Determination of Molecular Weight and Gel Content of Natural Rubber Using Thermal Field-Flow Fractionation

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Introduction

The determination of the molecular weight (MW) and molecular weight distribution (MWD) of natural rubber has been studied by several workers. Examples of some of the techniques used are fractionation by solvent extraction,[1-3] fractionation by precipitation,[4] stress relaxation,[5] electron microscopy,[4] and size-exclusion chromatography (SEC).[1,4,6-8] Of these, SEC has been most frequently used because it is fast and simple and is a routinely used technique in the MWD determination of many polymers. However, it has been recognized by some authors that the high MW and microgels present in natural rubber put the SEC results to question.[1,8] High-MW fractions and microgels are susceptible to shear degradation in the SEC columns[10] and can also lead to the blockage of the SEC columns.[8] For this reason, most workers attempt to remove the gel fraction from the natural rubber prior to SEC analysis, but, even in these cases, the extent of shear degradation of the high-MW species is difficult to quantify. Indeed, it is found that the SEC result for the average MW of natural rubbers is often lower than that found by other techniques such as osmometry[1,8] of fractionation,[8] suggesting that shear degradation does take place.

Thermal-field-flow fractionation (ThFFF) is a relatively new separation technique that is particularly suited to the characterization of ultrahigh-MW polymers that are difficult to analyze by SEC.[11-14] As in SEC, the components of an injected sample are separated as they are carried along the flow channel, leading to the elution of different MW components at different times. The difference in mechanism between two techniques leads to opposite elution orders (retention time increases with MW in ThFFF) and different resolution levels for different MW ranges. ThFFF is claimed to offer higher resolution than SEC,[15] particularly for MW higher than a million. Unlike SEC columns, ThFFF channel is open. The open-channel geometry minimizes shear degradation and adsorption of polymers. It also allows the passage of microgel particles through the channel. ThFFF has recently been used to characterize the MW distribution of a microgel-containing acrylate elastomer.[13]

Recognizing that natural rubber is usually a high-MW material with some microgel, it is clear that ThFFF would be ideally suited to its MWD characterization. In this paper the feasible use of ThFFF in characterizing the MWD of virgin and processed natural rubber is reported.

Experimental Section

The ThFFF system was a Polymer Fractionator Model T100 from FFFractionation, Inc. (Salt Lake City, UT). SEC columns were Permagel 500, 10^3, 10^4, 10^5, 10^6, and 100 Å columns (Column Resolution, Inc., San Jose, CA) connected in series. HPLC-grade tetrahydrofuran (THF) from JT Baker Inc. (Phillipsburg, NJ) was used as a carrier for both ThFFF and SEC, and the effluent was monitored by a refractive index detector (Hewlett Packard Model 1037A, Palo Alto, CA). The flow rate was 0.2 and 1.0 mL/min for ThFFF and SEC, respectively.

Natural rubber samples were cut in small pieces and added into THF at a concentration of approximately 0.2% (w/v). The solutions were placed on a wrist-action shaker for about 12 h. For SEC analysis, the rubber solutions were filtered through a 0.2-μm PTFE disposable syringe filter (25 mm). The rubber solutions were analyzed in ThFFF with and without filtration. Filtered solutions for ThFFF analysis were prepared by filtering the rubber solutions through a 5-μm PTFE filter without applying pressure. A series of narrow *cis*-polyisoprene standards having nominal MW's between 6.0×10^4 and 3.3×10^6 (Polymer Laboratories Ltd., Church Stretton, U.K.) was used to calibrate both ThFFF and SEC. All the standards have nominal polydispersities (M_w/M_n) less than 1.06.

The gel content of the natural rubber was measured by soaking 0.2–0.3 g of the rubber (one or two pieces) in an excess of toluene for 24 h and then passing the solution through a wire mesh with 125-μm openings. The weight of the dried material remaining on the mesh was regarded as gel, and percent gel was calculated from this weight as a percent of the original rubber weight.

The natural rubber sample is a ribbed smoke sheet (RSS1) obtained through Cargill (New York, NY). The processed rubber sample was obtained by passing the as-received RSS1 natural rubber through a thermomechanical degradation (mastication) process.

Results and Discussion

Retention time in ThFFF depends on both the mass diffusion coefficient, D, and the thermal diffusion coefficient, D_T.[11] Various experimental parameters affect D and D_T. Solvent is one of the retention parameters in ThFFF as it affects D_T of the polymers. Among the solvents tested (toluene, chloroform, cyclohexane, and THF), THF was chosen as a solvent (and also as a carrier) because the use of THF yielded a higher retention time, and thus higher resolution, for the natural rubber samples used in this study. The field strength (temperature drop across the channel, ΔT) is also one of the important retention parameters in ThFFF. Generally, the retention time, and thus the resolution, increases as the field strength increases. However, the use of higher field strength requires longer analysis time. An optimum condition was found for the analysis of the natural rubber by gradually decreasing the field strength during a run ("power programming"[16]). The power programming was selected to prevent excessive retention of high-MW components and microgels of natural rubber. The programming parameters were initial $\Delta T = 50$ °C, predecay time $t_1 = 6$ min, time constant $t_a = -12$ min, and the hold $\Delta T = 3$ °C.

For the analysis of an unknown sample using ThFFF, the D/D_T value of the sample is first calculated from its measured retention time, and the MW is determined using the calibration curve ($\log(D/D_T)$ vs log MW). Figure 1 shows a ThFFF calibration curve constructed using narrow linear *cis*-polyisoprene standards. Open circles represent the $\log(D/D_T)$ values calculated from measured retention times of the standards (nominal MW = 2.9×10^5, 4.6×10^5, 1.2×10^6, and 3.3×10^6, respectively), and the straight line is the result of the first-order linear regression of the data points. As expected from ThFFF theory, the calibration plot shows an excellent linearity for the MW range of the standards. Natural rubber usually contains branched molecules and microgel particles, and thus the MW data reported in this study cannot be regarded as absolute as they were determined using a calibration curve

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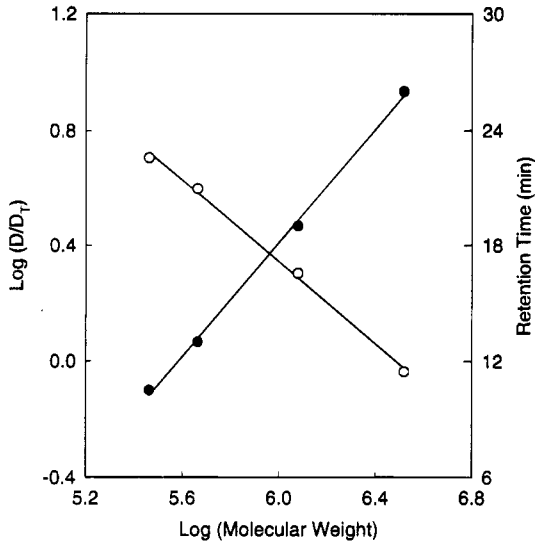

Figure 1. ThFFF calibration curve constructed using narrow *cis*-polyisoprene standards having nominal MW's of 2.9×10^5, 4.6×10^5, 1.2×10^6, and 3.3×10^6.

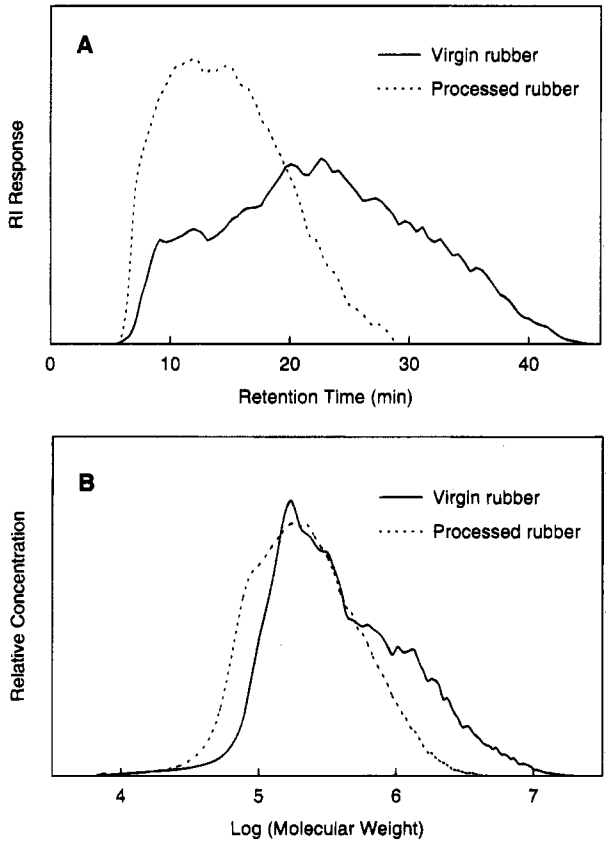

Figure 2. ThFFF elution curves (A) and MWD's (B) of natural rubbers obtained without prior filtration.

constructed with linear molecular standards. The filled circles represent the retention times measured for the same series of standards, and the straight line is the result of the first-order linear regression. As mentioned earlier, the retention time increases with increasing MW in ThFFF.

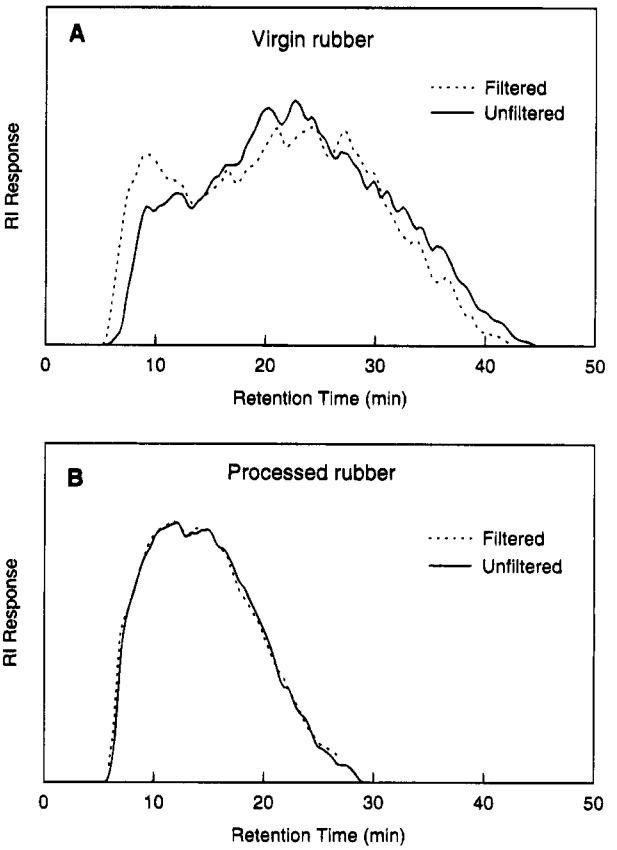

Figure 3. ThFFF elution curves of filtered and unfiltered samples of virgin (A) and processed rubber (B).

Figure 2A shows ThFFF fractograms of the processed and virgin rubber samples obtained without prior filtration. The elution of the processed rubber was completed in a shorter period of time (~30 min) than that of the virgin rubber (~45 min), which indicates the MW of the processed rubber is lower than that of the virgin rubber. It is also noted that the fractogram of the processed rubber is smoother than that of the virgin rubber. As a result of the rubber breakdown during the mastication process, the MW of the natural rubber was significantly decreased and the MWD became much smoother. The MWD's of the samples are shown in Figure 2B and the average MW's determined in Table 1. It is noted that the high end of the MWD of the virgin rubber reaches beyond 10 million.

Figure 3 shows ThFFF elution curves of filtered and unfiltered solutions of virgin (A) and processed rubber (B) obtained at the same experimental conditions as in Figure 2. For the virgin rubber (Figure 3A), the fractogram of the filtered sample (dotted line) is shifted toward lower retention time (or lower MW) from that of the unfiltered sample (solid line). The shift to lower MW is probably due to the removal and/or degradation of microgels (or ultrahigh-MW species) during the filtration. The growth of the low-MW shoulder in the filtered sample suggests that the degradation of the rubber has occurred as a result of the filtration. Unlike the virgin rubber, the processed rubber shows no

Table 1. Average MW's of RSS1 Natural Rubber Determined by ThFFF and SEC[a]

		ThFFF			SEC		
	filtration	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-5}$)	M_z ($\times 10^{-5}$)	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-5}$)	M_z ($\times 10^{-5}$)
virgin natural rubber	no	8.1	29	59			
	yes	5.1	25	51	3.0	8.8	15
processed natural rubber	no	3.3	7.3	13			
	yes	3.1	7.3	13	2.0	6.5	11

[a] M_n = number-average MW; M_w = weight-average MW; M_z = z-average MW.

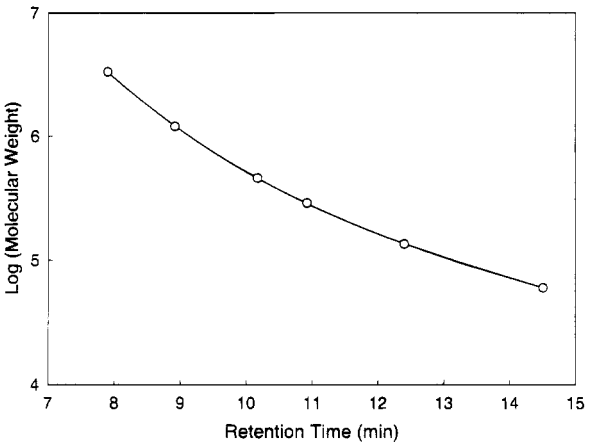

Figure 4. SEC calibration curve constructed using narrow *cis*-polyisoprene standards having nominal MW's of 6.0×10^4, 1.4×10^5, 2.9×10^5, 4.6×10^5, 1.2×10^6, and 3.3×10^6.

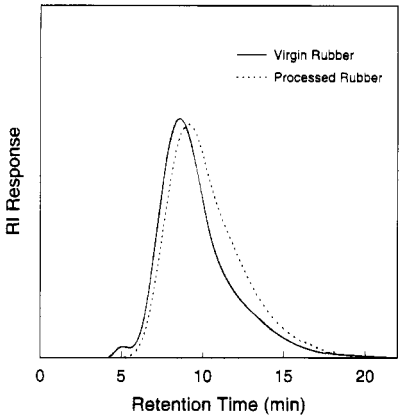

Figure 5. SEC chromatograms of virgin and processed natural rubber (THF, 1 mL/min, 6 column set).

significant difference between the filtered and unfiltered samples (Figure 3B). This is probably because there is no significant amount of microgel or ultrahigh-MW species left after the mastication of the virgin rubber. As seen in Table 1, there is about 15% reduction in both weight-average and *z*-average MW's after the filtration of the virgin rubber, while there is no significant difference in the average MW's for the processed rubber.

The results obtained for the rubber samples using SEC are also shown in Table 1. No SEC data are available for unfiltered samples as it was impossible to run the unfiltered rubber solutions without plugging SEC columns. The MW's determined from SEC are lower than those obtained from ThFFF for both processed and virgin rubber. It is noted that the difference in MW's obtained from ThFFF and SEC is greater for the virgin rubber than for the processed rubber. This is probably due to the lack of resolution in SEC for the high-MW components of the virgin rubber. Figure 4 shows a SEC calibration curve constructed using the same series of *cis*-polyisoprene standards as those used in ThFFF experiments. Circles represent measured retention times of the standards (nominal MW = 6.0×10^4, 1.4×10^5, 2.9×10^5, 4.6×10^5, 1.2×10^6, and 3.3×10^6, respectively). The first-order linear regression did not result in a good fit to the data points. The line shown in Figure 4 is the result of the third-order linear regression of the data points. Figure 5 shows SEC chromatograms of the rubber samples. The small shoulder at the beginning of the chromatogram of the virgin rubber indicates a small fraction of high-MW components are excluded from the column pores. In ThFFF, the resolution usually remains constant for the entire elution range, while that of SEC deteriorates as the MW approaches either the column exclusion limit or the total permeation limit. The MW tends to be underestimated in SEC as it approaches the column exclusion limit. The SEC column set used in this study is similar to those used for the analysis of natural rubber in previous reports.[9]

The difference in the peak areas of the filtered and unfiltered sample allows a gel content estimation to be made.[13,17] The gel content measured from the relative peak area was 15% for the virgin rubber and 0% for the processed rubber. When measured by a more accurate, conventional solvent extraction method with toluene as an extracting solvent, the gel content was 13 and 0% for the virgin and processed rubber, respectively. The gel content measured by ThFFF is not expected to yield an accurate data as it assumes the detector signal is proportional to the solute concentration throughout the whole range of the elution profile, including the microgels. Although it may not yield an accurate gel content data, the ThFFF method is simple and less time-consuming than conventional solvent extraction methods and is expected to be useful for comparative studies among similar materials.

Conclusion

ThFFF provides distinct advantages over SEC for the determination of MW and MWD of natural rubber. First, there is no need for sample filtration. Filtration eliminates the microgels and some ultrahigh-MW species. Second, ThFFF is expected to yield more accurate MWD data for natural rubber as it offers higher resolution than SEC for high-MW polymers, particularly for polymers with MW near or higher than a million. Third, an estimate of the gel content of natural rubber can be obtained using ThFFF.

The MW's presented in this study are not absolute but based on polyisoprene calibration. More work will be needed for the determination of the absolute MW of natural rubber.

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