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METHODS FOR INCREASING THE RESISTANCE OF POLYMERS TO LOW-TEMPERATURES

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1. INTRODUCTION

The rapid growth of technology places increasing demands on the properties of polymeric materials; in particular, an increase in the temperature limits of their applicability is needed.

This article reviews the methods for increasing their low-temperature resistance, *i.e.* the ability of parts made from polymeric materials to retain their serviceability at low-temperatures. An insufficient low-temperature resistance in polymers may be due to vitrification or crystallisation†, which produce increased hardness, brittleness, and loss of elastic properties. According to modern views[1,2], the vitrification of polymers is caused by a sharp decrease in the intensity of the thermal motion of the polymer chains, a decrease in their flexibility, closer approach of the molecules, and an increase in their interaction. The temperature at which the polymer becomes vitreous is called the glass point (T_g). Polymers typically show a range of glass points, and not a single temperature T_g, since the values of T_g obtained by different methods do not coincide. Moreover, as Aleksandrov and Lazurkin[3], Lazurkin[4,5], and Bartenev[6-8] have shown, the temperature at which the material loses its properties can vary by several tens of degrees, depending on the rate of deformation: T_g increases with the rate of deformation; thus in evaluating T_g for polymers, the actual conditions of use must be taken into account‡.

As the temperature is reduced, the tendency of crystallising polymers to vitrify increases. Crystallisation takes place over a range of temperatures, and its rate increases sharply over a definite section of this temperature range[2]. Thus for unstretched natural rubber this range extends from +15° to -50°, with a maximum rate of crystallisation at -26°. No crystallisation occurs below -50°, since the mobility of the macromolecular chains is too small to form orderly structures. Polychloroprene polymers crystallise over the temperature range +32° to -32°, with a maximum rate of crystallisation at 0°.[2]§

Articles made of polymeric materials often cannot be used even at temperatures above the glass point, because of crystallisation. Thus goods of natural rubber, which has a glass point of the order of -73°, sometimes cannot be used at -10° to -40°, because of incipient crystallisation and loss of elastic properties. Methods are now known for reducing the glass point and decreasing the extent of crystallisation in polymeric materials.

2. REDUCTION OF THE GLASS POINT IN POLYMERS BY PLASTICISING

Until recently the only method for increasing the low-temperature resistance of polymeric materials was by plasticising them, which comprises compounding the polymer with substances which reduce the glass point of the initial polymer. The most widely used plasticisers were phthalic, sebacic, and phosphoric esters.

For a long time, however, the experimental data on the plasticising of polymers had no theoretical foundation, because of the absence of any clear views on the structure of polymers. The investigation of the physical basis of plasticising became possible after the studies of Kobeko[1], Aleksandrov and Lazurkin[3], and Kargin and Slonimskii[15] on the structure of polymers and their behaviour on deformation.

According to modern views there are two mechanisms for the action of plasticisers, for polar and non-polar polymers. After studying the plasticisation of polar polymers by polar or easily polarised plasticisers, Zhurkov[16-19] concluded that the plasticising effect is independent of the chemical nature or molecular dimensions of the plasticiser. The plasticising effect was directly proportional to the molar concentration of the plasticiser:

$$\Delta T = kn,$$

where ΔT is the plasticising effect and n is the molar concentration of plasticiser. k was constant for several plasticisers (tetrachloroethane, acetone, benzyl alcohol, and others). Zhurkov explained this action of plasticisers on polar polymers as the blocking of the individual active centres in the polymer molecule, and showed that this should be determined only by the number of molecules introduced, irrespective of their nature or shape. This is known as the Zhurkov rule of molar concentrations.

† For polymers which crystallise.

‡ The processes occurring in vitrification have been described in more detail in special publications[9,10].

§ The processes occurring in crystallisation have been described in more detail[2,11-14].

The same dependence of the plasticising effect on the number of molecules introduced, irrespective of their chemical structure or shape, was found by Sokolov and Fel'dman[20] in the plasticising of poly(vinyl chloride) with various phthalates and phosphates, and by Kozlov and Russkova[21,22] on cellulose nitrate and acetate.

Kargin and Malinskii[23,24] have shown that the rule of volumetric concentrations applies for non-polar or weakly polar polymers: the decrease in the glass point is proportional to the volumetric concentration of the added plasticiser; this rule was established in the plasticising of poly(vinyl chloride) and polystyrene.

According to Kargin and Malinskii, vitrification of a polymer system is due to a sharp decrease in the mobility of the macromolecular chains; with non-polar or weakly polar polymers, when the plasticiser is introduced there is a purely geometric decrease in the steric hindrance to motion of the polymer chains, because of the increased mean distance between them. Nielsen and Levreault[25] obtained analogous data on the dependence on the plasticising effect on the volume concentration of the plasticiser.

The volumetric and molar concentration rules indicate that the plasticising effect is independent of the type of plasticiser, but recent published work has shown that the chemical structure, and the molecular size and shape of plasticisers can influence the plasticising effect.

On the basis of a study on the deformational properties of polymers, Slonimskii[26] has shown that the various properties of plasticised compositions depend as a whole on the types of plasticiser used; in this respect plasticisers are not mutually interchangeable.

TABLE 1. Mechanical properties of films prepared with various plasticisers.

Plasticiser	Poly(vinyl chloride) : plasticiser : : stabiliser ratio	Tensile strength, kg cm^{-2}	Elongation, %
1*	100 : 100 : 1.5	166.5	203
2	100 : 100 : 1.5	105.5	175
3	100 : 100 : 1.5	101.5	168

* 1) 1-Nitromethyl-2-chlorocyclohexanol;
2) acetyl 1-nitromethylcyclohexane;
3) 1-nitromethylcyclohexanol.

TABLE 2. T_g of polymers and plasticisers.

Property	Polymers			
	styrene – acrylonitrile copolymer	poly(vinyl chloride)	poly(vinyl acetate)	poly(chloroprene)
T_g of polymer, °C	+151°	+116°	+84°	−9°
	Plasticiser			
	dimethylcyclohexyl phthalate	tricresyl phosphate	di-n-heptyl phthalate	dibutyl adipate
T_g of plasticiser, °C	+6°	−30°	−57°	−85°

Voskresenskii and Kozlov[27] have studied the influence of the chemical nature of plasticisers on the plasticising effect in poly(vinyl chloride), and found it to vary with different plasticisers, being dependent on their chemical nature and structure (particularly their polarity). Equimolecular proportions of different plasticisers (see Table 1) give films with different mechanical properties.

Films obtained using equimolecular amounts, or the same contents by mass, of different plasticisers show different low-temperature resistances. Films plasticised with tributyl phosphate are more resistant (T_{brit} = -45°) than those plasticised with tricresyl phosphate (T_{brit} = -15°).

Jenckel[28,29] has shown that the plasticising effect depends not only on the chemical structure of the plasticiser, but also on the glass point of the plasticisers themselves. Table 2 gives the characteristics of the polymers and plasticisers which he studied. The results obtained with 16 different compositions fit the equation:

$$\frac{1}{T_g} = C_{pol}\frac{1}{T_{g\,pol}} + C_{plast}\frac{1}{T_{g\,plast}},$$

where T_g is the glass point of the mixture, and C_{pol} and C_{plast} are the concentrations of polymer and plasticiser respectively.

It follows from the above equation that the greater the difference $T_{g\,pol} - T_{g\,plast}$, the greater will be the reduction in T_g. If this difference is negative, the plasticiser acts as a "thickener", *i.e.* its addition will increase T_g for the mixture.

Pollack[30] has shown that some plasticisers form eutectic mixtures with polymers, and in this case the plasticising effect is a maximum. Forman[31] has investigated the influence of some plasticisers on neoprene rubbers; his results are given in Table 3. He showed that the best plasticising effect at low temperatures is given by plasticisers of high viscosity, high boiling point, and as low vapour pressure as possible.

In his study of the plasticising effect of esters of organic acids, Felix[32] showed that the most effective were esters of C_{6-8} acids. Esters of higher acids tend to freeze out.

TABLE 3. Mechanical properties of neoprene films with various plasticisers.

Plasticiser	Amount added, %	GN neoprene				FR neoprene			
		tensile strength, kg cm^{-2}	elongation, %	molecules at 300%** kg cm^{-2}	T_{brit}, °C	tensile strength, kg cm^{-2}	elongation, %	molecules at 300%** kg cm^{-2}	T_{brit}, °C
—	—	235	995	12	−51	85	785	59	−57
Dibutyl sebacate	15	110	770	40	−62	88.5	1000	28	−57
ditto	30	—	—	—	—	74	1055	19	−68
Tributoxyethyl phosphate	15	119	640	38	−51	89	975	22	−62
ditto	30	105	655	24	−62	80	1160	8.5	−68
Flexol 360*	30	109	820	32	−62	—	—	—	—
Tricresyl phosphate	15	—	—	—	—	82	1010	32	−57
ditto	30	107	730	28	−57	—	—	—	—
Dicapryl phthalate	30	112	800	32	−46	75	1075	15	−68
Petroleum oil	30	124	875	32	−57	—	—	—	—

* Flexol 360 is triethyleneglycol di-2-ethylhexyl ether [made by Union Carbide Corp. (Ed. of Translation)].

** In the rubber industry, modulus at 300% denotes tensile stress to produce 300% strain; it is not the modulus of elasticity (Ed. of Translation).

Lel'chuk and Sedlis[33-35] have attempted to generalise the theory of the action of plasticisers on polar and non-polar polymers. They suggest that the plasticiser molecules penetrate between the polymer macromolecules, force them apart, solvate them, separate the reacting groups, and destroy the regularity and order of the macromolecules; this weakens the intermolecular and intramolecular forces and increases the mobility of the molecules and polymer chains. Consequently, the greater the length, degree of branching, and volume of a molecule, the greater will be its efficiency as a plasticiser. However, increasing the size of the plasticiser molecule decreases its mobility and hinders its penetration into the polymer. Table 4 gives results[33-35] which support these suggestions.

For the quantitative determination of the compatibility of the polymer with the plasticiser, the usual method is to measure the free energy of mixing or the lowering of vapour pressure or change in specific viscosity of the mixture[36,37].

The above data relate to low-molecular plasticisers, the main disadvantage of which is that in addition to reducing the glass point of the polymer, they worsen its mechanical properties, electrical conductivity, dielectric properties, etc.

Recently, polymeric plasticisers have come to be used for plasticising polymers, since they reduce the glass point but do not worsen the other properties[20,38,39]. Thus Voyutskii and his coworkers[38,39] have plasticised poly(vinyl chloride) with high-molecular butadiene–nitrile copolymers as plasticisers; they consider that the plasticising of poly(vinyl chloride), which is a polar polymer, requires a plasticiser containing both polar and non-polar groups, the polar groups reacting with the polar groups of the polymer and so increasing the compatibility of the plasticiser with the polymer. The non-polar groups of the plasticiser screen the polar groups of the polymer and so decrease the interaction between its molecules.

If the plasticiser molecule has a large number of polar groups, it will be highly compatible with the polymer, but its plasticising effect will be slight. It was found that in plasticising poly(vinyl chloride) with butadiene–nitrile copolymers, the optimum effect is obtained with the copolymer containing two butadiene groups for each nitrile group, and that the use of a high-molecular plasticiser provides a poly(vinyl chloride) of considerably better mechanical properties than the use of the low-molecular plasticiser dibutyl phthalate.

In the light of new theories on the structure of amorphous polymers — the micellar structure[40] — two mechanisms have been proposed for the action of plasticisers, an intramicellar and in intermicellar mechanism[41].

TABLE 4. Main properties of plasticisers.

Plasticiser	Efficiency, °C	Compatibility (swelling); tricresyl phosphate = 1	Plasticiser	Efficiency, °C	Compatibility (swelling); tricresyl phosphate = 1
Tricresyl phosphate	9.4	1	Dibutyl adipate	12.4	1.60
Diethyl phthalate	9.8	3.75	Dioctyl adipate	13.1	0.01
Dibutyl phthalate	10.6	1.5	Dibutyl sebacate	13.8	0.275
Dioctyl phthalate	11.9	0.438	Dioctyl sebacate	15.1	0.0087

Intramicellar plasticising takes place when the interaction between the plasticiser and the polymer is stronger than that between the polymer molecules. This occurs with complete miscibility of the polymer and plasticiser.

Intermicellar plasticising takes place when the intermolecular interaction in the polymer is greater than that between the plasticiser and the polymer. This is found when there is a limited compatibility of the polymer with the plasticiser.

The mechanical properties of the plasticised polymer will depend on the type of plasticising which takes place. With intramicellar plasticising one would expect to find increased elasticity in the polymer, a reduction in its glass point and reduced mechanical strength. With intermicellar [intra- in Russian (Ed. of Translation)] plasticising, the glass point would not be reduced, the mechanical strength would be high, and the elasticity of the plasticised polymer would be determined by the Hooke elasticity of the "clusters", which are highly asymmetric in shape, *i.e.* by the elastic deformation of these secondary structural formations.

3. REDUCTION OF THE TENDENCY OF POLYMERS TO CRYSTALLISE

As the literature cited above shows, plasticising can reduce the T_g of a polymer and therefore increase its resistance to low-temperatures. Crystallising polymers lose their elastic properties at reduced temperatures because of increasing crystallisation.

Ritter[42,45] has shown that when crystallising polymers are plasticised their tendency to vitrify increases, because of the increased mobility of the chains and the creation of more favourable conditions for the formation of crystal structures.

One of the known methods for reducing the tendency of polymers to crystallise is the copolymerisation of monomers[10,46]. Recent investigations[42-76] have shown modifying a polymer can reduce its tendency to crystallise by a factor of hundreds or even thousands. The low-temperature resistance of the modified polymer is considerably increased thereby.

A. Copolymerisation

The close connection between crystallisability and regularity of molecular structure is well known. Reduction in the regularity of structure produces a sharp decrease in the tendency of the polymer to crystallise. The introduction of side groups of various structure in the linear polymer chain (by copolymerisation) is often used in practice to obtain non-crystallising polymers.

By copolymerising chloroprene with styrene Mayo[46] obtained a new non-crystallising rubber, neoprene FR. The destruction of the regular structure of the rubber by adding small quantities of styrene prevented the rubber crystallising. Mayo gives comparative data on the tendency of neoprene rubbers to crystallise (Figs. 1 and 2). The diffraction patterns were taken after conditioning the films at 15° for 4 days (Fig. 1) or after straining the vulcanised films 400% (Fig. 2). The full lines indicate the tendency of the various types of rubber to crystallise, and the broken lines indicate the amorphous halo formed when the crystals are destroyed (Fig. 1) or before they appear

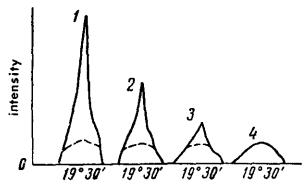


Fig.1. X-Ray diffraction intensity before and after 4 days exposure of the specimen at 15°:
1) neoprene CG; 2) neoprene CN;
3) neoprene RT; 4) neoprene FR;
broken lines: before conditioning; full lines: after conditioning.

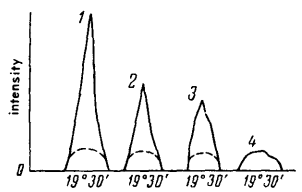


Fig.2. X-Ray diffraction intensity before and after stretching by 400%:
1) neoprene CG; 2) neoprene CN;
3) neoprene RT; 4) neoprene FR;
broken lines: unstretched; full lines: stretched.

(Fig. 2). The greatest tendency to crystallise is shown by neoprene CG, and is less with neoprene CN and slight with neoprene RT; the neoprene–styrene copolymer FR has no tendency to crystallise.

B. Modification

Another and comparatively new method for greatly reducing the crystallisation effect at low temperatures is by modifying the polymers. This can be carried out with thio-acids[42-44,47-53,55-65], butadiene sulphone[5,67], sulphur dioxide[54,67], titanium tetrachloride, triisobutylamine, or powdered selenium[68]. The reactions of polymers with thio-acids were first described in du Pont patents[47-49]. This work was carried out to stabilise polymers to the action of solvents by the saturation of the double bonds¶.

The reaction of natural rubber with thio-acids to prevent its crystallisation has been described by Ritter and Cunneen in patents[51,52]. Commencing in 1956 there have been a large number of investigations by Ritter[42-44], Cunneen[53-56,63-65], and others, on the conditions for the reaction of thio-acids with solid rubber (in the roller mill, Banbury mixer, and extruder), in solution, and in latex; in each case the modified rubbers crystallised hundreds and sometimes thousands of times more slowly than the initial natural rubber.

Gent[57-59] has studied the kinetics of crystallisation of natural rubber at low temperatures, and has evaluated the effect of the degree of cross-linking on the rate of crystallisation, showing that the formation of chemical cross-links reduced the rate of crystallisation. Moreover, Gent showed that combined sulphur in the side groups can also substantially reduce the rate of crystallisation.

On this basis, Ritter[44] suggested that the thio-acids react with natural rubber at the double bonds to form side chains which hinder crystallisation because of the resulting irregular structure.

If the side groups contain more carbon atoms than thiobenzoic acid, they tend to crystallise themselves, so that high-molecular-weight modifiers are ineffective.

According to Ritter[44], the addition of thio-acids to natural rubber proceeds as follows:

$$\mathrm{RCOSH} \rightarrow \mathrm{RCOS^*}$$

$$-\mathrm{CH_2C(CH_3)=CH-CH_2^-} + \mathrm{RCOS^*} \rightarrow -\mathrm{CH_2C^*(CH_3)CH(SCOR)CH_2}-$$

$$-\mathrm{CH_2C^*(CH_3)CH(SCOR)CH_2}- + \mathrm{RCOSH} \rightarrow$$

$$\rightarrow -\mathrm{CH_2CH(CH_3)CH(SCOR)CH_2}- + \mathrm{RCOS^*},$$

where R is alkyl or aryl.

Thiobenzoic acid was the most effective modifier in respect of reducing the rate of crystallisation and yielding products of satisfactory strength and technological properties. The addition of 0.5–2 moles of thiobenzoic acid per 100 isoprene groups reduces the rate of crystallisation by a factor of hundreds.

Since the changes were considerably greater than would be expected from the "action of side group mechanism"[57,72], it had to be assumed that thio-acids produce some other structural changes in the isoprene macromolecules.

Ritter's suggestion[44] that the double bonds in the macromolecule are transposed to form side methylene groups has not been confirmed by infra-red spectroscopy.

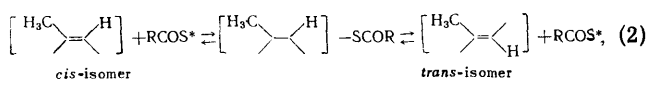
Cunneen[63-65], Cunneen and Shipley[53,54], Watson[67], and Golub[61] and others have observed that the action of thiol acids on natural rubber causes isomerisation, some of the *cis*-bonds becoming *trans*-bonds. Earlier attempts to isomerise natural rubber by the action of ultra-violet light or various chemicals did not give substantial *cis*-*trans*-isomerisation[73,74]. Before Golub's work[75] configurational changes of polyolefines with non-conjugated double bonds were unknown. The method of infra-red spectroscopy used by Cunneen and coworkers[64] was specially developed by them, and could only be used for homopolymers and for mixtures of homopolymers of *cis*-*trans* 1–4 polyisoprenes; it is based on differences observed in the spectra at frequencies of 1125 and 1145 cm^{-1}, and can give a quantitative analysis of the configurational changes taking place in natural rubber and gutta-percha, even with less than 5% isomerisation.

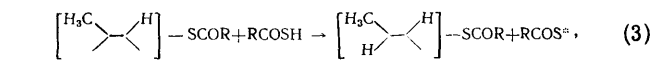
¶ For similar work on the modification of polyisoprene by saturating it with mercaptans to obtain a product stable to the action of ozone, ultra-violet light, and sunlight, see Meyer and coworkers[69-71].

Fig. 3 shows detailed stereochemical results. After reaction with sulphur dioxide, natural rubber and gutta-percha were converted into products containing 57% *trans*-bonds and 43% *cis*-bonds. Analogous isomerisation can be achieved by treating the polymers with thio-acids or butadiene sulphone.

The isomerisation, according to Cunneen and his coworkers[53], must proceed as follows:

$$A^* + RCOSH \rightarrow AH + RCOS^*, \quad (1)$$





where A* is a radical formed either by the action of initiators (in solution or in latex) or by rupture of the rubber molecules on the roller mill. The isomerisation thus proceeds through a reversible stage in the addition reaction. The addition proceeds by a free-radical mechanism; in step (2) the thioacyl radicals add across the double bonds to form a complex radical, which can then either react further with the acid to form the addition product, as shown in step (3), or can undergo *cis-trans*-isomerisation. If step (2) is much more rapid than step (3), a considerable number of double bonds will be isomerised for each thio-acid molecule added on to the chain. These structural changes, as would be expected, considerably reduce the tendency of natural rubber to crystallise at low temperatures.

This has been confirmed by Kraus[76], who showed that polybutadienes with a high content of *cis*-bonds crystallise rapidly at low temperatures, while those containing 20–75% *trans*-bonds are amorphous.

The rate of crystallisation has been determined by various methods: by measuring the stress relaxation in the specimen[55], dilatometrically[59], and by measuring the temperature retraction[44].

The stress relaxation has been measured at -26°, the temperature at which the rate of crystallisation of unvulcanised and vulcanised natural rubber is maximum[55]. The vulcanised specimens were held under a constant strain (usually 150%) at this temperature. The time for the volume to decrease by 50% of the total change (in the dilatometric method), or for the tension in the stretched specimen to decrease to a half of the initial value (in the stress relaxation method), is called the crystallisation half-life[55].

Fig. 4 shows the crystallisation half-lives for modified and unmodified natural rubber[64]. The former is seen to be greater than the latter. The retardation factor (the ratio of the crystallisation half-life for the modified rubber to that for the corresponding control) is in this case 100:1.

The rate of crystallisation can also be determined by the standard ASTM procedure[77,78] by the temperature retraction of specimens. In this procedure the specimen is stretched by 400–500%, cooled to between -70° and -80° and held at this temperature for a definite period of time. The stretching force is then removed and the temperature of the specimen raised. The temperatures are recorded at which the specimen contracts by 10, 30, 50, and 70% of the initial length (TR 10, TR 30, TR 50, and TR 70 respectively).

Fig. 5 shows the temperature retraction of unmodified natural rubber.

Using this procedure, Ritter[44] has determined the degree of crystallisation as follows: the specimen was stretched by 50–100% (crystallisation does not occur, even in unmodified rubber) and held at -70°. TR 70 was measured, the specimen stretched by 400–500%, and TR 70 again measured. The difference between these two values of TR 70 characterises the tendency of the rubber to crystallise; the greater the difference, the greater the tendency. For a non-crystallising rubber the difference is zero. To obtain additional information on the rate of crystallisation at low temperatures, Ritter[44] has slightly modified the above TR method. The specimens were not stretched at

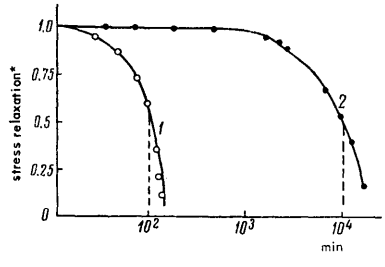


Fig. 4. Comparison of the crystallisation half-lives of vulcanised rubbers:
1) unmodified; 2) modified natural rubber.

* Stress/initial stress (Ed. of Translation).

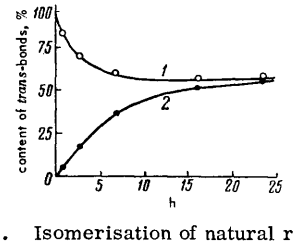


Fig. 3. Isomerisation of natural rubber and gutta-percha at 140° under the action of sulphur dioxide:
1) gutta-percha; 2) natural rubber.

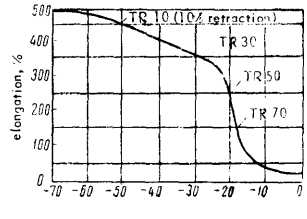


Fig. 5. Temperature retraction (TR) of unmodified natural rubber.

room temperature, but were first cooled to the desired low temperature, and then stretched at that temperature; the stretched samples were held under these conditions for a definite period of time, the straining force was removed, and the permanent set measured as a function of crystallisation time at the given temperature.

At -50° the permanent set of modified rubbers containing 0.5 and 1% thiobenzoic acid was 28 and 16% respectively. Unmodified rubbers had a permanent set of 32% at -20°, 200% at -30°, 300° at -40° and 280% at -50°.

Fig. 6 shows the permanent set curves for modified rubbers; low-temperature plasticisers increase the rate of crystallisation of the unmodified natural rubber. This cannot be detected with the normal TR techniques described above, since the vulcanised rubbers crystallise very rapidly at room temperature and the increase in the rate of crystallisation when the plasticiser is introduced is negligible at this temperature.

Moreover, it was found[44] that the temperature at which the crystallisation rate is a maximum, which is -26° for unstretched natural rubber, may be different when the rubber is stretched, *e.g.* -50°. The introduction of low-temperature plasticisers shifts this optimum crystallisation temperature towards higher temperatures (Fig. 7).

Modification of natural rubber in the solid. Ritter[42-44] has modified natural rubber with thio-acids in the roller mill and the Banbury mixer, using thioacetic, thiocaprylic, thiostearic, thiochloroacetic, thiobenzoic, thionaphthoic, benzoic [*sic.* (Ed. of Translation)], bromothiobenzoic, nitrothiobenzoic, and dinitrothiobenzoic acids. The thio-acids were added to the plasticised rubber in amounts of 0.1, 0.25, 0.5, 1, and 2 mole% and mixed for 10 min. The vulcanising agents were added the following day. The addition of more than 2 mole% of the thio-acids was difficult because of scorching. The rate of scorching could be reduced by replacing the sulphur used for vulcanising by Sulfasan R† (4, 4′ dithiodimorpholine). Figs. 8 and 9 show Ritter's results on the rate of scorching[47].

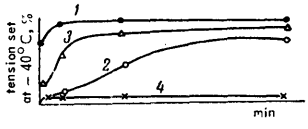


Fig. 6.* Low-temperature tension set at -40° and 400% elongation; racking periods 5, 30, 120, and 380 min:
1) dried latex film, unvulcanised; 2) smoked sheet, vulcanised; 3) smoked sheet + tributyl phosphate; 4) rubber (1 mole % added thiobenzoic acid) + + tributyl phosphate, vulcanised.

* Captions taken from original paper[44] (Ed. of Translation).

† Made by Monsanto Chemical Co.

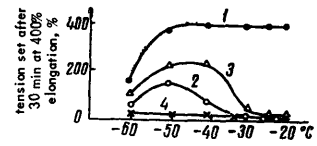


Fig. 7.* Dependence of the low-temperature tension set on the test temperature.
1)–4) See Fig. 6.

* Captions taken from original paper[44] (Ed. of Translation).

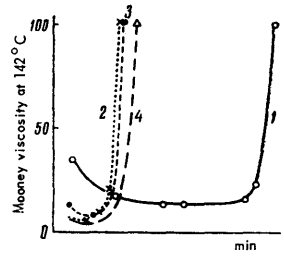


Fig. 8.* Tendency to scorching as a function of the content of various thio-acids:
1) smoked sheet; 2) thiobenzoic acid modified rubber; 3) trichlorothioacetic acid modified rubber; 4) β-thionaphthoic acid modified rubber. (At 2, 4, etc. up to 20 min).

* Captions taken from original paper[44] (Ed. of Translation).

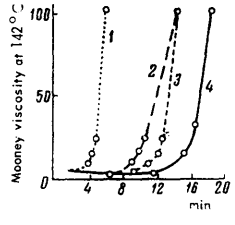


Fig. 9.* Influence of substitution of sulphur by Sulfasan R on the vulcanisation of rubber. 100 g of thiobenzoic acid-modified rubber contain:
1) 2.5 g of sulphur; 2) 1 g of Sulfasan R;
3) 2 g of Sulfasan R; 4) 4 g of Sulfasan R.

* Captions taken from original paper[44] (Ed. of Translation).

Thiobenzoic acid was the most effective of those studied in reducing the crystallisability of natural rubber; the addition of up to 2 mole% produced a sharp reduction in the tendency towards crystallisation.

Fig. 10 shows the effect of thiobenzoic acid on the crystallisation of natural rubber. The rate of crystallisation

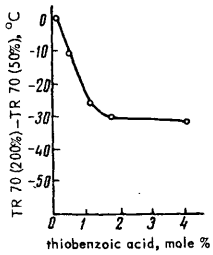


Fig.10. Crystallisation of natural rubber as a function of the thiobenzoic acid content.

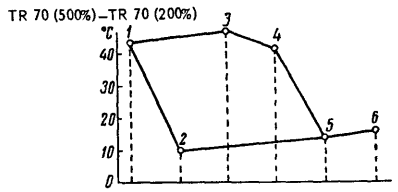


Fig.12. Influence of plasticisers and modifiers on the tendency of smoked sheets to crystallise: 1) unmodified sheet; 2) thiobenzoic acid-modified rubber; 3) rubber + tributyl phosphate; 4) rubber + + plasticiser TP90B; 5) thiobenzoic acid-modified rubber + tributyl phosphate; 6) thiobenzoic acid--modified rubber + plasticiser TP90B.

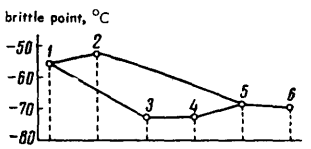


Fig.13. Influence of plasticisers and thiobenzoic acid on the brittle point: 1)–6) see Fig.12.

decreases as increasing amounts of thiobenzoic acid are added, the glass point of the mixture is simultaneously raised (Figs. 11–13); this increase is negligible with up to 2 mole% of the thio-acid, but the tendency to crystallisation is reduced by a large factor by the addition of these amounts. Moreover, Ritter[44] has shown that when a modifier and a plasticiser are used together, non-crystallising rubbers with a low glass point can be obtained. The strength of the rubber decreases as the thio-acid is added to natural rubber.

By analogy with SBR-type copolymer rubbers reinforced with carbon black, Ritter[44] considered modified natural rubber as a "quasi-polymer" and used carbon black to reinforce rubber modified with thiobenzoic acid. Table 5 shows his results.

Modification of natural rubber in latex. The isomerisation of natural rubber in the latex has been studied in detail by Cunneen[53], who used ordinary concentrated latex, containing 60% rubber, preserved with ammonia. To avoid immediate neutralisation of the thio--acid by the ammonia, the stabilised latex was acidified with dilute hydrochloric acid to pH 0.6. The most effective stabilisers were (ethylene oxide)–amine condensation products, particularly the condensation product of stearylamine with 50 moles‡ of ethylene oxide used in an amount of 2–2.5% by weight of the rubber. Ascaridole§, t-butyl hydroperoxide, cumene hydroperoxide, and α,α'-azo-bis-isobutyronitrile were used as catalysts for the reaction.

The catalyst was usually added in an amount of 10–20 wt.% of the thio-acid as a benzene solution or as an emulsion; the thio-acids were also added in benzene solution or as an emulsion. The addition of catalyst and thio--acid in solution gave products whose crystallisation rates were lower than those of products obtained when the additives were used in emulsion. The reaction was continued for 5 h at 60° when using 0.16 wt.% thiobenzoic acid. Above 60° the latex thickened or coagulated, while below 40° the reaction was very slow. Reaction for more than 5 h did not give products with a further reduction in the rate of crystallisation. The latex was coagulated with a polar solvent, such as ethanol or acetone, and the coagulum was extracted with acetone and dried in vacuum, or washed on a wash mill and dried in a thermostat. The rate of crystallisation was determined as described above, or dilatometrically for unvulcanised samples, or by the stress relaxation method[59].

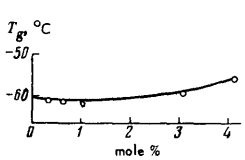


Fig.11. Dependence of the glass point of natural rubber as a function of the thiobenzoic acid content.

TABLE 5. Comparative data on the mechanical properties of modified natural rubber reinforced with carbon black.

Added thiobenzoic acid, mole %	Combined acid, mole %	Modulus at 100% elongation, kg cm^{-2}	Modulus at 300% elongation, kg cm^{-2}	Modulus at 500% elongation, kg cm^{-2}	Tensile strength, kg cm^{-2}	Elongation, %	Tear strength, kg cm^{-2}	Hardness Shore A
With carbon black								
0	0	43	106	—	307	425	109	66
1.2	0.8	47	100	—	221	410	96	67
2.5	1.8	41	83	—	224	500	89	65
4.9	3.2	48	90	—	216	450	95	70
9.8	4.6	89	—	—	135	175	—	83
Without carbon black								
0	0	10	24	78	304	700	29	43
1.2	0.8	5	12	24	140	820	14	35
2.5	1.8	5	11	25	141	825	13	14
4.9	3.2	6	16	23	168	750	14	37
9.8	4.6	6	14	30	72	675	11	35

‡ Mole % ? (Ed. of Translation).

§ 1,4-Peroxido-*p*-menth-2-ene (Ed. of Translation).

TABLE 6. Influence of thiobenzoic acid on the crystallisation half-life.

Added thiobenzoic acid, %	Crystallisation half-life, days
0.04	0.15
0.08	0.69
0.16	28

TABLE 7. Influence of thio-acids on the crystallisation half-life.

Thio-acid	Amount used, %	Crystallisation half-life, days	Thio-acid	Amount used, %	Crystallisation half-life, days
Thiostearic	0.16	0.42	2-Thionaphthoic	0.32	14
»	0.64	1.08		1.28	69
o-Hydroxythiobenzoic	0.16	2.6	2-Hydroxy-3--thionaphthoic	0.32	9.7
	0.32	8.3		1.28	140
	5.12	210			

TABLE 8. Dependence of the retardation factor on the properties of the latex.

Catalyst	pH 1.0	pH 0.6	Precipitated latex, pH 0.6	Repeatedly centrifuged latex, pH 0.6
—	no retardation	6:1	300:1	12:1
Ascaridole	2:1	110:1	750:1	1000:1

TABLE 9. Influence of thio-acids on the crystallisation half--life.

Thio-acid	Amount used, %	Crystallisation half-life, days	Thio-acid	Amount used, %	Crystallisation half-life, days
Thiochloracetic	0.4	3.1	α-Thionaphthoic	0.1	1.2
»	0.6	8.3		0.2	4.2
»	0.8	21		0.4	140
Thiotrichlor-acetic				0.6	140
	0.3	0.83		0.8	140
»	0.7	5.4			
»	1.0	29			

Table 6 gives data on the influence of thiobenzoic acid on the crystallisation half-life, and Table 7 gives similar data obtained with other thio-acids. The hydroxythio-acids are considerably less effective than thiobenzoic acid.

Products prepared under identical conditions from different batches of latex often have very different crystallisation retardation factors (the ratio of the crystallisation half-life of the modified rubber to that of the corresponding untreated rubber). According to Cunneen[62] this difference is due to the different reactivities of the latex. Considerably better results were obtained when the pH of the latex was reduced to 0.6 using precipitated latex, or by using latex which had been repeatedly centrifuged. Table 8 gives some results obtained by these methods.

Reaction in solution. Cunneen[63] and Ritter[44] have reacted natural rubber with thio-acids in solution; the thio-acids were added to 2% solutions of deproteinised crepe in benzene. No catalysts were used. The reaction mixtures were evacuated and heated at 100° for 6 h; the modified rubbers were precipitated with methanol, extracted with acetone in a Soxhlet apparatus for 20 h in an atmosphere of nitrogen, and dried in vacuum. Table 9 gives the results obtained[59] by modifying rubber in solution. The crystallisation half-life increases with the amount of thio--acid added.

Natural rubber can also be isomerised by treatment with sulphur dioxide[67] or butadiene sulphone. The latter is more convenient for modifying natural rubber in the dry state on an industrial scale[65,68]. This method of isomerisation consists in heating the natural rubber for several minutes at 160° with 2% butadiene sulphone. The reaction can also be carried out in internal mixers or injection moulders. The resulting product has properties identical with those of rubber obtained by modification with thio-acids.

This review has shown that three methods exist for increasing the low-temperature resistance of polymeric materials: plasticising, copolymerising, and modifying. Plasticising reduces the glass point of the polymer. Modification and copolymerisation are used to increase the low--temperature resistance of crystalline polymers (to reduce their tendency to crystallise at low temperatures). Modification and copolymerisation do not reduce the glass point of the polymer, so that if it is necessary to increase the low-temperature resistance of a crystallising polymer which has a comparatively high glass point, plasticisers and modifiers must both be used, or copolymerisation must be followed by plasticising of the copolymers.

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USE OF INFRA-RED SPECTROSCOPY TO INVESTIGATE ADSORPTION AND THE STRUCTURE OF SURFACE CHEMICAL COMPOUNDS

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