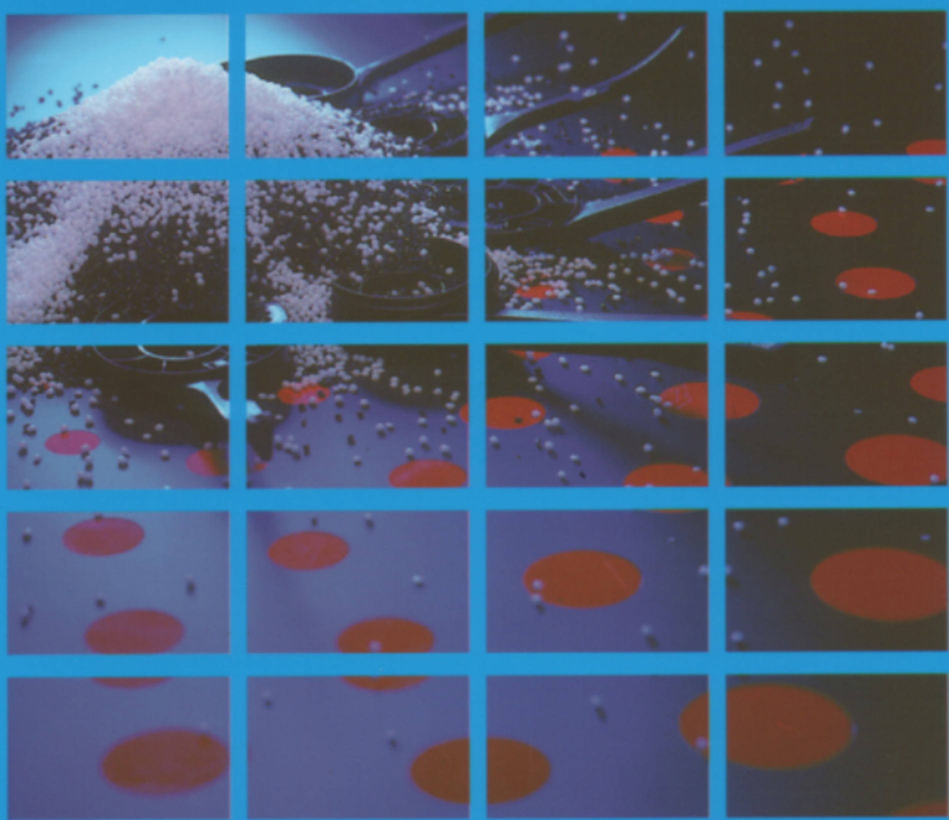
TARNOFORM®

THE MODERN POLYACETAL



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Tarnoform® - the modern polyacetal

1. INTRODUCTION

Polyacetals, first used in engineering practice in the sixties, quickly received wide recognition thanks to their specific features overcoming many limitations and constraints imposed on the designers by other engineering plastics, for example polyamides. The plant producing polyacetal with trade name **Tarnoform®**, (started-up at Zakłady Azotowe w Tarnowie-Mościcach, Tarnów, Poland in 1994) introduced ZAT into an exclusive group of companies manufacturing this excellent resin. Typical properties of **Tarnoform®** are following:

- negligible change of impact strength at temperatures between -40°C and 110°C,
- high stiffness and mechanical strength,
- high fatigue endurance,
- no influence of air humidity on mechanical properties,
- excellent dimensional stability,
- resistance to most organic solvents, bases and acids of pH > 4,
- high hardness and abrasion resistance,
- low friction coefficient in connections involving typical materials,
- high resistance to warping, even at high temperatures,
- outstanding electrical and dielectric properties, virtually unaffected by changes of ambient temperature and humidity,
- high resistance to water, bacteria, fungi and insects (in applications requiring resistance to prolonged exposure).

These properties of **Tarnoform®** result from the regular structure of its main polymeric constituent, chemical composition of additives and high crystallinity. **Tarnoform®** belongs to the group of acetal copolymers obtained by polymerisation of trioxane (cyclic formaldehyde trimer) in the presence of co-monomers providing global stability of polymer chains.

1.1. Tarnoform® - production programme

Six grades of **Tarnoform®** are currently being manufactured:

- **Tarnoform® 200** - standard **extrusion** grade, which may be also used to produce thick-walled parts of simple shape by **injection moulding**
- **Tarnoform® 300** - standard **injection moulding** grade
- **Tarnoform® 400** - easy flowing grade for high precision and thin-walled parts produced by **injection moulding**
- **Tarnoform® 411** - easy flowing, internally strengthened grade for **injection moulding** of thin-walled parts of very high mechanical requirements
- **Tarnoform® 500** - very easy flowing grade for complex, high precision parts and thin- walled shapes made by **injection moulding**; useful in case of long flow paths
- **Tarnoform® 700** - extremely easy flowing grade for **injection moulding** of very thin-walled parts or for very long flow path

Tarnoform® is available in pellets (about 3 mm in diameter) in natural (milk-white) colour. Coloured grades are also available (six basic colours), as well as modified grades: reinforced, mineral filled, high impact, wear&friction and UV stabilised (black and natural colour). Also we have in offer colour concentrates on Tarnoform® basis for self-colouring during processing stage.

1.2. Packaging

Tarnoform® is packed in polyethylene valve bags containing 25 kg of the product. It may be also packed to octatainers containing 1000 kg of pellets each.

2. TARNOFORM® PROPERTIES – SUMMARY

Table 1 - Mechanical properties

Property		ISO test method	Unit of measure	Tarnoform®					
				200	300	400	411	500	700
Melt flow index	190°C 2.16 kg	1133	g/10 min	2.5	9	13	13	27	48
Tensile yield point	23°C	527	MPa	60	62	62	68	65	64
Yield point elongation	23°C	527	%	14	13	11	10	8	7
Elongation at break	23°C	527	%	65	50	45	30	30	9
Nominal elongation at break	23°C	527	%	40	30	25	20	20	9
Tensile modulus	23°C	527	MPa	2350	2700	2800	3000	3000	2900
Flexural strength	23°C	178	MPa	57	61	64	68	68	69
Flexural modulus	23°C	178	MPa	2100	2400	2500	2600	2600	2700
Impact strength (notched, Charpy test)	23°C	179/1eA	kJ/m^2	8	7	6	6	5	4
Impact strength (notched, Izod test)	23°C	180/1A	kJ/m^2	9	7.5	7	6	6	5
Ball indentation hardness	23°C 358 N 30 s	2039-1	MPa	135	140	140	150	140	150
Rockwell hardness	23°C	2039		M82 R114	M82 R114	M82 R114	M82 R114	M82 R118	M82 R114

Table 2 - Thermal properties

Property		ISO test method	Unit of measure	Tarnoform®					
				200	**300**	**400**	**411**	**500**	**700**
Heat distortion temperature	1.8 MPa	75	°C	110	115	115	115	120	120
Melting point	DSC	3146	°C	167	167	167	170	167	167
Vicat softening point	50 N 10 N	306 B50 306 A50	°C	150 163	150 163	150 163	160	150 163	153 165
Coefficient of linear thermal expansion	30-60°C	ASTM D696	1×10^{-5} K^{-1}	11	11	11	11	11	11
Specific heat	20°C		J/(g K)	1.48	1.48	1.48	1.48	1.48	1.48
Maximum temperature of continuous operation			°C	100	100	100	100	100	100

Table 3 - Electrical properties

Property		ISO test method	Unit of measure	Tarnoform®					
				200	**300**	**400**	**411**	**500**	**700**
Volume resistivity	20°C	IEC 93	Ω cm	10^{15}	10^{15}	10^{15}	10^{15}	10^{15}	10^{15}
Surface resistivity	20°C	IEC 93	Ω	10^{15}	10^{15}	10^{15}	10^{15}	10^{15}	10^{15}
Dielectric constant at 20°C	50 Hz 1 kHz 1 MHz	IEC 250		3.9 3.9 3.9	3.9 3.9 3.9	3.9 3.9 3.9	3.9 3.9 3.9	3.9 3.9 3.9	3.9 3.9 3.9
Dissipation factor at 20°C	50 Hz 1 kHz 1 MHz	IEC 250		20×10^{-4} 10×10^{-4} 85×10^{-4}	20×10^{-4} 10×10^{-4} 85×10^{-4}	20×10^{-4} 10×10^{-4} 85×10^{-4}	20×10^{-4} 10×10^{-4} 85×10^{-4}	20×10^{-4} 10×10^{-4} 85×10^{-4}	20×10^{-4} 10×10^{-4} 85×10^{-4}
Dielectric strength	20°C	IEC 243	kV/mm	25	25	25	25	25	25
Arc resistance	21°C, 65% RH	ASTM D495	mm	1.9	1.9	1.9	1.9	1.9	1.9
Leak resistance	21°C, 65% RH	IEC 167	Ω	7.5×10^{14}	7.5×10^{14}	7.5×10^{14}	7.5×10^{14}	7.5×10^{14}	7.5×10^{14}
Comparative tracking index		IEC 112	CTI	600	600	600	600	600	600

Table 4 - Other properties

Property		ISO test method	Unit of measure	Tarnoform®					
				200	300	400	411	500	700
Density	23°C	1183	g/cm^3	1.41	1.41	1.41	1.41	1.41	1.41
Flammability		UL. 94 FMVSS		HB B50	HB B50	HB B50	HB B50	HB B50	HB B50
Water absorption	23°C	62	%	0.7	0.7	0.7	0.7	0.7	0.7
Moisture absorption	23°C 50% RH	62	%	0.2	0.2	0.2	0.2	0.2	0.2
Colour	23°C	ASTM E 313	L* a* b*	76 -0.5 -0.5	76 1.0 -5.5	76 1.0 -5.5	76 1.0 -5.5	76 1.0 -5.5	76 1.0 -5.5
Injection shrinkage	24 h 4 mm	flow direction perpendicular	% %	2.9-3.1 1.9-2.2	2.8-2.9 2.1-2.4	2.7-2.9 2.1-2.3	2.8-3.0 2.2-2.4	2.5-2.7 2.0-2.2	2.8-3.0 2.2-2.4

The values given in the tables are the average values calculated for many production batches of Tarnoform® and should not be regarded as guaranteed for any specific batch. They also cannot be used as the basis for quality requirements, technical specifications and strength calculations. As there are a significant number of factors influencing the properties of the products during production and in operation, it is recommended that the purchasers should test finished products in order to determine their usefulness in the envisaged applications or in order to determine their specific properties.

3. PHYSICAL PROPERTIES

The list of properties of individual Tarnoform grades, presented in the previous section, provides a global overview of this resin. In this section, a more detailed description of individual properties is provided, and changes of these properties as functions of temperature and time are outlined.

3.1. Mechanical properties

The main characteristic feature of materials described as plastics (and therefore Tarnoform as well) is their complex behaviour in response to external forcing factors. In order to describe their properties taking into consideration temperature changes, three basic states of plastics may be defined:

1. Glassy state (at temperatures between 0 K and glass transition temperature Tg) - plastics behave like glass, their impact strength is minimal, they virtually do not flow when loaded (in applicable time intervals).
2. Viscoelastic state (at temperatures between glass transition temperature Tg and melting point Tm) - depending on the strain speed, Tarnoform shows elastic behaviour resulting in high resistance to impact loads or it demonstrates viscous characteristics, flowing under prolonged static loads. This range corresponds to the use of Tarnoform as an engineering resin.
3. Plastic state (above the melting point) - Tarnoform is a highly viscous non-Newtonian fluid and its viscosity depends on external factors. This state is present during the production and processing of Tarnoform.

The glass transition temperature Tg, determining the minimum temperature at which Tarnoform may be applied, is **-60^{o}C**. In comparison with other plastics, this figure is very low and it may be explained by the chemical structure of the polymer chain. It gives a relatively broad range of operating temperatures (160^{o}C).

In the following subsections the variability of main mechanical properties of Tarnoform will be described for three basic load types: impact, short- and long-term.

3.1.1. Short-term strength

Short-term strength is the most frequently used property of plastics, since it is determined during the quality control process. Table 1 contains basic data for all Tarnoform grades obtained by applying short-term loads. Tensile tests carried out on standard specimens are used to determine the following parameters:

- yield point - the value of stress which ends the linear part of the stress/strain curve of a plastic; this point also limits the range of its engineering applications;
- yield point elongation;
- elongation at break- defined as the elongation of a test length of 50 mm situated in the middle of the specimen;
- nominal elongation at break- defined as the elongation of the whole specimen;
- Young’s modulus (tensile modulus).

Standard tensile tests (according to ISO 527 - 1/2) are carried out on Tarnoform specimens at a strain rate of 50 mm/min (except for tensile modulus determination, carried out at 1 mm/min), which may be classified as tests under static, short-term loads. Results of these tests may be regarded as a definition of short-term strength of the plastic. The numbers given in table 1 shows a pronounced tendency towards the change of properties as a function of variable flowability of the plastic (growing MFI). Above mentioned tendency can be most clearly seen in increasing stiffness (increasing yield point, decreasing elongation at break, increasing tensile modulus), which is related to the decreasing molecular weight of the resin and the growing number of features specific to low molecular crystalline substances.

Bending tests are another tests conducted under short-term loads. These tests determine the following properties:

- bending stress at a deflection equal to 1.5 times the specimen thickness;
- flexural modulus.

Standard bending tests (according to ISO 178) are carried out on Tarnoform specimens, sized 80×10×4 mm, loaded at three points, at a strain rate of 10 mm/min (except for flexural modulus determination, carried out at 2 mm/min).

The last groups of tests carried out under short-term loads are hardness tests. The following standard hardness tests are used to determine Tarnoform properties:

- Ball indentation hardness (according to ISO 178). During the test a steel ball (5 mm in diameter) is pressed (with 358 N force) in a specimen and test force is applied for 30 seconds. Next the depth of the indentation is measured and the area of the indentation is used to determine the hardness index (product of the force and the indentation area).

- Rockwell hardness (according to ISO 2039). This test consists of indenting the specimen with a steel ball (diameter 6.35 mm for scale M or 12.7 mm for scale R) under a specific load (980.7 N for scale M or 588.4 N for scale R). First, the steel ball placed on the specimen (minimum thickness of the specimen 6 mm) is pre-loaded with 10% load. Next, the test load is applied, and after that the load is released to the value of the preliminary load, the depth of the indentation is measured. The hardness index (*HR*) is calculated from the following formula:

  $$HR = 130 - e$$

  where e is the depth of the indentation measured in 0.002 mm units.

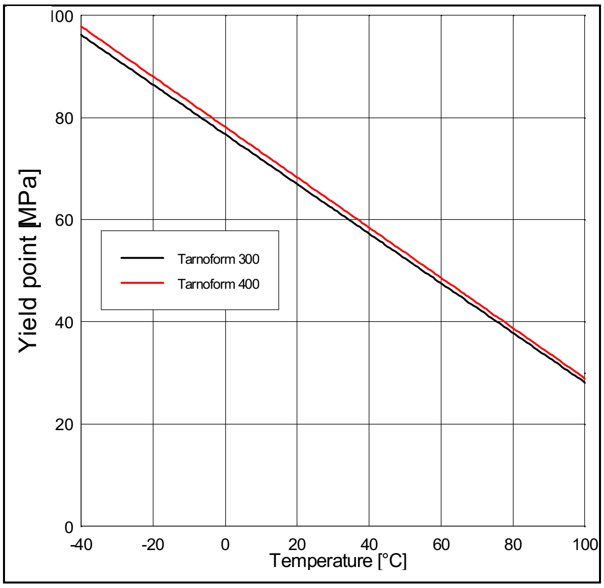

Figure 1. Temperature dependence of the tensile yield point of Tarnoform 300 and Tarnoform 400; strain rate 50 mm/min; sample acc. to ISO 527

Temperature is the main parameter influencing the changes of individual properties of the plastics. Relationships between the yield point and temperature for the basic Tarnoform grades (i.e. Tarnoform 300 and Tarnoform 400) are presented in the attached graph.

3.1.2. Long-term strength

The design and application of plastic parts requires the knowledge of long-term behaviour characteristic for the specific resin. The influence of the duration of stress on the dimensional stability of parts may be described by the following parameters:

- creep characteristics - describing the influence of stress on the elongation of the part as a function of time;

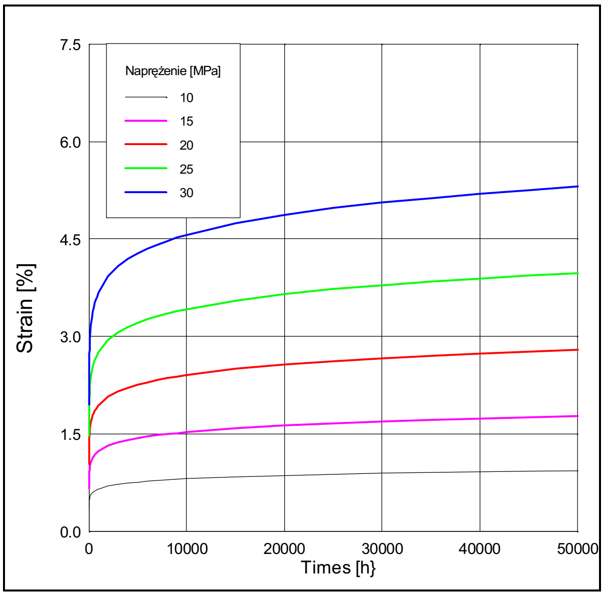

Figure 2. Creep characteristics of Tarnoform for selected loads (23°C)

- creep compliance - standardised creep index of plastics, denoted by J and described by the following formula:

$$J(\sigma_0, t) = \frac{\varepsilon(\sigma_0, t)}{\sigma_0}$$

where: σ_0 - input stress,
ε - resulting strain,
t - duration of stress.

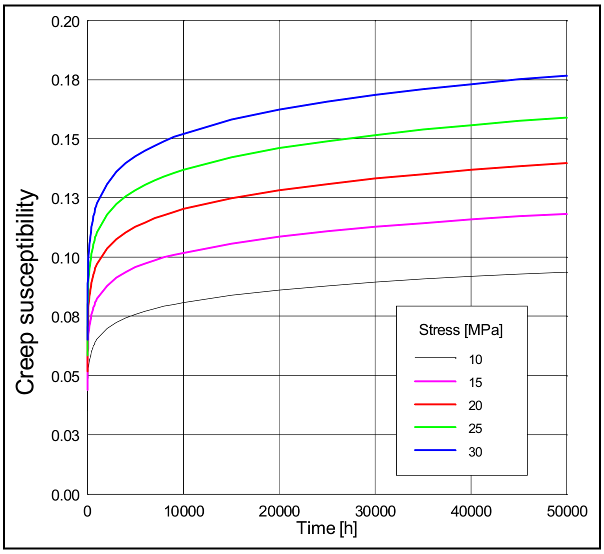

Figure 3. Creep compliance for selected loads (Tarnoform 300, 23°C]

- isochronous curves - describing the relationship between stress and strain at selected time points.

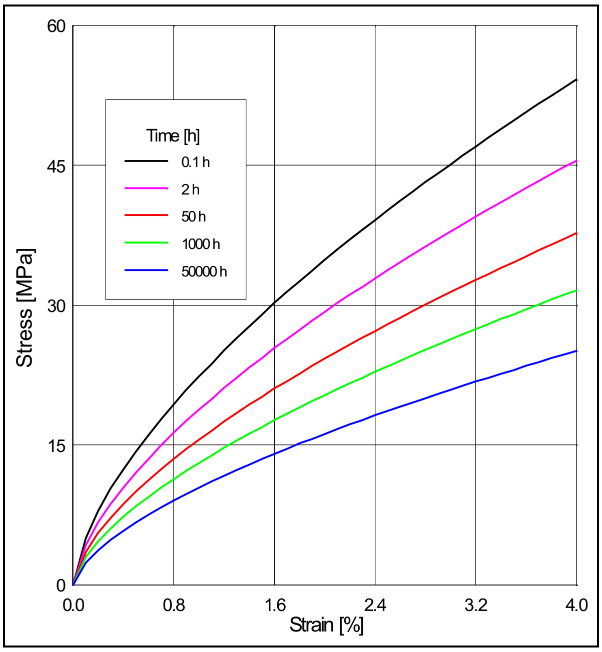

Figure 4. Isochronous curves for Tarnoform 300 (23°C)

Owing to viscoelastic properties of the plastics, apart from the phenomenon of flow caused by stress in the plastic, another phenomenon may be observed, namely the recovery after strain unloading, called relaxation. In case of all plastics (and therefore Tarnoform as well), the relaxation of stresses within a predictable observation time is not complete, which means that when a long-term load causing a measurable strain is removed, the part does not return to its original shape. In order to describe this phenomenon the following parameters have been used:

- relaxation characteristics - determining the influence of the initial strain on the stress remaining in the tested part as a function of time;

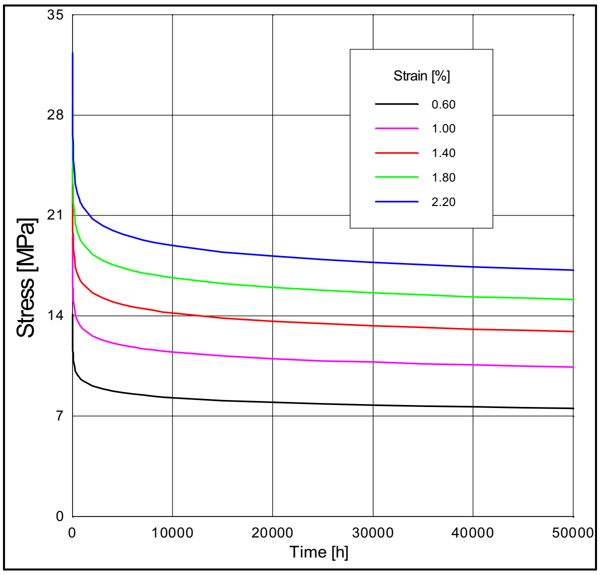

Figure 5. Relaxation characteristics of Tarnoform 300 for selected initial strains at 23°C

- relaxation modulus - standardised relaxation index of plastics, denoted by E and described by the following formula:

$$E(\varepsilon_0,\, t) = \frac{\sigma(\varepsilon_0, t)}{\varepsilon_0}$$

where: σ - residual stress in the part,
ε_0 - initial strain,
t - duration of the relaxation process;

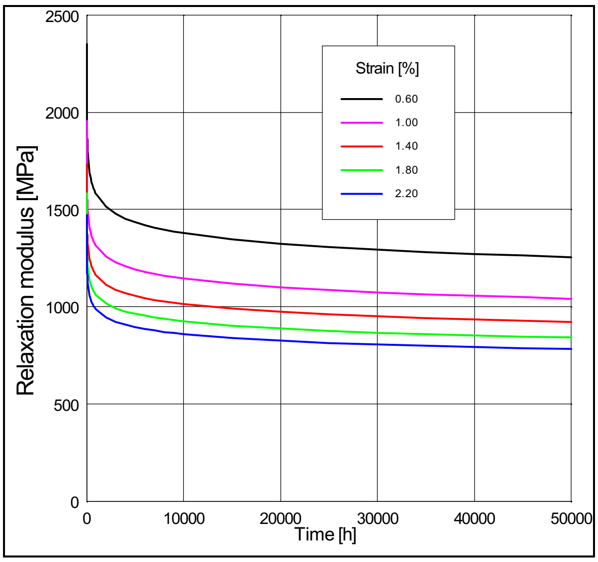

Figure 6. Time dependence of relaxation modulus of Tarnoform 300 for selected initial strains at 23°C

In practical application for designing parts, knowledge of the maximum permissible stresses (σ_{max}) for long-term loads (up to 50 000 hours) is very significant, as well as the knowledge of the maximum stresses (σ_{min}) which allow the phenomenon of flow to be neglected as having only a marginal effect. These parameters for Tarnoform 300 are given below as a function of temperature:

Temperature [°C]	σ_{max} [MPa]	σ_{min} [MPa]
23	30	8
40	24	6
60	19	6
80	15	3

3.1.3. Fatigue strength

Real loads are usually much or less variable, therefore the influence of variability factor on the strength properties of parts must be considered. The relationship between fatigue strength σ_Z and the number of cycles is described by Wöhler's curve. Fatigue strength σ_Z is defined as the maximum stress that can be withstood by a part on which a specific load is exerted for the specific amount of time, without leading to the complete damage. It is necessary to specify the input load characteristic precisely, as plastic parts demonstrate significant differences in behaviour for various input loads. As the model input load, sinusoidally variable tension is used, the mean value of which equals zero. For this type of load, at a frequency of 10 Hz and 10^7 load cycles, the fatigue tensile strength (σ_Z) of Tarnoform, as well as of the majority of plastics, reaches about 25% of the short-term tensile strength. In general, in response to the changes of the most important parameters, the fatigue strength tends to vary as follows:

- σ_Z decreases when the temperature increases,
- σ_Z decreases when the load amplitude increases,
- σ_Z decreases when part has elements causing stress concentration

3.1.4. Impact strength

Impact loads may be classified as short-term loads lasting less than 10 ms. Impact strength is one of the most important characteristics of Tarnoform, as the parts made of this resin are frequently used where it is highly probable that such action may occur. Two basic test used to evaluate the impact strength of plastics are following:

- Charpy impact strength (according to ISO 179/1eA) - the test specimen have a shape of a small beam sized 80×10×4 mm, mounted horizontally; impact energy equals 1 J.
- Izod impact strength (according to ISO 180/1A) - the test specimen have a shape of a small beam sized 80×10×4 mm, mounted vertically and secured on one side; impact energy equals 1 J;

In both cases it is possible to make a standardised notch on the specimens, which provide stress concentration. Impact strength tests of Tarnoform are conducted on notched samples, because unnotched specimens do not break without artificial stress concentration. The influence of temperature on the impact strength of notched specimens, determined in Charpy tests, is presented in fig. 7. This strength remains practically unchanged in the whole range of test temperatures, thus providing an excellent basis for the use of Tarnoform in applications involving impact loads in a wide range of temperatures.

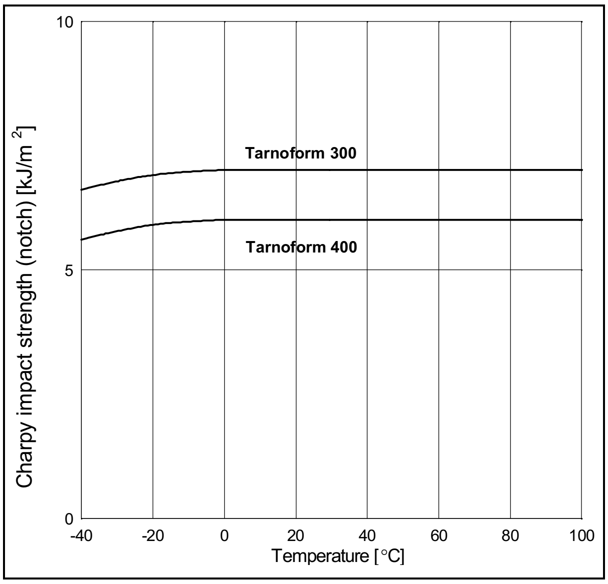

Figure 7 Temperature dependence of Charpy impact strength (notched) of Tarnoform 300 and 400 (testing acc. to ISO 179/1eA)

3.1.5. Tribological properties

Thanks to excellent tribological properties, Tarnoform is used in the construction of plain and rolling bearings, gears and cams. The main tribological properties are following:

- static coefficient of friction (sCOF)
- dynamic coefficient of friction (dCOF),
- wear resistance - defined as linear or volumetric loss on friction.

Tribological parameters determined in typical tests usually are functions of significant measurement conditions, such as sliding velocity, pressure, roughness and hardness of the counter-specimen as well as the test temperature (the ambient temperature and the temperature of the specimens). Therefore these parameters might be regarded as system parameters, not as material-specific parameters. However, when the test parameters are kept constant, the results of such tests reflect in some way the behaviour of the tested material itself. The factors discussed above, influencing the tribological properties of Tarnoform, should be taken into consideration when designing sliding joints made of Tarnoform, in order to locate the operating point of such joint optimally in respect of its minimum wear and the lowest possible coefficient of friction. Design tasks may be aided by the graphs presenting the full characteristics of the dynamic COF and linear wear between a specimen made of Tarnoform 300 and a counter-specimen (steel with roughness of 0.34 µm and hardness of 45 HRC).

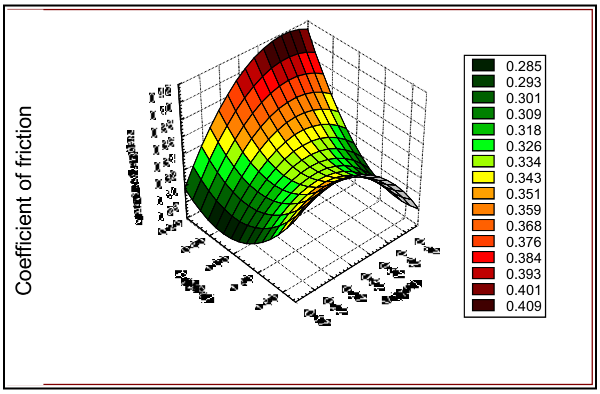

Figure 8a Dynamic coefficient of friction of Tarnoform 300 - 3D characteristics

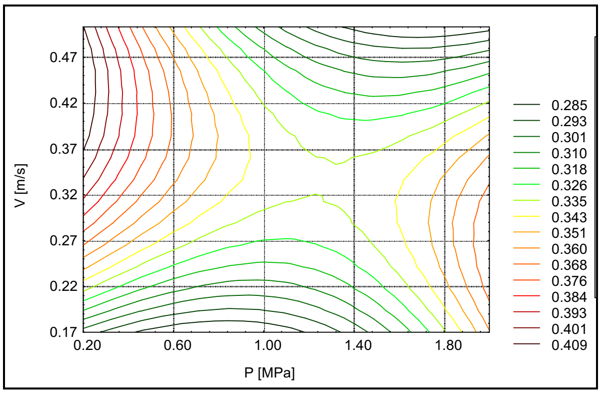

Figure 8b Dynamic coefficient of friction of Tarnoform 300 - contour plot

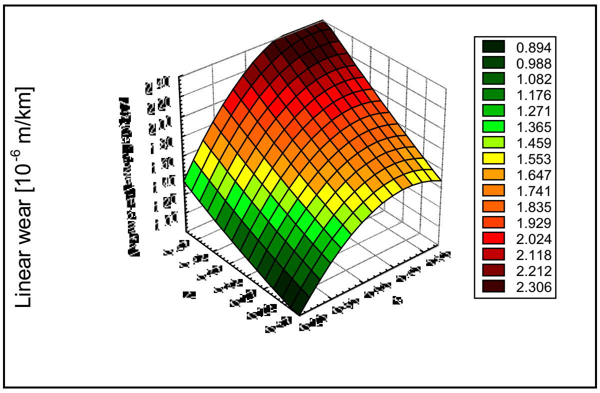

Figure 9a Linear wear of Tarnoform 300 - 3D plot

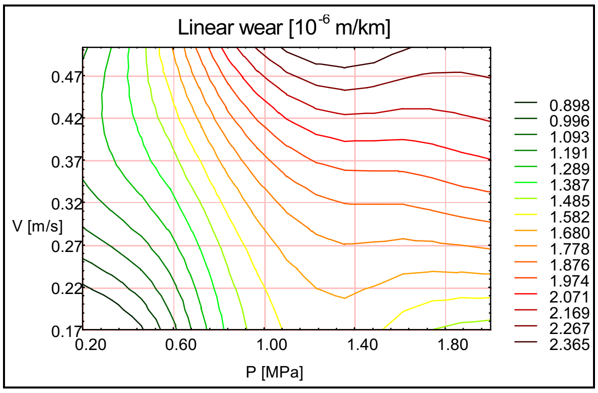

Figure 9b Linear wear of Tarnoform 300 - contour plot

A typical value of the static coefficient of friction between Tarnoform and Tarnoform is 0.35. The dynamic COF equals to 0.25.

3.2. Thermal properties

The basic thermal properties of Tarnoform may be characterised by the following parameters:

- glass transition temperature T_g,
- melting point,
- specific heat,
- enthalpy,
- thermal conductivity,
- coefficient of linear thermal expansion,
- heat distortion temperature,
- Vicat softening point

At present, the first four parameters are determined by Differential Scanning Calorimetry on micro-samples (weighing about 20 mg) of Tarnoform. A typical DSC curve for Tarnoform 300 is shown in fig. 10.

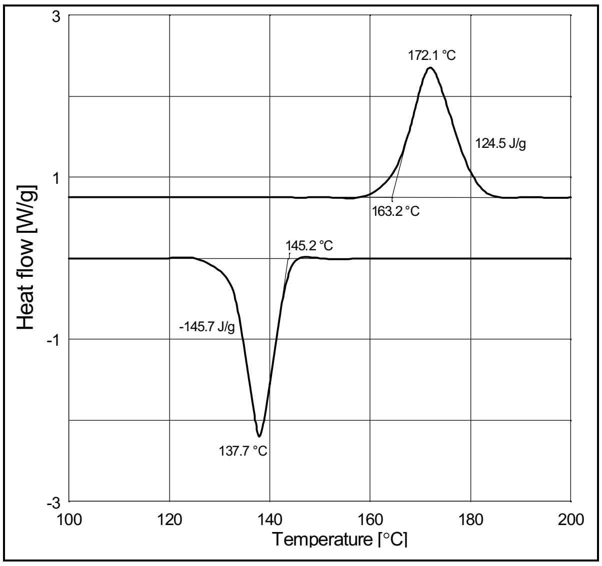

Figure 10 Typical DSC curve for Tarnoform 400

Between -50°C and +200°C the only visible peak in the heating phase is the melting peak at a maximum of about 172°C. This permits short-term application of parts made of Tarnoform even at temperatures close to the melting point. The crystallisation peak visible in the cooling phase permits the determination of the temperature and the heat of Tarnoform crystallisation, equal to 138°C and -142 J/g respectively. The maximum deviations from these parameters, occurring in practice, are following:

- ± 2°C in case of the melting point and crystallisation temperature,
- ± 15% in case of the heat of fusion and heat of crystallisation.

Specific heat is the quantity of heat, which should be supplied in order to heat up a unit mass of Tarnoform by 1 K. At room temperatures (23°C), the specific heat capacity equals to 1.48 kJ/kg·K for all Tarnoform grades. The changes of Tarnoform specific heat capacity as a function of temperature are presented in the form of a graph. 11.

The relative specific heat is often presented as a dimensionless quantity, taking the specific heat of water at a given temperature as the reference value. The relative specific heat of Tarnoform at 23°C is 0.35 for all grades.

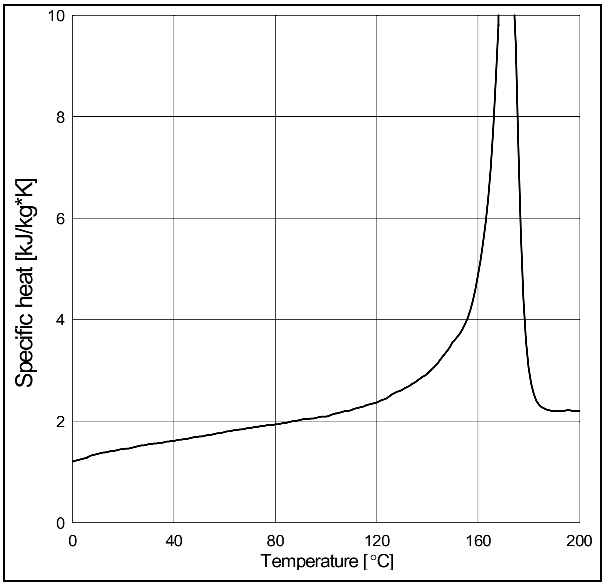

Figure 11. Temperature dependence of specific heat

For practical purposes, it is more convenient to use another quantity describing the amount of heat transferred during heating or cooling of Tarnoform, namely enthalpy. Enthalpy is usually referred to room temperature, at which it equals 0. Consequently, the amount of heat exchanged during heating or cooling of Tarnoform is represented by the difference between enthalpies determined for the initial and final process temperatures.

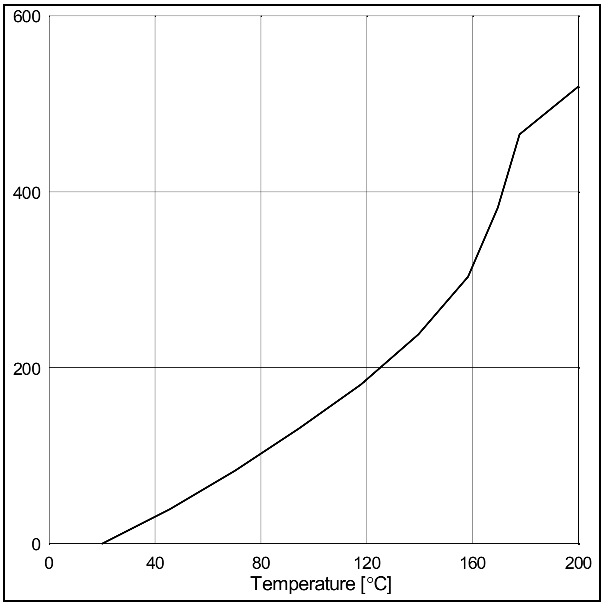

Figure 12. Temperature dependence of Tarnoform enthalpy

In order to design processing equipment and to evaluate the ability of Tarnoform parts to suppress the heat transfer, it is necessary to know the thermal conductivity of Tarnoform.

For all Tarnoform grades, this conductivity equals 0.33 W/m·K (at 23°C) and situates Tarnoform among thermal insulators.

Thermal expansion coefficient α of Tarnoform is presented in the form of graph.13.

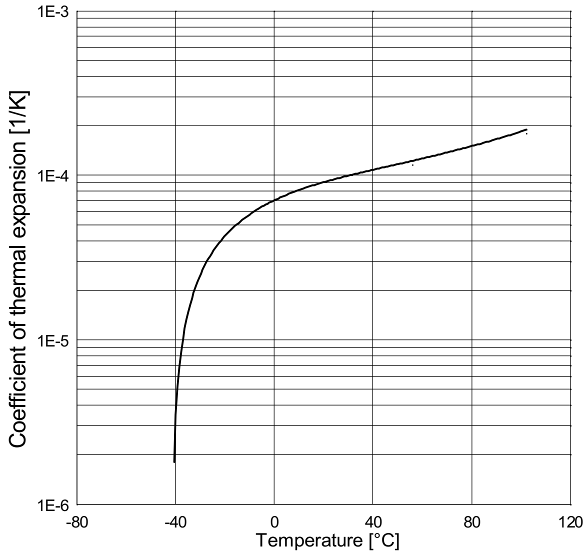

Figure 13 Temperature dependence of coefficient of linear thermal expansion of Tarnoform

As in case of other plastics, this coefficient too increases with temperature. For practical purposes, it is more convenient to use the average coefficient of thermal expansion (α_m) for a given temperature range. It permits simple calculations of part dimensions changes when the temperature increases or decreases by a specified value, according to the following formula:

$$l_{\Delta T} = l_0 [1 + \alpha_m \Delta T]$$

where: $l_{\Delta T}$ - linear dimension of the part after temperature change,
l_0 - initial linear dimension of the part,
α_m - average coefficient of thermal expansion,
ΔT - temperature change.

For all Tarnoform grades, the value of the average coefficient of thermal expansion equals $70 \cdot 10^{-6}$ K^{-1} in the temperature range of -40°C to 30°C; $110 \cdot 10^{-6}$ K^{-1} in the temperature range of 30°C to 60°C and $150 \cdot 10^{-6}$ K^{-1} in the temperature range of 60°C to 105°C.

Heat distortion temperature (HDT) defines the point at which a standard bar deflects under specific load (1.8 MPa for HDT A or 0.45 MPa for HDT B). Based on the test results we can describe ability of the resin to sustain in high temperatures. Typical HDT values for all Tarnoform grades are given in table 2. Addition of reinforcement (glass or carbon fibres) or certain fillers drastically increase values for HDT, so we can say that HDT is a good indicator of compound thermal resistance.

Softening point according to Vicat (VSP) gives temperature at which a special needle penetrates a specimen under load (50 N for Vicat A or 10 N for Vicat B). Typical softening point temperatures for all Tarnoform grades are presented in table 2. In this case there is no change in VSP values for modified grades of Tarnoform, so we can call VSP a “matrix resin” property.

3.3. Electrical properties

Electrical properties of Tarnoform situate this plastic among good dielectric materials. In combination with excellent mechanical properties, even in increased temperatures, parts made Tarnoform find a broad range of applications in the electric and electronic industries. The basic electrical properties of Tarnoform are as follows:

- volume and surface resistivity,
- dielectric constant and dielectric loss factor,
- dielectric strength,
- electric arc resistance,
- leak resistance,
- drift current resistance.

Electrical properties of all Tarnoform grades are collected in table 3. In the figures below, selected properties are presented as functions of time and frequency. Attention should be given to the invariability of dielectric constant for a wide range of frequencies (graph 19) and to the constant characteristic of dielectric strength in the vast range of temperatures (graph 16).

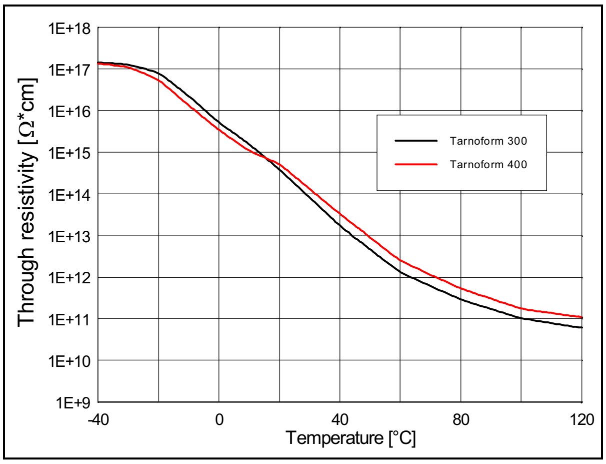

Figure 14 Temperature dependence of volume resistivity for Tarnoform 300 and Tarnoform 400

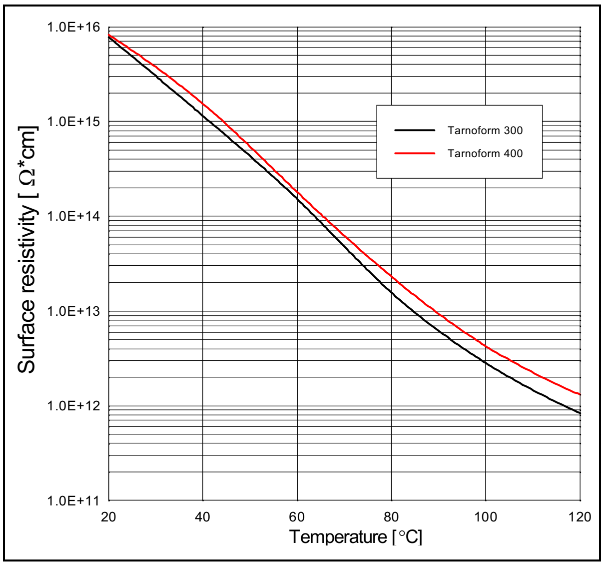

Figure 15 Temperature dependence of surface resistivity of Tarnoform 300 and Tarnoform 400

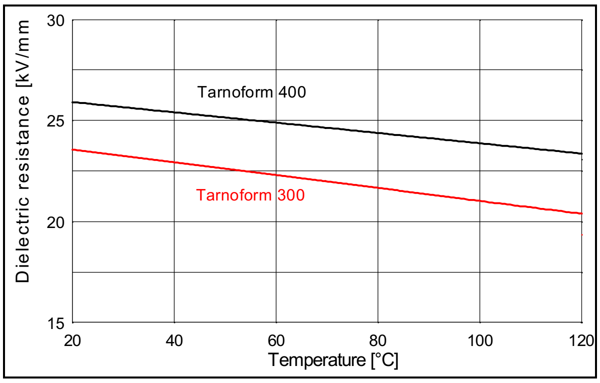

Figure 16 Temperature dependence of dielectric resistance of Tarnoform 300 and Tarnoform 400

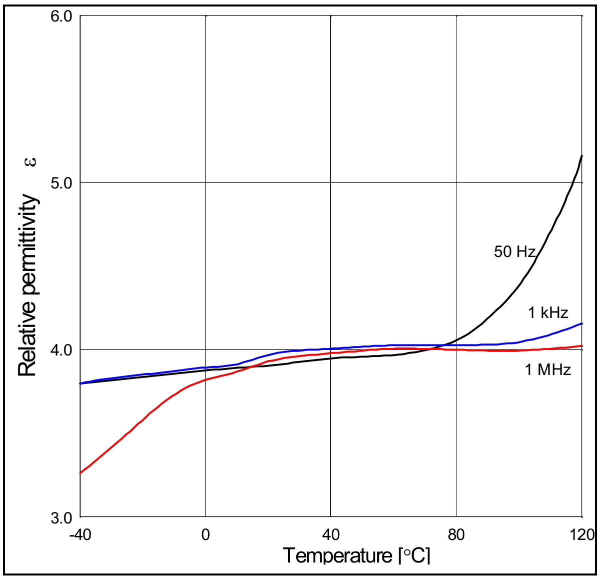

Figure 17 Temperature dependence of relative permittivity of Tarnoform for the frequencies of 50 Hz, 1 kHz and 1 MHz

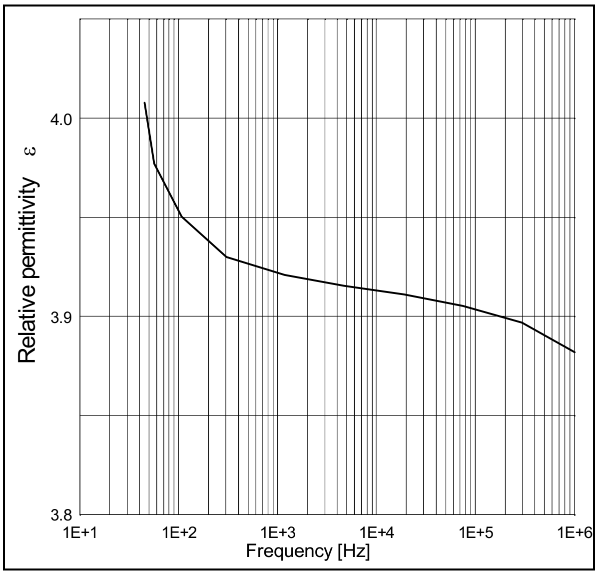

Figure 18 Relative permittivity of Tarnoform 400 as a function of frequency

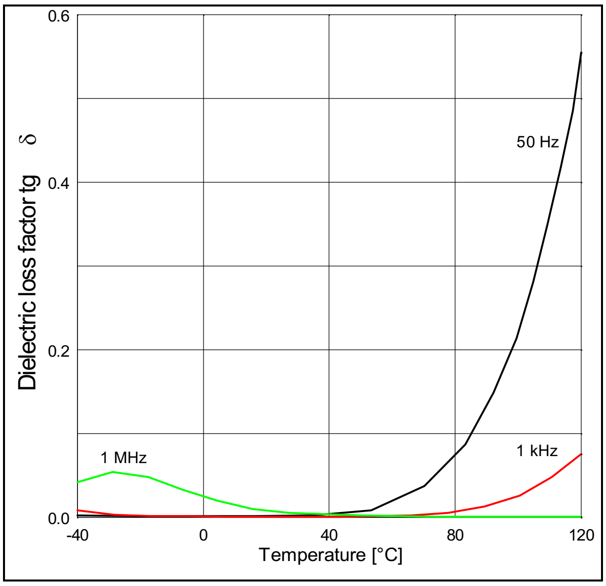

Figure 19 Temperature dependence of dielectric loss factor of Tarnoform 400 for the frequency of 50 Hz, 1 kHz and 1 MHz

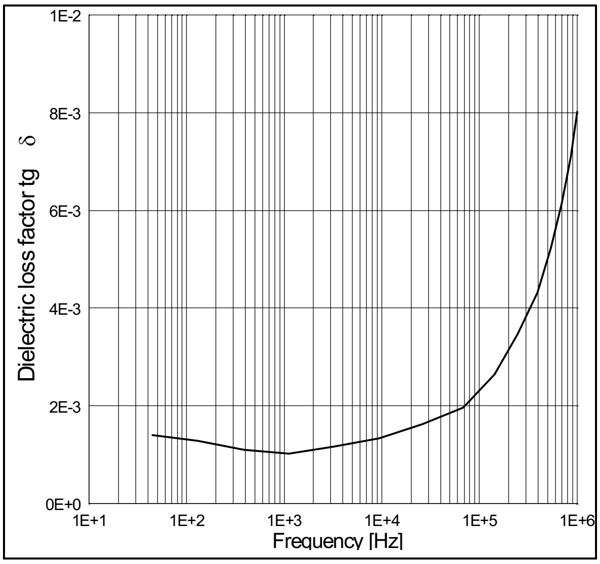

Figure 20 Dielectric loss factor of Tarnoform 400 as a function of frequency

3.4. Optical properties

The main quantity determining the optical properties of Tarnoform is its refraction index equal to 1.48 for the visible range of light. This index defines the relative speed of light in a given medium (compared with the speed of light in vacuum), according to the following formula:

$$n = \frac{c}{v}$$

where: n - index of refraction,
c - speed of light in vacuum ($2.99792 \cdot 10^8$ m/s),
v - speed of light in Tarnoform, in m/s.

Tarnoform may be classified as a translucent plastic, as it transmits different amounts of light depending on the sample thickness (see table below):

thickness [mm]	light transmission [%]
1	65
2	50
3	45

Parts made of Tarnoform are usually in milk-white colour; their gloss depends on the finish of the mould surfaces. The results of typical colour determination procedures obtained instrumentally are collected in table 4.

4. EFFECT OF THE ENVIRONMENT ON TARNOFORM® PROPERTIES

Tarnoform parts are subject to environmental factors, such as oxygen (oxidation), light (photo degradation) and temperature (thermal degradation), which usually leads to deterioration of its mechanical properties and change in colour. Nevertheless, use of the instructions given below permits a long-term and effective utilisation of all valuable properties of Tarnoform without any significant degradation. The influence of processing parameters on the properties of Tarnoform will be described in detail in chapter 5.

4.1. Chemical resistance

Chemical structure of Tarnoform, containing repeatable components of ether type, influences the main features of Tarnoform chemical resistance, such as:

- resistance to hydrocarbons,
- susceptibility to thermal oxidation,
- chemical inert in the presence of most non-oxidising chemicals.

The first of these features determines the applicability of Tarnoform in the automotive, fuel processing and power industries.

Degradation by thermal oxidation in air takes place only at temperatures above 150°C and therefore above the range of operating temperatures. So high resistance of Tarnoform has been achieved by the optimum selection of stabilising additives.

High chemical resistance of Tarnoform is confirmed by almost complete stability towards organic solvent. The only solvents known to dissolve Tarnoform at room temperature are those two exotic: hexafluoroacetone sesquihydrate and hexafluoroisopropanol.

4.1.1. Resistance to fuels

Typical automotive fuels are mixtures of hydrocarbons, the boiling points of which are suitable for the given type of engines. In case of petrol, additives improving resistance to ”knocking” are often used. Typical antiknocks include lead tetraethyl (being withdrawn from use owing to its high toxicity), oxygen compounds (methyl alcohol and ethyl alcohol, ketones) and aromatic hydrocarbons.

Resistance of Tarnoform to typical fuel mixtures is high, which is confirmed by the lack of noticeable changes in its mechanical properties. The only visible effect is a minimum (about 2%) and completely reversible absorption of these media demonstrated by Tarnoform. Thus Tarnoform may be successfully used in the automotive industry, in components remaining in constant or intermittent contact with fuels (flow meters, filling systems, tanks and floats). Exceptionally low permeability demonstrated by Tarnoform in contact with fuel mixtures vapours (0.015 $cm^3/m^2 \cdot h$ at 23°C) is an additional advantage.

Increasing importance of natural gas as an ecological engine fuel initiated the search for materials having high strength combined with high resistance to this medium. Similarly as in case of petrol type fuel, properties of Tarnoform suits very well to all the requirements mentioned above, enabling the construction of gas-tight supply systems for the automotive industry and gas distribution systems (pipe joints, various fittings, gas meters).

4.1.2. Resistance to chemicals

Chemical composition of Tarnoform, ensuring high resistance to corrosive chemicals, permits the use of parts made of Tarnoform in applications involving long-term exposure to chemical substances. Tarnoform is resistant to chemicals having acidity pH>4, therefore only strong acids are capable of damaging its structure. Tarnoform chemical resistance was tested by measuring changes of its mechanical properties during exposure. Data presented in the table were collected for 4-mm thick injection moulded specimens. Unless otherwise specified, pure substances (100% concentration) were used. The specimens were completely immersed in these media for 2 months, at room temperature. When any of the properties changed by more than 20%, the plastic was classified as not resistant (denoted by -), otherwise it was classified as resistant (denoted by +). Borderline results were denoted by +/-. Figures 21 and 22 show changes in Tarnoform properties caused by two opposite type chemicals (10% sodium hydroxide and 10% nitric acid).

Substance	Resistance	Substance	Resistance
acetic acid	-	leaded petrol	+
acetic acid 10%	+	methyl acetate	+/-
acetic acid 80%	+/-	methyl alcohol	+
acetone	+	methylene chloride	+/-
ammonia 10%	+	n-hexane	+
ammonia 30%	+	nickel sulphate 10%	+
ammonium sulphate 10%	+	nitric acid 10%	-
aniline	+	olive oil	+
benzene	+	oxalic acid 10%	+
brake fluid	+	phenol	-
butyl alcohol	+	phosphoric acid 25%	+/-
calcium chloride 10%	+	potassium hydroxide 10%	+
calcium nitrate 10%	+	potassium hydroxide (saturated solution)	+
carbon disulphide	+	potassium permanganate 10%	+
carbon tetrachloride	+	sea water	+
chlorinated water	+	silicone oil	+
chloroform	-	sodium carbonate 10%	+
citric acid 10%	+	sodium chloride (saturated solution)	+
copper sulphate 10%	+	sodium chloride 10%	+
crude oil	+	sodium dihydrogen phosphate 10%	+
cyclohexane	+	sodium hydrogen carbonate 10%	+
detergents	+	sodium hydrogen phosphate 10%	+
diesel oil	+	sodium hydrogen sulphite (saturated solution)	-
distilled water	+	sodium hydroxide 10%	+
engine oil	+	sodium hydroxide (saturated solution)	+
ethyl acetate	+/-	sodium hypochlorite (bleach)	+/-
ethyl alcohol 96%	+	sodium nitrate 10%	+
ethyl ether	+	sodium phosphate 10%	+
ethylene glycol	+	soybean oil	+
formalin 37%	+	sulphuric acid 10%	+
formic acid 10%	+	sulphuric acid 50%	-
fruit juices	+	tetrahydrofuran	+/-
fuel oil	+	thiophene	+/-
glycerine	+	toluene	+
hydrochloric acid 10%	-	transformer oil	+
hydrogen peroxide 1%	+	trichloroethylene	+/-
hydrogen peroxide 30%	+/-	turpentine	+
instant coffee	+	unleaded petrol	+
isopropyl alcohol	+	unleaded petrol with alcohol content	+
jet fuel	+	urea 5%	+
lactic acid 10%	+	white oil	+
lactic acid 90%	+	xylene	+

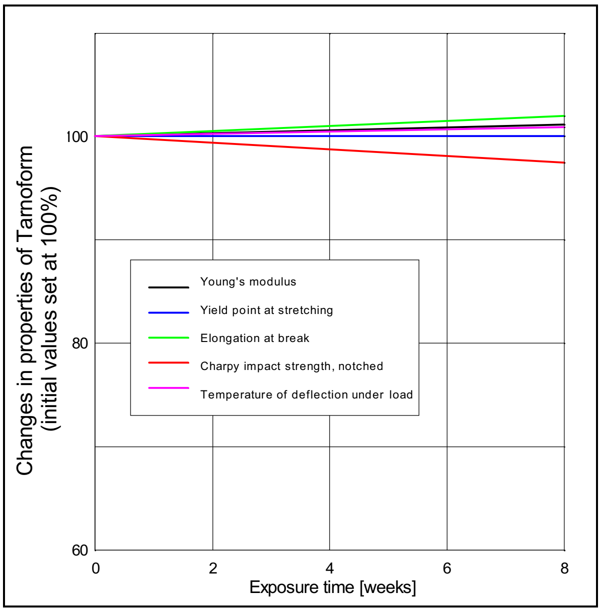

Figure 21 Exposure time effect on Tarnoform properties (medium - 10% solution of sodium hydroxide)

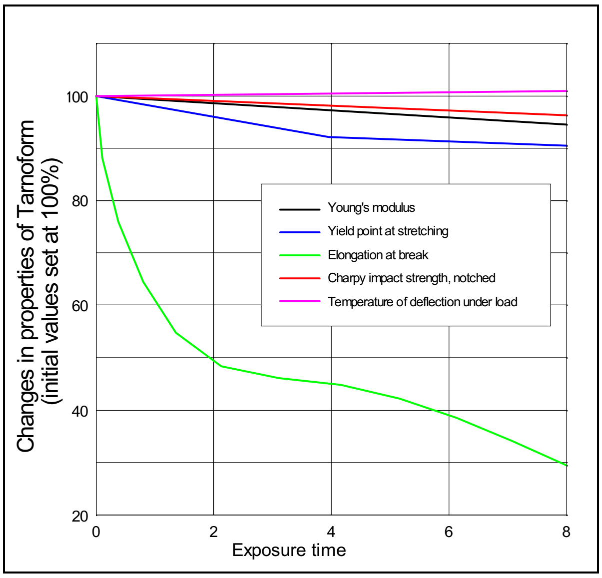

Figure 22 Exposure time effect on Tarnoform properties (medium - 10% solution of nitric acid)

4.2. Effect of water and steam

As indicated in the table (section 4.1.2), Tarnoform demonstrates excellent resistance to water (both distilled and sea) at room temperature. Higher temperatures do not cause any significant changes in the classification, which is illustrated in fig. 23. It is clearly visible that only continuous exposure to a temperature of 100°C for more than 1.5 year caused the tensile strength of Tarnoform to decrease to 80% of the initial value. This allows Tarnoform to be used in the production of parts remaining in permanent contact with water, such as plumbing fittings and washing machine parts.
As it is shown in table 4, Tarnoform absorbs minimum amounts of water from the environment. Even in long-term tests this absorption did not exceed 1.6% (at 100°C). Chemical structure of Tarnoform causes that the absorbed water cannot be permanently bounded in the resin, thus a complete desorption of moisture always take place in suitable conditions.
Long-term contact with steam at high temperatures causes changes similar to those caused by water acting at increased temperatures, i.e. deterioration of strength. In case of occasional exposure of parts or products made of Tarnoform to overheated steam (for example during sterilisation), significant changes of strength properties take place only when the temperature of steam exceeds 140°C.

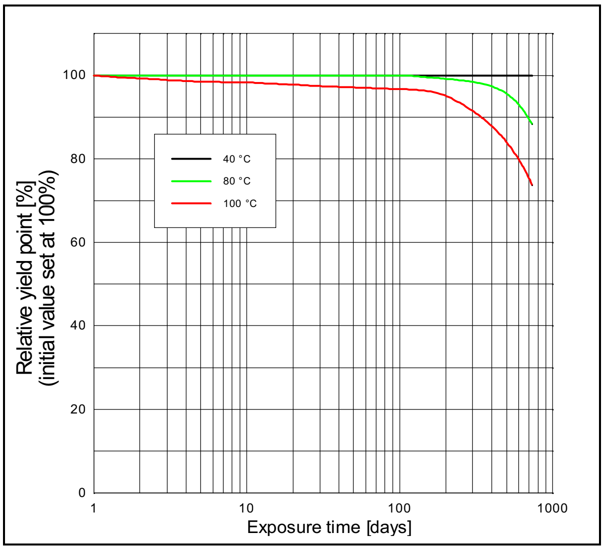

Figure 23 Effect of the time of holding in water at selected temperatures on the tensile strength of Tarnoform

4.3. Resistance to ageing (effect of light and air)

Tarnoform, similarly as other plastics, is subject to degradation in the natural environment, mainly as a result of combined action of air's oxygen and ultraviolet radiation from sunlight. Applications involving such exposure resulted in the introduction of stabilised Tarnoform grades, which are resistant to ultraviolet radiation. High quality of Tarnoform UV (in black colour) was confirmed by a positive result of test, consisting of a 300-hour exposure of plastic parts to a simulated sunlight. After such tests, parts made of Tarnoform demonstrated neither changes in colour (which is the main indication of deterioration on coloured polyacetal without UV additives) nor surface chalking, characteristic for polyacetals in natural colour.

In order to illustrate the behaviour of Tarnoform in the air as a function of temperature and duration of exposure, a characteristic is shown indicating that it is possible to use parts made of Tarnoform at a temperature of 100^{o}C for over two years.

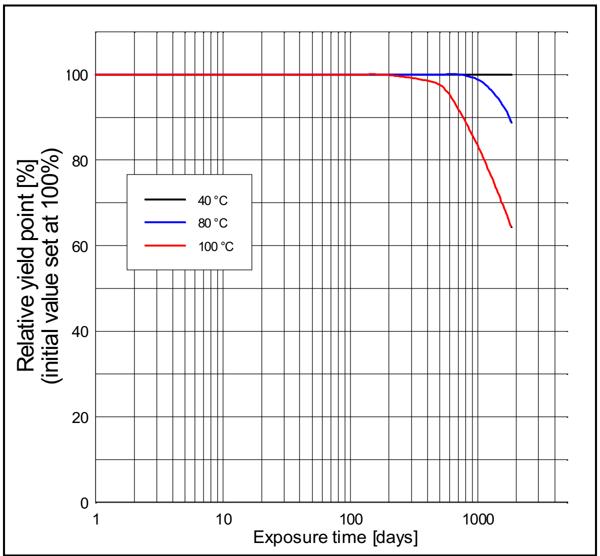

Figure 24 Effect of the time of holding in air at enhanced temperature on the yield point of Tarnoform

Thus this temperature is the temperature of continuous operation, presented in table 2. However, in order to determine the operating temperature of particular parts, the effects of stresses and their nature should be taken into consideration as well. The maximum instantaneous operating temperature of Tarnoform is 140^{o}C.

4.4. Effect of high-energy radiation

Apart from ultraviolet radiation described in the previous section, typical high-energy radiation includes gamma-, X- and beta rays. Similarly as in case of ultraviolet radiation, exposure of parts made of Tarnoform to high-energy radiation results in such symptoms as damage to the polymer structure causing deterioration of mechanical properties and decolourisation (of coloured Tarnoform) or yellowing (of natural Tarnoform). The degree of damage is a function of radiation dose absorbed. When the total dose of radiation is about 25 kGy, the tensile strength does not change at all, but elongation at break decreases by 10 - 15% as a result of certain damage done to the polymer structure. Thus this is the maximum dose which can be absorbed by a part made of Tarnoform without a risk of any significant drop in mechanical properties.

4.5. Flammability

Tarnoform ignites in the presence of flames and still burns after removing the fire source, with a bluish, almost invisible flame. During combustion, the plastic melts and drips with burning drops. When the supply of air is sufficient, products of combustion include carbon dioxide and water. When the amount of air is insufficient, carbon monoxide and decomposition products may be released, mainly including formaldehyde, also being the main constituent of gases emitted by the plastic when extinguished. Tarnoform combustion rate depends mainly on the thickness of plastic parts and decreases when the thickness grows.

Flammability classification for all Tarnoform grades is following:

- UL 94: HB
- FMVSS 302: B 50 (1 mm)

In case of testing according to UL94, V-0 classification is not possible, mainly due to the high oxygen content in polymer structure.

4.6. Toxicological aspects of Tarnoform®

Basic approvals include situations when Tarnoform should be in contact with food or drinking water. For European market there are today three basic Directives issued by the European Commission:

- 82/711/EC - stating permissible levels of migration of components of plastic into foodstuff
- 85/572/EC – regarding simulants of foodstuff used in migration tests
- 90/128/EC – containing list of allowable starting materials for manufacturing of food contacting plastics

On the German market those directives are collected as a Consumer Articles Regulations (Bedarfsgegenständeverordnung, BGVO), which states that plastic could be used for manufacture of consumer articles (as defined in Food and Consumer Articles Law, Lebensmittel- und Bedarfsgegenständegesetz, LMBG) in case of fact that:

- resin is made of approved monomers
- migration of resin constituents doesn't exceed allowable limits
- final article is used in accordance with they intention and doesn't change contacting food taste an odour

Additionally there is a range of polyacetal specific requirements, i.e. for Germany there are recommendations of Federal Institute for Consumer Health Protection and Veterinary Medicine (BgVV):

- XXXIII – Acetal resins
- IX – Colorants for the coloration of plastics and other polymers for
- LII – Fillers for consumer articles from plastics

In United States of America the same requirements could be found in 21 CFR § 177.2470 issued by Food and Drug Administration (FDA).

Based on our today knowledge we can declare that all natural grades of Tarnoform meet all above requirements, i.e. EC laws, especially BGVO and BgVV, as well as FDA.

Requirements to be met by plastics used in the production of toys for the European Union market are defined by EN 71-3 standard ”Safety of toys”. On the basis of conducted tests we can confirm suitability of all grades of for this purposes.

Composition of Tarnoform doesn't include any heavy metals and ozone depleting compounds as defined by Montreal's Protocol.

5. PROCESSING

Tarnoform may be processed by all methods typical for thermoplastics, such as injection moulding, extrusion and compression moulding. Injection moulding is the most common method for processing of Tarnoform.

DRYING

Drying Tarnoform before processing is not necessary, if the process of transportation and storage is conducted according to the relevant requirements, i.e. transportation by means of covered vehicles, storage at temperatures below 50°C in dry places, far from heat sources. Long-term storage or contact with moisture causes the water content of the granulated product to increase up to 0.2 %, which may make processing difficult. The common symptoms include yellowing during processing and poor appearance of product surface (silver smudges, microblisters). In such situations it is necessary to dry Tarnoform at temperatures between 100°C and 120°C for 2 to 3 hours (the layer of Tarnoform being dried on shelf dryers should not be thicker than 3 cm). If the plastic is stored at temperatures below 20°C, before processing its temperature should be equalised with the ambient temperature, as steam contained in the air is likely to condense on cold Tarnoform.

MELT TEMPERATURE

Melt temperature of Tarnoform during processing should be in the range of 180°C to 230°C, but the appropriate temperature should be adjusted empirically by the processor depending on the specific features of the processing machine, manufactured products and process type. Thermal stability of the resin should be also taken into consideration, as it determines the maximum allowable time that Tarnoform may be kept in a given temperature, according to the characteristic presented in fig. 25.

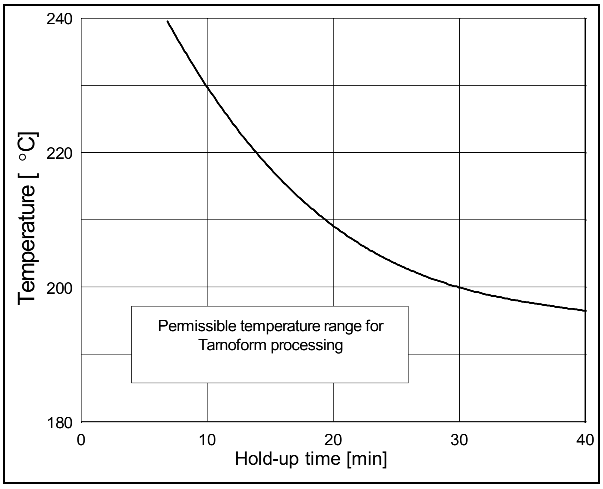

Figure 25 Thermostability curve of Tarnoform during the processing - permissible temperature range is below the thermostability curve

A period for which the plastic is held in the cylinder of the injection moulding unit may be calculated from the following formula:

$$t = \frac{m_{cylinder}}{m_{injection\ cycle}} \times t_{cycle}$$

where: $m_{cylinder}$ - weight of the plastic contained in the cylinder,
$m_{injection\ cycle}$ - weight of the plastic injected into the mould in one injection cycle,
t_{cycle} - injection cycle duration.

For practical purposes, this period may be calculated from the following, simplified formula:

$$t = \frac{l_{max} \times 2}{l_{cycle}} \times t_{cycle}$$

where: l_{max} - maximum stroke of the screw,
l_{cycle} - effective stroke of the screw in the dosing phase (screw stroke combined with its rotation),
t_{cycle} - injection cycle duration.

Current temperature of the melt may be determined by a temperature sensor, which is built in the processing machine (usually in the nozzle). When such sensor is missing, melt temperature may be determined in the following manner:

- During steady running phase of the machine in the automatic cycle, the cycle should be interrupted after the dosing phase (fully retracted screw) and the melted material should be injected into a container made of insulating material (wood, ceramic or plastic having melting temperature much higher than the expected temperature of melted Tarnoform).
- Immediately after injection, a temperature sensor (a thermocouple or a thermistor) having a very low time constant (an instantaneous sensor) should be inserted into the melted plastic. The sensor should be formerly heated up to a temperature similar to the expected level)
- Next, the maximum instantaneous temperature should be read on the sensor.
- When the conditions described above are maintained, the temperature reading accurately reflects the real temperature of Tarnoform melt.

Exceeding the allowable time for a given temperature may cause decomposition of the plastic, involving emission of detrimental gaseous products (formaldehyde). In such situation the cylinder should be emptied, its heating system should be cut off and ventilation should be switched on. Degraded material may be immersed in water in order to limit the emission of gaseous products of decomposition.

In case of downtime, the cylinder temperature should be lowered to 150°C. Longer downtimes (lasting several days) require the cylinder to be emptied in order to avoid a potential thermal degradation.

CHANGE FROM TARNOFORM TO ANOTHER RESIN

The material remaining in the cylinder should be removed by ending the cycle, retracting the injection unit from the mould, moving the screw forward to its extreme position, setting a high counter-pressure and manual switching of the dosing action (the screw rotates, but does not retract). In order to remove Tarnoform residue, the machine should be flushed (by performing injection) with polyethylene, polypropylene, polystyrene or another appropriate cleaning material. The cleaning process should be conducted in the range of Tarnoform processing temperatures (between 180°C and 230°C).

CHANGE FROM ANOTHER RESIN TO TARNOFORM

Such procedure, as mentioned above, (purging, flushing etc.) is to be conducted at the processing temperatures of the former plastic, and subsequently the temperature of the machine should be switched to the range suitable for Tarnoform. When switching from PVC to Tarnoform occurs, apart from the procedure described above it is necessary to clean (mechanically) at least the nozzle, as Tarnoform contaminated with PVC residue may potentially decompose and emit detrimental gaseous products of such decomposition.

RECYCLING

Recycling of uncontaminated Tarnoform waste products (runners, short shots, defective mouldings and products) is possible by milling them in slow-speed mills and mixing with fresh material. The amount of the recycled material added may reach even 100% in case of unsophisticated products with low quality requirements, thus complete recycling is possible at this processing stage. However, the manufacturer should evaluate the effects of the recycled material content on the important product properties. Other issues concerning recycling of Tarnoform are discussed in section 5.6.

COLOURING

Tarnoform may be coloured during the injection moulding process, but the following requirements must be fulfilled:

- A colour concentrate designed for injection moulding should be used (carrier: polyacetal or universal compatible with Tarnoform), containing colorants having thermal resistance at least 240°C. Chemical properties of colorants should be neutral, in order to avoid any potential degradation of Tarnoform.

- The resin should be homogeneously mixed with the colorants by selecting appropriate parameters of the dosing cycle (relatively low rotational speed of the screw) or by using a mixing head which forces the dispersion of the pigment by repeated changes of the direction of flow of the melt.

An optimum solution is, however, to use mass-coloured material, in which optimum dispersion of the pigment is ensured.

5.1. Injection moulding

MACHINE

Tarnoform may be processed on all types of injection moulding machines equipped with universal screws. However, a screw conforming to the specification given below provides the optimum processing conditions as well as high output:

- screw length: 18 - 22 D
- feed zone: 6 - 10 D
- compression zone: 6 - 9 D
- dosing zone: 4 - 5 D
- screw pitch: 0.8 - 1.0 D
- compression ratio (ratio of the screw coil depth in the feed zone to the depth in the dosing zone): 1.9-2.4 (Tarnoform 200), 2-3 (other grades)

Tarnoform may be processed on injection moulding machines equipped with open nozzles (in such design it is recommended to use a non-return valve installed between the nozzle and the cylinder) or needle-type closing nozzles.

MOULD

The design of the mould should take into account relatively high moulding shrinkage of Tarnoform. The total shrinkage, being the sum of the processing shrinkage (measured 24 hours after the injection) and the after-shrinkage (occurring during the whole lifetime of the product) is a function of four parameters: mould temperature (strong relationship), hold pressure, hold pressure time and part wall thickness (weaker relationships).

These relationships are graphically illustrated on graphs.

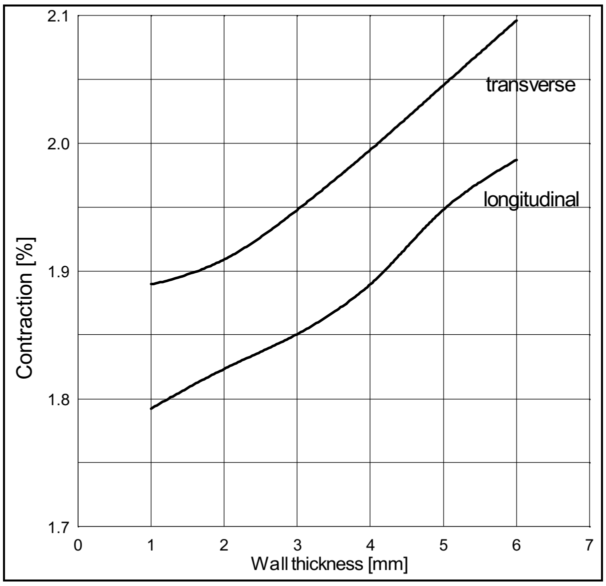

Figure 26 Dependence of Tarnoform shrinkage on the wall thickness of a moulding part (mould temperature 90°C, hold pressure 100 MPa, melt temperature 205°C)

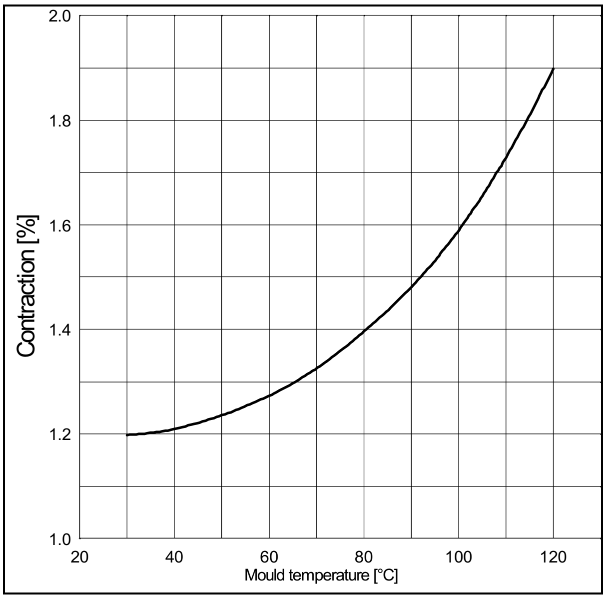

Figure 27 Tarnoform shrinkage characteristics as a function of the mould temperature (wall thickness of a moulding part 1.5 mm, hold pressure 100 MPa, melt temperature 210°C, the measurement after one hour since the injection)

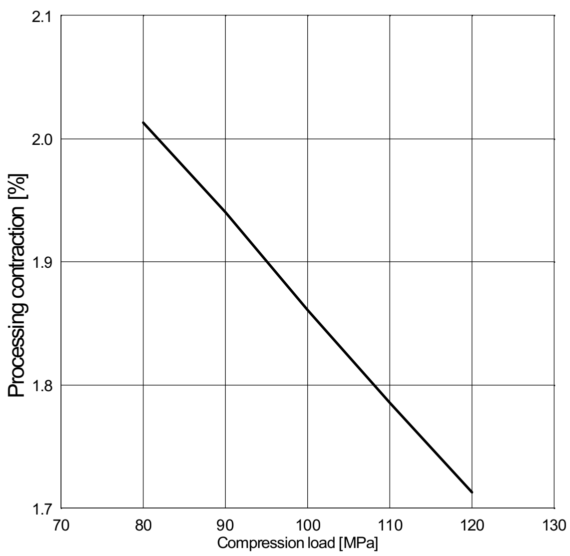

Figure 28 Processing shrinkage of Tarnoform as a function of hold pressure (wall thickness of a moulding part 3 mm, mould temperature 90°C, melt temperature 205°C)

In practice, three types of injection are considered: regular (tolerance limit: ±1%, mould temperature: 60°C), technical (tolerance limit: ±0.6%, mould temperature: 90°C) and precision (tolerance limit: ±0.3%, mould temperature: 120°C). The tolerance limits specified above apply to sizes above 10 mm. When all injection parameters are selected according to the characteristics of the resin, it is possible to produce moulded pieces having dimensional precision required by their envisaged applications. In case of thick-walled moulded parts, seasoning at a temperature of 140°C for a period of 10 minutes per each 1-mm of wall thickness is recommended, as this leads to a reduction of internal stresses.

Another significant issue influencing the process of injection moulding of Tarnoform is the design of mould runners and gates. The following recommendations should be observed:

- Gates should be placed in the thickest part of the moulded part.
- The diameter of the gate should be at least equal to a half of the thickness of the moulded part near to the gate.
- The length of the gate should be minimised (maximum length 0.8 mm).
- The diameter of the runner should be at least 120% of the largest thickness of the moulded part.
- The system of runners should ensure unconstrained flow of the melt during the filling phase and the hold pressure phase.

In case of using metal inserts, it is necessary to heat up initially all metal parts at least to the temperature of the mould. This will protect the moulding against high internal stresses, frequently leading to product damage.

PROCESSING CONDITIONS

Achieving the best parts during injection moulding of Tarnoform is possible as a result of appropriate crystallisation conditions of the resin, i.e. injection mould temperature between 60°C and 120°C, clamping pressure between 60 MPa and 120 MPa and hold pressure time selected experimentally as a function of the product weight.

Optimisation of the process parameters for a given product made of Tarnoform should be performed according to the following scheme:

- Set the temperatures in the feed cylinder so as to obtain the appropriate range of melt temperatures from 180°C to 220°C (230°C for mouldings with complex flow paths). An example of temperature profile is shown below (numbering of zones from the feed hopper side):

zone 1	175°C
zone 2	185°C
zone 3	195°C
nozzle	200°C

After initial setting of the parameters, they should be corrected during the cycle by reading the measured melt temperature (recommended temperature of melted Tarnoform: 205°C). The influence of heat generated by the shear of the melt in the dosing phase and during flows through gates should be also taken into account (10 MPa pressure drop at the gate rises the temperature of the melt by 3.6°C).

- The temperature of the mould inner surface should range between 60°C and 120°C (depending on the desired dimensional tolerance of the moulded part). To reach this temperature, proper adjustment of the thermostat is required (the temperature set on the thermostat should be higher than the expected mould temperature, as some heat is loss to the environment). After reaching thermal equilibrium during the process of injection, the temperature of mould cavities should be measured by an instantaneous thermometer and the setting of the thermostat should be adjusted correspondingly.

- Set the peripheral speed of the screw (*u*) during the dosing phase in the range of 0.1 to 0.4 m/s, which gives the following rotational speed of the screw (*D* is the screw diameter expressed in metres):

$$n = \frac{60 * u}{\pi * D_s} \text{ [rpm]}$$

  For the range of Tarnoform melt temperatures specified above, an optimum rotational speed of the screw should ensure proper homogenisation. In order to assess the accuracy of homogenisation the following test may be conducted:

  - When the machine runs steadily in the automatic cycle, interrupt the cycle after the dosing phase (fully retracted screw) and perform a free injection of the material;
  - Feed a dose of material and perform a free injection again;
  - Repeat this operation until unmelted particles can be observed in the melt;
  - When the process settings are correct, at least three first injections should be free of unmelted pellets (optimum settings provide six such injections);
  - If unmelted material appears earlier that after three injections, the temperature of the melt should be increased, the rotational speed of the screw should be decreased or the backpressure should be increased.

- The backpressure should be between 0 and 3 MPa (0 - 30 bar).
- The injection pressure should be equal to the hold pressure and should be in the range of 60 to 180 MPa (600 to 1800 bars).
- The injection rate should ensure proper filling of the mould, without disturbances caused by premature crystallisation of the resin. However, the influence of the injection rate on the important strength parameters of the product should be evaluated experimentally, because when the injection rate decreases (the time of injection is longer), the impact strength of the products grows. Thus the optimum injection rate is a compromise between the expected strength properties of the product and the simplicity of the injection process. In general, the injection time for thick-walled mouldings is shorter than for thin-walled parts.
- The duration of the hold pressure phase should be optimised by the evaluation of the moulding sizes and weights, according to the characteristic given below.

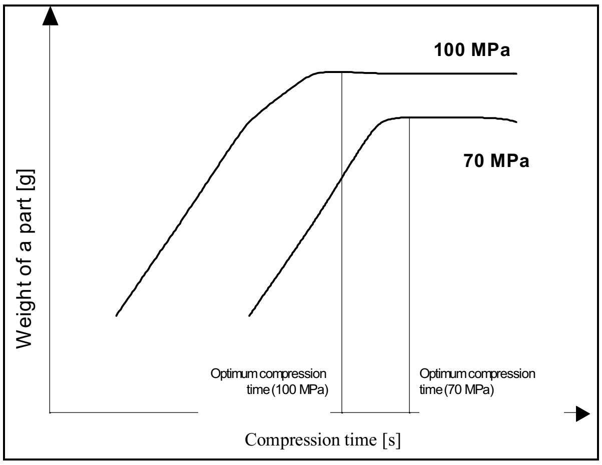

Figure 29 Principle of the optimum hold pressure time choice for selected hold pressures

- The cooling time should be initially computed from the following formula:

$$t = \frac{s^2}{\pi^2 * 0.057} * \ln\left(\frac{4}{\pi} * \frac{T_m - T_w}{T_e - T_w}\right)$$

  where: s - maximum wall thickness of the part [mm],
  T_m - melt temperature,
  T_w - mould temperature,

T_e - demoulding temperature (150°C),

and next corrected according to the desired dimensional tolerance of the product (longer cooling time reduces the scatter of product dimensions).

- As it is necessary to compensate the moulding shrinkage losses, it is recommended to maintain a resin cushion in the cylinder having a volume up to 10% of the dosing stroke.

As an example of the injection process parameters, the requirements of ISO 9988 standard may be specified, concerning the process of injection moulding of specimens for tensile tests, made of acetal copolymer:

- melt temperature 195 ± 5°C
- mould temperature 85 ± 5°C
- complete cycle time 35 to 45 s
- average injection rate v 200 ± 100 mm/s computed from the following formula

$$v = \frac{\pi * D^2 * v_w}{4 * n * A}$$

where D - screw diameter [mm],
v_w - linear speed of the screw during injection [mm/s],
n - number of cavities in the mould,
A - cross-sectional area of the moulded part in the tested range [mm^2]

- hold pressure time 25 to 35 s
- hold pressure 85 to 95 MPa
- cooling time 10 to 15 s
- back pressure 0.0 to 1.0 MPa

Optimally selected parameters of the injection process ensure dimensional stability and high mechanical properties of parts made of Tarnoform. In order to select these parameters for small, precision parts, we advise to perform a computer simulation of the injection process before the mould is made. This prevents from additional costs involved by necessary corrections of the tooling, resulting from specific features of Tarnoform, particularly from its shrinkage characteristic.

5.2. Extrusion

MATERIAL

Tarnoform 200 is a standard extrusion grade. It is used in semi-finished products requiring further mechanical processing, such as pipes, rods and plates.

MACHINE

Extrusion of Tarnoform is conducted exclusively on single-screw extruders having the following specifications:

- screw length: 20 - 25 (30) D
- feed zone: 8 - 9 D
- compression zone: 3 - 5 D
- dosing zone: 9 - 10 D
- screw pitch: ≈ 1.0 D
- compression ratio (ratio of the screw coil depth in the feed zone to the depth in the dosing zone): 2.75 - 3.0

Temperature settings should ensure that the temperature of the melt is between 175°C and 185°C. A considerably long time for which the material remains in the extruder should be taken into account.

RODS

Typical line consisting of a single-screw extruder, an indirect water-cooled calibrating head, a cooling bath and a jaw-type pull-off device applying high back pressure to the section being extruded, in order to prevent it from the formation of contraction cavities. Typical pull-off speeds are between 5 and 20 mm/min at outputs of 7 to 10 kg/h for single extrusion dies and about 20 kg/h for multiple dies. Typical rotational speeds of the screw do not exceed 40 rpm. Rods manufactured in this manner have relatively high internal stresses and require thermal treatment in the form of annealing in air, nitrogen, wax or oil, at temperatures between 140°C and 145°C. The duration of such treatment depends on the section dimensions: each millimetre of thickness requires 10 minutes of treatment. In order to avoid secondary stresses during heating and cooling, these processes should be carried out at a rate of 35°C/h (heating) and 15°C/h (cooling).

PIPES AND HOLLOW PROFILES

Pipes are made on a line consisting of an extruder, die head, calibrator (vacuum water bath with set of draw plates for outside diameters below 10 mm, vacuum device only for larger diameters), a cooling bath, a pull-off device and a measuring device controlling pipe diameter and wall thickness. Moulding shrinkage reaches 2.5%, thus the inner diameter of the calibrator should be larger than the desired outside diameter by this value. The extrusion die gap should be 3 to 4 times larger than the expected wall thickness.

PLATES

Plates are made on a line consisting of an extruder, a sheet die, a triple rolling mill, a pull-off device and a thickness control device. It is important to reduce the gap between the extrusion die and the take-up roll to minimum (few millimetres). In the manufacturing of plates which are 1 to 6 mm thick and up to 1000 mm wide, extruders with screw diameter between 90 and 120 mm are most common. In order to improve the quality of plate surface, plastic melt may be degassed in the degassing zone (0.5 D long) installed in the middle of the extruder. In such configuration the screw has two segments corresponding to the specifications given above. The first segment has a compression ratio of 2.7, while this parameter for the second segment (after the degassing zone) equals 3.0. The temperature of the rolls should be not higher than 145°C to 170°C (take-up rolls) and not lower than 120°C to 140°C (finishing rolls). Plates received from the rolling mill are being subsequently cut to a determined size and may be further processed by thermoforming or used as a semi-finished product for machining.

5.3. Machining

Machining as a method of processing is used in the short-run production, as well as in the production of large-size parts (screw conveyors, conveyors rollers, etc.) which cannot be manufactured using typical plastic processing methods. Usually semi-products used for machining have form of rods, pipes and profiles made by extrusion. Tarnoform may be machined on all typical machines, but the following factors should be taken into consideration:

- Lower stiffness in comparison with metals requires supports for thin-walled parts in order to avoid deflection during machining.
- Lower thermal conductivity and lower melting point in comparison with metals requires suitable cooling in order to avoid thermal distortion or even melting during machining.
- In general, Tarnoform should be machined at high tangential velocities and low feeds.

Typical machining parameters are collected below:

Turning:
- tangential velocity 200 - 300 [m/min]
- feed 0.1 - 0.3 mm/rev.
- tool rake angle 0 - 5 [°]
- tool orthogonal clearance angle 5 - 15 [°]

Drilling:
- tangential velocity 50 - 150 [m/min]
- feed 0.1 - 0.3 mm/rev.
- tool rake angle 0 [°]
- drill lip clearance angle 10 - 30 [°]

Milling:
- tangential velocity 1000 [m/min]
- feed 0.3 mm/rev.
- tool rake angle 0 - 5 [°]
- tool orthogonal clearance angle 5 - 15 [°]

Cutting:
- tangential velocity 500 - 1500 [m/min]
- feed 0.1 - 0.3 mm/rev.
- tool rake angle 0 - 5 [°]
- tool orthogonal clearance angle 10 - 30 [°]

5.4. Joining

Parts made of Tarnoform may be joined using following techniques:

- riveting,
- welding,
- bonding with adhesives,
- bolting,
- snap- and press-fits.

RIVETTING

Parts made of Tarnoform may be joined by ultrasound riveting and by riveting with a hot punch. In the former case, the device generating ultrasound waves serves simultaneously as a riveting die forming the head of the rivet. In the latter case, hot riveting is a two-stage process: in the first stage a hot punch, coated with PTFE and heated up to a temperature between 220^{o}C and 230^{o}C, heats up the rivet, which is formed in the second stage by a cold die, at the same time cooling the rivet down to the ambient temperature.

WELDING

Parts made of Tarnoform are usually welded using three of various welding techniques: fusion bonding with a heating platen, friction welding and ultrasonic welding. Induction welding is not possible owing to a low value of dielectric loss factor of Tarnoform.

Fusion bonding with a heating platen is carried out in the following manner: the parts to be joined are heated up by applying a heating element, the shape of which corresponds to the surfaces being bonded. The heating platen, coated with PTFE, is heated up to a temperature between 220^{o}C and 240^{o}C. Next, the heating platen is removed and the parts are pressed against each other. The parts are cooled down to a temperature, which prevents the bond from deformation, by an accidental external disturbance (100-130^{o}C). The heating time for the bonded parts should ensure melting of the bonded part surfaces (5 to 30 s) and depends on the weight and shape of the parts and on the heating capacity of the heating element. In the design of fusion-bonded components changes of dimensions resulting from the loss of material forced out of the bond must be taken into account.

Rotating one (or both) part(s) forced together effect friction welding. Typical process parameters are following:

- peripheral speed 100 - 300 m/min
- pressure 0.2 - 0.5 MPa

Each specific joint should be, however, considered individually and the parameters should be selected experimentally, according to the required properties of the joint (mechanical strength, gas tightness). In case of ultrasonic welding, the selection of the optimum parameters is closely related to the characteristics of the welded parts and it is difficult to provide more detailed recommendations at this point.

ADHESIVE BONDING

The process of adhesive bonding of Tarnoform parts is difficult owing to high chemical resistance of the resin and difficulties in achieving the required adhesion force. It is possible to activate the surface by etching at an increased temperature, with a dilute solution of hydrochloric acid, sulphuric acid or phosphoric acid. Before the surface is usually degreased with a solvent (acetone, ethyl acetate). At present, the following adhesives are available, producing a relatively strong bond (all on basis of cyanoacrylate):

- LOCTITE 406, LOCTITE 406 and LOCTITE 460,
- Uniflex-Technical AI 402.

The optimum solution in terms of the strength of the adhesive bond may be achieved by using substances dissolving Tarnoform, available on the market, i.e. hexafluoroacetone sesquihydrate and hexafluoroisopropanol. Applying a layer of the solvent on both joined surfaces and pressing the surfaces together until the solvent evaporates effects bonding with such solvents. One must, however, remember that these solvents are toxic and when working with them, the recommendations of the manufacturer concerning the ventilation requirements at the workplace should be observed.

TIGHTENING BY SCREWS

Bolted and screwed joints of parts made of Tarnoform should fulfil the following requirements:

- Threaded parts of injection moulded components should be made in risers, should have smooth undercuts and consistent thread pitch in case of co-axial threads.
- In precision parts it is necessary to make threads in the form of metal inserts.
- In case of provisional joints self-tapping screws may be used.

SNAP-FITS

Thanks to high strength and high flexibility of Tarnoform it is possible to make permanent and temporary snap-in and snap-on joints. The main principle utilised in such joints is instantaneous deformation of a pair of elements, forming the joint. The permissible deformation of Tarnoform in such joints is 6% for permanent and 2-3% for unclutchable joints.

5.5. Surface decoration

Tarnoform surface may be decorated by the following methods:

- silk-screen printing,
- pad printing,
- hot stamping,
- painting,
- metallization,
- laser marking.

In the majority of surface decoration techniques, preconditioning of the plastic surface is necessary. Such procedure is usually made by etching with acid solutions (similarly as in case of adhesive bonding, see section 5.4).

PRINTING AND STAMPING

The processes of silk-screen printing and stamping are conducted using conventional machines and paints - the paint sticks well to properly prepared surfaces. In case of hot stamping, the characteristics of the plastic must be taken into account and process parameters must be adapted to the narrow melting point range and relatively high hardness of the products made of Tarnoform. The following parameters are proposed as the starting point:

- stamp pressure 0.35 - 0.55 MPa,
- stamp temperature 185°C,
- penetration time 0.1 - 2 s.

The optimum set of parameters should be determined experimentally.

PAINTING

Parts made of Tarnoform may be painted using typical paints and lacquers (nitrocellulose, polyurethane, acrylic, epoxide and phenolic lacquers), but the surface must be preconditioned in the manner described above. In order to accelerate the process of drying or curing the coating applied, the parts may be held at a temperature of 145°C, however it is necessary to test the influence of thermal treatment on part dimensions.

METALLIZING
Metallizing, apart from its decorative function, may be also used to form a conductive layer, which is important in electrical applications. In the first stage the surface is etched with acids; in the subsequent stage metallizing is performed by vacuum plating or electroplating - similarly as for ABS resins. The metallic layers usually contain aluminium, chromium, copper, silver and gold.

LASER MARKING
Laser marking is the most modern of surface modification processes. This technique is used mainly in case of considerable variability of the pattern applied (e.g. numbering of subsequent parts) and produces various effects (interaction with plastic - carbonisation or evaporation of the surface layer, reaction with pigments - thermal decolourisation, photochemical reactions). Thus either colour effects may be obtained or the possibility of engraving is provided, being a decoration itself or allowing different paints to be applied selectively. The most commonly used laser types include excimer lasers, gas lasers (based on carbon dioxide) and crystalline lasers (Nd: YAG).

5.6. Recycling

As it was mentioned in section 5, there is a possibility of complete recycling of Tarnoform, but this possibility is limited to uncontaminated Tarnoform waste products (runners, defective mouldings). The charts shown below present changes in the properties of Tarnoform subjected to complete material recycling repeated 10 times.

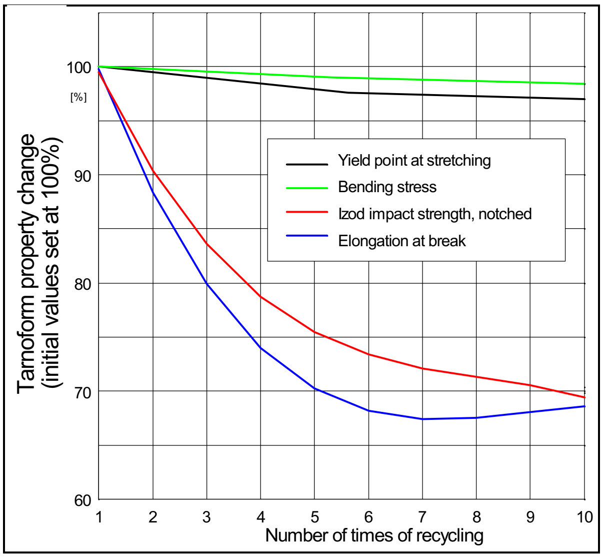

Figure 30 Effect of the number of recycle processes on basic mechanical properties

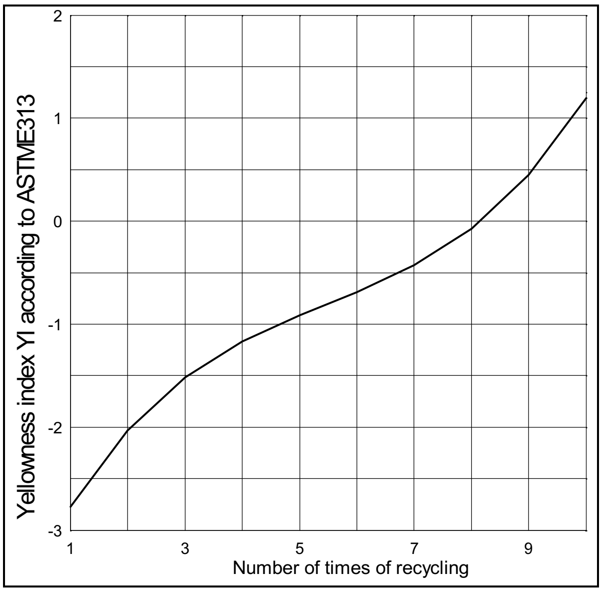

Figure 31 Yellowness degree of Tarnoform recyclate as a function of number of recycles

These data might lead to the conclusion that the observed changes of properties are not critical and permits the application of the closed material cycle in the processing phase in case of unsophisticated products with low quality requirements. However, the effects of the recycled material content and the number of recycles on the important product properties should be evaluated experimentally by moulder.

For other forms of Tarnoform waste (post-production waste and used parts) the only alternative is recycling by combustion (taking advantage of its high heat of combustion), as the recovery of substrates on a commercial scale is only possible in the monomer manufacturing plant. Recycling by combustion requires a sufficient amount of air, as otherwise detrimental products of incomplete combustion (carbon monoxide) and decomposition (mainly formaldehyde) are produced.

6. APPLICATIONS OF TARNOFORM® - EXAMPLES

- gears, cams, plain and ball-bearings
- zips, snap-in fasteners
- lighters bodies
- vertical blinds components
- electric switch sliders
- automotive industry (impellers and casings of blowers; door handles, switch levers for lights, indicators and ventilation/heating system; mirror housings and fasteners; sun-roof parts, window motion systems; Bowden cables casings; fuel supply system components)
- bodies and impellers of pumps for corrosive media and sewage
- hydraulic and pneumatic fittings (pipe connectors, valves, taps)

Resins and plastics products offer:

Resins:

TARNAMID®	Polyamide 6	PA6
TARNOFORM®	Acetal copolymer	POM
TARFLEN® S	Poly(tetrafluoroethylene) suspension	PTFE
TARFLEN® D	Poly(tetrafluoroethylene) dispersion	PTFE
FLUOTAR® DP	Fluorinated elastomer – vinylidene fluoride/perfluoropropylene copolymer	FPM –VDF/PFP
FLUOTAR® TP	Fluorinated elastomer – terpolymer vinylidene fluoride/perfluoropropylene/ /tetrafluoroethylene	FPM – VDF/PFP/TFE

Plastics semi-finished goods:

TARFLEN® S – rods, plates, pipes, tubular bars,
TARNAMID® B– rods, plates, tubular bars
TARNOFORM® C– rods, plates, tubular bars

Plastics goods:

TARFLEN® S – sealings, demisters, bellows, sealing tapes,
TARFLEN® D – sealing cords, tubes, insulating mates

Tubes:	polyamide 11 i 12 –	automotive air braking and fuel lines, pressure tubes
	polyamide 6 –	bowden casings, pressure tubes
	polyethylene LDPE –	pneumatical control tubes, pressure tubes

Meat industry packaging – polyamide casings:

STANDARD Ż	/PA6/
NYLFLEX	/PA66/
NYLFLEX 12	/PA12/

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