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APPLICATION OF TMA FOR RAPID EVALUATION OF LOW-TEMPERATURE PROPERTIES OF ELASTOMER VULCANIZATES*

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ABSTRACT

Many elastomeric products are required to function at low temperatures and although numerous ASTM Standard procedures have been developed to evaluate low-temperature properties of vulcanizates, none is suitable for routine rapid batch-to-batch testing. Expansion, identation and tension TMA/DTMA have been used to establish low-temperature characteristics of a variety of elastomer vulcanizates (polyacrylates, neoprenes, nitriles and BR/SBR/NR blends) and it is shown that these techniques offer a rapid approach to testing for quality control.

The lowest temperature at which adequate elastomeric properties can be monitored is determined by the glass transition of the elastomer; however, the rate of change of properties with temperature (e.g. increase in modulus with decreasing temperature) is significantly affected by type and amount of plasticizer (extender, softener, etc.). TMA and DTMA results are in good agreement with Gehmen rigidity modulus determinations. TMA results can be obtained in about ten minutes.

INTRODUCTION

Numerous standard procedures have been developed for determining the low-temperature characteristics of plastics and elastomer vulcanizates and the basic principles of each procedure have been outlined by Nielsen[1]. The most often quoted ASTM procedures[2] for rubber and related materials are D-746 Brittle Temperature by Impact, D-797 Young's Modulus in Flexure, D-1053 Torsional Modulus and D-1329 Temperature-Retraction Properties. In general, some property of the system is determined at a series of isothermal temperatures and the temperature at which the property attains a value considered representative of its limit for adequate field performance is determined. The time involved in such testing is considerable and cannot be considered on a routine basis for the release of products. Further, the large sample size and refrigerant system (air or liquid) results in poor temperature control and time delay in moving from one isothermal condition to another. Many

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of these problems can be overcome by the use of thermomechanical analysis (hereafter TMA) which utilizes a small sample and sample holder together with a reproducible and accurate dynamic heating program. The purpose of this paper is to describe in some detail the TMA methods and observations made on a variety of elastomer vulcanizates.

The use of a linear dimensional analyser to determine second-order transitions in high polymers was described by Floyd[3] and later by Dannis[4]. Current commercial TMA instruments employ the same technique but have the advantage of recording a continuous dimensional change under a rigorous and reproducible heating or cooling thermal program. A further advantage of commercial instrumentation is the simultaneous recording of the first derivative of the dimensional change.

Numerous applications of TMA have been reported. Manz and Creedon[5], for example, have used TMA to determine the degree of cure in thermosetting resins from expansion profiles. Other applications include measurement of thermal shrinkage of aromatic polymers[6], effect of thermal history on expansion properties of plastics[7], measurement of swelling and dissolution of plastics[8, 9] and rheological compatibility of polymer blends[10]. In elastomer studies, Miller and Saunders[11] used TMA to observe the effects of structure on the molecular interactions of segmented polyurethanes. TMA expansion and tension data were reported over a wide temperature range (−160 to +250°C). Miller and Fitzsimmons[12] have also compared transitional behaviour in block copolymers as observed by several thermoanalytical procedures (TMA, dilatometry, DTA, thermal depolarization, etc.) Using a hemispherical probe indentor, Hwo and Johnson[13] used TMA to determine the Young's modulus of an acrylic elastomer. It was suggested that experimental slip problems could be overcome by the use of a flat-ended probe of the type used in this work.

TMA has been evaluated as a low-temperature test method for plastics. Yanai et al.[14] have shown that TMA data obtained in penetration allow calculation of the deflection under load temperature (ASTM D-648), the Vicat softening temperature (D-1525) and the Clash Berg T_F temperature (D-1043)[15]. Values obtained by the TMA procedure are in excellent agreement with those obtained following the ASTM procedures. Interlaboratory studies on the reproducibility of TMA measurements have also been reported[16]. Thermal expansion and glass transition temperatures of polycarbonate and poly(methyl methacrylate) were determined by a number of laboratories using standard samples. For the glass transition temperature, interlaboratory agreement was within 5% variation. For expansion coefficient measurements, TMA is not as precise, intralaboratory results agreeing within ±5% and interlaboratory precision running from 12 to 15%.

Elastomer studies have been made with instrumentation closely resembling some of the TMA modes of operation. Stevens and Ivey[17] constructed an apparatus to allow stress–temperature (constant strain) and length–temperature (constant stress) measurements. Heating and cooling rates as low as 1K/0.5 h were used with an NBR polymer. Similar determinations were reported by Briggs et al.[18] for a wider range of vulcanizates (BR, NR, SBR, NBR and IIR). Normal heating and cooling rates of 5°C/min were used. In their conclusion, the authors stated that the use of such simple mechanical tests proves to be a valuable approach to the preliminary study of rubber compositions. Dilatometry is also used to study low-temperature transitions in polymers. Data obtained from linear expansion in TMA should agree well with volume measurements made by dilatometry. For vulcanizates, linear expansion measurements are experimentally more easy and much more rapid. Henderson and McLeod[19] and Breitman[20] have reported data on the effect of a number of plasticizers on the T_g of SBR. These data are useful for comparing the results obtained by TMA with dilatometry.

EXPERIMENTAL

Materials

A series of vulcanizates (polyacrylates, medium and low nitrile NBRs, neoprene, BR/SBR/NR and BR/SBR blends) were supplied by Dunlop Research Centre, United Kingdom. The low-temperature properties of these vulcanizates had been determined using a Gehman torsional pendulum. All other vulcanizates were prepared using standard rubber laboratory equipment following ASTM D-15 procedure[2]. Commercial elastomers (SBR 1500, Krynac 800 and 34:60 SP, Neoprene W), curatives, fillers and plasticizers were used throughout.

Thermomechanical analyzer

The TMA used was a DuPont 942 with temperature programming and recorder facilities provided by a 990 module. Displacement of a probe is measured by the core displacement of a linear variable differential transformer. Details of the instrument are given in the literature[13]. Maximum sensitivity of the instrument is 5×10^{-5} cm/cm of chart. (Note: The system is calibrated in British units, but in this paper all values have been corrected to conform with SI units.) The first derivative of the displacement is simultaneously recorded on the x–y–y' recorder. Maximum derivative sensitivity is 1.27×10^5 cm/min per cm of chart.

The heating rate can be varied in seven steps from 0.5 to 50°C/min. Programmed cooling is not available.

Probes and sample preparation

Three types of probe were used in this work. All probes and sample holders were constructed of quartz. The expansion probe was 0.254 cm in diameter with a flat end. This probe was used for thermal expansion measurements with no applied load. When used with load, indentation of the sample also occurs. For penetration measurements, a probe with a 0.06 cm diameter tip was used. In tension studies, a standard DuPont tension probe was used. Maximum loading on all probes was 100 g or typically for the expansion probe ~1.98 kg/cm^2 at the probe–sample interface.

Samples were die cut from 0.127 to 0.254 cm thick compression moulded sheets. Maximum sample thickness that the instrument can accommodate is 2.54 cm.

Discs of 0.38 cm diameter were used for expansion and penetration measurements. For tension measurements, ring samples in the shape of a running track were die cut. The distance between suspension points of the ring was 1.27 cm at room temperature. width of the sample arms was 0.32 cm.

In order to obtain reproducible results, the following procedure was followed. The sample was mounted in the TMA at room temperature and a small load ($\sim$0.2 mg) placed on the probe. This load maintained the probe in contact with the sample as it was cooled. Water-free nitrogen was purged through the system as the furnace was cooled in liquid nitrogen. Any moisture condensed on the sample surface significantly affected the data. Thin films of moisture were readily detected by rapid displacements of the probe at 0°C resulting in a very sharp DTMA peak.

At the required temperature, usually 50°C below the transition of interest, load was applied to the probe and the heating program started. The temperature was measured by a thermocouple placed near ($\sim$0.2 cm) the sample but not touching it.

RESULTS AND DISCUSSION

The general features of the experimental data obtained in each mode of operation of the TMA are illustrated in Fig. 1. The data was obtained for a neoprene vulcanizate scanning the range −100 to +20°C at 5°C/min.

Figure 1(a) illustrates the free expansion thermogram. The slope of the displacement versus temperature curve, measured directly by the derivative offset from zero, is the rate of expansion at any given temperature. The linear expansion coefficient, α, is thus readily calculated at any temperature. Ideally, as the glass transition region is scanned, a smooth transition from one expansion rate to another would be observed as in dilatometry. In practice, this smooth transition was difficult to achieve experimentally with elastomer vulcanizates, an apparent shrinkage generally being observed as the T_g region was scanned. This shrinkage is actually indentation of the sample resulting from the non-zero mass of the probe. Although the probe mass is balanced at the starting temperature, the sample expands against the probe and continued adjustment is necessary to observe a thermogram as shown in Fig. 1(a). In experiments with a macro expansion probe (probe area greater than sample surface area) smooth transitions were still difficult to obtain. In this case, compression of the sample was the cause.

Reproducible results are obtained by loading the probe to guarantee indentation. Figure 1(b) illustrates data obtained with 50 g ($\sim$1 $\mathrm{kg/cm^2}$ on sample). A comparison of expansion coefficients below the onset of the glass transition calculated from free expansion and expansion with load were in good agreement, indicating the low compressibility of the glassy state. Significant indentation is observed as the T_g region is scanned, the DTMA exhibiting a peak. The temperature at which the maximum occurred, i.e. maximum rate of indentation, is quite characteristic of the sample under given experimental conditions. Above the glass transition range, the observed slope depends upon the competition between indentation and thermal

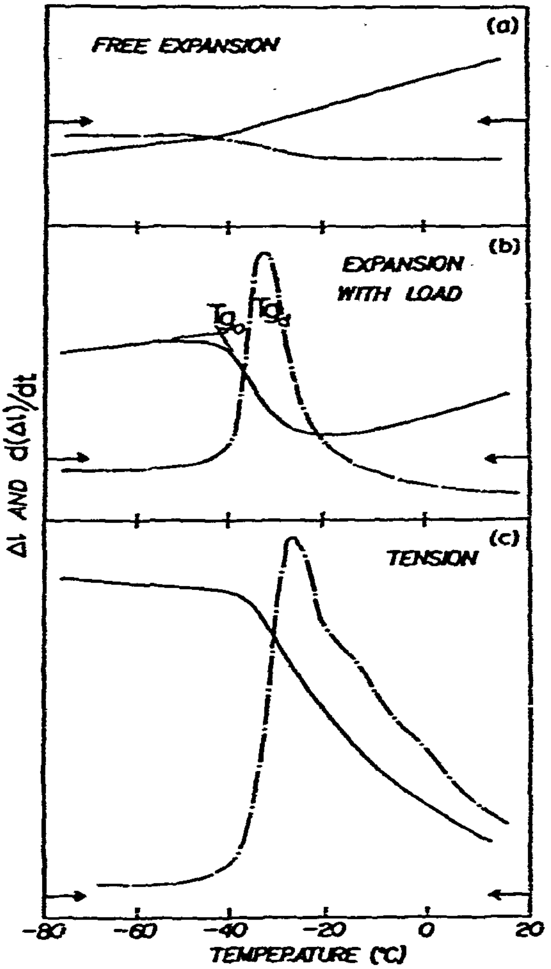

Fig. 1. TMA free expansion, indentation and tension thermograms neoprene vulcanizate. 5°C/min, 50 g load in indentation and tension. ——, Δl versus temperature; ——, $d(\Delta l)/dt$ versus temperature.

expansion. The behaviour in this temperature region is related to the hardness of the vulcanizate and is affected by the type of plasticizer used (see later.).

Figure 1(c) illustrates the development of tensional strain for the same neoprene vulcanizate as the temperature is raised through the T_g. Below the T_g, the tension data again simply reflects the thermal expansion of the sample. Tensional strain begins to develop as the temperature reaches the T_g and again the DTMA curve exhibits a peak which is characteristic of the sample. For all vulcanizates studied, the DTMA peak in tension occurs at a higher temperature than that observed in compression. With some vulcanizates, particularly blends, several tension DTMA peaks are observed.

The usual method of calculation of T_g is by extrapolation, illustrated in Fig. 1(b). Construction of the correct tangents can be difficult, but the DTMA thermogram can be used to determine the point on the TMA curve at which the maximum rate

TABLE 1

THERMOMECHANICAL ANALYSIS OF VULCANIZATES

Vulcanizate	*a* (°C^{-1}) × 10^4 ± 0.03 below T_g ± 0.1 above T_g	*Expansion* (°C)		*Tension* (°C)		*Gehman* (G_T)
		T_{gd}	T_{go}	T_{gd}	T_{go}	
Polyacrylate 1.	0.54 (−120 to −40), 2.3 (+80)	−8	−16	0	−11	−11
2.	0.53 (−120 to −60), 1.8 (+60)	−11, 22	−21, 16	−4	−15.5	−15.5
Medium nitrile NBR 1.	0.45 (−80), 1.8 (+40)	−18	−24	−15	−21	−21
2.	0.51 (−80), 1.8 (+40)	−22	−30	−18	−26	−26
Neoprene WRT	0.49 (−60), 1.69 (+40)	−33	−40	−27.5	−36	−34.5
Low nitrile NBR	0.45 (−120 to −60), 1.47 (+40)	−32	−40	−28	−36	−39.5
BR/SBR/NR	0.46 (−110), 1.57 (+20)	−74	−89	−58, −38, −5	−70	−65
BR/SBR	0.60 (−110), 1.53 (+40)	−78	−70±5	−57, −27, −6	−70	−75

occurs. The tangent to the curve must be drawn through this point. Two characteristic temperatures are reported here, T_{g0}, the extrapolated temperature and T_{gd}, the temperature of the DTMA peak corresponding to the maximum rate of indentation or tensional strain development.

General vulcanizate properties

Typical results obtained for α, T_{g0} and T_{gd} by both expansion and tension measurements are shown in Table 1 for a range of vulcanizates. Also included in Table 1 is the Gehman temperature, G_T, which is defined as the temperature at which the rigidity modulus is 1000 kgm/cm^2/radian.

Although TMA is a rapid method for determining α, it is clear that reproducibility of the method is only of the order of ±6%. This is in agreement with results obtained on poly(methyl methacrylate)[16]. The reproducibility might be improved by using thicker samples (up to 2.54 cm maximum) rather than the 0.127–0.254 cm sheets used here. Measured maximum rates of expansion were of the order of 0.30–1.50 × 10^{-4} cm/min at 5°C/min scan rate.

For several vulcanizates (polyacrylate, neoprene and the blend compounds)

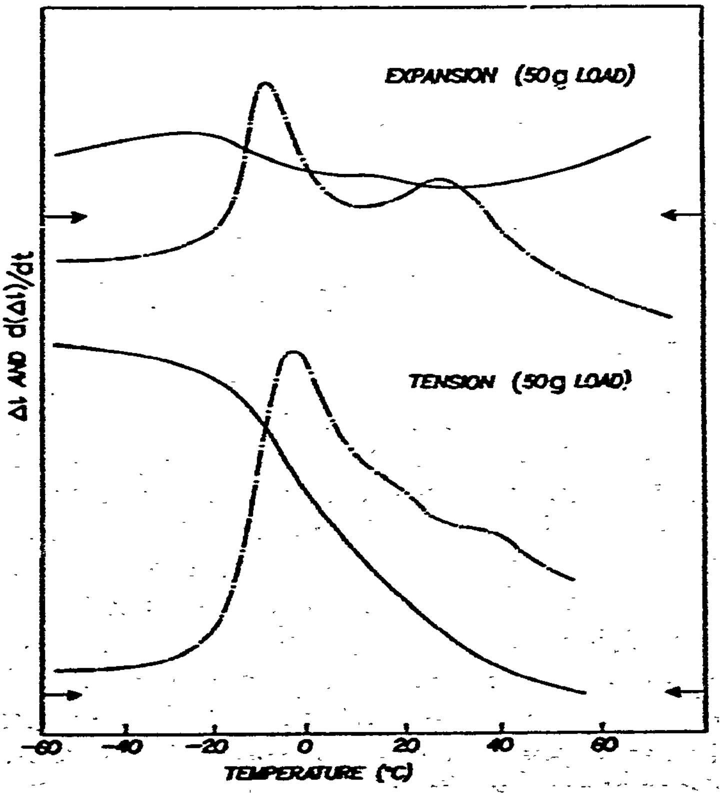

Fig. 2. TMA thermograms polyacrylate vulcanizate. 5°C/min, 50 g load in indentation and tension sample thickness 0.217 cm. Sensitivity: expansion Δl, 5 × 10^{-4} cm/cm chart. —·—, $d(\Delta l)/dt$, 5 × 10^{-5} cm/min. Tension Δl 5 × 10^{-3} cm/cm chart. ———, $d(\Delta l)/dt$ 5 × 10^{-4} cm/min. Arrow indicates derivative zero.

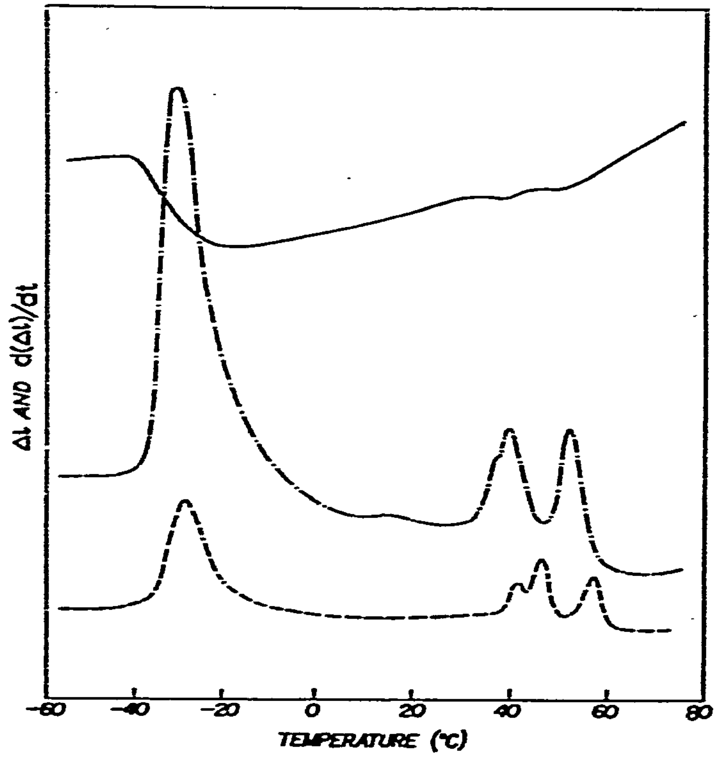

Fig. 3. TMA thermograms neoprene vulcanizate effect of scan rate indentation with 50 g load. ———, 10°C/min Δl; ———, 10°C/min $d(\Delta l)/dt$; ———, 2°C/min $d(\Delta l)/dt$.

more than one peak is observed in the DTMA thermogram. Polyacrylates exhibit two maxima as illustrated in Fig. 2, for results obtained in expansion and tension, both with 50 g load. The second event is clearly seen with expansion but appears only as a plateau in tension measurements.

Neoprenes also exhibit thermal events in TMA other than the main glass transition. These are illustrated in Fig. 3, where results obtained in loaded expansion over the temperature range −60 to +80°C are shown. Apparent indentation of the sample is observed at 40 and 52°C. The 40°C event also appears to be a composite of two which can be separated using low scan speeds. The general effect of heating scan rate is considered later. The main glass transition temperature and the DTMA peak are unaffected by the scan rate variation. DSC scans on neoprenes show endothermic transitions at 42 and 47°C which have been related to crystallization[21]. TMA experiments using an expansion probe with no load support this, as even with very careful balance to remove residual probe mass, the 40°C doublet and the 52°C event are accompanied by volume reduction in the system. Further, as observed, a scan rate dependence would be expected for crystallization effects.

Figure 4 illustrates typical results obtained with a BR:SBR blend vulcanizate. As would be expected, vulcanizates containing BR:SBR or BR:SBR:NR exhibit an indentation and tensional strain development over a much wider temperature

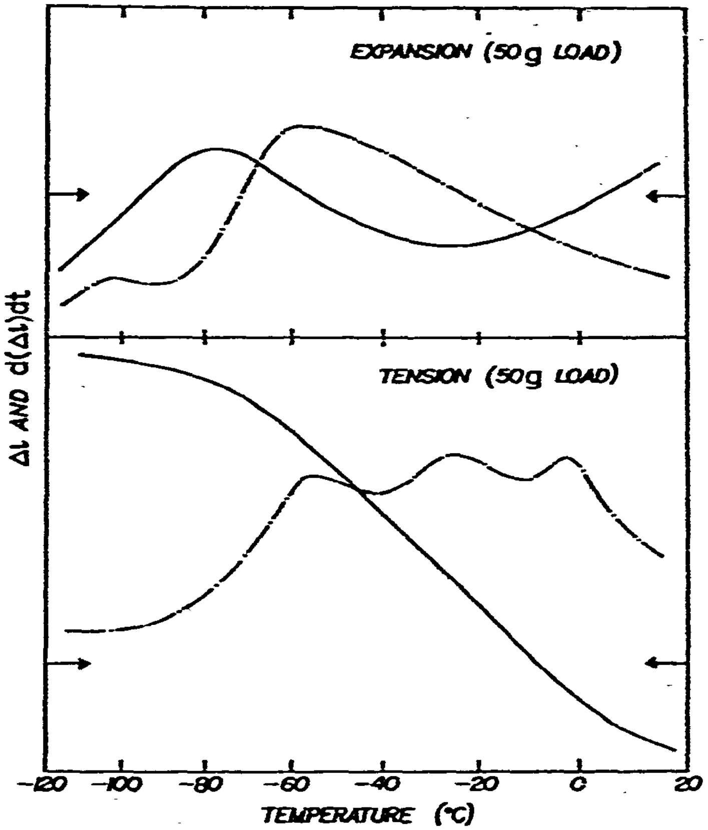

Fig. 4. TMA thermograms NR:SBR vulcanizate. 5°C/min, 50 g Load, Sample thickness 0.153 cm. Indentation: —, 5×10^{-4} cm/cm chart, Δl; ———, 2×10^{-5} cm/min, $d(\Delta l)/dt$. Tension: ———, 1×10^{-2} cm/cm chart, Δl; ———, 1×10^{-3} cm/min, $d(\Delta l)/dt$.

range because of the presence of several elastomer components. In indentation, only one broad DTMA peak is observed for both blends. DTMA in tension, however, shows three distinct peaks which are quite reproducible from run to run. These maxima are not observable by inspection of the primary TMA thermogram. Comparison of the temperatures at which the DTMA maxima are observed (Table 1) show only the centre peak is changed in an SBR:BR blend by the addition of NR. This moves from −27 to −38°C. The first two peaks are probably related to the T_g of the components; however, to assign definite values at this point in time would be speculative. The −5°C event is probably related to crystallization in the BR phase (reported values range from −14 to −6°C for 95 *cis*-1,4 BR, the values falling with decreasing *cis*-1,4 content[22].) All other vulcanizates in Table 1 exhibited only single peaks in TMA and DTMA.

In Fig. 5, the T_{go} and T_{ga} temperatures obtained in tension and indentation are plotted against G_T. Because of the differences in experimental method (tension/indentation versus modulus determination), the time–temperature conditions (isothermal versus dynamic heating) and the arbitrary modulus value chosen to define G_T, the TMA thermograms and the Gehman modulus–temperature curve are not

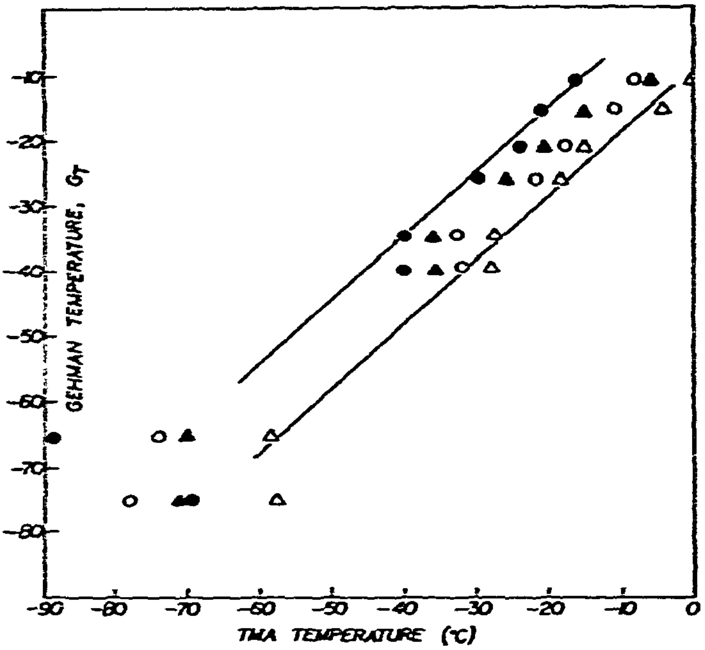

Fig. 5. TMA versus Gehman results. Vulcanizate in Table 1, 5°C/min. Tension: T_{gd}, △; T_{go}, ▲. Indentation: T_{gd}, ○; T_{go}, ●.

directly superimposable on the temperature axis. The result is a linear relationship between T_{go} or T_{gd} and G_T which is offset on the temperature scale. The apparent agreement between T_{go} tension and G_T is thus coincidental. Nevertheless, just as G_T is a characteristic of the vulcanizate, both T_{go} and T_{gd} can be used to determine relative vulcanizate low-temperature properties. The larger scatter in T_{go} and T_{gd} values for the SBR:BR and SBR:BR:NR vulcanizates arises from the presence of several transitions in these blends. In dilatometric work, a correlation between the lowering of the T_g of SBR gums by plasticizers and the lowering of the Gehman freeze temperature (extrapolation of twist angle versus temperature curve to zero twist angle) has been reported[20]. Although the effect of plasticizers on Gehman results has not been investigated here, TMA should give similar observations on vulcanizates.

Effect of scan rate

It is well known that the glass transition temperature of polymers is dependent upon the time scale in which it is determined[1]. In TMA, where a dynamic heating rate is used, variation in the observed T_g with scan rate is expected. Further, since the sample thermocouple is not in direct contact with the sample, a thermal lag between sample and recorded temperature would be expected. The thermal lag should increase as scan rate increases because of the increasing thermal gradients, both in the sample and in the furnace. Actual values recorded for a medium nitrile vulcanizate are given in Table 2. Over the scan rate range 2–20°C/min, T_{gd} remains constant

TABLE 2

EFFECT OF SCAN RATE ON TMA RESULTS

Compound: Medium Nitrile NBR. Expansion with 50 g load.

Scan rate (°C/min)	T_{go} (°C)	T_{gd} (°C)
2	−26	−19
5	−26	−18.5
10	−28	−19
20	−30.5	−18.5
50	−26	− 8

within experimental error whilst T_{go} moves to lower temperatures. The shift is ~4°C as scan rate changes from 2 to 20°C/min. This shift is in the opposite direction to that anticipated but is quite reproducible. At 50°C/min, both T_{go} and T_{gd} shift to higher temperatures suggesting the temperature gradient has become too high. In order to obtain reproducible results at 50°C/min, extreme care in positioning the sample thermocouple is necessary. The cause of the T_{go} moving to lower temperatures as scan rate increases is not understood. It was noted that as scan rate increased, indentation of the sample started at lower temperatures. This might be related to thermal gradients within the sample itself.

Effect of plasticizers

It is well known that the addition of certain plasticizers to polymers results in a lowering of the polymer's T_g and that the magnitude of the observed shift is dependent upon structure and physical properties (viscosity, free volume, etc.) of the plasticizer. Having established that TMA and DTMA are rapid and reproducible techniques for determining the T_g of vulcanizates, the effect of plasticizers on T_g was studied to ascertain whether compositional changes could be readily detected by TMA. Compared with plastics, little information is available in the literature on the absolute magnitude of T_g shifts with plasticizer variation in vulcanizates. Since the observed T_g depends not only on the plasticizer content but also on other factors such as degree of cure, concentration of diluents, method and frequency of measurement, it is unlikely that exact agreement in literature values would occur.

Table 3 illustrates TMA/DTMA results obtained for several plasticizers in an SBR vulcanizate. The plasticizers used were dioctyl phthalate (DOP), dibutyl phthalate (DBP) and a naphthenic oil, Circosol 4240. Although ester plasticizers are not used commercially in SBR, they do produce the largest T_g shifts and are useful for comparing the ability of the TMA to detect such shifts. The high viscosity naphthenic oil (2525 SUS at 37.8°C) does not affect T_{go} or T_{gd}, in agreement with the dilatometric observations[19, 20]. DOP and DBP both lower T_{go} and T_{gd}, DBP being the

TABLE 3

EFFECT OF PLASTICIZERS ON TMA T_g OF SBR AND NBR VULCANIZATES

Vulcanizate	*T_{go} (°C)*	*T_{gd} (°C)*	*Literature values (°C)*
SBR 1500			
No plasticizer	−54	−43	−62.5
10 phr Circosol 4240	−54	−44	
20 phr Circosol 4240	−54	−43	
10 phr DOP	−55	−44	−65
20 phr DOP	−57	−47	−67
10 phr DBP	−56	−48	−65
20 phr DBP	−63	−52	−69
Krynac 800			
No plasticizer	−27	−19.5	
10 phr DOP	−31	−22.5	
20 phr DOP	−34	−25	
10 phr Paraplex G-50	−28.5	−20.5	
20 phr Paraplex G-50	−30	−23.5	

more effective at the 20 phr level (ΔT_{go} of 9°C). The values for the shift are in fair agreement with those observed in uncured SBR, although the absolute T_g of the latter (28% styrene) is 8.5°C lower than that of the SBR 1500 (23.5% styrene) vulcanizate. Similar results were found for DOP and a polyester ester plasticizer in commercial Krynac 800 (34% ACN) vulcanizates (Table 3). All results given in Table 3 were obtained using a temperature base with which temperature readability is ±0.5°C in the −100°C to 0°C range. Actual reproducibility in the observed T_g was better than this (~±0.2°C) as determined by operating the instrument on a time base (thus expanding the temperature axis.) Thus, for quality control purposes, TMA/DTMA affords a rapid check on plasticizer content if a shift in T_g is produced by the plasticizer in use.

Many plasticizers, extenders, softeners, etc. are used in the rubber industry which do not affect the T_g of the vulcanizate, but are added primarily for improved processing (viscosity reduction, easier mastication, etc.) and subsequent modification of the vulcanizate physical properties. Thus, simple determination of the T_g will not give any information on the presence, absence or amount of plasticizer present. For this purpose, the use of TMA/DTMA over a wider temperature range was investigated. Figure 6 illustrates TMA thermograms of nitrile vulcanizates (Krynac 34:60 SP) containing various resin plasticizers. Each vulcanizate is identical except that the resin has been substituted at the 10 phr level. The resins compared are coumarone–indene, a hydroxy and a hydrocarbon. Below the T_g, the expansion coefficients were identical for all vulcanizates. Further, T_{go} and T_{gd} were identical and independent of the resin type. As the temperature increased above the T_g, the extent of the in-

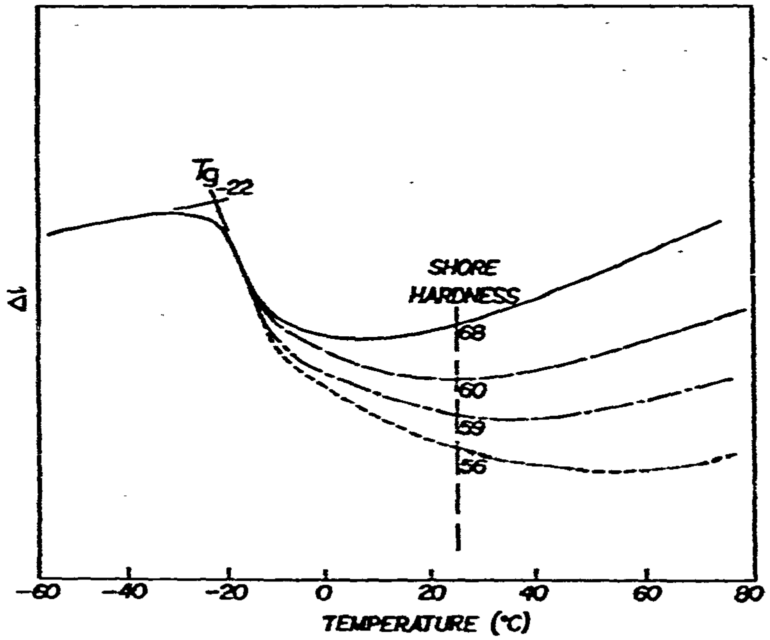

Fig. 6. Effect of plasticizer resin on indentation of nitrile vulcanizite, 5°C/min. ———, No plasticizer; ———, 10 phr coumarone indene resin; ———, 10 phr hydrocarbon resin; ———, 10 phr hydroxy resin; Formulation: Krynac 36:40 SP 100, Mt Black 85, FEF Black 15, Betanox Special 2.0, Antioxidant MB 2, Dicup 40 C 3.5.

dentation and the temperature range over which it occurred, varied with the plasticizer used (Fig. 6). The results shown were obtained under standard conditions of 5°C/min with 50 g load, and 0.20 ± 0.01 cm thick samples, and are therefore directly comparable. The actual maximum indentation amounts to 0.003 cm or ~1.5% of the sample thickness. It was found that using a penetration probe (see experimental), the thermogram was not as reproducible although the penetration was considerably higher. As the temperature rises further, thermal expansion eventually predominates over indentation and the thermogram of each vulcanizate becomes parallel. Apparent expansion coefficients calculated in this region are approximately 10% lower than those obtained from free expansion measurements. Observation of Fig. 6 shows that for each resin plasticizer, the vulcanizate gives a characteristic but different thermogram above the T_g. The characteristic shape of the thermogram is determined by the physical properties of the vulcanizate and in particular, the hardness. Also shown in Fig. 6 is the hardness (Shore A) of each vulcanizate determined at room temperature (25°C). From this limited study, a direct correlation between hardness and extent of indentation appears to exist. Gent[23] has derived a relationship between Young's modulus, calculated from indentation of a rigid sphere and BS 903 and Shore hardness. The mathematics of indentation versus modulus for a flat probe of the type used here has been derived[24]. Use of these relationships with the TMA/DTMA data is now being evaluated. Although the T_{gd}, i.e. the temperature at maximum rate of indentation, does not appear affected by the type of resin, the higher indentation above T_{ga} for the resin vulcanizates is reflected as an extensive shoulder on the high temperature side of the DTMA peak.

CONCLUSIONS

Static thermomechanical analysis has been investigated as a method for determining the low-temperature properties of vulcanizates. Dimensional changes of a sample in free expansion, indentation or tension are monitored as the sample is heated at a known and reproducible rate. The first derivative of the dimensional change is simultaneously recorded.

TMA/DTMA data obtained in free expansion gives the linear thermal expansion coefficient at any temperature during the experiment. The glass transition is observed as a change in slope as in dilatometric determinations. In the indentation mode, the thermogram is the result of competition between thermal expansion and indentation. For tension measurements, the thermogram records the additive sum of thermal expansion and tensional strain development. For indentation and tension, the glass transition is obtained by a standard extrapolation method. A maximum in the DTMA thermogram is also observed which represents the maximum rate of change as the sample is heated through the glass transition range. The temperature of this maximum T_{ga} is characteristic of a vulcanizate. Variation in scan rate between 2 and 20°C/min has little effect on T_{go} and no effect on T_{ga}. At 50°C/min, thermal gradient effects predominate.

For a wide range of vulcanizates in tension or indentation, T_{go} or T_{ga} versus the Gehman rigidity modulus gives a linear relationship. Exact temperature agreement is not observed because of differences in the experimental techniques. In blends, several T_{ga} values are observed.

Plasticizer effects can either be observed by a shift in the T_{go} or by a change in the thermogram profile, the extent of indentation and temperature range over which it occurs. The extent of indentation correlates with vulcanizate hardness as expected. The indentation of a rubber sample by a flat probe has been treated mathematically in the literature[24], and the determination of Young's modulus by TMA/DTMA is now being investigated.

In conclusion, the ease of sample preparation and the rapidity of TMA/DTMA measurements offers a quick approach to assessing the low-temperature properties of vulcanizates. At 20°C/min scan rate, actual runs can be completed in as little as four minutes (80°C total scan) if the sample has a single transition.

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