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# INFLUENCE OF TEMPERATURE ON COMPRESSION SET OF NR VULCANIZATES

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Compression set (CS) of natural rubber vulcanizates was measured under different conditions. The temperature regime ranged from –30 to 70°C. The effects of cure system, filler, plasticizer and antioxidant on CS were also evaluated. At lower temperatures, peroxide-cured natural rubber showed higher CS than the conventionally cured rubber. Fillers, naphthenic oil and the antioxidant PBNA increased CS at all the temperatures studied.

*Key words* :- Natural rubber, Compression set, Cure system, Filler, Plasticizer, Antioxidant.

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## INTRODUCTION

Set is a measure of recovery of a rubber specimen after removal of an applied stress or strain and that which occurs on compression is called compression set (CS). This is an important parameter influencing performance of seals, gaskets, and mountings made from rubbers and has been extensively studied. Jahn (1965) studied CS behaviour of some synthetic elastomers in comparison with that of natural rubber (NR). Baldwin (1970) developed a simplified model for CS and compared the results of high temperature CS of ethylene-propylene terpolymer (EPDM) rubber with the model. Improved CS resistance of a fluoro elastomer was reported by Moran and Pattison (1971). In most of these studies the test method employed was ASTM D 395, method B, with appropriate modifications. The test involves compression of a disc by 25 per cent of its thickness for a fixed time at a fixed temperature, followed by release at test temperature recovery for 30 min at room temperature and measurement of final thickness. The advantages and disadvantages of this test method were described by Turner and Loraine (1972). Although the test provides for measurement of set at any desired temperature, in the literature one normally finds CS data only at 20°C, 70°C and 100°C. However, for a proper evaluation of the set behaviour, a vulcanizate has to be tested over a wider range of temperature. For practical performance, CS both at low and at high temperatures will be of special interest. It is also quite likely that the ranking of rubber vulcanizates based on CS measured at a particular temperature may not hold good at another. In this context the extensive study by Jahn and Bertram (1973) on the CS behaviour of nitrile rubber over a wide range of temperature and the influence of compounding variables on set under such conditions, assumes importance. Although natural rubber is used in many engineering applications, data on CS behaviour at different temperatures are meagre. In the present investigation this aspect has been taken into account and CS of NR vulcanizates over the range of temperature from –30°C to 70°C has been studied. The influence of compounding variables like cure system, filler, plasticizer and antioxidant on CS under such conditions has also been included in the study. One set of SBR vulcanizates has been studied for comparison.

## EXPERIMENTAL

### Materials

Natural rubber used for the study was ISNR 5 (light colour) and all the other compounding ingredients were of commercial grade. Reagent grade benzene was used for estimation of volume fraction of rubber ($V_r$).

### Compounding variables

The formulations of the unfilled compounds with three different cure systems for NR and SBR are given in Table 1. The effects of the following parameters were studied:

(a) Cure system
(b) Type and quantity of filler
(c) Process oil
(d) Antioxidant PBNA

For studying the effects of fillers, process oil and antioxidant, appropriate quantities of the ingredients were added to the formulation. The compounds were prepared on a 15 x 30 cm size laboratory model two-roll mill at a friction ratio of 1:1.25. Optimum cure times were determined using a Monsanto rheometer R-100 at 150°C. Vulcanization to optimum cure was carried out in a 45 x 45 cm hydraulic press, having steam heated platens, at a pressure of 45 kg/cm$^2$ on the mould. Test buttons of 12.5 ± 0.5 mm thickness and 29.0 ± 0.5 mm diameter were moulded. Five minutes extra time over the optimum cure was provided. The test buttons were conditioned for 24 h at 30 ± 2°C and 60 ± 5 per cent relative humidity.

Table 1. **Formulations of unfilled compounds for NR and SBR**

| Ingredients | Conventional | | EV | | Peroxide | |
|---|---|---|---|---|---|---|
| | A | B | C | D | E | F |
| Natural rubber | 100.00 | — | 100.00 | — | 100.00 | — |
| SBR 1502 | — | 100.00 | — | 100.00 | — | 100.00 |
| Stearic acid | 2.00 | 2.00 | 2.00 | 2.00 | | — |
| Zinc oxide | 4.00 | 4.00 | 4.00 | 4.00 | — | — |
| N-cyclohexyl-2-benzothiazole-sulphenamide | 0.60 | 1.00 | 2.00 | 2.00 | — | — |
| Tetramethyl-thiuramdisulphide | — | — | 1.50 | 1.50 | — | — |
| Sulphur | 2.50 | 2.00 | 0.50 | 0.30 | — | — |
| Dicumyl peroxide (40% active) | — | — | — | — | 4.25 | 4.25 |
| Optimum cure time, $t_{90}$ at 150°C, min. | 12.5 | 40.0 | 14.0 | 13.0 | 42.0 | 37.5 |

### Compression set measurements

Measurements were made following ASTM D 395, method B. The period of compression was 22 h in all cases. However, to study the effect of prolonged application of load in the case of the unfilled vulcanizates the period was changed as 96 h. Measurements were made at -30, -20, -5, 10, 30 and 70°C. Load was released at the test temperature and the specimens allowed to recover at room temperature (30 ± 2°C) for 30 min, before the final thickness of the specimens was measured. However, in the case of tests below room temperature, recovery was carried out at the test temperature itself.

### Determination of $V_r$

Measurements of $V_r$ were made from equilibrium swelling following the method suggested by Ellis and Welding (1964) and the change in network structure of the vulcanizates for the three cure systems before and after compression was studied.

## RESULTS AND DISCUSSION

### Effect of cure system

The most important factor influencing CS of NR is the type of cure system. Three different types of systems - a conventional sulphur vulcanizing system (CV), an efficient vulcanizing system (EV) and a peroxide system using dicumyl peroxide - were employed in the present study. The physical characteristics of the three types of vulcanizates are presented in Table 2. Compression set of vulcanizates prepared from all the three compounds and tested at different temperatures is presented in Fig. 1a. At 70°C, the conventional vulcanizates exhibited maximum CS, while the peroxide vulcanizate gave the minimum set, the EV sample being in between. It is well known that among the three systems studied, the conventional system gives the least stable network and the peroxide system the most stable one. According to the model developed by Baldwin (1970) a stable network should give rise to minimum CS at an elevated temperature and the present results are in agreement with this. The results of $V_r$ measurements (Table 3) further confirm this. While $V_r$ increases appreciably in the case of conventional vulcanizate as a result of compression at 70°C, the change in $V_r$ is only marginal in the case of the peroxide vulcanizate, the EV vulcanizate being in between.

Table 2. **Physical properties of NR gum vulcanizates**

| Parameters | Conventional | EV | Peroxide |
|---|---|---|---|
| Modulus 300% (MPa) | 2.07 | 2.30 | 1.52 |
| Elongation at break (%) | 1140.00 | 789.00 | 705.00 |
| Tensile strength (MPa) | 23.20 | 14.10 | 11.00 |
| Tear strength (kN/m) | 26.40 | 24.20 | 17.50 |

Table 3. **Vr of gum vulcanizates before and after compression**

| Cure system | $V_r$ Before compression | $V_r$ After compression at 70°C for 22 h | $V_r$ After compression at -30°C for 22 h |
|---|---|---|---|
| Conventional | 0.1837 | 0.2006 | 0.1806 |
| EV | 0.1930 | 0.2014 | 0.1980 |
| Peroxide | 0.1657 | 0.1620 | 0.1672 |

As the test temperature is lowered, the differences among CS values of the three vulcanizates decrease and at about 20°C all the three vulcanizates exhibit more or less the same CS. However, below this temperature, the observations are contrary to those obtained above 20°C, the peroxide vulcanizate showing maximum set and the conventional vulcanizate the minimum. The trend continues as the temperature is further lowered and at -30°C, the observations are almost the reverse of those obtained at 70°C, as indicated by the bowl shaped curves of Fig. 1(a). It is to be pointed out here that the factors contributing to CS are different in the two temperature regimes. At temperatures above 20°C, the stability of the network is the most important factor influencing set, while at lower temperatures and especially at sub-zero level CS is influenced more by low temperature crystallization (Stevenson, 1986 and Gent, 1955). The fact that set at sub-zero temperatures is not contributed by changes in the network structure is further confirmed by the results of $V_r$ measurements (Table 3). After compression at -30°C, the changes in $V_r$ are only marginal. When the samples were held under compression for a longer period of 96 h, an identical trend was observed, although the absolute values of CS were higher both at high and at low temperatures, as shown in Fig. 1(b). The differences among the CS values of the three vulcanizates were also found higher at the extremes of the temperature range studied, as compared to those of the samples tested for a shorter period of 22 h.

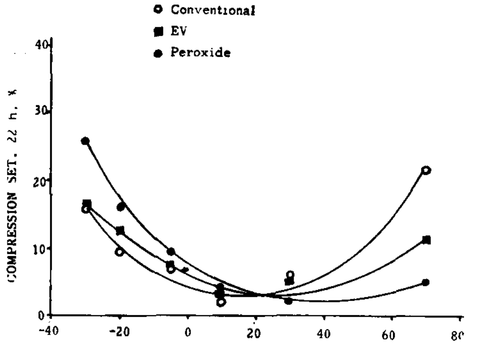

Fig. 1(a). Effect of curing system and temperature on CS of NR vulcanizates for 22 h.

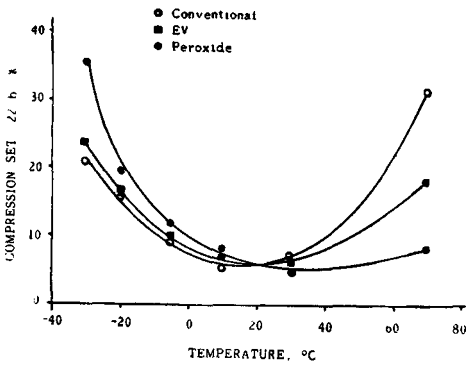

Fig. 1(b). Effect of curing system and temperature on CS of NR vulcanizates for 96 h.

When NR is exposed to sub-zero temperatures for long periods, crystallites are formed within the amorphous matrix and grow in a manner that depends both on strain (Stevenson, 1986) and temperature (Gent, 1955). When rubber is held at a fixed strain, crystallization is accompanied by a progressive relaxation of stress. It is already established that in sulphur vulcanization of natural rubber, main chain modifications also take place along with crosslinking (Crowther *et al.*, 1988). These modifications delay the process of crystallization and the extent of delay is proportional to the degree of main chain modification.

The fact that CS at low temperature is influenced more by crystallization is further supported by measuring CS of a non-crystallizing rubber like SBR, cured with the three different curing systems, at different temperatures. The results are depicted in Fig. 2. Here also at 70°C trend more or less comparable to that in the case of NR was noted, the peroxide vulcanizate exhibiting a minimum CS and the conventional sulphur vulcanizate giving the highest CS. Although the differences among the samples narrowed down as the temperature was lowered, the trend was not reversed at sub-zero temperatures as was observed in the case of NR.

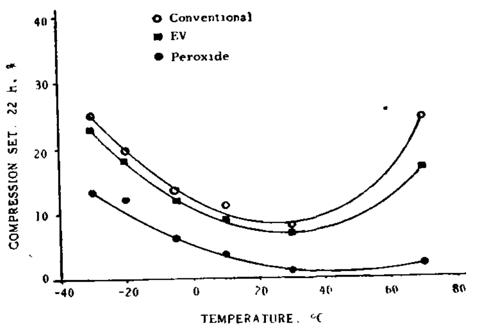

Fig. 2. Effect of curing systems and temperature on CS of SBR vulcanizates for 22 h.

## Effect of fillers

As most of the rubber products contain fillers, the effect of three different types of fillers (carbon black, precipitated silica and china clay) on CS behaviour was studied in the same temperature range and using the three cure systems.

## Effect of carbon black

The effects of temperature and cure system on CS of 50 phr HAF black-loaded vulcanizates are shown in Fig. 3. The observations are similar to those made in the case of the unfilled vulcanizates. However the absolute values of CS are higher. Here also the ranking of the vulcanizates based on CS values obtained at 70°C is reversed at temperatures below 20°C. The influence of crystallization on CS is evident from the results. The superiority of the conventional sulphur vulcanizates over the efficiently vulcanized sample with respect to CS is further confirmed by these results. While designing rubber compounds for low CS at 20°C or below, this aspect has to be considered. However at temperatures above 30°C, the superiority of EV and peroxide vulcanizates remains unchanged.

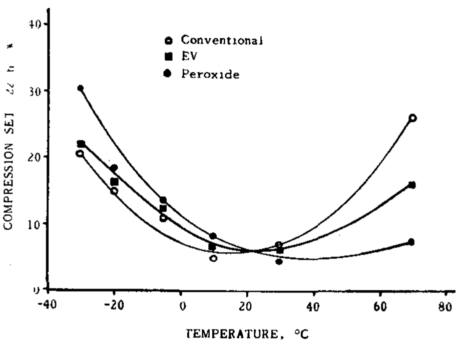

Fig. 3. Effect of curing systems and temperature on CS of 50 phr HAF-filled NR vulcanizates

The effect of different levels of loading of carbon black on CS, in the conventional system of curing, at different temperatures is depicted in Fig. 4. Similar bowl shaped curves are obtained at all the loadings studied. As expected CS is found to increase progressively as the loading is increased.

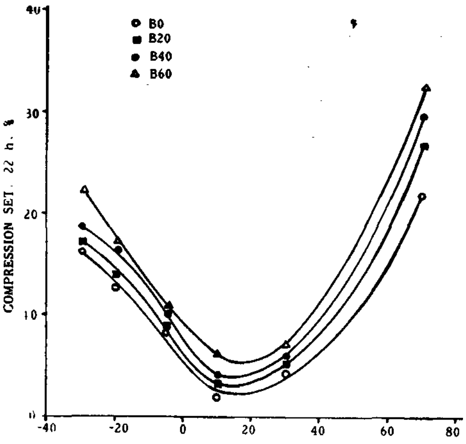

Fig 4. Effect of of HAF and temperature on CS

## Effects of China clay and precipitated silica

Similar to the effect of carbon black, the effects of china clay and precipitated silica on the CS of NR vulcanizates prepared using the three types of cure systems were also determined after loading 50 phr each of the fillers and the results are given in Figs. 5 and 6 respectively. The observations are similar to those made in the case of carbon black, the absolute values being different. In the case of precipitated silica, the CS values are found to be higher than the corresponding black or clay filled vulcanizates. This is probably due to the lower state of cure resulting from the adsorption of curatives by the filler (Pal and De, 1982).

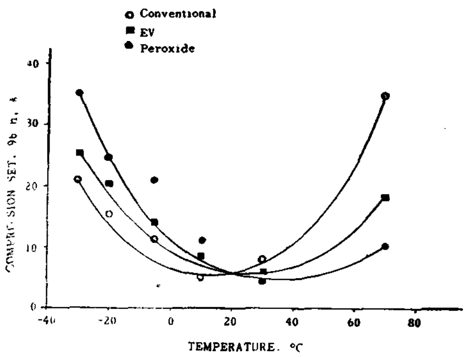

Fig. 5. Effect of curing system and temperature on CS of 50 phr china clay-filled NR vulcanizates

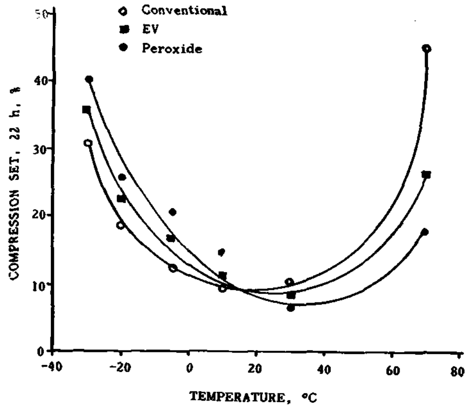

Fig. 6. Effect of curing system and temperature on CS of 50 phr precipitated silica-filled NR vulcanizates

The effects of different levels of loading in the case of china clay and precipitated silica are shown in Figs. 7 and 8 respectively. Here also only the conventional cure system was used. The results are similar to those observed in the case of carbon black.

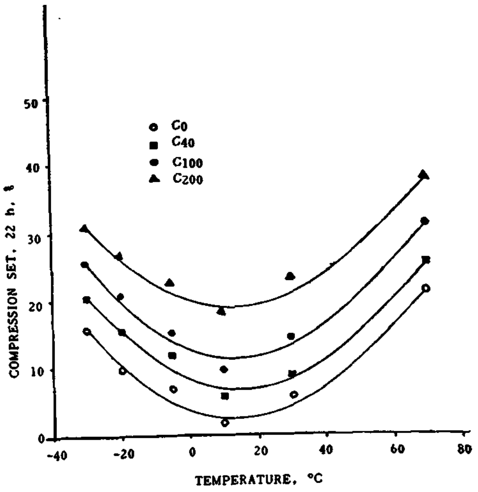

Fig. 7. Effect of china clay and temperature on CS

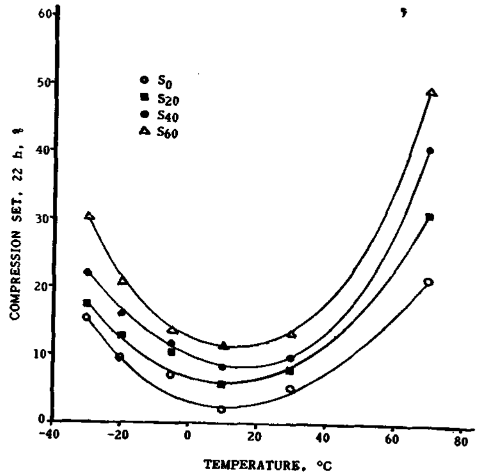

Fig. 8. Effect of precipitated silica and temperature on CS

## Effect of process oil

As process oils are invariably added in most of the filled rubber compounds, its effect on CS was also assessed at different temperatures. Naphthenic oil at 20 phr was added to a compound containing 50 phr of HAF black and the CS of these vulcanizates was compared with that of a similar compound containing no oil. The results are shown in Fig.9. Compression set is found to be higher in the case of the compound containing oil and this has been observed throughout the temperature range. At sub-zero temperatures, addition of process oils need not necessarily be helpful in resisting crystallization (Stevenson, 1988 and Fogg and Swift, 1962). It is probable that at 20 phr, naphthenic oil is incapable of influencing the rate of low temperature crystallization. Therefore the increase in CS caused by the presence of the oil in the high temperature region is observed in the low temperature region as well.

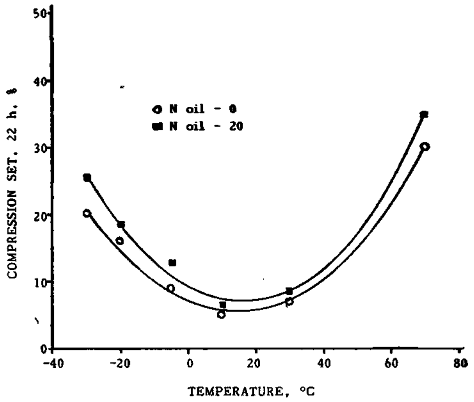

Fig. 9. Effect of naphthenic oil and temperature on CS

## Effect of antioxidant

The effects of adding 1 phr of phenyl-$\beta$-naphthylamine (PBNA) to the unfilled and HAF black-filled conventional vulcanizates are presented in Fig. 10. In both cases CS is found to increase and this has been observed throughout the temperature range. Nando and De (1980) and Mathew *et al* (1982) also reported similar observations, at 70°C. It is probable that addition of PBNA favours formation of a higher extent of polysulphidic type of crosslinks giving rise to a higher set.

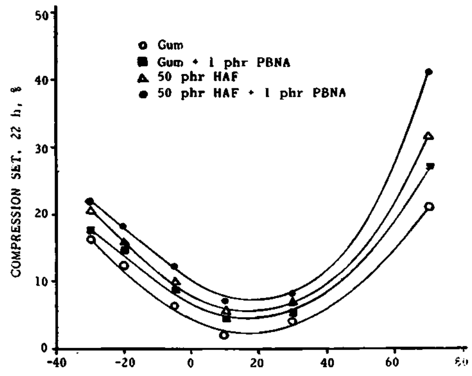

Fig. 10. Effect of antioxidant PBNA and temperature on CS of NR gum and HAF-filled vulcanizates

The $(CS)_{t, \min}$ (temperature at which CS is minimum) is found to be influenced by cure system and found to be 10°C for the conventional and EV systems and 30°C for the peroxide system. The value of minimum CS for vulcanizates containing different cure systems, types of fillers and their loadings, naphthenic process oil and antioxidant PBNA are also given in Table 4. Plots of CS vs filler loadings for three different fillers at different temperatures are given in Figs. 11, 12 and 13. Empirical relations

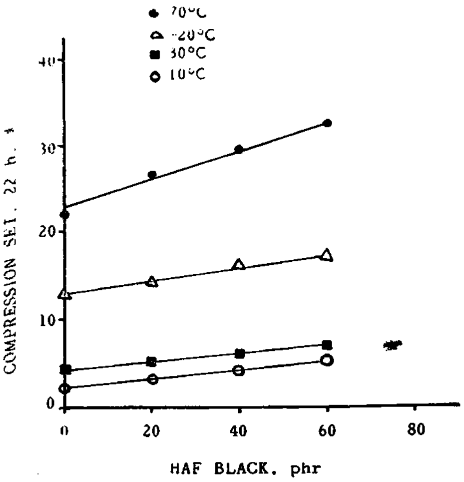

Fig. 11. Relationship between CS and HAF loading at different temperatures

Table 4. **$(CS)_{t,\ min}$ for different fillers and cure systems**

| System | $(CS)_{t,\ min}$ | Temperature, °C |
|---|---|---|
| **Conventional** | | |
| *HAF black* | | |
| $B_0$ | 2.1 | 10 |
| $B_{20}$ | 3.2 | 10 |
| $B_{40}$ | 4.3 | 10 |
| $B_{50}$ | 5.5 | 10 |
| $B_{60}$ | 6.0 | 10 |
| *China clay* | | |
| $C_0$ | 2.1 | 10 |
| $C_{40}$ | 5.5 | 10 |
| $C_{50}$ | 6.0 | 10 |
| $C_{100}$ | 9.8 | 10 |
| $C_{200}$ | 18.2 | 10 |
| *Precipitated silica* | | |
| $S_0$ | 2.1 | 10 |
| $S_{20}$ | 6.5 | 10 |
| $S_{40}$ | 9.8 | 10 |
| $S_{50}$ | 10.2 | 10 |
| $S_{60}$ | 14.0 | 10 |
| *Naphthenic oil* | | |
| $N_0$ | 5.0 | 10 |
| $N_{20}$ | 6.7 | 10 |
| *Antioxidant PBNA* | | |
| Gum + 1 phr PBNA | 4.5 | 10 |
| 50 phr HAF + 1 phr PBNA | 7.0 | 10 |
| **EV** | | |
| Gum | 3.4 | 10 |
| HAF, 50 phr | 6.8 | 30 |
| Clay, 50 phr | 6.5 | 30 |
| Silica, 50 phr | 8.0 | 30 |
| **Peroxide** | | |
| Gum | 2.1 | 30 |
| HAF, 50 phr | 5.0 | 30 |
| Clay, 50 phr | 4.8 | 30 |
| Silica, 50 phr | 6.7 | 30 |

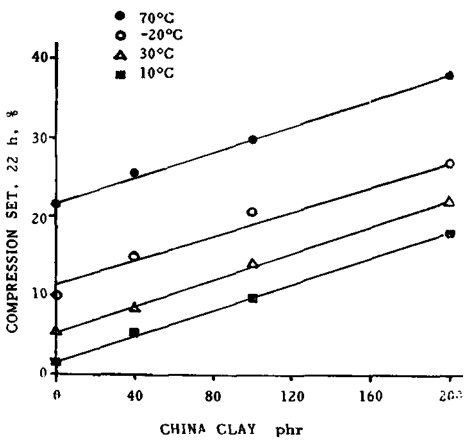

Fig. 12. Relationship between CS and china clay loading at different temperatures

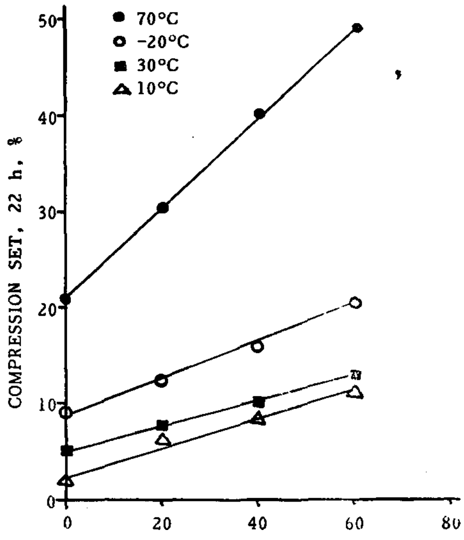

Fig. 13. Relationship between CS and precipitated silica loading at different temperatures

derived from the straight lines obtained are given in Table 5. Using these equations it is possible to predict CS at these four different temperatures and at any filler loading.

Table 5. **Empirical relations for compression set**

| Filler | Temperature, °C | CS |
|---|---|---|
| HAF black | 70 | 0.16x + 23.5 |
| ,, | 30 | 0.05x + 4 |
| ,, | 10 | 0.05x + 2 |
| ,, | -20 | 0.07x + 13 |
| China clay | 70 | 0.08x + 21.5 |
| ,, | 30 | 0.09x + 5.5 |
| ,, | 10 | 0.08x + 2 |
| ,, | -20 | 0.08x + 12 |
| Precipitated silica | 70 | 0.45x + 21 |
| ,, | 30 | 0.15x + 5 |
| ,, | 10 | 0.14x + 2 |
| ,, | -20 | 0.21x + 8.5 |

x = Corresponding filler loading, in phr

## CONCLUSIONS

The major factors contributing to compression set at elevated temperatures are those involving changes in network structure while at sub-zero temperatures CS is contributed mostly by low temperature crystallization. A stable network obtained through the use of peroxide will be advantageous at elevated temperature while a conventional sulphur cure could be better at sub-zero temperatures in applications where low CS is important. Although CS is increased by the presence of fillers like carbon black, precipitated silica and china clay, the superiority of the conventional system at sub-zero temperatures is still maintained. Naphthenic oil and antioxidant PBNA are found to increase CS throughout the temperature range studied.

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