

Ana PILIPOVIĆ, Ivan STOJANOVIĆ, Vesna ALAR

University of Zagreb

Faculty of Mechanical Engineering and Naval Architecture, Zagreb

## Impact of ageing on mechanical properties of polyamide castings

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### Summary

With longer exposure to atmospheric impacts the products lose their properties and the life cycle decreases. Consequently, there is need to determine the material properties after a longer exposure to atmospheric impacts. The paper has studied the impact of natural and laboratory ageing on the mechanical properties of the reaction cast polyamide 6 (PA6) with addition of oil. The tensile properties, hardness and toughness were studied. Since polyamide 6 with addition of oil was selected, the friction factor and the abrasion wear have been studied as well. In determining the required properties of castings from PA6 it should be taken into account that they are the result of the reaction primary shaping, which means that first there is primary shaping of product, and then primary structuring at molecular and higher levels.

### KEYWORDS:

abrasion wear  
ageing  
friction factor  
hardness  
impact strength  
polyamide 6 + oil  
reaction casting  
tensile properties

### KLJUČNE RIJEČI:

abrazijsko trošenje  
faktor trenja  
poliamid 6 + ulje  
rastezna svojstva  
reakcijsko lijevanje  
starenje  
tvrdoća  
žilavost

### Utjecaj starenja na mehanička svojstva poliamidnih odljevaka

#### Sažetak

Proizvodima koji su dulje vrijeme izloženi atmosferskim utjecajima opadaju svojstva i skraćuje se životni vijek. Stoga je potrebno odrediti njihova svojstva nakon duljeg izlaganja tim utjecajima. U radu je ispitan utjecaj prirodnog i laboratorijskog starenja na mehanička svojstva reakcijski lijevanog poliamida 6 (PA6) s dodatkom ulja. Određena su rastezna svojstva, tvrdoća i žilavost. S obzirom na to da je izabran PA6

s dodatkom ulja, određivan je i faktor trenja te je ispitivano abrazijsko trošenje. Pri određivanju potrebnih svojstava proizvoda odljevaka od PA6 treba uzeti u obzir da su oni rezultat reakcijskog praoblikovanja, što znači da se najprije praoblikuje tvorevina, a zatim se prastrukturira na molekularnoj i višim razinama.

### Introduction

In testing various types of polymers and composites quite a lot of consideration was shown for mechanical and tribological properties, which depend on the crystallinity, molecular mass, microstructure, water absorption, etc. Many types of polyamides, e.g. PA6, PA66, PA46, PA11, PA12 are applied when a moderate friction factor and high resistance to abrasion wear are required. In testing polyamides for abrasion wear Rajesh et al.<sup>1</sup> found out high impact of wear on different mechanical properties: ductility, formation of cracks, critical extension, module of elasticity, speed of crack propagation, and time to fracture of the test specimen. The combination of different additives to the parent material (polyamide) reduces the abrasion wear.<sup>1</sup>

Addition of oil reduces the friction factor and wear, but a significant change occurs after a longer time of sliding. The impact of the lubricant contents and the contact stress on the friction factor for cast polyamide was studied by De Baets et al.<sup>2</sup>, but the sliding time was limited to 10 minutes at a speed of 0.06 m/s and stress of 0.083 MPa. The test showed a low friction factor (0.08–0.12), but without taking into consideration different sliding times and temperatures. Lubrication depends on the quantity of oil in the polymeric material and its movement at the place of friction.<sup>2</sup>

Many studies have been carried out in order to understand the mechanism of the basic processes of radiation effects on polymers. Chemical changes by UV exposure result in a complex set of processes involving a combined effect of UV and oxygen, in which formation of a complex mixture of products is observed. Bond dissociation is initiated by the absorption of UV radiation, resulting in chain scission and/or crosslinking; subsequent reactions with oxygen result in the formation of functional groups such as carbonyl (C=O), carboxyl (COOH), or peroxide (O-O). The effects of UV exposure, or photo-degradation, are usually confined to the top few microns of the surface (50 - 100 microns). The effect of UV radiation is also compounded by the action of temperature, moisture, wind-borne abrasives, freeze-thaw and other environmental components. All UV light irradiation studies reported are mostly about the effect of long-time interval exposures in the range from one hour to a thousand hours.<sup>3</sup>

Most of the commercial organic-based polymers undergo photolytic and photo-oxidative reactions during exposure to solar UV radiation. The polymers contain chromophoric groups, such as carbon-carbon double bonds (C=C) and carbonyl groups (C=O), which are capable of absorbing UV energy and are involved in the photoreactions that result in the degradation of the polymer. These chromophoric groups can either exist within the regular structure of the polymer, or exist as a result of impurities present, or through thermal processing of the materials involved. This is the situation with the polyolefins, polyethylene and polypropylene, which are severely affected by the presence of UV radiation.<sup>4</sup>

Degradation effects that occur within polymer-based materials range from discolouration on the polymer surface, which affects the aesthetic appeal of the material, through to extensive mechanical damage to the polymers. The colour changes mainly occur as consequence of chemical changes within the polymer structure, resulting in yellowing or darkening of the polymer. Another adverse effect of weathering is the synergistic combination of water and UV radiation, which can lead to erosion and fading of the surface of certain types of polymers. This phenomenon is known as chalking.<sup>4</sup>

The impact of accelerated (laboratory) ageing of pure PA6 was tested by Kiliaris et al.<sup>5</sup> at temperatures of 120°C and 150°C in intervals of 35 days (0, 7, 14, 21, 28 and 35 days). After the exposure the test specimens were left in the dryer for 24 hours and after that their mechanical properties were studied. Before ageing, the test specimens had been dried for 4 hours at a temperature of 80°C. The results of mechanical properties have shown that at higher temperatures (150°C) all the mechanical properties are lower in comparison to the temperature of 120°C. At both temperature values of all the tested mechanical properties (tensile strength, module of elasticity and tensile strength at break) are significantly reduced with longer time of ageing.<sup>5</sup>

## Reaction primary shaping

### Reaction manufacture of polymeric products

Primary shaping is the production of solid bodies out of shapeless substances by creating connections between particles and creation of primary structure. Three groups of primary shaping may be distinguished:<sup>6-8</sup>

- primary shaping with chemical creation of material;
- primary shaping with transformation of materials from solutions or dispersions;
- primary shaping of melts.

Casting of PA6 is an example of chemical (reaction) primary shaping.<sup>6-10</sup>

In reaction production of polymeric products, the process and manufacturing technology are combined into production technology. The material input into the procedures of reaction primary shaping (primary shaping with chemical transformation of materials) can consist of the basic substances: monomer (e.g.  $\epsilon$ -caprolactam in reaction casting of mould made of polyamide 6 (PA6) or methyl-methacrylate), reaction suitable components (e.g. polyole and polyisocyanate, i.e. ingredients required in reaction injection moulding of polyurethane foam products), pre-polymer (e.g. direct moulding of thermoset resins (e.g. phenol-formaldehyde (PF)) and polymeric matter (e.g. rubber). Since the basic components of materials do not have the necessary performance characteristics of the products, the material input in the process consists also of the necessary additions (Figure 1).<sup>6-8,11</sup>

In cyclic procedures of reaction primary shaping, the mould serves as the batch reactor in which the polymeric materials and the polymeric product are produced concurrently during the cycle<sup>6,7</sup>. In this way one can produce: thermosets, elastomers and partly thermoplastics.

In case of reaction primary shaping the function of change is as follows:<sup>6</sup>

$$F_{MPR} = F_{MI,po} + F_{MP,psm} + F_{MP,psn} + F_{MP,rsm} \quad (1)$$

where:  $F_{MI,po}$  – function of primary shaping,  $F_{MP,psm}$  – function of primary structuring at molecule level,  $F_{MP,psn}$  – function of primary structuring at super-molecular and higher levels,  $F_{MP,rsm}$  – function of restructuring at molecular level.

The cyclic reaction primary shaping is the name for a group of procedures during which the substances of the required shear viscosity are fed (e.g. injection moulding) into the mould cavity of the given temperature

(primary shaping). The product is solidified by *polymerization* and/or *crosslinking* and/or *foaming* and it is then suitable for demoulding (structuring).<sup>7</sup>

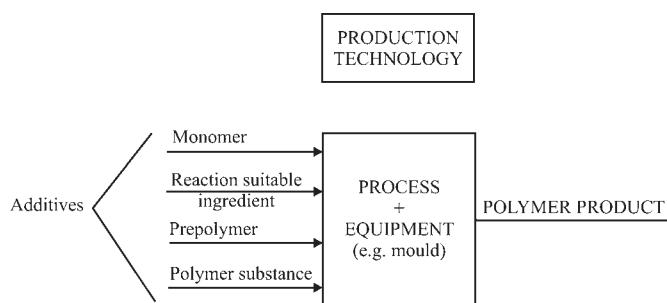


FIGURE 1 – Reaction production of polymeric products – thermosets, elastomers and partly thermoplastics<sup>6-8, 11</sup>

### Reactions of polymerization during reaction primary shaping of polyamide 6<sup>6-10</sup>

During reaction primary shaping in the mould as batch reactor the most common is the chain mass polymerization. Anionic polymerization by aid of chain initiators and catalysts and ion chain polymerization in reaction casting of  $\epsilon$ -caprolactam and additives is also possible for the production of PA6 mouldings.

In the mould as reactor by polyaddition and polycondensation, apart from the basic components, the presence of only those components that remain in the product is also possible, so that the only possible procedure is mass polymerization.

During polymerization and crosslinking heat is generated and it leads to reaction and thermal shrinkage of reactants, which needs to be considered in mould design.

In the production of products made of PA6 two basic procedures are known: casting and injection moulding. In both cases one starts from  $\epsilon$ -caprolactam, the reaction is activated anionically, lasts for a relatively short time and occurs at a relatively low temperature.

The basic characteristic of the reaction is the mutual independence of individual reaction level and release of simple low-molecular by-products (e.g. water), which are in gaseous state at the reaction temperature and which in case of completely closed moulds result in the occurrence of bubbles in the product. Therefore, mould design and managing of the primary shaping process require the possibility of degassing (i.e. opening of the mould in case of compression moulding or degassing channels in transfer and injection moulding).

### Production of Polyamide 6 (PA6) moulding<sup>9,10</sup>

In reaction production the most important is the area of the production of thermoset and elastomer products with two major exceptions: manufacture of cast polyamide 6 (PA6) products by anion polymerization of  $\epsilon$ -caprolactam and poly(methyl methacrylate) (PMMA) by chain polymerization of methyl-methacrylate.

In casting of  $\epsilon$ -caprolactam the reaction primary shaping is related to the creation of polymeric material by polymerization reaction and with the making of polymeric product by crystallization. Reaction casting of  $\epsilon$ -caprolactam proceeds in the following phases:

- preparation of reaction compound;
- feeding compound into the mould;
- progress of polymerization and crystallization.

The monomer is molten in the nitrogen stream in separate containers A and B (Figure 2) up to a temperature set in compliance with the mould

size (125–132°C). After the compound is fed into the pre-heated mould (150–155°C), where the exothermal reaction takes place, the melt temperature has to be maintained below the melting point of the polymer. Catalyst is added into one container, and initiator into the other. The compound is stable for a longer period of time, and it is possible to prepare an amount for several manufacturing cycles.

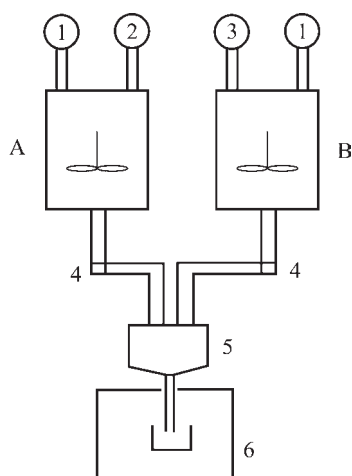


FIGURE 2 – Reaction casting of ε-caprolactam: 1 – nitrogen supply, 2 – catalyst supply, 3 – initiator supply, A, B – container with lactam compound and mixer, 4 – compound dosage, 5 – mixing of compound, 6 – furnace with pre-heated mould<sup>9</sup>

During compound preparation and while adding the ingredients the following conditions have to be met:

- maximal purity of all the reactants that enter the melt composition;
- oxygen from the atmosphere and humidity have to be completely eliminated;
- precise measuring of the amount of all reactants, in order to keep the given concentration of the catalyst and initiator;
- precise measuring of the melt temperature.

Immediately prior to feeding, the compounds are mixed, and then fed into the pre-heated mould. The mould is pre-heated in the furnace or directly by electrical heaters. In gravity casting the compound is supplied to the mould bottom in order to squeeze out the air from the mould cavity.

**Experimental part**

**Material of test specimens**

The testing was done on polyamide 6 with the addition of fine-dispersed oil droplets (PA 6 + oil), under the brand name Novilon-oilon, manufactured by Akripol, Slovenia. This is a self-lubricating material used in the industry usually to produce bearings, sliding segments of the universal joints, sliding sleeves, plates, gears, guides, chain tighteners, annular spacers, etc. Already in the initial phase of the production, microscopically tiny oil droplets are added to the polyamide, i.e. oil becomes the component of the entire material structure. The oil embedded in this manner cannot evaporate nor leak from the material regardless of the conditions of application and regardless of how much of the material is removed during machining.<sup>12</sup>

**Preparation and ageing of the test specimens**

Using the PA6 reaction casting procedure the plates of dimensions 500 · 1,000 mm were obtained, and the test specimens were cut out of them in order to determine the mechanical properties. For tensile strength at break, elongation at break, tensile modulus and abrasion wear four test

specimens were used and for impact strength five test specimens were used for all series (before ageing, after 20 and 42 days of laboratory ageing and natural ageing). For hardness, three test specimens with five measurements for each test specimen were done and for friction factor three pairs of test specimens were used.

The test specimens were exposed to accelerated ageing for 20 days and 42 days (i.e. approximately 500 h and 1,000 h) at the laboratory in a UV chamber Erichsen without wetting of the samples according to standard HRN EN ISO 4892: 2004 - 2.<sup>13</sup> The temperature in the chamber was 65°C with radiation of 550 W/m<sup>2</sup>.

For comparison, the naturally aged test specimens were taken, that were kept at the laboratory for 20 years (i.e. 7,300 days = 175 200 h) at a temperature of 16–20°C (depending on the season) and relative air humidity of 62%.

**Determining of tensile properties**

The tensile properties have been determined according to standard HRN EN ISO 527: 2012.<sup>14</sup> There are two basic types of test specimens, but for easier cutting from the plates, the flat test specimen was selected with the dimensions presented in Figure 3.

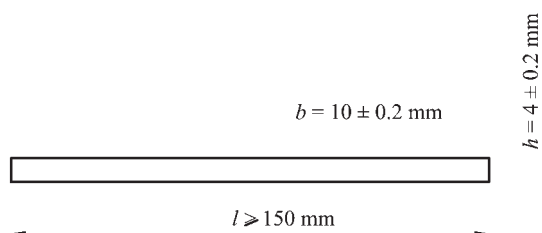


FIGURE 3 – Shape of tensile test specimen<sup>14</sup>

Tensile strength at break is calculated according to equation:<sup>14</sup>

$$R_p = \frac{F_p}{A_0} \tag{2}$$

where:  $R_p$ , MPa – tensile strength at break,  $F_p$ , N – breaking force,  $A_0$ , mm<sup>2</sup> – surface of specimen.

Elongation at break is calculated according to equation:<sup>14</sup>

$$\varepsilon_p = \frac{\Delta L_0}{L_0} \tag{3}$$

where:  $\varepsilon_p$ , % – elongation at break,  $\Delta L_0$ , mm – increase in the specimen length between the gauge marks,  $L_0$ , mm – gauge length of the test specimen.

Tensile modulus is calculated according to equation:<sup>14</sup>

$$E = \frac{R_2 - R_1}{\varepsilon_2 - \varepsilon_1} \tag{4}$$

where:  $E$ , MPa – tensile modulus,  $R_2$  and  $R_1$  – tensile stresses,  $\varepsilon_2 = 0.0025$  – strain,  $\varepsilon_1 = 0.0005$  – strain.

Tensile properties are determined on a tensile-testing machine of the measuring range from 0–2,400 N at the temperature of 23°C. In order to determine the tensile properties the test specimen is clamped into the tensile-testing machine jaws and extended by force  $F$ , at velocity  $v = 7$  mm/min.

The tensile properties (Figures 4, 5 and 6) were compared after the laboratory and natural ageing. The test specimens in the laboratory conditions were exposed to UV light for 20 days and 42 days, as specified by the standard.

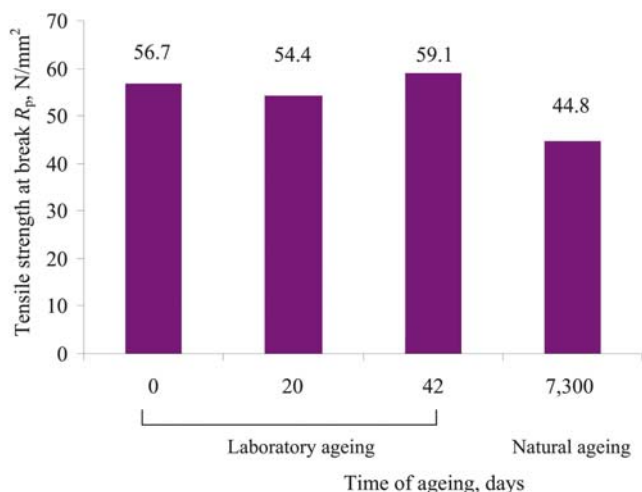


FIGURE 4 – Comparison of tensile strength at break after laboratory and natural ageing

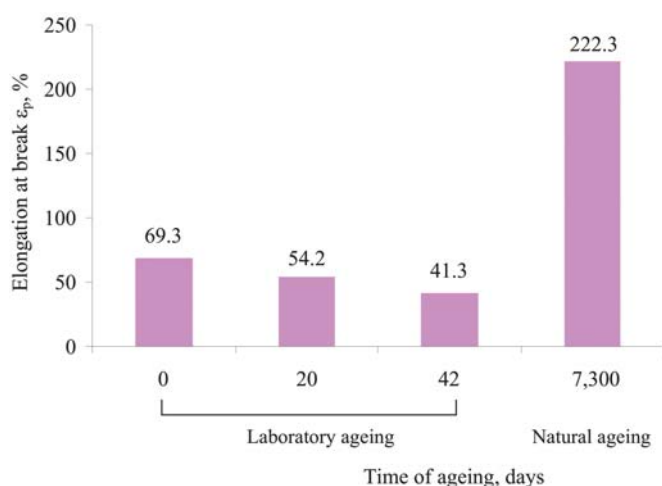


FIGURE 5 – Comparison of elongation at break after laboratory and natural ageing

By comparing the tensile properties one may conclude that over time there comes to a decline of properties. One can also notice that tensile strength at break and tensile modulus after 42 days of UV light exposure increase as compared to the time of 20 days. It is interesting to note that in case of tensile elongation at break by natural ageing there is an increase by more than 2.5 times. Such results can be explained by the fact that the test specimens had been stored over the 20 years at ambient temperature,

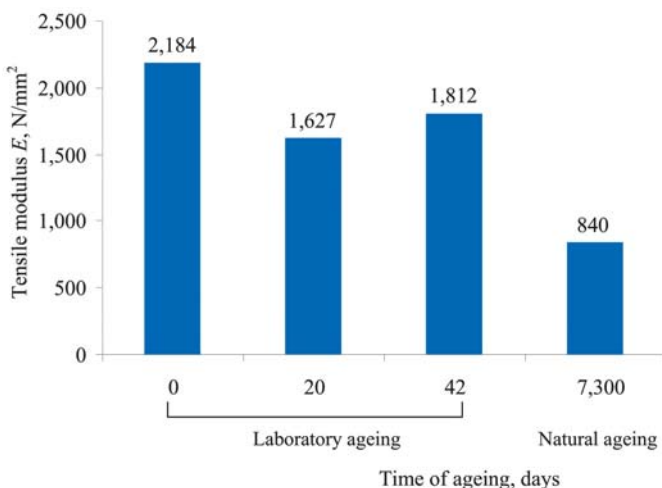


FIGURE 6 – Comparison of tensile modulus after laboratory and natural ageing

with relatively small changes in air humidity, and without the impact of weather conditions.

By comparing the obtained results with the data of polyamide 6 with oil guaranteed by the manufacturer one can notice that the tensile modulus is significantly different. According to the manufacturer’s data the tensile modulus should be within the interval  $E = 3,300 \text{ N/mm}^2 - 3,650 \text{ N/mm}^2$ ; however, the tests showed that it is significantly lower and amounts to  $E = 2,184 \text{ N/mm}^2$ .

**Determining of hardness**

The hardness was determined according to the standard HRN EN ISO 868:2008 – hardness according to Shore D by indentation of durometer after  $15 \pm 1 \text{ s}$  on five places on each test specimen. The measuring was done on the external and internal surface of the test specimens cut out from the plate.<sup>15</sup>

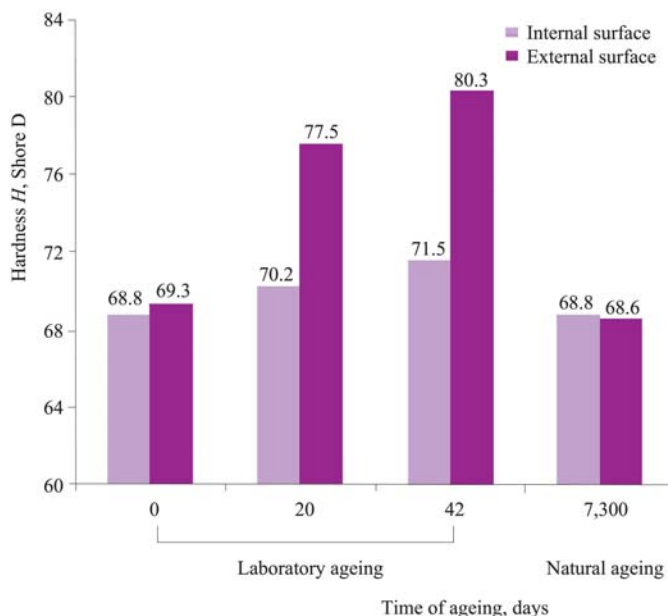


FIGURE 7 – Comparison of hardness after laboratory and natural ageing

Figure 7 shows the comparison of hardness on the internal and external surface in case of laboratory and natural ageing.

It may be noticed in Figure 7 that the hardness on the external surface after accelerated ageing is higher by approximately 10 Shore D compared to the internal surface. Before being exposed to UV light and after natural ageing the hardness is equal both on the internal and external surface. The exposure of test specimens made of PA6 to UV light results in an increase of hardness on the external surface and it is only then, that it reaches the hardness specified by the manufacturer (76-80 Shore D).

**Determining of impact strength**

Toughness is determined by the Charpy method according to the HRN EN ISO 179:2005 standard. The span of the supports on the device is  $L = 62^{+0.5}_{-0} \text{ mm}$ . The test specimen is made with a C type notch (Figure 8).<sup>16</sup>

Impact strength of test specimen with notch is calculated according to the equation:<sup>16</sup>

$$a_{CN} = \frac{E_C}{h \cdot b_N} \tag{5}$$

where:  $a_{CN}$ , kJ/m<sup>2</sup> – Charpy impact strength (notched test specimen),  $E_C$ , J – energy absorbed by breaking the test specimen,  $h$ , mm – thickness,  $b_N$ , mm – remaining width.

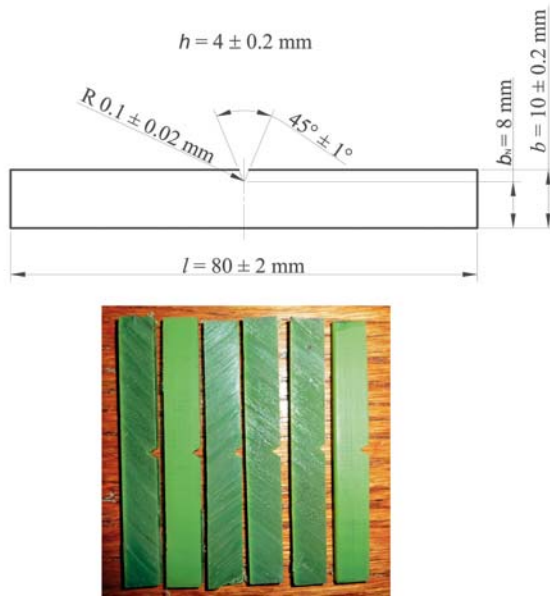


FIGURE 8 – Shape of test specimen for testing impact strength<sup>14</sup>

Due to UV light exposure the impact strength falls, but the slight increase between 20 days and 42 days of UV ageing is unexplainable. As is the case in tensile strength at break, impact strength increases with natural ageing, and the reason remains the same; the test specimens had been stored for 20 years at room temperature (Figure 9).

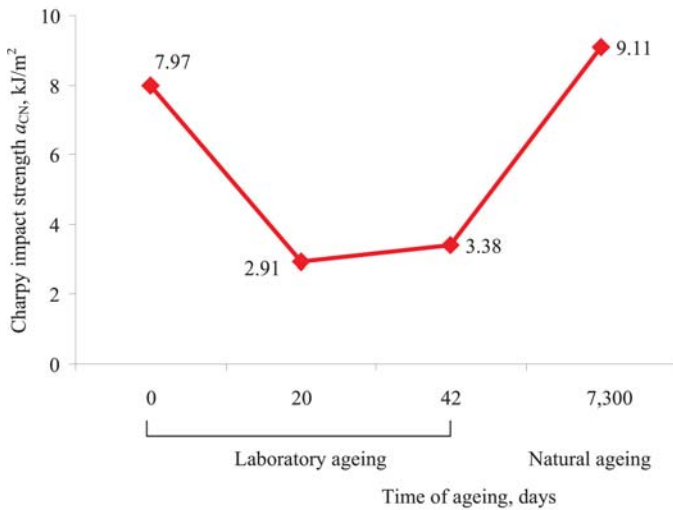


FIGURE 9 – Comparison of impact strength after laboratory and natural ageing

**Determining of friction factor**

The law of dry friction of two bodies in contact says that the force necessary to create friction is proportional to the normal force on the surface of these two bodies (Equation 6). Adhesion is determined so that one material slides over the other and this is how the friction factor is obtained. The tribological properties are affected by the heat generated due to friction, deformation, and other environmental impacts. For the needs of this study, the friction couple of both test specimens was made of the same material, PA6 + oil (Figure 10). The dimensions of the test couple are 16·8·8 mm and the internal diameter  $\phi$  30 mm with wall thickness of 4 mm.

The shift in a certain time period (0 s, 15 s, 30 s, 45 s, 60 s, etc.) is read on the device for determining the friction factor, and using the diagram the shift – friction force (Figure 11), which has been obtained by the

approximating curve for a certain initial mass, i.e. force and using its respective shift the friction force is read, and from the equation for the friction force the friction factor  $\mu$  is calculated.

$$F_{tr} = \mu \cdot F_N \tag{6}$$

where:  $F_{tr}$ , N – frictional force,  $\mu$  –friction factor,  $F_N$ , N – force on the surface.



FIGURE 10 – Determining of friction factor

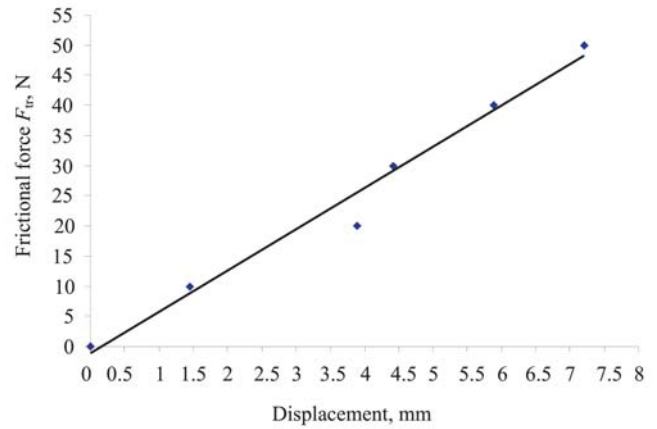


FIGURE 11 – Diagram displacement – frictional force

The testing was carried out with the weight of  $m = 2$  kg and the force on the base  $F_N = 100$  N.

Figure 12 presents the calculated values of the friction factor  $\mu$  in certain time period from 0 s to 120 s.

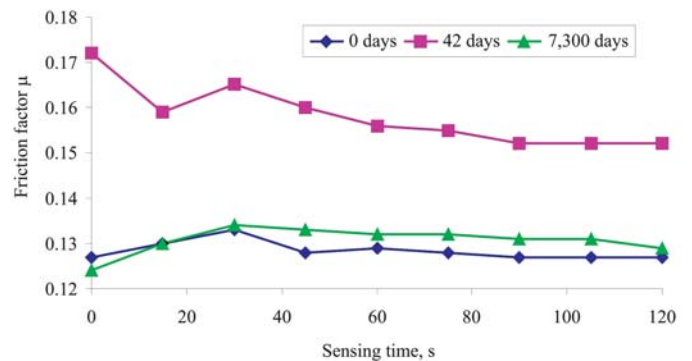


FIGURE 12 – Friction factor in dependence on the time of reading

The friction factor becomes constant after 80 s. At the beginning a small increase can be seen, but these differences are negligibly small (Figure 12). The manufacturer specifies the friction factor of  $\mu = 0.109$ , but the tests have shown that it is higher. Before ageing and natural ageing it is

approximately 0.13. UV light increases the friction factor up to approximately 0.16 (Figure 13). During the determination of the friction factor the mass of the test specimens has remained unchanged.

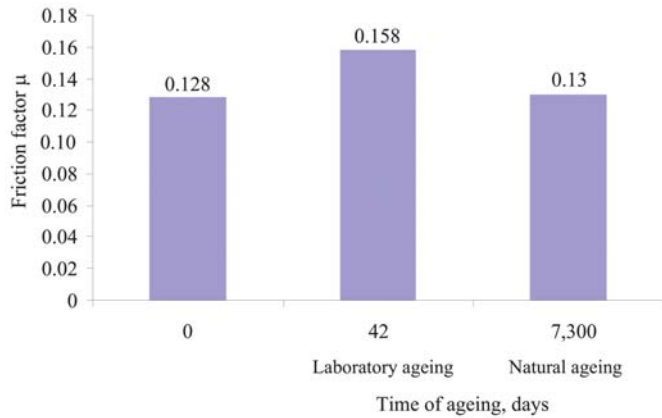


FIGURE 13 – Friction factor in dependence on the ageing time

Apart from UV radiation, the friction properties of the friction couple are also affected by the shear strength, module of elasticity, form and size of surface irregularities, heat and friction, as well as humidity and impurities of the friction surfaces.

**Determining of abrasion wear**

Friction of all polymeric materials is related to wear. Abrasion wear is determined according to the ASTM G 65 standard, i.e. the mass loss is determined. The smaller the mass loss, the smaller the wear is. The wear is calculated according to the equation:

$$AT = \frac{m_2 - m_1}{m_1} \cdot 100 \quad (7)$$

where:  $AT$  – abrasion wear,  $m_2$ , g – mass after testing,  $m_1$ , g – initial mass.

On the device the sand falls gravitationally between the test specimen of dimensions 90·25·15 mm and the wheel, thus wearing off a certain surface layer of the test body (Figure 14). After a certain number of revolutions the wheel stops, and the loss of mass is measured on the test specimen. In the performed test a force of 45 N was applied and it was empirically determined to stop the wheel after 100 revolutions.

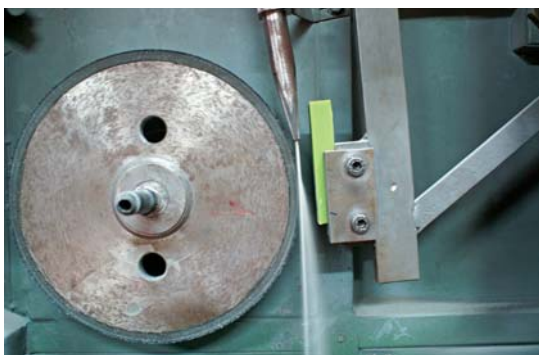


FIGURE 14 – Abrasion wear testing

The obtained results before ageing, after 20 days, 42 days and 7,300 days are presented in Figure 15.

The diagram in Figure 15 shows that there is a negligible loss of mass of the test specimen of PA6 + oil. After 42 days the loss of mass is somewhat greater ( $AT = 0.0775\%$ ) compared to the loss of mass without exposure to UV light ( $AT = 0.0651\%$ ). Still, the lowest loss of mass is on the test specimen after natural ageing. It may be concluded that even after a longer period of ageing the wear is negligible ( $AT = 0.0284\%$ ), which is at the

same time related to the material hardness and oil particles which have been added to the material. This enhances the material quality and at the same time the product quality as well.

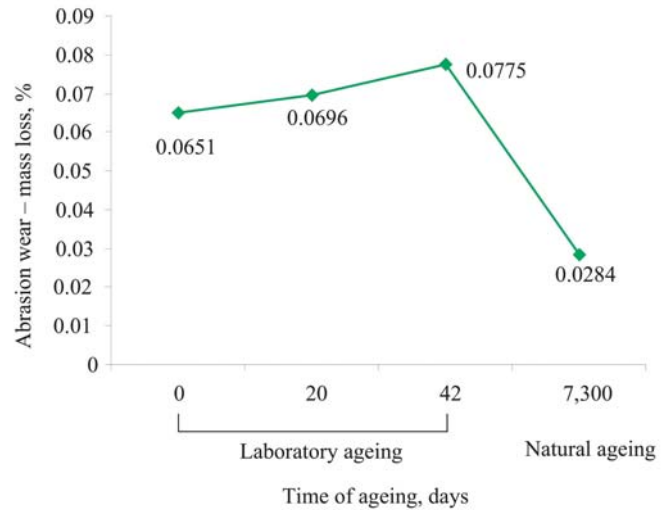


FIGURE 15 – Comparison of abrasion wear after laboratory and natural ageing

**Determination of glass transition temperature**

The glass transition temperature  $T_g$  determination was carried out on a DMA device *Mettler Toledo Triton* with parameters:

- heating rate 2°C/min;
- frequency 1 Hz;
- temperature interval: from room temperature to 160°C;
- displacement amplitude 5  $\mu\text{m}$ .

$T_g$  is determined as peak value of  $\text{tg}\delta$  curves measured by DMA (Figure 16).

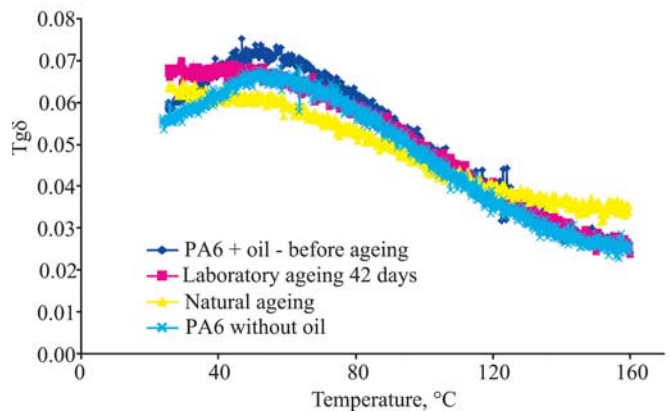


FIGURE 16 – Comparison of  $\text{tg}\delta$  after laboratory and natural ageing and for PA6 without oil

The obtained results suggest (Figure 17) that PA6 with and without oil have roughly the same value of the glass transition temperature  $T_g$ . It can be also noticed that the ageing time has a significant impact on the change of the glass transition temperature. The  $T_g$  value of 42 days in laboratory-aged specimens is reduced by almost 16%, while for 7,300-day natural aged specimens  $T_g$  value decreases by 40%.

**Statistical analysis of results**

For all the properties an analysis was made on how laboratory and natural ageing affect them (Tables from 1 to 6), using average  $\bar{x}$  and estimated interval of expectations  $d$  according to the method originally described in literature<sup>17</sup> (taken from<sup>18</sup>). To estimate the intervals of expectation for tensile strength at break, elongation at break, tensile modulus and abrasion

wear four test specimens, for hardness of the external surface three test specimens and for impact strength five test specimens were used.

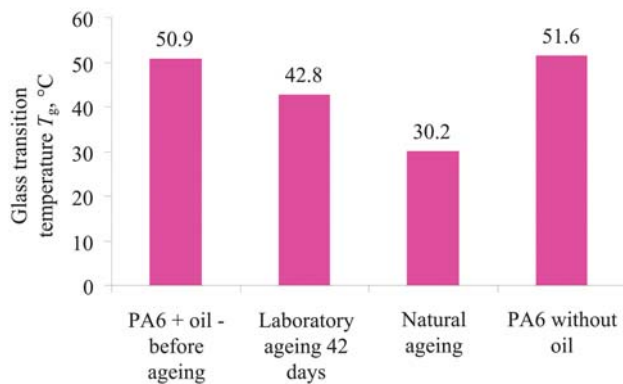


FIGURE 17 – Comparison of  $T_g$  after laboratory and natural ageing and for PA6 without oil

The results of the analysis show that the duration of laboratory ageing (20 or 42 days) did not affect the value of tensile strength at break as well as elongation at break (Tables 1 and 2). There are no differences between the series of laboratory-aged (20 and 42 days) and non-aged specimens. There were significant mean series

differences between the laboratory-aged and the naturally aged specimens.

The results of the analysis of tensile modulus (Table 3) show that there are no differences between the two series of laboratory-aged (20 and 42 days) test specimens. There was a significant mean difference between the series of laboratory-aged, non-aged and naturally aged test specimens.

As seen from Table 4, there are no differences between laboratory (20 and 42 days) and natural ageing for the hardness of the external surface, but there are significant mean differences between the series of laboratory ageing of 20 and 42 days.

The results of the analysis (Table 5) show that the duration of laboratory ageing (20 or 42 days) did not affect the value of the impact strength. There are no differences between the non-aged and aged specimens for 7,300 days. The difference between the laboratory-aged specimens and those non-aged and naturally aged ones shows to be mean significant.

The results of the analysis (Table 6) show that there are no differences between the series of laboratory-aged (20 and 42 days) and non-aged specimens, but there are significant mean differences with the naturally aged specimens.

The variation part in the analysis for the friction and hardness of the internal surface is not significant and because of that the series does not need to be compared.

TABLE 1 – Analysis of the influence of laboratory and natural ageing on tensile strength at break

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	54.4	59.1	56.7	44.8
Laboratory 20 days	54.4	+		+	
Laboratory 42 days	59.1		+	+	
Before ageing	56.7	+	+	+	
Natural ageing	44.8				+
$\bar{x} - d$		51.2	56.9	53.5	41.4
$\bar{x} + d$		57.5	62.9	59.8	47.8

TABLE 2 – Analysis of the influence of laboratory and natural ageing on elongation at break

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	54.2	41.3	69.3	222.3
Laboratory 20 days	54.2	+	+	+	
Laboratory 42 days	41.3	+	+	+	
Before ageing	69.3	+	+	+	
Natural ageing	222.3				+
$\bar{x} - d$		18.4	6.2	34.2	200.7
$\bar{x} + d$		88.6	76.3	104.3	270.8

TABLE 3 – Analysis of the influence of laboratory and natural ageing on tensile modulus

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	1,627	1,812	2,184	840
Laboratory 20 days	1,627	+	+		
Laboratory 42 days	1,812		+		
Before ageing	2,184			+	
Natural ageing	840				+
$\bar{x} - d$		1,342	1,598	1,918	626
$\bar{x} + d$		1,770	2,026	2,345	1,053

TABLE 4 – Analysis of the influence of laboratory and natural ageing on the hardness of the external surface

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	77.5	80.3	69.3	68.6
Laboratory 20 days	77.5	+			
Laboratory 42 days	80.3		+		
Before ageing	69.3			+	+
Natural ageing	68.6			+	+
$\bar{x} - d$		75.5	78.2	67.3	66.6
$\bar{x} + d$		79.6	82.3	71.4	70.6

TABLE 5 – Analysis of the influence of laboratory and natural ageing on impact strength

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	2.91	3.38	7.97	9.11
Laboratory 20 days	2.91	+	+		
Laboratory 42 days	3.38	+	+		
Before ageing	7.97			+	+
Natural ageing	9.11			+	+
$\bar{x} - d$		1.36	2.08	6.66	7.8
$\bar{x} + d$		3.96	4.68	9.26	10.4

TABLE 6 – Analysis of the influence of laboratory and natural ageing on the abrasion wear

Series comparison	Series number	Laboratory 20 days	Laboratory 42 days	Before ageing	Natural ageing
	Average $\bar{x}$	0.0696	0.0775	0.0651	0.0284
Laboratory 20 days	0.0696	+	+	+	
Laboratory 42 days	0.0775	+	+	+	
Before ageing	0.0651	+	+	+	
Natural ageing	0.0284				+
$\bar{x} - d$		0.0546	0.0625	0.0501	0.0134
$\bar{x} + d$		0.0845	0.0925	0.0801	0.0434

## Discussion

In naturally aged polyamide the changes of tensile strength, tensile modulus and elongation at break are as follows: tensile strength is lower by 22.7%, tensile modulus after ageing falls to only 42% of the initial value, whereas elongation at break increases by as much as 164%. This shows that over time there have been significant changes in the structure of the naturally aged polyamide 6.

In addition, PA 6 is a typical example of depolymerisable heterochain polymer and in spite of absence of elevated temperature, during a very long period of time, depolymerisation probably occurs. On the other hand, the continued presence of humidity during a very long period of natural ageing suppresses enthalpy relaxation i.e. the ageing process is therefore retarded.

Previous tests<sup>19</sup> have shown that there is somewhat greater share of crystal areas and those crystallites are more uniform regarding size, which certainly has a positive impact on the properties.

However, UV light in the presence of elevated temperature (650°C) probably induces some breaking of the main chain on the heteroatom position during artificial ageing. Therefore, the tensile strength at break in artificially aged polyamide, even after a longer period of ageing (natural ageing) remains almost unchanged (the difference being + 1%), whereas the tensile modulus (-11%) and elongation at break (-41%) decrease.

Toughness is reduced by half. The exposure of test specimens to UV light results in the increase of hardness on the external surface, whereas the internal surface remains unchanged.

The toughness of the naturally aged PA6 + oil has even risen (+17%). This can be assigned to the long-term exposure to 62% humidity, which positively acts on polyamide toughness. The increasing mobility due to lower  $T_g$  value contributes to that change. The hardness, external and internal, remains almost unchanged.

The wear causes the change in the mass, but there is a significant difference between the natural and artificial ageing of polyamide. Greater loss of mass of the artificially aged polyamide indicates harmful action of UV radiation, although polyamides are not especially sensitive to its action. The increase in the friction factor follows the difference in the loss of mass and it is less pronounced in the naturally aged polyamide. The low increase of the friction factor, in spite of the action of UV radiation, results also from the positive action of oil drops which can be found in the material structure regardless of how much of the material has been removed on the surface. By longer ageing this positive impact is somewhat reduced, but it is still present even after 7,300 days, since the friction factor after such a long period features an increase of as little as 1.5%.

The ageing impacts the glass transition temperature of polyamide 6 + oil decreasing  $T_g$  by 40% in comparison to the initial value before ageing.



## Conclusion

The use of oil in the polyamide is to improve some properties of which the most important is an excellent wear resistance and self-lubrication, making it ideal for manufacturing of bearings.

In equivalent applications, parts made of polyamide with the addition of oil droplets endure five to seven times longer than the same parts made of pure polyamide or polyamide filled with molybdenum disulphide.<sup>12</sup>

The paper deals with the impact of ageing time on the mechanical properties of polyamide 6 obtained by reaction casting with the addition of fine-dispersed oil droplets in order to enhance first of all the friction properties. The comparison has been done between certain properties for the artificially aged PA6 + oil and the same polyamide that has aged naturally by staying in laboratory with no daylight, i.e. without UV radiation with temperature intervals (depending on the season) from 16°C to 20°C and relative humidity of about 62%.

Polyamide products obtained by the casting procedure feature certain advantages over the products obtained by conventional moulding procedures, since they have better structural characteristics. The presence of oil additionally enhances the already good friction properties.

Based on the performed testing it may be concluded that UV radiation has nevertheless dominant impact on the ageing of polyamide 6 + oil.

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## CONTACT

Ana Pilipović, Ph.D.  
University of Zagreb  
Faculty of Mechanical Engineering and Naval Architecture  
Chair for Polymer Processing  
Ivana Lučića 5  
HR-10000 Zagreb, Croatia  
E-mail: ana.pilipovic@fsb.hr