PRACTICAL USE OF THE MOONEY-RILVIN EQUATION FOR DETERMINATION OF DEGREE OF CROSSLINKING OF SWOLLEN NR VULCANISATES

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ABSTRACT

The Mooney-Rilvin equation was used for determining the degree of crosslinking of rubbers based on their stress-strain behaviour. Non-linear bahaviour of the Mooney-Rilvin curve under valid elongation and change in the crosslink density for swollen NR vulcanisates were observed, this being not the case for unswollen vulcanisates. The non-linear bahaviour was caused by prior-extensibility of the rubbers whereas the change in the degree of crosslinking resulted from differences in the directional stresses in the NR compounds during swelling. The crosslink densities from the use of the Mooney-Rilvin equation were then compared to those from a swelling method based on the Flory-Rehner equation.

INTRODUCTION

The Mooney-Rilvin equation is widely used for assessing the degree of crosslinking (crosslink density) of rubbers based on their stress-strain behaviour. The Mooney-Rilvin equation can be applied to both unswollen (dry) and swollen rubber vulcanisates. For unswollen rubbers, such equations are based on the phenomenological theory of rubber elasticity[1-5] which can be obtained as follows.

$$F = 2A_o(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \tag{1}$$

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \tag{2}$$

In the case of swollen rubbers, equations 1 and 2 change to equations 3 and 4 respectively:[1-2]

$$FV_r^{1/3} = 2A_o(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \tag{3}$$

$$\frac{\sigma V_r^{1/3}}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \tag{4}$$

where F is the force required to stretch the rubber vulcanisate, A_o is the cross-sectional area of the unstretched rubber vulcanisate, V_r is the volume fraction of rubber at the fully swollen state [2], σ is identifiable with F/A_o, λ is the extension ratio (which is $1+\varepsilon$), ε is strain, and C_1 and C_2 constants are characterising the vulcanisate.

By performing the plot of $\sigma/(\lambda - \lambda^{-2})$ against $1/\lambda$ (for unswollen rubbers) **OR** the plot of $\sigma V_r^{1/3}/(\lambda - \lambda^{-2})$ against $1/\lambda$ (for swollen rubbers), the constants C_1 and C_2 can be determined i.e., the intercept of the curve on the $\sigma/(\lambda - \lambda^{-2})$ or $\sigma V_r^{1/3}/(\lambda - \lambda^{-2})$ axis corresponds to the value of C_1 and its slope corresponds to the value of C_2. The value of C_1 can be used to assess the physically manifested crosslink density (n_{phys}), which is simply determined by equation 5 as follows:[1-3]

$$n_{phys} = \frac{C_1}{RT} \tag{5}$$

where R is the gas constant (8.314 J.mole^{-1}.K^{-1}), and T is the absolute temperature.

However, users should be aware of the limitations of the Mooney-Rilvin equation. One of the well-known limitations of this equation is its invalidity at large strains.[2,4] In practice, the equation can only be used to accurately determine the crosslink density in the range of tensile elongation of 30-150% ($\lambda^{-1} \approx 0.4$-0.7), the tensile elongation being measured in the uniaxial direction.[2,5] The aim of this paper is to give a short practical concern regarding some discrepancies of the determinations of crosslink density of vulcanised rubbers before and after swelling in a solvent (toluene), within the limited range of the tensile elongation of 30%-150%. The paper is described using some experimental results whose experimetal methods were in part outlined, the details being referred to elsewhere.[6]

MATERIALS AND METHODS

Several dumbbell samples of unfilled sulphur-accelerated natural rubber (NR) vulcanisates were produced using the efficient vulcanisation system, thus the Efficient Vulcanisates (EV) being obtained.[1-2,6] The vulcanisates produced had the same initial degree of crosslinking, this being based on the fact that they were produced using the same vulcanisation system and mixing/curing conditions, which are explained elsewhere.[2,6] The vulcanisates used for testing in this work were in the form of dumbbell samples. The work was carried out by dividing the samples into two groups. Samples in the first group are called "unswollen samples" and those in the second group that were immersed in toluene until fully swollen (around 2 days) are called "swollen samples". From the swelling experiment, it was found that the samples swelled by approximately 70% (by sample length). Samples from both groups were used for the measurement of crosslinking density via the stress-strain measurement using an AGS-500 D (SHIADZU) tensile testing machine and the cross-head speed used was 500 mm/min, the results being the mean of at least five determinations.

The work was extended by using some related values obtained by the swelling method to calculate the volume fraction of rubber (V_r) which can be obtained using equation 6.[6]

$$V_r = \frac{(W_1/\ \rho_1)}{(W_1/\ \rho_1)+(W_2/\ \rho_2)} \tag{6}$$

Where W_1 and W_2 are the weights of the polymer (NR) sample and solvent respectively; and r_1 and r_2 are the densities of the polymer and solvent respectively.

Swelling studies are also widely used to determine rubber networks for many years. Crosslink density is frequently calculated from equilibrium swelling data by means of the Flory-Rehner equation, this equation relating swelling behavior to the kinetic theory of elasticity through the polymer-solvent interaction parameter or Huggins factor, c [7]. For the comparison purposes, crosslink density of the rubber is also calculated using the Flory-Rehner equation (equation 7).[8]

$$-\ln(1-V_r)-V_r-\chi V_r^2 = 2V_s\eta_{swell}[V_r^{\frac{1}{3}} - \frac{2V_r}{f}] \tag{7}$$

where V_r is the volume fraction of rubber in the swollen state,
         V_s is the molar volume of the solvent (toluene),
         η_{swell} is the number of effective network chains/cm^3 of rubber (crosslink density),
         f   is the functionality of the crosslinks

RESULTS AND DISCUSSION

Figure 1 shows typical Mooney-Rivlin plots $s/(\lambda - \lambda^{-2})$ and $\sigma V_r^{1/3}/(\lambda - \lambda^{-2})$ versus $1/\lambda$ for unstretched unswollen, prestretched unswollen and swollen vulcanisates. The prestretched sample is defined as a sample which has been stretched at a specified strain for a period of time (2 days) before being tested. The data in Figure 1 were experimentally obtained from the tensile elongation range of 30-150%. From the result, two significant features should be noted, these being:

Non-straight line of the Mooney-Rilvin curve on swelling

It can be seen from Figure 1 that the results of unswollen and swollen samples were different. The results of the unstretched and prestretched unswollen samples were very similar. In fact, they were the same, taking account of the experimental errors. However, the difference between swollen and dry (unstretched and prestretched) was significant. Considering unstretched dry and swollen samples, the dry sample showed the straight line, the $2C_1$ value (intercept) being approximately 0.161 MPa. For the swollen sample, the curve showed two separate regions. The first region was the $1/\lambda$ from 0.50 to 0.35 showing a non-straight line, whereas the other was the $1/\lambda$ from 0.70 to 0.50 showing a straight line, the value of $2C_1$(obtained using the straight region) being 0.144 MPa. The reason for showing the non-straight line in the first region was due to the limitation of the Mooney-Rilvin equation as stated earlier. That is for the Mooney-Rilvin equation to obtain a straight line, the values of elongation should remain between 30-150% ($\lambda^{-1} \approx 0.4 - 0.7$).[2,5] During the swelling experiment, it was observed that the vulcanisates had *already* swelled to approximately 70% elongation by length ($\lambda^{-1} \approx 0.6$). After swelling, the values of $2C_1$ and $2C_2$ obtained from tensile curves within an elongation
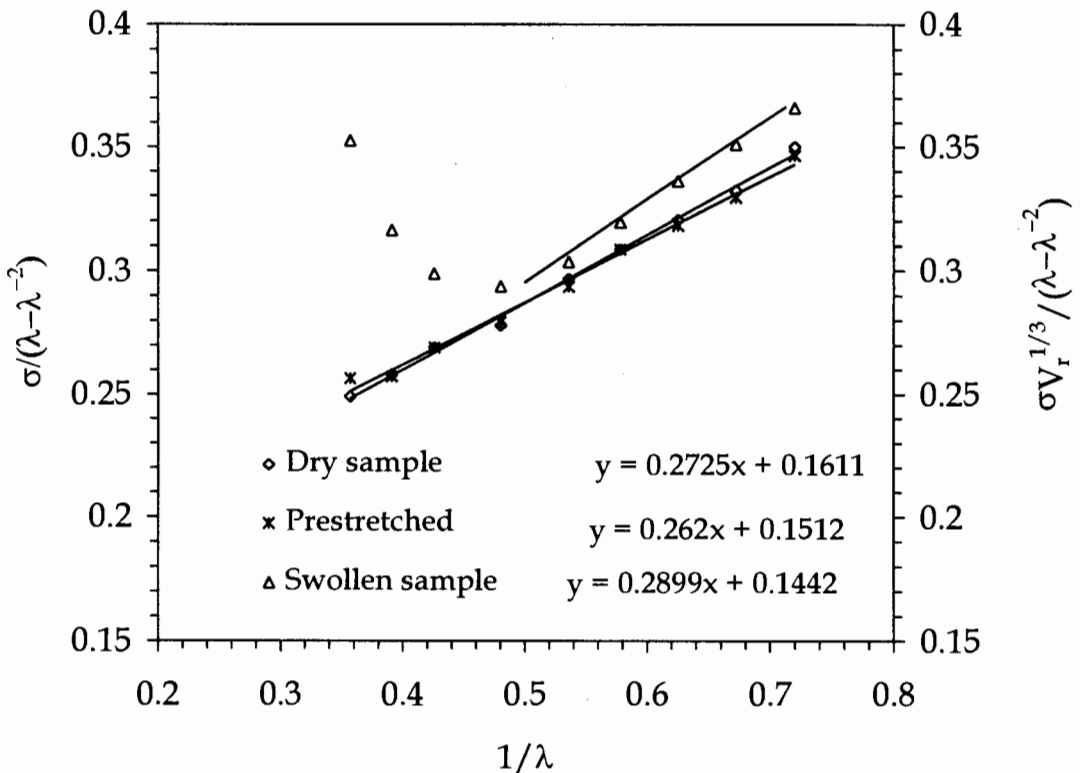

Legend (within figure):
- ◊ Dry sample $y = 0.2725x + 0.1611$
- × Prestretched $y = 0.262x + 0.1512$
- ▵ Swollen sample $y = 0.2899x + 0.1442$

x-axis: $1/\lambda$
left y-axis: $\sigma/(\lambda-\lambda^{-2})$
right y-axis: $\sigma V_r^{1/3}/(\lambda-\lambda^{-2})$

Fig.1   Typical Plots of $\sigma/(\lambda-\lambda^{-2})$ & λ^{-1} and $\sigma V_r^{1/3}/(\lambda-\lambda^{-2})$ versus λ^{-1} of NR Vulcanisates.

range of 30-150% needed calibrating based on the prior extensibility of the swollen sample. In this case, the sample has extended by 70% after swelling, then when tensile-testing the specimen, the valid elongation range will be up to 80%. Above this value, a non-straight line will occur, this behaviour corresponding to the results in the first region of the swollen curve in Figure 1. In this respect, it had a practical implication in that the use of Mooney-Rilvin equation for accurate determination of crosslink density of swollen rubbers needs calibrating based on the prior extensibility of the samples.

Change in degree of crosslinking

According to the theory of swelling of crosslinked polymers, strong bonds, such as the chemical crosslinks between the vulcanised rubber chains, prevent rubber molecules becoming completely surrounded by the fluids, but cause swelling.[6,9] In relation to this work, one would expect to observe the same degree of crosslinking from the dry and swollen samples in Figure 1. In other words, the values of $2C_1$ obtained from the dry and swollen samples (using the straight region) should be the same. However the values of $2C_1$ obtained from the dry and swollen samples were slightly different, the $2C_1$ values of the dry and swollen samples being 0.161 and 0.154 MPa respectively. This indicates that crosslink density of the rubbers reduced after swelling. This may be a consequence of the following:

- Prior extensibility (70% in this consideration) of the swollen specimen was different from the apparent extension of the dry sample whilst being stretched at 70% strain during testing. This was due to the fact that the extensibility of the swollen sample was three dimensional whereas, in the tensile test, it was uniaxial.[10] In this respect, the stress set up in the network structures was different which led to different tensile behaviour. This statement can be better-substantiated and proven by comparing the result of the swollen sample with that of the prestreched dry sample in Figure 1. The results were different. This confirmed that the prior extensibility due to swelling was different from that due to tensile-stretching.

- On swelling, there may be some soluble and uncrosslinked parts of rubbers which dissolved in toluene whereas this did not occur in the dry sample.[6] This resulted in some differences in the overall structure and stress distributions in the samples during testing.

- The interaction forces between polymer chain segments and the molecules of swelling solvents may probably affect the tensile results during the test, this then being the cause of the variations of the crosslink density.

These findings have practical implications in that, in order to obtain an accurate evaluation of crosslink density for swollen vulcanisates, prior extensibility of the compounds after swelling should be taken into consideration.

Comparison between the crosslink densities obtained by the Mooney-Rilvin and the Flory-Rehner equations

In order to calculate the crosslink density of the NR vulcanisates swollen in toluene by means of swelling, the values of χ, f and V_r are required. The first two values for NR-toluene system were obtained from the literature (at a temperature of 25°C)[11] whereas the last parameter was obtained using equation 7, which was previously carried out by the author.[6]

χ = 0.3795[11]

f = 4, this value being usually assumed[12]

V_r = 0.49

Table 1 Crosslink densities of NR vulcanisates obtained using the Mooney-Rilvin and Flory-Rehner methods.

Samples	Crosslink density by Mooney-Rilvin method (mole/cm³)	Crosslink density by Flory-Rehner method (mole/cm³)
Dry	3.24×10^{-5}	-
Prestretched	3.02×10^{-5}	-
Swollen	2.81×10^{-5}	3.15×10^{-4}

Table 1 shows crosslink densities of NR vulcanisates obtained from the two methods. It can be seen that the crosslink densities obtained from the two different methods, in the case of swollen samples, were found to be very different, the value obtained from the Mooney-Rilvin equation being considerably lower than that obtained from the Flory-Rehner equation by a factor of ten. This was also the case when comparing to the dry and pre-stretched samples. It was not surprising since it has been evident that crosslink densities determined using various means would be considerably different.[8] However, the discrepancy in the results (only for swollen samples) between the two methods observed in this work was thought to be caused by two possible factors, these being:

- Mode of deformations: The deviation of the results is dependent on the magnitude of the crosslink fluctuations affecting how loosely embedded the crosslinks are within the network structure.[7] In the case of the stress-strain method (Mooney-Rilvin), the polymer chains were fully swollen and stretched out whereas the stretching of the polymer chains did not occur in the case of the Flory-Rehner method.

- Errors in the calculations of the Flory-Rehner equation: Since all the parameters (χ, f and V_r) used in the calculations were obtained by various independent methods, this would result in an error in the calculations.

CONCLUSION

Non-linear bahaviour of the Mooney-Rilvin curve under valid elongation and change in the crosslink density for swollen NR vulcanisates, compared to dry NR vulcanisates, were observed. The non-linear bahaviour was caused by prior-extensibility of the rubbers whereas the change in the degree of crosslinking resulted from differences in the directional stresses in the NR compounds during swelling, in the chemical structures, and in the interactive bonding between dry and swollen samples. The crosslink densities from the use of the Mooney-Rilvin equation were found to be different when compared to those from the Flory-Rehner equation, this being due to differences in mode of deformations and error in the calculations.

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