

## Measurement of Brittleness Temperature of Neoprene by Proton Magnetic Resonance: Effect of Plasticizers

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### Synopsis

Proton magnetic resonance (PMR) line widths,  $\delta H$ , have been determined as a function of temperature for a number of neoprene (polychloroprene) samples. The measurements were made on raw neoprenes (type W, WRT, and GNA) and on neoprenes with plasticizers in both the unvulcanized and vulcanized states. An excellent correlation of the temperature of line narrowing with brittleness temperature found by mechanical tests is reported. The results indicate that PMR may be of value in studying plasticizer properties and in measuring glass temperatures in a manner dependent only on molecular motions rather than on the nature of a mechanical test or on sample statistics.

### Introduction

It is well known among polymer scientists that the addition of a plasticizer in compounding may affect the glass temperature  $T_g$  (and the associated stiffness temperature  $T_s$  and brittleness temperature  $T_b$ ) to a sizeable degree. Standard measurements of these quantities involve certain mechanical, thermodynamic or optical quantities. In general  $T_s > T_b > T_g$ .  $T_s$  and  $T_b$  are often used as a measure of  $T_g$ . In determining  $T_b$ , it is usually necessary to make mechanical measurements on a number of different samples. The need for a method which is independent of sample statistics and the nature of the mechanical test is apparent.

With this end in mind, proton magnetic resonance (PMR) measurements as a function of temperature were made on several samples of neoprene (polychloroprene) which is based on the monomer  $\text{CH}_2=\text{C Cl}-\text{CH}=\text{CH}_2$ .

### Samples and Experimental Methods

The samples were: (a) raw du Pont neoprenes GNA, W, and WRT in both a "heat-treated" and "cold-treated" state; (b) unvulcanized plasticized GNA neoprene; and (c) vulcanized plasticized GNA neoprenes.

The raw heat-treated samples were held at 70°C. for 30 min. in order to minimize crystallinity.<sup>1</sup> The cold-treated samples were held at about -10°C. in a refrigerator for 1-2 months, in order to maximize crystallinity.<sup>1</sup>

Three different plasticizers were used in the present experiments. These were: 10 parts of an aromatic hydrocarbon oil (Sundex 53) per 100 parts GNA, 10 parts dibutyl sebacate  $[(\text{CH}_2)_4\text{COOC}_4\text{H}_9]_2$  (designated DBS) per

100 parts GNA, and 10 parts di-2-ethylhexyl phthalate  $C_8H_4(COOC_8H_{17})_2$  (designated DEHP) per 100 parts GNA. The vulcanized samples contained 5 parts ZnO and 4 parts MgO as vulcanizing agents. Both unvulcanized and vulcanized samples were given the heat and cold treatments described above.

The PMR measurements, made at 40 Mcycles/sec. in a Varian dual-purpose NMR spectrometer, consisted of determinations of line width  $\delta H$  between absorption mode derivative extrema as a function of temperature. For the most part measurements were taken at progressively lower temperatures starting from room temperature and above.

### Results and Discussion

The results of measurements on the raw, heat-treated neoprenes are shown in Figure 1, where line width is plotted versus temperature. Also shown is the work of Kusumoto<sup>2</sup> on neoprene W. Although a discrepancy in magnitude between our work and that of Kusumoto exists, the temperature dependences of the two sets of data agree fairly well. The slightly lower values of line width for type WRT may be associated with a slightly more open structure of this type neoprene.

Two regions of line narrowing are seen in Figure 1. Kusumoto made no suggestions concerning the nature of the motions which produce the two line-narrowing regions. However, it is likely that the higher-temperature

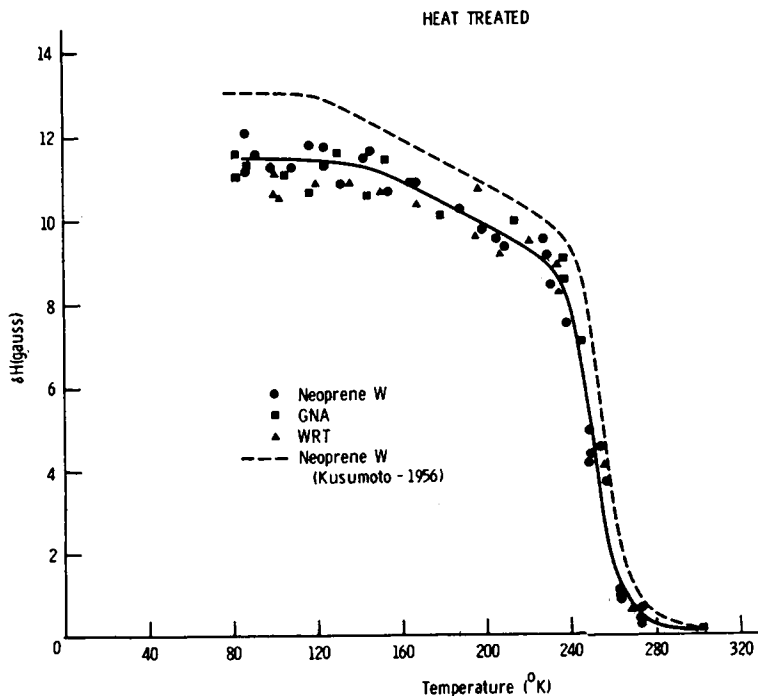


Fig. 1. Line width vs. temperature for heat-treated raw neoprenes.

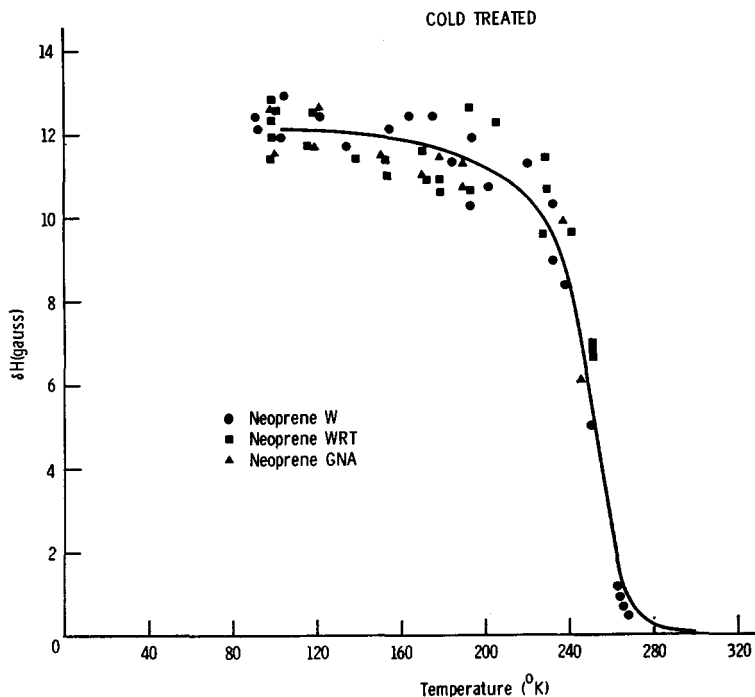


Fig. 2. Line width vs. temperature for cold-treated raw neoprenes.

region, like that of polyisoprene,<sup>3</sup> is associated with segmental motions related to the glass transition. (Gutowsky et al.,<sup>4</sup> who did the original work on isoprenes, associated the line narrowing with sample crystallinity, but Slichter,<sup>3</sup> in his interpretation, indicates that the line narrowing is not associated with crystallite melting.)

Inasmuch as neoprene contains no methyl groups, one cannot associate the lower-temperature line narrowing with methyl rotation. However, perhaps it is related to side chain motion or to motions in the amorphous portion of the neoprene. Indeed, in the raw samples which were cold-treated to increase crystallinity, the low-temperature line-narrowing transition appears to be gone (Fig. 2). This conclusion seems to be valid in spite of the sizeable experimental scatter in this temperature region.

In the heat-treated samples there was little evidence for the weak narrow component seen by Kusumoto.<sup>2</sup> Kusumoto ascribed this component to the presence of the monomer. It may be that in our samples, the amount of monomer may be lower than in the sample of Kusumoto. Signal-to-noise considerations also may have obscured the weaker narrow component. A weak narrow line was seen in one of the cold-treated raw samples (WRT), but this may have been due to a small quantity of moisture picked up in the refrigerator.

In the samples containing plasticizers two-line components were seen at high enough temperatures. Weak shoulders on the main central resonance

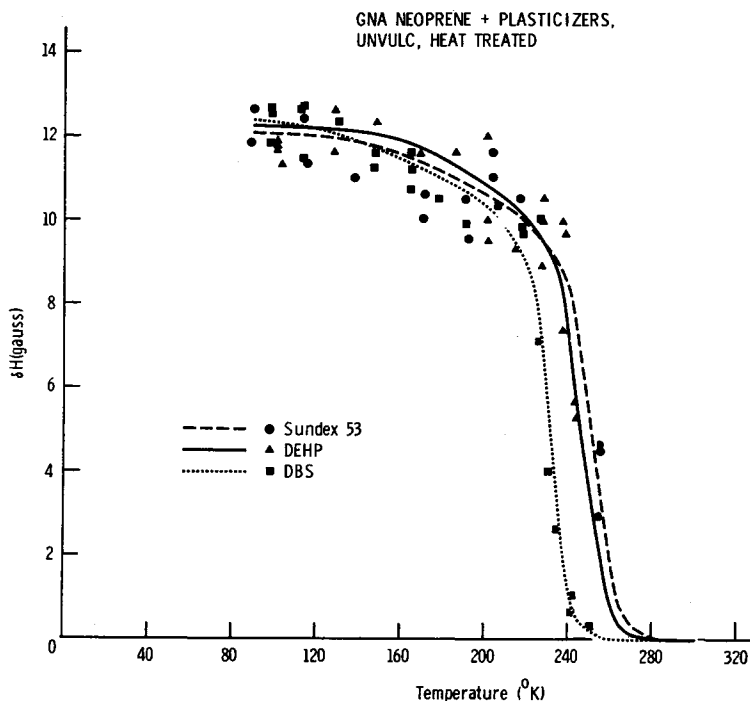


Fig. 3. Line width vs. temperature for heat-treated, unvulcanized, plasticized GNA neoprenes.

were visible at high enough temperatures. These shoulders were weakest in the unvulcanized heat treated samples. Perhaps the shoulders were due to crosslinking and crystallinity in the samples. When the lines were very narrow at high temperature, a chemical shift between the two components was apparent. The narrower line appeared to be at a somewhat higher field than the broad one. At lower temperatures the shoulders essentially vanished, usually by the time the line had broadened to a width of about 6-7 gauss (about one-half the magnitude at lowest temperatures). The shoulders were so weak in intensity that in our line width curves for plasticized samples only the narrow line widths are plotted. From these plots we obtain the temperature  $T_6$  at which  $\delta H = 6$  gauss, which we associate with the glass transition. In some samples, particularly the cold-treated plasticized ones, the presence of two-line components increased the uncertainty in the temperature. However, by using a value of  $\delta H = 6$  gauss, the amount of interference of the two-line components is made reasonably small. The use of the narrow component alone in a correlation with the glass transition is suitable, since it was done consistently for all samples. In addition, the broad component vanishes at low enough temperatures rendering it unsuitable for such correlations. At high temperature the broad component shows the same qualitative dependence on plasticizer as the narrow component. This fact further justifies our choice of method.

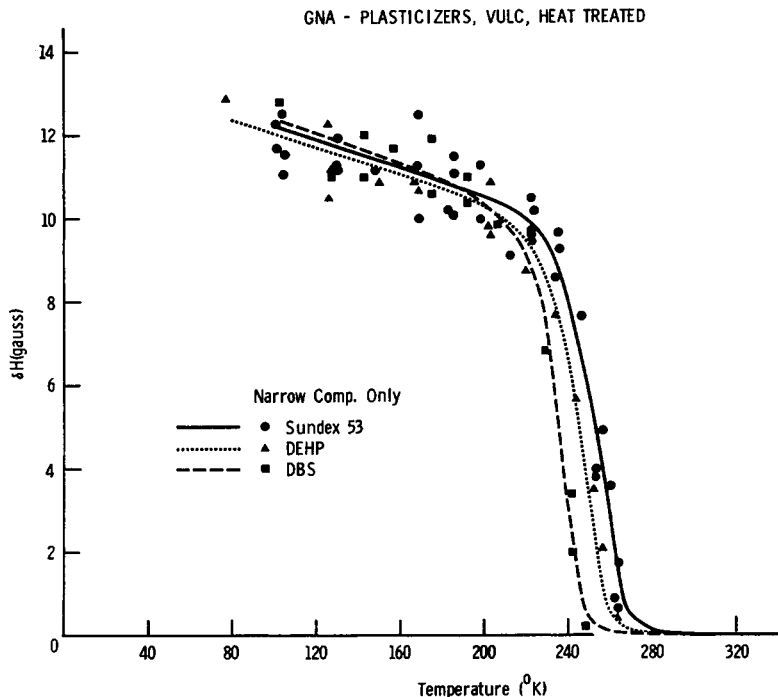


Fig. 4. Line width vs. temperature for heat-treated, vulcanized, plasticized GNA neoprenes.

Finally, as we shall see, the narrow component shows a relative independence of state of vulcanization and temperature treatment. This fact allowed us to derive  $T_6$  from just the heat-treated samples for comparison with the results of  $T_b$  from mechanical tests. It also allowed us to make a comparison of  $T_6$  for the raw GNA polymer and  $T_b$  for the vulcanized sample with no plasticizer.

Figure 3 is a plot of  $\delta H$  versus temperature for heat-treated, unvulcanized neoprene GNA with three different plasticizers. Figure 4 is a similar plot for heat-treated, vulcanized samples. It can be seen that segmental motion occurs at lowest temperature in the presence of DBS plasticizer and at somewhat higher temperature with DEHP. Figure 5 is a comparison of the plots for raw GNA (both heat- and cold-treated) and GNA with DBS plasticizer in unvulcanized and vulcanized, heat- and cold-treated samples. Data points have been left out for clarity. We see that the state of the sample has little effect on the line narrowing of the plasticized neoprenes.

Figure 6 makes a similar comparison for raw GNA and heat-treated unvulcanized samples with the three different plasticizers.

#### Comparison with Mechanical Tests

Mechanical measurements of  $T_b$  were made<sup>6</sup> on vulcanized neoprene samples by means of two ASTM tests. The results are shown in Table I,

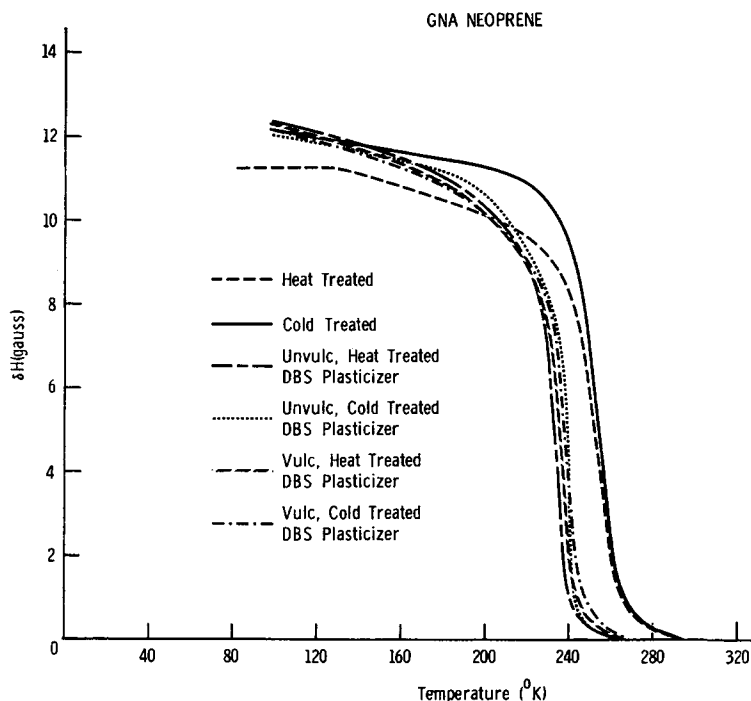


Fig. 5. Line width vs. temperature for raw GNA neoprenes and GNA neoprenes with DBS plasticizer.

where we compare  $T_b$  thus found with our NMR  $T_g$  values. In the case of  $T_g$  for the unplasticized sample we use the value for raw GNA since, as we saw in Figure 5 above, the state of the sample has little effect on the  $\delta H$  versus  $T$  plot—at least for plasticized samples. There may be some error in this assumption.

TABLE I  
Comparison of  $T_b$  from ASTM Tests<sup>a</sup> with  $T_g$  from NMR for GNA Neoprenes<sup>b</sup>

Plasticizer	$T_b$ , °C.		$T_g$ , °C.	
	D-746-A	D-746-B	Vulcanized	Unvulcanized
None	-30.2	-26	—	-26
Sundex 53	-26.2	-24	-24	-23
DEHP	-36.2	-34	-32	-29
DBS	-47.8	-44	-41	-43

<sup>a</sup> These tests were run at Inland Manufacturing Division, General Motors Corporation, in the laboratory of Mr. E. N. Ipiotis. The tests used were ASTM D-746-A and ASTM D-746-B.

<sup>b</sup> The ASTM tests were run on vulcanized compounds consisting of 100 parts GNA, 5 parts zinc oxide, 4 parts magnesium oxide, and 10 parts plasticizer. NMR data were taken using heat-treated vulcanized samples compounded in the same manner and heat-treated unvulcanized samples containing plasticizer only.

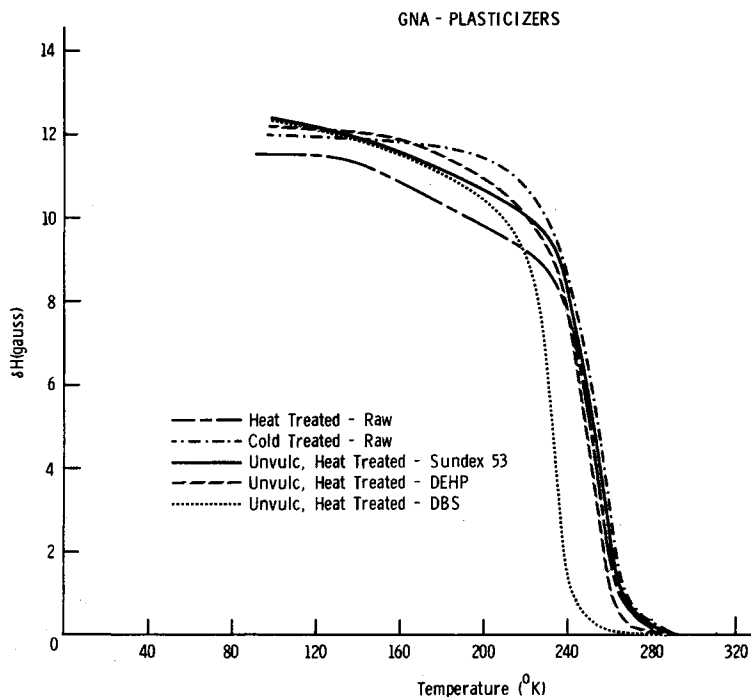


Fig. 6. Line width vs. temperature for raw GNA neoprenes and heat-treated, plasticized, unvulcanized GNA neoprenes.

It can be seen that a good correlation exists between  $T_g$  from NMR and  $T_b$  from mechanical tests. No particular significance is attached to the apparent equality of  $T_g$  and  $T_b$  (D-746-B). The important feature is the excellent agreement of the two methods in ranking the plasticizers for their low-temperature properties.

### Conclusions

From this work we conclude that PMR can be of value in determining glass transition temperatures and low-temperature plasticizer properties in neoprenes. In the present case we have shown by PMR that an aromatic hydrocarbon (Sundex 53) raises the glass temperature of neoprene GNA about  $2^{\circ}$ C while di-2-ethylhexyl phthalate lowers it some  $8^{\circ}$ C. and dibutyl sebacate lowers it about  $18^{\circ}$ C., in agreement with mechanical measurements. The method may well be applicable to other elastomers and polymers with various plasticizers.

PMR may have considerable value as a method for determining plasticizer properties in a way which is strictly dependent on molecular motions and not on experimental test methods and statistics, as is the case with mechanical methods.

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### References

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### Résumé

On a déterminé  $\delta H$  la largeur de raie de résonance magnétique protonique (PMR) à température variable pour un certain nombre d'échantillons de néoprène (polychloroprène). Les mesures ont été effectuées sur des néoprènes bruts (type W, WRT et GNA) et sur des néoprènes avec plastifiants, à la fois à l'état vulcanisé et non-vulcanisé. On note une excellente corrélation entre la température d'amincissement des raies et la température de transition. Les résultats montrent que la PMR peut être d'utilité pour l'étude des propriétés des plastifiants et pour la mesure des températures de transition vitreuse d'une manière dépendant seulement des mouvements moléculaires plutôt que de la nature des tests mécaniques ou de la statistique des échantillons.

### Zusammenfassung

Protonmagnetische Resonanz-(PMR)-Linienbreiten,  $\delta H$ , wurden in Abhängigkeit von der Temperatur an einer Anzahl von Neopren-(polychloropren)-proben bestimmt. Die Messungen wurden an Rohneopren (Typ W, WRT und GNA) und an weichgemachtem Neopren in unvulkanisiertem und vulkanisiertem Zustand ausgeführt. Es ergab sich eine ausgezeichnete Korrelation der Temperatur der Linienverengung zur durch mechanische Tests festgestellten Sprödigkeitstemperatur. Die Ergebnisse zeigen, dass PMR zur Untersuchung von Weichmachereigenschaften und zur Messung der Glasktemperatur insofern von Wert sein kann, als sie nur von Molekülbewegungen und nicht von der Natur eines mechanischen Tests oder von der Probenstatistik abhängen.

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