

# Dielectric behaviour and sulphur vulcanization of the crosslinked butyl (XL-50) rubber

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Dielectric losses of XL-50 vulcanizates were measured at four different frequencies, viz. 500 Hz, 1.0 kHz, 5.0 kHz and 10.0 kHz. The influence of curing temperature (140°, 150° and 160°C) and curing time were also investigated. The cure characteristics were studied with the help of a Monsanto rheometer at 150°, 160° and 170°C. There exists a close relation between the dielectric losses and the state of cure of the sulphur vulcanization. Maximum dielectric loss has been observed at the optimum cure time. Dielectric loss decreases as the curing temperature decreases. Low frequency of measurement is always accompanied by high dielectric loss. Rheometric results have been correlated with the dielectric measurements.

**Keywords** Dielectric loss; crosslinked butyl; cure characteristics; frequency; activation energy; vulcanization

## INTRODUCTION

Dielectric analysis is a technique that has been frequently used to study various aspects of polymerization. Recently this technique has been extended to investigate the vulcanization of a polar elastomer<sup>1</sup>.

The present study deals with the sulphur vulcanization of the XL-50 variety of crosslinked butyls<sup>2</sup> and the determination of dielectric losses over a wide range of frequency during the course of vulcanization. The effect of curing temperature on the dielectric losses at different frequencies have also been measured.

Cure characteristics of the sulphur vulcanization have been determined at different curing temperatures with the help of a Monsanto rheometer (R-100).

Efforts have been made to correlate the above studies with the help of activation energy determinations.

## EXPERIMENTAL

The polymer was compounded in a two roll laboratory (size 13 inch × 6 inch) mixing mill using the formulation (in phr): XL-50, 100.0; ZnO, 5.0; stearic acid, 2.0; sulphur, 2.0; MBT, 0.5; TMTD, 1.0. The compound was cured at 140°, 150° and 160°C for various times (10, 20, 30, 50 and 70 min). Dielectric constant and loss measurements were carried out using a Universal Bridge B-224 (Wyne Kerr, USA) fitted with a specially designed sample holder. This machine operates with an accuracy of about ±0.01%. Measurements were taken with both empty sample holder and the sample holder fitted with the vulcanizate. All measurements have been conducted at four different frequencies. Cure characteristics were determined from the rheographs at different temperatures.

## RESULTS AND DISCUSSION

### *Variation of the dielectric losses with cure time at different frequencies*

The dielectric losses measured at four different frequencies, viz. 500 Hz, 1.0 kHz, 5.0 kHz and 10.0 kHz, and three curing temperatures are shown as a function of curing time in *Figures 1, 2 and 3*. It is observed that the loss factor increases with increase in cure time, attains a maximum value and then decreases at all frequencies of measurement. However, the losses are very high at lower frequency, i.e. 500 Hz, and minimum losses are observed at high frequency, say 10.0 kHz. As the frequency of measurement decreases, the dielectric loss increases.

The results show that the peak values of dielectric losses occur at a particular time irrespective of frequencies of measurement for a particular curing temperature, i.e. varies with the curing temperature but independent of frequency of measurement. The figures show that the maximum loss value is observed at 30 min cure time at 160°C and at 45 min and 55 min cure times at 150°C and 140°C cure temperature respectively.

### *Variation of dielectric losses with curing temperatures*

*Figures 4, 5, 6 and 7* show the dielectric loss factor with cure time and temperature at 500 Hz, 1.0 kHz, 5.0 kHz and 10.0 kHz respectively. The figures reveal that at a particular frequency of measurement the rate of increase in loss factor increases with increase in curing temperature. The highest loss value has been observed at higher curing temperature. The maximum value in the loss factor shifts towards lower curing time as the temperature of cure increases.

At low curing temperature the variation of loss factor

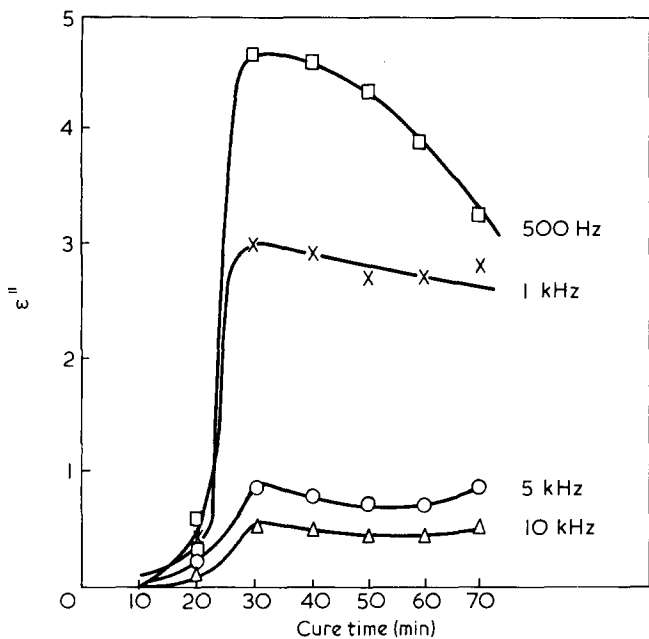


Figure 1 Variation of dielectric loss factor with curing time at 160°C

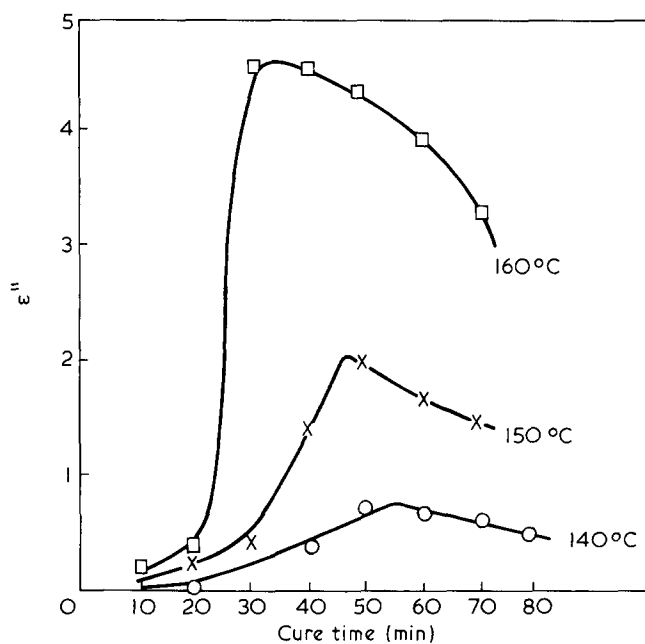


Figure 4 Variation of dielectric loss factor with curing time measured at 500 Hz

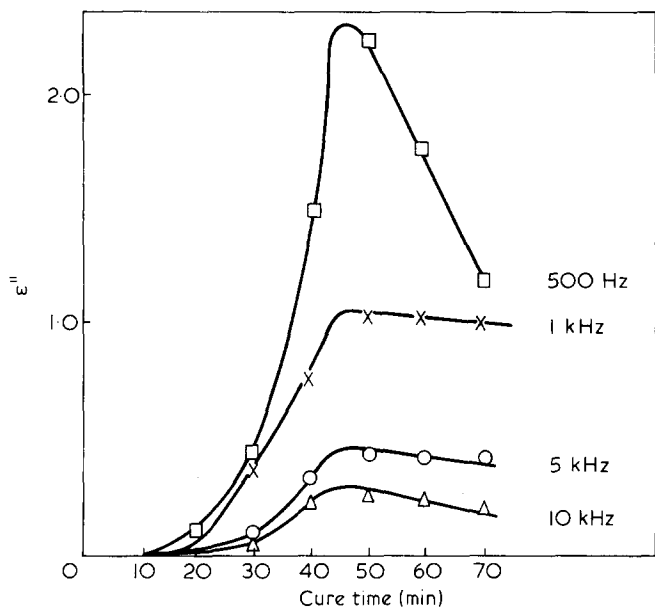


Figure 2 Variation of dielectric loss factor with curing time at 150°C

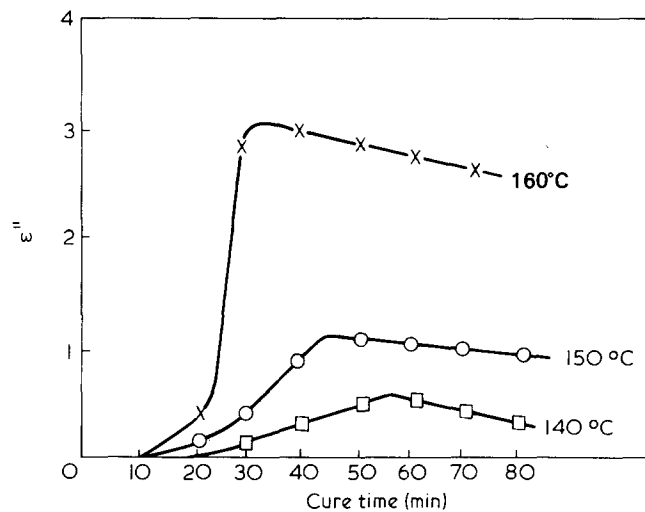


Figure 5 Variation of dielectric loss factor with curing time measured at 1 kHz

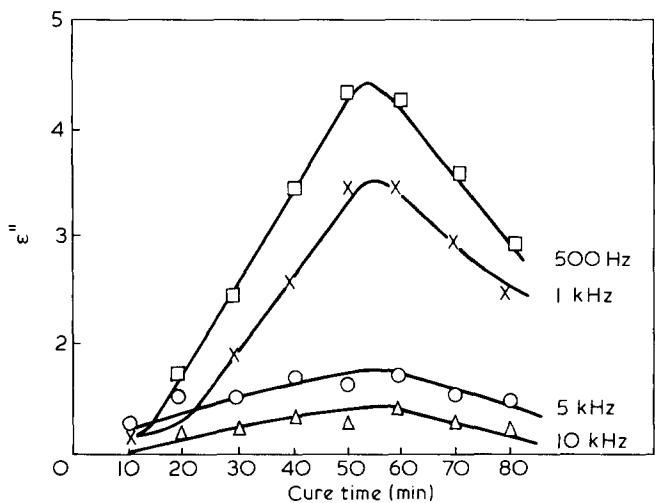


Figure 3 Variation of dielectric loss factor with curing time at 140°C

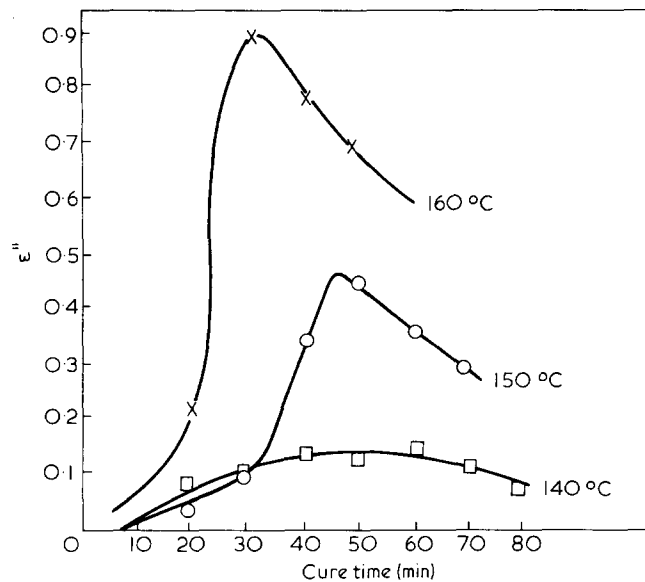


Figure 6 Variation of dielectric loss factor with curing time measured at 5 kHz

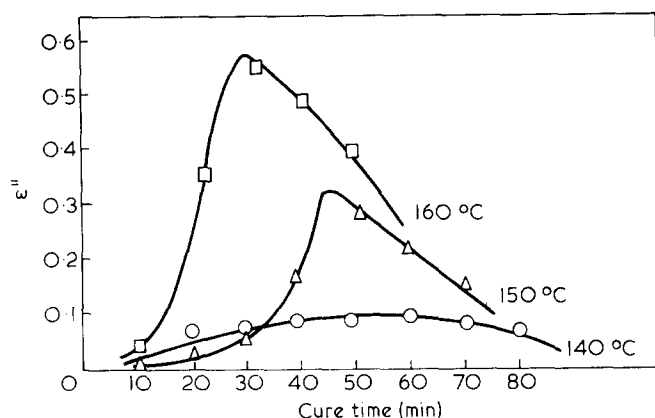


Figure 7 Variation of dielectric loss factor with curing time measured at 10 kHz

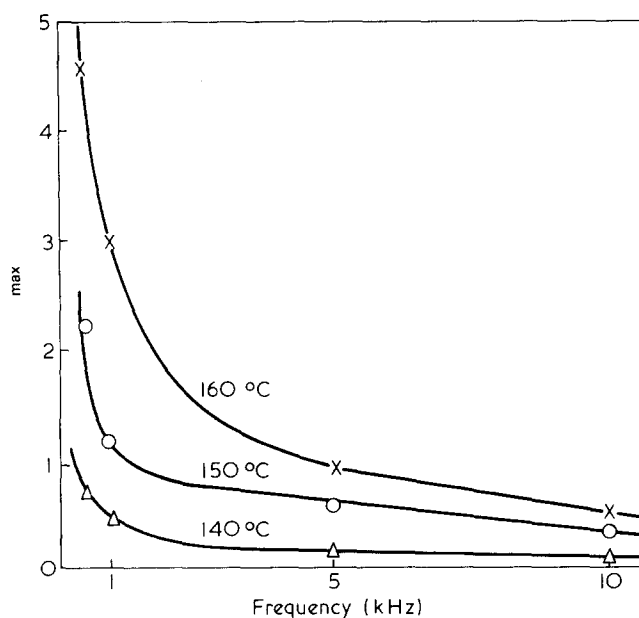


Figure 8 Variation of maximum dielectric loss factor with frequency at different temperatures

with curing times is not so well pronounced. A very sharp peak is observed at high curing temperature, viz. 160°C, when measured at high frequency. However, a comparatively sharp peak is observed at low temperature of cure when measured at lower frequency, viz. 500 Hz (Figures 4 and 7).

A sharp reversion in the loss factor above the maximum value was observed with increase in the temperature of curing at higher frequency of measurement (i.e. at 5.0 kHz and 10.0 kHz). At 500 Hz and 1.0 kHz frequency the rate of reversion is less. The rate of reversion at lower curing temperatures and at higher frequencies of measurement are not so well marked as at lower frequencies of measurement.

The peak value of the loss factor appears at the same curing time for all frequencies of measurement, but shifts towards lower curing time as the temperature of cure increases.

#### Variation of dielectric loss factor with frequency

The maximum dielectric loss values ( $\epsilon''_{\max}$ ) at different temperatures and at different frequencies of measurement calculated from the previous graphs and plotted against

the frequency (Figure 8) reveals that  $\epsilon''_{\max}$  decreases sharply with increase in frequency and finally levels off at very high frequency, particularly when the curing temperature is low (140°C). At higher curing temperature (160°C),  $\epsilon''_{\max}$  decreases continuously with increase in frequency. This rate of decrease in  $\epsilon''_{\max}$  is very high up to 3 kHz frequency and beyond 3 kHz it decreases at a much slower rate. This decreasing rate of  $\epsilon''_{\max}$  with frequency is very much more pronounced at higher cure temperature (viz. 160°C). At lower curing temperature (140°C) the frequency has no effect on  $\epsilon''_{\max}$  especially at higher frequencies.

At all frequencies the higher curing temperature gives rise to higher  $\epsilon''_{\max}$  values. However, this difference in  $\epsilon''_{\max}$  values with curing temperature narrows as the frequency increases. Large differences in  $\epsilon''_{\max}$  values with curing temperature have been observed in the lower frequency region. In the high-frequency region the difference in  $\epsilon''_{\max}$  values with curing temperature is not as well pronounced.

#### Rheometric study

The cure characteristics of the sample determined at 150°, 160° and 170°C (Figure 9) show that both scorch time and optimum cure times decrease with increase in cure temperature. The rate of cure also increases with increase in temperature. The state of cure increases with increase in cure times at a particular temperature, attains a maximum and then gradually decreases. This rate of reversion after the maximum cure increases with increase in temperature of cure. The optimum cure times at three different temperatures are shown in Table 1.

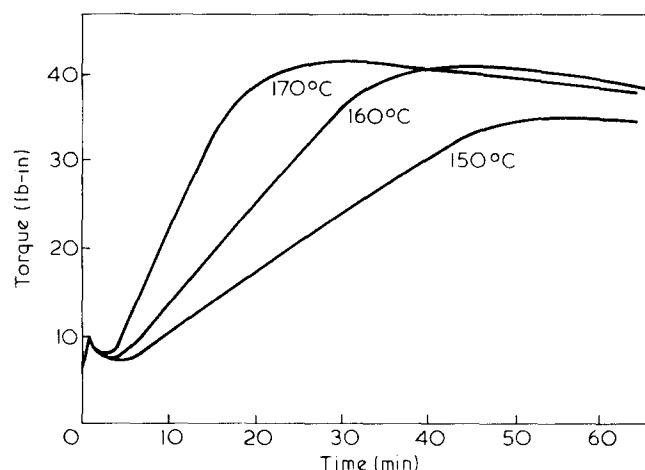


Figure 9 Rheometric study at 150°, 160° and 170°C

Table 1 Determination of activation energy

	Curing temperature (°C)				Activa- tion energy, $E$ (kcal mol <sup>-1</sup> )
	140	150	160	170	
$t_{90}$ (min) (from rheometric study)	—	43.5	30.5	17.5	16.3
$t'_{\epsilon''_{\max}}$ (min) (from dielectric study)	55.0	45.0	30.0	—	

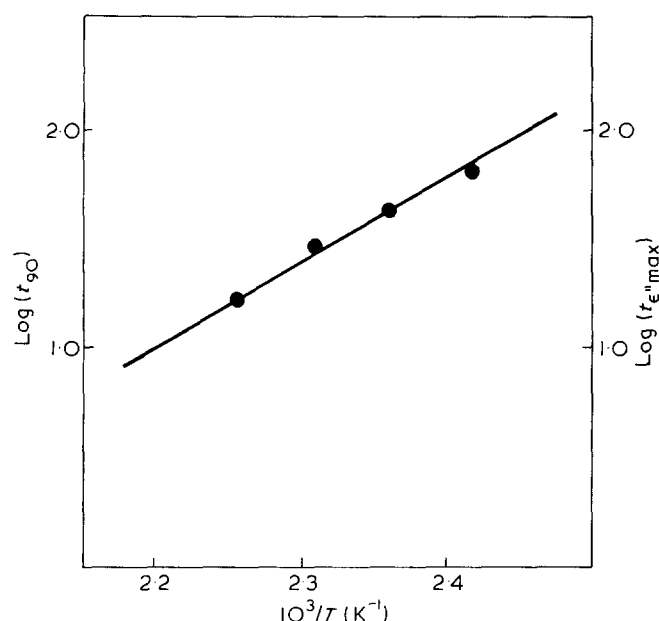


Figure 10 Determination of activation energy from rheometric and dielectric studies

Figures 4–7 and 9 suggest that there is a close relation between the state of cure and the dielectric loss. The dielectric loss as observed is due to the sulphur dipole formed during vulcanization. As the vulcanization proceeds the loss factor increases initially due to the combination of sulphur with the macromolecular chains. The sulphur which is combined with polymer during vulcanization forms two types of compounds<sup>3,4</sup>: (a) some of the sulphur forms sulphidic crosslinks and determines the elastic properties, but only a part of the combined sulphur can be accounted for in this way; (b) the remaining sulphur is combined in the form of heterocyclic groups arranged randomly among the rubber chains. The dielectric losses are mostly due to sulphur which has been combined in the form other than crosslinks. Dipolar crosslinks contribute little to the polarization of the rubber because of restricted mobility.

Dielectric loss factor changes arising from changes in the state of cure and the point where the change in loss factor with time of vulcanization reverses more or less correspond to the optimum cure time (Figure 9) as observed from Table 1. After the optimum cure time, the state of cure increases slowly up to the maximum and then reversion takes place depending on the temperature of cure. However, the loss factor starts decreasing after the optimum cure time. It may be that after the optimum cure time the dipolar combined sulphur, which was contributing to the losses, is transforming to the crosslinks up to the maximum cure. Reversion is the

combined effect of crosslink scission and slow crosslink formation, and hence from the decreased loss factor during the reversion period it may be assumed that the transformation of –S chains to –S ring occurs<sup>5</sup>. High losses at high temperature of cure may be attributed to vulcanization heterogeneity and may be quite pronounced at low frequency. At high frequency, although there are differences between the losses at different temperature of cure, these differences are not so well marked as observe at low frequency.

#### Activation energy

The activation energies determined from the rheometric study and dielectric measurement are shown in Table 1. The activation energy from the rheometric data has been calculated from the change of optimum cure time ( $t_{90}$  min) with curing temperature (Figure 10) as described earlier<sup>6</sup>.

In the case of dielectric measurements, the maximum portions of the dielectric loss curves have been considered<sup>1</sup> and the corresponding times have been taken as equivalent times. The activation energies have been calculated, at different frequencies, from the change of equivalent times with curing temperature (Figure 10).

The activation energies as calculated from the above two studies are found to be more or less the same, suggesting that the dielectric measurements can be utilized to determine the cure characteristics of the vulcanizates.

#### CONCLUSION

The dielectric behaviour of the sulphur vulcanization of the crosslinked butyl (XL-50) changes with the change in the state of cure, the curing temperature and the frequency of measurement. At the optimum cure time the dielectric loss is a maximum. High temperature of curing was always accompanied by high loss; however, this is more pronounced at low than at high frequency of measurement. In the high-frequency range, the power loss is less than at low frequency.

The dielectric measurements may be used to gain more insight into the vulcanization process and can be compared with the rheometric studies in order to evaluate the cure characteristics.

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