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DESCRIPTION OF POLYMER AND COMPOSITE HARDENING DURING TENSILE TESTS

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Tensile stress-strain curves of plastics and polymer composites are prepared and analyzed, the effects of temperature, water diffusion, heat treatment and notches being taken into account. The conditions are determined under which the tensile stress-strain diagrams may be described by rectilinear segments (schematization) in the entire loading range. The analysis was carried out at the set of 465 diagrams. The attempt was made to furnish a physical interpretation of the hardening effect of three types of materials: Polyamide 6 (Tarnamide T-27 and Block Tarnamide) and Polyamide 6 reinforced by glass microballs (Itamide 58-D). Polyesther-ether elastomers (KPEE) were also considered in the analysis.

LIST OF NOTATIONS

E	modulus of elasticity in tension [MPa],
α_s	shape factor,
ε	deformation [%],
ε_r	relative elongation at rupture,
ρ	depth of water diffusion in [mm] after submersion of specimens for $\tau_w = 0$, 3, 6 and 12 [months],
σ_z	maximum tensile stress [MPa], according to the Polish Standard PN-81/C-89034,
σ_z(NC)	maximum tensile stress of specimens conditioned in natural laboratory environment [MPa],
σ_z(358)	maximum tensile stress assessed at the temperature of 358 K [MPa].

1. INTRODUCTION

The strength parameters of 15 types of plastics including 10 types of polymer composites (Table 1) under static tension were analyzed and the influence of the conditions of tests and specimens preparation was investigated; the latter conditions included the temperature time of water sorption, heat treatment, notch effects and type of reinforcement (fibres and glass microballs). Within the group of materials and test parameters mentioned above, nonconventional behaviour of two polymers and one composite was observed (Table 2).

Table 1. Mechanical properties of the tested plastics assessed in the tensile test (50 mm/min).

Material	Glass reinforcement contents % by weight	σ_z [MPa]				
		Characteristics of specimens				
		NC (298 K)	NC (358 K)	$6H_2O$ (298 K)	HP (298 K)	with notch ($\alpha_s = 1.9$)
Tarnamide T-27	-	35	21	24	60	50
Itamide 25	25	92	64	72	139	100
Itamide 35	35	112	86	91	168	124
Tarnamide B	-	70	57	58	-	-
Elana 2	-	61	34	53	55	37
Elit 30 EX	30	135	80	133	141	109
Elit 30 PX	30	140	75	135	142	104
Bistan AS-20	20	79	62	72	84	56
Itamide 58-A	58	129	80	79	155	125
Itamide 58-B	58	107	63	63	129	100
Itamide 58-C	58	66	38	35	73	66
Itamide 58-D	58	27	15	13	31	30
Polipropylene	-	27	14	27	-	31
Arnite A-160	-	76	-	70	-	-
Makrolon 8030	30	72	-	62	-	-

NC – specimens held under normal laboratory conditions, ambient temperature and relative humidity,

Temperature of measurement 298 K and 358 K,

6 H_2O – before tensile test the specimens were submerged in water for 6 months,

HP – heat processed specimens.

The conventional behaviour, according to the author, means that the tension stress-strain curve is typical under normal conditions, i.e. the tested material has a distinct limit of proportionality (σ_H) or, in the case of composites, two distinct limits of proportionality (σ_{H1} and σ_{H2}) – maximum tensile stress (σ_z) and nature stress (σ_r), and furthermore Tarnamide T-27 exhibits fiber-forming properties on the stress-strain curve (large relative elongation at rupture, ε_r, and $2 \div 3$ necks).

The non-conventional behaviour denotes that when the specimens are submerged in water for three or more months before the strength tests,

Table 2. Strength yielding and sorption properties of PA6 and reinforced PA6.

τ_W [months]	0			3			6			12		
Properties / Material	σ_z	ε_r	ρ	σ_z	ε_r	ρ	σ_z	ε_r	ρ	σ_z	ε_r	ρ
Tarnamide T-27	35	220	-	24	200	1.40	24	180	2.25	26	-	3.0
Tarnamide B	70	-	-	-	-	0.65	58	-	3.80	-	-	>6.0
Itamide 58-D	27	2.4	-	14	40	1.00	13	50	3.00	11	-	>6.0

Results of σ_z measurements are arithmetic means for 10 specimens,

τ_W – time of water sorption.

i.e. when the plastifier (water) is introduced by diffusion, then with the stress-strain curves for tension the schematization with strength plateau and linear hardening can be carried out.

The aim of the work is then formulated as follows: describe the non--typical behaviour of the tested group of matarials under static tensile load with the view to their strength properties and explain the reason and mechanism of hardening.

2. Properties of plastics with linear hardening

Materials which exhibited non-conventional behaviour in the tensile test and are Tarnamide T-27, Black Tarnamide and Tarnamide T-27 reinforced with glass microballs, 58 % by weight (Itamide 58-D). Polyamide 6 obtained by the method of hydrolytic polymerization of caprolactam is produced for fibers, and is also used in small quantities for machine parts. The PA 6, however, which is obtained by anion polymerization of caprolactam (Block Tarnamide) is a typical construction material (Table 3). The differences in the polymerization methods determine the macroparticle length and such properties as resistance to stress, fatigue, creep etc.

Polyamide 6 reinforced PA6 are materials of large water absorbing power. Presence of water in a polymer or a polymer composite yields reduction of strength: very large in Itamide 58-D and large in Tarnamide T-27. Similar relations appear in tests at elevated temperature. The quantitative influence of water sorption and temperature on the maximum tensile stress σ_z

Table 3. Physical properties and material coefficients of PA6 and reinforced PA6.

Property	Measurement method or formula	Tarnamide T-27	Tarnamide Block	Itamide 58-D
Mean molecular mass	viscosity	14500	45000	-
Relative viscosity	Ubbelohde	2.7	2.3 ÷ 2.7	2.36
Monomer contents %	[3]	≤ 2	≤ 10	-
Crystality degree %	Hermans – Weidinger	43	46	-
Water sorption coefficient $K_W(6)$	$\frac{\sigma_z(6H_2O)}{\sigma_z(\mathrm{NC})}$	0.686	0.829	0.407
Heat stability coefficient K_T	$\frac{\sigma_z(358)}{\sigma_z(298)}$	0.600	0.814	0.556
Heat processing coefficient $(463\ K/10')\ K_{\mathrm{HP}}$	$\frac{\sigma_z(\mathrm{HP})}{\sigma_z(\mathrm{NC})}$	1.70	-	1.15
Notch stress concentration β_{N} $(\alpha_s = 1.9)$	$\frac{\sigma_z(\mathrm{smooth})}{\sigma_{zK}(\mathrm{with\ notch})}$	0.70	-	0.886

Heat process parameters: temp. 463 K, heating time 10 min.

can be described by material coefficients K_W and K_T (Table 3). Apparent reduction of these coefficients for Itamide 58-D in comparison with those for Tarnamide T-27 or Block Tarnamide indicates the importance of cohesion forces at the separation surface and their dependence on the action of water and temperature.

3. Stress-strain curves at tension

The stress-strain curves for tension of the specimens of Tarnamide T-27, Block Tarnamide and Itamide 58-D, held under natural laboratory conditions (NC), i.e. the specimens aged at the temperature 293 ± 3 K and in relative humidity 30 - 90 %, consist of a number of segments (a), (b), (c) (Figs. 1 and 2).

a. *The line segment OA*. Strains are of immediate elastic character ($\varepsilon_{\mathrm{ei}}$) and delayed elastic character ($\varepsilon_{\mathrm{ed}}$). The total strain is a sum of three components [3]:

$$\varepsilon = \varepsilon_{\mathrm{ei}} + \varepsilon_{\mathrm{ed}} + \varepsilon_{\mathrm{pl}} ,$$

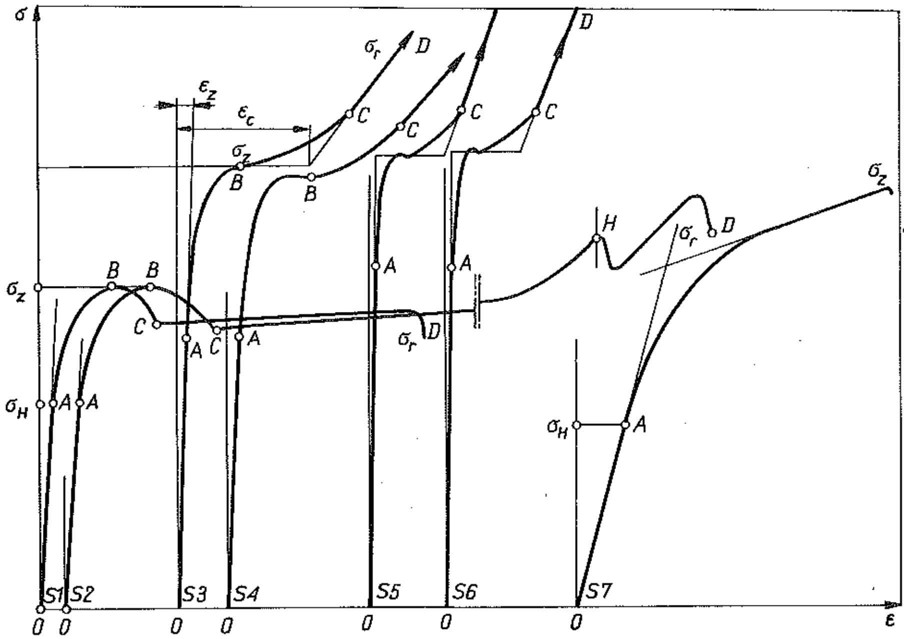

FIG. 1. Stress-strain curves for tension of Tarnamide T-27: S1 and S2 – specimens in natural state (NC); S3 and S4 – specimens submerged before tests in water for $\tau_w = 3$ months (3 H_2O); S5 and S6 – specimens submerged before tests in water for $\tau_w = 6$ months (6 H_2O); S7 – specimen after heat process (HP: 463 K/10′/oil).

ε_{ei} results from the changes of distances between atoms and changes of the valence angles; ε_{ed} results from the macroparticle straightening; ε_{pl} plastic strain appears as a result of change of mutual position of macroparticles.

b. *The curvilinear segment AB.* As the load increases, longer strains appear, including the plastic strain (ε_{pl}). The point B, which is the starting point of neck forming, corresponds to the maximum tensile stress σ_z (or resistance to tension R_m [4]). This corresponds to the opinions expressed in the papers by Cheng, Needleman et al., that for slender specimens of elastic-plastic material "the neck should form at the strain approximating that corresponding to the maximum force" [1, 5].

c. *The curvilinear segment BC.* Load decreases or increases as a result of hardening.

Further shape of the stress-strain curves depends on the kind of material and individual features of the specimen (statistical spread). For example, specimens of Tarnamide T-27 can vary in number of necks formed and, hence, in the value of the rupture stress σ_r (point D – specimens S1 and

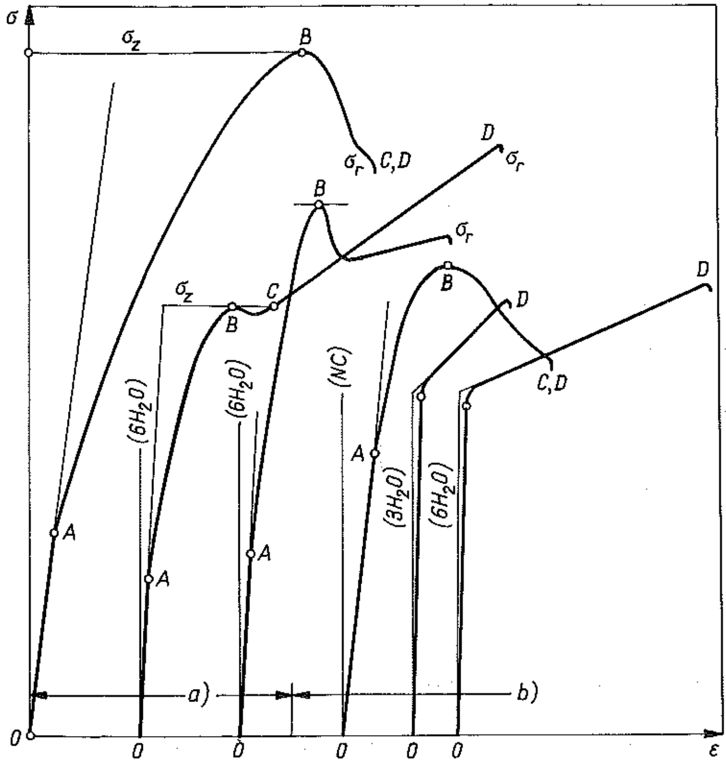

FIG. 2. Stress-strain curves for tension for Block Tarnamide (a) and Itamide 58-D (b). Notations as in Fig. 1.

S2 – Fig.1). In the specimen S1 one neck has formed along the line BCD, whereas in the specimen S2 there are two necks: the first one along BCH and the second one – along HD. In this case, plastic strain ($\varepsilon_r = 220\ \%$) develops according to the telescoping mechanism and results from the fiber-forming properties of the Polyamide 6. In the ten specimens set (Table 2) it has been observed that the development of more than one neck is of a random character and results from the action of a large number of factors, each of them having small influence on the total strain. The results are such that $\sigma_r > \sigma_z$. Therefore, to estimate the construction quality of plastics in the elastic-plastic state and in order to compare their properties, the application of σ_z should be recommended.

The stress-strain curves for the Block Tarnamide [6] and the Itamide 58-D are also characterized by the appearance and development of a neck, but plastic strain is significantly restricted: in the Block Tarnamide – by the specimen shape, and in the Itamide 58-D – by the presence of reinforcement (glass microballs).

4. Schematization of the stress-strain curves

The aim of the schematization of the stress-strain curves (according to [2]) is the preparation of data for strength calculations behind the limit of elasticity, i.e, the analytical description of complete tensile stress-strain curves by means of simple mathematical expressions, good conformity with experiments being simultaneously maintained.

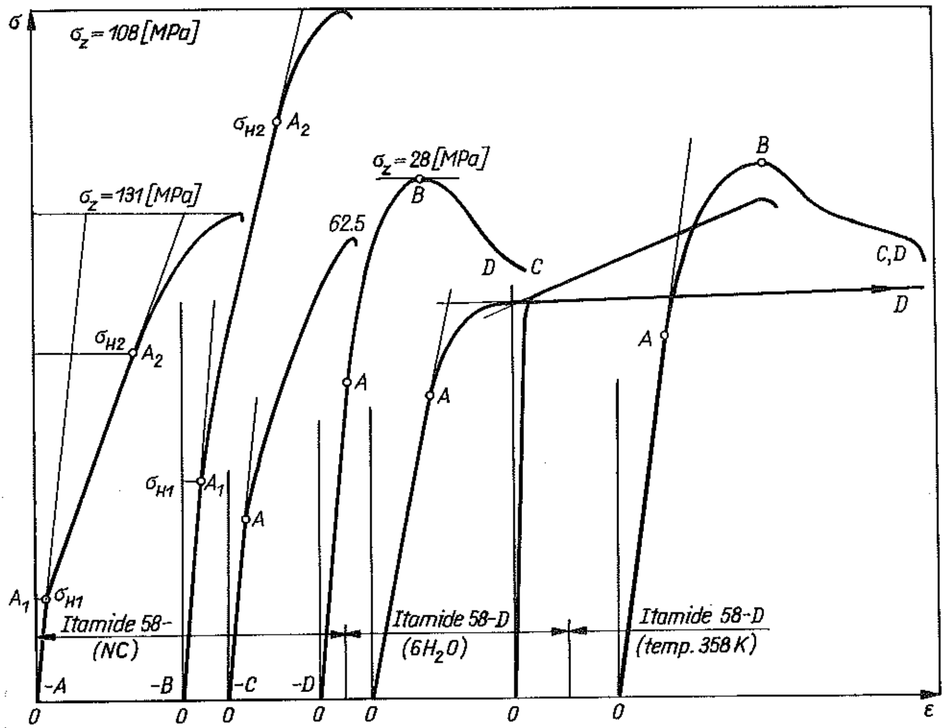

FIG. 3. Stress-strain curves for tension (50 mm/min, temp. 298 K, exposition time τ = 48 months, various scales for σ and ε axes-various): Itamide 58: A-B-C-D (specimens NC); Itamide 58-D, specimens after water sorption time τ_w = 6 months; Itamide 58-D (temp. 358 K).

Plots for which schematization according to the above aim can be carried out originate from the test of tensile loading of Tarnamide T-27, Block Tarnamide and Itamide 58-D, plastified with water by diffusion (Figs. 2 and 3). However, different from the case of stress-strain curves for various types of steel [2], it is more justifiable to talk about hardening of plastics than about their plasticizing, as in the stress-strain curves for plastics no clear yield point can be observed. Furthermore hardening is apparent at the tensile strength limit ($\sigma_z = R_m$) i.e. it emerges together with neck formation. As the hardening takes place along the curvilinear segment between the maximum tensile stress σ_z and the rupture stress σ_r, it makes schematization impractical in the case when in the calculations σ_z is considered as the critical state. However, schematization is useful in the case when a value belonging to the interval $\sigma_z < \sigma \leq \sigma_r$ is assumed as the critical state, i.e. a value connected with linear hardening.

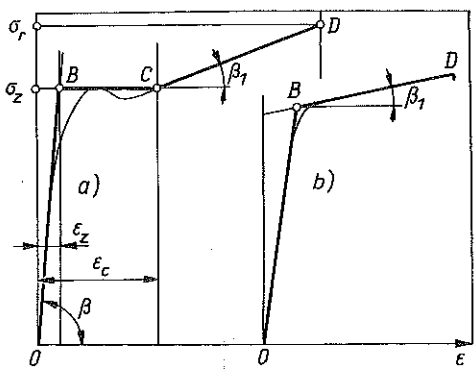

FIG. 4. Schematization of the stress-strain curves for tension: a) with the curve with strength plateau and linear hardening; b) with the curve with linear hardening (without the strength plateau).

Table 4. Analytic stress-strain relations for segments of schematized curves (Figs. 1 and 4).

Segment	Interval	Equation	
		Materials with strength stop	Materials without strength stop
OB	$0 \leq \varepsilon \leq \varepsilon_z = \frac{\sigma_z}{E}$	$\sigma = E \cdot \varepsilon$	$\sigma = E \cdot \varepsilon$
BC	$\varepsilon_z < \varepsilon \leq \varepsilon_c$	$\sigma = \sigma_z = E \cdot \varepsilon_z$	-
CD	$\varepsilon > \varepsilon_c$	$\sigma = \sigma_z + E_h(\varepsilon - \varepsilon_c)$ $\sigma = \sigma_z \left[1 - (1-\lambda)\frac{\varepsilon_c}{\varepsilon_z}\right] + E_h \cdot \varepsilon$	$\sigma = \sigma_z \cdot \lambda + E_h \cdot \varepsilon$

E_h – material hardening modulus ($E_h = \operatorname{tg} \beta_1$, Fig. 4),
$\lambda = 1 - (E_h/E)$ – hardening parameter.

Tensile stress-strain curves (Fig. 4) with the strength plateau (instead of the plastic plateau in the tests of metals) can be replaced with the broken line $OBCD$ (Tarnamide T-27 and Block Tarnamide), whereas the tension curves without the strength plateau can be represented by the broken line OBD (Itamide 58-D). With such schematization, the differences between the limit of proportionality, the limit of plasticity and the rupture point of plastics vanishes. The appropriate formulae are grouped in Table 4.

5. The hardening mechanism

The physical basis for the linear hardening of polyamide (Tarnamide T-27 and Block Tarnamide) is the ability of particles to straighten quickly (to orient themselves, [7]) under uniaxial load and with the participation of the absorbed water which plays the role of an accelerator and plastifier (increases the distances between the macroparticles). The process of orientation and hardening takes place also in the specimens held under natural laboratory conditions (NC); it is not of a linear character, however (e.g. because two necks emerge according to the telescopic mechanism). It is also slower and starts with a certain delay (point C – Fig. 1, specimens S1 and S2). Water accelerates the orientation, so that macroparticles straightening takes place before the point B is reached (Fig. 1, specimens S3-S6).

In the case of microballs reinforced polyamide (Itamide 58-D), water contained in the composite after sorption time $\tau_w = 3, 6$ and 12 months reduces the cohesion energy at the separation surface, and then the microballs become the cavities in the matrix to greater extent than the reinforcement (Table 5). Itamide 58-D behaves in such a manner because the strength plateau vanishes (Fig. 4b). The process of hardening of polymers and composites may also be explained by the phenomenon of yielding of the material; as a result, the neck is formed and a three-dimensional stress state (σ_r, σ_z, σ_θ) appears [5].

Table 5. Strength properties of Itamide 58-D after various water sorption times τ_w (exposition time $\tau \geq 48$ months).

Property	Water sorption time τ_w [months]			
	0	3	6	12
σ_z [MPa]	27	14	13	11
$Z_{g0}(10^7)$ [MPa]	16.1	6.4	5.0	5.0
ρ [mm]	0	1.5	3.0	6.0

From the observations carried out on 15 types of plastics it results that these materials exhibit hardening which in the tension test conditions are in the high-elastic physical state, contain considerable quantities of plastifiers (e.g water, monomer) or have the inclination and possibilities of macroparticle orientation. The material which fulfils these conditions whithout the presence of water is, e.g., the polyester-ether copolymer (KPEE, Table 6, Fig. 5). The KPEE macroparticle consists of elastic segments which form

Table 6. Mechanical and physical properties of the thermoplastic copolyester-ether elastomer (KPEE).

No	Property	Value
1	Maximum tensile stress σ_z [MPa]	17.00
2	Rupture stress σ_r [MPa]	26.00
3	Tensile modulus of elasticity E_t [MPa]	245.00
4	Bending stress R_b [MPa]	5.10
5	Relative elongation at rupture ε_r [%]	794.00
6	Water sorption after 24 h [%]	0.31
7	Crystallity degree (DTA) [%]	16.10
8	Glassy temperature T_g [K]	218.00
9	Morphological structure	spherolythic
10	Rigid segments contents [%]	60.00

No. 1 - 2: own investigations; No. 3 - 10: according to [8].

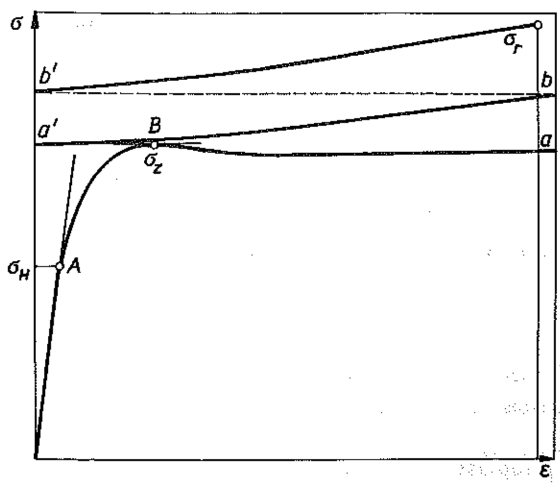

FIG. 5. Stress strain curve for tension of the KPEE; deformation rate 50 mm/min, temp. 298 K, specimen NC, σ_z = 17.3 MPa, σ_r = 24 MPa, ε_r = 790 %, exposition time τ = 2 months, a′ and b′ – continuations of the plots a and b.

amorphous regions alternately with rigid segments which form crystalline regions [8]. At the stress-strain curve (Fig. 5) the following points can be seen: the limit of proportionality σ_H, the maximum tensile stress σ_z and the rupture stress σ_r with the value larger than σ_z by more than 50 % (Table 5). At the point σ_z a single neck is formed and considerable orientation of macroparticles takes place, what results in linear hardening of the KPEE.

6. Conclusions

1. Among 16 types of plastics tested for tension in various conditions only three, after plasticization by water, exhibit linear hardening behind the tensile stress limit (maximum tensile stress σ_z). These are: Tarnamide T-27, Block Tarnamide and Itamide 58-D. Furthermore, one kind of material, namely, the thermoplastic elastomer (KPEE) shows linear hardening without the plastifier (water).

2. Water contained in the reinforced and non-reinforced polyamide and monomer and water in the Block Tarnamide accelerate the process of macroparticle orientation as a result of an instantaneous decrease of the particle cohesion energy level and the separation surface cohesion energy level (microballs - polymer).

3. Schematization extends the scope of the analytical description of measurement results to a number of plastics and, together with Hooke's law, constitutes the set of formulae for strength calculations in the whole range of the tensile stress-strain curve. Schematization contributes to the unification of calculations on the grounds of constitutive equations and should be applied in every case where appropriate possibilities exist.

4. From the viewpoint of strength of polymers, hardening means that the rupture stress σ_r is larger than the maximum tensile stress σ_z: for Tarnamide T-27 one obtains $\sigma_r/\sigma_z = 1.67$; for Block Tarnamide $\sigma_r/\sigma_z = 1.35$, and for Itamide 58-D $\sigma_r/\sigma_z = 1.25$.

5. Results of tensile strength measurements shown in the tables and figures can be used in strength calculations structures made of plastics working in various conditions and for a long time, according to conventional methods as well as with the use of schematized tension curves (for four plastics: Tarnamide T-27, Block Tarnamide, Itamide 58-D and polyester-ether copolymer KPEE).

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