

# Rheological study of crosslinking and gelation in chlorobutyl elastomer systems

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The multiple waveform rheological technique was used to study the crosslinking behaviour of a filled elastomeric system at various temperatures. The gel point could be precisely determined from a single experiment at each temperature using this technique. At the instant of gelation, the storage ( $G'$ ) and loss ( $G''$ ) moduli scale with frequency in an identical manner, i.e.  $\sim \omega^n$ . The relaxation exponent,  $n$  was found to be approximately constant (0.14) in the temperature range studied. Reported values of  $n$  for chemically crosslinking systems are typically higher; the low value in this case can be attributed to the high molecular weight of the prepolymer and the presence of filler. The gel times at various temperatures were used to calculate an apparent activation energy of the curing reaction, which was found to be approximately  $92 \text{ kJ mol}^{-1}$ . Copyright © 1996 Elsevier Science Ltd.

**(Keywords: crosslinking; gelation; gel point; filled system; rheology; multiwave form)**

## INTRODUCTION

Chlorobutyl rubber either exclusively or in blends with natural rubber, is widely used in the tire industry, e.g. for tubeless tire innerliners, tire sidewalls, or tire curing members<sup>1,2</sup>. Like its parent, butyl rubber, from which it is prepared, chlorobutyl rubber is a highly saturated polymer containing a limited level of reactive functionality in the form of an allylic chloride moiety<sup>1</sup>. The lower reactivity allows more control during the vulcanization (crosslinking) of chlorobutyl, as compared to natural rubber. Nevertheless the level of functionality is sufficient to provide a crosslinked network of high strength.

Chlorobutyl rubber is also widely used in biomedical applications<sup>3</sup>. Articles made from these rubbers are fabricated by compression moulding at temperatures of about  $150^\circ\text{C}$ . The material fed in to the compression mould consists of a compounded stock of rubber, crosslinking agent and other components such as fillers, plasticizers, and accelerators. The system does not cure at room temperature; it has to be heated to temperatures exceeding  $100^\circ\text{C}$  for crosslinking to occur. During cure, the material is transformed from a high molecular weight polymer, consisting of entangled macromolecular chains, to a branched network of infinite molecular weight. Rheological studies of the crosslinking process are essential for optimization of the processing cycle. In addition, such studies can be used to gain a fundamental

understanding of the crosslinking kinetics and the mechanical behaviour of the system.

Rheological properties such as the viscosity and the dynamic modulus can be directly correlated to the evolving physical and mechanical properties of the system during cure. In other techniques, such as calorimetry and spectroscopy, the state of cure cannot be directly related to the changes in mechanical behaviour. The preferred rheological technique for monitoring crosslinking has been dynamic mechanical spectroscopy, where sinusoidal shear at low strains is applied to the sample as it cures<sup>4</sup>. The response of the sample yields the shear storage modulus ( $G'$ ), which indicates the elastic character of the material, and the shear loss modulus ( $G''$ ), which is related to the viscous response of the material. This technique is non-intrusive, as compared to steady shear measurements, since the level of deformation is kept low.

Typically, the isothermal cure of elastomers is followed by a dynamic time sweep, where the moduli  $G'$  and  $G''$  are monitored as a function of cure time at constant frequency<sup>5</sup>. The  $G'$  vs time curve can then be fitted to an empirical kinetic model, such as that suggested by Hsieh and co-workers<sup>5,6</sup>. The ultimate modulus reached on cure can also be obtained from this experiment. However, it has been shown that a single time sweep at a constant frequency is not sufficient for accurate determination of the gel time<sup>7</sup>. The gel point ( $GP$ ) of a crosslinking polymer is an important parameter, both from scientific and technological standpoints. It can be determined precisely from appropriate rheological measurements, as described below.

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*Rheological criterion for gel point*

A crosslinking polymer at its *GP* is in a transition state between liquid and solid<sup>7,8</sup>. The *GP* is defined unambiguously as the instant at which the weight average molecular weight diverges to infinity. Additionally, at this juncture, the molecular weight (*MW*) distribution is infinitely broad ( $M_w/M_n \rightarrow \infty$ ), with molecules ranging from the smallest unreacted chain to the infinite, sample-spanning cluster. The polymer reaches its *GP* at a critical extent of crosslinking,  $p \rightarrow p_c$  which can be predicted for simple systems by the theories of Flory, Stockmayer etc.<sup>8</sup>. Before the *GP*,  $p < p_c$ , the polymer is called a sol, because it is soluble in good solvents. The polymer beyond the *GP*,  $p > p_c$ , is called a gel, and is not soluble even in good solvent. From a technological standpoint, it is necessary to know when the sol–gel transition occurs because the polymer can be easily processed only before the gel point while it can still flow and the stresses applied can relax to zero<sup>8</sup>. Accurate knowledge of the *GP* would also allow estimation of the optimal temperature and time for which the sample should be heated before being allowed to set in the mould.

Rheological methods to determine the *GP* have become quite popular, though often they are applied incorrectly. Obtaining the gel time by measurements of viscosity (which becomes infinite at the *GP*) or the equilibrium modulus (which is non-zero past the *GP*) involves a certain amount of extrapolation<sup>7,8</sup>. Alternatively, the *GP* has been associated with a change in slope of the developing modulus ( $G'$ ) vs time curve, or with the crossover point of  $G'$  and  $G''$ <sup>9–12</sup>. However changes in slope are not universally observed in all systems and some curing systems exhibit multiple slope changes<sup>12</sup>. Also, the crossover point coincides with gelation only in certain special cases<sup>7</sup>.

Recent studies by Winter have led to a general criterion that can be used to identify the gel point<sup>7,8</sup>. This criterion has also been verified by theoretical studies based on scaling theory. It has been found that the stress relaxation behaviour of a network polymer at the *GP*, follows a power law:

$$G(t) = St^{-n}; \quad p = p_c \quad (1)$$

Here, the strength of the gel,  $S$ , depends on the flexibility of molecular chains and crosslinks, and on the crosslink density at *GP*. The relaxation exponent,  $n$  can have values in the range  $0 < n < 1$  and is related to the geometry of clusters existing at the *GP*. From the above equation, the frequency dependence of the dynamic shear moduli at *GP* can be deduced to be:

$$G'(\omega) = \Gamma(1 - n) \cdot \cos(n\pi/2) \cdot S\omega^n \quad \text{i.e. } G'(\omega) \sim \omega^n \quad (2)$$

$$G''(\omega) = \Gamma(1 - n) \cdot \sin(n\pi/2) \cdot S\omega^n \quad \text{i.e. } G''(\omega) \sim \omega^n \quad (3)$$

Thus, the storage and viscous moduli do not coincide at *GP*, but they depend on frequency in an identical manner, corresponding to parallel lines in a frequency spectrum. Additionally, at *GP*, the loss tangent  $\tan \delta$  becomes independent of frequency:

$$\tan \delta = \frac{G''}{G'} = \tan(n\pi/2) \quad (4)$$

If the evolution of  $\tan \delta$  with cure time is measured at

different frequencies, the various curves would coincide at a single point, corresponding to the *GP*. The above behaviour at the *GP* is observed only at temperatures much above the glass transition temperature ( $T_g$ ) of the crosslinking polymer.

*Multiple waveform rheology*

In order to make use of these criteria for the gel point, the dynamic moduli must be obtained at different frequencies as crosslinking progresses. One possible way of accomplishing this is by using multiple waveform rheology where a compound waveform is applied on the sample<sup>13,14</sup>.

$$\gamma = \sum_{i=1}^m \gamma_i \sin(\omega_i t)$$

where  $\omega_1 = \omega_f$ ;  $\omega_2 = n_2\omega_f$ ;  $\omega_3 = n_3\omega_f$  (5)

$$\sum_{i=1}^m \gamma_i \leq \gamma_c \quad (6)$$

The strain applied,  $\gamma$ , is the sum of the Fourier series described by each individual strain. The frequencies chosen are harmonics (integer multiples) of a fundamental frequency,  $\omega_f$ . Equation (6) expresses the condition requiring that the sum of the individual strain amplitudes has to be below the critical amplitude,  $\gamma_c$ , corresponding to the linear viscoelastic limit.

From the stress response to this composite strain, the individual stress (and thus  $G'$ ,  $G''$ ) values at each discrete frequency can be obtained by means of a discrete Fourier transform. The technique is therefore known as Fourier Transform Mechanical Spectroscopy (*FTMS*). The principle of this technique is based upon the Boltzmann superposition principle, which in simplified terms, states that two or more mechanical waves can simultaneously pass through a material independent of each other<sup>13</sup>. Thus, the displacement (strain) at a point within the material is the sum of the strains caused by each wave. The 'multiwave' method offers the advantage of speed, since the experimental time,  $t_c = 2\pi/\omega_f$ , is determined by the fundamental frequency,  $\omega_f$ . Measurements at higher frequencies do not require additional time since they are conducted simultaneously.

From the results of the multiwave experiment, the *GP* can be detected by the criteria mentioned previously: (a) the equality of slopes in the frequency spectrum; (b) frequency independent loss tangent. Simultaneously, data for  $G'$  and  $G''$  as a function of curing time can be extracted, for use in an appropriate kinetic model.

**EXPERIMENTAL**

Chlorobutyl rubber samples were received from Becton Dickinson Research Center [Research Triangle Park, NC]. A typical composition, which includes accelerator and filler is shown in *Table 1*<sup>3</sup>. The molecular weight of the polymer (400 000–500 000), is well above the entanglement molecular weight for the system,  $M_{en} \sim 8000$ <sup>1,3</sup>. Samples were cut into discs of about 8 mm diameter and 1–1.5 mm thickness from a sheet of rubber, and used for the experiments.

Rheological studies were conducted on a Rheometrics Mechanical Spectrometer (RMS-800) using 8 mm parallel plates. The plates were zeroed at the temperature of

**Table 1** Typical composition of chlorobutyl rubber system

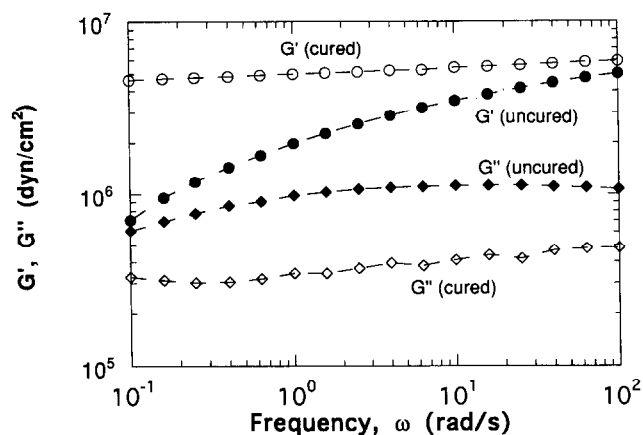
Component	Parts
Chlorobutyl rubber	100
Fillers:	50–60
Hi-sil 233	
Mistron vapour talc	
Whitetex clay	
Paraffin wax	2
Process aids	5
White oil	5
Stearic acid	1
Zinc oxide	5
SP-1055 resin	5
Mercaptobenzothiazole disulfite	2

interest, after which the pre-cut sample was placed between them. The time for loading the sample was kept to a minimum so as to reduce the lag time for temperature equilibration. The multiwave experiment was run with a fundamental frequency of  $1 \text{ rad s}^{-1} (\omega_f)$  and the strains ( $\gamma_i$ ) were kept at 0.5% at each harmonic. A total of eight waveforms were added to create the composite strain input, with the frequencies ranging from 1 to  $100 \text{ rad s}^{-1}$ . The instrument software had the capability to automatically perform the Fourier transformation of the raw data.

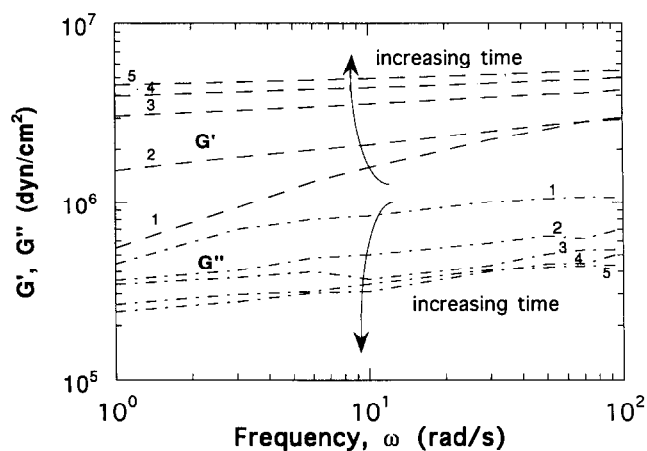
## RESULTS AND DISCUSSION

The initial filled rubber system with pre-mixed curing agent, is a viscoelastic material. Unlike most other crosslinking polymeric systems investigated using the Winter method<sup>15–21</sup>, the polymer molecular weight here is well above the entanglement limit, and the elastic nature of the system is enhanced by the presence of reinforcing filler. These aspects are reflected in the initial rheological properties of the system. Frequency sweeps prior to crosslinking, conducted at  $90^\circ\text{C}$  (a temperature at which no cure occurred over a long period of time, as verified by differential scanning calorimetry), are shown in *Figure 1*. The storage modulus,  $G'$  is greater than the loss modulus,  $G''$  over the entire frequency range. However,  $G'$  shows a marked dependence on frequency, especially towards the lower end of the frequency spectrum, thereby indicating the absence of any permanent crosslinked structure. On completion of curing, the ultimate moduli show frequency independent behaviour, with  $G'$  significantly larger than  $G''$ , characteristic of crosslinked systems. It should be noted that the increase in the level of  $G'$  due to crosslinking is less than an order of magnitude, and the ultimate loss modulus,  $G''$  is lower than its initial level.

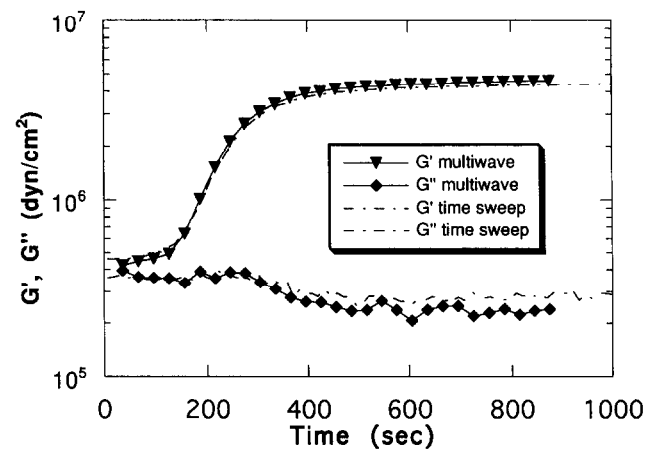
The multiwave technique generates frequency sweeps from  $1$  to  $100 \text{ rad s}^{-1}$ , as the sample cures. For isothermal cure at  $170^\circ\text{C}$ , the evolution of microstructure with time is shown in terms of the frequency sweeps (*Figure 2*). It is observed that  $G'$  increases in magnitude and becomes increasingly independent of frequency as the crosslinking progresses. Correspondingly, the level of  $G''$  drops steadily with cure time. These observations indicate that the polymer develops a predominantly elastic character and simultaneously loses its viscous characteristics. Qualitatively, the above behaviour of the storage and loss moduli with cure time (see also *Figure 3*) is



**Figure 1** Comparison of the storage ( $G'$ ) and loss ( $G''$ ) moduli of cured and uncured samples plotted as a function of frequency. Both the experiments were conducted at strains within the linear viscoelastic regime. The uncured sample was characterized at  $90^\circ\text{C}$ , while the crosslinked sample was tested after curing for 15 min at  $170^\circ\text{C}$



**Figure 2** Evolution of the storage ( $G'$ ) and loss ( $G''$ ) moduli during crosslinking at  $170^\circ\text{C}$ . The frequency sweeps shown were obtained from a single multiwave experiment at different instants of cure: 1, 6 s; 2, 220 s; 3, 300 s; 4, 400 s; 5, 900 s

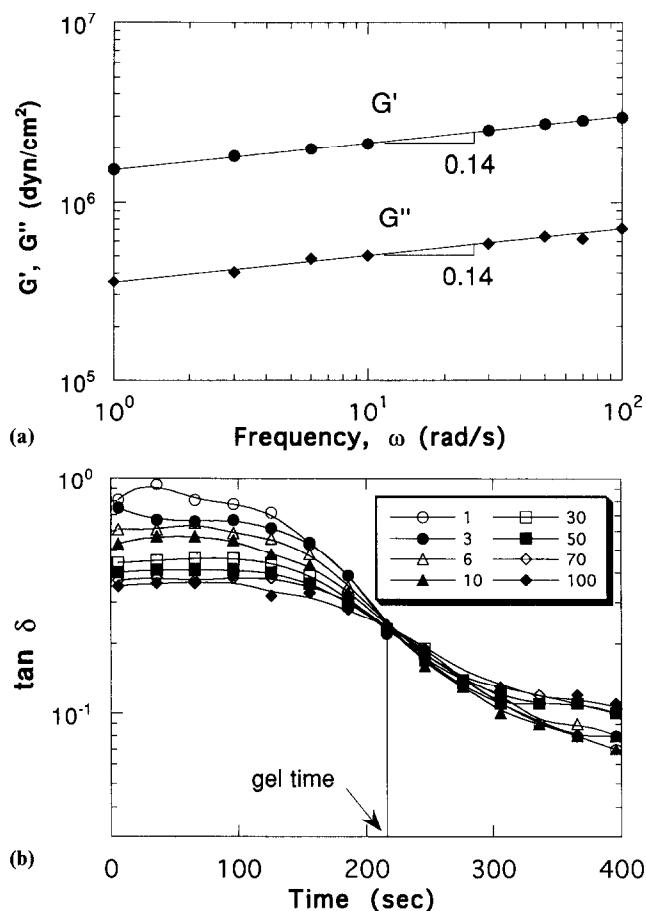


**Figure 3** Evolution of the time-dependent storage ( $G'$ ) and loss ( $G''$ ) moduli obtained through the multiwave technique compared with that obtained using a single frequency ( $\omega = 1 \text{ rad s}^{-1}$ ) time sweep. The data correspond to cure at  $170^\circ\text{C}$ . Excellent overlap is observed between the two sets of data

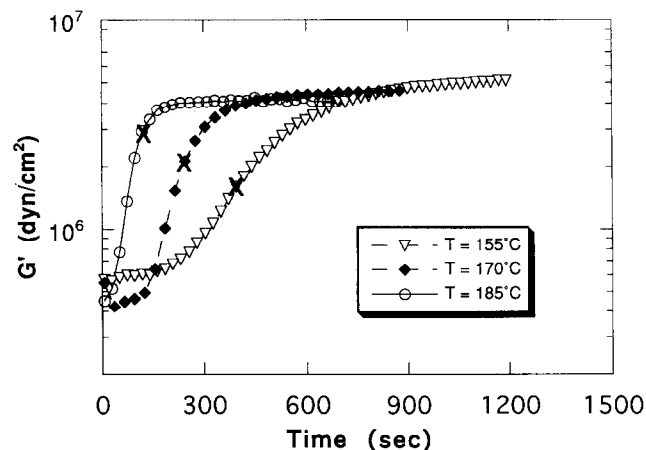
typical of many thermosetting systems, in particular filled rubbers<sup>5,6</sup>.

As crosslinking proceeds, at a certain instant, the  $G'$  and  $G''$  curves have the same slope, corresponding to the

formation of the critical gel (Winter criterion). This occurred at 220 s at 170°C and the corresponding value of relaxation exponent,  $n$ , given by the slope of the lines was found to be 0.14 (Figure 4a). Equivalently, the



**Figure 4** (a) Frequency spectrum at the gel point for crosslinking at 170°C. The data were obtained at a time of 220 s after the onset of crosslinking, which corresponds to the gel time. The slopes of the lines are identical and equal to 0.14. This is the value of the relaxation exponent  $n$ , characterizing the frequency-dependent behaviour of the moduli, i.e.  $G' \sim G'' \sim \omega^n$ . (b) Variation of  $\tan \delta$  during cure at 170°C. The lines corresponding to different frequencies intersect at the gel point (220 s), showing that  $\tan \delta$  is independent of frequency at this instant



**Figure 5** Evolution of the storage ( $G'$ ) modulus (at  $\omega = 1 \text{ rad s}^{-1}$ ) during cure at different temperatures. The data were obtained from multiwave experiments conducted at each temperature

gel time can be estimated from curves of  $\tan \delta$  vs time, with each curve corresponding to a different frequency (Figure 4b). The various curves intersect at one point, at which  $\tan \delta$  becomes independent of frequency. The time at which this occurs is the gel time and the value of  $n$  calculated by equation (4) is 0.14.

The Winter criterion thus seems to work remarkably well for our system. As mentioned earlier, this system is significantly different from others for which the sol-gel transition has been investigated in this manner. Most of the systems studied so far have been neat melts; no such study has been undertaken for filled polymers. Due to the high molecular weight of prepolymer and the presence of filler, the initial (pre-cure) slopes of the  $G'$  and  $G''$  lines are not 2 and 1 respectively (Figure 1). Moreover, in earlier studies  $G'$  and  $G''$  both increased with curing time, and the extent of increase was typically several orders of magnitude<sup>15-21</sup>. In contrast,  $G''$  decreases with time in our case, while  $G'$  increases only by a small amount.

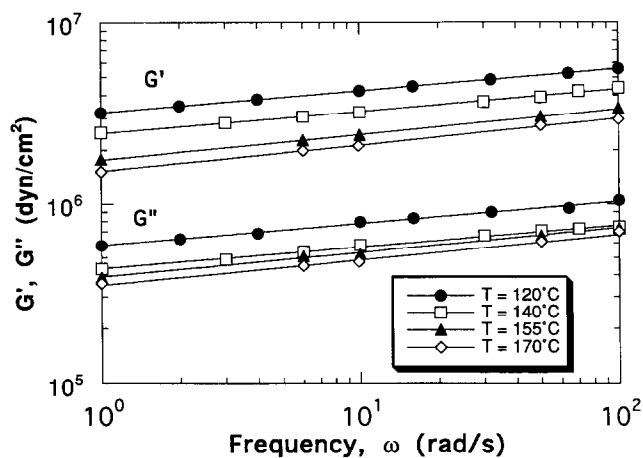
There has been some discussion in the literature regarding the applicability of the winter criterion for the crosslinking of high molecular weight pre-polymers. The power law behaviour at GP extends for time scales  $t > \lambda_0$ , or equivalently, for frequencies,  $\omega < 1/\lambda_0$ , where  $\lambda_0$  is a characteristic relaxation time of the material<sup>7,8,15,17</sup>. Earlier studies by Winter and Chambon identified  $\lambda_0$  as corresponding to the crossover to glass transition<sup>15</sup>. However, de Rosa and Winter<sup>17</sup> recently postulated that  $\lambda_0$  may mark the transition to the entanglement region (rubbery plateau). This implies that the Winter criterion cannot be used for prepolymers whose molecular weight significantly exceeds the entanglement value. The new postulate was invoked because the authors were unable to determine the GP, using the Winter method, for the crosslinking of prepolymers having  $MW_s > 97\,000$ . However, our experimental results seem to negate their argument. In our case, we are able to observe the power-law relationship at the GP over a frequency range of 1–100  $\text{rad s}^{-1}$ , despite the prepolymer molecular weight being well beyond the entanglement value. It is therefore likely that  $\lambda_0$  is related to the glassy limit, as postulated originally by Winter and Chambon<sup>15</sup>.

We have verified the validity of the data obtained using the multiwave technique by comparing it with continuous time sweeps conducted at the same temperature. A time sweep performed at 1  $\text{rad s}^{-1}$  frequency and 0.5% strain (Figure 3) shows excellent overlap with data from the multiwave experiment, corresponding to the same frequency. It should be noted that a single multiwave experiment can be used to generate data for  $G'$  and  $G''$  as a function of time at each of the eight different frequencies probed. We have checked our multiwave data with time sweeps at other frequencies as well.

One of the objectives of this study was to characterize the cure of chlorobutyl rubber at various temperatures. We have used the multiwave technique to follow the isothermal crosslinking of chlorobutyl rubber at several temperatures. Data for the storage modulus ( $G'$ ) as a function of cure time at different temperatures is shown in Figure 5. At higher temperatures crosslinking occurs faster, leading to a reduction in the gel time. The gel time at each temperature was obtained from plots of  $\tan \delta$  similar to Figure 4b and the values are provided in Table 2. The point of gelation has been marked with

**Table 2** Gel times at various temperatures obtained from multiwave experiments

Temperature of cure (°C)	Gel time (s)
120	5470
140	1270
155	420
170	220
185	100

**Figure 6** Frequency spectra at the gel point for crosslinking at different temperatures. The critical exponents,  $n$ , obtained from the slopes are nearly identical (0.12–0.14) in the temperature range of study

a cross on the  $G'$  vs time curves in *Figure 5*, and is observed to occur before the curves change slope. The characteristic time for slope change has been interpreted as the gel time by some researchers<sup>7</sup>. We have found that gelation occurs earlier at all temperatures investigated.

The frequency spectra at the *GP*, for different temperatures, display interesting features (*Figure 6*). The value of the critical exponent,  $n$ , is observed to be approximately the same in each case, varying slightly around 0.14. This indicates that the properties of the critical gel do not depend on the temperature at which the crosslinking is conducted. Thus, within the temperature range of the study, the reaction mechanism is unchanged and the extent of crosslinking,  $p$ , is expected to be the same at all temperatures<sup>19</sup>. The only difference is in the rate of reaction, i.e. the rate of evolution of network structure. The constancy of  $n$  with temperature has also been detected in other studies<sup>15,19</sup>.

*Figure 6* also shows that the values of the dynamic moduli at *GP* ( $G'_c$  and  $G''_c$ ) decrease with increasing temperature, a trend which has also been observed before<sup>19</sup>. The moduli at *GP* depend only on two parameters, the relaxation exponent,  $n$  and the gel strength  $S$ . Since  $n$  is identical over the temperature range, a decrease in  $G'_c$  implies a decrease in  $S$ . It has been shown that  $S$  depends solely on the modulus of the fully crosslinked material ( $G_c$ ) and the zero-shear viscosity ( $\eta_0$ ) of the prepolymer<sup>19</sup>. The decrease in  $S$  is then a consequence of the decrease in the above viscoelastic properties with temperature. Qualitatively,  $S$  reflects the mobility of chain segments at the *GP*, and therefore its decrease with temperature points to an enhanced chain mobility at higher temperatures.

The constancy of  $n$  simplifies the conduction of a study on temperature-dependent gelation of elastomers. The relaxation exponent,  $n$ , needs to be measured only once, for instance by a multiwave experiment. This can be done at a temperature most suited for experimentation, i.e. where the cure does not occur extremely fast. At other temperatures, the gel point can simply be determined by a conventional time sweep performed at a discrete frequency: it is the instant when the ratio  $G''/G'$ , i.e.  $\tan \delta$ , takes on the value  $\tan(\pi/2)$ .

#### Value of $n$ : comparison with literature

The exponent,  $n$ , observed for our system is very low (0.14); most studies have found  $n \geq 0.5$ . Values of  $n$  below 0.2 have been reported in only two studies so far, both of which were on thermoplastic elastomers, where gelation occurred by physical crosslinking<sup>20,21</sup>. However trends in  $n$  found for chemically crosslinking systems can be analysed to understand why the value obtained here is so low. Winter<sup>7</sup> has shown that if  $n > 0.5$ , the *GP* occurs earlier than the  $G'-G''$  crossover point. Conversely, if  $n < 0.5$  the crossover precedes the *GP*. This is consistent with the results for our system, where the polymer molecular weight is very high, and therefore the crossover of  $G'$  and  $G''$  is expected to have occurred before gelation.

The low value of  $n$  found for our system is possibly due to two reasons: the high molecular weight of the prepolymer and the presence of fillers in the system. The effect of molecular weight on gelation has been studied for a few systems, and the results are not conclusive<sup>16–18</sup>. In a study on polybutadienes, which crosslinked through sites along the chain backbone, de Rosa and Winter<sup>17</sup> found that  $n$  did not depend on  $MW$  in the range 18 000–70 000. It should be mentioned that this was the only systematic study conducted on polymers well above the entanglement  $MW$ . However studies on end-linking PDMS as well as end-linking polycaprolactones showed that  $n$  decreased with increasing prepolymer  $MW$ <sup>16,18</sup>. A value as low as 0.3 was found for the highest molecular weight (19 000) polycaprolactone investigated<sup>18</sup>. Scanlan and Winter<sup>16</sup> studied end-linking PDMS of only two molecular weights and obtained a low  $n$  value of 0.2 for the higher  $MW$  of about 125 000.

Since the molecular weight of the prepolymer is extremely high in our case in comparison to previous studies, the low value of  $n$  is not entirely unexpected. Izuka *et al.*<sup>18</sup> mention that a low value of  $n$  implies that the material at *GP* is a mostly elastic body, with the limit of  $G'' = 0$  at  $n = 0$ . This is reasonable in our case, because the initial unvulcanized rubber loses its viscous character as crosslinking proceeds.

A second contributing factor towards the low value of  $n$  could be the presence of filler molecules in the rubber. Reinforcing fillers, such as the silicates used in this case, are expected to provide physical crosslinks in the initial system<sup>22</sup>. This enhances the effective molecular weight of the initial rubber and leads to an initial frequency spectrum dominated by the storage modulus,  $G'$ . The system at *GP* will have physical crosslinks with a finite lifetime, in addition to the permanent chemical crosslinks formed by reacting functional groups. This leads to a denser network with amplified elastic character.

The power law at the *GP* represents the self-similar (fractal) behaviour of clusters at the *GP*<sup>23,24</sup>. This means that if a portion of the crosslinking system at *GP* were

magnified, its essential features would resemble those of the whole sample, however small the original portion might be. The statistical self-similarity of the polymer is quantitatively represented by a fractal dimension,  $d_f$ , which relates the molecular weight  $MW$  of the polymer to its spatial size (such as a radius of gyration),  $R$

$$R^{d_f} \sim MW \quad (8)$$

Theories relate the exponent  $n$ , characterizing the critical gel with the fractal dimension at  $GP$ . Different relations exist, depending on whether or not the excluded volume effects of polymer chains are screened. During the crosslinking of chlorobutyl elastomer, crosslinks are established between long strands of high molecular-weight polymer and the screening of the excluded volume is expected. The equation relating  $n$  to  $d_f$  is then given by<sup>24</sup>:

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \quad (9)$$

For  $n = 0.14$ , we get a value for  $d_f$  of 2.38 in three dimensions ( $d = 3$ ). This is very close to the value for  $d_f$  of 2.50 obtained in the case of complete screening of excluded volume interactions<sup>24</sup>.

#### Activation energy of crosslinking

It has been shown in the literature that an apparent activation energy for the crosslinking reaction can be calculated from a knowledge of the gel time at different temperatures<sup>9,25</sup>. Before the  $GP$ , crosslinking polymerizations are kinetically controlled, and can usually be represented by a single  $n$ th order kinetic expression. Since the network structure is a unique function of conversion, the conversion at the  $GP$  may be considered constant and independent of temperature. This is also corroborated by our rheological data. The kinetic equation can then be integrated in the following manner<sup>9</sup>:

$$dp/dt = k \cdot f(p); \quad k = Ae^{-E/RT} \quad (10)$$

$$\begin{aligned} \ln t_{gel} &= \left\{ \ln \left[ \int_0^{p_{gel}} \frac{dp}{f(p)} \right] - \ln A \right\} + E/RT \\ &= \text{const.} + E/RT \end{aligned} \quad (11)$$

The activation energy,  $E$ , of the cure can be calculated from the slope of a semi-logarithmic plot of the gel time against  $(1/T)$ , as shown in Figure 7. The value for our system is found to be approximately 92 kJ mol<sup>-1</sup> and correlates well with typical values reported for the crosslinking of chlorobutyl rubbers<sup>2</sup>.

#### Evolution of $G'$ during cure

A kinetic model developed by Hsich and co-workers, which has proved to be effective in describing the curing behaviour of filled elastomeric systems<sup>5,6</sup>, was used to describe the evolution of rheological properties in our system. In this model, the changes in mechanical properties, such as the elastic modulus ( $G'$ ), during crosslinking are interpreted in terms of the mean square fluctuations of thermodynamic ordering parameters:

$$\begin{aligned} \frac{G'_\infty - G'(t)}{G'_\infty - G'_0} &= \exp \left[ - \left( \frac{t - t_0}{\tau} \right)^\beta \right] \\ \tau &= \tau_0 \exp(E/RT) \end{aligned} \quad (12)$$

Here,  $\beta$  and  $\tau$  are fitting parameters, with  $\tau$  being interpreted as a characteristic relaxation time associated with the chemical reaction<sup>5</sup>. The induction time,  $t_0$  was negligible for all temperatures. We have used this model to fit our data, and a typical fit at 155°C is shown in Figure 8. As mentioned earlier, the multiwave experiment simultaneously provides time sweep data at eight different frequencies. For modelling purposes, a frequency of 1 rad s<sup>-1</sup> was chosen. We find excellent agreement between experimental data and model predictions in Figure 8, indicating the validity of the model.

Crosslinking data at various temperatures were fitted using the Hsich model and the values of the parameters,  $\tau$  and  $\beta$  were obtained (Table 3). The relaxation time,  $\tau$ , varies with temperature in a manner similar to the Arrhenius scaling of the gel time<sup>5</sup>. A semi-logarithmic plot of  $\tau$ , against  $1/T$  was constructed, to calculate the apparent activation energy,  $E$  of the crosslinking reaction. We find  $E$  in this case to be 97 kJ mol<sup>-1</sup>, which is in good agreement with the value obtained from gel time data.

The effect of different crosslinking temperatures on end-use properties of elastomeric systems is of particular interest with regard to their applications. This can be studied by measuring the shear modulus of the fully crosslinked network, under identical conditions. Izuka

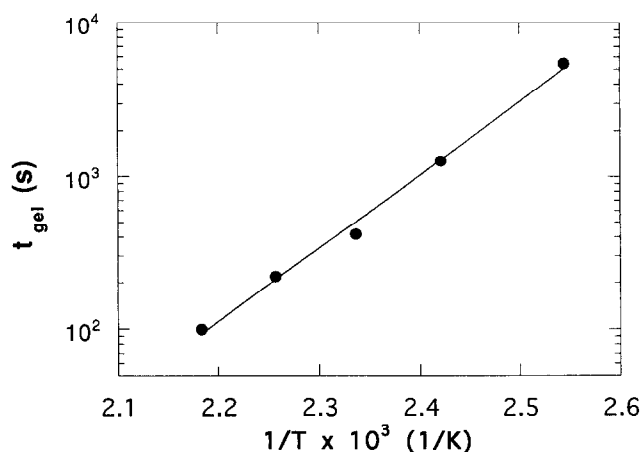


Figure 7 Semi-logarithmic plot of gel time versus  $(1/T)$  where the temperature  $T$  is expressed in Kelvin. The slope of the line is equal to  $(E/R)$  where  $E$  is the activation energy of the crosslinking reaction and  $R$  is the universal gas constant

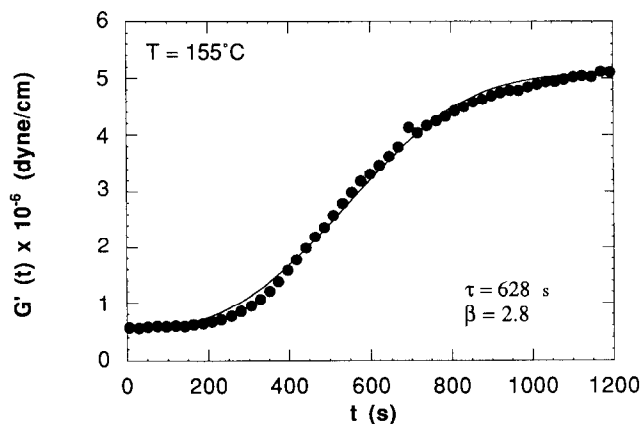


Figure 8 Data for the storage modulus ( $G'$ ) as a function of time, fitted to an empirical model due to Hsich<sup>5</sup>. The plot shown corresponds to crosslinking conducted at 155°C for which the model parameters were determined to be  $\tau = 628$  s and  $\beta = 2.8$ , as indicated

**Table 3** Values of parameters ( $\tau$ ,  $\beta$ ) in the Hsich model for cure at various temperatures

Temperature of cure (°C)	$\tau$ (s)	$\beta$
120	8345	2.3
140	1835	2.5
155	628	2.8
170	317	2.9
185	117	2.5

*et al.*<sup>19</sup> determined the value of the complex shear modulus,  $G^*$  after cure and found a negligible dependence of  $G^*$  on temperature of cure, within the range investigated. The same trend was observed in our system also, with the value of  $G^*$  for the cured samples being  $\sim 4.5 \times 10^6 \text{ dyn cm}^{-2}$ , irrespective of the cure temperature. It can be concluded that, in the temperature range of our study, the mechanical properties of the cured polymer are not affected by the temperature of the curing reaction. This means that the processing of the rubbers can be carried out rapidly at a fairly high temperature, to reduce overall cycle time in manufacture.

The above results are also consistent with the assertions of Martin and Adolf<sup>26</sup>. They declare that the nature of the critical gel largely dictates the properties of the fully cured network. The shear modulus of the ultimate network is intimately related to the reaction path, which occurs by a process of aggregation till gel point, when the infinite network is formed, and then onwards by network extension. Structures formed at the *GP* are not completely absent in the final gel, and hence play a role in determining the value of the ultimate modulus. It is possible that as long as the value of  $n$  remains independent of temperature, the properties of the fully crosslinked material will remain the same.

## CONCLUSIONS

The multiple-waveform rheological technique was found to be effective for studying the crosslinking of filled rubbers. Conventional techniques that monitor rheological properties during cure are limited to measurements of dynamic moduli at one particular frequency. The multi-wave method can be used to generate frequency spectra at various times during cure, and thus provides information on evolving microstructures. The *GP* can be obtained by using the Winter criterion, and a relaxation exponent,  $n$ , can be determined from the frequency spectrum at the gel point. This study is the first demonstration of the applicability of the above criterion for filled elastomeric materials. In contrast to earlier studies, the loss modulus,  $G''$  in the present case, decreased continuously with cure time.

The value of  $n$  for this system was found to be fairly low at  $\sim 0.14$ . The low value of  $n$  could be due to a combination of two factors: the high molecular weight of the prepolymer, and the presence of reinforcing filler. Cure occurred faster at a higher temperature, and the gel time decreased. The exponent  $n$  remained unchanged with temperature indicating that the same reaction (gelation) mechanism was operating over the temperature range of study. The level of moduli at gelation decreased with temperature, and this implies a decrease in the gel strength,  $S$ , at the *GP*. A model proposed by Hsich *et al.* to describe the evolution of  $G'$  with time, was successfully fitted to our data. This model was used to determine a characteristic relaxation time at each curing temperature, and an apparent activation energy of the crosslinking reaction. This activation energy ( $97 \text{ kJ mol}^{-1}$ ) was found to be consistent with the value of  $92 \text{ kJ mol}^{-1}$  calculated directly from gel time measurements at different temperatures.

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