THE EFFECT OF SIMULATED CLIMATIC CONDITIONS OF AGEING ON PROPERTIES OF SELECTED POLYMER COMPOSITES

Streszczenie

Nowadays designers and engineers readily turn to plastics because they offer combinations of properties not available in any other materials. Plastics offer advantages such as lightness, resilience, resistance to corrosion, colour fastness, transparency, ease of processing, etc., and although they have their limitations, their exploitation is limited only by the ingenuity of the designer. Degradation of the polymers under the influence of temperature, light, humidity and oxygen leads to changes in structures such as the increase in crosslinking, reducing the degree of polymerization, oxidation or recrystallization of the molecular chains. The result of the ageing process are reversibly or irreversibly a deterioration of processing and changing of properties. The aim of this paper was the comparison of change of selected properties of polymer composites used for the production of parts in the electrical industry in changing the thermal conditions. Materials ABS, PA6 and PBT were tested and the samples were exposed to different climatic conditions. Static tensile test and 3-point bend test were used for testing and samples were used by injection molding.

Key words: polymer composites, simulated climatic condition, ageing, polymer properties.

Introduction

In recent years, the lifetime of polymer materials and coatings has been extended continuously in many cases. In turn, this means that the times required for testing these materials have also increased. However, such extended testing times are very often unacceptable for economic reasons. Therefore it is an ongoing demand for material testing technology to shorten test times. One possible method of achieving this is to employ significantly increased levels of irradiance and temperature for testing under simulated conditions in weathering instruments. One of the key factors which make thermoplastics attractive for engineering applications is the possibility of property enhancement through fiber reinforcement. Composites pro-

duced in this way have enabled plastics to become acceptable in, for example, the demanding aerospace and automobile industries and they have offer a good combination of strength, stiffness and price\textsuperscript{3}.

**Degradation of polymers**

Polymer degradation is a change in the properties (tensile strength, color, shape, etc.) of a polymer or polymer based product under the influence of one or more climatic factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling\textsuperscript{4}. The changes in properties of polymers (based on degradation) are often termed "ageing, degradation, deterioration, corrosion or violation". We distinguish natural and artificial ageing. The term natural ageing means the slow ongoing change of plastics properties by light, air, carbon dioxide and water. These changes, first limits and ultimately make impossible to further use of plastic product. At most plastics are ageing appearing by yellowing and embrittlement\textsuperscript{5,6}. Degradation of polymers can be different, most commonly UV degradation, thermal degradation, chemical degradation etc.

Many natural and synthetic polymers are attacked by ultraviolet radiation, and products using these materials may crack or disintegrate if they are not UV-stable. The problem is known as UV degradation, and is a common problem in products exposed to sunlight. Continuous exposure is a more serious problem than intermittent exposure, since attack is dependent on the extent and degree of exposure. Exposure to ultraviolet (UV) radiation may cause significant degradation of many materials. UV radiation causes photooxidative degradation which results in breaking of the polymer chains, produces radicals and reduces the molecular weight and causing deterioration of mechanical properties\textsuperscript{7}.

**Thermal degradation** of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties\textsuperscript{8}.

\textsuperscript{5} T. Garbacz, A. Tor, *Wpływ zawartości środka porującego na właściwości użytkowe zewnętrznych powłok kabli*. Polimery 2007, 52, 4, 286.
Chemically degradation of polymers is a type of polymer degradation that involves a change of the polymer properties due to a chemical reaction with the polymer’s surroundings. There are many different types of possible chemical reactions causing degradation however most of these reactions result in the breaking of double bonds within the polymer structure. Ageing tests which enable the evaluation of the degree of changes in the performance (mechanical strength, hardness, brittleness, elasticity, color, texture, reliability, durability) occurring in the polymers is carried out under the conditions for this specially designed and controlled, for example, increased temperature, humidity, mechanical fatigue or exposure to light and different kinds of radiation. Significant deterioration in the mechanical properties of polyolefins are observed after two weeks of accelerated ageing at increased temperature, and for engineering polymers after a month. Objects undergone to accelerated ageing help to understand the mechanisms of degradation and allow for an accurate description of the phenomenon. After the test, follow the measurement of the change in functional parameters and compare it to the original parameters. Accelerated ageing method does not give the real picture of change (unknown factor of shorten the experiment time), such as ageing by weathering properties, therefore, must assume a large margin of error, but it is well suited for comparative studies of different types of materials.

Material lifetime is the period during which practically important properties are maintained at the sufficient level for the proper function of the product. It depends on the material properties and on the conditions under which the product is used. Self-degradation of polymers can occur as a result of exposure to light radiation polymer’s surface, temperature, cold, chemical compounds or microorganisms. The surface of the polymer can be disturbed and with the subsequent diffusion of the outside environment towards inside of the polymer. The polymer can react with the environment. As a result these reactions may also occur to diffusion on the surface of polymer or to their release into the environment from the polymer.

**Experimental procedure**

The samples for experiments were produced by injection molding on machine type Arburg – Allrounder 320C. Defective samples were excluded and all test specimens used in the experiments did not reveal any deficiencies. After the conventional injection molding process, the samples were exposed to different climatic conditions; they are having an impact on ageing of materials. For a period one

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month samples were exposed to the effects of ultraviolet radiation by intensity 4x 18W into UV chamber. The samples were irradiated continuously for 12 hours, followed by a 12 hour interval. Within one month of UV radiation worked to a total of 360 hours. The others part of the samples was placed in a freezer at BEKO CSA22020 -20°C ± 3°C for a period one month. Heat condition was carried out in a laboratory dryer ECOCELL 55. The samples were exposed to a temperature of + 50°C for 12 hour cycle for all tested materials for a period of one month.

Tensile properties of tested materials were evaluated according to STN EN ISO 527-1, 2 and test specimen of type 1A was used for tests. Static tensile test was performed on the test machine TIRA-test 2300. Sample was pinned to jaws of the ripper and was loaded with the force until the disruption. Determination of bending strength was performed according to STN EN ISO 178 on the test machine TIRA-test 2300 until the disruption of sample. Five (5) samples from each type of material and for the each condition were tested according to standards.

Materials

Three types of polymer composites - material ABS (marks LG ABS XR 401), material PA6 (marks Silamid SV30 364) and material PBT (marks Crastin PBT SK 605NC010) were used for experiments.

ABS (Acrylonitrile-Butadiene-Styrene) is a low cost engineering plastic that is easy to machine and fabricate. This material is a ter-polymer of acrylonitrile, butadiene and styrene. ABS is suitable for injection molding and contains flame retardant. ABS is an ideal material for structural applications when impact resistance, strength, and stiffness are required. It is widely used for machining pre-production prototypes since it has excellent dimensional stability and is easy to paint and glue. Impact resistance does not fall off rapidly at lower temperatures. Stability under load is excellent with limited loads. Thus, changing the proportions of its components ABS can be prepared in different grades. Main applications areas are automotive, engineering and electrical industry.

PA6 (Polyamide 6) is a tough, abrasion-resistant material. It has improved surface appearance, creep resistance, and processability compared to polyamide 6/6. It also can be molded about 30°C lower with less mold shrinkage because it is slightly less crystalline. Adversely, PA 6 has a lower modulus and absorbs moisture more rapidly than PA 6/6. Moisture acts as a plasticizer, reducing tensile strength and stiffness and increasing elongation. But, while absorbed moisture reduces many properties, nylon owes part of its toughness to the plasticizing effect of moisture. As moisture content rises, significant increases occur in impact strength and general energy absorbing characteristics.

PBT (Polybutylene Terephthalate) is a crystalline, high molecular weight polymer that has an excellent balance of properties. Crastin® SK605 NC01 is a 30% glass fiber reinforced, lubricated polybutylene terephthalate resin for injection moulding. Because the material crystallizes rapidly, mold cycles are short and molding temperatures can be lower than for many engineering plastics. Disadvantages of PBT is hard to fill thin parts, glass filled resin very prone to warp and poor resistance to acids, bases and hydrocarbons. PBT provides excellent dimensional properties and stability versus moisture (better than nylon from a molding and performance standpoint) and good heat resistance. These properties make it particularly well-suited for lighting bezels, connectors, relays, switches, distribution boxes and fiber optic cable jackets.
**Experimental results**

The results of the static tensile tests are presented in Fig.1-2. Graphical dependence of the average measured values of bending strength- $\sigma_f$ - of tested samples in selected simulated condition is shown in Fig. 3.

Electrical properties namely volume resistivity were measured on samples of the PBT material exposed to UV chamber. The device type teraohmmeter E6-13A was used for measurement. Measurement results are shown in Fig. 4.

![Graphical representation of tensile test results](image1)

**Fig. 1.** Tensile test results ($\sigma_M$) after ageing of tested materials

![Graphical representation of tensile test results](image2)

**Fig. 2.** Tensile test results ($\varepsilon_M$) after ageing of tested materials
Fig. 3. Bending strength ($\sigma_f$) after ageing of tested materials

Fig. 4. Volume resistivity of PBT material after ageing

Fracture of PBT material after testing is shown in Fig. 5. Fracture surfaces of test specimens were also observed on the scanning electron microscope JEOL JSM - 7000F – Fig. 6-8.

Fig. 5. Fracture of PBT material after a) tensile test, b) bend test
Figure 6 to Figure 8 shows the surface fracture of a polymer composite after tensile test. Holes after ripped fibers are marked with arrows. In glass fiber there was a cracking of fibers and the crack slowly expanded. The ridges and stream characterizes the direction of fracture development. Figure 8 shows the detail of ABS material breach, at which the fault is shown as the peeling of layers.
Conclusion

This paper deals with the impact of ageing on the selected properties of polymers composites in different simulated climatic condition. Based on performed tests to determine the properties of tested material were given next conclusions:

- Values of $\sigma_M$ at tested materials changed minimally compared to samples from the standard condition.
- The greatest difference values of $\varepsilon_M$ was observed at ABS material in low-temperature environments – an increase of 46% compared to samples from the standard condition. At the tensile test and bend test were created small cracks in different locations over the length of the samples.
- The greatest difference values of $\sigma_f$ was observed at PA6 material in $+50^\circ C$ temperature environments - an increase of 14% compared to samples from the standard condition.
- At the sample of PBT material after UV degradation is clearly visible the colour change - from white to yellow. In other investigated materials in various conditions the colour change didn’t occurred.
- The change in volume resistivity was only in the conditions at $+50 ^\circ C$ at PBT material, which should be taken into account when applying of material PBT in practice.

According to the tests carried out we can conclude that products made from the ABS and PA6 materials and exposed to different climatic condition do not significantly change their properties and may be exposed to the external environment. It is necessary to consider the use of PBT material in external environment because after UV degradation there was the colour change of the surface of samples. The product made from PBT material should not be used to the external environment in terms of design of products.

Acquired knowledge in this paper is only part of the broad field of engineering plastics testing. Mentioned experiments require further study of changes in the structure of plastic material as well as complement of other technological tests according to applications of the investigated materials in practice.

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Obecnie projektanci i inżynierowie chętnie sięgają po tworzywa sztuczne ze względu na kombinacje właściwości, które oferują, niesiągalne w przypadku innych materiałów. Tworzywa mają liczne zalety, takie jak: lekkość, sprężystość, odporność na korozję, trwałość koloru, przejrzystość, łatwość obróbki, itd. i mimo swoich ograniczeń, ich zastosowanie jest ograniczone tylko poprzez pomysłowość lub jej brak u projektanta. Degradacja polimerów pod wpływem temperatury, światła, wilgotności i tlenu prowadzi do zmian w strukturze, takich jak wzrost sieciowania, redukcja stopnia polimeryzacji, utlenianie czy też rekrystalizacja łańcuchów molekularnych. Skutki procesu starzenia to odwracalne bądź nieodwracalne pogorszenie przetwarzania i zmiana właściwości. Celem niniejszej pracy było porównanie zmian wybranych właściwości kompozytów polimerowych stosowanych w produkcji części w przemyśle elektrycznym przy zmieniających się warunkach termicznych. Badano materiały ABS, PA6 PBT, których próbki poddane działaniu różnych warunków klimatycznych. W badaniach wykorzystano statyczne próby rozciągania oraz 3-punktowy test giętkości, natomiast próbki były wykorzystane w procesie formowania wtryskowego.

Słowa kluczowe: kompozyty polimerowe, symulowane warunki klimatyczne, starzenie się, właściwości polimerów.