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COMPARATIVE ANALYSIS OF MOLECULAR-TOPOLOGICAL STRUCTURE OF ABS-COPOLYMER UNDER LIQUID-PHASE AND SOLID-PHASE EXTRUSIONS

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Abstract: The work is devoted to thermomechanical exploration (TMS-method) of a molecular-topological structure of ABS-copolymer, received by solid-phase extrusion in comparison with the material received by the method of liquid-phase extrusion.

Thermomechanical spectroscopy is a new way of molecular-topological structure diagnostics of copolymer without using any solutions. That way was developed in the Institute of Chemical Physics Problems (Russian Academy of Sciences). The diagnostics is based on the thermomechanical analysis (TMA) of polymers. It allows to implement the complex molecular-topological testing of polymers with different structures and compositions within one experiment for the time of a snap practically.

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1. Experiment

Experimental researches of solid-phase extrusion (**SPE**) [1, 2, 7–9] polymer materials based on ABS-copolymer were carried out on the trial type with the mesh of a high pressure designed in Tambov State Technical University [6, 10, 11] and in the Laboratory of Plastic Deformation ISMAN (Chernogolovka) on machine «Instron» in SPE mode at V = const at various speeds of an extrusion over the range $V = 7…200$ mm/min.

Thermomechanical analysis (**TMA**) [3–5] was run by the method of quartz hemispherical sonde penetration into polymer (the radius of a sonde was 1 mm). The dynamics of sonde interaction with polymer surface was analyzed in paper [12]. As one of the quantities being measured by this method is the change of linear specimen value between the substrate and the sonde, so then the specimen itself must meet the special requirements made for the form and aggregate state. The polymer specimen being in solid aggregate state must have the continuousness of structure in the whole volume. The polymer specimen can have any form but it must be with two parallel-sided facetways. The distance between the facetways can amount from a few dozens of microns to a few millimeters depending on the sensitivity of gaging equipment and the coefficient of polymer thermal expansion. Before the analysis powder-like polymers are to be pressed in a closed space mould under optimized pressure which is equal to 20 MPa.

The specimen is put into the heat-chamber of УИП-70М thermo-analyzer [13] or in a different one and then it is chilled with the speed of 5 °/min up to – 120 °C that is a few dozen of degrees lower than the expected temperature of polymer vitrification. Then the specimen was being kept in such conditions for 5–10 min. At the same time the vitrified polymer was under the pressure of 0,2–0,5 g weight depending on the presupposed polymer module. Then heating was started with the speed of rising at temperature which was equal to the speed of temperature reduction while freezing.

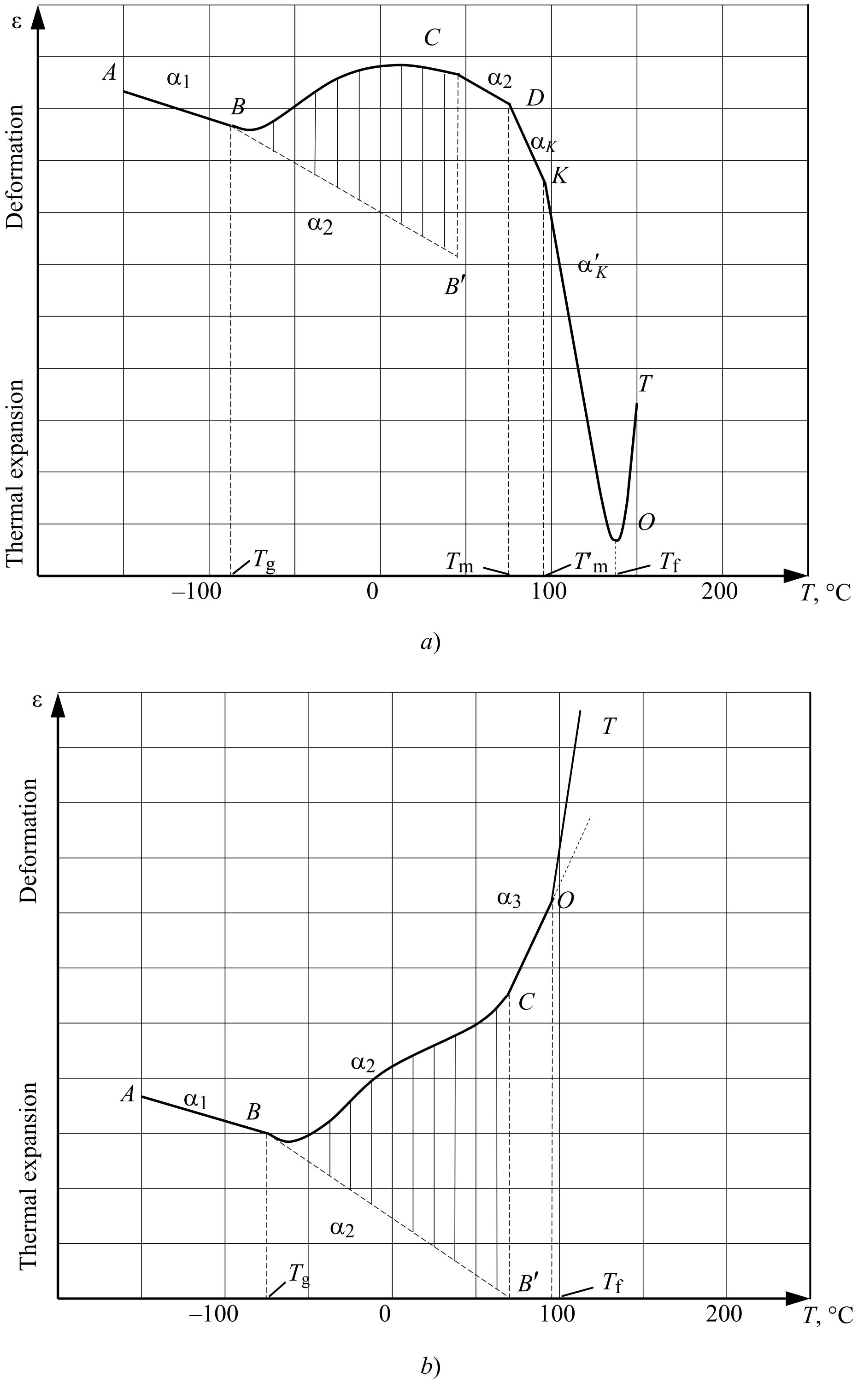
From this very moment according to the monitoring device (КСП-4) indices the registration of two functions was recorded: deformation – time and temperature – time, which are necessary for drawing of thermomechanical curve (**TMC**) in position data of deformation – temperature. TMA was finished when the temperature of fixed polymer molecular flow was achieved.

2. Molecular-topological structure of ABS copolymer after liquid-phase extrusion

Liquid-phase extrusion of plastics in general and copolymers ABC in particular is the basic technological process of processing rigid chain polymers and polymers of an amorphous-crystal structure such as polythene, polyamide-6 and many others. The structure of the target head in the extruders used for these purposes allows not only to change technological procedure of mixture at the static and dynamic modes, resulting to essential topological structure change of molecular-mass and relaxation characteristics of processed polymers [14, 15], but also to adjust their isotropic-anisotropic transformations proceeding at it. In this respect method of thermomechanical spectroscopy (**TMS-method**) gives the unequivocal information on these transformations by rather simple methodical reception, using the properties of macromolecules glass fragments of polymer to essential change of the specific volume at transition in a plastic condition [16]. And if to assume, that at an output of liquid melt from the head of the amalgamator the copolymer macromolecules are guided in the direction of a current vector and in the same direction they crystallize at cooling, then the structure of a copolymer generated at it becomes topologically anisotropic one. It is easy to interpret at TMA, having changed the vectors direction of the loading appendix of P_0 and the currents of liquid melt at extrusion. The crystallinity degree determined at it will differ depending on a degree of isotropic-anisotropic transformations of copolymer. And, at a coaxial direction (||) the crystallinity degree should be lower, than at mutual-perpendicular (⊥).

On Fig. 1 the TMC of copolymer is resulted after liquid-phase extrusion (**LPE**) at a coaxial variant of the analysis, registered at a temperature interval from – 100 °C up to 200 °C. It is the characteristic for topologically three-block amorphous-crystal polymer of a pseudo-mesh structure. At the temperature interval from – 100 °C up to – 83 °C the copolymer is in a glass condition and it extends at heating with constant speed (straight line AB), characterized in the factor of linear thermal expansion $\alpha_1 = 4{,}36 \cdot 10^5$ deg^{-1}.

At $T_g = -83$ °C in a copolymer the speed of its thermal expansion (dilatometer straight line BB') with the simultaneous occurrence of hermomechanical (penetration) deformations ε, measured concerning straight line BB' sharply increases. Its occurrence, according to the theory of physical grids [17, 18], is connected to the destruction of a grid of physical connections at heating polymer and at transition of its most low-molecular intercentral homologues into a condition of current or a sol-condition. With the rise of the temperature such processes proceed continuously with consecutive transition into the current condition of homologues of all molecular weights accompanied with deformation jump $\Delta\varepsilon_i$, starting with the length in Coon segment at T_g and finishing by the most high-molecular homologues at the temperature in the point ($T_\infty = 91$ °C). At temperature T_i bending around the deformation jumps occuring in



a)

b)

Fig. 1. Thermomechanical curves of ABS specimens after LPE (*a*) and specimens after SPE (*b*) at the extrusion speed of V_{ext} = 100 mm/min.
T_{ext} = 22 °C. A direction of test || to the direction of a specimen orientation at SPE

polymer at end of a segmental relaxation of all homologues with weight M_{ci} forms transitive area TMC (curve *BC*). Its coordinates are: on an axis of abscissas M_{ci} as the function $\Delta T = T_i - T_g$ and on an axis of ordinates φ_i as function $\Delta\varepsilon_i$ Being in coordinates of curves of molecular-mass distribution, the curve of transitive area of TMC is represented not than other as to pseudo-integrated MMD curve of intercentral circuits in a pseudo-grid of the amorphous block-matrixes of a copolymer. Its analysis allows to define average-numerical M_{cn} and average weight M_{cw} value of their molecular weight:

$$M_{cn} = 64500;\ M_{cw} = 113600;\ K = 1{,}76$$

and to construct their MMD curve (Fig. 2).

At temperature in a point *C* the processes of a segmental relaxation in intercentral circuits come to the end and the structure of a copolymer passes in a thermostable condition of its pseudo-grid that is the plateau of high-elasticity (straight line *CD*). Thus the direction of deformation processes changes again starting from penetration to thermal expansion, but already for the account increase in free volume V_f. The speed of this deformation is characterized by the factor of linear thermal expansion $\alpha_2 = 18{,}6 \cdot 10^5$ deg^{-1} which should not exceed the factor α_1 more than six times [19].

Such ratio is typical for polymers of a mesh and pseudo-mesh structure with heat–resistant units of a branching. The increase in free volume at heating begins with value at temperature of vitrification, equal [20] $3(\alpha_2 - \alpha_1)T_g = 0{,}081$. This value is the characteristic for pseudo-mesh structure of the amorphous block with the intercentral circuits inclined to crystallization.

At temperature in point *D* the thermostable condition area of pseudo-mesh structure of the block comes to an end, and its further increase leads to sharp increase of expansion speed of polymer. It extends with the speed α_K, equal to $30{,}1 \cdot 10^5$ deg^{-1}. Its

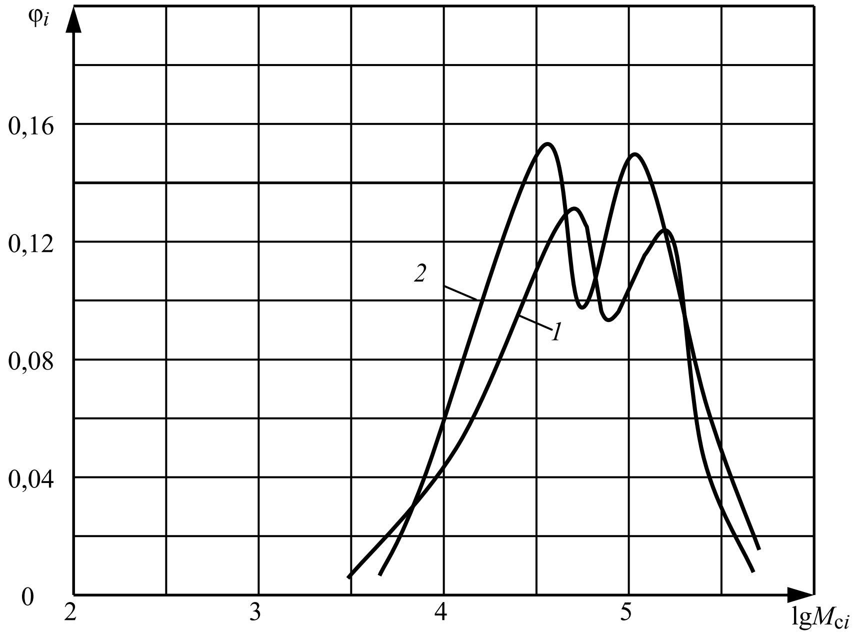


Fig. 2. MMD intercentral circuits functions of the matrix block of ABS copolymer of liquid-phase extrusion at coaxial || (*1*) and mutual-perpendicular ⊥ (*2*) orientations of vectors

ratio to α_1 exceeds the critical value equal to 6, and consequently all processes of expansion, proceeding in polymers with such speed, should be related to fusion of a crystal phase [19]. At the temperature of $T_\mathrm{m} = 119$ °C the crystallite fusion of low-melting updating starts and in the point K in which the speed of polymer expansion again changes at $T'_K = 144$ °C with the speed of $\alpha_K = 95{,}2 \cdot 10^5$ deg^{-1} the fusion of the second one, which is of more refractory crystal updating, begins. The process of fusion of this crystal updating comes to the end at temperature ($T_\mathrm{f} = 159$ °C) in the point O by the transition of a copolymer in a condition of molecular current (a curve OT). It is necessary to note the natural difference of this temperature from temperature of technological current which, as a rule, begins at temperature on 50–60 °C above.

Coming back to Fig. 2 on which MMD curve of intercentral circuits in a pseudo-grid of the matrix block is resulted, with good reason we can say, that its bimodal character is connected to the presence of two updatings at it as units of a crystallites branching. The intercentral circuits of two updatings have various masses and its distribution and they form its mesh structure. The molecular mass of glass circuits, as well as in the amorphous block, is proportional to a difference of temperatures between the beginning of current (T_f) and fusion (T_m) [21], i.e. basically the process of fusion of a polymer crystal phase than does not differ physically from the process of defreezing of segmental mobility in a glass condition of amorphous polymer [22, 23].

And the process of fusion should be represented as practically instant transition from the orientation of the first sort circuits into the second sort at the temperature which is already hardly above the temperature of fusion start with the subsequent process of its devitrification. In that case

$$\lg M_\mathrm{c} = 2{,}3 + 11(T_\mathrm{f} - T_\mathrm{m})/[100 + (T_\mathrm{f} - T_\mathrm{m})], \qquad (1)$$

and M_c and M'_c are equal accordingly 31600 and 63100.

Weight shares of circuits in structures of matrix and two crystal blocks are proportional to their total thermomechanical deformation (ε_a, ε_c и ε'_c). And they are defined from the ratio:

$$\varphi_\mathrm{a} = \varepsilon_\mathrm{a}/(\varepsilon_\mathrm{a} + \varepsilon_\mathrm{c} + \varepsilon'_\mathrm{c}),\ \ \varphi_\mathrm{c} = \varepsilon_\mathrm{c}/(\varepsilon_\mathrm{a} + \varepsilon_\mathrm{c} + \varepsilon'_\mathrm{c}) \ \text{ and } \ \varphi_\mathrm{c} = 1 - (\varphi_\mathrm{c} + \varphi'_\mathrm{c})$$

and they also correspond as 0,69 : 0,11 : 0,20.

The quantity of copolymer molecular mass can be as the first approximation designed by the method of block averaging according to the equations [24]:

$$M_\mathrm{n} = (\varphi_\mathrm{a} / M_\mathrm{cn} + \varphi_\mathrm{c} / M_\mathrm{c} + \varphi'_\mathrm{c} / M'_\mathrm{c}) = 64100;$$

$$M_\mathrm{w} = \varphi_\mathrm{a} M_\mathrm{cw} + \varphi_\mathrm{c} M_\mathrm{c} + \varphi'_\mathrm{c} M'_\mathrm{c} = 105000; \quad K = 1{,}6$$

and it can correspond to the true values provided that all topological blocks of a copolymer are formed not by the whole macromolecule, but only its fragments. Thus, in the structure of each macromolecule on the average there should not be more than one fragment of each type. Naturally the infringement of even one of these conditions leads to the error of the designed value from the true one. To these the average-numerical quantity of mass and average-weight quantity of mass in a smaller measure will be especially sensitive as the most probable is crushing of a crystal phase into fine crystallites connected by the through passage circuits of one macromolecule. Therefore, in any case analysing only one specimen of polyblock structure, the molecular mass of polymer designed by the method of block averaging is not certain always. At the analysis of logically connected series of polymers by the TMS-method one more additional parameter is received, except for a regular set of molecular-relaxation and quantitative characteristics. This additional parameter is the degree of crystallites crushing and an opportunity of specifications of uncertain value of polymer molecular mass in this connection.

What has happened to topological structure of copolymer ABC after its LPE? To answer this question, the analysis of a copolymer has been carried out by the same TMS-method, but at mutual-perpendicular orientation of vectors. In such variant of measurement the TMC of a copolymer is not resulted, as it is absolutely identical to a curve drawn on Fig. 1. Essential changes were not found in both molecular-relaxation and quantitative characteristics which are measured and designed directly. All of them are given in Table 1, 2. The character of MMD curves has not changed in intercentral circuits of a pseudo-grid of the copolymer matrix block (Fig. 2). Only values of the molecular masses average on blocks turned to a little bit different.

If we compare the concentration of intercentral circuits in a matrix pseudo-grid $\nu_e = \rho / M_{cn}$ (ρ – density) it shows, that at the coaxial orientation of vectors such circuits are found on 15 % more, than at the mutual-perpenducar orientation. Hence, it has the higher concentration of crystal units of a branching also. Actually, it was proved experimentally – $\varphi'_c\,(\|) > \varphi'_c\,(\perp)$. And though in its turn it has exceeded the probability of not disposable crossings (on the average) by each macromolecule of crystal blocks, but practically it was not reflected in value of the average molecular masses. The general conclusion from the comparative analysis of ABC copolymer is having a single meaning: under liquid-phase extrusion ABC copolymer keeps isotropic character of not only the general topological structure, but also of molecular-relaxation characteristics.

3. Molecular-topological structure of ABS copolymer after solid-phase extrusion (SPE)

We shall begin the analysis of a molecular-topological structure of ABC copolymer after its SPE with different speeds of extrusion (with the minimal speed 2 mm/min) and in the same methodical sequence of carrying out TMA, namely from the coaxial orientation of vectors. On Fig. 3 the TMC of copolymer is given. It was registered at the temperature interval from – 120 up to 200 °C. All the deformation processes occurring in it at rising temperature and under the influence of loading P_0 are unequivocal with which were described above at the analysis of a copolymer after LPE up to the finishing temperature of a segmental relaxation in it (T_∞). It is the area of glass state (straight line *AB*). The expansions of a copolymer in this area take place with the speed $\alpha_1 = 3{,}21 \cdot 10^5$ deg.$^{-1}$. The transition from the glass state into hyperelastic state takes place at $T_g = -89$ °C. Then with the temperature rise using the transition into the area of penetration deformation and formation of the TMC transitive area (curve *BC*), which was used as pseudo-integrated MMD curve of intercentral circuits in a pseudo-grid of the amorphous block, we have calculated their average molecular-mass characteristics:

$$M_{cn} = 143200,\ M_{cw} = 214100 \text{ and } K_0 = 1{,}50.$$

The function of their MMD is presented on Fig. 4. That is the procedure of carrying out TMA and getting the information on pseudo–mesh structure of the amorphous block for any polyblock polymer. As to units of a branching in the matrix block and their thermal stability, the information on it follows from the character of temperature area of hyperelastic expansion (a plateau of hyperelastic), namely its speed. So, if the ratio α_2 to α_1 is less 2,5 and further with inversion it reaches negative values it means, that in mesh (or pseudo-mesh) structure of the amorphous block except for heat-resistant units (chemical, crystal or cluster ones) of a branching, there are also thermolabile topological units of circuits crossing.

At TMA of SPE copolymer that case is found out just, when as units of a branching in a pseudo-grid of its matrix block on TMC there are the fragments of the cluster block (a straight line *CO* – a plateau of hyperelastic), as well as the interlacings of circuits. The segmental relaxation of the circuits forming the cluster block begins at

Table 1

Molecular-relaxation and quantitative characteristics of copolymer ABC after liquid- and solid-phase extrusion at || orientations of vectors

Characteristics ABC	ABC after LPE	ABC after SPE	
		Speed of extrusion, mm/min	
		2	100
Amorphous a block – matrix			
T_g, °C	-83	-60	0
$\alpha_1 \cdot 10^5$, deg.$^{-1}$	4,36	3,21	3,81
$\alpha_2 \cdot 10^5$, deg.$^{-1}$	18,6	12,2	15,4
V_f	0,081	0,052	0,066
$M_{cn} \cdot 10^{-3}$	64,5	143,2	297,9
$M_{cw} \cdot 10^{-3}$	113,6	214,1	390,0
K	1,76	1,50	1,31
φ_a	0,69	0,23	0,47
The crystal block 1 (unit of a branching)			
T_m, °C	119	–	–
$\alpha_K \cdot 10^5$, deg.$^{-1}$	34,1	–	–
$M_c \cdot 10^{-3}$	35,5	–	–
φ_c	0,11	0,0	0,0
The crystal block 2 (unit of a branching)		Cluster block (unit of a branching)*	
T'_m (T_{cl}), °C	144	63	75
$\alpha'_K \cdot 10^5$ ($\alpha_{cl} \cdot 10^5$), deg.$^{-1}$	43,9	219,8	228,6
$M'_c \cdot 10^{-3}$ ($M_{cl} \cdot 10^{-3}$)	63,1	70,8	35,4
φ'_c (α_{cl})	0,20	0,77	0,53
T_f, °C	159	90	92
ABC mass average on blocks			
$M_n \cdot 10^{-3}$	58,9	80,1	60,4
$M_w \cdot 10^{-3}$	94,9	103,8	202,0
K	1,6	1,3	3,4

[*] Characteristics symbols of the cluster block are given in brackets.

Table 2

Molecular-relaxation and quantitative characteristics of copolymer ABC after liquid- and solid-phase extrusion at ⊥ orientations of vectors

Characteristics ABC	ABC after LPE	ABC after SPE	
		Speed of extrusion, mm/min	
		2	100
Amorphous a block – matrix			
T_g, °C	-83	-86	-88
$\alpha_1 \cdot 10^5$, deg.$^{-1}$	3,33	5,05	4,65
$\alpha_2 \cdot 10^5$, deg.$^{-1}$	19,2	20,8	11,7
V_f	0,090	0,088	0,039
$M_{cn} \cdot 10^{-3}$	73,9	21,4	40,5
$M_{cw} \cdot 10^{-3}$	120,2	35,0	69,6
K	1,63	1,63	1,72
φ_a	0,79	0,08	0,16
The crystal block 1 (unit of a branching)			
T_m, °C	108	53	66
$\alpha_K \cdot 10^5$, deg.$^{-1}$	30,1	333,3	133,3
$M_c \cdot 10^{-3}$	31,6	10,0	12,6
φ_c	0,10	0,15	0,12
The crystal block 2 (unit of a branching)			
T'_m, °C	132	82	92
$\alpha'_K \cdot 10^5$, deg.$^{-1}$	43,9	400,0	833,3
$M'_c \cdot 10^{-3}$	63,1	100,0	63,1
φ'_c	0,11	0,77	0,72
T_f, °C	160	113	119
ABC mass average on blocks			
$M_n \cdot 10^{-3}$	64,1	37,8	40,2
$M_w \cdot 10^{-3}$	105,0	81,3	58,1
K	1,6	2,2	1,4

the temperature $T_{cl} = 63$ °C and comes to an end at $T_f = 90$ °C which is the certificate of practically unimodal distribution of their molecular mass equal to 70790. The relative content of topological interlacings to any other type of units is calculated from the ratio [25]

$$\varphi_T = 0{,}5 - 0{,}045(\alpha_{cl}/\alpha_1)P_0^{-1}. \qquad (2)$$

From this equation it follows, that a condition of topological units presence at a pseudo-grid only is the performance of an inequality $\alpha_{cl}/\alpha_1 \geq 3{,}2$. Such variant of pseudo-mesh structure of the matrix block of copolymer ABC after SPE with the speed of 2 mm per a minute is realized at coaxial orientation of vectors.

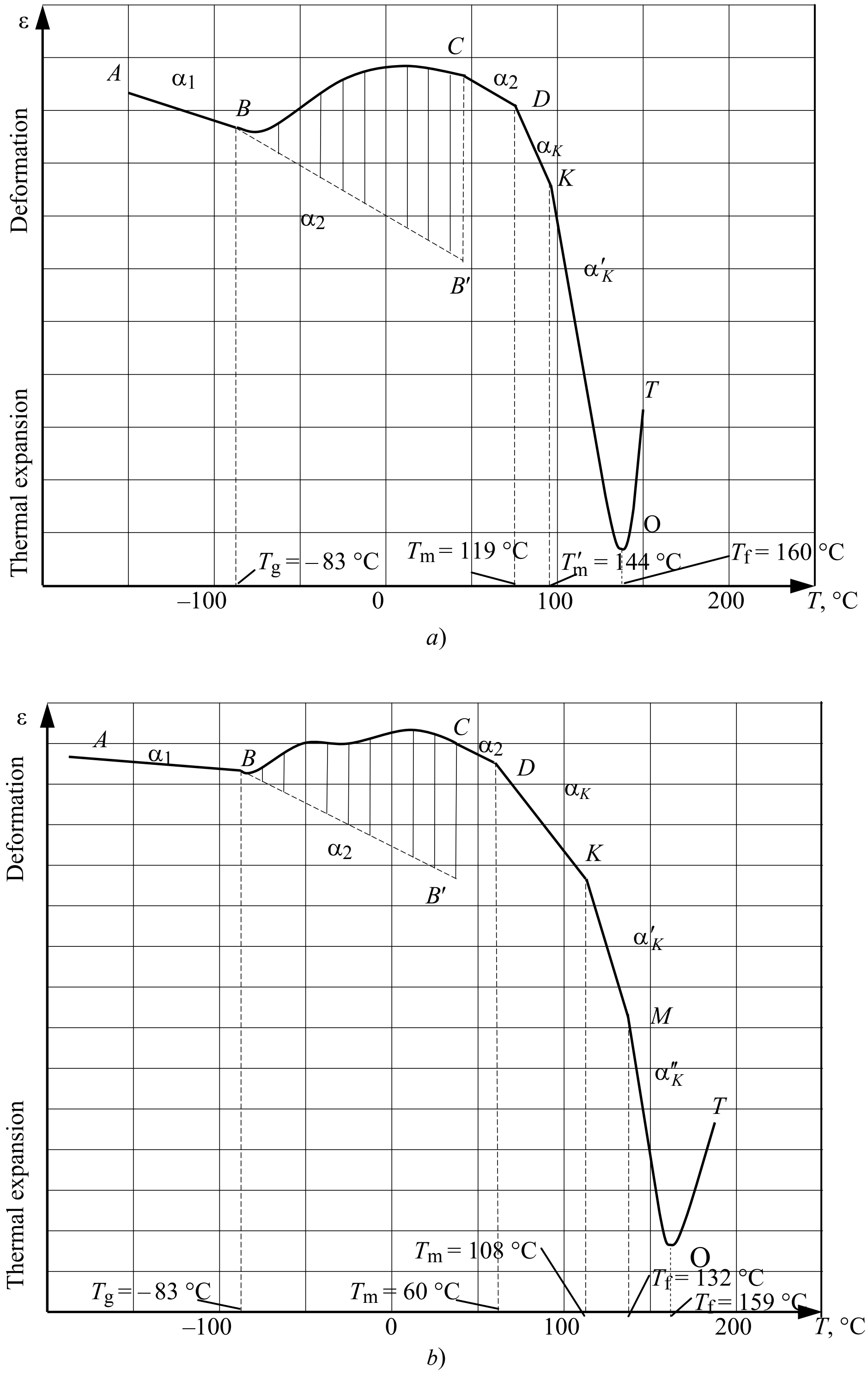
The weight share of intercentral circuits of macromolecules amorphous and clustered fragments in cluster blocks is proportional to total thermomechanical deformation ε_a and ε_{cl} (Fig. 3) and corresponds as 0,23 : 0,77. Molecular current of copolymer circuits (a curve *OT*) begins at temperature $T_f = 90$ °C (point *O*). Average–numerical and average-weight molecular masses averaged on blocks of a copolymer at coaxial orientation of vectors are equal accordingly to 80100 and 103800 with the factor of polydispersiveness $K = 1{,}3$.

The change of vectors orientation from coaxial into mutual-perpendicular one has essentially changed the character of copolymer analyzed structure. It was transformed from completely amorphous in the first case into amorphous-crystal in the second. Its TMC has the same character, as well as at a copolymer after LPE at any orientation of vectors. That is typical for three-block amorphous-crystal polymer of pseudo-mesh structures (Fig. 1) with two crystal updatings as units of a branching.

The speed increase in of copolymer extrusion from 2 up to 100 mm per a minute has not brought any basic changes in its topological structure in both modes of TMA. But essential changes have taken place practically in all its molecular-relaxation and quantitative characteristics in dependence on from the speed of extrusion and the orientation of vectors. All of them are given in Table 1, 2.

Before analyzing them, we shall define which of the molecular-topological characteristics of copolymers given in tables are vector values and can change the quantitative contents at its TMA in both methodical variants and which of them cannot. It was always considered, that the molecular mass of polymer is scalar value and cannot quantitatively change at modifying the geometrical conditions of the analysis. Undoubtedly the situation is the same for the monoblock polymers which do not have pseudo-mesh and topologically polyblock character, and as a method of the analysis of their molecular masses the grout variant is used. In the non-grout method what method TMS is, this restriction is most likely not rightful, but it also does not eliminate the appropriateness of a quantitative abnormity of the analyzed value from the true value. The matter is that the intercentral circuits in a pseudo-mesh structure are limited in the mobility by branching units and also fixed by the orientation as thermal and penetration deformation of polymer at TMA. In this case deformation of any circuit is projected on a recorder of the measuring device coaxially with a vector of an orientation applied to polymer through a quartz probe of cargo P_0. It is natural, that not all circuits react to this influence adequately to its value. Apparently, there are also such ones which absolutely ignore it. It occurs when the topological structure of polymer is obviously anisotropic as it was in our case to copolymer ABS.

The temperatures values of relaxation transitions in topological blocks presented in Table 1, 2 (T_g, T_{cl} and T_f) prove the thesis stated above unequivocally. So, if in the topological isotropic condition of a copolymer after LPE, the vitrification temperature of intercentral circuits of the matrix block is permanent at the change of TMA mode and corresponds to the mobility of circuits in chemical-block polybutadiene or in polybutadiene with the appreciable contents of a 1,4-trance isomers or diluted with more rigid styrene- or acrylonitrile fragments of macromolecules, then at SPE the situation is completely different in this sense. If at mutual-perpendicular orientation of vectors (Table 2) in both modes of a copolymer extrusion the content of adequately deformable and most mobile circuits are approximately equal as well as their T_g values are, then at coaxial orientation of vectors (now by virtue of anisotropic formation of topological copolymer structure and there of non-uniform distribution of circuits of various chemical block structure and, accordingly, mobility), the T_g value of a SPE



a)

b)

Fig. 3. Thermomechanical curves of ABS specimens after LPE (*a*) and specimens after SPE (*b*) at the extrusion speed of V_{ext} = 100 mm/min.

T_{ext} = 22 °C. A direction of test ⊥ to the direction of a specimen orientation at SPE copolymer appreciably raises. And it will be more powerful according to the rising speed of punching shear through draw plates. And it means that the most mobile low-molecular fragments of circuits leave the zone of an amorphous condition, passing in crystal area of structure. Thus not only molecular mass of intercentral circuits of the amorphous block (M_{cn} и M_{cw}) grows appreciably. The more it is the higher speed of punching shear of a copolymer mass is, but also the higher modality of their curves MMD is (Fig. 4). The weight share of the circuits, which have stayed in an amorphism condition (φ_{a}), is reduced (Table 1) not reaching the value, which is found in the analysis at mutual-perpendicular orientation of vectors.

Topological structure of a copolymer, which is found out at coaxial orientation of vectors in SPE copolymers, and molecular-relaxation characteristics (except for T_{g}), which are found out in a stationary condition (up to the analysis), do not exist and are realized only during heating of a copolymer. So, at TMA process begun at 53 °C and 66 °C in low-melting crystal updating in copolymers of various speed of their extrusion the process of fusion enriches the pseudo-mesh structure of the amorphous block with amorphism circuits. This structure is analyzed at coaxial orientation. By virtue of it the weight share of its intercentral circuits grows according to 0,08 till 0,23 and from 0,16 till 0,47. Also the values of their molecular mass (M_{cn} and M_{cw}) grow for the same reason and their curve of MMD is transformed from unimodal into bimodal one (Fig. 4). True values of molecular mass of intercentral circuits are much lower, than they are in a copolymer after LPE (Table 1, 2), and the curve of MMD is unimodal. Also as it was already marked it is connected to the loss of a part of the most mobile fragments of copolymer macromolecules after its SPE.

The total crystallinity degree of a copolymer has increased in the process of SPE approximately from 20–30 w. % after LPE up to 84–92 w. %. Thus the density of circuits packing in both crystal updatings has appreciably decreased. The temperature of their fusion start has decreased more than on 40 °C. By virtue of this the speed of fusion

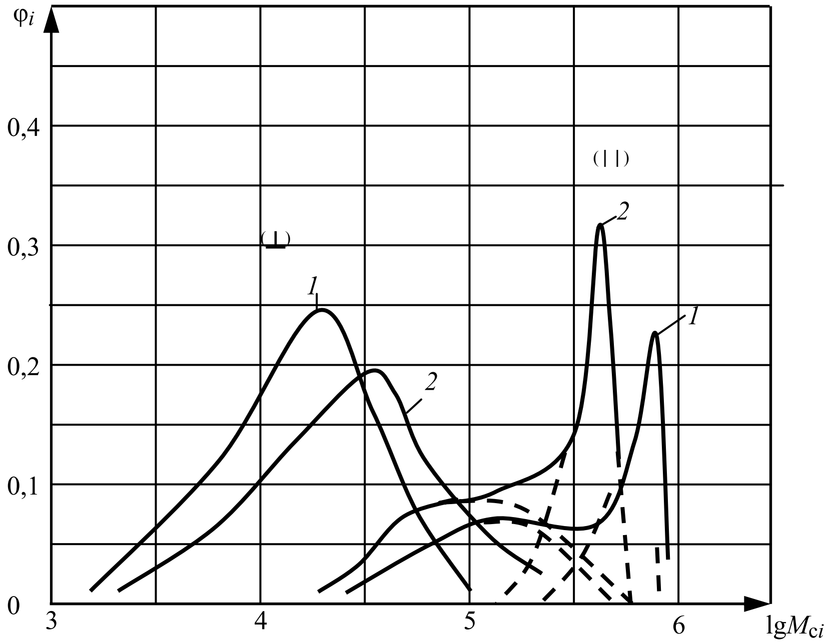


Fig. 4. MMD intercentral circuits functions of the matrix block of ABS copolymer after solid-phase extrusion with the speed 2 (*1*) and 100 mm/min (*2*)

(α_K и α'_K) has considerably increased also, though the molecular mass of glass circuits has not undergone essential changes. The cluster block formed from the crystal phase flux of SPE copolymer in the process of TMA at the coaxial orientation of vectors assimilates the basic part earlier glass fragments of copolymer macromolecules in the structure and has the molecular mass of the polyassociated circuits equal to 70800 and 35400 accordingly at 2 and 100 mm/min depending on the speed of extrusion. Molecular mobility of circuits in these two the cluster blocks, characterized at temperature T_{cl}, differs insignificantly and is average according to the temperature of the beginning of crystallites fusion in both updatings.

Being virtual the topological structure of copolymers after SPE, measured at coaxial orientation is more convenient in comparison with mutual-perpendicular by way of an estimation on the basis of their TMA averaged on the blocks of the copolymer molecular mass. The point is that at such methodical variant of the analysis the topological structure interpreted on its basis possesses a smaller degree of block structure and consequently allows receiving its value more corresponding to a true value. Thus, it is quite possible to say, that the received M_{n} values and M_{w} values averaged on blocks for LPE and SPE copolymers at the speed of extrusion in 2 mm/min are close to the true values. And the M_{w} value which has increased twice at the speed of extrusion in 100 mm/min allows to assume that the increase in the molecular mass of a copolymer depends on the extrusion speed. Besides the similar result was received earlier for LPE of polythene and polyamide-6 at processing in a compounding extruder of static type [14, 15].

Conclusions

1. The comparative research of a molecular-topological structure of ABS copolymers after liquid- and solid-phase extrusion with various speed of draw-plate punching shear was carried out with the method of thermomechanical spectrometry. In both ways of copolymer processing the three-block amorphous-crystal structure of a pseudo-mesh structure is found out in them topologically. In each topological block their molecular-relaxation and quantitative characteristics are determined.
2. It is shown, that after its liquid-phase the isotropic character of a copolymer molecular-topological structure with two crystal updatings is transformed into anisotropic one after solid-phase extrusion. Thus, independently of its speed, in a copolymer the glass degree sharply grows and the temperature is reduced of starting its molecular current. And with the increase of speed there might be the displays of mechano-destruction process bringing to the increase in its molecular mass.

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Сравнительное исследование молекулярно-топологического строения АБС-сополимера жидко- и твердофазной экструзии

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Ключевые слова и фразы: анизотропная структура; изотропная структура; кристаллическая фаза; массово-молекулярное распределение; пластичность полимера; псевдосетчатая структура.

Аннотация: Настоящая работа посвящена термомеханическому исследованию молекулярно-топологического строения АБС-сополимера, полученного твердофазной экструзией в сравнении с материалом, переработанным методом жидкофазной экструзии (традиционный метод).

Термомеханическая спектроскопия – новая безрастворная диагностика молекулярно-топологического строения полимеров, разработана в Институте проблем химической физики РАН. Она базируется на термомеханическом анализе полимеров и позволяет осуществлять комплексное молекулярно-топологическое тестирование полимеров любой структуры и строения в ходе одного эксперимента практически в режиме экспресс-анализа.

Vergleichende Forschung des molekullartopologischen Baus des ABS-Kopolymers der flüssig- und hartphasischen Extrusion

Zusammenfassung: Der vorliegende Artikel ist der thermomechanischen Forschung des molekullartopologischen Baus des ABS-Kopolymers, das durch hartphasischen Extrusion im Vergleich mit dem Stoff, der durch die verarbeiteten Methode der flüssigphasischen Extrusion (traditionelle Methode) erhalten ist, gewidmet.

Thermomechanische Spektroskopie – neue lösungslose Diagnostik des molekullartopologischen Baus der Polymere ist im Institut der Probleme chemischer Physik der rusischen Akademie der Wissenschaften entwickelt. Sie stützt sich auf die thermomechanischen Analyse der Polymere und erlaubt, die komplexe molekullartopologische Prüfung der Polymere einer beliebigen Struktur und den Bau im Laufe eines Experimentes praktisch im Regime der Express-Analyse zu verwirklichen.

Analyse comparative de la structure moléculaire et topologique du copolymère ABC de l'extrusion des phases solide et liquide

Résumé: Le présent article est consacré à l'analyse thermomécanique de la structure moléculaire et topologique du copolymère ABC de l'extrusion des phases solides en comparaison avec le matériel obtenu par la méthode de l'extrusion de phase liquide (méthode traditionnelle).

La spectroscopie thermomécanique est une nouvelle diagnose sans solution de la structure moléculaire et topologique élaborée à l'Institut des problèmes de la physique chimique de l'Académie des sciences. Elle est fondée sur l'analyse des polymères et permet de réaliser les tests moléculaires et topologiques complexes d'un expériment pratiquement dans le régime de l'express-analyse.