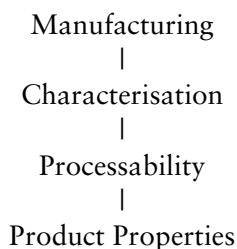


# 5 Characterisation of Gum Rubber Using Dilute Solution Methods

## 5.1 Introduction

The purpose of characterisation may be stated as, in the most general terms, elucidation of a structure-property relationship. The structural characteristics include MW, its distribution, branch patterns and gel types. Microstructure is also included in this category. In addition there are compositional differences among copolymers and blends. The term, property, implies static characteristics such as density and specific heat, although sometimes, dynamic characteristics such as viscoelastic behaviour, are called viscoelastic properties. In order to be all-inclusive the structure-property relationship may be restated as the relationship between the structure/composition and property/behaviour.

Why do we need to elucidate such a relationship? This question is seldom asked because the answer may be presumed to be obvious. In the industrial context, the answer lies in the relationship shown in the following sequence:



Specific gum rubber is manufactured to meet the requirements of a finished product having certain properties. This also requires the gum rubber to be processable with the available equipment. Therefore, the characterisation activity is a valuable and often indispensable link in the above relationship. When a problem arises because of an unsatisfactory property in the product or unsatisfactory processability, the final answer must be sought on how to alter the manufacturing process to produce a gum rubber with acceptable properties. In short, we need to establish the above relationship as the background knowledge needed for a day-to-day operation of the manufacturing process as well as for problem solving.

Table 5.1 Grades of NBR Manufactured by the BFGoodrich Company							
Type	DTA T <sub>g</sub> (°C)	Nominal % Acrylo- nitrile	Specific Gravity	Average Mooney Viscosity	Anti- Oxidant	Special Properties	Potential Uses
VT455	-18	40	1.00	55	Non- staining	High oil resistance. Low foul. Easy processing	Fuel hose, rolls, gaskets, packings, oil seals, food grade applications.
VT480	-18	40	1.00	80	Non- staining	High oil resistance. Low foul, easy processing	Fuel hose, rolls, gaskets, packings, oil seals, food grade applications.
VT330	-30	30	0.99	30	Non- staining	Good oil resistance, good water resistance, low foul, easy processing	Adhesives, moulding, extruding, calendering, non-corrosive to metal.
VT355	-30	30	0.98	55	Non- staining	Good oil resistance, good water resistance, low foul, easy processing	Print rolls, sheeting, gaskets, resin modification, blends of SBR, Hydrin®, PVC.
VT380	-30	30	0.98	80	Non- staining	Good oil resistance, good water resistance, low foul, easy processing	Hose, tubing and other extruded goods. Also adhesives and solution coatings.
1000 x 132	-12	51	1.02	55	Slightly staining	Very high acrylonitrile polymer; unusually good oil and fuel resistance	For better oil, fuel, and solvent resistance than with standard high acrylonitrile Hycar® rubbers: transformer gaskets, fuel lines, et. Hycar® 1000x88 makes outstanding adhesives in blends with thermosetting resins.
1000 x 88		43	1.00	95	Slightly staining	High acrylonitrile	Hycar® 1001CG, excellent for high strength adhesives. Available in several cement viscosity ranges and with non- staining antioxidants. Oil well parts, fuel cell liners, fuel hose, other uses requiring resistance to aromatic fuels, oils, solvents. Rolls, lathe-cut gaskets, packings, oil seals, O-rings, phenolic resin modification.
101CG	-18	41	1.00	85	Slightly staining	Excellent oil and fuel resistance, controlled cement viscosity	

Table 5.1 Grades of NBR Manufactured by the BFGoodrich Company (continued)							
Type	DTA T <sub>g</sub> (°C)	Nominal % Acrylo- nitrile	Specific Gravity	Average Mooney Viscosity	Anti- Oxidant	Special Properties	Potential Uses
1002	-31	33	0.98	95	Slightly staining	The original medium-high acrylonitrile copolymer	Compounds of Hycar® 1002 have very good water resistance during prolonged service.
1022	-29	33	0.98	50	Non- staining	Low Mooney viscosity, directly soluble, cement grade polymer. FDA applications	Adhesives. Moulded, calendered, extruded goods requiring relatively low moduli. Low heavy metal ion content.
1042x82		33	0.98	85	Non- staining	Nerve-free Hycar® 1042, non-soluble. Crosslinked	Gives minimum die swell in extrusion. Excellent calendering stock with low shrinkage. Recommended for tubing, sheet goods and print plates.
1014	-61 -39	21	0.95	80	Slightly staining	Easy processing polymer	Applications in which excellent low- temperature properties are critical.
1034-60	-30.5 -62.0	21	0.95	55	Slightly staining	Corrosion resistance and easy processing	Applications in which excellent low- temperature properties are critical.
1094-80	-43	21	0.95	80	Non- staining	Low nitrile with outstanding physical properties	Applications in which excellent low- temperature properties are critical.
1095-80	-52.5	-	0.98	80	Non- staining	Very low nitrile	Specialised low temperature applications.

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The BFGoodrich Company.

The characterisation activity may be divided into three kinds. The first is that requiring chemical analysis to find compositional differences. This activity is not dealt with in this book. The second is to find differences among gum rubbers having essentially the same chemical composition but different properties/behaviour. The third is an extreme case of the second; that is, in every respect two gum rubbers are supposed to be the same but either process differently or the properties of the finished products are different. This book deals with the second and the third, where the difference in the processability is the primary focus. Statements on the finished products are also included when they are important.

The commercial gum rubbers are made in different grades to satisfy the needs of different applications. The preceding is an example of the grades of NBRs manufactured around 1985 at the BFGoodrich Company, Table 5.1.

Among the 15 grades there are compositional differences as well as the differences in structure. Four representative samples, A, B, C, and D, are described in Chapters 2 and 4 with respect to their molecular structure and mill processability. Comparison between the different grades is the first and the second kind of characterisation mentioned earlier. Processability problems may arise within a given grade, if, for example, the processing latitude is very narrow. Matching a competitor's gum rubber with the same grade may not always work. Handling of these problems requires the third kind of characterisation activity.

The dilute solution methods have been used for characterising polymers since day one of polymer science. Measurements of dilute solution viscosity, osmotic pressure and light scattering have been well-established in theory as well as in practice. They are described practically in every textbook and in many review articles. More than 30 years have passed since the introduction of size exclusion chromatography (or gel permeation chromatography; GPC), which provides fractionation data very conveniently. This chapter is not intended to be a review of these methods. It is directed to examining how useful these methods are with respect to sensitivity, reproducibility, and reliability. Stated differently, the question is whether or not differences in processability can be explained on the basis of information available from the dilute solution methods.

## **5.2 Gel determination**

As described in Chapters 1, 2 and 4, gels are present in many gum rubbers, exerting a critical influence on their processability. For gel-containing rubbers, the dilute solution methods are not applicable, because gels are removed by filtration. Therefore, the determination of gel content is the first order of the business in the characterisation of gum rubbers.

ASTM D3616-95 [1] describes a method for determining of gel, swelling index and dilute solution viscosity (DSV). The method has been developed for E-SBR and NBR, and toluene and methyl ethyl ketone, respectively, are used as solvents. The method is for the determination of macrogel content but it may also be used for microgel, a particle of a crosslinked network.

A sample is taken from a bale without milling. Approximately 0.4 g of weighed sample is placed on a 50 mesh screen having 300  $\mu\text{m}$  opening, and soaked in 100 ml of solvent for 16-20 hours at 25 °C without stirring. During this period the soluble fraction is extracted. When the gel-content is high such as 50% or more the sample sitting on the screen is visible to the eyes. The reason why the solution is not stirred is because better reproducibility is obtained. Gels originate in emulsion droplets of less than 0.1  $\mu\text{m}$  diameter and, if stirring breaks up the gels, some of them would go through the screen of 300  $\mu\text{m}$  opening.

The gel content is determined indirectly from the amount of soluble fraction and directly by weighing the dried gel. Examples of the reproducibility of the data by round-robin tests are given for two SBR copolymers and three NBRs of 0 to 85% gel content. For the 'zero' sample the standard deviation is as high as  $\pm 100\%$  indicating that a very small amount of gel may be distributed non-uniformly. The standard deviations for 50-85% gel samples are at most  $\pm$  a few per cent.

The swelling index indicates a denseness of the branch point; the denser it is, the lower the swelling. The DSV of the soluble fraction is a measure of MW, but only an approximate one, because some molecules may have branches. For the selected samples mentioned previously, the soluble fraction of the higher gel-containing sample had a lower MW. This conforms with the mechanisms of generating branches and gels in free radical polymerisation, which were explained by Flory many years ago, [2]. Because the measured gel content depends upon the pore size of a filter, generally more gel is found with a gel permeation chromatography (GPC) filter having 0.1 - 0.2  $\mu\text{m}$  opening compared to the result from the ASTM screen having a 300  $\mu\text{m}$  opening.

The ASTM test is intended to give a pragmatic definition of gel content in such a way that if a sample is gel-free according to this analysis, the effect of gel on the processability is usually negligible. Strictly speaking, this statement may not be acceptable in some cases. For each processability requirement, the assumptions involved in the gel determination need to be examined. Also, the method is only for E-SBRs and NBRs. With ACM gum rubbers, the results from using the 300  $\mu\text{m}$  screen were not useful and the gel-content results obtained with 20  $\mu\text{m}$  opening of a filter paper agreed well with the results from various viscoelastic measurements [3].

Sometimes a gel is generated in the post-polymerisation process; it may come from hung up material somewhere in the reactor, dryer or in the passage-way. They may be hard or soft. They may appear sporadically and are difficult to catch.

### **5.3 Dilute solution method**

For gel-containing rubbers the dilute solution properties of the soluble fraction obviously do not represent the gum rubber.

On the other hand for completely soluble rubbers such as *cis*-1,4-BR and ethylene-propylene copolymer (EPM), useful information may be obtained. EPDM tends to have some fraction, which is filtered out with 0.1~0.2  $\mu\text{m}$  filter. The osmotic pressure and light scattering methods give absolute MW, the number-average  $\overline{M}_n$  and the mass-average  $\overline{M}_w$ , respectively. These values alone cannot be used to determine whether a polymer has branches or not. On the other hand, DSV depends upon the degree of branching, because a branched polymer gives a lower viscosity for a given MW. A degree of branching is defined as a ratio of the DSV of a linear sample and that of a branched sample at the same MW.

Scientific treatment of DSV is to use the intrinsic viscosity, which is the value extrapolated to zero concentration. For a reason of convenience a DSV at a fixed concentration, for example, 0.2 g/100 ml, is more frequently used in industry. Just which average MW should be used for this comparison may be a problem, if there is a large difference in the MW distribution. Usually a 'viscosity-average' MW is used. However, the averaging requires a prior knowledge of the degree of branching, which affects the exponent of Mark-Houwink-Sakurada equation. Original works in developing the method used narrow distribution samples such as a  $\overline{M}_w / \overline{M}_n$  ratio which was close to one. For finding a difference between samples of the same grade, the method may not be sensitive enough.

Because determination of osmotic pressure and light scattering requires special instrumentation and skill to operate, they are usually used for fundamental research only. Because of the convenience, DSV and GPC are more frequently used. GPC provides a fractionation curve, not just mass-average and number-average. DSV is usually just used to obtain a bench-mark of MW, without questioning a presence or absence of branching. The following discussion covers the reliability of information obtainable from GPC with processability in mind.

GPC is often described as a method for determining MW and its distribution. This is not true - it is a method for fractionation according to the hydrodynamic size of the swollen polymer coil. The fractionation uses columns packed with porous material; usually it is

porous polystyrene beads crosslinked to make them insoluble. Because commercial rubbers often have very broad MW distribution, as many as four columns are used in series, each having different pore size designation. A dilute solution of a sample polymer is injected to a solvent-stream, which is flowing slowly through the columns. Because smaller polymer-chains can diffuse into the pores, it resides in the columns for a longer time. Therefore, the larger molecules are eluted first. The concentration of polymer at any instant of elution is measured by the difference between the refractive index of the solution and that of the solvent. Because the elution time is the measure of the swollen size of the polymer chain, the elution time must be calibrated for the swollen size of polymer chain; then it must be converted to MW. For convenience, usually fractions of known MW of unbranched polystyrene are used for the calibration. If a sample in question is a linear polystyrene, this calibration is satisfactory. For branched polystyrenes the calibration samples must also be branched, because the branched polymer has a smaller hydrodynamic size than the linear one for the same MW. If the branch pattern is different, for example, an equal arm star against a comb-type, the hydrodynamic size is different. For evaluating the MW of a branched polymer by GPC, calibration samples having exactly the same branch pattern are required.

When the branch pattern of a sample in question is not known, there is no way to calibrate. The question of calibration is often ignored. The data of MW and MW distribution reported in the literature are often only relative values, based on the linear polystyrene standards. This may still be useful if a sample in question is unbranched. For branched polymers, such data does not have a precise meaning.

Some elaborate methods have been developed for obtaining information about the degree of branching from GPC data. It requires a rather tedious procedure. Moreover, degree of branching ignores the difference of branch patterns. Therefore, it has only a very limited use.

There are other problems concerning the calibration. The elution time is also a measure of elution volume. The rate of elution must be controlled so that it is constant all times. Earlier GPC instruments were deficient in this regard, contributing to the reproducibility problem. In the later models a satisfactory pumping system giving a steady flow-rate, is installed.

The advanced models of GPC are equipped to measure the MW of the eluting polymer with a low angle laser light scattering device (LALLS). This enables the calibration problem to be eliminated. A special attachment to measure the viscosity of the eluting solution is also available. From the above two measurements a degree of branching may be estimated. The information on the branch pattern is not obtainable, however.

Because the LALLS was not available for the earlier work and even at present it is not always used, the following discussion is given on the use of calibration curves.

Because a very high MW polymer and a very small gel accumulate in the columns, the column performance changes with time. This requires a frequent re-calibration or a running a reference sample. When columns lose satisfactory performance or eventually even plug up, the columns must be repacked and re-calibrated. For this reason a sample solution is carefully filtered through a 0.1-0.2 mm filter. If a very high MW fraction is removed by filtration, the resulting elution curve does not represent the sample in question.

This is a serious problem when we consider that the processability is often affected by the presence of a small amount of very high MW fraction. Most annoying is when it is not known whether the higher MW fraction is removed by filtration or not. Figure 5.1 is an example of the calibration curve [4].

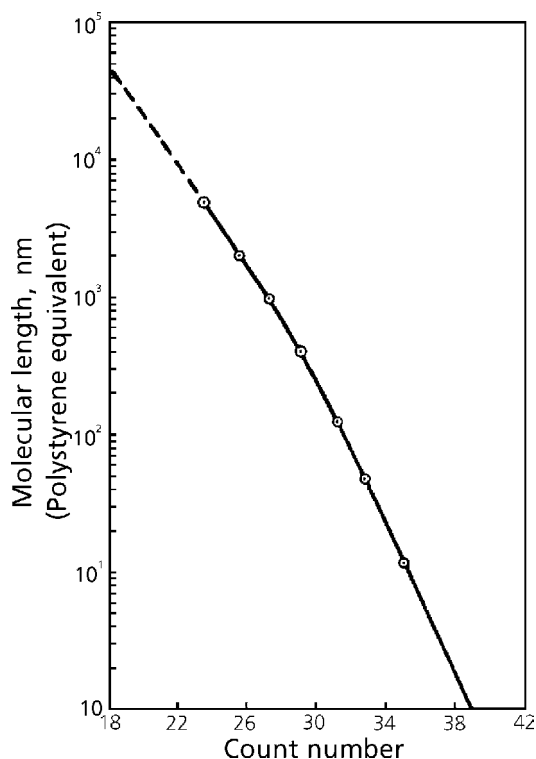


Figure 5.1 Calibration curve obtained using polystyrene standards.

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Because the calibration curve is a semi-log relationship, a small error in the elution volume is magnified at the MW scale. Another problem is a lack of the calibration standard at the very high MW. The significance of this is shown in Figure 5.2 [5].

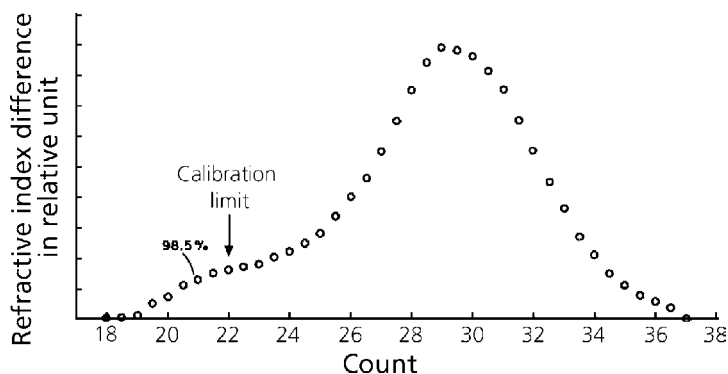


Figure 5.2 A typical 4 column GPC chromatogram of linear polyethylene. Solvent: trichlorobenzene. Temperature: 137 °C. Columns:  $7 \times 10^6$ ,  $3 \times 10^6$ ,  $10^5$ , and  $10^3$  Å. Solution concentrate: 0.5%. Injection time 130 s. Flow rate: 2 cm<sup>3</sup>/min. Refractive index difference in relative unit.

*Reprinted from N. Nakajima, Separation Science, 1971, 6, 2, 277, Figure 1, by courtesy of Marcel Dekker, Inc.*

It is evident that below count no. 22, there is no calibration. Assuming the extrapolated part of the calibration curve, is correct, the mathematical moments of the MW distribution were calculated according to Equations (5.1)-(5.5), where  $Q_i$ 's are zeroth to fourth moments,  $A_i$  is the relative MW based on the polystyrene standard and  $W_i$  is the mass fraction of polymer having MW,  $A_i$ . The corresponding curves for the area-integration are shown in Figures 5.3a-e [5].

$$Q_0 = \int 1/A_i (dW_i/dA_i) dA_i = \int (dW_i/dA_i) d \ln A_i \quad (5.1)$$

(Curve a)

$$Q_1 = \int (dW_i/dA_i) dA_i = \int A_i (dW_i/dA_i) d \ln A_i \quad (5.2)$$

(Curve b)

$$Q_2 = \int A_i (dW_i/dA_i) dA_i = \int A_i^2 (dW_i/dA_i) d \ln A_i \quad (5.3)$$

(Curve c)

$$Q_3 = \int A_i^2 (dW_i/dA_i) dA_i = \int A_i^3 (dW_i/dA_i) d \ln A_i \quad (5.4)$$

(Curve d)

$$Q_4 = \int A_i^3 (dW_i/dA_i) dA_i = \int A_i^4 (dW_i/dA_i) d \ln A_i \quad (5.5)$$

(Curve e)

$$\bar{A}_n = Q_1 / Q_0 \quad \text{or} \quad 1/Q_0 \quad (\text{number average}) \quad (5.6)$$

$$\bar{A}_w = Q_2 / Q_1 \quad \text{or} \quad Q_2 \quad (\text{weight average}) \quad (5.7)$$

$$\bar{A}_z = Q_3 / Q_2 \quad (z \text{ average}) \quad (5.8)$$

$$\bar{A}_{z+1} = Q_4 / Q_3 \quad (z + 1 \text{ average}) \quad (5.9)$$

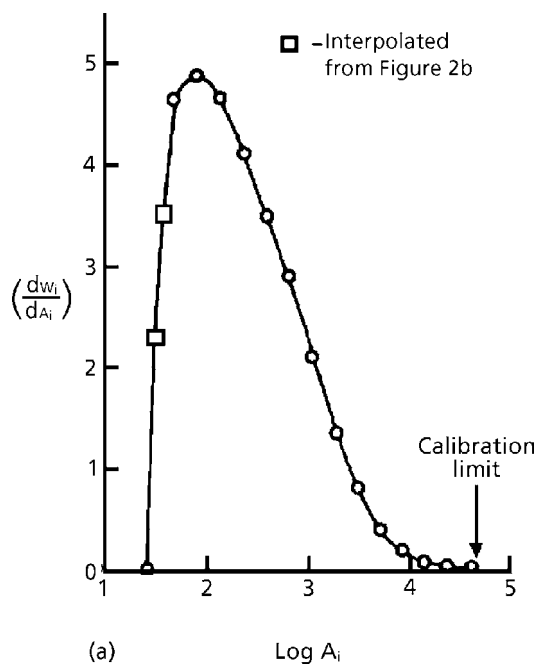


Figure 5.3a is based on Equation (5.1).

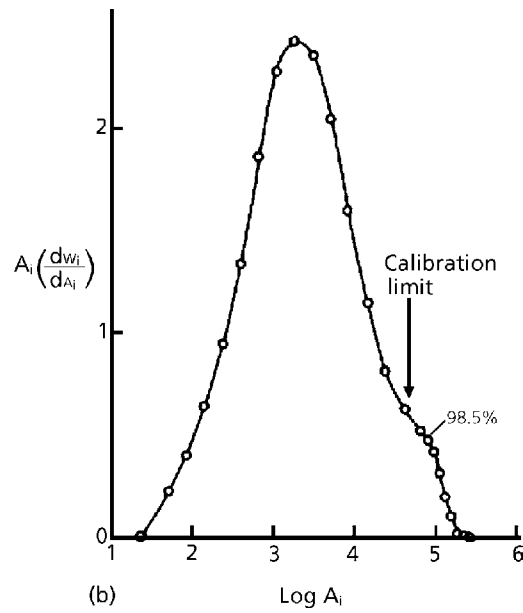


Figure 5.3b is based on Equation (5.2).

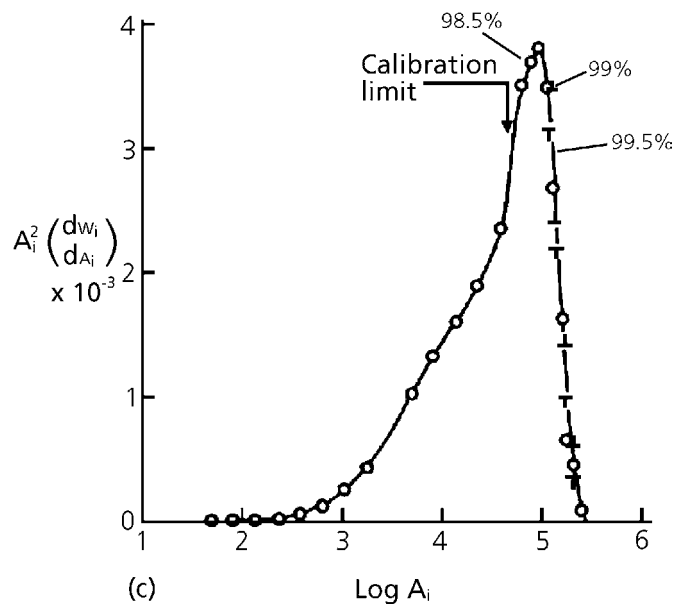


Figure 5.3c Based on Equation (5.3).

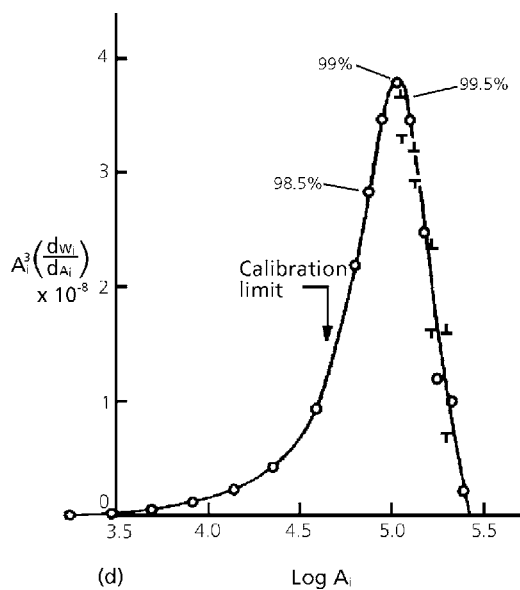


Figure 5.3d is based on Equation (5.4).

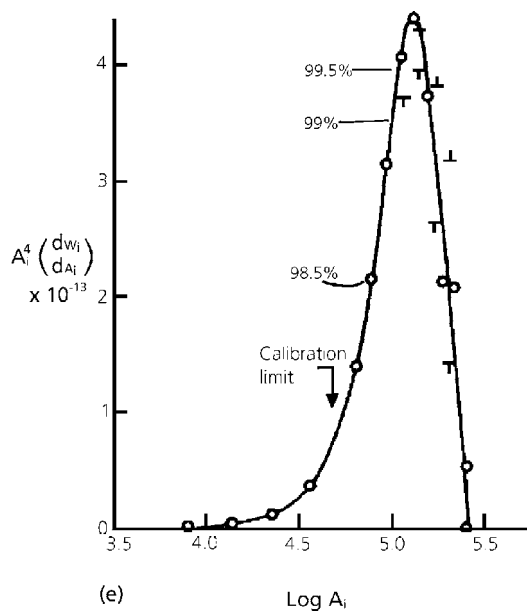


Figure 5.3e is based on Equation (5.5).

Figure 5.3 Moments, percentages shown are cumulative weight fractions.

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Table 5.2 Moments and Average Chain Length		
Quantity	Computer integration	Possible range of values resulting from baseline error (hand calculation)
$Q_0$	$1.59 \times 10^{-3}$	Negligible
$Q_1$	1.01	Negligible
$Q_2$	$8.95 \times 10^3$	Negligible
$Q_3$	$4.77 \times 10^8$	$4.52-4.85 \times 10^8$
$Q_4$	$4.82 \times 10^{13}$	$4.32-5.30 \times 10^{13}$
$\bar{A}_n$	$6.3 \times 10^2$	Negligible
$\bar{A}_w$	$8.9 \times 10^3$	Negligible
$\bar{A}_z$	$5.3 \times 10^4$	$5.05-5.4 \times 10^4$
$\bar{A}_{z+1}$	$1.01 \times 10^5$	$0.96-1.09 \times 10^5$

Integrating for  $Q_0$ , (see Figure 5.3a), the entire area falls within the calibration limit and for  $Q_1$ , (see Figure 5.3b), almost whole area is calibrated. Therefore, the number average MW,  $\bar{A}_n$ , given by Equation (5.6), is approximately correct. For  $Q_2$  (see Figure 5.3c), only one-half of the area falls within the calibration limit and therefore, the weight average MW,  $\bar{A}_w$ , Equation (5.7) is not very reliable.

For the  $Q_3$  and  $Q_4$  integration almost entire areas are not calibrated. Therefore, Z average  $\bar{A}_z$  and Z +1 average  $\bar{A}_{z+1}$ , Equations (5.8) and (5.9), are creations of the arbitrary calibration curve. Because the computer provides a neat printout of  $\bar{M}_w$ ,  $\bar{M}_z$  and  $\bar{M}_{z+1}$ , the values are often accepted without scrutinising whether they are the creation of the software or not.

One more problem with GPC is a possible lack of the resolution at the high molecular tail. In Figure 5.2 the elution appears to start at about count number 19. Is this because the MW distribution has a cut-off or is it the limit of the resolution of the column?

## 5.4 Relationship between dilute solution properties and processability

Because of the calibration problems, the information obtained from GPC is at best the relative values of MW and its distribution. The higher averages such as  $\bar{M}_z$  and  $\bar{M}_{z+1}$

are often meaningless. When the branching is involved, the credibility is reduced further. For example, when two samples have a difference in the apparent values of  $T_g$ , we are not sure whether there is a difference in the true  $\overline{M}_n$  or if one sample has more branches than the other.

There is a well-established relationship for polymer melts between the low shear Newtonian viscosity and MW,  $\eta_0 = k \overline{M}_w^n$  (Equation 5.6), where  $K$  is a constant and  $n$  is 3.4 or a very similar number [6].

Very high MW dependence, i.e., 3.4 power, comes from extensive entanglements of polymer chains, which are slipping through each of the other chains at low shear rate conditions.

The low shear Newtonian viscosity is sometimes called zero-shear viscosity. Strictly speaking the two are different. The zero-shear viscosity is a viscosity extrapolated to zero shear rate and the value depends upon the method of extrapolation. This is particularly true for a polymer having a very high MW tail or a polymer with long branches. On the other hand, the low shear Newtonian viscosity is an observed value. The relationship in Equation (5.6) was established with series of samples having different MWs and a very narrow MW distribution. In order to observe the relationship, a given gum rubber must be in the flow state. This often requires a temperature where degradation sets in, or it takes a very long time so as to be impractical. The exception to this is rubbers prepared via anionic polymerisation and polydimethyl siloxane (PDMS); in these rubbers the high MW tail of distribution is not extending very much.

In general, a gum rubber has a very high MW fraction, long branches or both. In the processing condition it is usually not in the flow state but it is in the rubbery state. In the latter state a rubber, having apparently a higher MW may have a lower modulus, if it has long branches. Likewise, a lower Mooney index does not necessarily mean a given rubber having lower MW. Instead, it may have more branches.

When there are large differences in the pattern of the MW distribution among the samples, GPC may provide information such as shown in Figure 5.4 [7].

A caution is that even in this case the fractionation curve of E-SBR does not represent MW distribution, because there are branches and probably gels in the sample.

The main purpose of this chapter is to caution the reader against over-reliance on the dilute solution properties, particularly on GPC. The methods are good for detecting relatively large differences. They often lack sensitivity required for problem solving in processability. Much time may be wasted in trying to interpret data and trying to obtain information, which is not really there.

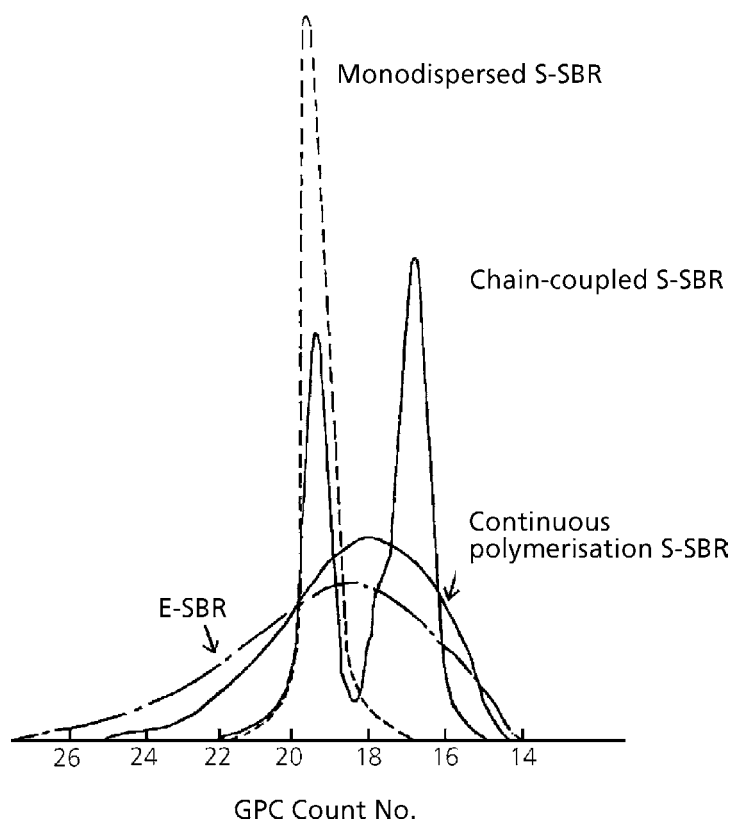


Figure 5.4 Examples of MW distribution of SBRs.

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