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One factor having an effect on greater utilization of plastics in machine-
building is the introduction of new brands of plastics with better strength
and thermal properties.

Among plastics which can be used most widely in machinebuilding, one
should distinguish reinforced plastics, especially plastics reinforced with
glass and carbon fiber, as well as new brands of plastics which are resistant
to high temperatures, such as polysulfone (PSU), which is resistant to temper-
atures up to 150°C, and acrylic polysulfone (PAS), which is resistant to temper-
atures up to 260°C. The strength properties of reinforced plastics are 2-4 times
greater compared with those of an unreinforced plastic.

Characterization of Selected Structural Plastics

Selected strength and thermal properties of structural plastics manufactured
in Poland are presented in Fig. 1 [1-10].

From Fig. 1 it follows that the tensile strength of some polyester plastics
reinforced with glass fiber is greater than the tensile strength of nonferrous
metals and some grades of steel. The following plastics are also characterized
by high tensile strength:
-- glass-fiber-reinforced polyamide with 25% and 35% glass fiber additive (Itamid 25 and Itamid 35);

-- glass-fiber-reinforced polycarbonate (Bistan AS);

-- glass-fiber-reinforced polyformaldehyde (polytrioxane) (Tarnoform S);

-- glass-fiber-reinforced ethylene polytetraphthalate (Elit-25).

Currently, research on the development of new polymers is oriented toward improving the properties of known polymers and developing composite materials from polymers, reinforcing fillers, or mixtures of various polymers.

Polymers displaying liquid crystal properties in the fused state are very promising. Some copolyester composites display liquid crystal properties in the fused state. Besides a high content of aromatic rings, these polymers can be easily molded in view of the capacity for orientation in the melt. Polymers in which sequences of monomers built from long, flat, and relatively stiff particles constitute liquid crystal melts. Large quantities of aromatic groups can be introduced in such a polymer without increasing the viscosity of the melt and molding difficulties associated with the latter.

Thanks to the liquid crystal character of the melt, polymers in the solid state are oriented to a great degree. Along the axis parallel to the orientation direction of the particles, their mechanical properties can exceed the mechanical properties of typical glass-fiber-reinforced thermoplastics.

It is considered that polymers displaying liquid crystal properties in the fused state may constitute the first step in solving the problem of obtaining thermoplastics with advantageous characteristics, which can be easily molded. Such polymers are representatives of the second generation of structural plastics [11].

In the next few years, the utilization of plastics reinforced with carbon or glass fibers will increase considerably. Originally these materials were used
Fig. 1. Comparison of some properties of plastics and metals:
A. tensile strength  B. longitudinal modulus of elasticity
C. thermal conductivity  D. coefficient of linear expansion
E. continuous utilization factor

Key: a. Elit-25 (polytetraphthalate reinforced with glass fiber)
b. (reinforced with glass fiber) c. Polypropylene  d. Polyvinylchloride (hard)
e. polycarbonate f. glass-fiber-reinforced polycarbonate
g. polyamide+glass fiber h. phenoplasts  i. aminoplasts
j. glass-fiber-reinforced polyesters  k. copper alloys  l. aluminum alloys
m. steel  n. tensile strength  o. longitudinal modulus of elasticity
p. thermal conductivity  q. coefficient of thermal expansion
r. continuous utilization factor
exclusively in astronautics and aviation; currently, they are being applied widely in the motor vehicle, chemical, electrical engineering, and other industries.

Carbon and graphite fibers are characterized by high strength properties, low specific gravity and coefficient of friction, and ideal resistance to aggressive media. Among these advantages, one should also include the small thermal expansion factor and high electrical and thermal conductivity. On the other hand, their serious shortcoming is the weak bonding with polymers, which gives rise to the low shear strength \( R_t = 14-28 \text{ MPa} \). The shear strength can be considerably increased by modifying the surface of the fibers by means of oxidation or application of special preparations or whiskers.

Epoxide polyester and phenol resins and polyamides are usually reinforced with carbon or graphite fibers.

Carbon-fiber-reinforced plastics compared with glass-fiber-reinforced plastics are characterized by greater tensile strength and flexural strength, a higher modulus of longitudinal elasticity, however, by lower impact strength.

The former are also characterized by smaller thermal expansion and molding shrinkage, which is equal to one-half the shrinkage of graphite-reinforced plastics, and about one-fifth the shrinkage of unreinforced plastics. The thermal conductivity of these plastics is two times greater than that of glass-fiber-reinforced plastics.

Effect of Temperature, Aging, and Heat Treatment of Plastics on Changes in Their Properties

Temperature has a significant effect on changes in the strength properties. Fig. 2 shows the change in the fatigue of polyamides with a change in the utilization temperature \([12]\). The decrease in fatigue strength \( Z_{go} \) of polyamides with increasing temperature is very large. The latter follows from the fact that the resultant cohesive force whose components represent the strengths of the principal and secondary bonds depends on the temperature. In the fatigue decohesion, in which temperature is the parameter, the following factors have an effect on the change in the properties:
-- crystalline phase content and its distribution in the cross-section of a specimen;

-- physical and mechanical properties, in particular, of the upper layer;

-- state of internal stresses and their relaxation rate at various temperatures;

-- content of monomers, small-particle fractions, and moisture;

-- activity of free, aggressive radicals in secondary chemical reactions, in particular, cross-linking and oxidation;

-- decrease in stiffness and increase in deformations of specimen;

-- filler content (for example, glass fiber).

The effect of aging on the strength properties of plastics has not been solved adequately. Aging investigations of domestically manufactured plastics must contribute to a more advantageous utilization of the latter in industry and to the development of plastics which are more resistant to aging.

Reference [12] discusses the results of investigations of the aging time of domestically manufactured polyamides on the fatigue strength $Z_{go}$ (Fig. 3).

The rate of fatigue strength changes can be subdivided into two periods: the first period, up to 3 years, and the second period, from 3 to 5 years. The decrease in $Z_{go}$ in the first period with respect to Itamids is about 25% and in the second period, the decrease is negligible. Water absorbed from the atmosphere, causing changes in the structure of the plastic, has a fundamental effect on the decrease in fatigue strength.

The advantageous effect of heat treatment (thermal stabilization) on the strength of plastics has been ascertained on the basis of various tests. Heat treatment is usually conducted in oil at maximum plastics recrystallization
Fig. 2. Effect of temperature on variation in fatigue strength of polyamides:

Key: a. Fatigue strength  b. Temperature

Fig. 3. Effect of natural aging time on fatigue strength of polyamides:

Key: a. Fatigue strength  b. Aging time, measured in years  c. Temperature  d. Frequency  e. Base \( N_g = 10^7 \) cycles

Temperatures. Heat treatment parameters of selected plastics are presented in the table [13].

The presented plastics can be subjected to normalizing, annealing, hardening, drawing, or other special heat treatment. Fig. 4 presents as an example a diagram of the course of polyamide annealing.
Heat Treatment Parameters and Increase in Tensile Strength Caused by Heat Treatment for Some Plastics [13]

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Heat treatment medium</th>
<th>Heat treatment parameters: temperature, °C/soaking time, h</th>
<th>Tensile strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyamide</td>
<td>olej wrzącym</td>
<td>130/3</td>
<td>57,0 ± 22,8</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>olej wrzącym</td>
<td>95/100</td>
<td>40,0 ± 25,0</td>
</tr>
<tr>
<td>Polyformaldehyde</td>
<td>szycąmek</td>
<td>90/2</td>
<td>40,0 ± 25,0</td>
</tr>
<tr>
<td>Poliester</td>
<td>szycąmek</td>
<td>76/2</td>
<td>57,3 ± 27,5</td>
</tr>
<tr>
<td>Poliester</td>
<td>powietrze</td>
<td>120/6</td>
<td>63,0 ± 23,0</td>
</tr>
</tbody>
</table>


Column b: 1. spindle oil  2. spindle oil  3. crystalline  4. glycerine  5. air

**Fig. 4.** Diagram of course of polyamide annealing: I. heating in water  II. soaking in water  III. cooling in water to 20°C (heating rate 0.89°C per min, cooling rate 0.58°C per min) [13]

Key: a. Time  b. Temperature
LITERATURE


Machine Tool Department, Institute of Machinebuilding Technology, Czestochowa Institute of Technology
POLYMERIZATION MOLDING OF POLYAMIDE STRUCTURAL ELEMENTS

Leszek Ciesielski, doctor of engineering

Traditional methods for molding polyamide products (i.e., mainly injection molding) limit their mass to several or 11 to 19 kg. This is a consequence of the existing typical molding machines. Frequently, however, it is required to obtain elements with a considerably greater mass. In addition, for example, in small-series production, machining turns out to be more advantageous than preparation of an expensive injection mold.

In such cases, pressureless die casting technology in simple and relatively cheap molds is indispensable. This technology (in a typical design) is limited to thermosetting plastics (epoxy, polyester resins) and does not allow one to utilize fine structural thermoplastics, for example, polyamides. This problem has been solved by developing a casting process using activated anion polymerization of caprolactam. This method makes it possible to obtain products with a great mass (even several hundred kilograms) and advantageous properties (see Table).

The simple production process technology (which makes it possible to conduct polymerization almost in all plants) and the availability of materials deserve particular emphasis.
Properties of Polyamide Castings Produced by the Method of Activated Anion Polymerization of Caprolactam (Basic Version of Process)

<table>
<thead>
<tr>
<th>Wymienioną a</th>
<th>Numa b</th>
<th>Wymienioną c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zawartość amoniaku, %</td>
<td>PN/C-88033</td>
<td>9</td>
</tr>
<tr>
<td>Twardość mączkowa, Pa</td>
<td>PN/C-88030</td>
<td>65,3-116</td>
</tr>
<tr>
<td>Ciśnienie wulkanizacji, N/m²</td>
<td>PN/C-88035</td>
<td>(11,16-11,20)10²</td>
</tr>
<tr>
<td>Temperatura miedziowy we Vm</td>
<td>PN/C-88034</td>
<td>680</td>
</tr>
<tr>
<td>Uderzenność bez korku, J/m²</td>
<td>PN/C-88039</td>
<td>29,24-60,010²</td>
</tr>
<tr>
<td>Uderzenność z korku, J/m²</td>
<td>PN/C-88029</td>
<td>nie pęka</td>
</tr>
<tr>
<td>Współczynnik sprężystości pręcia</td>
<td>PN/C-88051</td>
<td>62,1-10³</td>
</tr>
<tr>
<td>Współczynnik sprężystości próżniowej, Pa</td>
<td>PN/C-88034</td>
<td>600,7-10²</td>
</tr>
<tr>
<td>Współczynnik wierza wg Amsler</td>
<td>PN/M-90005</td>
<td>0,35</td>
</tr>
<tr>
<td>Źródło podania formowania, %</td>
<td>PN/M-90005</td>
<td>2,5</td>
</tr>
</tbody>
</table>


Anion Polymerization of Caprolactam

The polymerization reaction of epsilon-caprolactam depends on opening the ring and formation of an amide bond that is characteristic for polyamides. This change takes place for pure and dry caprolactam in an inert gas atmosphere at a temperature exceeding 520°K after about 200 h. The polymerization time is shortened by adding small quantities of additives initiating polymerization, which, depending on the initiator, proceeds as hydrolytic or ionic polymerization (anion or cation polymerization) [1].

Typical anion polymerization initiators are alkali metals (sodium, potassium, their hydrides and hydroxides). Water is a strong inhibitor of a polyreaction initiated in this manner [2]. Even trace amounts can make it impossible to carry out the process. However, some water content in caprolactam is permissible if bis-(methoxyethoxy)aluminum-sodium hydroxide is used as the initiator. The "drying" properties of the latter simplify considerably the process by eliminating laborious drying of caprolactam [3,4].
Polymerization takes place sufficiently fast only at a temperature of about 500°K. Addition of small quantities of activating compounds before polymerization accelerates the process and reduces its temperature. N-acetylocaprolactam and isocyanate are the most important compounds of this type. Application of these activators makes it possible to conduct the process at a temperature of about 400°K within 10 to 20 min.

The process of anion polymerization of caprolactam (Fig. 1) leading to the formation of a polyamide casting consists of the following operations:

- melting of monomer (caprolactam) at a 350°K temperature;
- addition of reaction initiator — about 380°K;
- addition of reaction activator — about 400°K;
- polymerization (about 430°K) combined with solidification of polymer and its crystallization;
- drawing out casting.

Depending on the shape of the casting, this process is subdivided into three versions [4,5]: free casting, centrifugal casting, and rotary casting.

![Fig. 1. Schematic diagram of polyamide polymerization casting process:
I. stationary process realized on industrial scale
II. simplified version of process
Key: a. Caprolactam  b. Initiator  c. Activator
d. Energy  e. Autoclave  f. Mold  g. Product
h. Activator  i. Molds  j. Products](image)

During production process tests (in the basic version of the process), the following input products were used:
--- caprolactam. This monomer is produced by the Nitrogen Plants in Tarnow. Top grade caprolactam with moisture content not exceeding 0.035% must be used in the process. A higher moisture content (from 0.03 to 0.07% as envisioned by the standard) prolongs the polymerization time, increases consumption of the reaction initiator and activator, and also worsens the properties of the product;

--- synhydrid. This is the commercial name of the bis-aluminum-sodium hydride constituting the initiator of the reaction. It is supplied in the form of a 65% solution in toluene by the Syntesia Company in Kolin, Czechoslovakia. This compound is sensitive to the effect of light and humidity; therefore, it must be stored in air-tight, dark packages and in dry rooms;

--- izocyn T-100 or T-80. This compound is the activator of the reaction. The activation effect of both compounds is identical. The compound is manufactured by the ZACHEM Chemical Plants in Bydgoszcz. Izocyn is sensitive to the effect of humidity and it must be stored in leakproof packing in a room at a temperature of about 300°K.

The process of anion polymerization of caprolactam carried out according to the production process technology presented above, in principle, does not give rise to side products. Only small quantities of hydrogen and glycol ethylene ether come out.

During the molding process, caprolactam vapors may be emitted, which must be drawn off. These vapors [6] are not toxic; nevertheless, they have an irritating effect.

Free Casting

Polymerization during this process takes place in a heated mold without pressure. In principle, only a heated vessel (mold, temperature to about 450°K), batch meters for measuring reagents, a mixer, and a temperature regulator are needed to realize the process. Individual castings can already be produced with such equipment. In the case of large-scale production, introduction of a separate set of autoclaves for melting the monomers and pouring the prepared reaction mixture in the molds placed below the autoclave facilitates the process (Fig. 2).
Molds used in this technology can be metallic, glass, or ceramic sealed molds. Application of separating agents on the surface is not required. The size of the obtained casting depends, in principle, only on the size of the made mold. This means that there are no restrictions of the plasticizing capacity or maximum molding pressure type, etc.

The minimum thicknesses of block castings obtained in this manner (during experimental production in the Plastics Plant of Poznan Institute of Technology) were 0.01-0.015 m, for a surface of about 1 m².

![Fig. 2. Schematic diagram of set of equipment for free casting of polyamide:](image)

I. autoclave for preparation of reaction mixture  
II. mold  
III. temperature regulator  
1. cover  
2. heating jacket  
3. heat insulation  
4. temperature measuring sensor  
5. draining valve  
6. melted caprolactam  
7. heating jacket  
8. insulation  
9. temperature measuring sensor  
10. casting undergoing polymerization

Rotary Casting

Rotary casting (Fig. 3) depends on inducing caprolactam polymerization in an enclosed mold set in rotary motion about two perpendicular axes. It has been established experimentally that the difference in rotation must be about 5 rpm and the rotary speed, about 0.6 m/s.

The reaction mixture undergoing polymerization swirls the walls of the mold and while building up layers forms the walls of the product. Elements of the
walls of the product. Elements of the enclosed container type with arbitrarily regulated wall thickness are obtained in this manner. Thickening at the corners, improving their strength properties, is characteristic of these containers.

This method requires equipment ensuring motion about the perpendicular axis, continuous regulation of the rotary speed, which is independent of both axes, heating of the rotating mold, and temperature regulation. Production efficiency in the case of the two molds mentioned above is 8 to 10 containers per shift from one piece of equipment. Finally, besides the mold for the caprolactam reaction mixture, at least a simplest installation for preparation of the mixture is also required.

Heating of the mold is realized in an enclosed chamber by infrared rays or without a chamber by electric resistance heaters wound on the mold. The production cycle for obtaining the product in this process consists of the following operations:

-- melting and, if necessary, drying of caprolactam with nitrogen;
-- heating to temperature at which initiator is introduced, and addition of initiator;
-- heating to temperature at which activator is introduced, addition of activator with simultaneous pouring in mold at defined temperature;
-- polymerization in rotating mold;
-- removal of casting and preparation of mold for next operation.

The drying, melting, and additional heating of caprolactam takes place outside the mold (in separate heated vessel) and overlaps in time with the operation of cooling, removing the casting, and preparing the mold for the next operation. Since polymerization conditions are more difficult than during free casting (intense contact of mixture with air as a result of swirling of the mold during its rotary motion), the strength properties of the product are 20% lower.
Centrifugal Casting

In this version of the process, polymerization takes place in a heated swirling mold. It has been established that a uniform distribution of wall thickness and a smooth inner surface is obtained at a linear velocity of the mold of about 0.6 m/s.

The reaction mixture undergoing polymerization uniformly distributed on the walls of the molds, subjected to the effect of pressure (depending on the diameter and the rotary velocity), stabilizes into a product with properties which are somewhat better than those obtained during free casting.

This method makes it possible to obtain pipe sections with much larger diameters than in traditional extrusion (even much larger than 1 m) with arbitrarily regulated wall thicknesses.

Here, the only constraints are due only to the structure or adaptation of the equipment inducing the swirling motion of the mold. However, the equipment is simple and its production is not beyond the capabilities of even small plants.

The centrifugal casting process proceeds as follows: melted caprolactam with the added catalytic polymerization system (prepared by preceding methods) is poured in the mold with temperature of about 440°C; the mold is set in rotary motion for about 10 min; and after 15 min, the casting can be removed. Shrinkage of the product, using this method, is about 3.5%.

Possible Applications

The production process technology described above can be used for molding large structural elements, slide elements, and also containers. For example, they are suitable for slidelinings, which are resistant to shock (even at relatively low temperatures), pulleys, semifinished products used in the production of large individual gears or pulleys, transporting elements (conveying worms) (Fig. 5), gripping elements, and feed elements in production lines, insulating elements, containers for aggressive liquids (for example, pesticides and herbicides), positive-gauge pressure and partial-vacuum tanks, and also for pipes with very high mechanical properties.
Fig. 3. Schematic diagram of equipment for rotary casting of polyamide:
1. mold 2. heating jacket 3. insulation
4. separation plane of mold 5. gear imparting swirling motion to mold 6. reaction mixture
7. collectors 8. rotary frame 9, 10. motors with continuous regulation of revolutions
11. temperature measuring sensor 12. heating energy input 13. temperature regulation signal down lead

Fig. 4. Schematic diagram of centrifugal casting of polyamide:
1. motor with continuous regulation of revolutions 2. collector 3. heating jacket 4. insulation
5. mold 6. reaction mixture undergoing polymerization 7. opening for introduction of reaction mixture 8. temperature regulation
Fig. 5. Examples of polyamide castings

LITERATURE


3. Team study "Wytwarzanie elementow konstrukcyjnych wielkowymiarowych na drodze polimeryzacji kaprolaktamu" [Production of Large-Scale Elements by Way of Polymerization of Caprolactam], Report of Institute of Machinebuilding Engineering, Poznan Institute of Technology, 1977.

