Temperature Coefficient of Vulcanization and Equivalent Cures for SBR Hard Rubber Polyblends

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Synopsis

The temperature coefficient of vulcanization for SBR hard rubber polyblends has been determined to be approximately 2.0 for 10°C. intervals of temperature. Higher percentages of sulfur give faster rates of cure and higher glass transition temperatures. T_i at 10^9 provides a convenient index to the degree of vulcanization of the mixtures. The response of hard rubber polyblends to variations in time and temperature of vulcanization and to changes in the proportion of sulfur in the recipe are similar to those found for conventional rubber recipes. Vulcanization parameters for hard rubber polyblends may therefore be estimated according to procedures found valid for non-polyblend hard rubber mixtures.

Background

The temperature span in which sulfur-vulcanized hard rubber polyblends maintain a level of modulus intermediate between glassy and rubbery behavior has been found to extend from the glass transition temperature of the rubbery component up to the glass transition temperature of the resinous component.[1] Because the glass transition temperature of the hard rubber depends upon the degree of vulcanization of the mixture, changes in the degree of vulcanization of hard rubber polyblends will produce corresponding changes in the length of the temperature interval in which the modulus remains at the intermediate level characteristic of the polyblend.[2] Sulfur content, time of vulcanization, and temperature of vulcanization are therefore important parameters which exert determining effects on the mechanical properties of the vulcanized mixture.

Experimental

Hard rubber polyblends were prepared by adding 4 phr of butyraldehyde–amine accelerator (du Pont Accelerator No. 808) to SBR 1000 and then adding sulfur to the accelerator mixture to obtain a hard rubber recipe containing 22% sulfur by weight. Butyl 365 (registered trade name for Enjay Chemical Co. isobutylene–isoprene copolymer containing 2.0–2.5 or mole-% unsaturation), 30 parts, was then blended with 70 parts of the hard rubber recipe and vulcanized to obtain polyblends which,

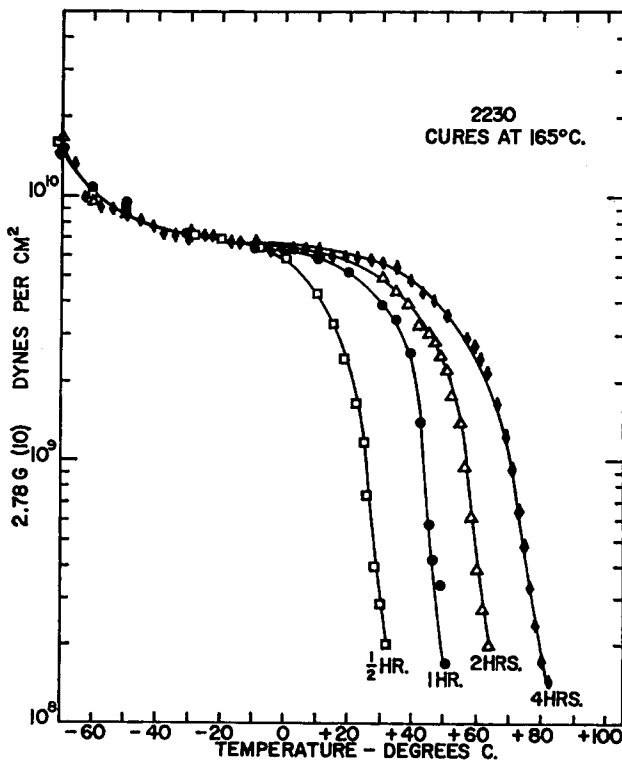* Present address: I. I. T. Research Institute, Chicago, Ill.

Fig. 1. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365, showing increase of T_g and T_i with degree of vulcanization at 165°C.

although all made from the same recipe, differed in mechanical properties due to differences in the degree to which each was vulcanized. Another series of polyblends was made from a hard rubber recipe containing 34% sulfur by weight but otherwise prepared as described above. Shear modulus[3] measurements were used to provide an index to the degree of vulcanization obtained with these mixtures for several time intervals at curing temperatures between 165 and 200°C.

Observations

The progressive increase in T_g which is produced as the degree of vulcanization of a hard rubber polyblend is increased is shown in Figure 1. Because of the gradual inception of transition as temperature increases, it is difficult to set an exact value for the glass transition temperature of this material at any one of the degrees of cure shown. The intercept temperature, T_i at which $2.78G(10) = 10^9$ dynes/cm.², can be determined precisely and thus provides a convenient means of comparing specimens for degree of cure. It is thus possible to follow the increase of T_i with time of cure as in Figure 1: $T_i = 24$ at $^1/_2$ hr., 43 at 1 hr., 55 at 2 hr., 70 at 4 hr. It is also possible to compare different curing conditions for equiv-
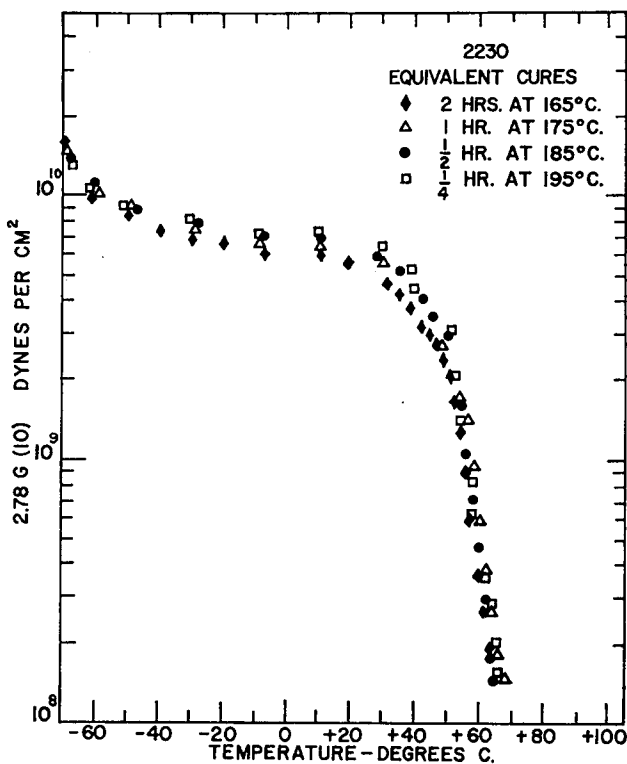
Fig. 2. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365 showing coincidence of modulus temperature curves at equivalent cures.

alence of cure as in Figure 2: $T_i = 55$ for 2 hr. at 165°C., 54 for 1 hr. at 175°C., 56 for $\frac{1}{2}$ hr. at 185°C., and 57 for $\frac{1}{4}$ hr. at 195°C. Full cures, as in Figure 3, are seen to give a better matching of modulus for even increments of time and temperature than do the partial cures shown in Figure 4.

Figure 5 shows the increase in degree of vulcanization with temperature of cure at constant time. Figure 6 shows the relationship of T_i to time of cure at 200°C. similar to that noted in Figure 1 for cures at 165°C.

In Figure 7 we see that T_i (and therefore degree of vulcanization) increases linearly as a log function of time for each of the temperatures within the range investigated. In Figure 8 we plot the corresponding relationship of T_i to temperature of vulcanization. The linear portions of the curves shown give good correspondence to the empirical equation:

$$\Delta t/\Delta T = 2^{-0.1n} \tag{1}$$

where ΔT is the difference in vulcanization temperature in degrees Centigrade and n is a number expressed in the same units as used to indicate the difference in time, Δt. Departures from linearity at short times, par-
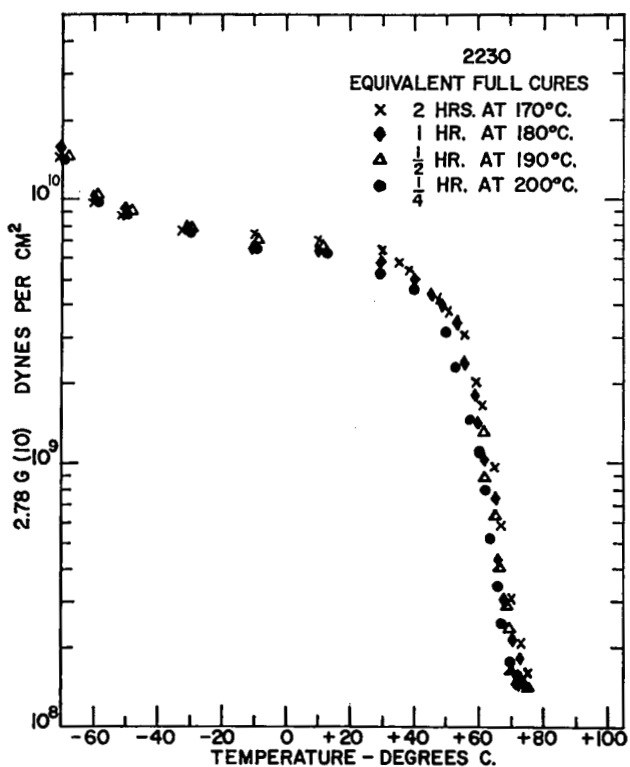
Fig. 3. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365 showing coincidence of modulus temperature curves at full cure.
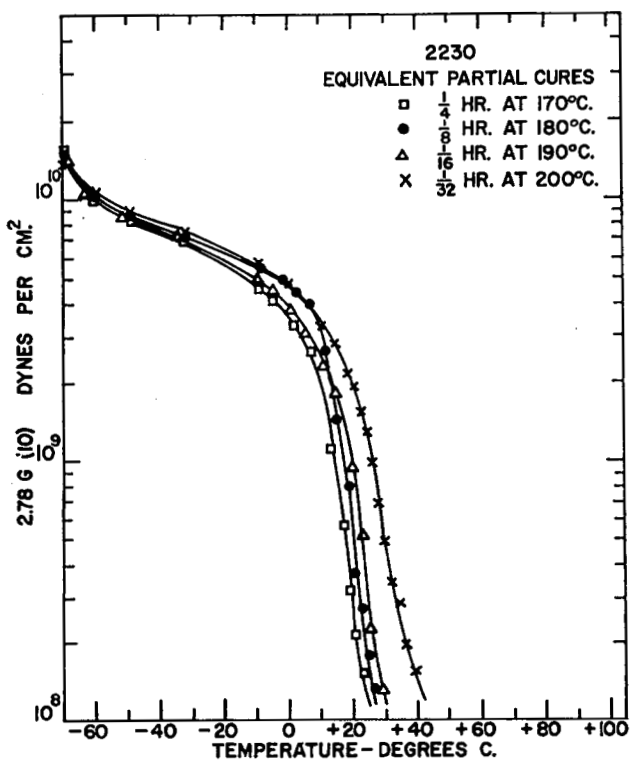

Fig. 4. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365 showing coincidence of modulus temperature curves at equivalent partial cures.
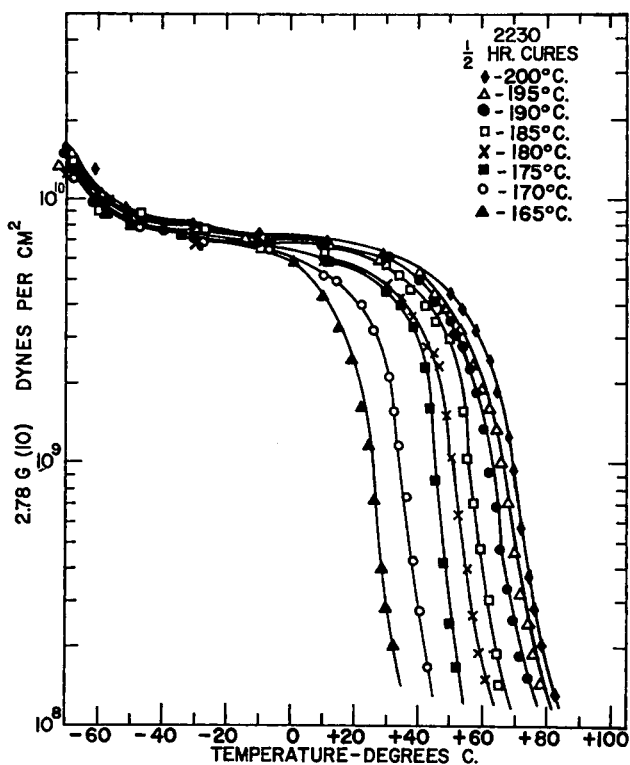
Fig. 5. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365 showing increase in degree of vulcanization with temperature of cure at constant time.
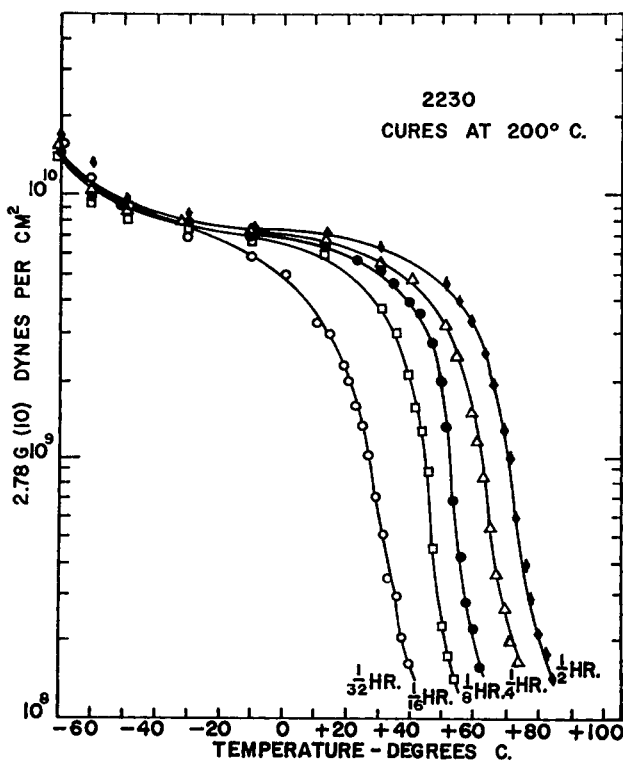

Fig. 6. 22% Sulfur hard rubber polyblend containing 30 wt.-% of Butyl 365 showing increase of T_g and T_i with degree of vulcanization at 200°C.
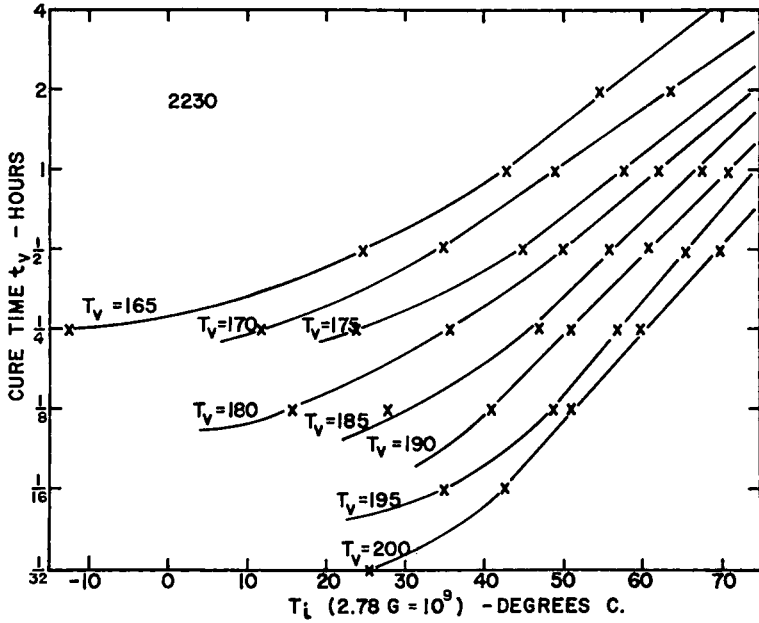
Fig. 7. Increase of T_i with time of vulcanization at constant temperatures in the range 165–200°C.
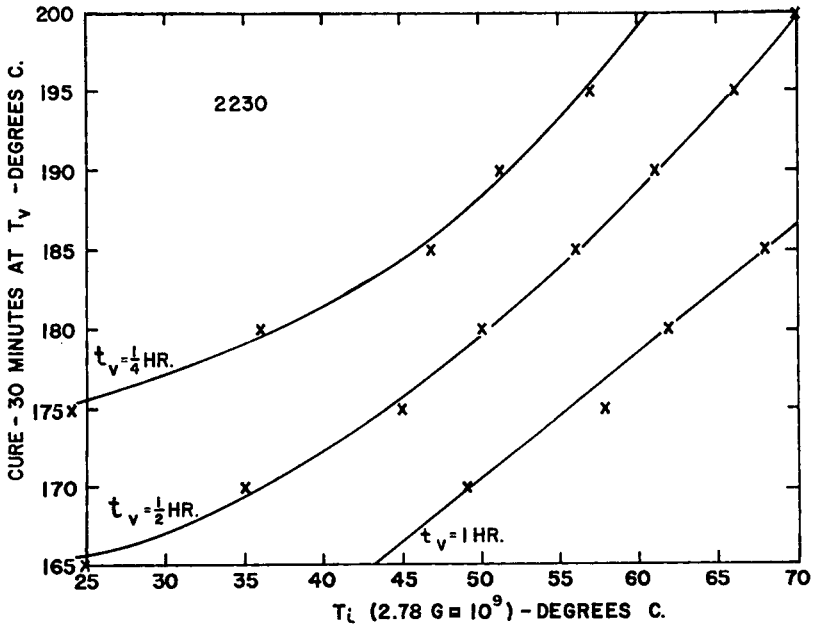

Fig. 8. Increase of T_i with temperature of vulcanization at three intervals of constant time.
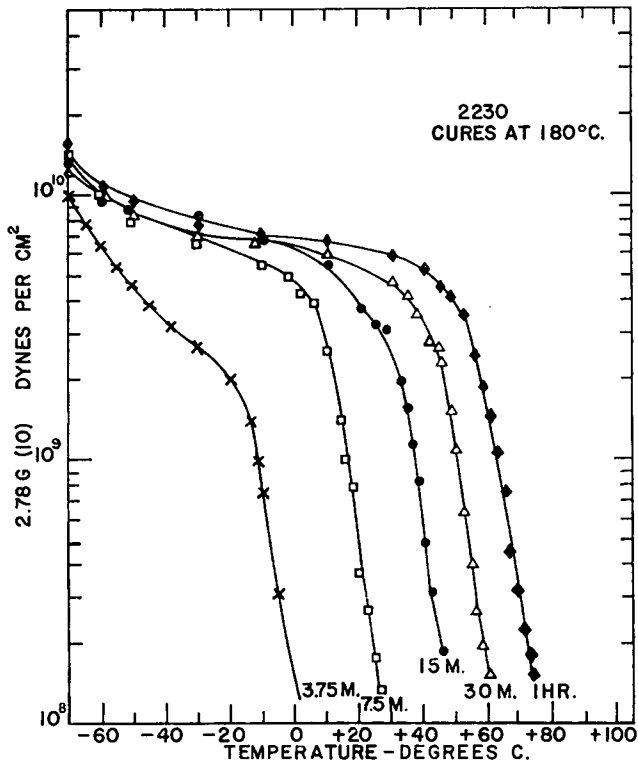
Fig. 9. Increase of T_g and T_i with degree of vulcanization for a low sulfur hard rubber polyblend vulcanized at 180°C.
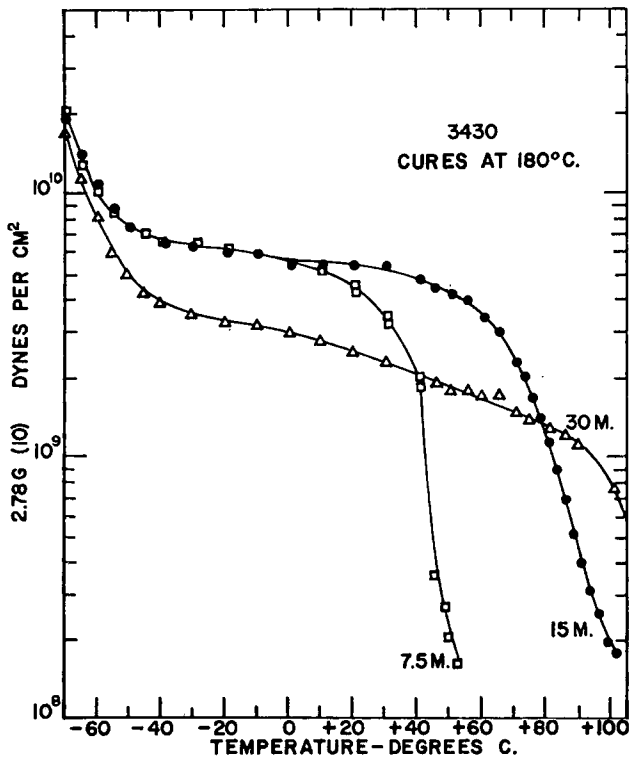

Fig. 10. Increase of T_g and T_i with degree of vulcanization for a high sulfur hard rubber polyblend vulcanized at 180°C.

ticularly at higher temperatures, are easily explainable on the basis of energy required to raise the specimens to vulcanizing temperature.

Figures 9 and 10 compare polyblends of low and high sulfur level at corresponding intervals of cure. The powerful accelerating effect of the additional sulfur in the high sulfur mixture is clearly evident, as is the complicating effect of reversion as evidenced by the 30-min. cure of the high sulfur material as shown in Figure 10

Conclusions

The response of hard rubber polyblends to variations in time and temperature of vulcanization is sufficiently similar to that found for conventional rubber recipes[4-6] to warrant the conclusion that the temperature coefficient of vulcanization for the polyblend is the same as that of the hard rubber portion of the mixture. The effects of increases in the sulfur content of the recipe are the same as noted previously[7] for SBR hard rubbers. Vulcanization parameters for hard rubber polyblends may therefore be estimated according to procedures found valid for nonpolyblend hard rubber mixtures.

References

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Résumé

On a déterminé le coefficient de température de vulcanisation de mélanges de caoutchoucs durs SBR; il est égal à 2.0 pour 10°C. d'intervalle de température. Des concentrations plus élenées en soufre donnent des vitesses de transformation plus grandes et des températures de transition vitreuse plus élevées. T_i à 10^9 fournit un indice utile pour le degré de vulcanisation des mélanges. Les réponse des échantillons vis-à-vis des variations du temps et des températures de vulcanisation et en regard des variations de proportion de soufre, sont similaires à celle trouvée dans les traitements de caoutchouc conventionnel. Les paramètres de vulcanisation pour des mélanges de caoutchouc dur peuvent, de ce fait, être estimés conformément à des procédés valides pour des mélanges non-traités de caoutchouc dur.

Zusammenfassung

Der Temperaturkoeffizient für die Vulkanisation von SBR-Hartgummipolymermischungen wurde zu etwa 2,0 für 10°C Temperaturintervall bestimmt. Ein höherer Schwefelgehalt liefert eine höhere Vulkanisationsgeschwindigkeit und eine höhere

Glasumwandlungstemperatur. T_i bei 10^9 ergibt einen brauchbaren Index für den Vulkanisationsgrad der Mischung. Das Verhalten von Hartgummipolymermischungen bei Änderungen von Vulkanisationsdauer und -temperatur und des Schwefelanteils im Rezept sind denjenigen bei konventionellen Kautschukrezepten ähnlich. Die Vulkanisationsparameter für Hartgummipolymerischungen können daher nach den bei Kautschukmischungen mit einem Polymeren anwendbaren Verfahren bestimmt werden.