

The Quantitative Determination of Oil in Impact Polystyrene

T. E. NOWLIN, A. J. UNGERMAH, and S. L. WALLACE, *Union Carbide Corporation, Chemicals and Plastics Division, Bound Brook, New Jersey 08805*

Synopsis

The combination of an extraction technique with proton magnetic resonance spectrometry (PMR) has provided an analytical method for the determination of hydrocarbon mineral oil blended into an impact polystyrene. The amount of extraction time necessary for quantitative removal of the oil has been shown to be dependent on resin particle size. A linear correlation has been found between the weight of the extract obtained from 10.00 g resin and the per cent oil found in the resin.

INTRODUCTION

A saturated hydrocarbon mineral oil is an important processing aid added during the production of impact polystyrenes (IPS). The addition of from 0.5 to 8 wt-% mineral oil to an IPS improves both injection molding and mechanical properties. Sufficient oil is blended to give an optimum melt flow value for injection molding.

It is necessary for both quality control and product optimization studies to have a method for the quantitative determination of oil that is blended into an IPS.

Chromatographic techniques are often utilized for the determination of additives to polymers.¹ However, because the mineral oil blended into an impact polystyrene is a mixture of several hydrocarbons, peak identification and resolution in a chromatographic procedure may not be possible. Interference from low molecular weight styrene-butadiene oligomers would most likely result.

The combination of an extraction technique with proton magnetic resonance (PMR) spectrometry has provided a method.

The extraction procedure separated the mineral oil from the bulk of the polymer material, and PMR spectrometry was utilized to differentiate between the hydrocarbon mineral oil and styrene-butadiene oligomers.

Long-term extraction studies and the examination of IPS resins that contained a known amount of mineral oil have indicated that the quantitative removal of the oil is achieved. The effect of resin particle size on the extraction time has also been examined.

A correlation has been found between the weight of the extract obtained from 10.00 g resin and the per cent oil found in the resin.

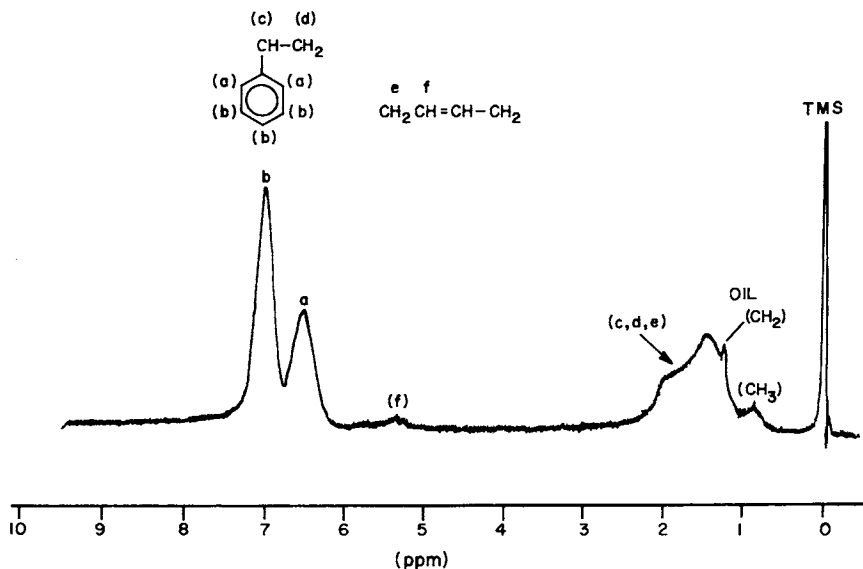


Fig. 1. 60 MHz PMR spectrum of an impact polystyrene resin with approximately 5 wt-% oil.

RESULTS AND DISCUSSION

Figure 1 shows the 60 MHz PMR spectrum of an IPS with about 5 wt-% blended mineral oil. The phenyl region from 6.8 to 7.2 ppm is characteristic of a block of polystyrene.^{2,3} The region at 5.3 ppm is due to the methinic protons of butadiene. The remaining backbone protons of the polymer give a broad resonance from 1.1 to 2.2 ppm. The partially resolved peaks at 0.9 and 1.1 ppm are due to the mineral oil. Adequate quantitative information concerning the amount of oil present in the sample can not be gained from this spectrum. Therefore, an extraction technique was employed to remove the oil from the bulk of the polymer matrix.

In most IPS resins, the mineral oil accounts for greater than 85% of all additives. Moreover, other additives such as antioxidants possess a different polarity than the oil and the extraction solvent (pentane) and were not extractable with pentane. Consequently, the extract contained styrene-butadiene oligomers and mineral oil. The absence of other additives in the extracted material was verified by comparing the pmr spectrum of the extracts with the pmr spectrum of authentic samples of other additives.

Figure 2 shows the PMR spectrum of a typical hydrocarbon mineral oil that is blended into IPS resins. The relatively large methyl resonance at 0.90 ppm shows that the oil is highly branched.

The PMR Spectrum of Typical Extracts

The spectrum of the extract obtained from a typical resin dissolved in deuteriochloroform is shown in Figure 3. The similarity of this spectrum with that of the mineral oil (Fig. 2) is immediately evident. The peaks near 7.0 and 5.3 ppm are due to the styrene and butadiene oligomers, respectively, which were extractable with pentane.

The relative areas obtained from the PMR spectrum allow one to calculate the per cent oil in a particular extract (P_e). The per cent oil in a resin (P_r) is,

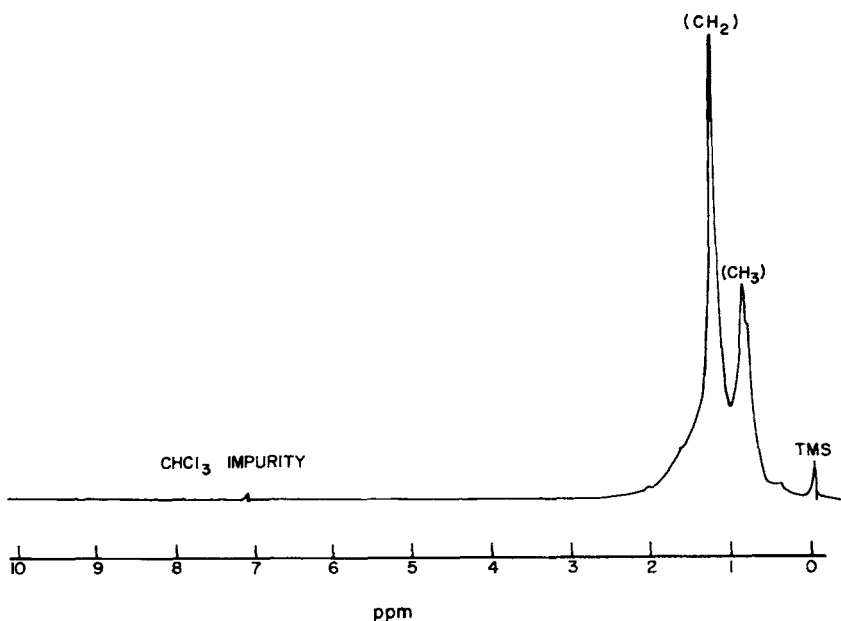


Fig. 2. 60 MHz PMR spectrum of the type of hydrocarbon mineral oil blended into an IPS.

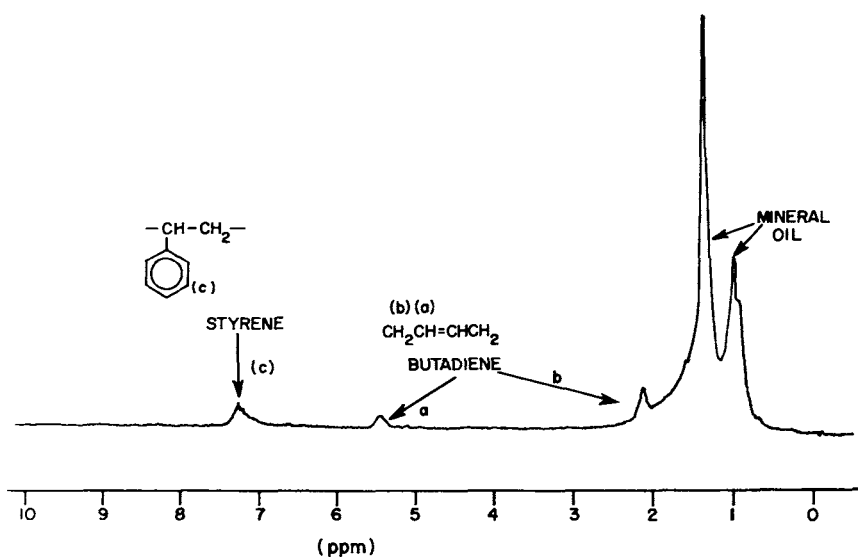


Fig. 3. 60 MHz PMR spectrum of a typical extract.

therefore, given by

$$P_r = \frac{W_e P_e}{W_r}$$

where W_r is the weight of the resin which was extracted with pentane and W_e is the weight of the extract. In all of the IPS resins examined in this work, 10.00 g resin was utilized.

The results obtained from five different resins with a range of oil contents are shown in Table I.

TABLE I
Results Obtained from IPS Resins with a Range of Blended Mineral Oil

Resin no.	Oil found, wt-%	Average
1	0.56, 0.61	0.58
2	1.23, 1.25	1.24
3	2.20, 2.13	2.16
4	4.81, 4.65	4.73
5	7.93, 7.63	7.78

TABLE II
Results of an Extraction Time Study on Resin 4

Extraction time, from hr to hr	Wt. of extract, g	Oil in extract, %	Wt. of oil extracted, g	Cumulative oil, % ^a
0-4	0.5846	72.1	0.421	90
4-8	0.0403	75.7	0.031	97
8-24	0.0248	48.1	0.012	99
24-32	0.0054	48.2	0.003	100

^a If it is assumed that the quantitative removal of the oil has taken place after 32 hr, then the per cent oil values given may be calculated. Resin was a #16 mesh particle size.

TABLE III
Results Obtained from Resins with a Known Amount of Mineral Oil

Oil added, wt-%	Oil found wt-% ^a
2.0	2.0 ± 0.17
4.0	3.8 ± 0.23
6.0	6.0 ± 0.41

^a Average of two separate determinations and corresponding average deviation. A baseline value of 0.55 was found in the control resin and subtracted from each value.

The reproducibility of the method was usually less than ±2%. In order to determine if the quantitative removal of the oil was taking place, several long-term extractions were performed and the extracts were examined at various intervals. The results are shown in Table II. After each time interval 4, 8, 24, and 32 hr, the pentane was removed from the apparatus and replaced with fresh pentane. The weight of the extract obtained from each interval was determined and the extract was examined by PMR. Examination of Table II indicates that for this sample, 90% of the oil was removed after 4 hr. An additional 4-hr extraction increased the figure to 97% and continued extraction for 24 additional hours yielded only a residual trace of oil.

This same experiment was carried out on four additional resins containing different amounts of oil. In all cases, similar results were obtained indicating that the oil is extracted after 8 hr. In addition, a series of standards were prepared and examined in which a known amount of mineral oil was added to a control resin. The results are summarized in Table III and indicate that almost quantitative recovery of the oil is achieved.

In order to determine the effect of particle size on the extraction time, resin

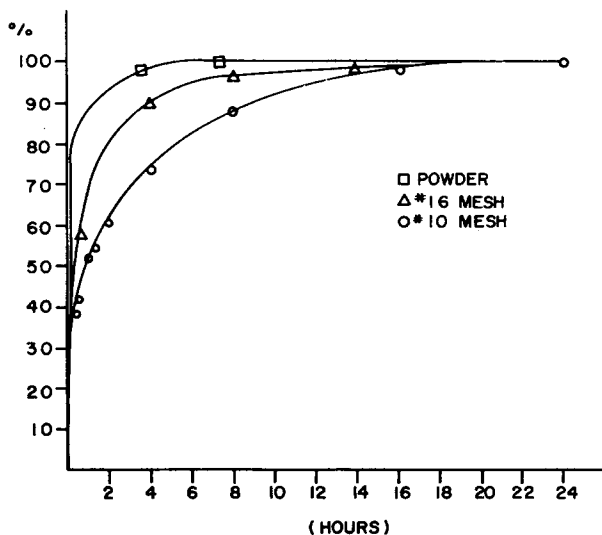


Fig. 4. Effect of particle size on extraction time.

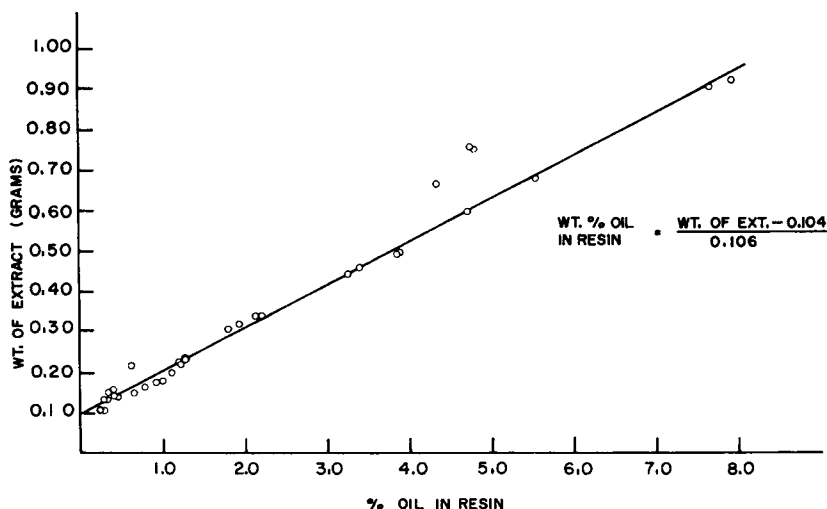


Fig. 5. Correlation between weight of extract and per cent oil in the resin.

4 (Table I) was ground into a powder, a #16 mesh, and a #10 mesh. The extracts were examined after various time intervals, and the results are illustrated in Figure 4. In all cases no additional oil could be extracted after 20 hr. However, the time required for complete removal was reduced to about 4 hr and 8 hr with the powder and #16 mesh particle size, respectively.

A least-squares analysis was carried out on the relationship between the per cent oil found in a resin and the weight of the extract obtained from 10.00 g resin (Fig. 5). A correlation coefficient of 0.99 was obtained.

Therefore, a reasonable measure of the oil content in a resin is given by the expression

$$\text{wt \% oil in resin} = \frac{(\text{wt. of extract}) - (0.104)}{0.106}$$

The significant advantage of this approach is that the extract does not need to be examined by PMR spectrometry after a correlation curve has been established. The results imply that any pentane extract obtained from 10.00 g resin will consist of 0.104 g (y -intercept) of butadiene-styrene oligomers and the oil. The deviation of the slope from 0.100 (actual value obtained 0.106) indicates a slight deviation from this idealized approach.

However, it must be emphasized that the highest confidence level will only be obtained if the extraction technique is used in conjunction with PMR spectrometry.

EXPERIMENTAL

The PMR spectra were obtained at ambient temperature on a Varian EM-360 (60 MHz) instrument. The extracts obtained were dissolved in CDCl_3 and the spectrum recorded from 0 to 10 ppm. In some cases, carbon disulfide was found to be a better solvent.

Resin was ground into the appropriate particle size in Dry Ice. Ten grams resin weighed to the nearest 0.1 g was used in all extractions.

Soxhlet assemblies were placed on a steam plate and 250 ml pentane was utilized. Excess solvent was removed with a stream of nitrogen, and the extracts were dried in a vacuum oven at 60°C for 16–20 hr.

Calculations

Let P_e = % oil in extract, P = area of phenyl region, B = area from 4.8 to 5.3 ppm, R = area from 0.9 to 3.0 ppm,

$$P_e = \frac{\frac{[R - (3P/5 + 2B)]478}{70}}{\frac{[R - (3P/5 + 2B)]478}{70} + (P/5)(104) + (B/2)(54)} \times 100.$$

The mineral oil is a saturated hydrocarbon with a molecular weight of ~ 478 amu with 70 hydrogen atoms.

The authors express their gratitude to Ms. A. D. Hammerich and Dr. L. E. Brydia for helpful discussions and suggestions.

References

1. J. Haslam, H. A. Willis, and D. C. M. Squirrell, *Identification and Analysis of Plastics*, Butterworth, London, 1972.
2. F. A. Bovey, *High Resolution NMR of Macromolecules*, Academic Press, New York, 1972, p. 124.
3. F. A. Bovey, G. V. D. Tiers, and G. Filiporich, *J. Polym. Sci.*, **38**, 73 (1959).
4. W. L. Senn, *Anal. Chim. Acta*, **29**, 505 (1963).

Received September 24, 1975

Revised October 6, 1975