

PHYSICAL AND TECHNOLOGICAL PROPERTIES OF CIS POLYBUTADIENE

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INTRODUCTION: The discovery of the stereospecific polymerisation processes, based on the use of metalorganic catalysts, led to results of great interest not only in the field of poly- α -olefins, but also of diolefins⁽¹⁾. The monomeric units deriving from the latter can assume many possible different stereo-isomeric structures: and thus a great variety of products may be formed according to the presence of more or less large amounts of different structured monomeric units in the same chain.

Up to 1954, only amorphous synthetic diolefin polymers were known, in which monomeric units corresponding to different types of enchainment and of steric structure are present in the same macromolecule.

Only after the discovery of the stereospecific polymerisation processes, was it possible to obtain different kinds of polymers in each of which the macromolecules are substantially formed by monomeric units having only one type of stereoisomeric structure. All these polymers are crystallisable and differ markedly from each other, according to their steric structure. Polymers of high steric purity differ from the less pure ones owing to crystallinity (percentage of crystalline polymer) and to melting tem-

perature, which both decrease with the decrease of steric purity.

Non-sterically pure crude polymers, having the same steric composition, may show remarkably different properties, according to the distribution of that impurity in the different macromolecules, and according to the mode of distribution of those impurities in each macromolecule. A random distribution of impurities in all the macromolecules causes a greater decrease of crystallinity and of melting temperature than any other type of distribution known up to now.

If we consider only butadiene polymers, the first crystalline polymers with a 1,4 enchainment have been prepared at the Institute of Industrial Chemistry of the Milan Polytechnic⁽²⁾.

The crude polymers obtained using heterogeneous catalysts mainly contained trans-1,4 macromolecules; by fractionation it was possible, however, to separate from the crude polymer not only fractions having a high content of trans-1,4 units and high melting temperature (145°C.), but also fractions rich in cis-1,4 units.

Whereas the trans-1,4 fraction is crystalline and high melting, the fractions of high cis-1,4 content are amor-

phous and, in spite of the prevailing cis-1,4 content, are scarcely interesting as rubbers owing to the poor mechanical properties of their vulcanisates.

Analogously, we have prepared trans-1,4 isoprene polymers,⁽²⁾ having a crystalline structure similar to that of gutta-percha, whereas cis 1,4 isoprene polymers show analogies with natural rubber⁽³⁾.

Shortly thereafter we also succeeded, for the first time, at the Milan Polytechnic, in the synthesis of polybutadiene with 1,2 enchainment. We obtained, depending on the catalytic system employed, two different products, both of very high content in 1,2 units⁽⁴⁾. These products show different properties, different melting temperatures, and different crystalline structures, depending on the type of steric order of the monomeric units. The structure of one of them is syndiotactic (m.p. 158°C.), that of the other is isotactic (m.p. 128°C.).

For all the types of the above-mentioned stereoisomeric polybutadienes, we have determined the crystalline structure, and, in particular, the chain conformations in the crystalline state⁽⁵⁾.

At the beginning, it was difficult to obtain crystallisable cis-1,4 polybutadiene. This depended, we thought, on the low melting temperature. Subsequently, a series of investigations was made with the purpose of obtaining polymers of high cis-1,4 content; in fact, it could be foreseen that a polymer of this structure and with high steric purity would have given a synthetic rubber superior to any other butadiene rubber.

In order to isolate a product of better properties and to examine the variation of properties dependent on steric purity, we first fractionated polymers made with titanium catalysts and which gave prevalingly 1,4 products⁽⁶⁾. For the first time, we isolated and described a polymer of high cis-1,4 content, which showed crystallinity under stretching—also at room temperature^(6, 7). Accurate fractionations carried out on these crude polymers allowed the isolation of fractions containing 97-98 per cent of cis-1,4 units (m.p. 0°C.)^{(8)*}. It is interesting to observe that these polymers, obtained by fractionation, are more crystalline than other polymers examined by us and prepared following other processes⁽⁹⁾, which also furnish products rich in cis-1,4 units.

This is due to the fact that, in our products, steric impurities are not distributed at random and longer chain segments with an exclusively cis-1,4 structure are present. Similar results

TABLE I
1,4 cis Polybutadiene: Melting Temperatures VS. 1,4 cis content with different Methods

Sample	1,4 cis % of total unsaturation	Melting Temperatures °C.		
		Dilatometric method	Differential thermal analysis	Dynamic method mechanical damping at sound frequencies
1	93	-5	-17	-11
2	96	-2	-11	-5
3	98	-1	-6	-0.5
4	99	+0.5	-3	—

TABLE II
Structural Properties of Different 1,4 cis Polybutadienes

	PB-M1	PB-P
Intrinsic viscosity dl.g ⁻¹ ...	2.39	2.75
Average viscosimetric molecular weight ($[\eta]=1.53 \times 10^{-4} M^{0.80}$)	180,000	215,000
Mw/Mn ...	~2.5	~2.5
Types of monomeric units:		
1,4 cis ...	97.5	95.2
1,4 trans ...	1.3	1.7
1,2 vinyl ...	1.2	3.1
1,4 trans/1,2 vinyl ...	ca.1	ca.0.6
Mooney viscosity ML-4 at 100°C. ...	45	45

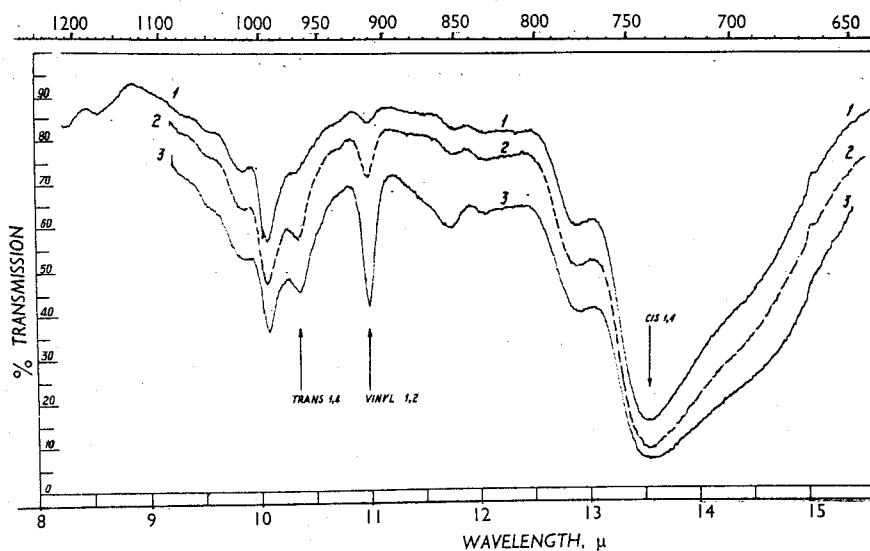


Fig. 1. Infra-Red Spectra of Cis 1,4 Polybutadienes. (1) 99 per cent Cis, 0.5 per cent Trans, 0.5 per cent Vinyl, PB-M1; (2) 97.5 per cent Cis, 1.3 per cent Trans, 1.2 per cent Vinyl, PB-M1; (3) 95.2 per cent Cis, 1.7 per cent Trans, 3.1 per cent Vinyl, PB-P

cannot be obtained, as it can be proved by dilatometric analysis⁽¹²⁾, with polymers prepared following other processes, e.g. using $TiCl_4$ as catalyst⁽⁹⁾. The change of properties observed in dependence of an increase of crystallinity led us to undertake systematic studies for the direct production of polymers of high cis-1,4 content and to develop a research programme also at the "Donegani" Institute in Novara.

This research work produced polymers of a cis-1,4 content higher than 95 per cent⁽¹³⁾ and, when employing particular improved catalytic systems, also polymers containing more than 98-99 per cent of cis-1,4 units⁽¹⁴⁾.

The study of the properties of these polymers proved our predictions concerning the influence of steric purity on the properties of cis-1,4 polybutadiene; in particular regarding the possibility of obtaining polymers which crystallise under stretch in the absence of reinforcing agents, and showing a stronger increase of modulus at high elongations and a higher tensile strength.

These results were in contrast with what was then generally believed; in fact, other investigators, on the basis of the extrapolation of results obtained from less pure polymers, foresaw only a modest improvement of properties for pure cis-1,4 polymer⁽¹⁵⁾.

* In the first I.R. investigations of the polymer structure, to determine the cis-1,4 content, coefficients which led to incorrect results, were used. The first coefficients used by us led to results lower than reality, whereas the coefficients used by other Authors⁽¹⁰⁾ led to results a little higher than those which are supposed to be correct nowadays⁽¹¹⁾. For instance, the spectra we presented at the First International Synthetic Rubber Symposium in London in 1957 correspond to a cis-1,4 content of about 92 per cent. At first a content lower than reality had been ascribed also to the fractionated product described in another paper⁽⁸⁾.

Physical Properties of Polybutadienes containing more than 97 per cent of cis-1,4 units

In the present communication, we refer to the properties of polybutadienes having a cis-1,4 unit content higher than 97 per cent, which are produced in the Montecatini pilot plant at Castellanza. Since large quantities of this polymer are available, it has been possible to study its properties thoroughly.

Purer polymers, containing 99 per cent of cis-1,4 units, have been prepared on a laboratory scale; they melt at about $+1^\circ C.$, as determined by a dilatometric

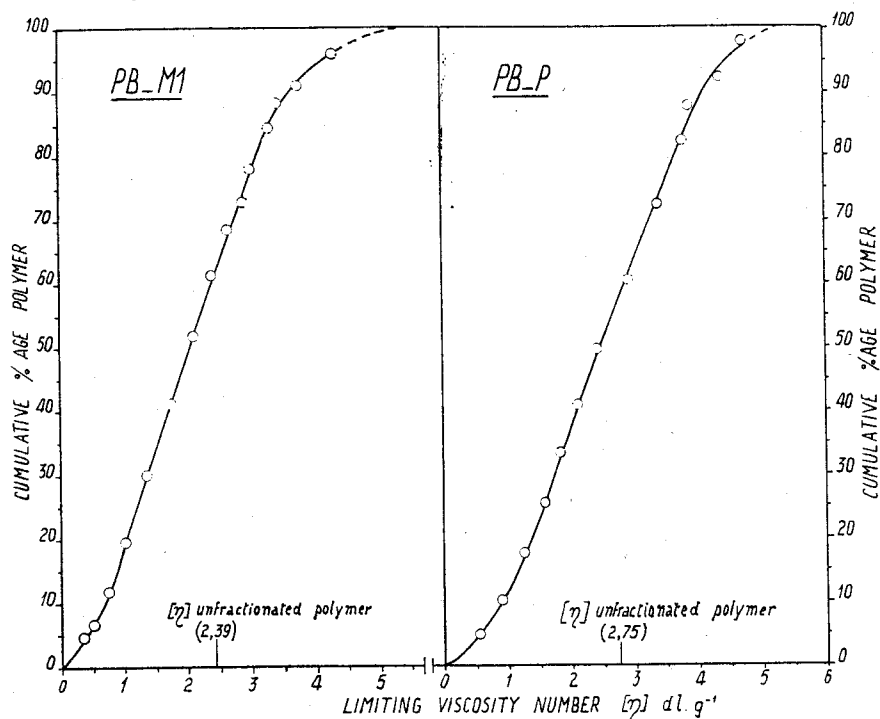
method using a very low rate of temperature increase. Higher melting temperatures have been observed sometimes, operating less accurately; but probably this increase of melting temperature depends on the internal stresses of the sample. This is confirmed by the fact that the melting temperature of cis-1,4 polybutadiene, analogous to what happens with natural rubber, varies according to the history and in particular to the thermal and mechanical treatment the samples have been subjected to. In fact, in strongly stretched samples of our polybutadienes melting temperatures higher than $80^\circ C.$ were observed.

Using the dilatometric method, the melting temperature is the temperature which corresponds to complete melting under conditions near to equilibrium. The values thus obtained, approach the values determined by X-rays, corresponding to the complete disappearance of diffractions in the crystalline phase.

In Table I are reported measurements obtained with the aid of a dynamic method (i.e. by measuring the mechanical damping at sound frequencies) and by differential thermal analysis. The lower values obtained by the latter method are due to the fact that, as melting temperature, the temperature has been considered in which the amount of heat absorbed by the melting is the greatest, and not the temperature corresponding to the total melting.

In Fig. 1 we show the I.R. spectra of samples of cis-1,4 polybutadiene obtained with cobalt catalysts, having a cis-1,4 content of 99 per cent and 97.5 per cent respectively, and the I.R. spectrum of a commercial sample having a cis-1,4 content of 95.2 per cent.

Fig. 2. Molecular Weight Distribution of Cis 1,4 Polybutadienes



Some data concerning the two last above-mentioned samples (which will be hereinafter called PB-M1 and PB-P), are reported in Table II.

The polymers we have obtained using soluble catalysts show a lower dispersion in comparison with that observed in polybutadienes obtained by other methods. In Fig. 2 we report the distribution curve of molecular weights expressed as intrinsic viscosity for both the PB-M1 and PB-P samples. When operating under well controlled polymerisation conditions, we can obtain crude polymers with a much more limited distribution, corresponding to a value of the MW/Mn ratio—1.2:1.5. Their properties will be described in a subsequent communication.

Table III shows the composition of the different fractions and, in particular, the cis-1,4 content as a percentage of the total unsaturation, and the ratio between trans-1,4 and 1,2 units for both the samples examined. The PB-M1 sample shows a more regular and homogeneous structure. In fact, the composition of the different fractions is found to be practically the same as the one of the original sample before fractionation. The PB-P sample, on the contrary, shows a higher content of units different from cis-1,4 in the first fractions of lower molecular weight.

Processing Properties

In order to evaluate different polybutadienes from a technological point of view, we have employed some tests which reproduce, as far as possible, industrial processing conditions. For this purpose, we chose typical machineries of the rubber industry, such as the open mill, the Banbury mixer and the extruder.

I. Mill mixing: Cis-1,4 polybutadiene shows a typical behaviour in mill processing: at first a smooth, tacky bright coloured band is formed, which adheres to the cylinder if this is kept cold by water circulation. When increasing the temperature, the band becomes dry and crumbled, and loses its adherence to the roll; under these conditions processing

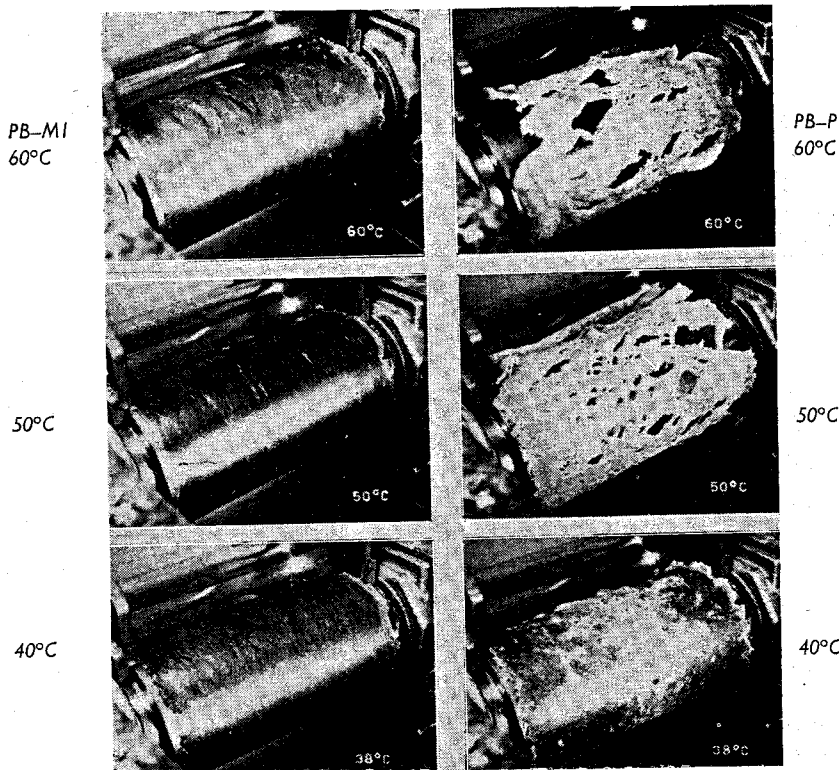


Fig. 3. Behaviour of Different Cis-1,4 Polybutadienes on Mill

becomes difficult and the incorporation and homogenisation of fillers in the polymer are practically impossible.

This phenomenon is quite reversible, since when lowering the temperature processing becomes easy again, and the band looks bright and homogeneous again. The temperature at which this transformation appears depends mainly on the steric and chemical structure of the polymer.

Fig. 3 shows the very different behaviour on the roll mill of the PB-M1 and PB-P samples, having a Mooney viscosity ML-4=45 at the temperatures of 40°C., 50°C. and 60°C.

The PB-M1 sample shows, at these

temperatures, a perfect band formation and adherence to the cylinders, whereas the PB-P sample at 40°C., already shows less adherence and an imperfect band formation.

On a laboratory mill, it is fairly easy to keep the roll temperature below 40°C., whereas on an industrial mill, when working larger amounts of polymer, it is more difficult to remove the heat caused by friction, and hence the temperature tends to increase. It follows that it is important that polybutadiene has as high as possible a transition temperature.

Mixes have been easily prepared with PB-M1 also on mills of 400 x 1.000 m.m.

TABLE III
Configurations in Fractionated Samples of Polybutadienes

PB-M1					PB-P				
Fractions	Fractions weight %	$[\eta]$ dl.g ⁻¹	1,4 cis % of total unsaturation	Trans/1,2	Fractions	Fractions weight %	$[\eta]$ dl.g ⁻¹	1,4 cis % of total unsaturation	Trans/1,2
1°	1.0	0.2	96.0	1.2	1°	0.9	0.2	0	2
2°	2.1	0.2-0.3	96.3	1.5	2°	1.5	0.2	80	2.3
3°	1.8	0.3-0.4	97.0	0.9	3°	0.5	0.3	91.8	1.5
4°	2.9	0.48	—	—	4°	1.0	0.3-0.4	93.1	1.1
5°	2.4	0.62	97.5	1.0	5°	1.0	0.4	93.4	0.9
6°	3.0	0.75	—	—	6°	0.6	0.4-0.5	92.8	0.8
7°	4.3	0.82	97.7	0.8	7°	0.7	0.5	92.0	0.8
8°	8.1	1.05	97.7	1.0	8°	0.7	0.6	93.4	0.7
9°	7.4	1.30	97.8	1.0	9°-26°	93.1	0.6-4.7	94.5-95.7	0.7-0.5
10°	6.3	1.65	98.0	1.0					
11°	6.4	1.75	98.0	1.0					
12°-20°	54.3	1.7-5.1	97-96	1.0-1.2					
		$[\eta]$ dl.g ⁻¹	PB-M1	PB-P			
		1,4 cis % of total unsaturation	2.39	2.75			
		1,4 trans/1,2 vinyl	97.5	95.2			
					1.1	0.6			

All these factors obviously contribute to better processability characteristics of PB-M1.

II. Banbury mixing. Table VI shows the results obtained from mastication tests in a 1 litre laboratory mixer (Banbury B type). These results demonstrate that PB-M1 undergoes a marked breakdown during high temperature mastication, without gel formation, contrary to what happens for the PB-P sample.

III. Extrusion tests. Extrusion tests have been carried out using a 60 mm. extruder fitted with a Garvey die having bigger sizes than the standard ones (reported in Fig. 5). Tests have been performed at temperatures of 120°C. and 55°C.; the former corresponds to the standard temperature prescribed in the Garvey test, the latter is nearer to the temperature usually employed in industry. The compositions of the mixes employed in tests are shown in Table VII.

From the results obtained from the extrusion tests shown in Table VIII, it is shown that the behaviour of PB-M1 is very similar to that of natural rubber and of SB-R. From this point of view, the difference between PB-M1 and PB-P is very marked; the former, with Mooney viscosities of the raw polymer ranging from 35 to 50, gives perfect extruded products both at 55°C. and 120°C., with output very near to those of natural rubber and of SB-R.

With regard to PB-M1, it is possible to observe that at 50°C. its output in kg/h is very near to that of natural rubber; the lower output in m/h may be ascribed to a greater swelling of the extruded product. At 120°C. the output decreases in comparison with the output at 50°C., especially considering samples having a higher Mooney viscosity.

Fig. 6 clearly shows differences in behaviour of the extruded products.

Characteristics of Gum Vulcanisates

1. Crystallisability under stretching: Cis-1,4 polybutadiene (PB-M1) cured without filler, easily crystallises under extension.

The X-ray diffraction pattern of this product (97.5 per cent cis-1,4 content) cured with sulphur and ZnO, and extended to about 800 per cent, is shown in Fig. 7.

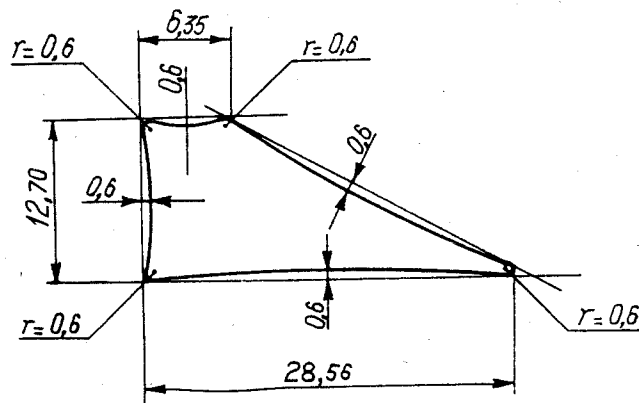


Fig. 5. Garvey Die Used in Extrusion Tests

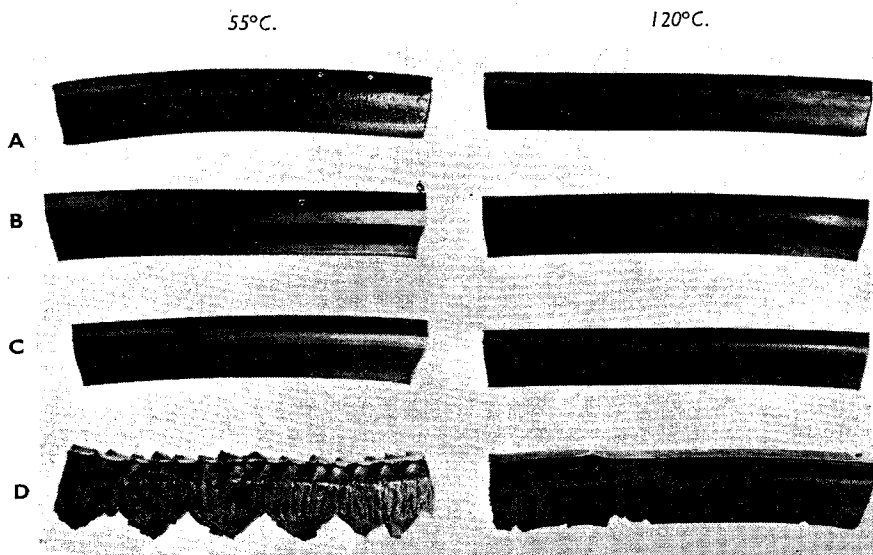


Fig. 6. Garvey Die Extrusion Tests at 55°C. and 120°C. (a) Natural Rubber; (b) SBR 1500; (c) PB-M1; (d) PB-P

Crystallinity, as a function of elongation is reported in the diagram of Fig. 8. Curves are S-shaped and the onset of crystallisation depends on the steric purity and on the vulcanisation conditions. Polybutadienes having a 99 per cent cis-1,4 content already crystallise at elongations lower than 350 per cent.

Crystallisability under extension can be measured by recording with a Geiger counter the X-ray intensity diffracted from lattice planes parallel to the stretch axis—that is from equatorial planes—and taking as a value of crystallisability the ratio between the diffraction due to the crystalline portion and the total diffraction. Therefore we prefer to indicate these conventional values as "equatorial crystallinity".

When heating the vulcanised samples, which were stretched to a high elongation, a reversible decrease of crystallinity has been observed, as can be seen from Fig. 9, which shows the change of the

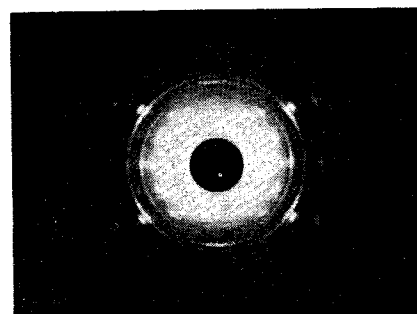


Fig. 7. PB-M1; X-ray Diffraction Pattern (Cu K α Radiation) of Pure Gum Vulcanisate at 800 per cent Elongation at 25°C.

peak intensity to $2\theta = 22.3^\circ$, by increasing the temperature of a sample stretched at 800 per cent. Such a decrease in crystallinity is accompanied by a decrease in tensile strength. From the

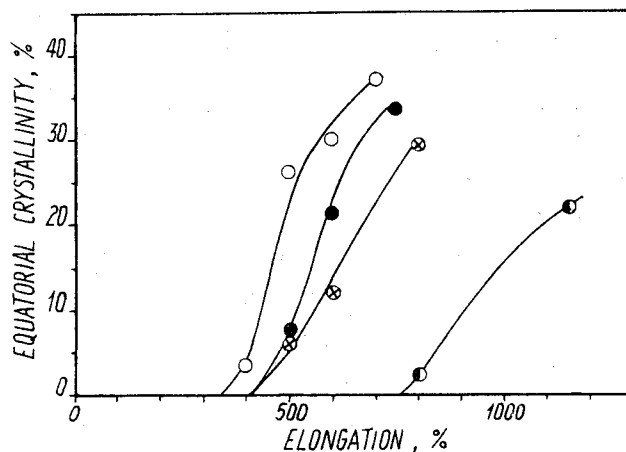


Fig. 8. Cis 1,4 Polybutadiene (Sulphur Cured) Equatorial Crystallinity vs. Elongation at Room Temperature. \circ 99.0 per cent Cis 1,4 Cross Linking $v = 2.0 \times 10^{-4}$ moles/cm³— \bullet 98.1 per cent Cis 1,4 Cross Linking $v = 1.2 \times 10^{-4}$ moles/cm³— \oplus 97.5 per cent Cis 1,4 Cross Linking $v = 0.9 \times 10^{-4}$ moles/cm³— \ominus 97.5 per cent Cis 1,4 Cross Linking $v = 0.2 \times 10^{-4}$ moles/cm³

same figure, it is possible to conclude that a certain degree of crystallinity is also present at temperatures which are far higher than the melting temperature of the unstretched product.

2. Properties of vulcanisates in the absence of reinforcing agents: Vulcanisation of cis-1,4 polybutadiene may be accomplished by means of the curing agents usually employed for highly unsaturated elastomers (NR and SBR).

The mechanical properties of the vulcanisates obtained from high cis-1,4 polybutadiene, in the absence of reinforcing fillers, are influenced by the steric purity of the raw polymer and by the vulcanisation conditions (ingredients of mix, temperature and time of vulcanisation, etc.). In fact, it has been observed⁽¹⁴⁾ that sulphur, during the vulcanisation process, may cause a cis-trans isomerisation of the monomeric units present in the macromolecules.

In our polymerisation tests we have observed that vulcanisation with sulphur and accelerators (of the type N-cyclohexyl-2-benzothiazolesulphenamide, di-2-benzothiazoledisulphide) gives vulcanisates having good mechanical properties for only a limited range of cross-linking density. Beyond the best cross-linking density, the tensile strength of vulcanisates undergoes a rapid decrease.

By curing cis-1,4 polybutadiene with vulcanising fillers in the absence of free sulphur, vulcanisates have been obtained which have excellent mechanical properties in a fairly wide range of cross-linking density.

In Fig. 10 we show the variation of tensile strength as a function of the cross-linking density (in this case, expressed as values of moduli at 300 per

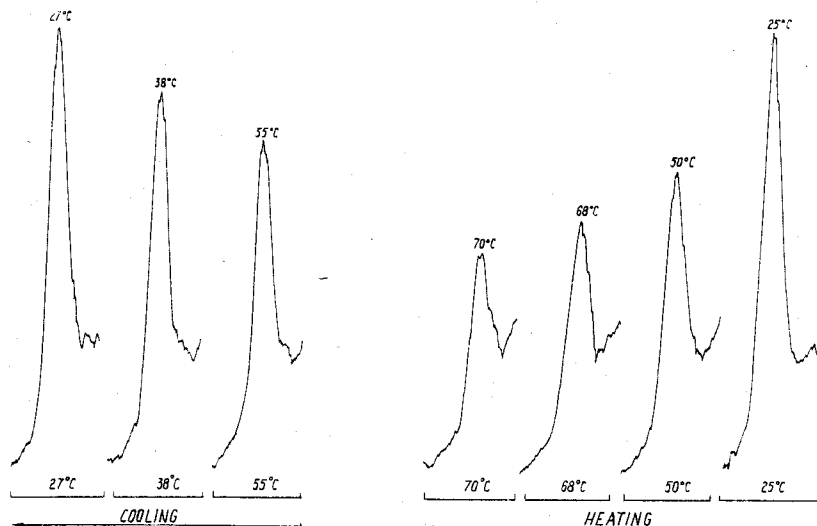


Fig. 9. PB-M1 Geiger Equatorial Registration of 800 per cent Elongated Sample: Effect of Variation in Temperature on the Crystallinity (Peak $2\theta = 22.3^\circ$)

cent), for vulcanisates obtained from PB-M1 polybutadiene, with a Mooney viscosity ranging from 40 to 50. Curve I refers to vulcanisates obtained from mixes with sulphur and accelerators; Curve II refers to vulcanisates obtained from sulphurless mixes. The variations of the cross-linking density have been obtained by varying the composition of the mixes and the vulcanisation conditions, according to statistical methods, and they represent the average value of a great number of results. These cures indicate that sulphurless systems, besides giving vulcanisates having better mechanical properties, show high tensile strengths for a fairly wide range of cross-linking density.

The high tensile strength of cis-1,4 polybutadiene is essentially due to its ability to crystallise under extension, similarly to natural cis-1,4 polyisoprene. As indicated above it clearly appears that both the recipe and the vulcanisation conditions exert a marked influence upon the characteristics of the vulcanisate. In Fig. 11 we report the stress elongation curves for vulcanisates (obtained in the absence of sulphur) of different cross-linking degree, prepared starting from PB-M1 polybutadiene having a Mooney viscosity (ML4 at 100°C.) of 40. They show the characteristic behaviour of a rubber which crystallises under stretch. In Table IX are reported the principal characteristics of some vulcanisates obtained with the aid of different recipes. These data refer to a first set of tests carried out by us on the vulcanisation of cis-1,4 polybutadiene. A careful study of the vulcanisation phenomena is probably necessary in order to improve the properties of the vulcanisates.

Mechanical Properties of Vulcanisates with Carbon Black

The mechanical properties of polybutadiene vulcanisates, reinforced with carbon black, are reported in Table X. Substantial difference between the PB-M1 and PB-P samples are not noticed; this indicates that the presence of the reinforcing agent, under the standard conditions of vulcanisation, reduces the effects of the difference in structure between the two products.

Conclusion

Polybutadiene obtained with soluble cobalt catalysts having a high cis-1,4 content and controlled molecular weight shows better properties than other polybutadienes.

The PB-M1 cis-1,4 polybutadiene produced by Montecatini on a pilot plant scale is characterised by very high cis-1,4 content (97-98 per cent), by a ratio between trans-1,4 and 1,2 configurations of about 1, by a narrow distribution of molecular weights and by a practically complete homogeneity of steric composition and structure in different fractions.

With this polymer gum vulcanised products are obtained which crystallise very

TABLE VII
Compounding Recipes used in Extrusion Tests

	1,4 cis Polybutadiene	Natural Rubber	SB-R 1500
Rubber	100	100	100
HAF	50	50	50
Circosol 2XH	5	—	5
Pine Tar	—	3	—
Antioxidant	1	1	1
Zinc Oxide	3	3	3
Stearic Acid	2	3	3

TABLE VIII
Extrusion Tests with Garvey Die on 60 mm. Extruder

	NR	SB-R 1500	PB-M1			PB-P
(A) Mooney viscosity ML-4 at 100°C.:						
Raw	90	53	35	40	45	50
Compounded	49	47	59	63	74	78
(B) Extrusion at 50°C.:						
Kg/h	28	21	22	26	28	27
m/h	115	69	72	73	72	69
Rating ⁽¹⁾	11	12	12	12	12	11
(C) Extrusion at 120°C.:						
Kg/h	26	23	21	21	16	16
m/h	125	96	94	86	65	58
Rating ⁽¹⁾	12	12	12	12	12	5

⁽¹⁾ Rated on surface, edge and corner; 12(4+4+4) is perfect.

⁽²⁾ Irregular Flow.

well under elongation and give high tensile strength. Increase in modulus with increasing elongation is comparable to natural rubber, owing to crystallinity under extension. The crystallinity of elongated products decreases with temperature, and disappears at very high temperatures.

Furthermore PB-M1 shows improved processing characteristics; in fact, it can be processed by conventional industrial machinery, even without adding natural rubber. Above all, it can be processed at temperatures even higher than 40-60°C., without loss of cohesion or tackiness.

The PB-M1 polymer undergoes breakdown by cold or hot mastication without gel formation. The increase of the compound Mooney viscosity, by adding carbon black, is much less than that of similar compounds obtained from other known polybutadienes.

Montecatini intends to produce cis-1,4 polybutadiene on an industrial scale in the near future.

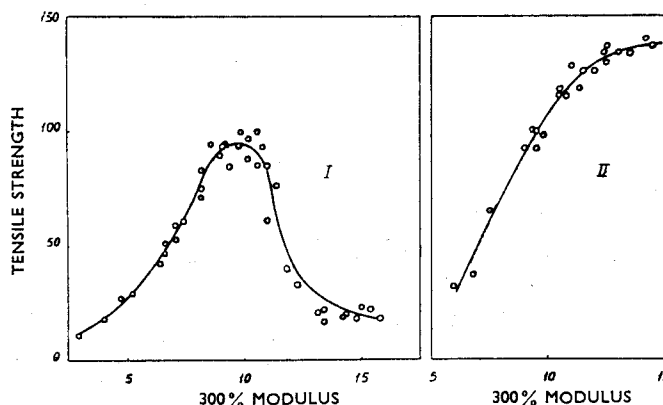
Discussion

Dr. W. Cooper, Dunlop:

Q.—Recently we have presented some evidence to show that the breakdown of these types of polybutadienes is related to the amount of branching in the polymer molecules, i.e. the more linear the polymer the less it breaks down upon the mill. Now, when you presented your data one of your samples showed little or no change in Mooney plasticity on milling and I would like to ask whether this particular sample was, or whether you have any evidence to show that it was, completely linear.

Fig. 10.

PB-M1 Gum
Vulcanisates:
Tensile Strength
Versus State
of Cure
(300 per cent
Modulus)
I, Sulphur
Vulcanisates;
II, Sulphurless
Vulcanisates



A.—Our polybutadiene is still under examination, but we have good reason to believe that on the basis of its behaviour it is very linear. We do not know at this moment a direct and sure method to decide on the degree of branching of a polybutadiene. However if branched and linear products in the mill behave as indicated by Dr. Cooper, I do not think that in our case conclusions could be drawn because the strong tendency of PB-P sample to cross-linking can mask degradation phenomena.

D. Bulgina, Dunlop:

Q.—Could I ask Dr. Leghissa if he has any information on the rate of crystallisation of the cis-polybutadiene he has described compared with that of natural rubber.

A.—I have not information about this question. The characteristics of crystal-

lisation's kinetics of cis-polybutadiene have not yet been examined by us.

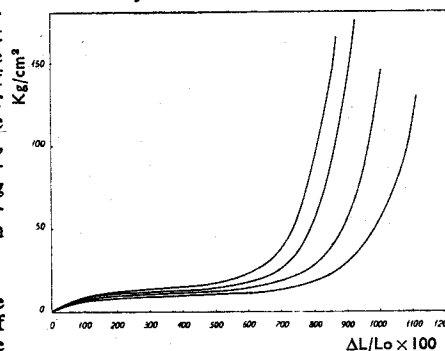


Fig. 11. PB-M1 Gum Vulcanisates in Absence of Free Sulphur: Stress Elongation Curves for Different States of Cure

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TABLE IX—Mechanical Properties of Gum Vulcanisates

Properties		1	2	3	4
Tensile strength	kg/cm ²	130	140	170	160
Elongation at break	%	980	890	880	860
Modulus at 300%	kg/cm ²	7	8.5	13	14
Modulus at 700%	kg/cm ²	20	27.5	34	36
Hardness, Shore A		46	50	49	51
Resilience at 20°C.	%	71	77	78	79
Resilience at 90°C.	%	75	79	80	82

TABLE X
Mechanical Properties Carbon Black Reinforced 1,4 cis Polybutadiene Vulcanisates

	Method	PB-M1	PB-P
Raw Mooney ML-4 at 100°C. ...	ASTM D927	45	45
Compounded Mooney at 100°C. ...	"	57	75
Tensile Kg/cm ² ...	ASTM D412	200	180
Elongation % ...	"	390-410	310-390
Tension Set % ...	"	3-5	3-5
300% modulus Kg/cm ² ...	"	132	122
Resilience ...	DIN 53512	46-47	47-48
Shore A Hardness ...	ASTM D676	63-64	67-68
Tear Strength Kg/cm ² ...	ASTM D634	32	34
Heat Build up (Δt) °C. ...	ASTM D623A	26-28	26-28
(1) Compounding Recipe:			
Rubber ...	100	Stearic acid ...	2
HAF ...	50	Antioxidant ...	1
Dutrex R55 ...	5	Nobs Special ...	0.9
Resin 731-D ...	5	Sulphur ...	1.76
Zinc Oxide ...	3		