ANNALS of the ORADEA UNIVERSITY.
Fascicle of Management and Technological Engineering, Volume X (XX), 2011, NR1

STUDY ON PROPERTIES OF POLYAMIDES USED IN MANUFACTURING OF COMPONENTS FOR THE AUTOMOTIVE INDUSTRY

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Keywords: polyamides, PA, properties, automotive industry

Abstract

This is an analysis of the significant properties of polyamides (PA) used in manufacturing of technical components for the automotive industry. Physico-chemical and mechanical properties were studied for polyamides, in pure (non-reinforced) state and reinforced with various reinforcing agents.

1. Introduction

The polyamides are semi-crystalline macromolecular compounds with a wide range of applications in technical fields, both as non-reinforced polyamides and polyamides reinforced with glass fibers, carbon fibers, molibden disulphur, silicium dioxide, metal fibers, etc. [1,2,3,4,5,6]. Polyamides are mainly used in automotive industry due to the following properties [7,8,9,10,11]:

- good mechanical strength
- moderate rigidity
- impact resistant
- resistant even when used at low temperature
- frictional wear resistance, especially if reinforced with molibden disulphur or graphite
- good adherability on steel
- easy processability
- agreeable look of the surface

In automotive industry polyamides are used in manufacturing of different types of housings, fans, complex-shape parts, fuel tanks, bushings, pivots, flexible cabling, level floats and brake fluid reservoirs.

2. Structure and properties

2.1. Structure

The characteristic feature of polyamides is the presence of the amidic group into the main chain:

(- CONH -), amidic group

There are two structural types of polyamides according to the corresponding two types of polyamidation reactions [12]:

a) polyamides obtained through polycondensation of dicarboxylic acids with diamines (e. g., polycondensation of adipic acid with hexamethylenediamine) and having the following structure:

$$-\!\left[NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO \right]_n\!-$$

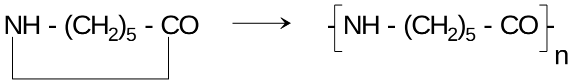
b) polyamides obtained through homopolymerization of an amino acid or through ring-opening polymerization (ROP) of lactams, having the following structural formula:

$$-\!\left[CO - NH - R \right]_n\!-$$

For the first time, polyamide was produced in 1939 - in U.S.A - by Dupont de Nemours company, as fiber under the brand name "Nylon".

Since there are several types of polyamides, their distinctive denomination is given considering the originating constituents and process, as follows:

- by one digit indicating the number of carbon atoms in amino acid for the polyamides obtained through homopolycondensation of amino acids:



$$NH - (CH_2)_5 - CO \longrightarrow \left[NH - (CH_2)_5 - CO \right]_n$$

poliamida - 6 sau PA 6

- by two digits indicating the number of carbon atoms in diamine and dicarboxylic acid for the polyamides obtained through polycondensation of dicarboxylic acid with diamine:

$$H_2N - (CH_2)_6 - NH_2 + HOOC - (CH_2)_4 - COOH \longrightarrow \left[NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO \right]_n$$ poliamida - 6,6 sau PA 6.6

The following types of polyamides are the most used in manufacturing of technical components for automotive industry:

$\left[NH - (CH_2)_6 - NH - CO - (CH_2)_4 - CO \right]_n$ poliamida - 6,6 sau PA 6.6

$\left[NH - (CH_2)_6 - NH - CO - (CH_2)_8 - CO \right]_n$ poliamida - 6,10 sau PA 6.10

$\left[NH - (CH_2)_6 - NH - CO - (CH_2)_{10} - CO \right]_n$ poliamida - 6,12 sau PA 6.12

$\left[NH - (CH_2)_4 - NH - CO - (CH_2)_4 - CO \right]_n$ poliamida - 4,6 sau PA 4.6

$\left[NH - (CH_2)_5 - CO \right]_n$ poliamida - 6 sau PA 6

$\left[NH - (CH_2)_{10} - CO \right]_n$ poliamida - 11 sau PA 11

$\left[NH - (CH_2)_{11} - CO \right]_n$ poliamida - 12 sau PA 12

Due to their structure with chains of high regularity, several linear polyamides have a high tendency to crystallize.

The (- CO-NH -) groups of the chain have a favorable effect for crystallization: these create the possibility of establishing hydrogen links which lead to an increase of intermolecular forces. The frequency of these links depends mostly on macromolecules' structure. Consequently, high degree of cristallinity (40-50%) will be at polyamides with high number of potential/possible hydrogen links. This is the case for PA 6.6, PA 6.10 and PA 6.

Good mechanical properties and high melting temperatures of polyamides are relying on the favorable effect of the internal hydrogen links. Generally, it was determined that polyamides containing an even number of methylenic groups amongst the amidic groups form the maximum number of hydrogen bridges, resulting in higher melting points than polyamides with an odd number of methylenic groups. The melting temperature decreases as the number of methylenic groups increases into the polyamide's macromolecule. A similar decrease of melting temperatures is produced in presence of side alchil-type groups in polyamides, as a result of lowering the macromolecules' packing capacity. The same effect has the replacement of a methylenic group with an oxygen atom. Introduction of aromatic nuclei in the sequence of polyamidic chains produce a significant increase of melting temperature.

2.2. Physical properties

- density ranging within 1010-1180 kg/m^3.
- as solid products, polyamides are transparent or translucid (at thin thickness) and opaque (at high thickness).
- moisture absorption from air: 2,5% (in conditions of normal relative humidity, 50%HR) and 8.5% (in conditions of maximum relative humidity, 100%HR). Water acts as a plasticizer for polyamides, respectively the higher is the moisture absorption, the lower is the vitrification temperature. For example, the vitrification temperature for PA 6.6 is 50ºC at 50% HR and 0ºC at 100% HR. A high moisture absorption - resulting in swelling of polyamide - worsen the mechanical, thermal, electrical properties and dimensional stability.

The interval of melting temperature is very narrow (10ºC) - if this interval is exceeded, the polyamides decompose easily.

All types of polyamides in molten state have a good fluidity.

PA 4.6 has the highest degree of crystallinity (70%).

The average molar mass of polyamides for technical use is ranging between 10000 and 35000 g/mole,

Polyamides are smell-less, tasteless and inert (physiological wise).

2.3. Mechanical properties

Polyamides have very good mechanical properties which put them on the leading places amongst thermoplastic materials.

Considering their relatively low molar mass, polyamides have – especially, the oriented polyamide – extremely high values of resistance.

Polyamides are very sensitive to moisture in the air. In order to be processed properly, polyamides must be stored in an environment with 50% relative humidity where the moisture absorption is only 2,5%. An atmosphere too dry make polyamides brittle and one too wet leads to overplastification.

The moisture absorption is depending on the ratio $–CH_2-/-CONH-$, meaning that the higher is this ratio, the lower is the moisture absoption. At the same time, the moisture absoption decreases as the polyamide's crystallinity increases.

The mechanical strength and rigidity of polyamides are influenced by temperature and moisture.

Increasing percentage of the moisture content results in increase of polyamide's flexibility (through decrease of elastic moduli) and impact strength, but also in decrease of its tensile strength.

• *Elongation and compression*

For designers of automotive technical components, it is important to know the behaviour of plastics solicited to elongation (tensile/stress) and to compression (compressive stress) because - in certain cases- these components can be exposed to both. The stress-strain curves for pure (non-reinforced) PA 6.6 both at tensile/elongation testing and compression testing are represented in Fig.1. The test was performed on polyamide, grade Zytel 101, at 23˚C [8]. Zytel 101 is the trade mark of DuPont De Nemours for non reinforced PA 6.6 having a Charpy impact strength of 20 KJ/m² and a modulus of elasticity E=1200 MPa.

It can be noticed that the stress required for compression is higher than the stress required for elongation within a wide range of strain. For example, the specimen B, requires a tensile/stress of 50 MPa for 8% elongation strain and a compressive stress of 75 MPa for 8% compression strain.

At low strain values, the stress-strain curves in tension (elongation) and compression are identical because the elastic modulus for compression is equal with the elastic modulus for tension.

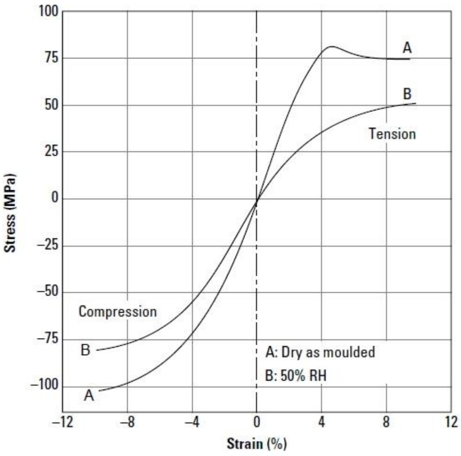


Fig.1 Stress-strain curves in tension and compression of Zytel 101 (PA 6.6), 23˚C.

• ***Flexural modulus***

The flexural modulus of pure (non-reinforced) polyamides is influenced by temperature and moisture.

In Fig.2 the DMA diagram shows the variation of storage modulus and tan δ with temperature and frequency for a specimen of PA 6.6, grade TECHNYL A 221 molded at 270˚C.

The lower is the temperature, the higher is the value of polyamide's elastic modulus (i.e., polyamide has higher rigidity). These values make polyamides suitable for manufacturing of various automotive components which are used both at high temperatures and low temperatures.

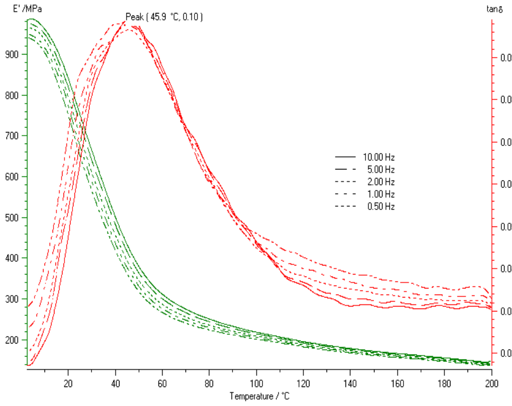


Fig.2 DMA diagram for PA 6.6, specimen grade TECHNYL A 221 (Dry) molded at 270˚C.

• *Impact strength*

The impact strength of polyamides is influenced by temperature and moisture. Increasing the moisture content in polyamide results in increase of elasticity, and impact strength respectively, because the absorbtion of energy required for breaking is higher.

Increasing the temperature is also causing the increase of polyamide's impact strength.

The repetitive impact strength of polyamides is higher than strength of many other plastic materials The optimum degree of reinforcing polyamides with glass fiber is 35%.

• *Creep resistance*

At long term stress, the behaviour of polyamides is characterized by creep deformation. Creep occurs in conditions of constant stress/load and the strain is measured relative to time.

The creep rate is dependent on polyamide type (i.e., structural composition of polyamide), temperature, moisture and amount of applied stress.

Resulted over a long period of time, at constant stress, the creep deformation of polyamides is very low recommending them for use in manufacturing of automotive parts and high performance sport items.

• *Fatigue resistance*

Fatigue resistance of polyamides is lower than the one of polyoxymethylenes and it is influenced by moisture (Fig.3) and temperature (Fig.4) [8].

Increase of temperature or moisture in polyamide specimens results in decrease of fatigue resistance.

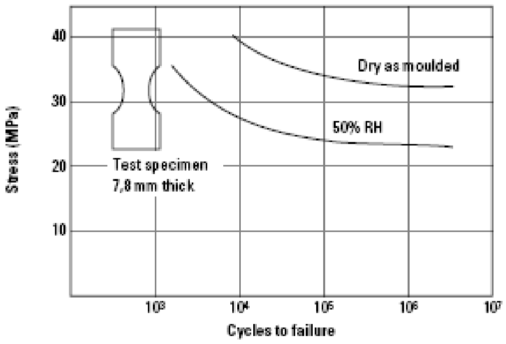


Fig.3 Flexural fatigue data for Zytel 101 using Sonntag machine. Constant maximum stress and 1800 cycles per minute at 23˚C.

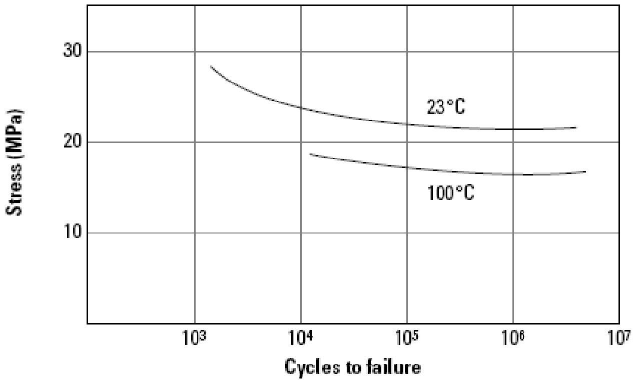


Fig 4. Effect of temperature on Sonntag axial fatigue of Zytel 101 with alternate tension and compression, 1800 cycles per minute. Tests at 23˚C and 100˚C

2.4. Chemical properties

Polyamides have a poor behaviour under the action of atmospheric agents (especially, sunlight) and their life cycle is limited in presence of boiled and highly oxygenated water.

Polyamides have a remarkable chemical stability against a large number of chemical products: oil, gear grease (for transmission parts), paints, varnishes, aldehydes, ketones, esters, petroleum products, etc. Poor resistance against metal salts

Polyamides have few solvents due to their high cristallinity. Polyamides are dissolved in phenol, cresol, concentrated sulphuric acid, concentrated phormic acid, alcoholic solutions of calcium chlorine or magnesium chlorine. All these substances have a strong polar character and they are able to solvate the amidic groups of macromolecules. At cold temperature, polyamides can be consided as stable under the action of diluted acids and bases. At hot temperature, polyamides are hydrolysed by acids and bases, The hydrolysis rate increases rapidly as temperature increases.

2.5. Electrical properties

Polyamides are used as electrical insulators for voltage up to 600 V and frequencies lower than 400 Hz. The dielectric losses are influenced by the percentage of humidity.

PA 11 and PA 6.12 are the most used as electrical insulators. Increasing the temperature or frequency results in decrease of polyamide's resistivity.

2.6. Thermal properties

Polyamides have a narrow melting interval (i.e., to pass from solid to fluid state) with high fluidity when melt and they decompose over 300ºC.

In melt condition, polyamides are sensitive to oxidation, fact that can be easily noticed due to the rapid change of colour (yellow turns into brown). Addition of copper powder or copper compounds, aromatic amines, etc is recommended in order to improve the thermal stability of polyamides.

Polyamides are considered as hard flammable materials, but they continue to burn after removal of flame releasing black smoke and smell of burned wool.

Polyamides have high mold shrinkage (up to 2,4%).

2.7. Reinforcing materials

Polyamides are reinforced with various materials in order to ameliorate certain properties.

Polyamides are treated with anti-UV protection agents for increasing their resistance against the action of atmospheric agents (especially, sunshine).

The frictional wear properties are improved using molybdenum disulphide, graphite, oil, etc.

Increasing of impact strength and electric properties is done through short glass fiber (3-200 mm) reinforcement.

Also reinforcing with powder materials (talc, kaolin, etc) improves the polyamides' dimensional stability.

The main properties of polyamides PA 6, PA 11 and PA 12 are presented in Table 1.

Table 1. Properties of PA 6, PA11 and PA 12

Properties	Unit	PA 6	PA 11	PA 12
Density	Kg/m^3	1130-1150	1040	1010
Water absorption at equilibrium, 50%RH	%	1,3-1,9	0,23	0,7
Water absorption at saturation	%	9,5	2,9	1,5
Breaking strength	MPa	80-90	34-65	47-65
Break elongation	%	23-50	20-300	5-250
Flexural strength	MPa	50-115		
Tensile elastic modulus	MPa	3200		1450
Flexural modulus	MPa	2200	970-1200	1200-1600
Melting temperature	ºC	218-220	183-187	172-180
Vitrification temperature	ºC	50-60	30	55
Continuous resistance temperature interval	ºC	95-100	-70,+65	80-110
Mold shrinkage	%	1,2	0,7-2	1,3-1,5
Thermal conductivity	W/mK	0,24	0,29	0,35
Transversal resistivity	Ωcm	$6 \cdot 10^{13}$	$7{,}8 \cdot 10^{13}$	10^{15}
Dielectric constant at 10-50 MHz		3,4-3,8	3,7	3,0-3,2

Advantages of polyamides PA 6, PA 11 and PA 12:

- good mechanical properties (frictional wear and fatigue resistance, tensile strength)
- hydrocarbon-resistant
- good thermal resistance
- good electrical insulators
- PA 12 has good behaviour at low temperatures, good dimensional stability.

Disadvantages of polyamides PA 6, PA 11 and PA 12:

- poor behaviour in boiling hydrogen peroxide
- For processing purpose, polyamides must be dried 2-4h at 110ºC or 6-12h at 90ºC.

The main properties of polyamides PA 6.6, PA 6.6 + 30% glass fiber, PA 4.6, PA 6.10 and PA 6.12 are presented in Table 2.

Table 2. Properties of polyamides PA 6.6, PA 6.6 + 30% glass fiber, PA 4.6, PA 6.10 and PA 6.12

Properties	Unit	PA 6.6	PA 6.6 +30%GF	PA 4.6	PA 6.10	PA 6.12
Density	Kg/m^3	1130	1370	1180	1090	1060
Water absorption at equilibrium, 50% HR	%	2,8	1,9	3,7	0,4	1,3
Water absorption at saturation	%	8,5	6	13	3,5	3
Breaking strength	MPa	83-120	208	10-80	70	52-61
Break elongation	%	5-60	3	3-30	100-300	7
Flexural strength	MPa	120	240			
Tensile elastic	MPa	2800	10800	3300	1200-	2700

modulus					1900	
Flexural modulus	MPa	2840	8400	3300	2500	2000
Melting temperature	ºC	255-260	255	295	210-220	208-216
Vitrification temperature	ºC	77	215-240	160	57	166
Continuous resistance temperature interval	ºC	-65,120		135	80	120
Mold shrinkage	%	1,1-1,5	0,5-1,3	1,5-2,4		1,5
Thermal conductivity	W/mK	0,25	0,23	0,3	0,21	0,22
Transversal resistivity	Ωcm	10^{13}-10^{15}	10^{12}-10^{15}	10^{9}-10^{14}	10^{12}-10^{15}	10^{13}-10^{15}
Dielectric constant at 10-50 MHz		3-3,9	4,1-4,3	3,5-3,9	3,5-3,9	3,5-4

Advantages of polyamides PA 6.6, PA 6.6 + 30% glass fiber, PA 4.6, PA 6.10 and PA 6.12:

- all these types of PA have very good mechanical properties (i.e., impact and tensile strength, fatigue and frictional wear resistance)
- good chemical inertia
- good thermal behaviour (especially, PA 6.6 + 30% glass fiber)
- good thermal insulators in absence of atmospheric humidity.

Disadvantages of polyamides PA 6.6, PA 6.6 + 30% glass fiber, PA 4.6, PA 6.10 and PA 6.12:

- their properties are declining in a wet atmosphere
- compulsory drying of material prior processing
- narrow melting temperature interval

3. CONCLUSIONS

Several types of polyamides were studied, both in pure (non-reinforced) state and reinforced with various reinforcing agents. The study revealed that the majority of polyamides have remarkable properties and can be successfully used for manufacturing of technical components for the automotive industry.

Bibliography

[1] Mişca, B., R., H., Materiale compozite polimere, Presa Universitară Clujană, Cluj-Napoca, 2001.
[2] Şereş, I., Materiale termoplastice pentru injectare, tehnologie, încercări., Editura Imprimeriei de Vest, Oradea, 2002.
[3] Trotignon, J., P., Verdu, J., Dobracginsky, A., Piperaud, M., Matieres Plastiques, Editions Nathan, Paris, 1996.
[4] Pichon, J., F., Injection des matieres plastiques, Dunod, Paris, 2001.
[5] Mărieş, Gh., R., E., Elemente de ştiinţa prelucrării termoplastelor, Editura Universităţii din Oradea, Oradea, 2004.
[6] Jacksch, E., Chetaru, D., Manca, Gh., Materiale plastice poliamidice, Editura Tehnică, Bucureşti, 1988.
[7] DuPont De Nemours, Product & Market Literature, DuPont Engineering Polymers, From Concept to Commercialization, 11, 2003.

[8] DuPont De Nemours, Product & Market Literature, DuPont Engineering Polymers, DuPont Minlon and Zytel, nylon resins, Design Information-Module II, 05, 2001.
[9] ***, BASF, Ultramid/Capron, Polyamide (PA), BASF Plastics key to your success, BASF The Chemical Company, 09, 2004, p. 10-28.
[10] ***, BASF, Ultramid, Polyamide (PA), BASF Plastics key to your success, BASF The Chemical Company, 09, 2004, p.4-17.
[11] Mărieş, Gh., R., E., Mărieş, I., Study on the properties of some thermoplastic polymers recommended in manufacturing power transmission components for engineering and automotive industries, Proceedings - The 3rd International Conference “Power Transmissions `09”, Pallini Beach Hotel, Kallithea, Greece, 1-2 october 2009, Editor: Athannassios Mihailidis, pp. 255-260
[12] Manoviciu, V., Mărieş, Gh., R., E., Materiale compozite cu matrice organică, Editura Universităţii Oradea, Oradea, 2005, p.135 -141.