

severed particles were detected, while deformed particles were absent. These findings appear consistent with the crazing mechanism of rubber reinforcement<sup>2</sup>, where the crazes are initiated by the rubber particles and where the specimen deformation is primarily due to the extension of the crazes. In this fashion, the craze fracture would produce fractured particles but no per-

manently deformed whole particles. Deformed particles may be expected, however, with polymers, where shear yielding is a predominant mechanism.

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## Elastomer structures and 'cold crystallization'

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#### INTRODUCTION

In a great number of applications an ideal elastomer should satisfy, to a certain extent, both of the following requirements: (i) nearly instantaneous crystallization upon application of strain (strain induced crystallization) and (ii) slow or no crystallization when cooled at the temperature of maximum crystallization rate (cold induced crystallization). A noteworthy case of (ii) is elastomer crystallization in a strained state.

The connection between the points (i) and (ii) has not been clearly understood up to now, but it is known that some crystallizable elastomers fulfil the requirements of both (i) and (ii) better than others. From an experimental point of view, cold induced crystallization kinetics are substantially easier to measure than those of very fast strain induced crystallization.

The phenomenon of cold induced crystallization in natural rubber, NR, has been known since the very beginning of elastomer technology and the tendency of natural rubber to crystallize by cooling has been overcome by crosslinking it with sulphur (vulcanization) without impairing its ability to crystallize by stretching (Goodyear 1836).

The synthesis of *cis*-polyisoprenes, IR, and *cis*-polybutadiene, BR, of different microstructural purity (different *cis* content) gave the possibility of changing the crystallization rate<sup>1</sup>. It has also been reported that the very

fast cold crystallization of *trans*-polybutadiene, TPA, could be reduced by lowering the *trans* content<sup>2</sup>. The same fact had been observed earlier for *trans*-polychloroprene<sup>3</sup>.

There is a general agreement in postulating that the reduction of the crystallization rate, obtained either by crosslinking or by chain regularity reduction, can be linked with the lowering of the melting point<sup>4</sup>. In both cases the low level of structural defects introduced in the chains does not affect the glass transition temperature in such a way as to vary the crystallization rate.

The aim of this paper is to emphasize the importance of the variations of the glass transition temperature and melting point on the elastomeric cold crystallization rate and the way these may be used in planning new elastomer structures.

#### DISCUSSION

We have shown<sup>5</sup> that the crystallization rate of several different uncrosslinked elastomers, expressed in terms of crystallization half time  $t_{1/2}$ , essentially depends on three variables. Two of these are peculiar to the elastomer structure, i.e. the glass transition temperature ( $T_g$ ) and the 'melting temperature'  $T_m^0$ , defined below. The third is the experimental crystallization temperature ( $T_c$ ).

The expression connecting  $t_{1/2}$  with these variables is:

$$\log_{10} \frac{t_{1/2}}{a_T} = a + b \frac{T_m^0}{T_c(T_m^0 - T_c)} \quad (1)$$

with  $a = -4.61$  and  $b = 338$ .  $a_T$  is a reduction factor to refer all elastomers to a state of uniform segmental mobility. The reduction factor employed is the Williams, Landel and Ferry relation:

$$\log_{10} a_T = -8.86(T_c - T_s) / (101.6 + T_c - T_s)$$

with  $T_s = T_g + 50K$ .

$T_m^0$  is an adjustable parameter which we call 'melting point', chosen so that all the experimental results lie on the same straight line when equation (1) is plotted as  $\log_{10} t_{1/2}/a_T$  versus  $T_m^0 / T_c(T_m^0 - T_c)$ . The  $T_m^0$  found in this way are related to the experimental ones, although they are slightly higher<sup>9</sup>.

Equation (1) is similar to that obtained by Hoffman<sup>6</sup> in which  $b$  is a function of the melting enthalpy and the interfacial free energy for lateral and end surfaces of the crystal. The novelty, in our approach, lies in the

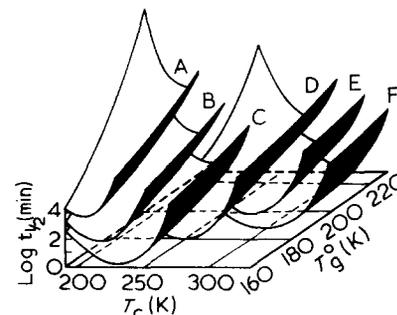


Figure 1 Plot of  $\log t_{1/2}$  vs.  $T_c$  and  $T_g$  for different values of  $T_m^0$ .  $T_m^0$  values: A, 260K; B, 280K; C, 300K; D, 320K; E, 340K; F, 360K

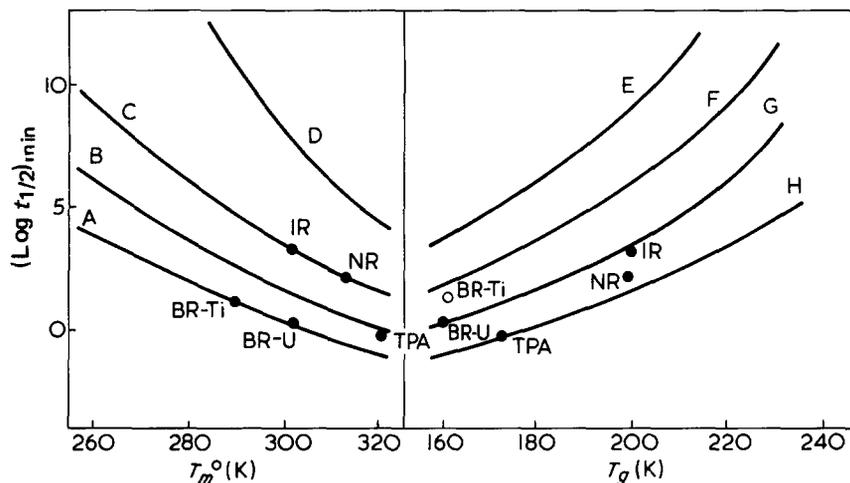


Figure 2 Plot of  $(\log t_{1/2})_{\min}$  vs.  $T_m^0$  or  $T_g$  for different values of  $T_g$  and  $T_m^0$ , respectively.  $T_g$  values: A, 160K; B, 180K; C, 200K; D, 230K.  $T_m^0$  values: E, 260K; F, 280K; G, 300K; H, 320K

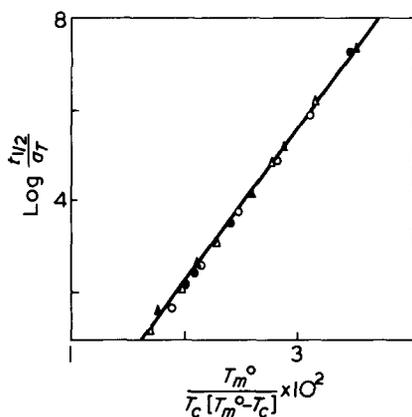


Figure 3 Plot of  $\log t_{1/2}/aT$  vs.  $[T_m^0 / (T_m^0 - T_c)] \times 10^2$  for *trans*-polyisoprene (Gent's data) crystallized at different crosslinking density.  $\nu \times 10^4$  (mol/cm<sup>3</sup>):  $\blacktriangle$ , 1.89;  $\nabla$ , 1.52;  $\blacksquare$ , 0.83;  $\blacklozenge$ , 0.67;  $\bullet$ , 0.47;  $\times$ , 0.28-0

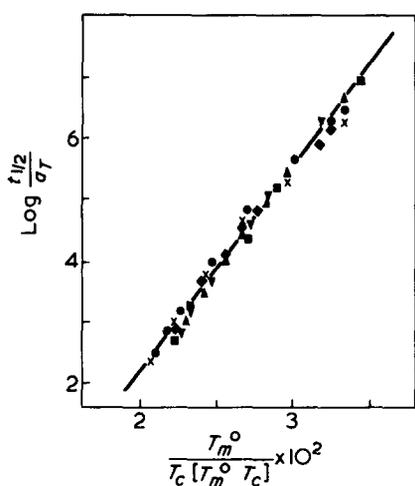


Figure 4 Plot of melting point depression versus crosslinking density for elastomers vulcanized with different recipes and our theoretical data.  $\blacktriangle$ , PB-U vulcanized with sulphur;  $\circ$ , PB-Ti vulcanized with sulphur;  $\times$ , PB-Ti vulcanized with Sulphasan R;  $\bullet$ , *trans*-PI vulcanized with DCP;  $\triangle$ , our work

fact that  $a$  and  $b$  are constant for all the examined elastomers within the limit of accuracy necessary for good forecasting of the cold crystallization rate. Therefore, the behaviour of every elastomer can be defined by the two variables  $T_m^0$  and  $T_g$ .

Going back to the relation between cold induced crystallization and structural purity it can also be shown (see Experimental) that the experimental data obtained on crosslinked and strained samples are well fitted by equation (1) and explained in terms of change of  $T_m^0$  due to microstructural purity, crosslinking or strain. The change in  $T_m^0$  agrees with experimental data<sup>1,7,8</sup>.

For tailoring new elastomeric structures, less prone to cold crystallization, it is useful to examine closely any possible significance of equation (1).

Equation (1) has been plotted in three dimensions in Figure 1 as  $\log_{10}$  versus  $T_c$  and  $T_g$  instead of a concise plot previously reported<sup>5</sup>, in which the various elastomers were represented in the form of half-straight lines.

For each  $T_m^0$  we have a surface in the form of a 'bent tile'. This representation clearly shows the importance of the minimum of  $\log_{10} t_{1/2}$ , which is characteristic for every elastomeric structure, defined by the two variables,  $T_g$  and  $T_m^0$ . If the value of  $t_{1/2}$  corresponding to the minimum is larger than the time of permanence at low temperature, specific for the elastomer end used, the problem of cold crystallization is overcome.

$(\log t_{1/2})_{\min}$  has been reported in Figure 2 as a function of  $T_g$  for different  $T_m$  and as a function of  $T_m$  for different  $T_g$ .

These two sets of theoretical curves

are approximately mirror-like, i.e. similar variations of  $T_g$  or  $T_m^0$  are necessary for the same variation of  $(\log_{10} t_{1/2})_{\min}$ .

In synthesizing a new crystallizable elastomer, both  $T_m^0$  and  $T_g$  should be taken into account with reference to the temperature range experienced by the elastomer in the application, and with reference to the duration of low temperature exposure. The locations corresponding to several elastomeric structures synthesized so far are reported in Figure 2. For IR and NR the experimental points coincide with the theoretical ones but for other polymers there are no experimental data. It appears that most elastomers have too low a  $T_g$ , except *cis*-polyisoprene and *trans*-polychloroprene. It is inferred that a control of cold crystallization of low  $T_g$  elastomers can be achieved only by lowering the  $T_m^0$  which could affect the possibility of having good strain crystallization.

In conclusion, it appears that there is a lack of crystallizable elastomeric structures having  $T_g$  comparable to that of *cis*-polyisoprene available to test

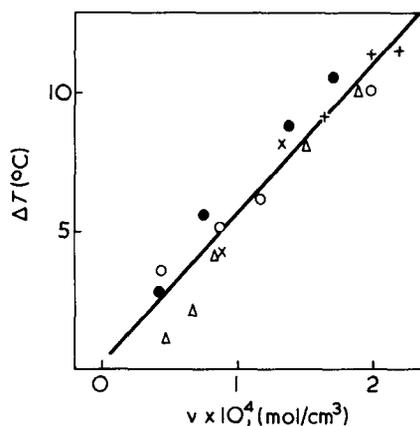


Figure 5 Plot of  $\log t_{1/2}/aT$  vs.  $[T_m^0 / (T_m^0 - T_c)] \times 10^2$  for *trans*-polychloroprene stretched and crystallized at different elongation (Gent's data).  $\alpha$  values:  $\bullet$ , 1;  $\circ$ , 2;  $\triangle$ , 3;  $\blacktriangle$ , 4

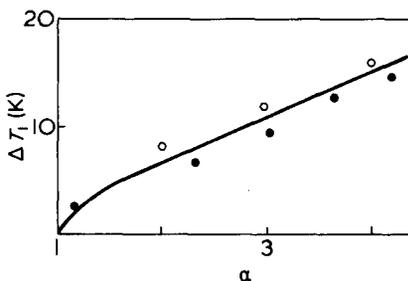


Figure 6 Plot of melting point increment for *trans*-polychloroprene.  $\bullet$ , Gent's data;  $\circ$ , our theoretical data

their response to the requirements (i) and (ii) in comparison with the low  $T_g$  structures synthesized so far.

## EXPERIMENTAL

Equation (1) has already been tested for elastomers subjected to small variations of chain regularity<sup>1</sup>. Data available in the literature also allows us to extend the validity of equation (1) for cross-linked elastomers.

Gent's data<sup>8,7</sup> on crystallization of 1,4-*trans*-polyisoprene and 1,4-*trans*-polychloroprene with different cross-linking density ( $\nu$ ) fit equation (1) well, as shown in *Figure 3* for the case of *trans*-polyisoprene, showing a decrease of  $T_m^0$  only as  $\nu$  increases. These  $\Delta T$  are plotted (*Figure 4*) together with those found experimentally by Gent<sup>8</sup> for 1,4-*trans*-polyisoprene and those obtained for polybutadienes with different 1,4-*cis* content (BR-U and BR-Ti are polymerized with uranium

and titanium catalyst, respectively) and crosslinked using different recipes (DCP = dicumylperoxide; Sulfasan R = 4,4'-dithiomorpholine).

The validity of equation (1) for elastomers strained at different elongation ratios ( $\alpha$ ) was also tested using Gent's data<sup>7</sup> on 1,4-*trans*-polychloroprene as shown in *Figure 5*, showing an increase of  $T_m^0$  only with  $\alpha$ .

The differences,  $\Delta T$ , between  $T_m^0$  for  $\alpha \neq 1$  and  $T_m^0$  for  $\alpha = 1$  as a function of  $\alpha$ , together with the experimental  $\Delta T$  obtained by Gent<sup>7</sup> and reported in the same paper are plotted in *Figure 6*.

Of course, the fact that the slope of equation 1 does not depend on enthalpy of fusion  $\Delta H_u$ , which is different for different elastomers, does not mean that it is not important for elastomer crystallization.

The influence of  $\Delta H_u$  should play a very important role in determining the variation of  $T_m^0$  as a function of elongation as represented by the well known equation due to Flory:

$$\frac{1}{T_{m,1}^0} - \frac{1}{T_{m,\alpha}^0} = \frac{R}{\Delta H_u} \left[ (6/m\pi)^{1/2} \alpha - \frac{1}{m} \frac{\alpha^2}{2} + \frac{1}{\alpha} \right]$$

where  $m$  is the number of equivalent freely jointed links per network chain.

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## On lamellar organization in banded spherulites of polyethylene

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### INTRODUCTION

One of the central problems in polymer materials science is to understand the lamellar organization within spherulites. Until very recently little progress had been made in this area for more than a decade but the introduction of two new morphological techniques has radically altered the situation. For example, elsewhere<sup>1</sup> we have described the highly ordered lamellar organization shown by polyethylene spherulites of intermediate molecular weight grown very slowly under Regime I conditions<sup>2</sup>. This consists of radiating sheets, composed of alternating {201} facets, growing out along  $b$  as spherulitic radius. A preliminary, as yet unpublished, survey of polyethylene spherulites grown under other conditions has shown that

the above is an optimum morphology in the sense that lamellae are less ordered in all other cases examined. In particular the regular faceting tends to disappear and is replaced at lower crystallization temperatures by sheets whose end-on profile (i.e. viewed down  $b$ ) is approximately a shallow S. Lamellar lengths along the radius also decrease. This note concerns further aspects of lamellar organization in banded spherulites, as typically produced by quenching molten polyethylene, and especially the question of whether they contain ribbon-like lamellae helicoidally twisted about the radius.

Detailed optical<sup>3-6</sup> and X-ray<sup>7</sup> studies in the past reached the conclusion that the molecular orientation in banded spherulites of polyethylene rotated continuously about the  $b$  axis

in travelling along a radius. The corresponding lamellar geometry has still not, however, been determined. There is little beyond Fischer's famous photograph<sup>8</sup> showing that the optical banding corresponds to an alternation of regions having radial lamellae lying successively in and perpendicular to the plane of the page. All this evidence in combination with what has been believed to be a radial fibrosity has led to the well-known airscrew model according to which the spiralling molecular orientation is accommodated within helicoidally twisted lamellar ribbons lying parallel to the radii. Two such airscrew-like lamellae are depicted in the figure of Kawai<sup>9</sup> which has been widely reproduced despite the obvious problems of packing greater numbers of helicoids that this particular representation would entail. Keller and Sawada<sup>10</sup>, in their studies of banded polyethylene spherulites degraded by nitric acid uncovered some lamellar stacks which were apparently compatible with this twisted lamellar model. They also con-