dichlorobenzene was added as an internal marker

and the solutions were filtered through a 0.2 micron polyamide membrane.

Sample solutions of PP and GFPP were prepared by adding boiling solvent and gently boiling for 20 min. The solutions were then filtered through a fiber pad at 160°C under an atmosphere of nitrogen and the filtered solutions were reheated to boiling immediately prior to the chromatography.

The results of a GPC analysis are in the form of a relative concentration vs. the elution time through the column. In the runs for which results are presented here, the concentration was measured at 500 equally spaced elution times, beginning 5 min after injection into the column and ending at a preset time that depended on the known characteristics of the column and the material under examination, usually between 15 and 25 min after injection. An example is given in Figure 1. The solvent flow rate should be kept constant and a monodisperse internal marker is included to monitor this. The position of the internal marker peak acts as a check on the solvent flow rate and allows corrections to be made for minor fluctuations in the flow rate; for the analysis of PP and GFPP samples, the peak due to the antioxidant was used as an internal marker.

In computing the results from the concentration distribution, it is first necessary to define the base line. This is partly subjective and can lead to significant differences in the results obtained by different operators even if they use the same data; even if the same equipment and the same calibration is employed, there is still scope for significant scatter in the results obtained. The effect of this is examined in detail below.

Each elution time corresponds to a particular molecular weight and the transformation of the concentration vs. elution time into the molecular weight distribution is normally conducted using a computer that also computes the corresponding number-average molecular weight,  $M_n$ , and weight-average molecular weight,  $M_w$ . The continuous distribution contains the most information, but for quantitative or semiquantitative assessment of the difference between samples, it is convenient to work with one of the molecular weight averages. In studies of molecular degradation,  $M_n$  is a useful parameter because it can be interpreted in terms of the number of random chain scission events.

The GPC-PRO software requires the operator to select an appropriate base line for the concentration vs. elution time plot. For the majority of the analyses performed in the study reported here, the concentration plot was flat at both low and high elution times and a straight base line joining these two re-

gions was chosen. This was usually horizontal or nearly horizontal. In the analyses performed here, the positioning of the base line was fairly straightforward and unlikely to be the source of serious operator error. To derive the molecular weight distribution, the operator must also choose the limits between which the transformation of the chromatogram is executed. In the chromatogram shown in Figure 1, the lower (left-hand) limit is set to the left of the point at which the steep curve intersects with the base line. Because there appears to be a sharp cutoff, the exact position of the left-hand limit may not be very important, but it is recommended that a single value is chosen and adopted for all chromatograms obtained for a series of samples within which comparisons are sought. The elution time lower limit corresponds to an upper limit in molecular size. The choice of the limit on the right-hand side of the chromatograph is not as easy to make. The curve does not fall to such a well-defined cutoff, and in the study described here, the tail sometimes encroached onto the internal marker/antioxidant peak.

In the case of weathered polymer samples, small molecular fragments are expected to be present and will have elution times in this area. The cutoff position must be to the left of the internal marker peak to prevent it from contributing to the molecular size analysis, but the exact location chosen is somewhat arbitrary. A cutoff limit was chosen, then adopted for all runs made with the same column and operating conditions. This limit effectively sets a lower limit to the molecular size in the analyzed distribution. An attempt was made to develop a method to scale the cutoff limits for chromatograms made using different columns based on the different elution times for standard samples; although this improved the agreement in results obtained using reference samples, we are not convinced of its accuracy. More details of the methods adopted for processing the chromatographic data to obtain the molecular weight information are given in the Results section.

### Example Application

The results given here were obtained as part of a larger study on the weathering of injection-molded PS, PP, and GFPP. Sample bars were illuminated by UV radiation using as the source fluorescent tubes (Q-Panel UVA-340) from which the output matches quite closely the spectral distribution of solar radiation at the Earth's surface in the wavelength range below 360 nm, with a similar cutoff at around 290 nm. Illumination was generally set at  $4 \text{ W m}^{-2}$  in the

wavelength range  $< 320$  nm (an extreme tropical level) and irradiation took place in a constant temperature room at  $30 \pm 0.5^\circ\text{C}$ . A special feature of the investigation was that many samples were irradiated while under stress, applied in tension, compression, or bending. The major objective of the investigation was to determine how stress affects the degradation, and molecular weight analysis was seen as a key characterization requirement. Selected samples for each of the materials used in the investigation were subjected to in-depth study by GPC and it is these results that are discussed here.

The samples extracted from the weathered bars for molecular weight analysis could have suffered molecular degradation in several ways. First, mechanical and/or oxidative degradation could have occurred during injection molding. The thermomechanical history of material within an injection molding differs at different depths and it is possible that molecular degradation will vary through the bar thickness direction as a consequence. Second, UV exposure promotes photooxidative degradation, and this also will vary with distance from the surface because of the falling intensity level and the depletion of oxygen in the interior. Molecular degradation caused by this source is of major concern here and should be separated from the other sources if possible. Third, molecular degradation might occur during the machining operation used to extract the sample. To investigate the relative importance of the three sources of molecular degradation, the following samples were subjected to GPC analysis in addition to the samples prepared from weathered bars:

- (a) Material removed by scalpel from a bead of virgin molding resin.
- (b) Samples prepared by milling as described above from an injection-molded bar that had not been exposed to any weathering treatment.

Samples from this program were dealt with in fairly large batches (50–150 samples in each) and a sample of virgin molding resin was included in each batch as a control.

## RESULTS

### Gel Permeation Chromatography (GPC)

To investigate the level of reproducibility of the GPC method, a series of analyses were conducted on data

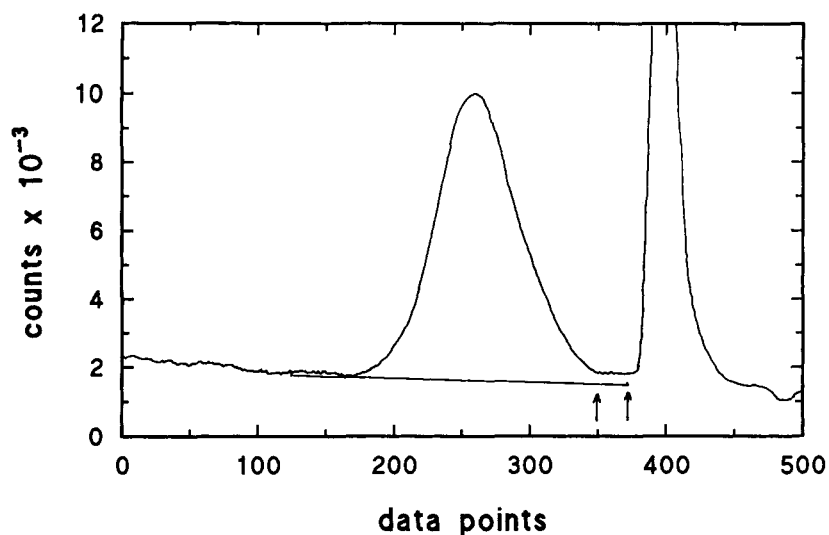
from GPC runs made on PP virgin resin over a period of about 2 years, including data using different columns and calibrations. The values of  $M_n$  and  $M_w$  obtained using the base-line selection procedure described above are given in Table II.

The standard deviation of  $M_n$  expressed as a percentage of the mean is 6%, whereas the value for  $M_w$  is 4%. There is therefore an acceptable degree of agreement but the absolute values may be in serious error. The cutoff at high elution times sets a lower limit on the molecular-size measurement. This may not be important with the virgin material but the degraded samples may contain significant amounts of low molecular weight material that does not contribute to the analyzed distribution and derived averages. This will cause a much greater error in the value of  $M_n$  than in  $M_w$ .

To investigate the effect of changing the higher cutoff limit, data from a heavily degraded PP sample was chosen. Compared to measurements made on less degraded samples, the chromatogram showed much higher concentrations at high elution times, corresponding to low molecular weight material (Fig. 1). For the cutoff limits of 125 and 350 used to obtain the results with virgin PP shown in Table II, the molecular weight averages were  $M_n = 13,900$  and  $M_w = 70,500$ . Inspection of Figure 1 indicates that it might be "reasonable" to select the datum point 370 as the upper cutoff limit instead of 350, still keeping to the left of the antioxidant peak. Reanalyzing with this condition gave  $M_n = 11,850$  and  $M_w = 70,800$ . As expected,  $M_n$  is much more sensitive than is  $M_w$  to the choice of the elution time upper

**Table II** Values of  $M_n$  and  $M_w$  for Virgin PP Recorded at Intervals Over a Period of Two Years

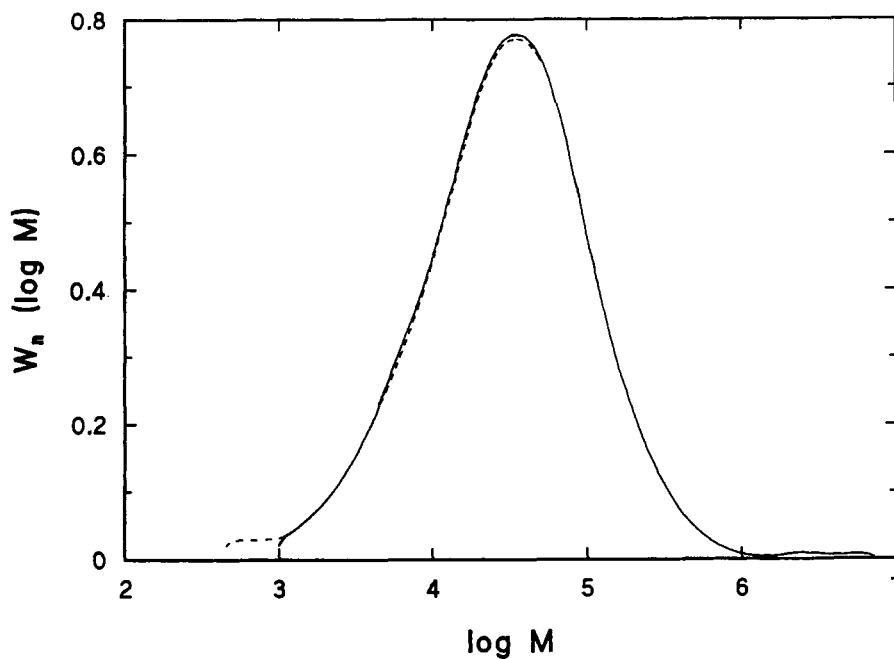
	$M_n$	$M_w$
	37,800	350,000
	42,400	352,000
	43,300	387,000
	41,700	377,000
	43,700	371,800
	43,400	403,000
	43,000	396,000
	42,200	378,000
	40,400	382,000
	40,350	385,000
	39,900	386,000
	48,900	372,000
Mean	42,250	378,300
Standard deviation	2,610	15,000



**Figure 1** Relative concentration vs. elution time for a PP sample taken from the surface of a bar degraded by UV irradiation for 6 weeks while under a tensile stress of  $10 \text{ MNm}^{-2}$ , expressed in terms of data points recorded at 500 equal intervals between two set times. The internal marker peak is at approximately data point 400. The base line chosen is shown together with cutoffs at 350 and 370 data points, respectively (see text).

limit, especially when there is a greater fraction of low molecular weight material present. The molecular size distributions for the two cutoff limits given

are inseparable except that there is a more extensive low molecular tail for the one based on a cutoff limit of 370 (Fig. 2).



**Figure 2** Molecular-size distributions derived from the chromatogram shown in Figure 1: The solid line corresponds to the cutoff at 350 data points and the dashed line to the cutoff at 370 data points.

The principles outlined above were applied when obtaining the molecular-size information presented in the following sections.

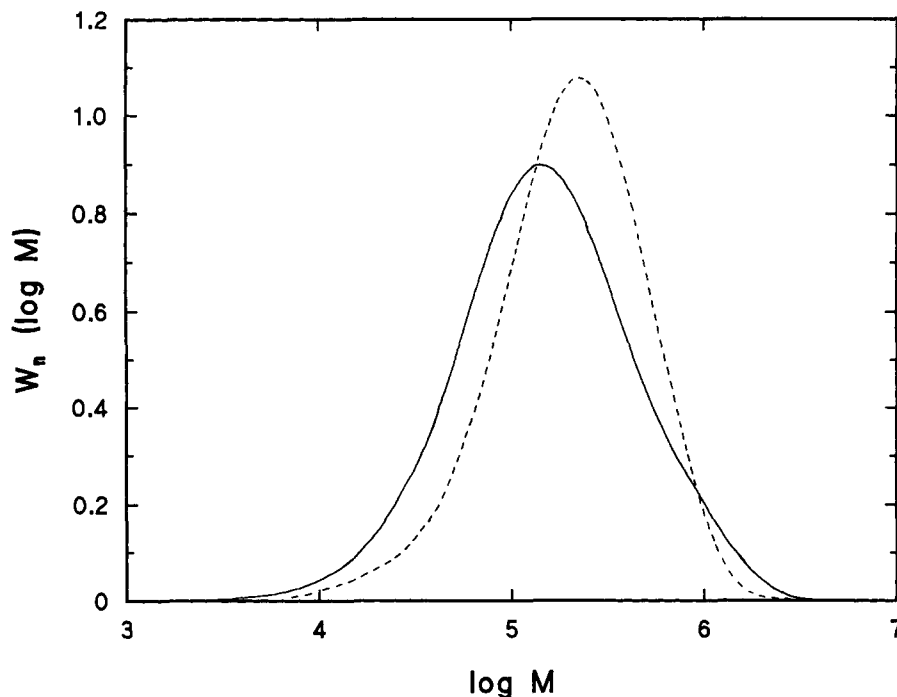
### Polystyrene (PS)

Typical molecular-size distributions for virgin PS and a degraded sample are shown in Figure 3. The degraded sample was removed from the surface (0.33 mm) of a bar that was UV irradiated for 6 weeks. Degradation is shown to have caused a shift to lower molecular weights. Of particular interest is the low molecular weight end because the presence of this fraction will be particularly detrimental to the properties of the material. This part of the GPC size distribution is most prone to inaccuracies, as discussed above, and careful assessment of the results must be made.  $M_n$  is much more sensitive than is  $M_w$  to errors in the measurements of concentration of the low molecular weight species and, as was the case with PP discussed above, it was found that scatter in the  $M_n$  values from the control samples was greater than that in the  $M_w$  values. The scatter in  $M_n$  in PS was acceptably small when compared to the magnitude of the changes in values observed to be caused by photodegradation. Shown in Figure

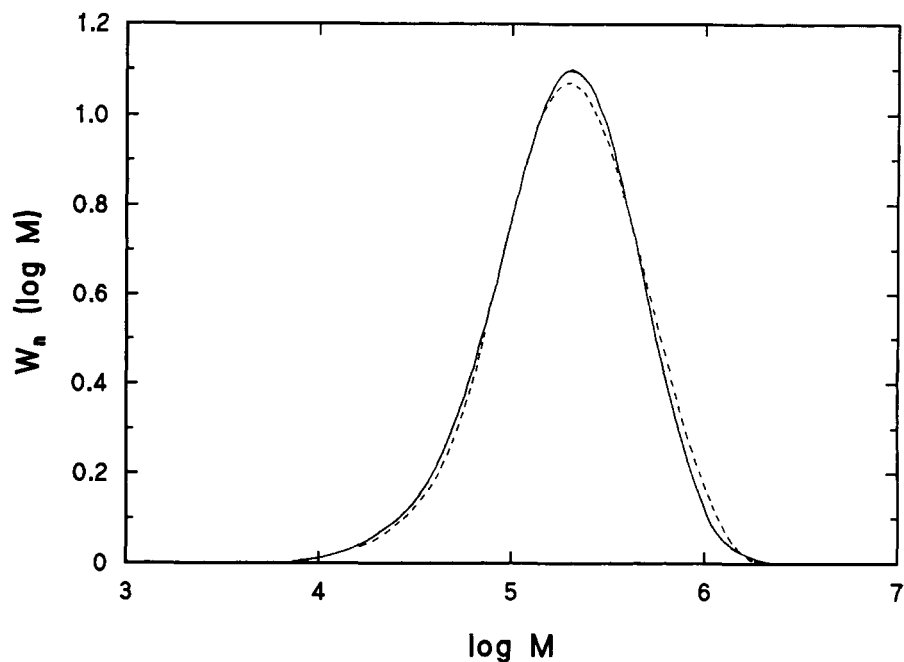
4 is the size distribution measured for a sample removed from the surface (0.3 mm) of an as-molded bar. The difference between this distribution and that obtained with the reference sample is negligible in comparison with that obtained with the exposed sample.

Figure 5 shows plots of  $M_n$  vs. depth for an as-molded PS injection-molded bar and for a similar bar after 6 weeks exposure to UV radiation. The values of  $M_n$  measured for the as-molded material are close to the value obtained with virgin material ( $1.21 \times 10^6$ ) and it is deduced that little or no molecular weight degradation occurred during molding. There is no evidence for depth-dependent differences in molecular weight in the as-molded material; this indicates not only that degradation is not significant but also that there is no significant molecular size segregation caused by flow during molding. It should be noted that the sample taken from one side of the as-molded bar was in the form of machine chippings, and that from the other side in the form of a tapelike remainder. The agreement in the molecular weight measurements from both samples is further evidence that the milling operation causes minimal molecular damage.

Significant molecular weight degradation has been caused by the UV treatment. The effect is



**Figure 3** Molecular-size distributions for virgin PS (broken line) and a degraded sample removed from the surface (0.33 mm) of a bar that was UV-irradiated for 6 weeks (solid line).



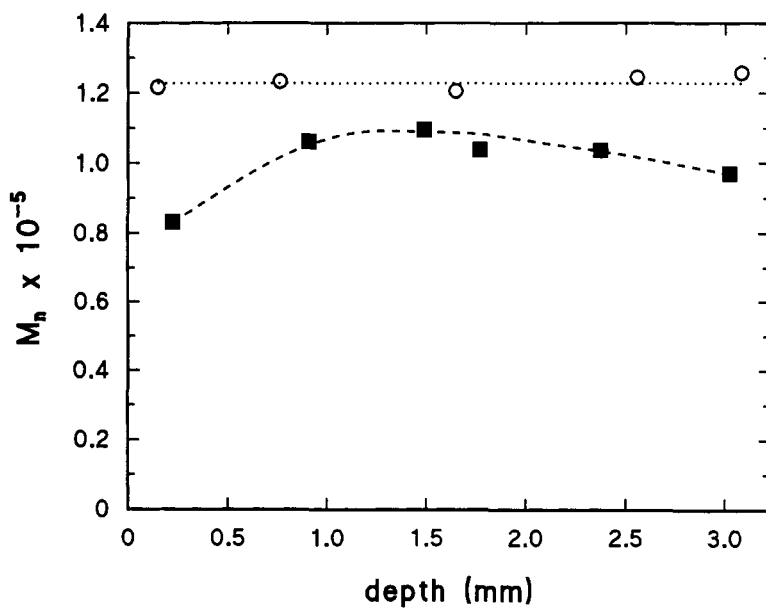
**Figure 4** Molecular-size distributions for virgin PS (broken line) and a sample removed from the surface (0.3 mm) of an as-molded bar (solid line).

greatest near the exposed surface. Degradation near the center of the bar is small but significant degradation is present near the surface that faced away from the UV source. It is deduced that oxygen depletion in the center inhibited reaction. In other experiments it has been shown that tensile stress accelerates molecular weight degradation under con-

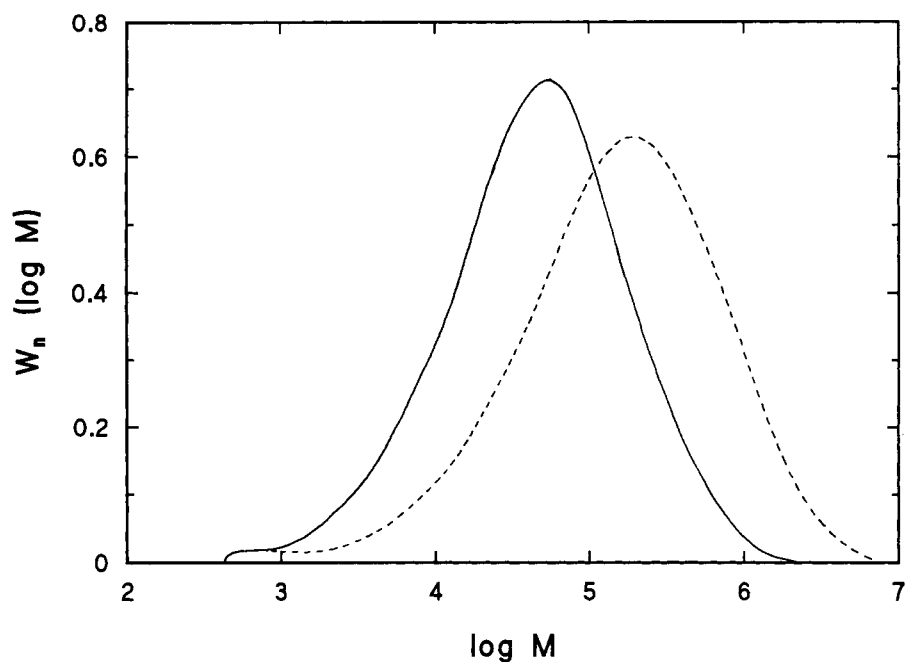
ditions of photooxidation; these results are presented elsewhere.<sup>7-9</sup>

#### Polypropylene (PP)

Figure 6 shows the molecular-size distribution for virgin PP and for a sample cut from the surface



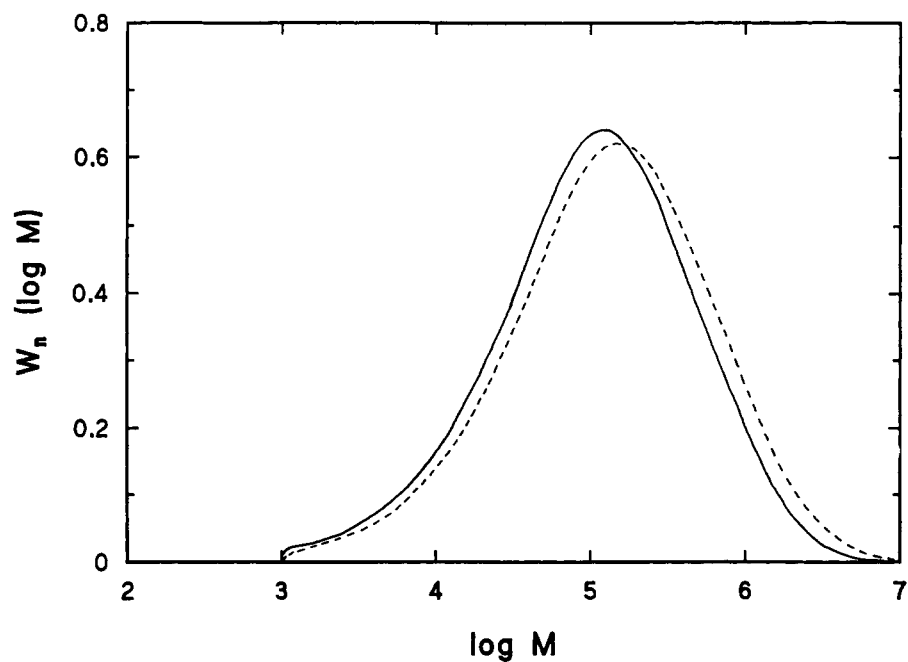
**Figure 5** Plots of  $M_n$  vs. depth for (O) an as-molded PS injection-molded bar and (■) for a similar bar after 6 weeks exposure to UV radiation.



**Figure 6** Molecular-size distributions for virgin PP (broken line) and a degraded sample removed from the surface (0.35 mm) of a bar that was UV-irradiated for 6 weeks (solid line).

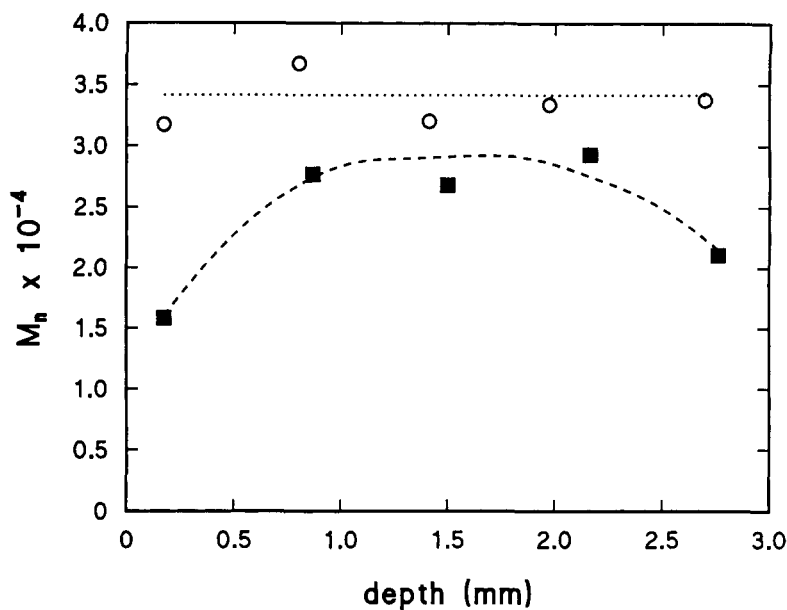
(0.35 mm) of a bar exposed to UV radiation for 6 weeks. The shift to lower molecular weights shows that significant degradation has occurred; the large increase in concentration at low molecular weights

(< 1000) is of particular interest. A much smaller yet significant degradation of molecular weight was found to have occurred on injection molding (Fig. 7).



**Figure 7** Molecular-size distributions for virgin PP (broken line) and a sample removed from the surface of an as-molded bar (solid line).

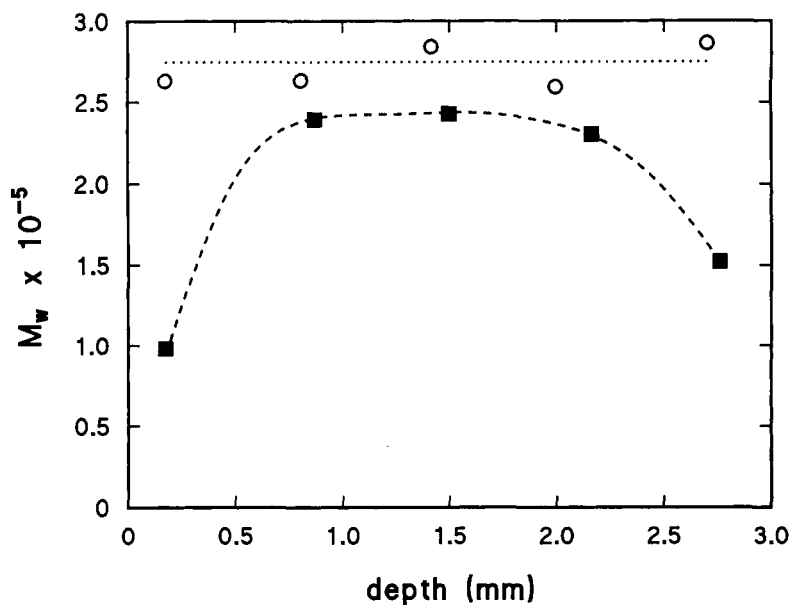




**Figure 8** Plots of  $M_n$  vs. depth (○) for an as-molded PP injection-molded bar and (■) for a similar bar after 6 weeks exposure to UV radiation.

Plots of  $M_n$  vs. depth for an as-molded PP bar and for one exposed to UV radiation for 6 weeks are given in Figure 8.  $M_n$  values for PP showed more scatter than those for PS, making the changes caused by degradation less easy to resolve.  $M_w$  showed less scatter and an example of a set of measurements of  $M_w$  made on samples cut through the depth of a degraded bar is plotted in Figure 9.

Both  $M_n$  and  $M_w$  show that molecular degradation is most severe near the exposed surface but that significant degradation is also present near to the unexposed surface. In the case of PP, the penetration of UV radiation is much less than in PS and measurements made with a photoradiometer (Bentham Instruments) show that the level of UV near the back surface from direct transmission plus reflection



**Figure 9** Plots of  $M_w$  vs. depth (○) for an as-molded PP injection-molded bar and (■) for a similar bar after 6 weeks exposure to UV radiation.

from external surfaces in the exposure room amounts to no more than 5% of the incident radiation. Thus, it is even more apparent with PP that oxygen depletion in the center is the most likely cause of the much lower degradation recorded there, though consideration may have to be given to the distribution of products of the reaction that may promote further degradation.

### Glass Fiber-reinforced Polypropylene (GFPP)

The survey of data obtained on GFPP virgin material over the period of study yielded a similar result to that for PP. The data for six virgin GFPP samples were reanalyzed and gave the following results:  $M_n = 44,200 \pm 2,260$  (i.e.,  $\pm 5\%$ );  $M_w = 358,000 \pm 12,300$  (i.e.,  $\pm 3.4\%$ ). The results obtained with samples extracted from bars molded from GFPP showed similar scatter to the PP samples. Size distributions for virgin GFPP and a degraded sample are given in Figure 10. Considerable degradation is indicated and, as with PP, a smaller yet significant amount of degradation occurred during injection molding.

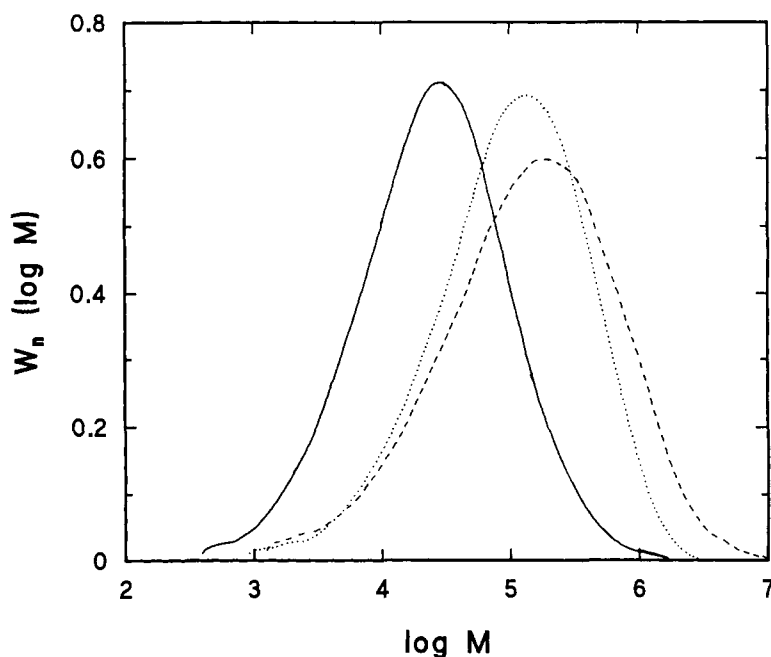
UV transmission is much less in GFPP than in PP because of (i) absorption in the glass and (ii) scattering, and photoradiometer measurements showed that negligible penetration occurred beyond 0.8 mm of the exposed surface. This is consistent

with the distribution of degradation indicated in Figure 11 in which  $M_w$  is plotted vs. depth for a bar exposed for 5 weeks. Very little degradation is indicated beyond a depth of 0.8 mm from the exposed surface.

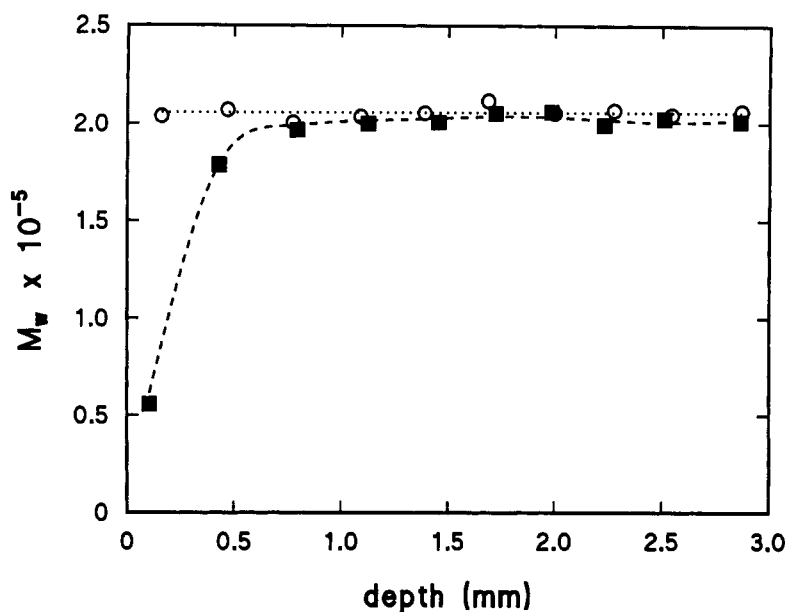
### DISCUSSION

The results presented here are from a much larger investigation in which a range of exposure times were used, and the mechanisms of degradation and the materials aspects of these studies will be discussed elsewhere.<sup>7-9</sup> Of concern here is the method of conducting the molecular weight analysis and the reliability of the results. A fairly comprehensive discussion of the operation and limitations of GPC is given by Ouano et al.<sup>10</sup> There have been refinements in many aspects of the method since the preparation of their chapter, including the development of numerical optimization methods made possible by the use of dedicated computers.<sup>11,12</sup> Methods suitable for measuring small differences in similar samples, as may be produced in studies of the aging behavior of polymers, have been reviewed by Cooper.<sup>13</sup>

In the study of weathering from which the current work is extracted, several hundred samples were surveyed and it would not have been practical to



**Figure 10** Molecular-size distributions for virgin GFPP (broken line), a sample removed from the surface of an as-molded bar (dotted line), and a sample taken from the surface of a bar after 5 weeks weathering (solid line).



**Figure 11** Plots of  $M_w$  vs. depth (O) for an as-molded GFPP bar and (■) for a similar bar after 5 weeks exposure to UV irradiation.

adopt time-consuming procedures. Thus, it was considered essential to base comparisons on results obtained using fast, easily operated commercial software; some of the absolute values may be inaccurate, but the use of standardized routines make sample-to-sample comparisons of good reliability. The discussion presented below concentrates on those aspects that are of particular importance in the application to measurements of degraded polymers.

GPC is the simplest and most effective manner of monitoring the changes in molecular weight distribution occurring during artificial weathering or any similar degradation process. However, the technique has inherent shortcomings with respect to the level of reproducibility.

The short-term reproducibility of GPC is generally reasonable and does permit the effective comparison of the different sections within a test bar. Furthermore, the data are generally comparable for a number of test bars analyzed within a reasonably short period of time, of the order of days. It is, however, essential to standardize a method for choosing the base line and to keep the same datum limits when transforming the chromatograph to the molecular-size distribution.

Problems arise when the average molecular weights are compared for samples measured over an extended period of time (say several months). By scaling the datum limits using the calibration information obtained at the different times, this effect

can be reduced and meaningful comparisons can be made between samples analyzed at widely different times and on different columns.

The experiments reported here have been conducted in a manner that takes account of the poor long-term reproducibility of GPC and demonstrates, in particular, the depth variations in molecular weight in degraded samples. The changes in  $M_n$  have the advantage of correlating with the number of random chain scission events. Changes in  $M_n$  are generally more marked than those in  $M_w$ , though more confidence can be placed on  $M_w$  measurements because they are fairly insensitive to low molecular weight content and therefore less dependent on the choice of the base-line limit at long elution times.

It is noted that the molecular weights measured on PS samples removed with a scalpel from virgin molding resin granules were indistinguishable from those prepared by milling from an injection-molded bar made from the same material. This implies that no significant molecular weight degradation occurs either during the molding operation or during milling. The good agreement between measurements made on machined chippings and tapelike remainders from equivalent depths is further confirmation of the suitability of this method of sample preparation. Thus, we regard the differences in measurements found in bars exposed to UV to be a true reflection of the degradation that had taken place during artificial weathering. In the case of PP, significant degradation was indicated to occur during

injection molding, but, again, there was no evidence to indicate that the degree of damage differed from one location to another within the molding.

## CONCLUSIONS

Great rigor must be observed both with the practical execution of GPC and of the analysis of the data if meaningful results are to be obtained, particularly if comparisons are to be made of a series of samples run over an extended period of time and on different columns. Inaccuracies are inevitable at the low molecular weight end and the absolute values obtained for the molecular weight averages are probably seriously in error when highly degraded polymers are measured, especially  $M_n$ .

High-speed milling is a satisfactory method of providing samples for the determination of the depth profile of molecular weight degradation in a weathered polymer bar. With samples having an exposed area of ca. 1000 mm<sup>2</sup>, sufficient material can be gathered to make two satisfactory GPC runs if a depth as little as 0.1 mm is machined away. This gives an acceptable depth resolution for the current investigations. Very little molecular weight degradation is suffered by PS during injection molding, but significant molecular weight reduction takes place when injection molding both PP and GFPP.

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isation Centre at Rapra Technology Ltd. is also supported by SERC.

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