SOME RESULTS OF TESTING OF MECHANICAL PROPERTIES
AND POLYAMIDE MODIFICATION

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1. Introduction

Polyamide is a thermoplastic of partially crystalline structure. It has found a wide application as the material for machine elements. As most of plastics, it exhibits distinctive rheological properties, ageing and self-heating under cycling loads. Its fatigue strength relative to tensile stress is lower than in metals. In the course of fatigue process, strength characteristics change (Mazurkiewicz (1986))—see Fig. 1.

![Fig. 1. The scheme for polyamide PA-6 of the modulus E, ultimate tensile stress R, elongation \( \varepsilon_r \), and temperature \( \Delta T \) as a function of fatigue strength employing \( n_r = \frac{n}{N(\sigma)} \), where \( n \)-the number of transferred load cycles, \( N(\sigma) \)-fatigue strength under a certain level of stress \( \sigma \), in bending test.]

Its yielding point depends on temperature and the deformation rate (Mazurkiewicz(1975))—see Fig. 2. Polyamide absorbs up to 10 per cent of moisture from its surroundings. This exerts a significant impact on the change of its properties.
Fig. 2 Yielding point versus temperature and deformation rate for polyamide PA-6.

Fig. 3 Change of strength characteristics for polyamide Tarlon X-4 (a), after 23 years (b).

Also ageing taking place under normal climatic conditions over a period of time changes the strength characteristics — see Fig. 3.
2. The possibilities of estimation of fatigue properties

Despite of the differences in the mechanism of destruction in immediate and fatigue tests, some correlations can be observed between them. It seems that it is not merely empirical but also of physical nature.

Fig. 4 Dependencies of the parameters estimating fatigue strength as a function of $T_0-T_9$.

$T_0$ - temperature of experiment

$T_9$ - glass temperature

- Polyamide

- an other thermoplastics.

The parameters estimating fatigue strength are: relative fatigue strength $K_m=Z_9/R_m$, coefficient of fatigue resistance $K_r=Z_9/\sigma_r$, fatigue coefficient of deformation $K_e=c_k/c_k^*$

where:

$R_m$ - tensile strength,

$\sigma_r$ - true ultimate tensile stress,

$c$ - deformation at the breaking point,

$c^*$ - ultimate fatigue deformation corresponding to the fatigue strength $Z_9$. 

The best correlation effects have been obtained for the fatigue resistance coefficient $K$ - see Fig. 4.

Also by testing the changes of relaxing properties in the course of fatigue process the degree of the process can be established. The changes are associated with the successive processes of structure deformation. It results in the initial increase of rigidity (the process of strengthening) and the decrease (the process of weakening) (Milewski and Mazurkiewicz (1988)) - see Fig. 5.

![Graph showing the change of relaxation times curves as a function of fatigue strength](image)

**Fig. 5** The change of relaxation times curves as a function of fatigue strength; 1 - for origin specimen; 2 - for specimen tested after the incubation of microcracks (induction period) Material polyamide PA-6, $T=295$ K, $\sigma=25$ MPa, symmetric bending test.

Two opposite processes of strengthening and weakening the structure take place in the process of fatigue. Their intensity changes in the time and depends on the structure of polymer. The destruction is the result of relaxation processes lagging behind the tensile changes.

3. Some methods of polymer modification

Under modification of plastics, such physical or chemical processes are understood for which the resulting plastics undergo the changes of structure improving certain of their utilization properties. Semi-crystalline thermoplastics are particularly easy modified. It is also feasible to change both the degree of crystallization as well as the dimen-
sion of shape of molecular structures. What is more, in some modifications substances acting as lubricant are introduced in such a way that they retard the process of thermo-oxidation. Some examples of changes of the mechanical properties of polyamide shown as the function of time and the concentration of quinol can be found in Fig.6.

![Fig.6 Change of the mechanical properties for polyamide PA-6 as a function of time stabilization τ: 1-5 %, 2-25 % hydrochinon solution. N - fatigue strength, Rm - tension stress, εr - elongation.](image)

From physical modifications the mechanical working has been selected (burnishing with rolls) which resulted in the changes of the surface layer (Mazurkiewicz (1987)). The results have been presented in Fig.7.

![Fig.7 Fatigue strength — and tensile strength ... as a function of pressure in burnishing for polyamide T-27 (1) and T-B (2).](image)
The positive effects of the mechanical working consists in the fact that in the conditions of locally increased temperature and pressure crystalline phase α undergoes polymorphic change into γ which is more elastic, hence better from the standpoint of fatigue properties. Also secondary crystallization and formation of structure of line spherolites takes place, there.

In turn, the thermal working by means of long thermal treatment increases the quantity of phase α, improving tribological properties.

Also ion implantation can be classified among the physical methods of modification. The implantation of ionized atoms of nitrogen N₂, a few hundred μm deep, causes selective and durable changes within the surface layer. General improvement of friction coefficient and hardness have been observed. High energy ions diminishes the grains of crystallites and significantly improves the order of structure. It is also very likely that the new free radicals may cause the reticulation effect. This type of modification calls for further research to explain physics of the occurring phenomena.

Chemical modification has been accomplished by treatment of the surface layer with quinol and potassium iodide (Mazurkiewicz et al. (1989)). Quinol does not penetrate compactness and rigidity. It renders difficult displacement of structure elements under high stresses. In the result, the values of temporary strength and deformations drop. However, fatigue strength is considerably improved (Mazurkiewicz (1988)).

Potassium iodide penetrates spherolites, weakening physical bondage and plastifying structure. This makes the displacement of structure elements easier and it improves the possibilities of its orientation under high values of stresses. In effect temporary strength and deformations increase, yet to the decreasing of fatigue strength. Polyamide structure with weakened bonds and diminutive spherolites proves to be improper under cyclic loads.

Modification significantly improves tribological properties. The results of lowering the friction coefficient of modified polyamide treated by burnishing and diffusion stabilization with potassium iodide have been shown in Fig.8. Modification, best suited for Itamide (PA-6 + WS), proved
Fig. 8 Dependencies of friction coefficient on pressure $p$ for non modified polyamide (PA), modified by burnishing (B-1) and diffusion stabilization with KJ (J2).

to be moderate stabilization by quinol.

Extensive modification should be applied in those cases when it is justified by technological aspects. Quinol introduced into the whole volume of a sample (in treatment) affects the supramolecular organization plasticizing its structure in "inter-crystalline" way. This reduced the friction coefficient by approx. 20-30%. However by the application of potassium iodine side by side with quinol reduced the wear by 13%.

Another method of modification consisted in introducing into the volume of polymer silicon oil together with pore-making additive. This resulted in very positive tribological effects. Oil settling in the micropores made a specific composite form which in terms of effects was comparable to the beneficial effects of very expensive modification with PTFE powder.

4. Conclusions

Mechanical properties of polymers depends considerably on the degree of the physical state of their structure. The changes taking place within
structure trigger the changes of some mechanical properties. Those effects can be used as descriptors of the advancement of the fatigue process. The condition of structure may be changed in the way of application of certain external agents, the changes being positive with regard to particular mechanical properties. Relatively simple technological treatment allows to obtain considerable economic effects.

References


Summary

WYNIKI BADAŃ PEWNYCH WŁASNOŚCI MECHANICZNYCH I SPOSOBÓW MODYFIKACJI POLIAMIDU

Własności mechaniczne poliamidu zmieniają się w wyniku starzenia i oddziaływania fizyko-chemicznych czynników. Ich zmiana w trakcie procesu zmęczenia może być deskryptorem stopnia zaawansowania tego procesu. Moddyfikacja struktury powoduje poprawę jego właściwości mechanicznych.