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THE GLASS TRANSITION TEMPERATURE OF NATURAL RUBBER

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In view of the lack of precise experimental data in the literature concerning the determination of a defined *Tg* value for natural rubber (NR) and the differences when such data are given, a reference definition of *Tg*(Vo) is offered and a procedure for obtaining it described in detail.

It is proposed that the value obtained for uncured NR of 200.5 K be used as a low temperature standard in the study of other polymer *Tg*'s which occur in this region.

The expression "Glass transition temperature" (*Tg*) defines a familiar property of every polymer and can be described as the temperature at which there is a sharp discontinuity in the otherwise smooth relationship between properties such as volume, elasticity etc. with temperature. It represents the boundary between glassy and rubbery states of the polymer. The transition occurs over a relatively narrow temperature range and, because many changes in property are effected at the transition, several methods of measuring it have been developed [1]. These in turn have led to a variety of definitions of the event.

One technique has predominated for routine measurement over the last twenty years, differential scanning calorimetry (DSC), although it should be noted that this includes two distinctly different methods [2] of instrumental operation, defined as power compensated DSC and heat-flux DSC. Even within this area variations in experimental technique and interpretation of data have resulted in a spread of results being quoted for any particular polymer whilst the fact that many publications give no indication of the means used to obtain the quoted value, or the method of calibration, renders the quoted values of *Tg* of dubious significance. Indeed of the publications which quote *Tg* values for uncured natural rubber (NR) only two [3, 4] appear to give relatively full details of both the experimental technique and calculations used. Others [5, 6] offer values without these highly relevant details although Maurer [5] defined and discussed many of the problems of both experimentation and interpretation as early as 1968.

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Much of the published data is used to show how changes, or shifts, in *Tg* are brought about by modification of the polymer structure. These shifts are completely valid, all other things being equal, but the quoted (undefined) *Tg* values can offer little more than a guide to the true *Tg* of the polymer in question.

The purpose of this paper is to consider the factors which may affect *Tg* values and to describe in detail an experimental procedure and method of calculation whereby a closely defined value may be assigned to the *Tg* of uncured NR. This polymer may then be used for the subsequent low temperature calibration of an instrument for *Tg* measurements of other polymers.

Factors affecting *Tg* values

Temperature measured

The energy changes associated with the heating of a polymer through the temperature region of its glass transition are as illustrated in Fig. 1.

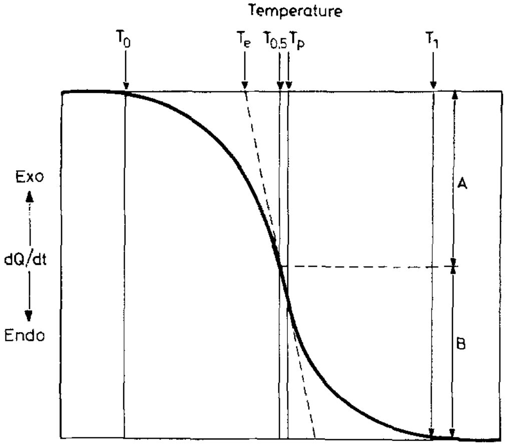

Fig. 1 Representative curve of heat flow *vs.* temperature in the region of the *Tg* of a polymer
To: Temperature of departure of base line from its linear extrapolation. *Te*: Temperature of intercept of extrapolated base line and tangent to steepest slope. $T._5$: Temperature at 50% transition ($A = B$). T_p: Temperature at maximum slope (peak of derivative plot). T_1: Temperature at completion of transition

Each of the temperatures indicated (*To*, *Te*, $T._5$ etc.) has variously been described as 'the *Tg*'—often with no further definition. Modern convention [2] equates *Te* with *Tg* and this will be followed here. In the same way the 'melting point' (*Tm*) of a standard is defined as the intercept of the extrapolated base line with the tangent to the maximum slope of the melting curve.

Thermal pre-history

The precise temperature of the *Tg*, and its shape, can be influenced by the presence of crystallites, [4] by slow cooling through the region of the *Tg*, [7] and by annealing of the quench-cooled polymer close to the *Tg* [5, 8].

The experimental procedure adopted here to eliminate these sources of variability was to heat the sample to 370 K prior to each run, hold at this temperature for one minute, and then crash-cool (320 deg/min^{-1}) to some 30 K below the *Tg*. The run was commenced at the chosen scan speed as soon as the recorder indicated a stable base line, a situation usually taking some five minutes.

Heating rate (V)

The transition which occurs when a polymer is heated through its *Tg*, and indeed when a crystalline chemical is melted, is a dynamic process and therefore there must be a dependency of the position of the observed transition on the heating rate. This can be resolved into two quite separate effects, instrument and sample related.

Instrumental effects are those such as the rate of heat transfer between the heat source and the sample (and reference), relative rates of heat losses between the sample or reference holders, and the rate of response of the monitoring device to thermal changes within the sample.

In general the electronic and engineering design of modern equipment is such that there is little displacement of the Observed T_e, for a relatively rapid event such as a

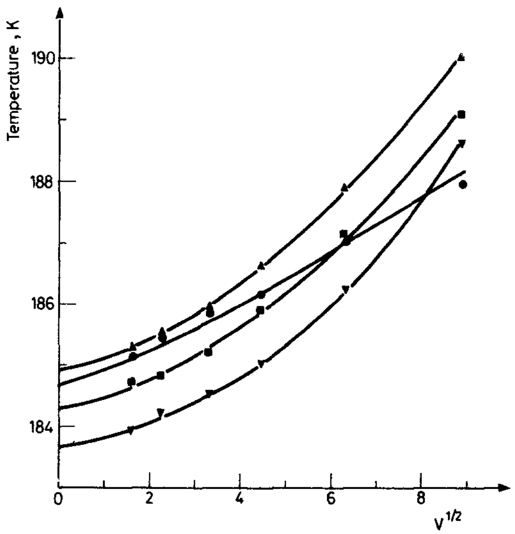

Fig. 2 Effect of mis-matching sample holder covers on the low temperature transition of cyclohexane at various heating rates

melting point, when the heating rate changes by 1 to 2 orders of magnitude but, as is described later (see Fig. 2), it is possible to deliberately mis-match the sample and reference holders to induce appreciable instrumental effects and then study their effect on the reproducibility of the experimental data.

Sample effects include such factors as the rate of heat transfer through the sample, and the rate at which the event being monitored reaches equilibrium at the indicated temperature. Rates of heat transfer do not appear to offer a problem, as the effect on *Tg* of varying the sample weight about small limits is not significant. For this study samples were taken as flat discs weighing some 8–10 mg.

The rate of the relaxation process as a polymer is converted from a glass to a rubber is slow however, due to the limited mobility of the high molar mass polymer chains, and this is evidenced by the significant heating rate dependence of this transition, in excess of that of the sharp transition of cyclohexane (see Table 5). It is this factor, together with the absolute low temperature calibration of the DSC, which probably accounts for most of the variation in literature values for glass transitions.

Structure

Natural rubber is some 93–95% polyisoprene, which is in a 100% *cis* 1–4 configuration. There appears to be no effect on the *Tg* by the non-rubbers present in raw NR, different grades of NR showing the same *Tg* value. This does not hold however if NR is replaced with synthetic polyisoprene, because, whilst there may be a very small variation in *Tg* due to the presence of *trans* isomers [1], there is a well documented linear relationship between the 3,4-content and the *Tg* of synthetic polyisoprenes [3, 9].

Molar mass

Fox and Flory [10, 11] first established the existence of a linear relationship between *Tg* and the inverse of the number average molar mass ($\bar{M}n$). Kow *et al.* [3] showed that, in the case of polyisoprenes, a limiting value for the *Tg* is reached with $\bar{M}n$*'s* of 5000 or more. $\bar{M}n$ values for NR are in excess of 10^5 and thus this factor can be discounted.

Cure

Although we are here concerned with the *Tg* of *uncured* NR, it is worth noting that curing, or vulcanization, increases the *Tg* significantly. This author finds that typical sulphur cures, using either a conventional (2.5 pphr S; 0.6 pphr accelerator) or an efficient vulcanizing system (0.5 pphr S; 2.5 pphr accelerator) will both increase the *Tg* by some 3 K whilst a peroxide cure will give an increase of almost 1 K for each part of peroxide used per hundred parts of rubber.

Calibration

It is obvious that suitable standard material which cover the temperature region of interest must be used to calibrate the instrument. It is not sufficient to rely solely on high temperature standards such as indium. Unfortunately the only glass transition standard currently available [2] is polystyrene ($Tg \sim 380$ K) thus low temperature crystalline standards with sharp melting points must be used and corections applied as described. Those chosen for this study were cyclohexane, which shows a transition at 186.3 K and *Tm* at 279.9 K, and mercury with *Tm* 234.3 K.

Calculation of *Tg* from experimental data

As noted previously, only two publications give experimental details for the determination of the *Tg* of uncured NR and also include information both on calibrants and on the method of calculation. Kow *et al.* [3] calibrate with mercury, run this and the samples at a range of heating rates and "Extrapolate to zero heating rate" to obtain a *Tg* of 202.2 K, whilst Burfield and Lim [4] calibrate with a range of materials including mercury and cyclohexane, measure *Tm's* and *Tg's* at a range of heating rates, and discuss various ways of presenting the data so obtained. They prefer to quote a '*Tg*' of 206.3 K at a heating rate of 20 deg/min^{-1} whilst drawing an extrapolated $Tg(Vo)$ value of 206.5 K on a plot of *Tg* *vs.* $V^{1/2}$ and a *Tg* of 203.6 K for a scan rate of 1 deg/min^{-1} on a plot of Tg^{-1} *vs.* log. *V* by extrapolation to log zero. This appears confusing.

Experimental

Materials

The natural rubber was of SMR 5 grade and was used without purification. Burfield and Lim [4] confirm that purification by reprecipitation has no effect on the *Tg* shape or value.

DSC measurements

All measurements were made with a Perkin–Elmer DSC 2 (power compensated DSC) equipped with a sub-ambient accessory cooled with liquid nitrogen. Helium was used as purge gas and the reference holder contained 10 mg of aluminium in a sample capsule. The instrument was allowed two hours to stabilize after its initial filling, and the liquid nitrogen reservoir was maintained at least half full at all times.

Although the sample and reference holder covers are usually matched to minimize instrument effect, in this series of experiments deliberate mis-matching was used to introduce substantial instrumental effects so that their significance could be determined on the *Tg* of NR as finally calculated. At each mis-match the cyclohexane standard transition temperature was measured, at a range of heating rates, at the beginning and end of the working period, with the samples run between at a random selection of heating rates, each at least in duplicate. These results showed no significant drifting (see Table 2).

For three of the mis-matches the linearity of the relationship between the indicated and true temperature was checked using cyclohexane and mercury, each sealed in a 'high pressure' aluminium capsule supplied by Perkin Elmer. The heating rate was 20 deg/min^{-1}. The absolute temperature calibration for each mis-

Table 1 Effect of altering the sample holder covers on the temperature linearity of the instrument at a heating rate of 20 deg/min^{-1}

	Literature	Transition temperature, K		
		(a)	(b)	(c)
Cyclohexane				
Low temperature *Te*	186.3	185.8	186.1	186.0
Cyclohexane *Tm*	279.9	280.5	280.6	281.2
Mercury *Tm*	234.3	234.7	234.5	233.6

Table 2 Reproducibility of *Te* measurement within one day, at various heating rates

Heating rate, deg min^{-1}	Cyclohexane *Te*		NR *Te* (*Tg*)			
80	188.7	188.5	213.5	213.5	213.3	213.2
40	186.3	186.2	209.8	209.6	209.8	209.6
20	185.0	185.0	207.2	207.4	207.1	207.1
10	184.5	184.4	205.2	205.0	205.1	205.2
5	184.2	184.2	203.5	203.7	203.0	203.5
2.5	183.9	183.9	201.5	201.7	202.0	—
1.25	183.7	183.7	—	—	—	—
0.62	183.7	183.7	—	—	—	—

match was obtained from the data on cyclohexane, extrapolated, using the most common plot of *Te vs.* $V^{1/2}$, [9, 12] to zero heating rate (*Vo*) (Fig. 2).

Polymer samples were cut into thin slivers (8–10 mg) and also sealed in high pressure aluminium capsules similar to those used for the calibrants. Before each run the sample was heated to 370 K for one minute, crash-cooled to 180 K and the run carried out at the selected heating rate as soon as the recorder indicated that the system was in thermal equilibrium.

Results and discussion

Temperature linearity

Literature and experimentally determined values for the transitions of cyclohexane and mercury are listed in Table 1. The experimental data are from runs with three different combinations of sample holder covers.

These clearly show that although some small variations in indicated temperature may occur, the relatonship between indicated and true temperature remains essentially linear over the region with which we are concerned.

Whilst there is some indication of a slight degree of 'slew' in the experimental values relative to the literature ones, this is insignificant considering the closeness of the NR *Tg* to the cyclohexane transition.

Reproducibility under specific conditions

Table 2 illustrates a typical series of results, obtained during one working period (6 hr), with the same covers being used for sample and calibrant and being replaced in identical positions each time the sample was changed.

There is somewhat more variation in the *Tg* measurements, compared with those of *Te*, particularly at slow heating rates. This probably reflects the increasing difficulty of drawing tangents to the less well defined transition. Nevertheless an error in the constructed intercept of less than ±0.3 K is generally obtained.

Absolute calibration

The low temperature transition (*Te*) of cyclohexane was measured at a range of heating rates, as already described, for each set of covers used.

Various methods have been proposed for handling these data, including the plotting of *Te vs.* $V^{1/2}$ [9, 12], *Te vs.* log *V*, [13] *Te vs. V*. [14] and Te^{-1} *vs.* log *V* [15] and in this instance the results, tabulated in Table 3, are illustrated in Fig. 2 where the indicated temperature (*Te*) is plotted *vs.* $V^{1/2}$. Regression analysis to a third order polynomial gives the calibration value for the transition $Te(Vo)$ for each combination of covers used and this is then applicable to the appropriate set of data for NR.

The glass transition of NR

Mean values obtained for the observed Tg of NR, at various heating rates and with the same combination of covers that were used for studying the cyclohexane, are given in Table 4. The magnitude of the discontinuity, as illustrated by the height of the displacement $(A+B)$ in Fig. 1, is dependent upon the heating rate, making it difficult to measure, with accuracy, Tg values at slow rates; 2.5 deg/min^{-1} is a realistic lower limit on this instrument.

Table 3 Variation in the observed low temperature Te of cyclohexane induced by changing the sample holder covers

Heating rate, deg/min^{-1}	Low temperature Te			
	1*	2	3	4
80	187.9	188.6	190.0	189.1
40	187.0	186.3	187.9	187.1
20	186.1	185.0	186.6	185.9
10	185.9	184.5	185.9	185.2
5	185.4	184.2	185.5	184.8
2.5	185.1	183.9	185.2	184.7
extrapolated to '0'	184.6	183.6	184.8	184.2

* Matched covers in their usual positions.

Table 4 Variation in the observed NR Tg induced by changing the sample holder covers*

Heating rate, deg/min^{-1}	1	2	3	4
80	214.5	213.4	214.5	212.7
40	211.0	209.7	210.2	208.7
20	208.2	207.2	208.3	206.8
10	206.5	205.1	205.3	204.9
5	204.5	203.4	203.5	203.7
2.5	—	201.7	202.8	—

* Columns 1–4 correspond with those in Table 3.

One set of results (column 2) is illustrated in Fig. 3, again as a plot of Tg *vs.* $V^{1/2}$, and it will be appreciated that extrapolation to zero heating rate (Vo) leaves some margin for error. However regression analysis to a third order polynomial gives intercepts for the four columns of 199.2 K; 197.0 K; 198.8 K and 198.8 K respectively. These then require correction based on the difference between the appropriate cyclohexane literature and determined $Te(Vo)$ values to give $Tg(Vo)$ values of 200.9 K; 199.7 K; 200.3 K and 200.9 K (mean value 200.4 K).

It is however possible to adopt another approach and argue that as the differences between the cyclohexane values brought about by using different covers are due to instrumental effects, and, as it has been shown [4] that heat transfer through NR (at the weight of sample used in these studies) is neither significant in broadening nor shifting the NR Tg, the difference in heating rate dependency between the transition of cyclohexane and the NR Tg must be related to the time dependence of the glass transition itself. In this case the equation:

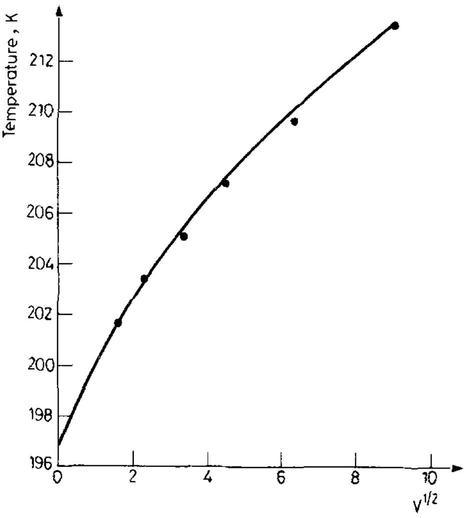

Fig. 3 Representative plot; Tg *vs.* $V^{1/2}$ (Table 4, column 2)

$$\log V = A - B\,Tg^{-1} \tag{1}$$

as derived by Wunderlich *et al.* [15] should apply.

Table 5 presents the combined data for Tables 3 and 4, where the ΔTe values represent the differences between the measured value for the NR Tg, at a particular heating rate and combination of covers, and the exactly analogous transition (Te) of the reference cyclohexane.

Figure 4 illustrates the linear relationship that exists from the application of equation 1 to those data and regression analysis gives the intercepts from which ΔTe at 1 deg/min^{-1} (i.e. log 0) can be obtained. Figure 2 suggests that the Te for cyclohexane at 1 deg/min^{-1} will be some 0.3 K above the literature $Te(Vo)$ value thus the addition of 186.6 (not 186.3 K) to the ΔT values will give the NR Tg at a scan rate of 1 deg/min^{-1}: 203.0 K; 203.4 K; 202.7 K; 203.5 K (mean 203.1 K).

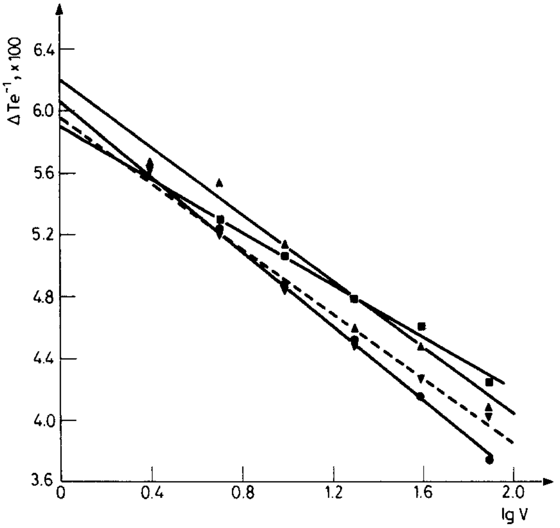

Fig. 4 Removal of instrument effects; Linear plot of $\Delta Te^{-1} \times 100$ *vs.* log V

Table 5 Difference between the temperatures of the cyclohexane Te and NR Tg at various heating rates (ΔTe)

Heating rate, deg/min^{-1}	ΔTe			
	1	2	3	4
80	26.6	24.8	24.5	23.6
40	24.0	23.4	22.3	21.6
20	22.1	22.2	21.7	20.9
10	20.6	20.6	19.4	19.7
5	19.1	19.2	18.0	18.9
2.5	—	17.8	17.6	—

Inspection of Fig. 3 shows that the difference in observed $Tg(Vo)$ and $Tg(V = 1$ deg/min$^{-1})$ is 2.7 K in excess of the cyclohexane contribution, thus the values can be further corrected to give $Tg(Vo)$:

200.3 K; 200.7 K; 200.0 K; 200.8 K (mean 200.4 K)

Because of the appreciable heating rate dependence of the cyclohexane *Te*, plots of ΔTe *vs.* $V^{1/2}$ show distinctly different curvature from those of *Te* *vs.* $V^{1/2}$. However, regression analysis of the former, again to a third order polynomial, followed by the addition of the cyclohexane *Te*(*Vo*) value of 186.3 K to each, give *Tg*(*Vo*):

200.6 K; 200.0 K; 200.6 K; and 201.1 K (mean 200.6 K)

The three methods of calculation thus give completely consistent results indicating a *Tg*(*Vo*) of 200–201 K for NR.

It is of practical interest to note that linear regression analysis of the data in Fig. 4 to a heating rate of 0.1 deg/min^{-1} (Log $V = -1$) gives intercepts which enable *Tg's* to be calculated which are within the spread for *Tg*(*Vo*) obtained using the three methods described above. It could be that linear regression analysis to log $V = -1$ is the better procedure to use when data from slow heating rates are not available, and the curvilinear regression analysis will necessarily be liable to increased error.

It is apparent that it will be time consuming to determine the absolute *Tg* of a polymer using the procedures described. This point is taken up by Burfield and Lim [4] who recommend running the polymer and calibrant at a moderate heating rate (20 deg/min^{-1}) and using the difference in *Te's* together with the literature value for the calibrant to obtain the defined polymer *Tg*; they quote 206.3 K for NR at 20 deg/min^{-1} using cyclohexane as calibrant. It is of note that their cyclohexane calibration shows no temperature dependence and thus their standard *Te* at 20 deg/min^{-1} is the same as *Te*(*Vo*). Inspection of the data given here in Tables 4 and 5 shows that, at a scan rate of 20 deg/min^{-1}, the NR *Tg* occurs some 21–22 K above the cyclohexane *Te*, whilst the cyclohexane *Te* itself is some 1.4–1.8 K above *Te*(*Vo*). On the basis of ΔT values alone this would give the NR *Tg* at about 208 K whilst, if the cyclohexane *Te* at 20 deg/min^{-1} was corrected to zero heating rate the value would be nearer 210 K.

It is therefore recommended that this type of arbitrary definition should be avoided as it could have a marked instrument dependency and it is proposed that, in a manner consistent with the quotation of melting points, the only numerical value given to the property designated '*Tg*' is that at zero scan rate *Tg*(*Vo*).

Comparative studies of glass transitions are most simply carried out at convenient scan rates in the range 10–20 deg/min^{-1} and here differences between *Tg's*, due to structural modification and molar mass variation etc. may be precisely measured. If absolute values are to be quoted the NR *Tg*, obtained at the same heating rate as the samples, should be used as a calibrant with its *Tg*(*Vo*) of 200.5 K.

Comparison with published data

It is interesting to compare these data with those published ones [3, 4] where reasonably full experimental details are supplied.

Burfield and Lim [4] present two different sets of data, one in tabular form and the other graphical. Our recalculation of their $Tg(Vo)$ using linear regression analysis of the Tg^{-1} *vs.* log V plot as described herein, and taking the displacement of cyclohexane Te with heating rate as zero (and hence the NR Tg shift between heating rates of zero and 1 deg/min^{-1} as 2.7 K), gives the data shown in Table 6.

Table 6 Comparison of literature data using the extrapolation procedure described herein (Tg^{-1} *vs.* log V)

Source	$Tg(Vo)$ K
Burfield and Lim [4]	
Table	200.0
Graphs	201.0
Kow et al [3] (L–11B)	203.4*

* Although Kow *et al.* do not define their extrapolation procedure, the difference which they quote between the synthetic polyisoprene (L–11B) and NR is 3 K, thus it may reasonably be assumed that their "equivalent NR Tg" would be 200.4 K.

The detailed data of Kow et al. [3] only refer to synthetic polyisoprenes, offer no details of calibrant Te displacement with heating rate, and claim a reproducibility of ± 1 K. Nevertheless recalculations from their data were carried out and the value obtained for $Tg(Vo)$ is also shown in Table 6.

Conclusions

The appreciable difference in heating rate dependency between any sharp transition of a standard such as cyclohexane and the broader glass transition of NR, obtained under identical operating conditions, contains a contribution due to the instrument. Whilst this may be small in terms of the variability of results from one instrument it could render invalid the comparison of data, quoted only at specific heating rates, when obtained on different instruments.

In our opinion this problem is best overcome by extrapolating glass transition data to zero heating rate, using one or more of the methods described, to obtain

Tg(*Vo*). Following the ICTA definition of *Tg*, various calculations from a wide range of experimental data consistently indicate that the *Tg*(*Vo*) value for NR is 200.5 K with probable limits of ±0.5 K.

* * *

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Zusammenfassung — Mit Hinblick auf das Fehlen genauer experimenteller Literaturdaten bezüglich definierter *Tg*-Werte für natürlichen Kautschuk und auf die Unterschiede, wenn solche Angaben gemacht werden, wird eine Bezugsdefinition für *Tg*(*Vo*) vorgeschlagen und das Verfahren, nach dem diese erhalten werden kann, in Einzelheiten beschrieben. Es wird vorgeschlagen, den für ungehärteten natürlichen Kautschuk erhaltenen Wert von 200.5 K als Tieftemperatur-Standard für die Untersuchung anderer in diesem Bereich auftretender polymerer *Tg's* zu verwenden.

Резюме — Из-за отсутствия в литературе точных данных по определению значений T_g для природного каучука или же из-за больших различий приводимых данных, предложено четкое обозначение $T_g(V_0)$ и подробная методика определения. Значение, полученное для невулканизированного природного каучука при 200,5 K, предложено использовать в качестве низкотемпературного стандарта при определении T_g для других полимеров.