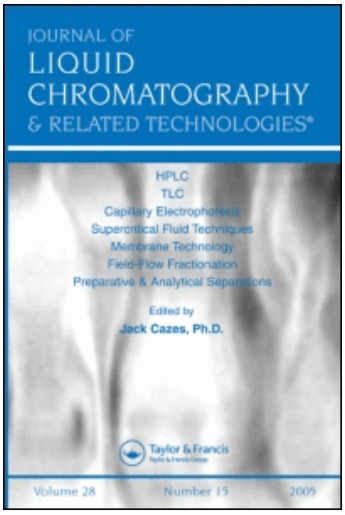

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DETERMINATION OF GEL CONTENT OF ACRYLIC LATEXES BY SIZE EXCLUSION CHROMATOGRAPHY*

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ABSTRACT

The percent gel of a number of acrylic latexes was measured by size exclusion chromatography (SEC). Latexes studied were emulsion polymerized butyl acrylate/methyl methacrylate copolymers with up to 70% gel content. Tetrahydrofuran (THF) was used as the solvent for the latex and chromatographic mobile phase. To optimize the separation, various pore sizes of controlled porosity glass (CPG-10) column packing were tested. Best results were obtained for a combination of three columns (3/8 inch I.D. and 4 foot long) packed with 75Å, 370Å and 729Å porosity CPG packings. The SEC results with analysis time of less than 2 hours compared favorably with those of the conventional gravimetric gel content method.

INTRODUCTION

An accurate and reliable method for the determination of gel content is important in the characterization and quality control of latexes used in coatings formulations. It is known that the

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mechanical properties of the final film are influenced by this highly crosslinked fraction of the latex. The stiffness or toughness of the film has been shown to increase with an increase in gel content.[1-2]

A number of techniques have been reported for the determination of the gel content of polymers. These techniques include gravimetric (solvent extraction),[1] centrifugal,[3] light scattering,[4-5] and chromatographic methods.[6-8] The choice of a given gel content analysis method is determined by its applicability to a particular polymer, convenience of operation and the speed of the analysis.

Among these methods the chromatographic approach, initially applied to a series of nitrile elastomers by Gaylor and coworkers[6], is of particular interest. It combines adequate sensitivity, ease of operation and considerable improvement in the speed of analysis when compared to the gravimetric gel content test. In this method the gel and soluble fraction of the latex, initially dissolved in a suitable solvent, are separated on a controlled porosity column packing on the basis of effective hydrodynamic size. Solvent swollen gel particles, which are considerably larger than dissolved molecules, elute through the interstitial volume of the packing much faster than the dissolved polymer molecules which enter the pores of the stationary phase and are temporarily retained in the pores.

This work reports the results of the application of the chromatographic gel content method to a series of acrylic latexes

with different gel contents. Results are compared with those of the gravimetric gel content method.

MATERIALS AND METHODS

Latex Samples

The latexes used in this work were emulsion polymerized butylacrylate/methyl methacrylate copolymers containing various levels of a plasticizer included in the synthesis to control the gel content level of the latex. The non-volatile (NV) and gel content of the three latexes used in this study are listed in Table 1.

Sample Preparation

The latex solutions for chromatographic analysis were prepared in Burdick and Jackson distilled in glass THF in the following manner. The aqueous latex (about 50% non-volatile by weight) was

TABLE 1.

NV and Gel Content of Three Latex Samples

SAMPLE	NV[a] (%)	GEL CONTENT[b] (%)
A	45.83	64
B	44.79	18
D	44.47	1.7

[a] As determined by the method ASTM D-1644-75
[b] As determined by the gravimetric gel content test method

directly added to a known volume of THF up to 1% solids. The solution was stirred with a magnetic stirring bar at room temperature, while dropwise adding the latex. At this point the latex may be present in three distinct forms; as soluble polymer, suspended microgel particles (crosslinked structure of colloidal size) and large macrogel particles which are not colloidally dispersable and sediment to the bottom of the container. Further agitation (about 1 hour in a shaker bath) is necessary to disperse the macrogel and bring the soluble fraction into complete solution. The solutions were then filtered through a 0.45 μ Fluropore* membrane. The proportions of microgel and macrogel in the latex affected the sample preparation and the accuracy of results. The presence of large amounts of microgel may cause difficulties in sample filtration and, therefore, is critical in the applicability of the chromatographic method to other systems. Finally, 0.5 to 2.0 ml of the 1% (W/V) samples were injected into the chromatograph.

Gravimetric (Solvent Extraction) Gel Content Method

Latex samples were initially analyzed for gel content by the gravimetric technique. A brief description of this method is given here. Initially about one drop of latex is used to cast a film on a pre-weighed sheet of aluminum foil. The film is dried for two hours at room temperature. The weight of dried film is

* Fluropore is a Registered Trademark of the Millipore Corp., Bedford, MA

determined and the foil is placed for three days in a suitable solvent (reagent-grade acetone in this case) to leach out the soluble fraction. The insoluble gel fraction is then removed by filtration through a 0.45 μ Fluropore filter. The gel content is calculated from the amount of polymer left on the filter and the initial weight of latex film. Although this method has good reproducibility, it suffers from the long analysis time, particularly the time associated with drying the latex and solvent exposure. Furthermore, some functional latex systems may undergo additional crosslinking during drying and film formation, which will result in higher gel content values by the gravimetric technique.

Chromatography Instrumentation and Quantitation

All chromatographic analysis were performed using an apparatus assembled in our laboratory. The system components included a Milton-Roy minipump, a Valco Model (CV-6-H-PAX) loop injector, Waters Associates Model R-4 differential refractometer and a Perkin Elmer Model NFLC-250 UV absorbance detector. Later for improved quantitative analysis a Waters Associates M6000 pump, a Varian Aerograph differential refractometer (DRI) and a Varian fixed wavelength (254 nm) UV absorbance detector were used. The system was interfaced to a Data General NOVA Model 1230 minicomputer for real time data aquisition and subsequent analysis. Details of the data analysis system is given elsewhere.[9] The quantitative information provided by the minicomputer system includes the relative areas of each peak of

the chromatograms as well as the molecular weight distribution of the soluble fraction. The chromatographic apparatus was operated at room temperature with Burdick and Jackson distilled in glass THF as the mobile phase solvent. Flow rates were adjusted between 1.0 and 2.5 ml/min.

The SEC columns were packed with CPG-10 controlled porosity glass particles (Electro-Nucleonics Inc.) according to a procedure described by Kirkland.[10] Stainless steel columns, 4 ft. long with 3/8" I.D. were used. The best peak resolution was achieved with the combination of columns with 75Å, 370Å and 729Å porosity CPG packings.

The resolution (R_S) for the optimum column set was determined from the expression derived by Bly[11]

$$R_S = \frac{2(V_{R_2} - V_{R_1})}{W_{b_1} + W_{b_2}} \cdot \frac{1}{\log_{10}(M_1/M_2)} \qquad (1)$$

where V_{R_2} and V_{R_1} are retention volumes, W_{b_1} and W_{b_2} are baseline widths and, M_1 and M_2 are peak molecular weights for polymer standards 1 and 2, respectively. For the above column set polystyrene standards of molecular weights 670,000 and 37,000 (Pressure Chemical Co., Pittsburg, PA) were used for standards 1, and 2. The value obtained for R_S was 2.22 at a flow rate of 2.27 ml/min.

TABLE 2.

Characterization Data of Polystyrene Standards Used for GPC Molecular Weight Calibration

Sample Designation[a]	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Peak Retention Volume DRI (counts)
PC-12b	2.05	2.12	≤ 1.10	42.6
PC-11b	3.10	3.60	≤ 1.10	42.1
PC-8b	9.43	10.0	≤ 1.06	40.7
PC-7b	36.0	38.0	≤ 1.06	36.7
ArRo - 500 - 16	97.6	98.1	≤ 1.06	32.3
PC-1c	193.	200.	≤ 1.06	29.0
PC-13a	640.	670.	≤ 1.10	23.2
PC-14a	1610.	1900.	≤ 1.20	22.3
Duke-2575	3730.	4100.	≤ 1.1	22.0

[a]
PC - Pressure Chemical Co., Pittsburgh, Pennsylvania
ArRo - ArRo Laboratories, Inc., Joliet, Illinois
Duke - Duke Standards Co., Palo Alto, California

To estimate the molecular weight of the latex, the column set was calibrated with polystyrene standards. Table 2 lists the characterization data of the standards used. The molecular weight calibration curve constructed by plotting $\log_{10}$ (molecular weight) vs. retention volume is shown in Figure 1.

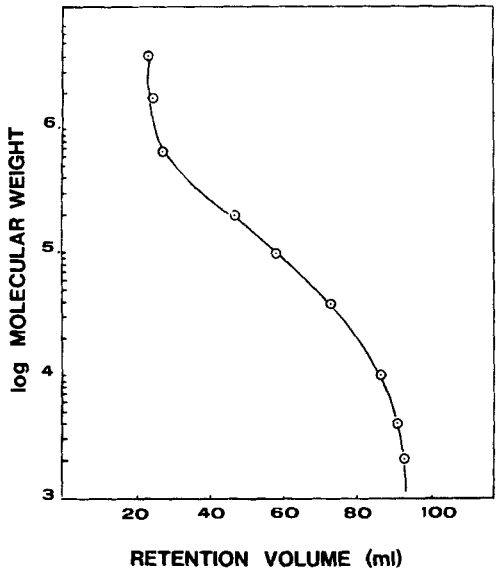

FIGURE 1. MOLECULAR WEIGHT CALIBRATION CURVE FOR THE COLUMN SET

RESULTS AND DISCUSSIONS

Separation of the Gel Fraction and System Optimization

Preliminary results using a single column packed with either CPG-729Å or CPG-370Å packing demonstrated the feasibility of the chromatographic method to separate gel and soluble fractions of the latex. These results are shown in Figure 2 for the sample B with moderate gel content (18% gel as obtained by the gravimetric gel test). Three distinct peaks were observed with the DRI detector. The first peak (1) represents the large swollen gel particles which were excluded from either 370Å or 729Å pores. The second peak (2) primarily is due to the low molecular weight

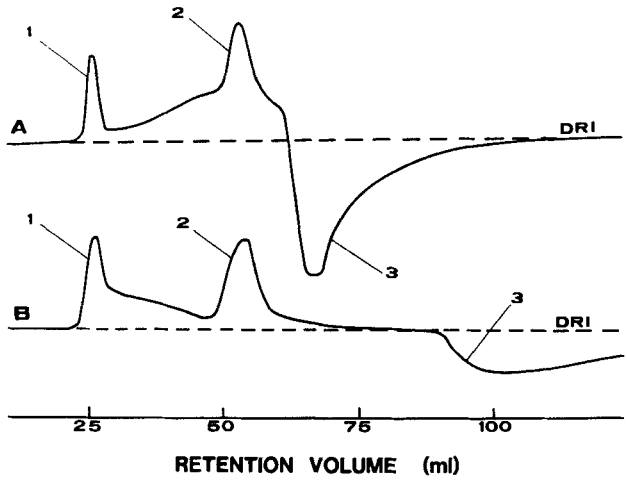

FIGURE 2. EFFECT OF COLUMN PACKING TYPE ON SEPARATION OF LATEX B.

A: 4 FT X 3/8 IN. I.D., CPG-729Å, B: 4 FT X 3/8 IN. I.D., CPG-370Å SAMPLE CONCENTRATION 1%, FLOW RATE 2.3 ml/min.

species present in the latex including unreacted monomers, plasticizer and surfactant molecules. The third peak, which is negative with respect to the baseline, is water. These partially separated peaks were identified by independent experiments in which water and polystyrene standards with molecular weights of 2000 to 6.7 x 10^5 were injected on the column. Visual observation of the collected latex fractions also provided evidence of correct peak identification (i.e., the initial fraction appears more turbid which indicates the presence of larger gel particles). Furthermore, comparing the DRI and UV detector responses suggested that the soluble portion of the latex covers the area between the first and second peaks.

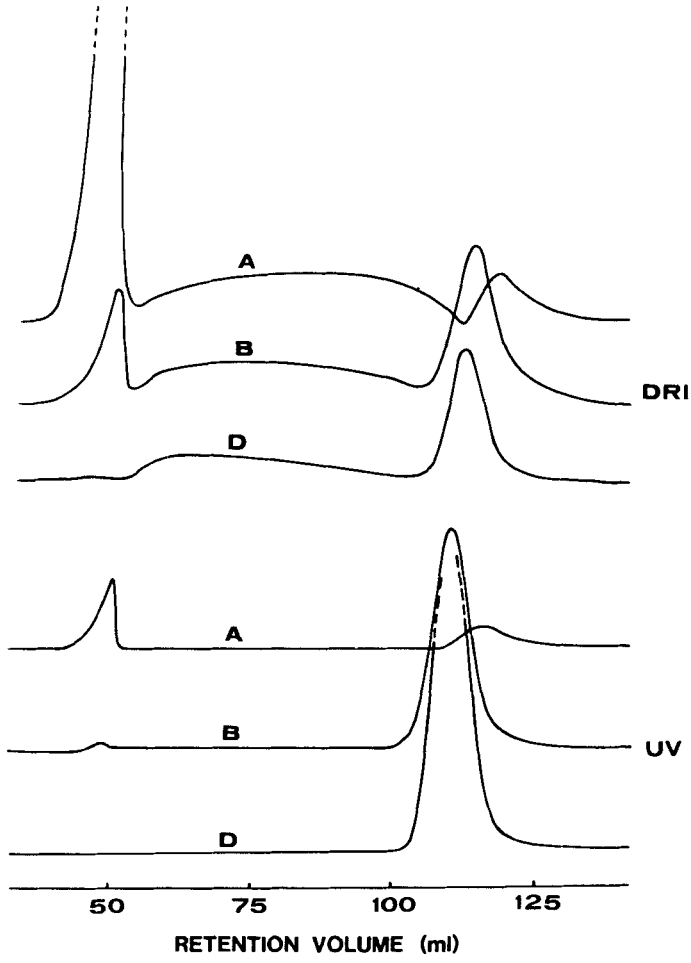

FIGURE 3. COMPOSITE CHROMATOGRAMS FOR LATEXES WITH DIFFERENT GEL CONTENTS

COLUMN: CPG 75Å/370Å/729Å SAMPLE CONCENTRATION 1%, FLOW RATE 2.3 ml/min.

Such results although encouraging, did not provide adequate resolution between gel and soluble latex fractions for accurate quantitative analysis. To optimize the peak resolution per unit time, the effect of operational variables including column packing porosity and flow rate were investigated. The separation performance of columns packed with various porosity packings were compared individually and as connected in series with each other. From this study the combination of columns packed with 370Å and 729Å in series with a 1 ft. x 3/8" I.D. precolumn packed with 75Å porosity was most effective in separating the latex fractions. Results obtained with this column set are shown in Figure 3 for latexes with different amounts of gel content as initially determined by the gravimetric gel content method. It can be seen that the relative peak areas clearly reflect the differences in gel content of each latex. Furthermore the chromatographic technique, as shown in Figure 2, was unable to detect minute amounts of gel (less than 2%).

Quantitative Analysis

Two methods can be used for the quantification of chromatograms and the determination of percent gel present in the latex. One method is to measure the area under the gel peak and divide that by the total area under the chromatogram which reflects the total solids injected.

The % of gel is calculated as follows:

$$G = 100 \cdot \frac{\text{Area of gel peak}}{\text{Total area under the chromatogram}} \qquad (2)$$

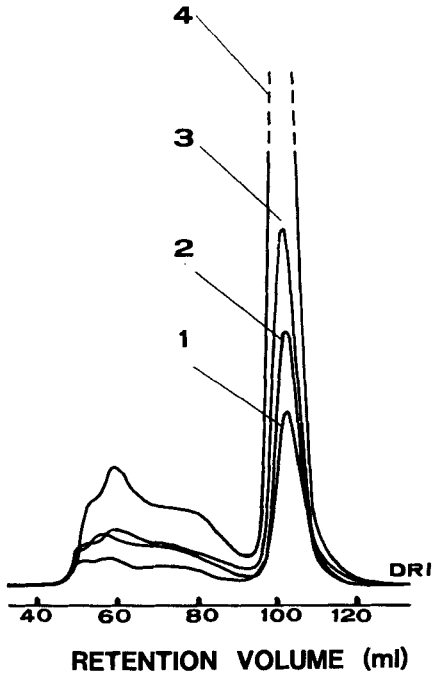

FIGURE 4. COMPOSITE CHROMATOGRAMS FOR VARIOUS INJECTED AMOUNTS OF LATEX D

(1): 5 mg, (2): 8 mg, (3): 10 mg, (4): 20 mg

Since some of the gel particles may be retained and lost during the filtration process, this approach may not provide the total amount of gel in some cases. A more reliable technique is to construct a calibration curve which relates the detector response to the amount of soluble polymer. A latex with no detectable gel content (in this case sample D with less than 2% gel) was used for this purpose. The calibration curve can be established by varying the weight of the injected latex and obtaining the corresponding area under the peak to the

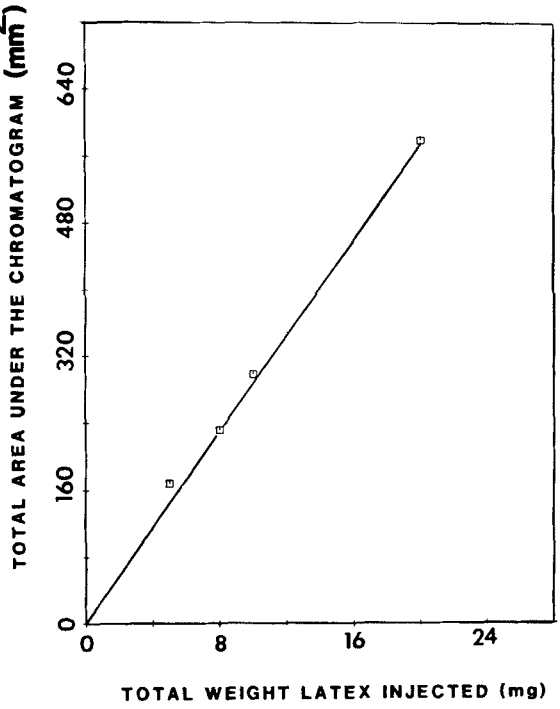

FIGURE 5. DETERMINATION OF DRI DETECTOR RESPONSE FACTOR WITH LATEX D

corresponding polymer soluble fraction. Figure 4 illustrates the composite chromatograms obtained by this procedure. The resulting calibration curve is shown in Figure 5. Using this calibration, the amount of soluble latex is directly measured and the gel content is calculated by difference. The following equation provides the calculation for determination of gel content.

$$G = 100 \cdot \frac{W-(A/K)}{W}, \qquad (3)$$

Where G is the % gel, W is the amount of latex injected, A is the area

TABLE 3.

Experimental and Calculated Data for the Determination of the Percent Gel in Acrylic Latexes by the Chromatographic Gel Test

Sample	% Gel by Gravimetric Gel Content Method	% Gel by Chromatographic Gel Content Method[a]	
		G_a	G_b
D	1.7	--	--
B	18	16.5	27.5
A	64	71	78.9

[a] : Weight of sample injected equals 10 mg.
G_a: Calculated from the relative area under the gel peak.
G_b: Calculated from the detector calibration curve.

under soluble fraction of the chromatogram, and K is the detector response factor (the slope of the detector response calibration curve). A linear least squares fit of the data resulted in a detector response factor of 2.86×10^{-2} (mm^2/g) with a correlation coefficient of 0.999.

Table 3 summarizes the quantitative data analysis for samples A, B and D. The two techniques discussed above, 1) relative area under the chromatogram and 2) the detector calibration curve, are used to quantify the chromatographic results. In comparison the percent gel obtained from the detector calibration curve is (G_b) is larger than the one calculated from the first method (G_a). This lends support to the conclusion that some of the gel is

retained on the filter during filtration of the sample prior to chromatography. The difference between the two approaches for the quantification of chromatograms (i.e., G_b-G_a) is an indication of the fraction of gel retained on the filter. This amounts to 11% for sample B and 8% for sample A.

Table 3 also indicates that the results of the chromatographic method are consistent with the gravimetric test initially performed on each latex.

In general the percent gel obtained from the chromatographic test (using detector calibration procedure for data analysis) tend to be higher than the gravimetric test. One may explain this discrepancy in terms of the microgel fraction which may go through the filter and consequently not accounted for in the gravimetric method.

In addition to the gel content analysis, the molecular weight characterization of these latexes were performed in each run. Using the calibration curve shown in Figure 1. in conjunction with the soluble polymer peak for sample B resulted in the average molecular weight as follows:

$$\bar{M}_n = 80,300 \quad (4)$$

$$\bar{M}_w = 390,000 \quad (5)$$

CONCLUSIONS

The feasibility of using size exclusion chromatography (SEC) to determine latex gel content was demonstrated for a series of

acrylic latexes. Results of the chromatographic analysis were in good agreement with conventional gravimetric gel test (solvent extraction) method. The proportions of microgel and macrogel in latex proved important in sample preparation and accuracy of results.

Using the chromatographic method each analysis is performed in less than two hours including the sample preparation. This analysis time is considerably less than gravimetric test which involves at least 3 days to complete. Further reduction in analysis time may be possible by using smaller I.D. (i.e. 1/8") columns and higher flow rates. The instrumentation described in this paper using a differential refractometer can detect % gel levels greater than 5%. The detectability can be improved by using more sensitive detectors such as a low angle laser light scattering detector.

In comparison to the gravimetric method, the SEC method provides a substantial improvement in analysis time and accuracy of measurements. In addition to the gel content, information on the molecular weight distribution and the composition of the latex can be obtained. Short analysis times and automated data analysis provided by this technique make it a valuable tool for applications concerning process and quality control of emulsion polymers.

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