

# Investigation of the influence of natural weathering factors on the properties of polyamide thermoplastic materials

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Resistance of injection pressurized specimens of polyamide 66 with 20% glass fibres and polyamide 12 to natural weathering was investigated. The process of natural outdoor weathering, in two climatically different areas was followed by determining the physical, mechanical and thermal properties of polyamide 66 before and during eight and a half years of exposure and of polyamide 12 before and during three years of exposure. Main factors of natural weathering in the open and the expected material degradation mechanism were described.

*Key words:* thermoplastic materials, polyamide 66 with glass fibres, polyamide 12, natural weathering, influence of atmospheric conditions.

## Introduction

NATURAL weathering as a process comprises all phenomena that lead to the degradation of materials and reduction of the life cycle of construction parts. Weathering, or more precisely degradation, depends on the way and extent to which materials interact with their surroundings.

Results of investigation of the influence of natural weathering meteorological factors on the properties of polyamide 66 with glass fibres and polyamide 12 in the open at two climatically different areas are described.

Climate presents the integration of the types of weather for an observed period within a specific area i.e. climate is a group of atmospheric states over a geographic area in a specified period of time.

The main components of weather i.e. the main meteorological factors, which can cause degradation are sunlight, temperature, water, wind and pollutants.

**Sun** is the main source of energy mostly transformed into thermal energy. Solar spectrum on the Earth's surface consists of ultraviolet light (about 5 % of the overall radiation of wavelength from 200 nm to 400 nm), visible light (45 % of the overall radiation of wavelength from 400 nm to 750 nm) and infrared light (50 % of the overall radiation of wavelength from 750 nm to 4.000 nm).

Temperature of an object in the sunlight (in this case, polyamide specimen) depends on factors such as radiation intensity, wind speed, object's shape and material properties (thermal conductivity and heat capacity). Higher temperature causes faster degradation rate.

**Water** has a negative influence on the polymeric properties of the materials, regardless of the fact that it is in gaseous, liquid or solid state, especially over a long period of time. Water has unique physical characteristics and such a chemical reactivity that it is an important factor in the deterioration process of organic and of course polymeric materials.

**Wind** represents horizontal and vertical movement of air. Wind causes temporary changes of temperature, air moisture and cloudiness and can also transfer thermal energy, water vapour and pollutants and spread them all over the Earth's surface.

**Pollutants** are particles of solid matter, biologically active materials and reactive gases. Particles of solid matter are dust, carbon black, ash, sand and coarser particles made by erosion of wind on the ground furnished by wood fires and volcanic eruptions. Since over 40 % of land surface of the world is defined as moisture-deficient and a further 40 % is seasonally dry, dust must be expected all over the land surface.

Coating of dust can have a number of effects on the material's stability. On one hand, dust traps moisture and hydrolytic degradation process can happen on the material's surface. Dust can also act as a trap for biologically active materials and, in the presence of moisture and warmth, microbiological growth can appear. This phenomenon exists at glass-filled polyamide because considerable erosion of the exposed surface occurs as the polyamide surface layer is carried off. On the remaining fibres, which are above the surface of the material, particles of dust are trapped so hydrolytic process occurs and microbiological growth appears.

On the other hand, dust can protect the material by absorbing a significant amount of solar radiation thus having a dual effect of decreasing the temperature attained by the material and decreasing the extent of photolytic degradation.

The most present volatile pollutants in the atmosphere are sulphur compounds, ammonia, oxides of nitrogen, saturated and unsaturated aliphatic and aromatic hydrocarbons along with their derivatives, carbon monoxide and carbon dioxide and ozone. It is said that the oxides of nitrogen, especially nitrogen dioxide, have a negative effects on the polyamide 66 [1-6].

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### Degradation of materials

Regarding synthetic macromolecules, the term "degradation" is used to denote the changes in physical properties caused by chemical reactions involving bond scission in the backbone of macromolecule and weakening of secondary intermolecular bonds. In linear polymers, among others are polyamides, these chemical reactions lead to reduction in the molecular weight i.e. to diminution of chain length.

Alterations of physical properties are, of course, not caused only by bond scissions in the polymer backbone, but also by very often simultaneously occurring chemical reactions in pendant groups or side chains. With the exception of intermolecular cross-linking, chemical reactions in pendant groups of linear polymers affect the physical properties only to a minor extent relative to reactions in the backbone.

Depending on the cause of the chemical reactions which lead to the changes of physical properties, there are different modes of polymer degradation: chemical, thermal, biological, light induced, mechanical and radiation induced.

It is known that heat ageing of polyamide 66 causes changes of both macro-structural and crystal properties. Changes of characteristics include decreasing of tensile properties and introduction of holes and deposits on the material's surface.

Injection-moulded specimens of polyamide 66 were exposed to high and low temperature. In both cases similar changes (deterioration of material) were observed i.e. the reduction in elongation at break and loss of impact resistance were found.

Heat ageing of aliphatic polyamide brings about microfissures on the surface, which has a negative effect on tensile properties.

At glass fibre polyamide 66, after exposure to tropic warm/wet conditions, changes in the appearance and mechanical characteristics were observed. After a certain period of exposure, dust and microbiological growth were observed.

In terms of accelerated thermal ageing polyamide 66 with 30 % glass-fibres exhibited a 50 % decrease in the ultimate stress [6].

During isothermal ageing of 33 % glass-fibres polyamide 66, an increase of strength was initially observed. This observation indicates a presence of physical ageing. However, at higher temperatures, the effect of isothermal ageing was a significant decrease of the ultimate strength (about 50 %), which indicates a chemical degradation i.e. oxidation of samples [7].

Regardless of the mode of degradation involved, beside bond scission in the back-bone of polymers, weakness of secondary bonds and concurrently cross-linking of chains appeared and essential changes of initial polymer properties appeared [1, 7-11].

A strong inter-relation between various modes of polymer degradation should be emphasized. Depending of the circumstances, different modes of polymer degradation simultaneously occurred.

Typical examples are:

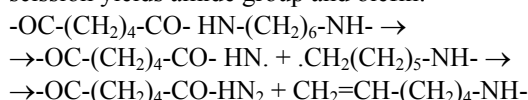
- environmental processes which involve simultaneous action of weathering factors, UV light and oxygen,
- oxidative deterioration of thermoplastic polymer during processing which is based on simultaneous action of heat, mechanical forces and oxygen.

Chemical reactions that lead to degradation of polymeric materials can be single step reactions or chain reactions.

In single-step reaction, the reaction rate is directly proportional to the rate of initiation. There are photochemical reactions where the main-chain bond is ruptured per absorbed photon.

A characteristic feature of the chain reaction is the self-propagation of the process. In other words, the initiation reaction yields products that are themselves capable of undergoing spontaneous reactions with intact molecules. Depolymerization and oxidative degradation processes occur by chain reaction. Sometimes, even low conversion can cause significant changes in physical properties, especially if main-chain scission or cross-linking processes occur in linear polymers, whose physical properties are strongly dependent on the average molecular weight.

It is considered that the carbon-nitrogen bond is weakest in the polyamides and, at elevated temperature, bond scission yields amide group and olefin:



Dehydration process of primary amide group yields formation of water, which can cause hydrolysis of other amide groups to COOH groups. Decarbonisation process of the carbonyl group, at higher temperatures, can cause the formation of carbon dioxide [8].

Depending on the structure of the macromolecules and mode of environmental influence, a random and non-random degradation of polymers occur.

A typical example of a random process is the photolytic main-chain scission. Upon irradiation with light of wavelength from 300 nm to 370 nm, the carbonyl group, present in the polyamide structure, acts as chromophers and, if a polymer sample is thin enough to permit a homogenous distribution of the absorbed energy, main-chain scission occurs in a random manner. Such main-chain scission degradation is induced by the absorption of light, by high energy radiation or via attack by chemical agents.

Non-random main-chain scission has been observed with linear polymers subjected to mechanical forces. In the reactions, the centre portions of the polymer chains are much more likely to undergo main-chain scission than other parts of macromolecules.

### Thermoplastics engineering polymers

Polyamides, polyacetals, polycarbonates, polyphenylene oxides, polysulfones and thermoplastic polyesters are referred to as thermoplastics engineering polymers because they are used for production of stressed parts and often employed as alternatives or replacements for metals in load-bearing applications.

Polyamides are denoted with a number that represents the number of carbon atoms in a monomer.

Polyamides, produced by aminoacids, are denoted by one number (for example, polyamide 12 means that monomer 12-aminoundecane acid, i.e.  $\text{H}_2\text{N}-(\text{CH}_2)_{11}-\text{COOH}$  has twelve C-atoms.).

Polyamide produced by dibasic acids and diamines, are denoted by two numbers (for example, polyamide 66 means that both monomer i.e. hexamethylene diamine  $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$  and adipic acid  $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$  contain six C-atoms).

Polyamide structure consists of extended chains, which are interconnected by hydrogen bonds. Oxygen atoms of carbonyl groups in one chain are always opposite to nitrogen atoms of amide groups in neighbouring chains, as it is shown in Fig. 1 [12]:

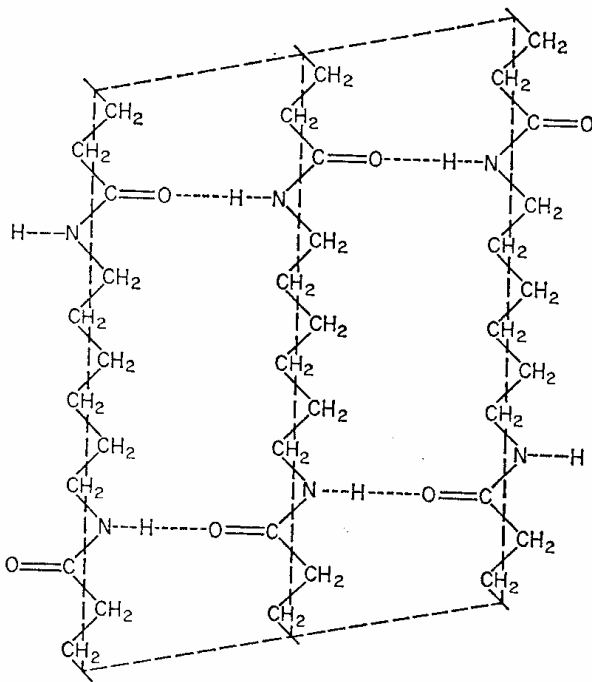


Figure 1. Structure of polyamide 66

Ageing under the influence of water and thermal energy reduces the effectiveness of the interfacial bonds.

Of all polyamide materials, polyamide 66 and polyamide 12 are chosen for investigation of the influence of natural weathering factors in the open in two different climatic areas.

### Experiment

Investigation and properties determination presented in this paper, are planned in such a way as to examine the resistance of polyamide 66 and polyamide 12 to a direct influence of meteorological factors in the continental (location Nikinci) and marine environments ((location Kumbor).

#### Materials

Polyamide 66 and polyamide 12 specimens are produced by injection moulding technology.

Polyamide 66 with 20 % glass fibres was obtained using appropriate quantities of polyamide 66 ULTRAMID A 3K without glass fibres, produced by BASF, and polyamide 66 VERTON RF 700-10 with 50 % glass fibres, produced by ICI. Homogenized mixture of these two materials was dried at the temperature of 105°C in HERAUS LTU 60/60 chamber for 2 hours.

Polyamide 66 specimens were produced by ANKERWERK V 17-65 injection moulding machine with 4 mm diameter nozzle and thermostat Single for constant mould temperature, according to parameters:

Temperature of the cylinder:

- zone I 270°C
- zone II 285°C
- zone III 300°C

- injection speed 1 circle
- injection pressure 15 MPa
- additional pressure 1,5 MPa
- additional pressure time 5 s
- dose 15 mm
- mould temperature 90°C
- cooling time 40 s.

Polyamide 12 VESTAMID 2160, produced by HULS, was dried at the temperature of 105°C in KS Belišće chamber for 2 hours. Polyamide 12 specimens were produced by KS BELMATIK 600/230 injection moulding machine with 4 mm diameter nozzle and thermostat TG 75-150 ILLIFE for constant mould temperature, according to parameters:

Temperature of the cylinders:

- zone I 228°C
- zone II 230°C
- zone III 232°C
- injection speed "small"
- injection pressure 12 MPa
- additional pressure 5 MPa
- additional pressure time 8 s
- dose 20 mm
- mould temperature 50°C
- cooling time 45 s.

Polyamide 66 and polyamide 12 specimens, exposed to outdoor natural weathering in two different climatic areas (continental location Nikinci and marine location Kumbor), were fixed to carrier equipment which is at an angle of 45° facing the Equator. It is considered that this is an optimum angle of exposure in temperate latitude for the whole year. In this case (Nikinci 44'51" N and Kumbor 42'26" N), the statement that the angle of exposure of specimens to natural weathering factors should be equal to the latitude of the site where specimens are exposed, was almost fulfilled.

The angle of exposure also depends on the natural weathering factors, whose influence is the subject of the research. If it is of particular interest to examine the influence of temperature, the angle of exposure should be 0°, because in this position the specimen reaches maximum temperature.

If it is of particular interest to research the influence of ultraviolet radiation (wavelength <400 nm), it is stated that the optimum angle of exposure should be 45° [1].

For the determination of tensile strength ( $\sigma_m$ ), elongation at break ( $\varepsilon_1$ ), impact resistance without notch ( $a_n$ ), density ( $\rho$ ), Vicat softening temperature (VT) and water absorption ( $a_a$ ) polyamide 66 specimens were exposed to the outdoor natural weathering at Nikinci and Kumbor during 8.5 years i.e. 102 months, and polyamide 12 specimens at the same locations during 3 years i.e. 36 months.

Based on the changes of the determined properties, the resistance of these two polyamide materials was estimated.

Tensile strength and elongation at break were examined using "dog bone" shaped 4 mm thick specimens of overall length of 150 mm with width and length of narrow parallel-sided portion of 60 mm and 10 mm, respectively, and gauge length of 50 mm. Impact resistance without notch was determined using 50 mm x 6 mm x 4 mm specimens. Vicat softening temperature, density and water absorption were

examined using 50 mm x 50 mm x 4 mm specimens.

Tensile strength and elongation at break were examined on ZWICK dynamometer at 100 mm/min cross-head speed. Impact resistance without notch was determined on CEAST impact tester and speed of falling hammer was 2.9 m/s. Vicat softening temperature was determined on HERAEUS chamber, KP/M type with the rate of temperature rising of 50°C/h. Density and water absorption were examined on METTLER analytical balance.

## Results and discussion

Physical, mechanical and thermal properties of polyamide 66 before and during eight and a half years of non-stressed outdoor natural weathering in both climatic areas (Nikinci and Kumbor) are shown in Table 1

Physical, mechanical and thermal properties of polyamide 12 before and during three years of non-stressed outdoor natural weathering in both climatic areas (Nikinci and Kumbor) are shown in Table 2.

Physical, mechanical and thermal properties of polyamide 66 and polyamide 12 were determined according to the appropriate JUS standards.

**Table 1.** Results of investigation of polyamide 66 before and during eight and half years of exposure to natural weathering

Time of exposure to weathering (months)	PHYSICAL, MECHANICAL and THERMAL CHARACTERISTICS					
	$\sigma_m$ (MPa)		$a_n$ (kJ/m <sup>2</sup> )		VT (°C)	$a_a$ (mg/100cm <sup>2</sup> )
	$\bar{X}$	s	$\bar{X}$	s		
<b>0</b>	<b>117,1</b>	<b>7,2</b>	<b>25,3</b>	<b>2,9</b>	<b>255</b>	<b>350</b>
<b>Continental climate (Nikinci)</b>						
6	121,2	4,2	26,1	1,8	253	286
12	107,0	4,7	25,1	3,9	253	246
18	107,9	6,3	23,3	1,8	251	239
24	104,5	5,6	24,7	3,2	252	205
30	101,5	3,0	19,1	1,1	251	201
36	93,0	7,3	17,3	1,0	252	202
42	90,0	2,4	16,1	2,8	251	211
48	84,5	4,4	15,1	2,0	250	208
54	85,1	5,2	14,9	2,1	252	161
60	85,2	6,8	14,2	2,8	251	131
66	86,7	3,3	13,7	3,1	249	119
72	89,2	3,0	13,0	1,5	246	115
78	84,5	3,5	12,8	1,0	250	112
84	86,3	1,9	10,1	0,5	245	111
90	85,1	2,3	8,6	0,5	247	106
96	84,3	2,7	7,4	0,9	242	103
102	83,1	2,2	6,7	1,3	241	99
<b>Marine climate (Kumbor)</b>						
6	118,5	6,3	25,8	2,1	251	282
12	109,1	7,9	25,1	1,9	254	238
18	107,9	7,3	22,0	1,8	253	228
24	104,4	2,4	18,0	2,4	253	204
30	97,6	4,0	17,6	1,2	250	209
36	95,4	4,8	16,1	2,0	252	209
42	90,6	3,9	16,2	1,2	250	214
48	90,4	3,1	15,3	1,6	251	202
54	91,5	3,2	14,8	1,7	251	213
60	88,7	2,8	14,6	2,1	250	128
66	90,8	2,3	13,9	3,0	247	119
72	90,0	1,0	13,2	1,1	248	115
78	87,1	2,8	13,0	1,0	247	110

84	86,5	2,1	9,6	1,2	244	108
90	84,6	2,4	8,1	0,4	245	102
96	85,2	2,7	7,5	1,1	242	100
102	81,3	3,1	6,9	1,2	240	95

**Table 2.** Results of investigation of polyamide 12 before and during three years of exposure to natural weathering

Time of exposure to weathering (months)	PHYSICAL, MECHANICAL and THERMAL CHARACTERISTICS					
	$\sigma_m$ (MPa)		$\varepsilon_1$ (%)		VT (°C)	$a_a$ (mg/100cm <sup>2</sup> )
	$\bar{X}$	s	$\bar{X}$	s		
<b>0</b>	<b>55,7</b>	<b>3,0</b>	<b>320</b>	<b>34,0</b>	<b>180</b>	<b>28</b>
<b>Continental climate (Nikinci)</b>						
6	52,5	1,4	310	10,0	181	25,2
12	45,0	2,7	247	10,3	180	24,9
18	29,7	1,8	147	9,7	175	24,3
24	18,6	1,3	88	6,1	171	23,5
27	15,2	2,4	67	7,1	171	21,3
30	13,9	1,4	58	5,3	172	17,9
33	13,0	1,6	53	7,0	170	17,6
36	12,7	2,0	47	4,3	170	16,9
<b>Marine climate (Kumbor)</b>						
6	51,2	2,4	300	14,8	180	23,9
12	44,8	2,4	243	11,6	178	24,6
18	28,2	2,8	140	7,8	174	23,9
24	19,2	2,2	101	8,0	170	23,6
27	16,1	1,9	64	6,9	172	21,6
30	14,0	1,6	56	6,5	171	17,6
33	13,2	1,3	51	7,3	168	17,1
36	12,4	2,1	48	6,2	169	16,7

Results of the determination of tensile strength and impact resistance of polyamide 66 before exposure are arithmetic mean values for 32 specimens.

Arithmetic mean values for tensile strength and impact resistance of polyamide 66 during exposure for the specified periods of time, are determined on the bases of 8 single specimens.

Results of determination of elongation at break ( $\varepsilon_1$ ), density ( $\rho$ ), Vicat softening temperature (VT) and water absorption ( $a_a$ ) of polyamide 66 before and after the specified periods of exposure are arithmetic mean values for 3 single specimens.

Results of the determination of tensile strength, elongation at break and impact resistance of polyamide 12 before exposure are arithmetic mean values for 40 specimens.

Arithmetic mean values for tensile strength, elongation at break and impact resistance of polyamide 12 during exposure for the specified periods of time, are determined on the base of 8 single specimens.

Results of determination of density, Vicat softening temperature and water absorption of polyamide 12 before and after the specified periods of exposure are arithmetic mean values for 3 single specimens.

Statistical analysis of tensile strength and impact resistance of polyamide 66 and tensile strength, elongation at break and impact resistance of polyamide 12 have been done and arithmetic mean values and standard deviation were calculated.

Changes of physical, mechanical and thermal properties of polyamide 66 in the specified terms of natural weathering in continental and marine locations, expressed

in percents of the initial value before exposure, are shown in Figures 2 and 3.

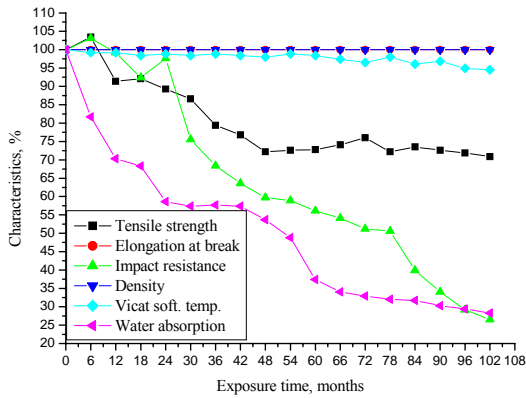


Figure 2. Changes of physical, mechanical and thermal properties of polyamide 66 as a function of exposure time in the continental area (Nikinci)

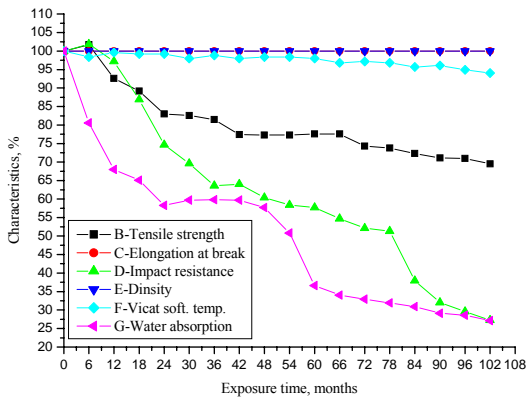


Figure 3. Changes of physical, mechanical and thermal properties of polyamide 66 as a function of exposure time in the marine area (Kumbor)

Dependence of tensile strength of polyamide 66 versus exposure time at continental (Nikinci) and marine (Kumbor) locations is shown in Fig.4.

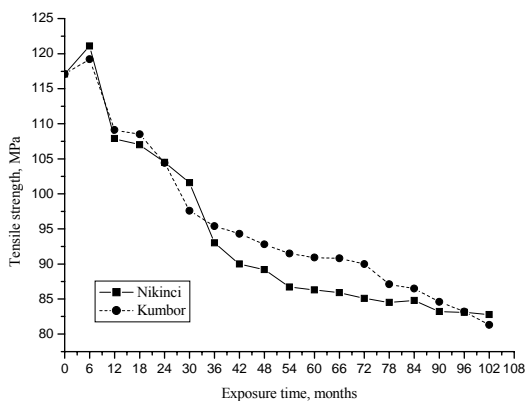


Figure 4. Dependence of tensile strength of polyamide 66 versus exposure time in continental (Nikinci) and marine area (Kumbor)

Impact resistance of polyamide 66 as a function of exposure time in the continental (Nikinci) and marine (Kumbor) areas is shown in Fig.5.

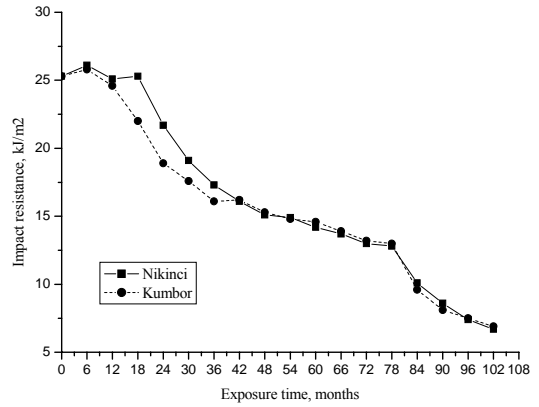


Figure 5. Changes of impact resistance of polyamide 66 as a function of exposure time in continental (Nikinci) and marine areas (Kumbor)

Changes of physical, mechanical and thermal properties of polyamide 12 in the specified terms of natural weathering in the continental and marine locations, expressed in percents of the initial value before exposure, are shown in Figures 6 and 7.

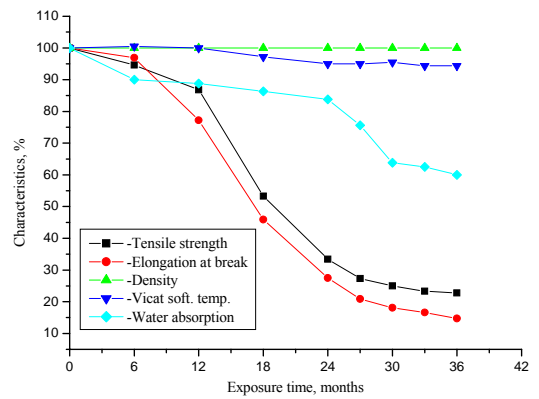


Figure 6. Changes of physical, mechanical and thermal properties of polyamide 12 as a function of exposure time in the continental area (Nikinci)

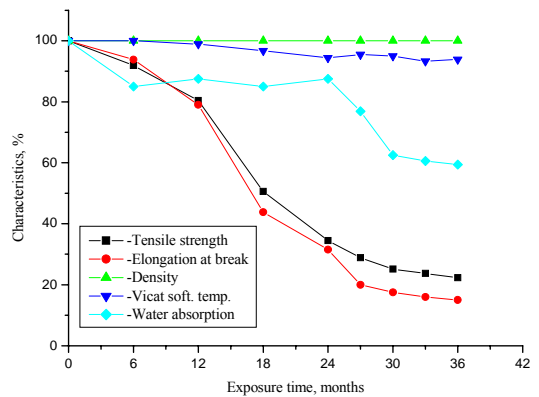
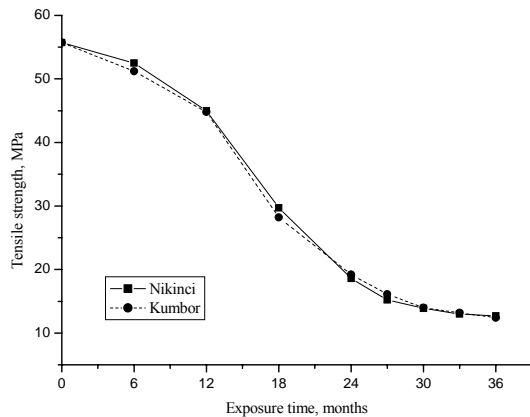


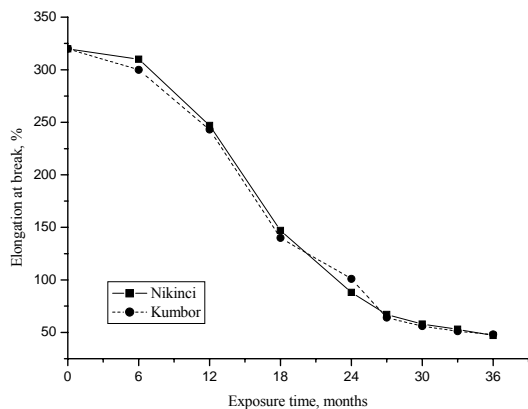
Figure 7. Changes of physical, mechanical and thermal properties of polyamide 12 as a function of exposure time in the marine area (Kumbor)

Tensile strength of polyamide 12 as a function of exposure time in the continental (Nikinci) and marine (Kumbor) areas is shown in Fig.8.

Elongation at break of polyamide 12 as a function of exposure time in continental (Nikinci) and marine (Kumbor) areas is shown in Fig.9.

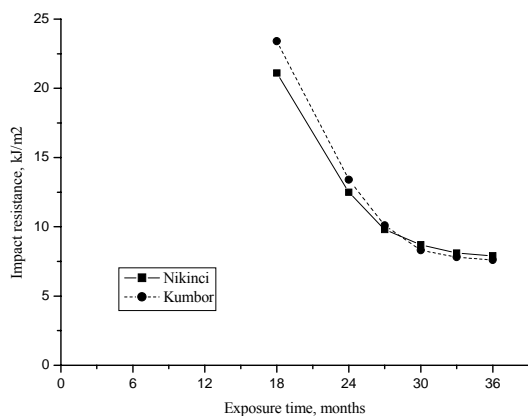


**Figure 8.** Changes of tensile strength of polyamide 12 as a function of exposure time in the continental (Nikinci) and marine (Kumbor) areas



**Figure 9.** Changes of elongation at break of polyamide 12 as a function of exposure time in the continental (Nikinci) and marine (Kumbor) areas

Impact resistance of polyamide 12 as a function of exposure time in the continental (Nikinci) and marine area (Kumbor) is shown in Fig.10.



**Figure 10.** Changes of impact resistance of polyamide 12 as a function of exposure time in the continental (Nikinci) and marine (Kumbor) areas

Results of determination of physical, mechanical and thermal properties of polyamide 66 indicate a drop of tensile strength and impact resistance (after a small growth after 6 months of exposure) and a drop of water absorption. There are practically no changes in density, elongation at break and Vicat softening temperature of polyamide 66 during eight and a half years of exposure to natural weathering in both different climatic areas.

Small growth of tensile strength and impact resistance in the first six months of exposure can be attributed to the enlarged water absorption i.e. achieving the equilibrium of moisture content, at which polyamides have optimum properties.

After 78 months of outdoor exposure in the continental (Nikinci) and marine (Kumbor) environments, polyamide 66 has retained about 70 % of initial values of tensile strength, but a drop of impact resistance and water absorption to about 50% of their initial values, indicate a more significant degradation of material.

A microbiological growth on the surface of specimens of polyamide 66 with 20 % glass fibres after 24 months of exposure to the outdoor natural weathering at Nikinci and 30 months at Kumbor was observed. Microbiological growth appeared on the surfaces at which, owing to erosion activities of meteorological factors, an outer layer was carried away. Glass fibres, remaining above the specimen surface, allow the piling of dust and biological active material, which, in the presence of moisture and warmth initiated the process.

It is stated that, on the polyamide 66 glass fibres specimen, after 2 years of outdoor exposure in tropic warm/wet conditions, a microbiological growth and layer of dust, were observed. On the same material in the same conditions, after 4 years of exposure, a drop of tensile strength of 40 % was registered [1].

Specimens of polyamide 66 with 20 % glass fibres, which were exposed to the outdoor conditions at Nikinci and Kumbor, has exhibited a drop of tensile strength of about 25 %.

The obtained results indicate that the degradation process of polyamide 66 with 20 % glass fibres was faster in tropic warm/wet conditions than in conditions at Nikinci and Kumbor

Results of determination of physical, mechanical and thermal properties of polyamide 12 indicate a constant reduction of tensile strength, elongation at break and water absorption, while there is almost no change in the density and Vicat softening temperature during three years of exposure to natural weathering in both different climatic locations. Owing to the fact that the tensile strength and elongation at break of polyamide 12, after first six months of exposure, are about 90 % of their initial values, it can be observed that the equilibrium moisture absorption process was finished and degradation process has started.

Specimens of polyamide 12 were broken, during the testing of impact resistance, for the first time after 18 months of the outdoor exposure in the continental (Nikinci) and marine (Kumbor) environments. After the same period of outdoor exposure (18 months), a tensile strength and elongation at break suffered a drop of 50 % compared to their original values. These two statements indicate that polyamide 12 has degraded to a significant extent in the conditions mentioned.

A drop of tensile strength and impact resistance of polyamide with 20 % glass fibres and reduction of tensile strength, elongation at break and impact resistance of

polyamide 12 indicate that bond scission in polymeric backbone and weakness of hydrogen bonds between macromolecules chains of these polyamide materials has occurred.

### Conclusions

Based on the obtained results and their analysis, it can be concluded that:

A drop of tensile strength, impact resistance and water absorption of polyamide with 20 % glass fibres began after 6 months of the outdoor exposure in continental (Nikinci) and marine (Kumbor) climates, while density, elongation at break and Vicat softening temperature remained almost at their initial values. This reduction / retention trend of values was observed during the whole period of exposure.

A drop of impact resistance of about 50 %, water absorption of about 70 % and tensile strength of about 30 % of polyamide 66 with 20 % glass fibres compared to the initial values indicate that this material should not be used in the open longer than 78 months of the outdoor exposure to continental and marine climates.

Microbiological growth appeared as a consequence of the erosion influence of the climate factors and taking off the surface layer of polyamide 66 with 20 % glass fibres specimen i.e. remaining glass fibres on the surface after 24 months of exposure at Nikinci and 30 months at Kumbor.

At polyamide 12 specimens the permanent decrease of tensile strength, elongation at break and water absorption started basically from the moment of exposure, while density and Vicat softening temperature remained at the initial values level.

A drop of tensile strength and elongation at break of about 50 % compared to the initial values and the fact that the specimens were broken, for the first time while testing the impact resistance indicate that polyamide 12 has degraded in such a way that it is not suitable for application in the outdoor conditions longer than 18 months.

Microbiological growth was not observed at polyamide 12 during the whole period of exposure neither in the continental nor in marine location.

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## Istraživanje uticaja faktora prirodnog starenja na svojstva poliamidnih termoplastičnih materijala

Ispitivana je otpornost injekciono presovanih epruveta poliamida 66 sa 20% staklenih vlakana i poliamida 12 prema dejstvu faktora prirodnog starenja. Proces prirodnog starenja na otvorenom prostoru, u dva klimatski različita područja praćen je određivanjem fizičkih, mehaničkih i toplotnih svojstva poliamida 66 pre i tokom osmoipogodišnjeg izlaganja, a kod poliamida 12 pre i tokom trogodišnjeg izlaganja. Opisani su glavni faktori prirodnog starenja na otvorenom prostoru i očekivani mehanizam degradacije poliamidnih materijala.

*Cljučne reči:* termoplastični materijali, poliamid 66 sa staklenim vlaknima, poliamid 12, prirodno starenje, uticaj atmosferskih uslova.

## Исследование влияния фактора естественного старения на характеристики полиамидных термопластичных материалов

Здесь исследована прочность инъекционно-спрессованных бюреток полиамида 66 со 22% стеклянных волокон и полиамида 12 под действием фактора естественного старения. Процесс естественного старения в открытом пространстве в двух климатически различных средах, был сопровожён определением физических, механических и тепловых характеристик полиамида 66 перед и в течении восемь с половиной лет выставления, а у полиамида 12 перед и в течении трёх лет выставления влиянием этих факторов. В этой

работе тоже описаны и главные факторы естественного старения в открытом пространстве и ожидающий механизм деградации полиамидных материалов.

*Ключевые слова:* термопластичные материалы, полиамида 66 стекляных волокон, полиамиды 12, естественное старение, влияние атмосферных условий.

## **La recherche de l'influence du vieillissement naturel sur les propriétés des matériaux polyamides thermoplastiques**

On a examiné la résistance des éprouvettes pressées à injection des polyamides 66 avec 20% de fibres de verre et polyamide 12 à l'action des facteurs du vieillissement naturel. Le procès du vieillissement naturel en plein air dans deux différentes régions climatiques était suivi par la détermination des propriétés physiques, mécaniques et thermique du polyamide 66 avant et pendant huit ans et demi d'exposition et chez le polyamide 12 avant et pendant 3 ans d'exposition. On a décrit les facteurs principaux du vieillissement naturel en plein air et le mécanisme attendu de la dégradation des matériaux polyamides.

*Mots clés:* matériaux thermoplastiques, polyamide 66 de fibres de verre, polyamide 12, fibre polyamide, vieillissement naturel, influence des conditions atmosphériques.