Influence of gel and molecular weight on the properties of natural rubber

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The influence of gel and molecular weight on the properties of natural rubber has been described. Crystallization, stress relaxation and orientation properties of different samples have been studied. Samples having different gel contents but similar molecular weights and samples having the same gel content with varying molecular weights have been prepared by extracting whole natural rubber. The gel content was varied from 1.5 to 29% and molecular weight from 1×10^5 to 9.9×10^5 g mol^{-1}. The gels reduce the overall crystallinity measured by differential scanning calorimetric experiments after freezing the samples for different time periods at $-15°C$. They also have a stiffening effect on the tensile relaxation modulus and decrease the rate of relaxation significantly. Birefringence, which measures the orientation and stress-induced crystallization, increases with time at high elongation for samples containing gels. At lower elongation, however, the birefringence of unvulcanized samples decreases with time. This decrease is less for gel samples. Natural rubbers of high molecular weight behave similarly in the above properties when compared to low molecular weight samples. The effect of gel is more predominant than that of molecular weight.

INTRODUCTION

Elastomers with unsaturation on the backbone chain tend to react on storage and form branched molecules and gels. Gels are also formed during synthesis of unsaturated elastomers in the absence of proper termination. Gels can be defined as particles obtained by combination of large polymer molecules into chemically connected finite groups or physically knotted groups that are expected to show significantly different properties than the linear chains in the sense that they produce more network defects and may affect transport properties.

The question of gels and their behaviour is very important to understand the physical properties of natural rubber. Gel formation is undesirable during extraction of natural rubber from shrubs such as guayule, but it is good and necessary for processing and properties of rubber in actual applications. In fact, it is well known that the rubber obtained from *Hevea brasiliensis* is superior to synthetic Natsyn and guayule rubber in terms of mechanical and rheological properties, although all these rubbers have the same isoprene backbone chain. Compared to the importance of the subject, little experimental work has been carried out to investigate the effect of gel on rubber properties. Moreover, the effect of molecular weight on the physical properties of natural rubber in the absence of gels has not been studied thoroughly. This paper aims to highlight the effect of gel and molecular weight on natural rubber properties.

It is industrial practice to incorporate gels in rubber to reduce die swell, to have better shape retention and higher extrusion rates, and to make a smoother surface finish. The advantages have been described by Hofman[1]. The flow behaviour of raw elastomers containing gel particles was studied for nitrile rubber[2] and guayule rubber[3].

These authors reported a decrease in viscosity with the addition of gel, especially at low shear rates. Gel contents of 100, 75, 50, 25 and 0% in nitrile rubber were examined. The incorporation of crosslink particles of the same rubber reduced the elastic response as well as the viscous response at higher rates of extrusion. At low gel contents (less than 40%) the results of viscosity of poly(ethyl acrylate) elastomer[4] and that of nitrile rubber[2] are not in agreement with each other. This means that the effect of gel particles on the properties of rubber is not the same for all elastomers. Moreover, the properties will depend very much on the size, shape and chemical nature of the gel particles, which are not easy to characterize. Hence, further study is needed in this area to investigate the effect of well characterized gels in rubber. These studies are now in progress in our laboratory. The present study is also important to understand the re-use of scrap rubber (which is made up of macrogel particles) in rubber vulcanizates[5] and commercially available superior processing rubbers[6].

Most of the studies reported above discuss rheological properties in general. Only recently has a systematic investigation been carried out to study the effect of gel on the mechanical properties of rubber[7]. Stress relaxation behaviour of raw natural rubber—fractionated and solvent extracted—was investigated. The gel had a stiffening effect on the relaxation behaviour of rubber. A gel phase in *Hevea* natural rubber has also been reported from the same laboratory[8].

EXPERIMENTAL

SMR-5 supplied by the Malaysian Rubber Bureau, USA, was used as the starting material. *Trans*-polyisoprene (t-PIP) obtained from Polysar was used in one mix.

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Preparation of rubber samples with varying gels and molecular weights

Hevea natural rubber was dissolved in toluene to make a 0.5% solution. Methanol was added at room temperature, until a turbidity developed. The mixture was then warmed to 50°C in a fractionating funnel with stirring to make a transparent solution. The warmed rubber solution was allowed to cool to room temperature. The high molecular weight rubber fraction precipitated out from the solution and was removed from the bottom of the funnel after siphoning out most of the supernatant liquid. The precipitated rubber was redissolved in toluene and the dilute solution after filtering through glass wool was dried in a nitrogen atmosphere. The rubber was stored in vacuum. The procedure was repeated with the collected supernatant solution, to obtain samples with varying molecular weights and gel contents.

A few low molecular weight samples were made from masticated natural rubber using the same procedure.

Preparation of film

Rubber fractions were dissolved in toluene to make a 2% solution. A wet piece of cellophane was stretched over a ring and dried at room temperature. A glass cylinder was placed on the smooth levelled cellophane surface. The solution was poured into the cylinder and covered with a piece of paper to ensure slow evaporation of the solvent. This takes about three weeks at room temperature. The prepared specimens were kept in vacuum for physical measurements.

Determination of molecular weight

A Waters Associates Ana-Prep gel permeation chromatograph was used for determination of molecular weights. Intrinsic viscosity was also determined for very high molecular weight fractions and fractions containing gels.

Two sets of columns—set A (10^7, 10^6, 5×10^5, 10^5 and 10^4 Å) and set B (10^6, 5×10^5, 10^5, 3×10^4, 10^4, 3×10^3 and 10^3 Å) were used in g.p.c. Samples were prepared at 0.125% concentration and filtered through 0.45 μm Metricel membranes. The flow rate of 1 ml min^{-1} at 30°C, THF as solvent, and a differential refractometer were used.

The intrinsic viscosity [η] was measured by using a single-bulb Ubbelohde viscometer. A stock solution of toluene of 0.48 g dl^{-1} was used and filtered through 10 μm Millipore type LS membranes. A viscosity average molecular weight (M_v) was calculated from the well known Mark–Houwink equation:

$$[\eta] = KM_v^a \qquad (1)$$

where $K = 50.2 \times 10^{-3}$ and $a = 0.667$ were used. In cases where molecular weights are difficult to determine, values of molecular weight were estimated (*Figure 1*) from a plot of weight average molecular weight *versus* viscosity average molecular weight using a gel-free guayule rubber of varying molecular weights. This has been done for rough comparison of different samples.

Determination of gel content

The gel content in each fraction was measured. About 0.1 g of rubber was dissolved in 25 ml of toluene. The initial concentrations were evaluated by drying 2 ml of the
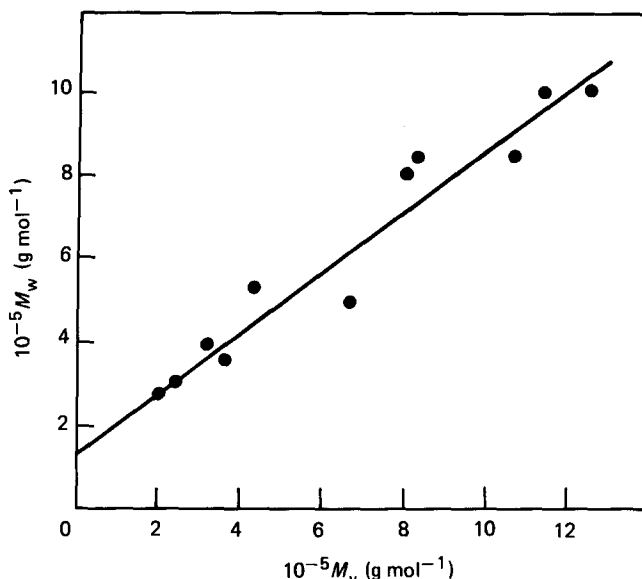

Figure 1 Plot of weight average molecular weight (M_w) from g.p.c. *versus* viscosity average molecular weight (M_v) for guayule samples

solution. The rest of the solutions were placed in polyethylene centrifuging tubes and capped. The solution was centrifuged at 7000 r.p.m. for 2 h using a Sorvall Ultracentrifuge. The solution was separated into a supernatant phase and gel particles. The concentration of the supernatant phase was measured, assuming that it does not include gel. The gel content was reported as percentage gel present in the original rubber.

Measurement of crystallinity

Crystallinity of natural rubber fractions was measured in a nitrogen atmosphere using a du Pont 1090 differential scanning calorimeter. For this, 10 mg samples, initially kept at -15°C for different periods, were used. The experiments were conducted at 10°C min^{-1}. The degree of crystallinity of the samples was obtained from the heat of fusion.

Measurement of stress–strain, stress relaxation and orientation properties

Stress–strain properties were measured on thin dumbbell samples. By means of a Statham force transducer, to which the upper clamp was attached, changes in tensile force at different extensions (rate of extension 8.5×10^{-3} m s^{-1} and test temperature 22°C) or at constant extension but at different times were followed.

On-line birefringence measurements were made following the deformation process. An optical bench containing polarizer, analyser and Babinet compensator was used. Details are reported elsewhere[9].

RESULTS AND DISCUSSION

Characterization of rubber

Measurement of molecular weight, molecular weight distribution and gel contents of rubber has been done on six fractions (R_1–R_6) having different molecular weights and gel contents (*Table 1*). Three low molecular weight fractions (R_7–R_9) extracted from masticated rubber have also been reported. High molecular weight samples have been characterized by viscometry due to problems of plugging the g.p.c. columns and low molecular weight

Table 1 Molecular weight and gel content of rubber fractions and the whole rubber (WHR)

Sample	Molecular weight (g mol^{-1})				
	From g.p.c. data			From viscosity $M_v \times 10^{-5}$	Gel content (%)
	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n		
R_1	–	8.4^a	–	9.9	29
R_2	–	6.7^a	–	7.6	16
R_3	–	6.3^a	–	7.0	4
R_4	–	5.7^a	–	6.1	2
R_5	–	5.0^a	–	5.2	7
R_6	–	2.4^a	–	1.7	2
R_7	2.2	4.9	2.3	5.0^a	4
R_8	1.5	2.1	1.5	1.2^a	1.5
R_9	0.6	0.8	1.3	–	2
WHR	–	7.2^a	–	8.1	8

^{a} Estimated value from *Figure 1*

samples characterized by g.p.c. Estimated molecular weights (M_w or M_v) from *Figure 1* are also reported in *Table 1*.

The gel content for different samples varies from 1.5 to 29%. The molecular weight varies from 1×10^5 to 9.9×10^5 g mol^{-1}. Samples R_2 and R_3 have similar molecular weights but different gel contents while samples R_4 and R_6 have similar gel contents but varying molecular weights. The whole natural rubber contains about 8% gel. In this particular study, high molecular weight fractions are always associated with high gel, because of the fractionation procedure adopted.

Crystallization of rubber fractions

The crystallinity of different samples with varying amounts of gel has been reported in *Table 2*. The samples were kept at $-15°C$ for different time periods to observe large differences in crystallinity. D.s.c. scans of some samples are reported in *Figure 2*. With increase in freezing period, the crystallinity increases for all samples. In general, the crystallinity decreases with increase in molecular weight. At similar gel content (samples R_4 and R_6), this is particularly evident. At similar molecular weight (samples R_2 and R_3), the sample with higher gel content gives lower crystallinity. A 7% increase in crystallinity is observed by reducing the gel content by one-fourth. *Figure 3* shows a plot of percentage crystallinity with gel content. There is a continuous decay of crystallinity with the addition of gel. These results could be explained in terms of chain mobility. A short chain moves easily and helps nucleate crystals. As discussed later, the motion of the chains in the gels or high molecular weight samples is hindered because these are physically knotted or chemically tied molecules. When these gels are put into molecules having linear chains, the overall crystallinity is affected corresponding to the amount of added gel.

Stress–strain data

Stress–strain plots have been made on R_1–R_6 samples (*Figure 4*). The stress at 60 min after stretching fresh samples to various elongations was measured here. At a particular elongation, stress values are much higher for samples containing gel or for high molecular weight samples. The effect of gel is very prominent from the behaviour of R_2 and R_3 samples. The sample with 16%

gel (R_2) at similar strain shows much higher stress than R_3 with 4% gel, especially at higher elongations. The effect of gel is very similar to that of *trans*-polyisoprene (t-PIP) in natural rubber (broken curve). The sample with *trans*-polyisoprene is more resistant to breaking than samples R_3, R_4 or R_6. At similar gel level, the higher molecular weight sample (R_4) shows superior stress–strain properties than the lower molecular weight sample (R_6). It seems that the effect of gel is more prominent on the stress–strain properties than that of molecular weight. The enhancement of properties with the incorporation of gels is probably due to (1) higher modulus of the gels, because these gels are chemically entangled systems (as detailed later), and (2) compatibility of these particles with the matrix.

Stress relaxation measurements

Stress relaxation experiments have been carried out on samples R_1–R_6. Representative plots on a double logarithmic scale have been shown in *Figures 5* and *6* for samples R_2, R_3 and R_4, R_6 at different elongations. The sample with high gel content (R_2) always shows higher modulus than the sample R_3 at similar elongations over a

Table 2 Crystallinity of rubber fractions

Sample	Crystallinity (%)^a		
	1 day	15 days	30 days
R_1	3.8	3.7	5.2
R_2	–	5.1	5.8
R_3	5.0	5.5	6.2
R_4	–	5.5	6.2
R_5	4.1	5.4	6.1
R_6	4.5	5.9	6.6
R_7	–	–	6.2
R_9	5.1	5.9	–
WHR	4.2	–	6.2

^{a} $\pm 0.5\%$
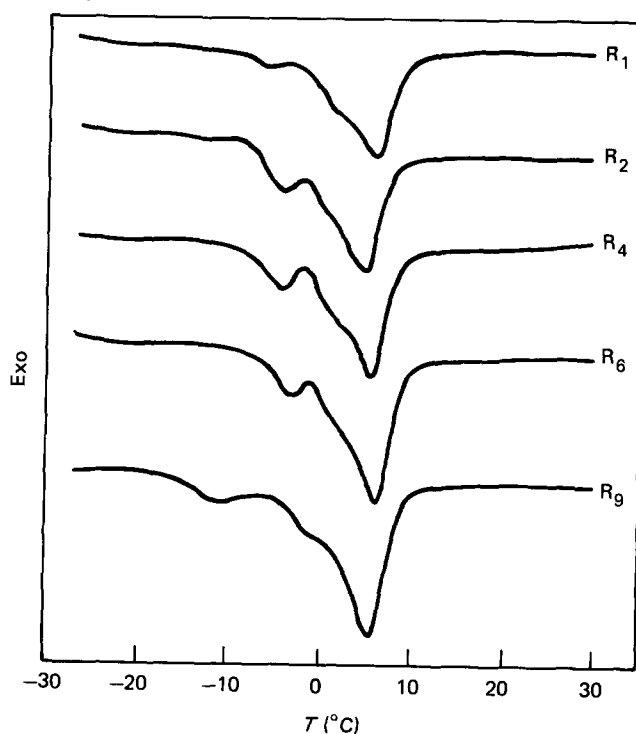
Figure 2 D.s.c. scans of natural rubber samples of varying molecular weights and gels over a range of temperatures (-30 to $+30°C$)
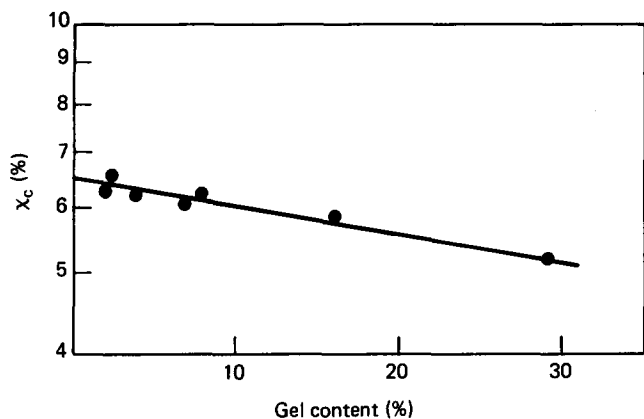
Figure 3 Plot of percentage crystallinity obtained from d.s.c. measurement *versus* gel content

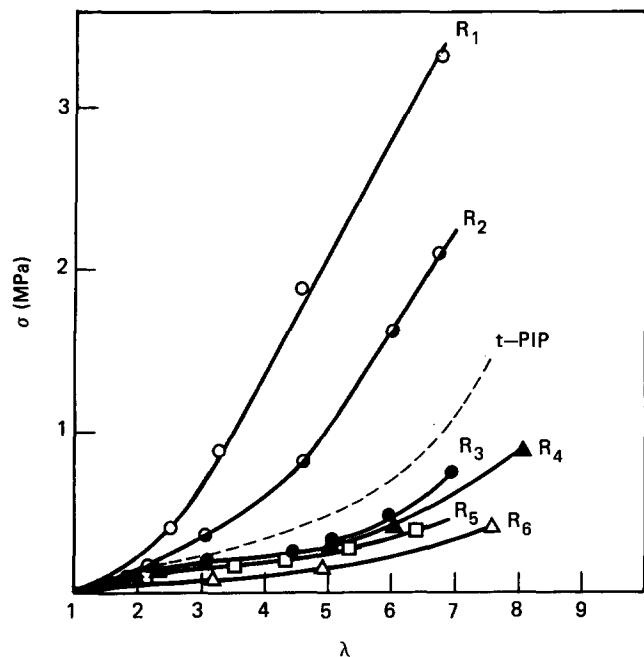range of time periods (*Figure 5*). A similar effect of high molecular weight has been shown in *Figure 6* for samples R_4 and R_6 at different elongations. It is quite apparent that the gel and high molecular weight have a stiffening effect on the relaxation modulus and these reduce the rate of relaxation quite markedly. The low molecular weight and low gel samples on the other hand influence the time variation of relaxing stress, increasing the rate of relaxation. Both the 'high gel samples' and the 'high molecular weight samples' can be treated on the same level in the sense that these are highly entangled samples (gel being more tangled).

For given elongation, the straight lines could be well represented by:

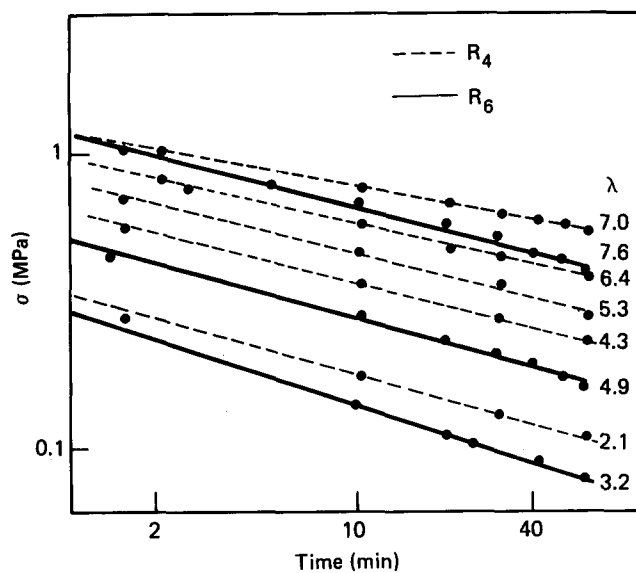$$\log \sigma - \log \sigma_0 = x(\log t - \log t_0) \qquad (2)$$

Figure 4 Stress–strain curves of natural rubber samples

Figure 6 Plot of tensile stress *versus* time for natural rubber samples having same gel contents but different molecular weights (R_4, $M_v = 6.1 \times 10^5$ g mol^{-1}, gel content 2%; R_6, $M_v = 1.7 \times 10^5$ g mol^{-1}, gel content 2%)

Figure 5 Plot of tensile stress *versus* time for natural rubber samples having similar molecular weights but varying gel contents (R_2, $M_v = 7.6 \times 10^5$ g mol^{-1}, gel content 16%; R_3, $M_v = 7.0 \times 10^5$ g mol^{-1}, gel content 4%)
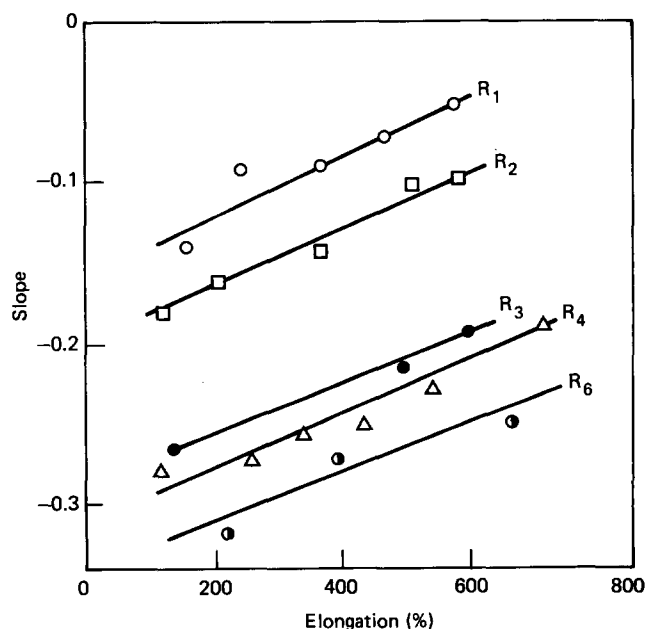

Figure 7 Slope of the stress relaxation plot of equation (2) *versus* elongation for natural rubber fractions

where σ is the stress at time t, σ_0 that at initial time t_0 and x is the slope of the plot. The value of x is found to be dependent on elongation and gel content as well as molecular weight (*Figure 7*). For high molecular weight samples and samples with higher gel content, slower stress relaxation occurs. Similar results have been obtained by Campbell and Fuller[7]. As discussed before, a higher molecular weight sample and a high gel sample, because of high entanglement density—either physical or chemical—and of the compatibility of chain structure, hold molecules together, causing very slow molecular flow and releasing stress slowly compared to low gel and low molecular weight samples.

Orientation of molecules in presence of gel

Measurement of birefringence has been carried out on the natural rubber fractions to observe the orientation in the presence of gel and entanglement. *Figure 8* shows a logarithmic plot of birefringence with time. Birefringence decreases with time for samples stretched at low
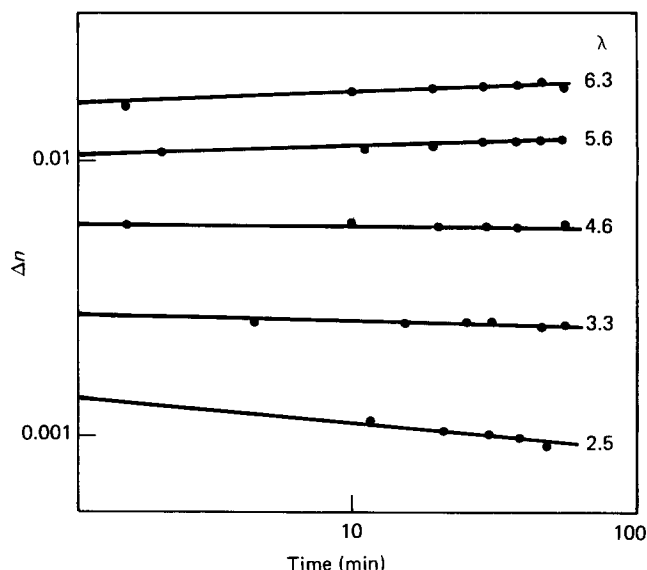
Figure 8   Plot of birefringence with time for natural rubber sample R_1 ($M_v = 9.9 \times 10^5$ g mol^{-1}, gel content 29%) at different elongations
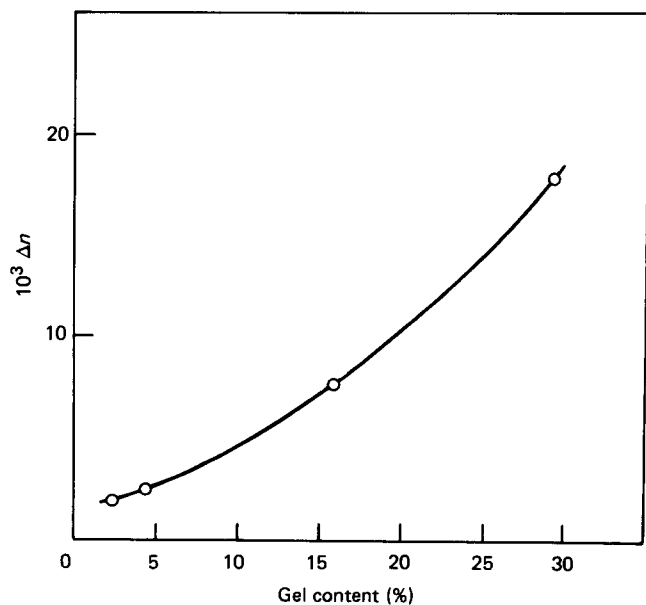
Figure 9   Variation of birefringence with gel content at elongation $\lambda = 6.8 \pm 0.1$ and time of 60 min
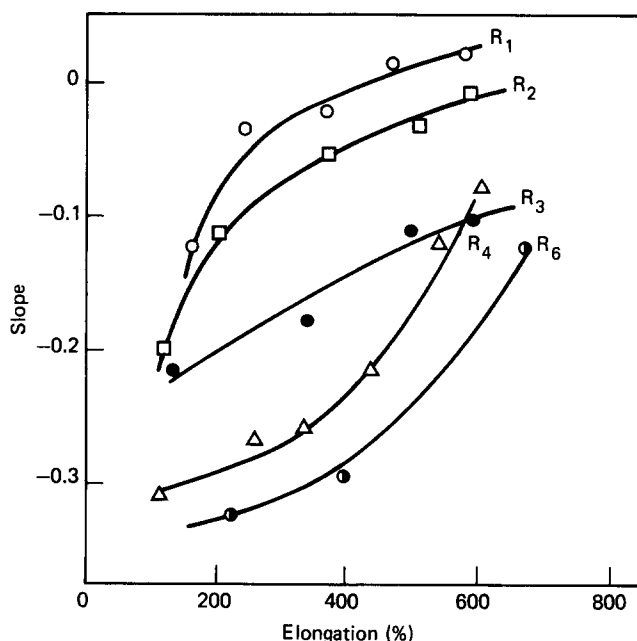
Figure 10   Plot of the slope using equation (3) *versus* elongation for different rubber samples

elongations, more so with the lower molecular weight samples. But the birefringence increases with time at higher elongations. Similar observations have been made previously on polyisoprene samples[9,10]. The variation of birefringence with gel content or molecular weight at a particular time (60 min) and elongation ($\lambda = 6.8 \pm 0.1$) has been shown in *Figure 9*. High molecular weight samples and high gel samples have higher birefringence.

When a rubber is stretched and held at constant strain, the molecules orient in the direction of stretching. At some strain, depending on temperature and material, the molecular chains align themselves and crystallize. Birefringence measures the combined effect of strain-induced crystallization and deformation of molecules. The non-crystallized molecules, however, start to flow after some time and take random orientation. Gel particles act as crosslinks and resist the flow of the matrix, which is also reflected in the stress–time plot. The rate of flow is so high for low molecular weight samples and low gel samples that the increased birefringence due to time-dependent crystallization will be overshadowed by the random orientation of the chain. Hence, birefringence decays with time for low gel samples.

Birefringence–time plots have been made for all samples at different elongations. The relationship can be expressed as:

$$\Delta n(t) = \Delta n(0)(t/t_0)^m \tag{3}$$

where m is the absolute value of the slope. As shown in *Figure 10*, the value of m increases with increasing elongation, molecular weight or gel content.

ACKNOWLEDGEMENTS

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