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PARTIALLY CRYSTALLIZED ELASTOMER AS A NANOCOMPOSITE MODEL

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Data on the influence of crystallization on the mechanical properties of elastomers — the elastic modulus, the relaxation properties, in particular, restorability in compression, and the tensile strength — have been generalized. These data have been compared to those on the influence of active fillers and a much higher crystallization efficiency has been shown. The size of single crystals has been evaluated for most crystallizable rubbers. It has been inferred that the nanosize of single crystals of elastomers and their direct bond with the elastomer matrix influence the mechanical properties of elastomer materials. In considering a partially crystallized elastomer as a nanocomposite model, one can formulate requirements imposed on efficient nanofillers for elastomer materials.

Recent years have been seen an increasing number of works showing the efficiency of the presence of nanosize particles in polymers. At the same time, it is well known how efficiently the mechanical properties of elastomers change in the presence of the crystalline phase. As early as the 1940s, Aleksandrov and Lazurkin [1] and then Treloar [2] clearly substantiated an analogy between the influence of crystallization and filling. However, the reasons for the higher crystallization efficiency are still not clearly understood. The present report seeks to generalize data on the difference in the influence of crystallization and filling on the mechanical properties of elastomers, to analyze the role of the size of crystallites and to compare this role to the role of the size of filler particles, and to make an attempt at formulating requirements imposed on fillers (meeting these requirements improves the efficiency of fillers).

Crystallization of elastomers has been studied quite adequately. Its influence on the mechanical properties of elastomers is also known [3–5]. Experiments have shown that an increase in the degree of crystallization C to 30% leads to an increase of three orders of magnitude in the elastic modulus of unvulcanized crystallized natural rubber (NR). Figure 1 gives data on a change of more than 1.5 orders of magnitude in the modulus of unvulcanized NR in the process of crystallization to 21% [3, 6]. (Here, apparently, the initial values of the modulus are somewhat overstated, since the initial crystallization (that before the beginning of measurements) is disregarded; this crystallization virtually does not influence the results of measurements of changes in the volume). In the case of polychloroprene (PCP), whose maximum degree of crystallization amounted to 10%, a growth of the order of magnitude in the shear modulus was observed (Fig. 2) [3, 7, 8]. The tensile [2] and torsional [9] moduli change in the process of crystallization in the same manner. Addition of the most active filler to the rubber, even in dosages at the compatibility level, cannot ensure such an effect.

The addition of a filler in the amount $C_1 = 5\%$ virtually does not change the mechanical properties, whereas the presence of a 5% crystallization leads to a twofold increase in the modulus (Table 1).

In vulcanized rubber whose initial modulus is a more definite quantity, changes in the modulus are somewhat smaller. Thus, a change from 0 to 30% in the modulus leads to a growth of two orders of magnitude in the modulus of compression of natural rubber. For rubbers of special-type polychloroprene the modulus grows by 2.5 orders of magnitude with increase in the degree of crystallization to $C = 18\%$; when $C = 10\%$ the increase observed in the modulus is the same as that for unvulcanized rubber, i.e., it is one order of magnitude, which is certainly unattainable (and unnecessary) in the case of the corresponding values of C_1. For an unfilled vulcanizate of polydimethylsiloxane (PDMS) whose degree of crystallization attains values of $C = 45\%$ the tensile modulus increases by nearly 3.5 orders

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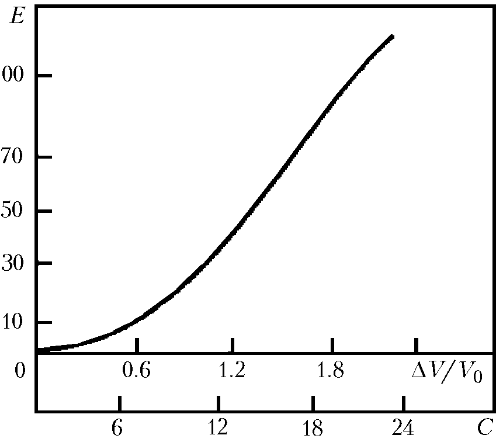


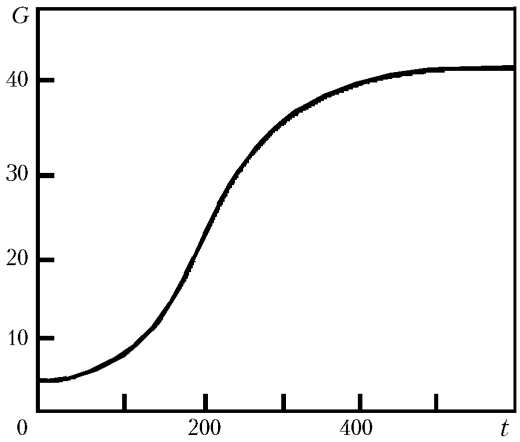


Fig. 1. Tensile modulus E vs. relative change in the volume $\Delta V/V_0$ and degree of crystallization C for an unvulcanized NR (from the data of [6], see [3]). E and G, MPa; $\Delta V/V_0$, %; C, %.

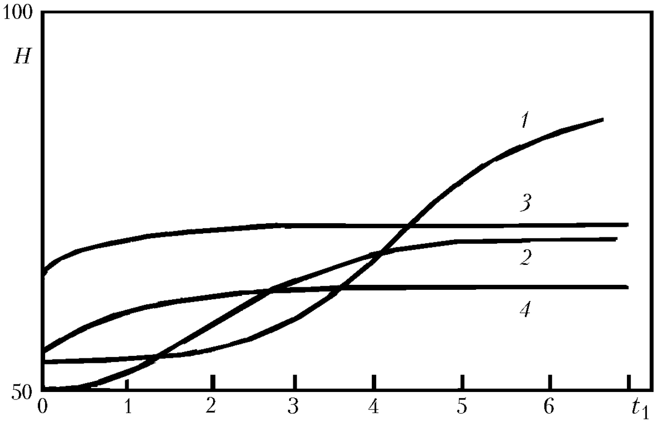
Fig. 2. Shear modulus G vs. crystallization time t for PCP; the limiting degree of crystallization is $C_\infty = 10\%$ (from the data of [7], see [3]). G, MPa; t, min.

TABLE 1. Interrelation between the Degree of Crystallization C and the Modulus M in the Amorphous (M_{am}) and Partially Crystallized ($M_{\mathrm{p.cr}}$) States for Crystallizable Rubbers, Unfilled Vulcanizates, and Filled Rubbers Based on Them

Rubber	C, %	Form of strain	M, MPa		T, °C	t, days
			M_{am}	$M_{\mathrm{p.cr}}$		
NR	30	Compression	0.5	$5 \cdot 10^2$	–25	20
NR	21	Extension	4.0	$1.1 \cdot 10^2$	–25	≈15
NR (vulcanizate)	30	Compression	1.1	$1 \cdot 10^2$	–25	28
NR (vulcanizate)	17	»	1	70	–25	11
PCP	10	Shear	4	40	–5	0.4
PCP	5	Compression	2	4	–10	1
PCP (vulcanizate)	10	»	2.5	$2 \cdot 10^2$	–10	0.1
PCP (vulcanizate)	18	»	2.5	$5 \cdot 10^2$	+20	1
PDMS (vulcanizate)	45	Extension	0.1	$4 \cdot 10^2$	–55	0.3
SKÉPT (rubber)	11	Compression	10	$1.5 \cdot 10^2$	–25	0.5
SKÉPT (rubber)	5	»	7	85	–40	0.1
SKÉPT (rubber)	3	»	7	65	–40	0.05

of magnitude. Some data on the change in the tensile and shear moduli and in the modulus of compression are given in Table 1. The data on the change in hardness confirm the conclusion on the higher crystallization efficiency than that for commercial carbon (Fig. 3 and Table 2).

Particularly pronounced is the efficiency of the influence of the process of microcrystallization, i.e., the formation of a small number of crystals with a nearly critical size, on the mechanical properties of elastomers. Thus, the presence of microcrystals in a number smaller than 3% (which cannot be determined by the x-ray method) leads to a growth from 50 to 80 Shore A units in the hardness H of rubber based on SKÉPT ethylene-propylene rubber [10]. For rubbers based on oxygen-containing fluoroelastomers (FEs) we have an increase from 58 to 67 and from 69 to 80 units, apparently with an even smaller degree of crystallization (of the order of 2%) (Fig. 3) [11].



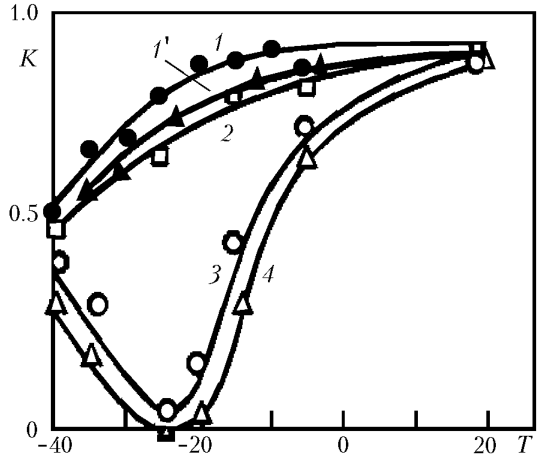


Fig. 3. Hardness H vs. crystallization time t_1 for rubbers based on PCP (1), SKEPT (2), and FE (3, 4). $T = \pm 20^\circ C$. H, Shore A units; t_1, days.

Fig. 4. Restorability K vs. temperature T for NR-based rubbers; 1–4) unfilled rubber [1) $t_1 = 2$ h and $C = 0$; 2) $t_1 = 5$ h, at $T = -25^\circ C$ and $C = 3\%$; 3) $t_1 = 16$ h, at $T = -25^\circ C$ and $C = 12\%$; 4) $t_1 = 48$ h, at $T = -25^\circ C$ and $C = 22\%$]; 1$'$) filled rubber, $C_1 = 30$ wt. parts of commercial carbon. $t_1 = t_2 = 10$ min and $\varepsilon = 0.3$. T, °C.

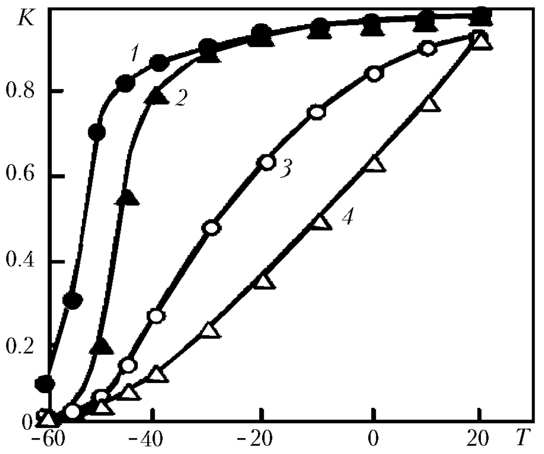
TABLE 2. Interrelation between the Degree of Crystallization C and the Hardness H in the Amorphous (H_{am}) and Partially Crystallized ($H_{\mathrm{p.cr}}$) States for Unfilled Vulcanizates and Crystallizable-Rubber-Based Filled Rubbers

Rubber	C, %	H, Shore A units		T, °C	t, days
		H_{am}	$H_{\mathrm{p.cr}}$		
NR (vulcanizate)	30	35	98	–25	20
NR (rubber)	30	52	98	–25	20
NR (rubber)	30	65	98	–25	20
PCP (vulcanizate)	18	45	95	+20	1
PCP (vulcanizate)	10	55	95	+20	7
SKEPT (rubber)	3	50	80	+20	7
FE (rubber)	2	58	67	+20	7
FE (rubber)	2	69	80	+20	7

Significant is the difference in the action of crystallization and filling on the relaxation properties of elastomers. The restorability K is the most sensitive index. The decrease in the restorability of unfilled and filled rubbers with different bases in the region of vitrified-to-highly elastic transition is not very large, even in the case of limiting filling with the most active fillers. In the process of crystallization, the restorability may decrease to 0 (Fig. 4) [3–5]. The temperature dependence of the restorability for ethylene-propylene-based rubbers with different contents w of propylene, therefore containing different numbers of microcrystals — from 0 with the highest content to 7% with the lowest one of those presented in Fig. 5 — also differs [5, 10].

It is not by accident that mechanical methods, including relaxation ones, are widely used for study of crystallization because of their high sensitivity [3–5].

A comparison of the data of regular crystallization and microcrystallization shows that the smaller the minimum possible size of crystallites, the higher the efficiency of their influence on the hardness and relaxation properties of elastomers. The influence of crystallization on the strength properties of elastomers is also more efficient. The use of fillers in noncrystallizable forms of rubber makes it impossible to attain the tensile strength ensured by the development of orientational crystallization in rubbers based on crystallizable forms. The same is true of both fatigue



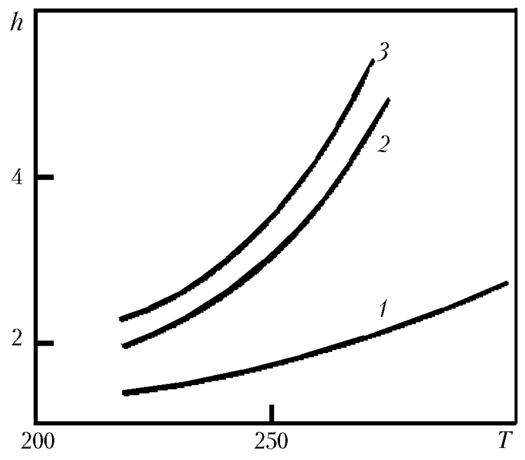


Fig. 5. Restorability K vs. temperature T for SKÉPT-based rubber with different molar contents of propylene w, %: 1) 48.6; 2) 46.7; 3) 43; 4) 29.7. $t_1 = 5$ min, $t_2 = 10$ min, and $\varepsilon = 0.3$. T, °C.

Fig. 6. Size of crystallites h in ethylene-propylene rubber vs. temperature of their formation T under the assumption of different values of the equilibrium melting temperature T_m^0, K: 1) 414; 2) 335; 3) 333. h, nm; T, K.

TABLE 3. Evaluation of the Crystallite Size h in Different Rubbers at Different Supercoolings $\Delta T = T_m^0 - T$

Rubber	T_m^0, K	σ, erg/cm^2	ΔH, J/g	T_m, K	ΔT_m, K	T, K	ΔT, K	h, nm
NR	313	19.9	64.6	281	32	248	65	6.1
				282	31	263	50	6.1
PCP	353	23.4	94.6	333	20	263	90	8.7
				342	11	295	58	15.9
PB	283	42.3	73.6	263.5	19.5	218	65	16.7
				272	11	263	20	29.6
PDMS	238	34.0	62.7	233	5	195	43	51.6
				235	3	218	20	86.0
SKÉPT	414*	87.4*	68.3*	263	151	253	161	7.0
				323	91	293	121	11.6
FE	483**	150**	104.5**	295	188	253	230	7.4
				333	150	293	190	9.2

*Polyethylene.

**Vinylidene fluoride.

strength and abrasive wear, although here the difference is not so great since, under test conditions, orientational crystallization develops only in the mouths of the cracks formed and the time it takes them to form and hence their number are much smaller.

The appearance of fillers whose particles have a nanosize and their high efficiency make it possible to assume that one reason is the small size of single crystals in elastomers. Not very numerous direct electron-microscopic data show that, in an unstressed state, the size of single crystallites does not exceed tens of nanometers [3, 12]. This is also demonstrated by the evaluation of the crystallite size by the change in the melting temperature, which leads to values of the order of a few nanometers in the case of microcrystallization. Such an evaluation was carried out with the use of the Thomson–Gibbs equation [13]:

$$T_m = T_m^0 \left[1 - 2\sigma/(h\Delta H)\right] .$$

Figure 6 [10] gives the results for one type of ethylene-propylene rubber that have been obtained with the use of different literature data for T_m^0 of polyethylene. The most correct seems to be the value used in constructing curve *1*, i.e., the microcrystal size characteristic of this type of ethylene-propylene rubber changes from 1.5 to 2.2 nm as a function of the crystallization temperature. Using this equation and knowing the quantities T_m^0, σ, and ΔH for other crystallizable elastomers, we can calculate the crystallite size h for them. Depending on the type of rubber and the temperature, the values of h change from 6 for natural rubber to 90 nm for polymethylsiloxane; the quantities h have intermediate values equal to 16–30 nm for polybutadiene (PB) (Table 3).

Under certain conditions, single crystallites, i.e., single crystals, can unite into polycrystals — spherulites or large-size grains [3]. However, there is always an amorphous phase inside such polycrystals; in the case of elastomers its content can attain 80%, whereas the size of single crystals is within the nanolimits.

Single crystallites formed in the process of orientational crystallization also have a nanosize [3, 12]. In this case, too, polycrystals — oriented axial fibrils or aggregates of transverse lamellas — can be of much larger size [3, 12, 14].

The above data show that crystallites are natural nanofillers of elastomers. However, their high efficiency is not only related to the excess surface energy, which is determined by their small size. A very significant factor is their direct bond with the elastomer matrix, whose macromolecules bordering the crystallites can be part of their composition. Both of these factors enable the crystallites to move together with the matrix under the action of stresses (including thermoelastic ones). It follows that to improve the efficiency of nanofillers in elastomers one must both decrease the size of their particles and improve the conditions of bonding between the surface of these particles and the elastomer matrix.

Works on the use of precipitated silica (a large number of such works have appeared in recent years), in particular, take this path. We give only one example: the addition of *in situ* silica to natural rubber makes it possible to obtain a filler-particle size of about 40 nm and rules out the formation of filler aggregates; the hardness attains 72 Shore A units as compared to 48 for the regularly filled elastomer [15]. However, in our opinion, the size of filler particles in this case is still larger than the optimum size and their interaction with the rubber matrix can be improved.

Thus, the crystallites in elastomers represent a convenient model of nanofillers; an analysis of their behavior in the elastomer matrix makes it possible to most efficiently use the advantages of fillers with nanosize particles.

In closing, we must note that the possibility of substantially changing properties by introducing of small amounts of nanoadditions does not rule out the simultaneous use of large amounts of regular fillers, improving properties and making products manufactured from elastomers less expensive.

NOTATION

C, degree of crystallization, %; C_∞, limiting degree of crystallization, %; C_1, content of the filler, %; E, tensile modulus, MPa; G, shear modulus, MPa; H, hardness of rubbers, Shore A units; h, crystal size, cm or nm; H_{am}, hardness of rubbers in the amorphous state, Shore A units; $H_{p.cr}$, hardness of rubbers in the partially crystalline state, Shore A units; K, restorability, dimensionless quantity; M, modulus in any state under any form of strain, MPa; M_{am}, modulus in the amorphous state under any form of strain, MPa; $M_{p.cr}$, modulus in the partially crystalline state under any form of strain, MPa; T, crystallization temperature, K or ^oC; t, crystallization time, sec, min, h, or days; t_1, time of storage of a compressed sample, sec, min, h, or days; t_2, time of restoration of the sample after its release, min; T_m, actually measured melting temperature of crystals, K; T_m^0, equilibrium melting temperature of crystals, K; V, volume of the sample after crystallization, cm^3; V_0, volume of the sample before crystallization, cm^3; w, content of propylene in SKÉPT, %; ΔH, heat of melting; J/g; ΔT, supercooling, $\Delta T = T_m^0 - T$, K, or ^oC; ΔT_m, difference between the equilibrium and actually measured melting temperatures, $\Delta T_m = T_m^0 - T_m$, K, or ^oC; ε, degree of compression, dimensionless quantity; σ, energy of formation of the crystal–melt interface, erg/cm^2. Subscripts: am, amorphous; p.cr, partially crystalline; m, melting. Superscript: 0, equilibrium melting temperature.

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