The effect of temperature and storage time on mechanical properties of polyamides

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Abstract. This work is deals with the influence of temperature and storage time on selected mechanical properties of polyamides. These properties were determined using an impact test Charpy hammer and static test strength. The tests were carried out on three types of polyamides PA 6 BT, PA 6 GF 20 and PA 6 CF 20. The samples were stored for 2, 5, 7, 14, 28, 56, 84 and 120 days with a storage temperature of -20 °C (the freezer), 21 °C (room temperature) and 70 °C (furnace, heated at a given temperature). At the indicated times, we performed the test set and evaluated the mechanical properties observed.

1. Introduction

The use of polymers as materials for manufacture of many everyday items is constantly increasing. However, all polymers are ultimately susceptible to degradation and aging under exposure to various conditions of commonly encountered environments [1]. The aging of polymers is the sum of irreversible changes in the properties of the polymers that occur due to effects of light, sun, ambient air, oxygen, radiation and heat [2]. Often multiple factors act simultaneously, making the overall effect of aging more significant. Aging is manifested by permanent changes in some properties, in particular loss of ductility, impact strength, and sometimes also a decrease in strength and loss of polymer mass. Basic definitions of terms in the field of polymer aging are [3, 4]:

- natural aging – the effect of the environment during storage or use,
- artificial aging – the effect of an environment with artificial conditions,
- climatic aging – the effect of climatic conditions of the given earth environment,
- resistance of polymers – ability to retain properties to some extent in the environment,
- biological aging – the effect of activity of living organisms that are in contact with polymers,
- mechanical aging – effect of long-term static or dynamic load,
- thermal aging – the effect of temperature or temperature changes without presence of oxygen,
- thermos-oxidative aging – the effect of temperature in the presence of oxygen,
- oxidative aging – the effect of oxygen
- ozone aging – the effect of ozone,
- light aging – effect of the visible and ultraviolet part of the electromagnetic spectrum,
- photo-oxidative aging – effect of the visible and ultraviolet part of the electromagnetic spectrum in the presence of oxygen,
- chemical aging – effect of chemically aggressive substances.
2. Material and methods

Generally speaking, polyamide is a semi-crystalline thermoplastic with low density and high thermal stability. Polyamides are among the most important and useful technical thermoplastics due to their outstanding wear resistance, good coefficient of friction, and very good temperature and impact properties. In addition, polyamide exhibits very good chemical resistance and is an especially oil resistant plastic. This excellent balance of properties makes the PA polymer an ideal material for metal replacement in applications, such as automotive parts, industrial valves, railway tie insulators and other industry uses, whose design requirements include high strength, toughness and weight reduction. Polyamide shows a propensity to absorb moisture and thus has poorer dimensional stability than other engineering plastics. Polyamide properties vary from the hard and tough PA 66 to the soft and flexible PA 12. Furthermore, there is a distinct difference between polyamide shapes produced by extrusion and those produced by casting. Extrusion typically provides for smaller, higher volume machine parts, while casting typically allows for low volume, larger parts containing lower levels of internal stress. Both extruded and cast polyamides can be modified through the use of fillers to enhance certain properties [5]. Polyamide plastic offers [6]:

- high wear resistance,
- high thermal stability,
- very good strength and hardness,
- high mechanical damping characteristics,
- good sliding properties,
- good chemical resistance.

The requirements for products made of polymeric materials can be met with a good knowledge of their mechanical, physical, electrical, chemical, optical and bio-logical properties. Test methods are used for evaluation, most of which are standardized. As a rule, test specimen with the prescribed shape and dimensions are used for testing according to the standards. Information about the mechanical properties of polymeric materials can be obtained from standards and manufacturers' brochures and catalogues [7]. This work deals with the evaluation of the effect of temperature and storage time on the mechanical properties of polyamides using the Charpy hammer impact test and static tensile test.

3. Experimental part

The tests were carried out on three types of polyamides PA 6 BT, PA 6 GF 20 and PA 6 CF 20. The samples were stored for 2, 5, 7, 14, 28, 56, 84 and 120 days with a storage temperature of -20 °C (the freezer), 21 °C (room temperature) and 70 °C (furnace, heated at a given temperature). At the indicated times, we performed the test set and evaluated the mechanical properties observed. In the table 1 is presented table values of tested materials properties. Characteristics of tested materials:

- Basic type PA 6 BT for injection moulding, modified for general use, with excellent manufacturing properties. Used in the automotive, engineering, electrical and consumer-goods industry – electrical tools, fasteners, clamps, hobby tools, toys.
- PA 6 GF 20 for injection moulding, chemically coupled with 20 % glass fiber. Application: impacted mouldings and mouldings with high strength applied in automotive, electrical, engineering and consumer-goods industry, e.g.: grips for electro tools, hobby tools, gears, cases of the electrotools, cooling screws of blowers, electromotors, carrying parts in the automotive industry. With the increasing content of GF also the toughness, flexural and tensile strength increase as well as the heat application increases up to 150 °C and the shrinkage decreases.
- PA 6 CF 20 for injection moulding chemically reinforced with 20 % carbon fiber, suitable for mouldings with high strength and toughness also at minus temperatures. Used in the automotive, engineering and electrical industry. Application: hobby tools, covers of electrotools, electromotors, cooling screws of blowers, gear wheels, carrying parts in the automotive industry like e.g. brake cables.
Table 1. Table values of tested materials properties.

| Properties                                         | PA 6 BT | PA 6 GF 20 | PA 6 CF 20 |
|----------------------------------------------------|---------|------------|------------|
| Tensile strength (MPa)                             | 85      | 135        | 230        |
| Tensibility (%)                                    | 3.5     | 4          | 2.5        |
| Tensile modulus (MPa)                              | 3100    | 6800       | 17000      |
| Charpy notched impact strength, +23 °C (kJ m⁻²)    | 1.6     | 8          | 6          |

Tensile strength (MPa), tensibility (%), and tensile modulus (MPa) were determined from the tensile curves. From the impact test using a Charpy hammer, we determined the Charpy notched impact strength (kJ m⁻²).

3.1. Tension strength

Tension strength is the face value of the tension given by the fraction of the biggest burdensome strength, which a test bar bears, and by the original section of a bar. Figures 1, 2 and 3 show the tensile strength values (MPa) of polyamides materials PA 6 BT, PA 6 GF 20 and PA 6 CF 20. All three materials behaved very similarly, the tension strength values increase for the first 28 days due to secondary crystallization and chain molecular alignment. The highest values were measured at elevated storage temperatures. Temperatures below 0 °C caused a slight increase of strength values.

![Figure 1](image1.png)

**Figure 1.** Tensile strength values (MPa) of the material PA 6 BT stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.

![Figure 2](image2.png)

**Figure 2.** Tensile strength values (MPa) of the material PA 6 GF 20 stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.
3.2. Tensibility

Tensibility is the relative elongation expressed in the percents of the original length. In the figures 4, 5 and 6 there are tensibility values (%) of polyamides materials PA 6 BT, PA 6 GF 20, and PA 6 CF 20, depending on the temperature and the number of days exposed to it. The tensibility of all three materials decreases with increasing days, which is due to secondary crystallization after manufacturing of the specimen, as well as rearranging the molecules and reducing the defect concentration. The values stabilize after 28 days of storage. Tensibility values decreased at lower and higher storage temperatures.

**Figure 4.** Tensibility values (%) of the material PA 6 BT stored for 0–120 days at storage temperatures -20°C, 21°C and 70°C.

**Figure 5.** Tensibility values (%) of the material PA 6 GF 20 stored for 0–120 days at storage temperatures -20°C, 21°C and 70°C.
3.3. Tensile modulus

Tensile modulus is a measure of the resistance to elastic deformation that material has. Materials that require higher stresses to induce elastic deformation have higher tensile modulus. The tensile modulus is commonly measured by taking the amount of stress applied to a material and dividing it by the strain the material undergoes. The figures 7, 8 and 9 show the tensile modulus values (MPa) of PA 6 BT, PA 6 GF 20 and PA 6 CF 20. The tensile modulus of all three materials increased and it can be conclude that all tested materials exhibit similar behavior. The biggest changes occurred in the first 28 days. The lowest values were measured at 70 °C and the highest at minus temperatures. The material loses stiffness at higher storage temperatures.
Figure 9. Tensile modulus values (MPa) of the material PA 6 CF 20 stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.

3.4. Charpy notched impact strength
Charpy notched impact strength – charpy impact testing involves striking a standard notched specimen with a controlled weight pendulum swung from a set height. The amount of energy absorbed in fracturing the test-piece is measured and this gives an indication of the notch toughness of the test material. In the figures 10, 11 and 12 there Charpy notched impact strength values (kJ m⁻²) of polyamides materials PA 6 BT, PA 6 GF 20 and PA 6 CF 20. At a storage temperature of -20 °C, the notch toughness values dropped significantly, and the material becomes brittle due to minus temperatures.

Figure 10. Charpy notched impact strength values (kJ m⁻²) of the material PA 6 BT stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.

Figure 11. Charpy notched impact strength values (kJ m⁻²) of the material PA 6 GF 20 stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.
Figure 12. Charpy notched impact strength values (kJ m\(^{-2}\)) of the material PA 6 CF 20 stored for 0–120 days at storage temperatures -20 °C, 21 °C and 70 °C.

4. Results and discussion

The static tensile test were used to determine and evaluate the tensibility, the tensile modulus, tensile strength and Charpy impact test was used to determine and evaluate Charpy notched impact strength. The effect of storage at minus, room and elevated temperatures was evaluated on materials PA 6 BT, PA 6 GF 20 and PA 6 CF 20 with a focus on their mechanical properties. From the experiments it was found that after the chain molecular alignment, tensibility of the material PA 6 BT depending on the temperature did not change significantly, while tensibility of PA 6 GF 20 and PA 6 CF 20 was significantly lower at -21 °C and 70 °C. It can be concluded, that the value of tensile modulus of the used samples had an increasing tendency at each storage temperature. The lowest values were reached at 70 °C and the highest values were reached at -21 °C. The material has higher stiffness at minus storage temperatures. It was found that the tensile strength for all materials grew, with the highest values being reached at 70°C and the lowest at room temperature. The evaluation of Charpy notched impact strength shows, that the longer the samples were exposed to a temperature of -21 °C, the greater the brittleness of the material was. Although the effect of temperature was examined for 120 days, it can be stated that after about 28 days the examined values did not change significantly due to a chain molecular alignment. The measured values correspond to the table values. As these materials are commonly used, the results of the work are usable in practice. However, the results of the experiments cannot be interpreted in general because the behavior of the polymer materials is individual.

5. Conclusions

Polymeric materials change and age over time. Experimental methods can be used to monitor the time dependence of a number of properties and also changes of molecular and supramolecular structures that determine macroscopic properties. All of these changes, whether spontaneous or caused by the environment, are collectively referred to as aging. During the lifetime of plastics, there are spontaneous and in many cases irreversible changes in their structure and properties due to the time, external storage conditions and use of the product. These changes are referred to as degradation, aging, corrosion or damage. The meaning is similar, but it is not exactly the same. The term aging emphasizes the time factor, properties do not necessarily deteriorate. In a narrow sense, degradation refers to a change in the structure and properties of polymers due to effects of heat, light, oxygen or mechanical load. Polymers are exposed to at least two important degradation stages during their lifetime. The first one is short but very intense. It takes place in a processing machine where the plastic melt is subjected to both high temperature and mechanical shear stress at the same time. The second stage of degradation takes place in the solid state during application of the final product. The development of polymers in the world is constantly progressing and it is necessary to continuously test their properties.
6. References

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