

Stress Relaxation in Natural Rubber Bale Crystallisation During Storage at Low Temperatures

P. BENOIST*, R. CHASSET* AND H. DE LIVONNIERE**

To assess natural rubber crystallisation during storage at low temperatures, measurements were taken using the stress relaxation method. This method makes it possible to assess the overall crystallisation rate over a wide range of temperatures, characterised by a 'melting point' at the T_m equilibrium point, which is determined by an empirical equation.

In this study, samples used differed in terms of clonal origin, collection date, processing and drying temperature. A statistical study of these factors showed differences in performance, particularly due to drying temperature. Drying rubber at 125°C rather than 65°C seems to reduce rubber bale crystallisation during storage at low temperatures.

During storage, natural rubber gradually crystallises^{1,2}, even at temperatures of 5°C to 10°C. This phenomenon can be reversed, and prolonged heating at a sufficiently high temperature enables rubber to recover its original consistency. Experience has shown that the 'background' of natural rubber bales – in both mechanical and heat terms – particularly influences crystallisation. This is the case with residual stress induced by stacking bales on pallets, which constitutes highly propitious sites for crystallisation³. Apart from these effects, it was also interesting to look at the effects of the planting material, latex collection conditions and processing treatments at the plantation on the rate of crystallisation of rubber.

Many studies^{4,5,6} have shown that the crystallisation process can be broken down into several phases:

- the induction period, corresponding to germ formation
- primary crystallisation, when crystallites develop from the germs

- secondary crystallisation, a slow phenomenon in which no more germs develop and crystallites do not grow any larger, but probably rearrange themselves to form a more perfect crystalline structure.

It is not always possible to study germ formation and crystallite growth separately; an overall study is therefore carried out of the conversion from the amorphous to the crystalline phase. The crystallisation rate is governed by competition between two processes: germ formation, which is faster the lower the temperature, and crystallite development, linked to molecular mobility, which decreases in line with temperature. It therefore depends on temperature¹, and reaches a maximum, as shown in *Figure 1*.

Crystallisation is accompanied by variations in some physical properties of the material, each of which can be used to measure crystallinity. This study used the stress relaxation method. In effect, if the polymer is kept under a constant strain, crystallisation leads to an additional gradual

*IRAP (Institut de Recherche Appliquée sur les Polymères) – 72, avenue Olivier Messiaen, 72000 Le Mans, France

**IRCA/CIRAD (Institut de Recherches sur le Caoutchouc) – 42 rue Scheffer, 75116 Paris, France

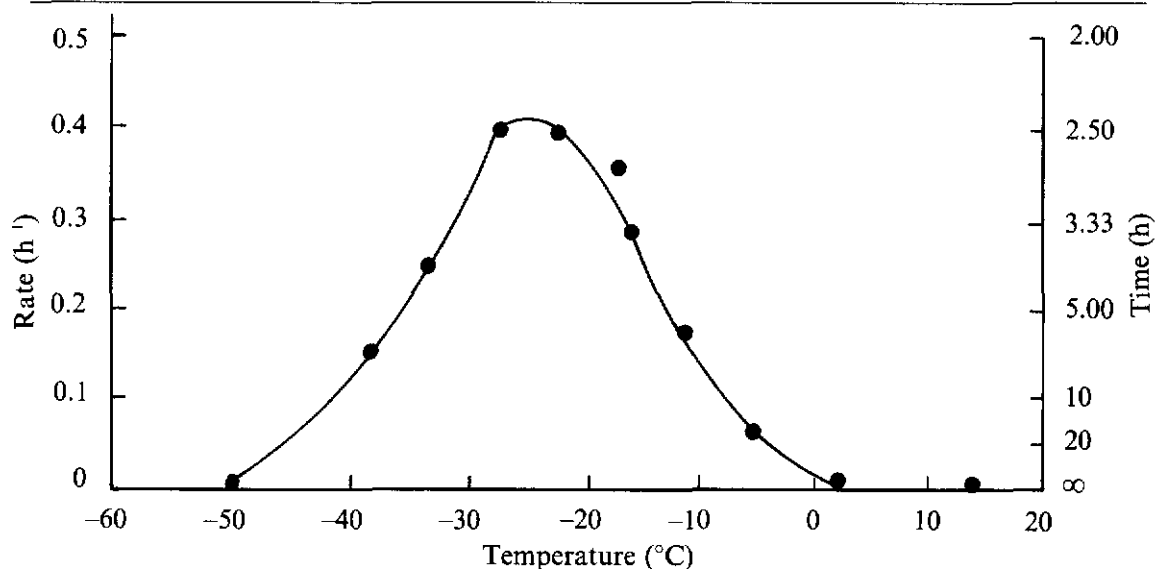


Figure 1. Natural rubber crystallisation rate ($1/t^{1/2}$) versus temperature (according to L.A. Wood and N. Bekkedahl¹).

stress relaxation, which also makes it possible to study the phenomenon over time.

MATERIALS AND METHODS

Definition of the Rubbers Studied

The rubbers were prepared at the IRCA Experimental Station in the Ivory Coast. Two clones were chosen: GT 1 and PR 107. All the latex was collected from the same groups of trees *Block A₃* for GT 1 and *Block D₇* for PR 107 – at two different periods: July and November. Three latex coagulation methods were used:

- **Method I**: Initial d.r.c., acidification to pH 5.2, 16 h maturing. *Method I* is the most commonly used method in the Ivory Coast.
- **Method II**: 15% d.r.c., coagulation by 10 g of acetic acid/kg of dry rubber (pH 4.5 after acidification), 16 h maturing. *Method II* is used to

coagulate smoked sheets (RSS) or air-dried sheets.

- **Method III**: Initial d.r.c., natural coagulation for four weeks in polythene bags under *Hevea* cover. *Method III* is a simulation of the coagulum collection method used by smallholders.

After coagulation, the rubber was processed as follows: dry crumbing in *Methods I* and *II*, creping (fed through ten times under water), followed by wet crumbing in *Method III*. The crumb was then split into two batches, one of which was dried at 65°C and the other at 125°C.

Table 1 gives the conditions for preparation of the main rubber samples and some characteristics of the raw gum produced: Mooney viscosity (MV), Wallace plasticity (P_o), plasticity retention index (PRI), nitrogen and volatile matter content size as per standard *ISO 2000*. The average molecular weight (\bar{M}_v), determined by viscosimetry*, is also given.

*Measurements were made at 25°C in toluene, based on the intrinsic viscosity value $[\eta]$, \bar{M}_v was calculated according to the equation $[\eta] = K\bar{M}_v^a$, where $K = 5.02 \times 10^{-4}$ and $a = 0.667$

TABLE 1. CONDITIONS OF PREPARATION AND SOME CHARACTERISTICS OF THE RUBBERS STUDIED

Rubber sample	Clone	Latex collection date	Coagulation method	Drying temp. (°C)	M.V.	P ₀	PRI (%)	N ₂ cont. (%)	Volatile matter (%)	$\bar{M}_v \times 10^{-6}$
22-1	GT 1	July	II	65	83	51	69	0.45	0.31	1.10
23-1				125	85	49	79	0.45	0.20	0.99
24-4		November	III	65	94	56	43	0.26	0.54	0.97
24-4B				125	83	31	31	0.23	0.25	0.56
30-2	PR 107	November	I	65	85	51	76	0.51	1.20	1.11
31-2				125	94	51	74	0.51	1.01	0.92
32-1		July	II	65	82	53	80	0.39	0.22	1.15
33-1				125	86	51	83	0.43	0.19	1.00
32-2		November	II	65	82	50	79	0.44	0.59	1.08
33-2				125	89	53	76	0.44	0.59	0.72
34-2		November	III	65	95	58	47	0.25	0.27	1.23
35-2				125	77	36	17	0.25	0.18	0.735

Stress Relaxation

Description of the relaxometer. This apparatus has already been used several times in previous studies^{7,8}. It comprises an atmospheric chamber ensuring a constant temperature – accurate to 0.2°C – within a range of –30°C to +10°C. The test-pieces are placed under strain rapidly: less than 1/10 s for extensions of 50% or less. Tensile load is measured using a stress gauge sensor. The apparatus is microcomputer-controlled, ensuring direct data input and processing.

The test-piece is a 50 mm long parallelepiped with a cross-section of 4 × 2 mm², with two rectangular end-pieces, which are fixed into stirrup clamps. This prevents the pieces slipping during the trial, as proved by a cathetometer study. The test-pieces are punched from a block of homogenised rubber (ISO 1796), moulded at 100°C in a heat cycle which cancels out the rubber's 'mechanical background' and destroys most of the residual stress and crystallite germs.

Relaxation kinetics. If there is no crystallisation, the relaxation kinetics of non-vulcanised rubbers follow a relationship of

the following type, over several decade periods:

$$f = f_{st=n} \text{ (where } n \text{ is constant).}$$

The curves obtained have a linear part on a double logarithmic scale, which slopes more sharply the higher the temperature: molecular chain slipping in relation to one another – the main cause of stress relaxation – is favoured by increased temperature. When the temperature decreases, the curve points downwards, since the chain segments are gradually incorporated into the crystallites and are no longer part of the elastic reaction. At the end of crystallisation, tensile load tends towards a nil value. Figure 2 gives an example of these curves, with variations over time in the $F = f/f_1$ ratio, where f is the strength at time t and f_1 the strength of the test-piece after 1 min strain. Time t_1 was chosen as the start of crystallisation; it corresponds to the point when deviation compared with the linear relationship is first observed. It is then easy to determine the half crystallisation time: $t^{1/2} = t_2 - t_1$ (if F_1 is the value of f/f_1 at t_1 , t_2 is the time for which $F_2 = 1/2 F_1$). It gives an overall characterisation of the rate of crystalli-

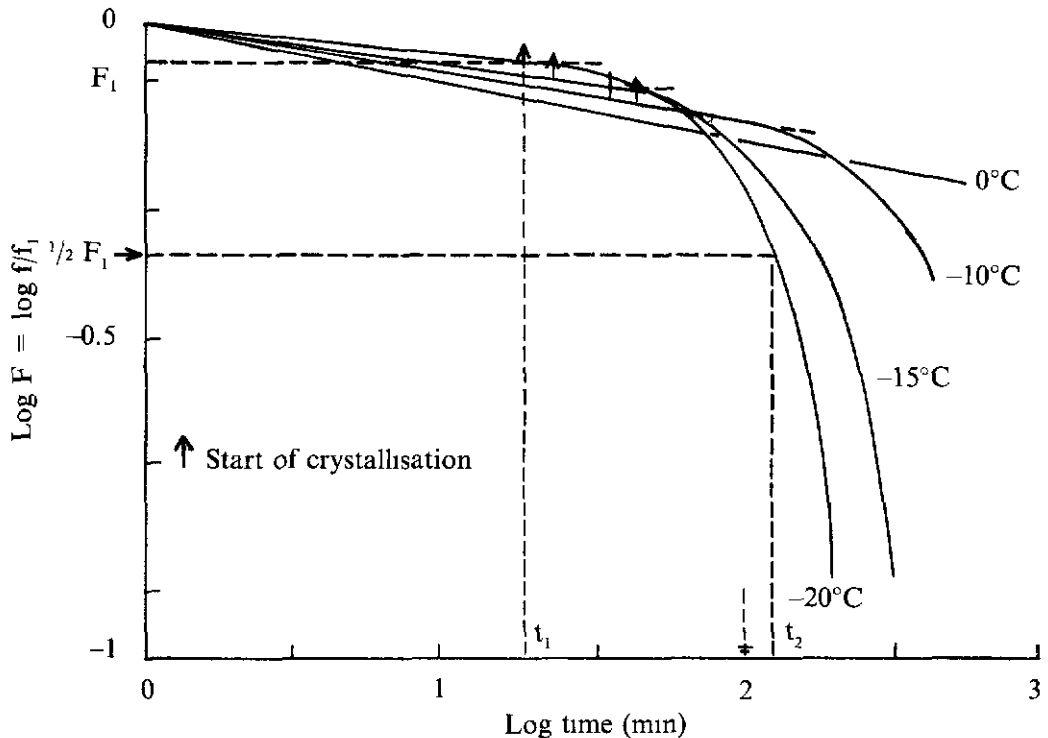


Figure 2. Stress relaxation curves for a non-vulcanised natural rubber.

sation under good conditions of reproducibility.

Exploitation of results (Bruzzone and Sorta's equation) Particular attention was paid to a quantitative description of the variations in the overall rate of crystallisation, estimated by half-time $t^{1/2}$, depending on the crystallisation temperature T_c . Based on previous theoretical work⁹ on non-stressed polymers, Guilian, Bruzzone and Sorta^{10,11} proposed a semi-empirical equation

$$\log \frac{t^{1/2}}{a\tau} = a + b \frac{T_m}{T_c (T_m - T_c)}$$

where a and b are constant. Temperature T_m is known as the 'melting point' at the point of equilibrium; $a\tau$ designates the reduction factor proposed by William *et al.*¹²

$$\log a\tau = \frac{8.86 (T - T_s)}{101.6 + T - T_s}$$

where T_s is conventionally a temperature characteristic of each polymer and equal to $T_g + 50K$. By applying this equation to the rate of crystallisation of eight different polymers, including natural rubber, the authors found that all the experimental data could be correctly represented if the same values were taken for a and b , irrespective of the polymer:

$$a = -4.61, b = 338.$$

Under these conditions, T_m becomes an adjustable parameter making it possible to simply characterise the rate of crystallisation of the sample in question. It is worth noting that the T_m values determined in this

way are higher than those given in literature, as pointed out by Kim and Mandelkern⁹. It is possible that the differences between the two sets of determinations could be explained by the different ways in which the equilibrium was prepared.

Using Bruzzone and Sorta's equation, a set of $t^{1/2}$ values were measured at x crystallisation temperatures $(T_c)_i$, on a polymer sample. To assess the melting point T_m of a sample, it is possible to calculate the $(T_m)_i$ corresponding to each temperature $(T_c)_i$, simply by applying Bruzzone and Sorta's equation and then taking the average of the $(T_m)_i$ values determined. The distribution of results can be explained by the standard deviation σ in the distribution of $(T_m)_i$ values.

EXPERIMENTAL RESULTS

Effect of Extension

Variations in $t^{1/2}$ depending on extension of between 10% and a maximum of 100% were determined on *Sample 22-1*. As extension favours macromolecular chain orientation, $t^{1/2}$ values are lower the greater the test-piece extension. This means that the rate of crystallisation $1/t^{1/2}$ is faster the greater the extension, as shown in *Figure 3* at three temperatures: -10°C , -15°C and -20°C . In addition, there is a close correlation between $\log 1/t^{1/2}$ and extension, which tallies with Gent's observations¹³.

Hence, for the rest of the study, a relatively moderate uniform strain of 30% was taken so as not to alter the classification

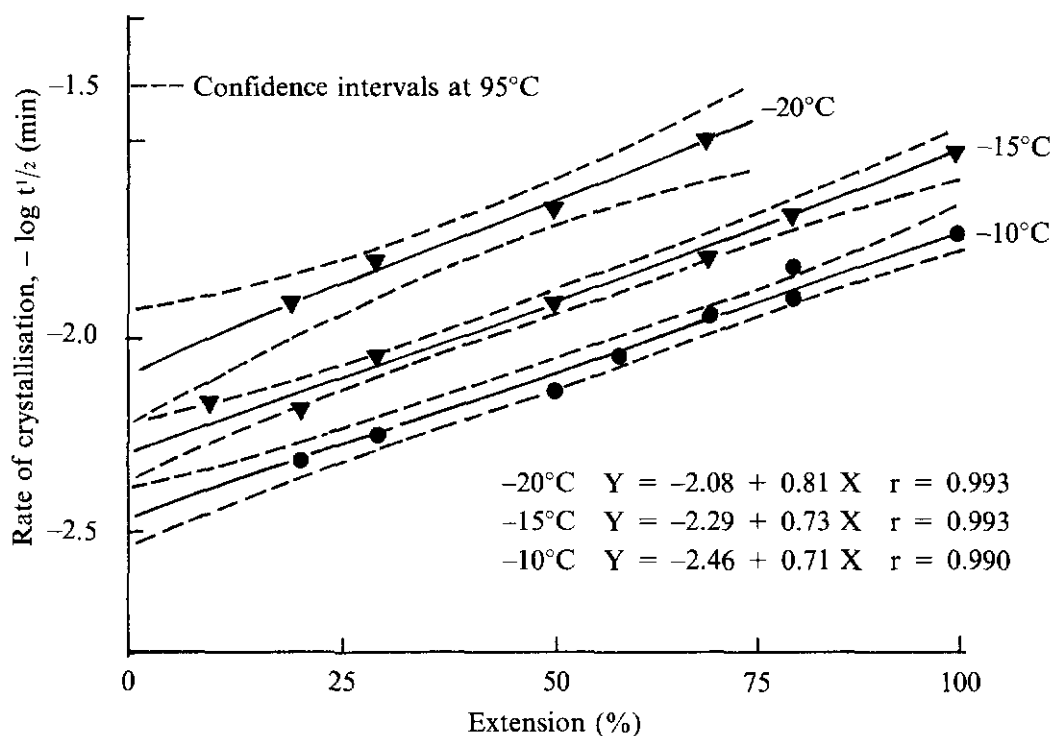


Figure 3. Effect of extension on rate of crystallisation of rubber sample 22-1.

of the various rubbers examined, but enough to accurately measure strength variations over time.

Rate of Crystallisation of the Samples Studied

For each of the above natural rubber samples, the half crystallisation time $t^{1/2}$ were measured by stress relaxation, depending on the temperature within a range of -27°C to -5°C , the upper limit depending on the rate of crystallisation.

Based on these experimental data and using Bruzzone and Sorta's equation, as in the above procedure, it was possible to give each sample a melting temperature T_m , for which values are given in Table 2, in addition to the standard deviation σ of the (T_m) values, the coefficient of distribution $e\%$, the $t^{1/2}$ value (min), calculated at -5°C and the rate $V = 1/t^{1/2}$ (day^{-1}), again at -5°C . Examination of Table 2 shows a very wide distribution of the standard deviation σ , which ranges from 0.23 (Sample 24-4) to 1.64 (Sample 32-2), a marked Gaussian distribution which is difficult to explain

except by the inevitable sources of error when taking particularly difficult measurements. Nevertheless, the curves in Figure 4 show that a melting temperature T_m , based on Bruzzone and Sorta's equation, makes it possible to satisfactorily represent experimental results, except for Sample 32-2, where there is a certain distortion, and – to a lesser degree – for Sample 30-2. In addition, variations in temperature T_m are relatively large: 5° (from 311.8K for Sample 25-4B to 316.8K for Sample 32-2), corresponding to rates of crystallisation at -5°C which can vary within a ratio of 1:6.2. Based on T_m values and distribution, it is worth looking at the effect – on a statistical level – of certain natural rubber production factors on the rate of crystallisation.

'Clone' effect. Only two clones were considered in this study: GT 1 and PR 107, with only one 'sheet' type coagulation method (Method II): Samples 22-1 and 32-1 (dried at 65°C) and Samples 23-1 and 33-1 (dried at 125°C). Table 3 gives a statistical analysis of the results based on a comparison of mean T_m values, according to Student's method, which uses the 't test'.

TABLE 2. RESULTS OBTAINED BY APPLYING BRUZZONE AND SORTA'S EQUATION TO THE RUBBERS STUDIED

Rubber sample	\bar{T}_m (K)	σ	$e\%$	$t^{1/2}$ at -5°C (min)	$v = 1/t^{1/2}$ at -5°C (days^{-1})
22-1	315.8	1.22	0.39	245	5.88
23-1	312.1	1.09	0.35	960	1.50
24-4	313.0	0.23	0.07	675	2.13
25-4B	311.8	0.59	0.16	1085	1.33
30-2	314.6	1.26	0.40	375	3.84
31-2	313.6	0.52	0.16	540	2.67
32-1	316.0	1.15	0.36	230	6.26
32-2	316.8	1.64	0.52	175	8.22
33-1	312.5	0.47	0.15	820	1.76
33-2	315.4	0.67	0.21	280	5.14
34-2	316.7	0.83	0.26	180	8.00
35-2	312.2	0.42	0.13	925	1.56

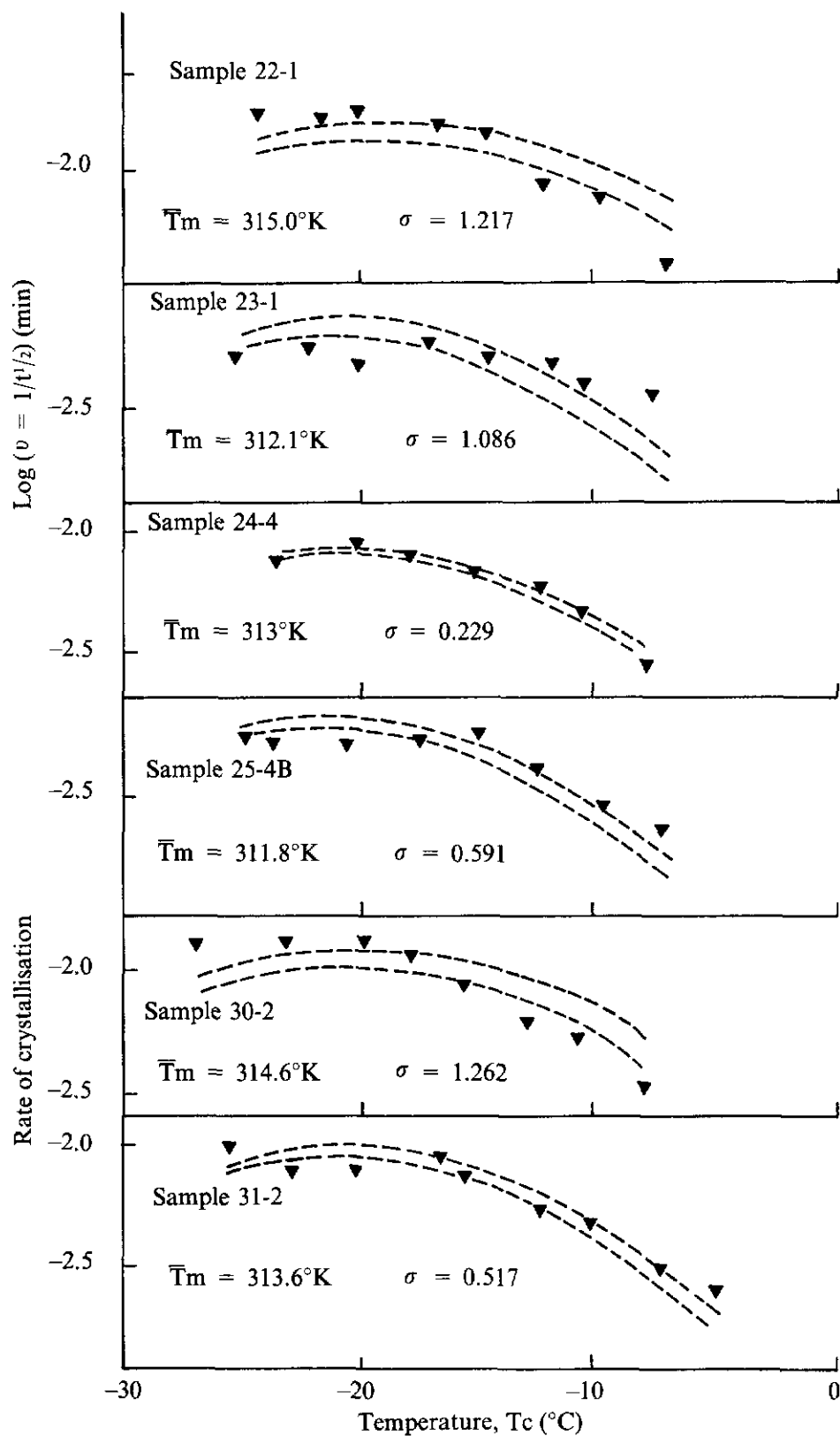


Figure 4. Bruzzone and Sorta's equation applied to experimental results: rubber samples 22-1, 23-1, 24-4, 25-4B, 30-2, and 31-2,

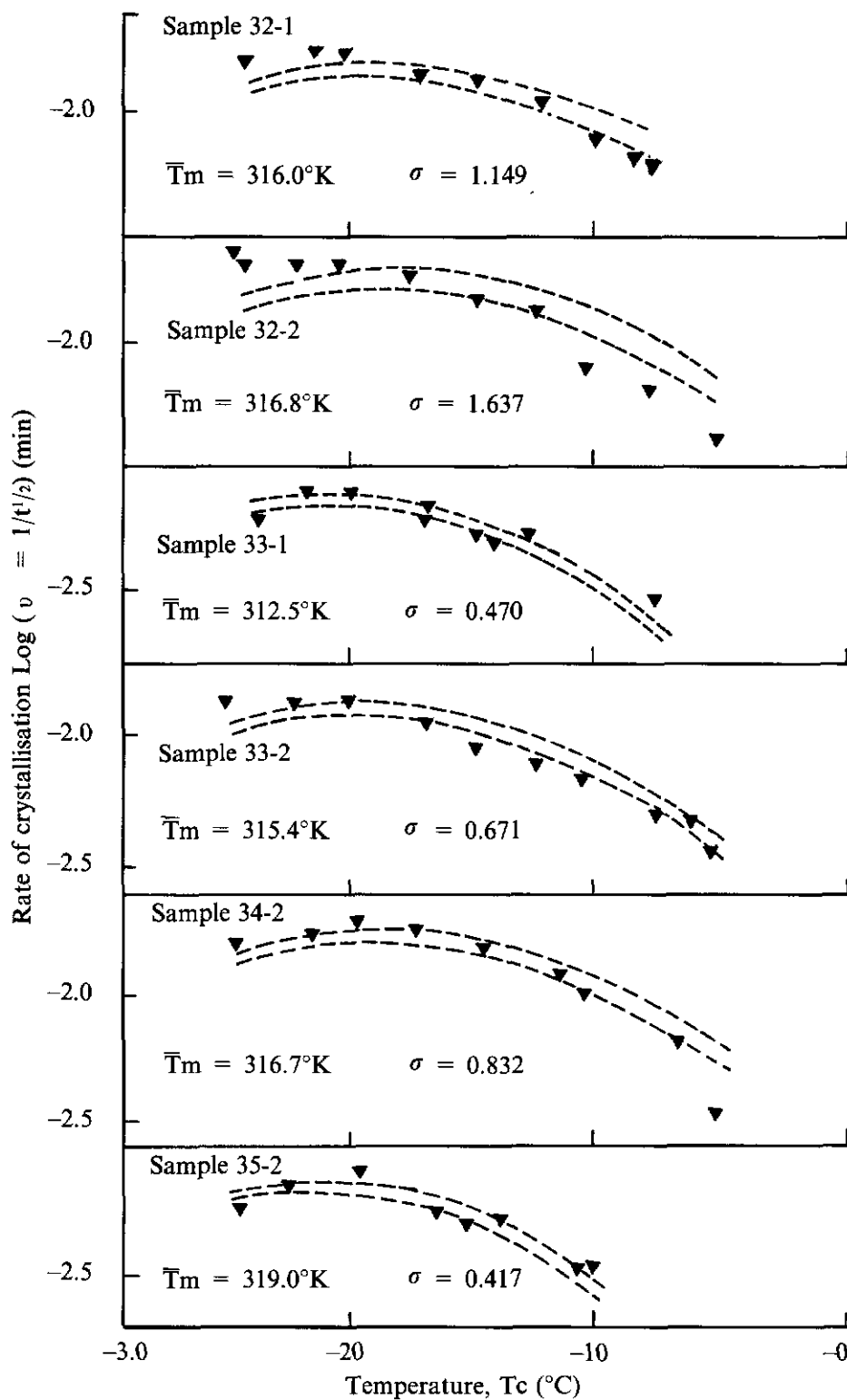


Figure 4 (contd.) Bruzzone and Sorta's equation applied to experimental results: rubber samples 32-1, 32-2, 33-1, 33-2, 34-2 and 35-2.

TABLE 3. STATISTICAL ANALYSIS - 'CLONE' EFFECT

Rubber sample	Clone	Drying temp. (°C)	T _m (K)	σ	n	t	Ø	Significance	v (d ⁻¹) at -5°C
22-1	GT 1	65°C	315.8	1.22	8	0.35	15	Not significant	5.88
32-1	PR 107		316.0	1.15	9				6.26
23-1	GT 1	125°C	312.1	1.09	8	1.01	15	Not significant	1.50
33-1	PR 107		312.5	0.47	9				1.76

Under the experimental conditions in question, there was no significant difference between the rubbers produced from GT 1 and PR 107 latex.

'Collection date' effect. This study also only involved a limited number of samples, all produced from clone PR 107, 'sheet' type coagulation (*Method II*): *Samples 32-1* and *32-2* (dried at 65°C) and *Samples 33-1* and *33-2* (dried at 125°C). The statistical analysis is given in *Table 4*. There is no difference between the two samples dried at 65°C. However, for the samples dried at 125°C, the rubber prepared in July crystallised about three times less quickly than the rubber collected in November of the same year.

'Coagulation method' effect. The six samples considered came from the same clone - PR 107 - and corresponded to the three methods of coagulation studied:

- *Method I* : *Samples 30-2* and *31-2*
- *Method II* : *Samples 32-2* and *33-2*
- *Method III* : *Samples 34-2* and *35-2*

Three rubbers (*Samples 30-2*, *32-2* and *34-2*) were dried at 65°C and the others

(*Samples 31-2*, *33-2* and *35-2*) at 125°C. *Table 5* gives a statistical analysis of the results.

There are highly significant differences, except for the *Samples 32-2/34-2* pair, dried at 65°C after coagulation as in *Method II* and *Method III* respectively. In other words, based on the rate of crystallisation at -5°C, it is possible to sum up the 'coagulation method' effect as follows:

$$\begin{array}{ll} \text{Drying at 65°C} & \text{Drying at 125°C} \\ v_{II} \ v_{III} > v_I & v_{II} > v_I > v_{III} \end{array}$$

Taking the lowest rate - *Sample 35-2* - as a reference, the following quantitative classification is obtained (in increasing order of rate):

$$\begin{array}{ll} v_{III} & = \ 1) \\ v_I & = \ 1.7) \text{ dried at 125°C} \\ v_{II} & = \ 3.3) \\ v_I & = \ 2.5) \text{ dried at 65°C} \\ v_{II} \ v_{III} & = \ 5.2) \end{array}$$

TABLE 4. STATISTICAL ANALYSIS - 'LATEX COLLECTION DATE' EFFECT

Rubber sample	Latex collection date	Drying temp. (°C)	T _m (K)	σ	n	t	Ø	Significance	v (d ⁻¹) at -5°C
32-1	July	65	316.0	1.15	9	1.24	18	Not significant	6.26
32-2	November		316.8	1.64	11				8.22
33-1	July	125	312.5	0.47	9	10.8	17	Highly significant	1.76
33-2	November		315.4	0.67	10				5.14

TABLE 5. STATISTICAL ANALYSIS - 'COAGULATION METHOD' EFFECT

Rubber sample	Coagulation method	Drying temp. (°C)	\bar{T}_m (K)	σ	n	t	ϕ	Significance	v (d ⁻¹) at -5°C
30-2	I	65	314.6	1.26	9	3.30	18	Highly significant	3.84
32-2	II		316.8	1.64	11				8.22
30-2	I		314.6	1.26	9	4.17	16	Highly significant	3.84
34-2	III		316.7	0.83	9				8.00
32-2	II		316.8	1.64	11	0.17	18	Not significant	8.22
34-2	III		316.7	0.83	9				8.00
31-2	I	125	313.6	0.52	9	6.50	17	Highly significant	2.67
33-2	II		315.4	0.67	10				5.14
31-2	I		316.6	0.52	9	6.10	15	Highly significant	2.67
35-2	III		312.2	0.42	8				1.56
33-2	II		315.4	0.67	10	11.8	16	Highly significant	5.14
35-2	III		312.2	0.42	8				1.56

'Drying temperature' effect. Six sets of two samples, one dried at 65°C and the other at 125°C, were examined. Two sets were from clone GT 1, coagulated as in *Method II* or *Method III*; the other four sets were from

clone PR 107 coagulated as in *Methods I, II* and *III*. For *Method II*, latex collected at two different times was used (*Table 6*). *Table 6* shows that irrespective of the clone, and allowing for the coagulation method

TABLE 6. STATISTICAL ANALYSIS - 'DRYING TEMPERATURE' EFFECT

Rubber sample	Drying temp. (°C)	Coagulation method	\bar{T}_m (K)	σ	n	t	ϕ	Significance	v (d ⁻¹) at -5°C
22-1	65	II	315.8	1.22	8	6.41	14	Highly significant	5.88
23-1	125		312.1	1.09	8				1.50
24-4	65	III	313.0	0.23	7	5.03	13	Highly significant	2.13
25-4B	125		311.8	0.59	8				1.33
30-2	65	I	314.6	1.26	9	2.20	16	Significant	3.84
31-2	125		313.6	0.52	9				2.67
32-1	65	II	316.0	1.15	9	8.46	16	Highly significant	6.26
33-1	125		312.5	0.47	9				1.76
32-2	65	II	316.8	1.64	11	2.51	19	Significant	8.22
33-2	125		315.4	0.67	10				5.14
34-2	65	III	316.7	0.83	9	13.8	15	Highly significant	8.00
35-2	125		312.2	0.42	8				1.56

and the collection date, rubbers dried at 65°C crystallise more rapidly than those dried at 125°C. The differences observed are generally highly significant, except for two cases, where they are only significant:

- Samples 30-2/31-2 PR 107 latex collected in November, coagulated as in *Method I*
- Samples 32-2/33-2 PR 107 latex collected in November, coagulated as in *Method II*.

In quantitative terms, the mean rates of crystallisation at -5°C were 5.72 and 2.33 for the samples dried at 65°C and 125°C respectively. On the whole, rubbers dried

at 65°C crystallise about 2.5 times faster at -5°C than those dried at 125°C.

DISCUSSION

The study of the 'drying temperature' effect involved twelve rubbers; it has been seen that: $v_{65^\circ\text{C}} > v_{125^\circ\text{C}}$ with a ratio of 1:2.5. It is worth comparing this observation with the correlation between the melting point at equilibrium T_m , which gives an overall characterisation of rate of crystallisation, and average molecular weight \bar{M}_v (Figure 5): the greater the \bar{M}_v value, the higher the T_m value, corresponding to a rubber which crystallises more slowly. In fact, all else being equal, drying at 125°C

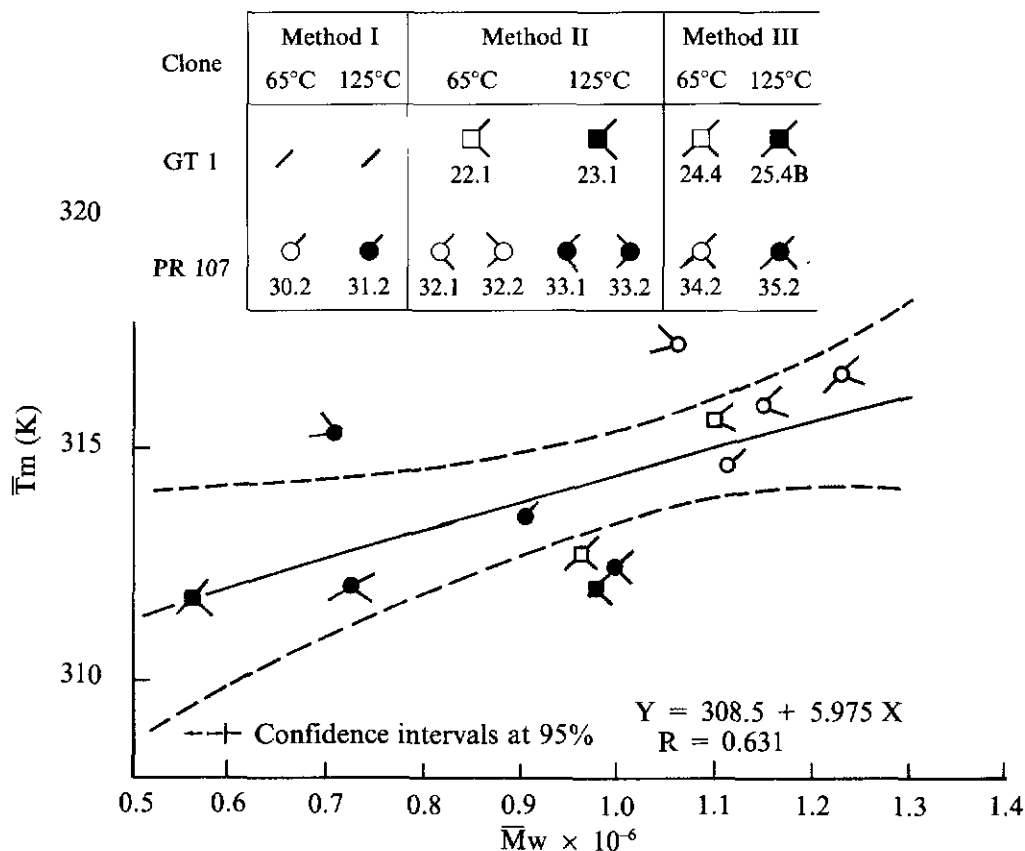


Figure 5. Correlation between melting point \bar{T}_m and average molecular weight \bar{M}_v .

reduces molecular weight to some extent, as shown in *Table 1* and *Figure 5*. This reduction in \bar{M}_v leads to a larger number of chain ends, which act as a dilutant as crystallisation develops⁵, hence reducing the rate of crystallisation. In other words, drying rubbers at 125°C is worthwhile, since it tends to slow crystallisation during storage at low temperatures, without altering the mechanical properties of vulcanisates. As far as the other effects are concerned, differences are harder to find.

The study of the 'coagulation method' effect only considered clone PR 107. The statistical analysis showed that irrespective of drying temperature $v_{II} > v_I$ (can be as much as double), rubber coagulated as in *Method III* and dried at 65°C crystallises rapidly (as with *Method II*), whereas rubber dried at 125°C crystallises more slowly.

Methods I and *II* differ in terms of latex dilution and the more acidic medium used in *Method II* (where the pH is 4.5 after acidification as against 5.2 for *Method I*). The lower the pH, the higher the non-rubber element content, and non-rubber elements, particularly fatty acids, are all possible germination sites and crystallisation triggers, which could explain the different rates of crystallisation observed between rubber prepared by *Methods I* and *II*. To confirm this hypothesis, the method should be developed so as to systematically titrate fatty acids. However, it is difficult to explain the classification of samples coagulated naturally (*Method III*).

As far as the 'latex collection date' effect is concerned, too few trials were carried out. Whereas there is no difference between the two rubbers dried at 65°C, the samples dried at 125°C perform differently: the rubber produced from latex collected in July ($v = 1.76 \text{ days}^{-1}$) crystallises around three times less quickly than rubber prepared in November ($v = 5.14 \text{ days}^{-1}$). According to monthly rainfall records,

1636 mm of rain fell in the three months up to the July collection, whereas only 159 mm fell during the three months up to November. Although this had no notable effect on d.r.c., this significant difference in rainfall necessarily affected the water balance in the tree and consequently latex composition. However, this phenomenon has not yet been explained.

As regards the 'clone' effect, there is no difference between GT 1 and PR 107 with respect to the treatments studied. It is worth noting that Bristow and Sears³ mentioned that by looking at a larger number of clones, they had detected a degree of clone effect, but as all commercial rubbers are blends of various clones, this is of no practical relevance.

CONCLUSION

The stress relaxation method seems to be appropriate for measuring the rate of crystallisation of natural rubber during storage at low temperatures, and can easily be used to record trial results. The study of samples prepared on plantations under clearly defined conditions made it possible to put forward hypotheses on seasonal and coagulation method effects. It was also shown that drying at high temperatures, for example 125°C, tends to slow the rate of crystallisation.

From a practical point of view, the effect of these various factors combines with that of residual mechanical stress within the rubber bales, due to actual storage conditions.

ACKNOWLEDGEMENTS

The authors thank J.L. Mary and J. Roboam for assistance in conducting the experiments and J.P. Villette for his contribution in molecular weight measurements.

Date of receipt: February 1992

Date of acceptance: April 1992

REFERENCES

1. WOOD, L.A. AND BEKKEDAH, N. (1946) *J. appl. Phys.*, **17**, 362.
2. TRELOAR, L.R.G. (1975) *The Physics of Rubber Elasticity*. Oxford University Press.
3. BRISTOW, G.M. AND SEARS, A.G. (1982) The Freezing and Thawing of Natural Rubber. *NR Technology*, **13**, 73
4. FLORY, P.J. (1953) *Principles of Polymer Chemistry*. New York: Cornell University Press.
5. MEARES, P. (1965) *Polymers, Structure and Bulk Properties*. London: D. Van Nostrand Co. Ltd.
6. AVRAMI, M. (1939) *J. Chem. Phys.*, **7**, 1103; (1940) **8**, 212; (1941) **9**, 177.
7. CHASSET, R. (1973) *CNRS Conf. Obernai, France No. 231*, 193.
8. CHASSET, R., LEROY, G. AND THIRION, P. (1977) Relaxation de vulcanisats de caoutchouc naturel comportant differents types de liaisons pontales. *Caoutchs. Plast.*, **54**(573), 109.
9. KIM, H. AND MANDELKERN, L. (1968) Temperature Dependence of the Bulk Crystallization Rate of Polymers. *J. Polym. Sci.*, **A2**, **6**, 695.
10. GIULIANI, M. AND SORTA, E. (1974) *Polym. Lett. Ed.*, **12**, 375.
11. BRUZZONE, M. AND SORTA, E. (1978) *Polymer*, **19**, 467.
12. FERRY, J.D. (1980) *Viscoelastic Properties of Polymers*. New York: Wiley.
13. GENT, A.N. (1966) Crystallization in Stretched Polymer Networks. II. *Trans-polyisoprenes*. *J. Polym. Sci.*, **A2**, **4**, 447.