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Effect of Accelerated Ageing Conditions on the Protective Properties of Anti-Blow Products

Abstract
This article presents research on protective packets of anti-blow vests in use among law enforcement services of the Polish Police. Basic information on the ageing process of polymer plastics are given. The types of ageing are presented as well as the phenomena causing the process within the plastics. The approved programme of accelerated ageing tests of the protective packets of anti-blow vests was characterised. The conditions of the tests were defined as well as the groups of properties to be tested, which are the criteria of the resistance of the test objects to ageing. The results of the research on the protective properties of anti-blow packets before and after tests of laboratory ageing are presented. The results of the research on packets of anti-blow vests after 10 years of real-time ageing are also presented. A concluding analysis of the research results and impact of ageing processes on the protective properties of the products tested was performed.

Key words: *ageing, accelerated ageing, anti-blow products, protective properties.*

Introduction

The law enforcement services of the Polish Police use some anti-blow protective products in operations, including helmets, vests, limb protectors, as well as products featuring a multi-layer and multi-material structure.

Virtually, every element of anti-blow protection is made of plastics like polyethylene, polypropylene, polyvinyl chloride, polycarbonate, polyesters, polyamide, etc. Plastics are subject to ageing i.e. they change their properties as time passes by. This is caused by the impact of many factors - physical, chemical or biological, among which the following may be mentioned: visible light within all the range of the spectrum, ionising radiation, oxygen, heat, humidity and active chemical compounds – both organic and inorganic [1].

Due to the origin of the process, two types of ageing might be distinguished: real-time and simulated at accelerated conditions. Ageing is also classified depending on the source of the phenomena that cause the process and on the kind of environment in which it occurs. In the case of materials exploited outdoors, the impact of climatic agents (sunlight, heat, rain and wind) causes the progressive deterioration of a material's properties. Such a process is called atmospheric ageing, which occurs according to two basic mechanisms: photo-oxidation and thermal oxidation. Photo-oxidation is a result of radiation, mainly of the UV band, whereas thermal oxidation happens on exposure to oxygen at raised temperatures [2].

The rate of ageing mainly depends on the kind of plastic and conditions of usage. Ageing may be of a chemical or physical nature. Every plastic is subject to chemical ageing, which means alterations in the chemical structure of the polymer on exposure to light, UV radiation, oxygen from the atmosphere, temperature or humidity [3 - 7]. Chemical ageing is characterised mainly by a loss of good mechanical properties. Other symptoms are tarnishes, crazings and bronzes. Chemical ageing causes plastic degradation, consisting of a line of chemical processes linked to the creation of oxides and peroxides, cracking macromolecular chains, cross-linking, and the creation of chemical double bonds (reason for bronzes). Manufacturers of plastics prevent early chemical ageing by adding a packet of stabilisers, anti-oxidants and UV-stabilisers, volumes and combinations of which depend on the kind of plastic and its use.

Physical ageing is a process which only plastics exploited below their glassy temperature are subject to. The nature of physical ageing is a change in the compaction of macromolecules at the amorphous phase, which leads to brittleness and the easy cracking of the material [8 - 12]. The process of physical ageing is inherently reversible: heating the material above the glassy temperature and cooled back, may restore its good properties. Unfortunately, you cannot do this with ready-made goods since they lose their shape upon heating. Partially-crystalline plastics display other kinds of changes, time-related and temperature-related, which consist in re-crystallising or improving the crystallisation of the material. Re-crystallisation also usually causes some deterioration of mechanical properties and loss of the material's ability to become deformed in a malleable way.

The assessment of materials' resistance, including plastic products, to environmental conditions requires prior execution of research on ageing under real conditions anticipated during exploitation i.e. so-called proving ground tests, consisting in locating samples of a given material or ready-made product outdoors and exposing them to ageing for a period no shorter than a year. The minimum time of real-time ageing assumed for the research of plastic is 5 years. The time-consumption of such research has forced the development of accelerated ageing methods which simulate natural conditions inside of laboratory apparatus, thus

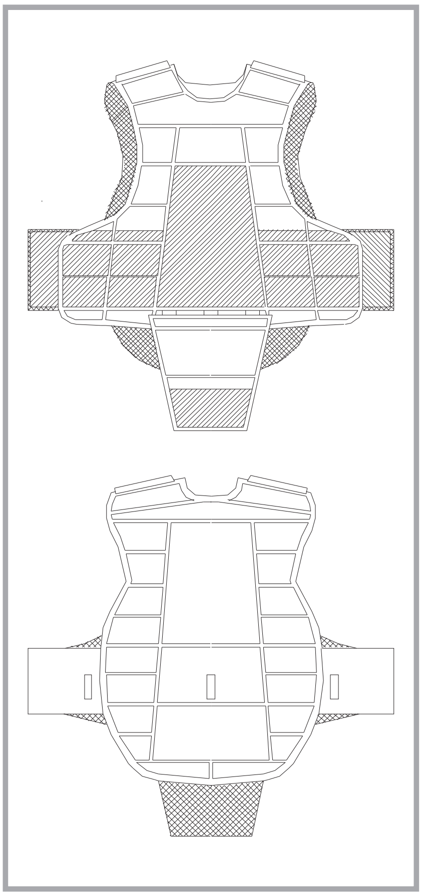

Figure 1. Anti-blow protective vest.

allowing the intensifying action of agents to impact the polymer and accelerate the process of ageing [1].

Object of research

The objects of the present accelerated ageing research were protective packets of anti-blow vests (protection of the Patent Office of the Republic of Poland – P 327897):
- new and
- after 10 years of usage under Central European climate conditions.

The design i.e. the arrangement and thickness of layers and material composition as well as the materials and their properties of all the packets tested were the same.

Currently the anti-blow vest (***Figure 1***) is in use among the law enforcement forces of the Polish Police. All of its area consists of anti-blow protective packets (items A, B i C at ***Figure 2***) that feature a multi-layer segmental structure [13]. The packets differ in the thickness and kind of materials applied. The anti-blow packets marked "B" in ***Figure 2*** were chosen for testing for two reasons: They cover the largest part of the vest area, and the protective function they perform. They consist of the materials specified in ***Table 1***.

Programme of research on ageing

Determining the conditions of ageing tests

The protective properties of an anti-blow packet are mainly determined by three, chemically different materials i.e. foamed polyethylene with closed cells (PE foam), panels of polyvinyl chloride (PVC), and foamed polyurethane plastic of tubular structure (PU foam).

Presumably the subject of analysis of the ageing tests is the change in the protective properties of the packet, considered as a whole, but not variations in its components. The impact of ageing conditions on the individual materials of the packet is caused by multiplanar phenomena, specifically their multiplicity and variety, thus requiring separate study.

Standard PN-EN ISO 2440: 2001: "Flexible and rigid cellular polymeric materials. Accelerated ageing tests" [14] was the basis for the development of an ageing test programme for the ternary packet.

The ageing of the anti-blow packets was conducted in two ways:
- under hot and dry conditions in a thermal chamber from BINDER GmbH

Parameters of the ageing process:
  - temperature – 70.0 ± 0.5 °C, which is the temperature recommended by Standard PN-EN ISO 2440: 2001 for olefin polymers. Since the

Table 1. *List of materials included in the B-packet of an anti-blow vest.*

Item	Name of material
1	External fabric: thickness – 0.6 mm, mass per unit area – 265 g/m^2
2	Flexible foamed plastic of tubular structure (PU foam): thickness – 5.0 mm, apparent density – 25 kg/m^3
3	Lining fabric: thickness – 0.4 mm, mass per unit area – 215 g/m^2
4	PVC impact-resistant hard panel: thickness – 1.0 mm, apparent density - 915 kg/m^3
5	Foamed polyethylene with closed cells (PE foam): thickness – 20.0 mm, apparent density - 30 kg/m^3

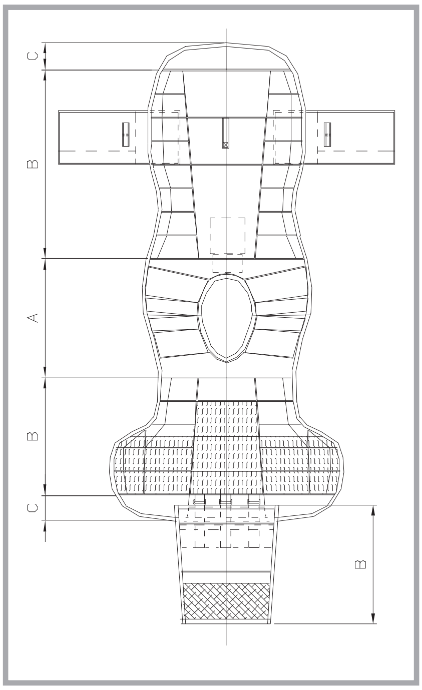

Figure 2. *Location of anti-blow protective packets in the vest.*

main compound of the packets was PE foam, a temperature of 70.0 ± 0.5 °C was assumed as the ageing temperature of the whole packet,
  - ageing time – 168 days subdivided into the stages:
    - stage I – 8 cycles, 7 days each (total 56 days),
    - stage II (continued ageing) - 8 cycles, 14 days each (total 112 days),
  - number of samples – 8 packets of A4 size for each ageing cycle,

- under hot and humid conditions in the thermal chamber

Parameters of the ageing process:
  - temperature 70.0 ± 0.4 °C,
  - ageing time 5 cycles, 28 days each (total 140 days),
  - humidity 50.0 ± 1.5% (safe level for this type of chamber),
  - number of samples 1 packet of A4 size for each ageing cycle.

Methods and criteria for the assessment of the test products' resistance to ageing

The anti-blow packets aged under laboratory conditions were tested at the end of every ageing cycle for changes in the following properties :
- *resistance to impact* – according to procedure PBB-07 'Impacting tests. Estimating the level of energy attenuation by body protectors" of the „MOR-

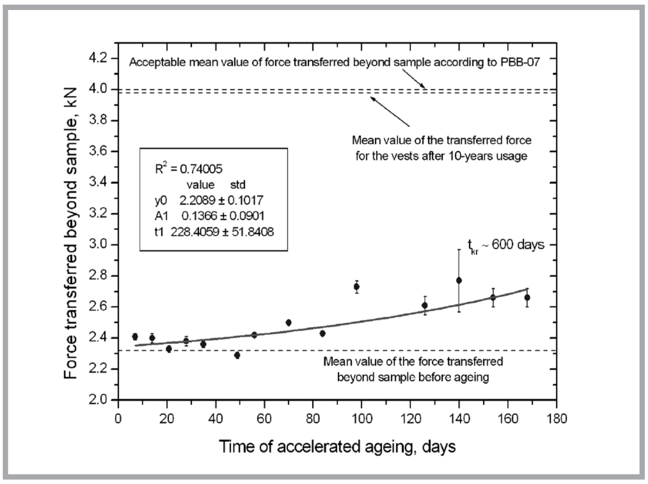

Figure 3. Dependence of aged packets' resistance to blow on the ageing time under hot and dry conditions (temp. 70.0 ± 0.5 °C).

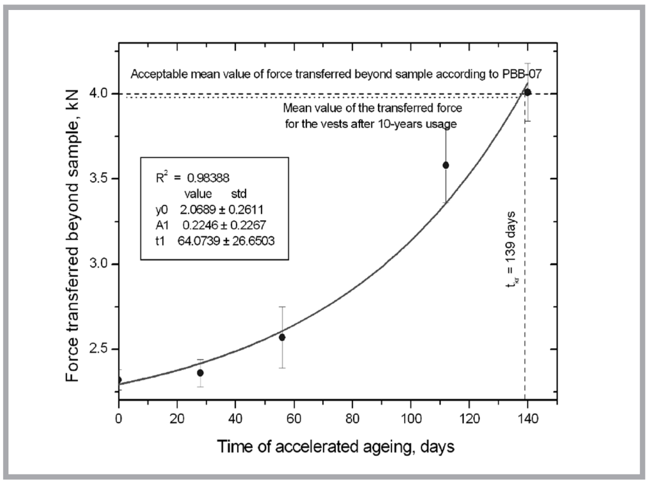

Figure 4. Dependence of aged packets' resistance to blow on the ageing time under wet (50.0 ± 1.5% humidity) and hot (70.0 ± 0.4 ºC) conditions.

ATEX" Institute, developed on the basis of Standard BS 7971-8: 2003 [15]. Tests were executed using a drop tower testing machine manufactured according to the requirements of Standard BS 7971-4: 2002 [16]. The main components of the workstation are an anvil with a sensor for measuring the magnitude of the impact force transferred, and a hammer for impacting the surface subjected to testing. Testing consisted in placing an A4-size packet sample on a cylindrical anvil of 150 mm radius and hitting it with a flat impactor with an energy of 20 J at 3 different points on the packet, determined with respect to the boundary conditions. The magnitude of the force transferred beyond the sample was registered, which typifies the resistance of the product to blow and should not exceed the critical value (4 kN).

- *stress-strain characteristics in compression* – according to Standard PN-EN ISO 3386-1: 2000 "Polymeric materials, cellular flexible. Determination of stress-strain characteristics in compression. Low-density materials" [17].

A tension tester from ZWICK was used for the testing, which allowed to compress the test samples of the packet of 10 × 10 cm size between the base plate the sample was placed on and the pressing plate. The sample was subjected to pressing at a constant velocity of 100 ± 20 mm/min. Each test was executed on 3 samples. The force in N which caused 40% compression was registered, and the value of the pressing tension in kPa was calculated according to the formula stated in the Standard.

Results and discussion

On the basis of the test results obtained from anti-blow packets both before and after each ageing process cycle, graphs of the impact of the ageing time were drawn with respect to the following:

- the force in kN transferred beyond the sample tested, according to PBB-07. The force reflects the resistance of the packet to blow. ***Figure 3*** shows a graph of the dependence under hot and dry conditions, while ***Figure 4*** depicts that under hot and humid ones. The results of the tests, shown in ***Figures 3*** and ***4***, were approximated with the exponential function:

$$y = y_0 + A_1 e^{x/t_1}$$

where: y_0, A_1 and t_1 are coefficients calculated for the function chosen on the basis of experimental data

- the stress tensile required to compress the packet down to 40% of its original thickness – CV_{40} in kPa under hot and dry conditions (***Figure 5*** see page 64) and humid and hot ones (***Figure 6*** see page 64) .

It should be emphasised again that because of the assumption made before (see page 62 - **Determining the conditions of ageing tests**), they are the results of tests of a whole packet. The analysis of the impact of the ageing of each of the materials applied in the packet on the behaviour of the whole packet, regarding their diversity, both the chemical and physical properties is the subject of separate research presently carried out by us.

Table 2 presents the results of tests on packets after a 10-year period of usage.

The resistance of the test protective packets to blow was measured with the magnitude of the force transferred beyond the sample. Its critical magnitude of 4 kN is defined in Standard BS 7971-8: 2003. On the basis of the analysis of the test results and graphs presented in ***Figures 3*** and ***4***, one may state that the impact of the ageing time on the resistance to blow of anti-blow packets depends significantly on the conditions of the ageing process. Under hot and dry conditions, despite the long time of ageing (168 days), only in-

Table 2. Results of tests on packets after real-time ageing (10 years).

Item	Parameter	Results of tests of vest no.			
		1	2	3	4
	Pressing tension at 40% compression CV_{40}, kPa:				
1	measurement 1	48.2	46.5	40.8	41.5
	measurement 2	40.7	41.3	37.7	37.0
	measurement 3	39.3	39.8	36.9	35.4
	measurement 4	39.7	39.4	36.6	35.4
	Mean value	**42.0 ± 4.2**	**41.7 ± 3.3**	**38.0 ± 1.9**	**37.3 ± 2.9**
	Resistance to blow (maximum force transferred beyond test sample), kN				
2	measurement 1	3.3	3.6	4.4	4.0
	measurement 2	3.4	3.6	4.7	3.8
	measurement 3	3.5	3.8	5.4	4.1
	Mean value	**3.4 ± 0.1**	**3.7 ± 0.1**	**4.8 ± 0.5**	**4.0 ± 0.2**

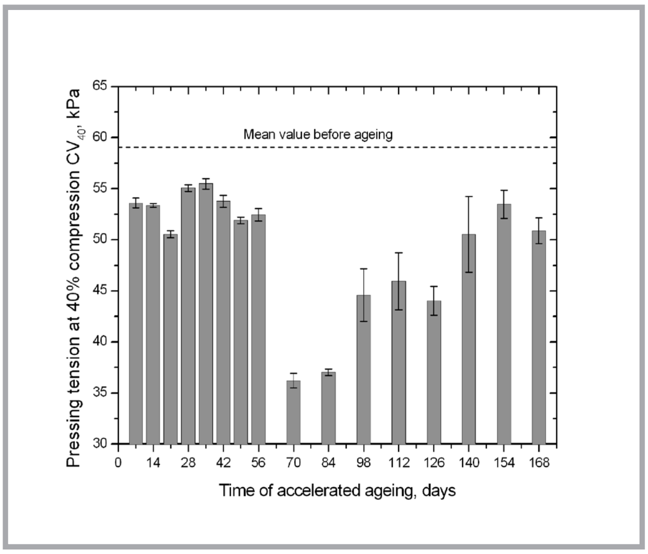

Figure 5. Effect of the ageing time on the pressing tension at 40% compression under hot and dry conditions (70.0 ± 0.4 °C).

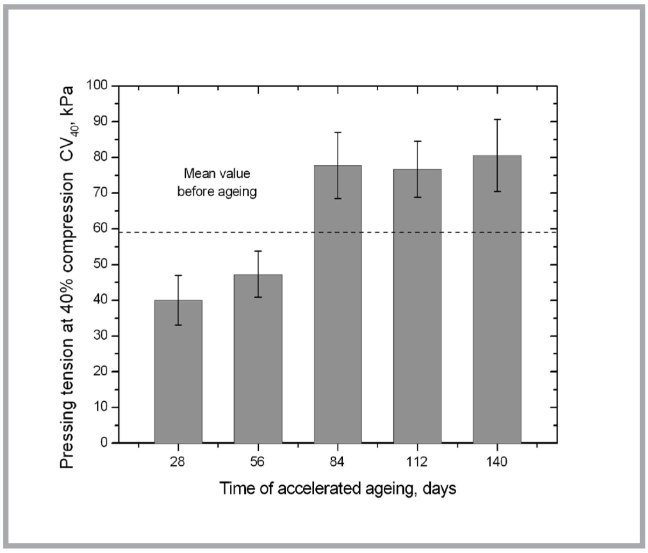

Figure 6. Effect of the ageing time on the pressing tension at 40% compression under hot and wet conditions.

significant changes in the parameter were observed (maximum ca. 21%), whereas at high temperature (70.0 ± 0.4 °C) and under humid conditions, the critical time, after which the magnitude is passed, is more than 4-times shorter than under hot and dry conditions.

The results of testing the packets of used vests (***Table 2***) show that after 10 years of real-time ageing, the resistance to blow of those products reaches the critical magnitude i.e. 4 kN.

The pressing tension at a compression of 40% also shows remarkably faster changes under hot and wet conditions (***Figure 6***) than under hot and dry ones (***Figure 5***). The former case shows a remarkable increase in the parameter as the time of ageing passes (feeling of the packet getting harder). The latter case i.e. hot and dry conditions, shows some decrease in CV_{40} during the first cycles of ageing, but as time passes, an increase in the parameters is observed.

The effect observed is new, and its explanation requires further research e.g. at the level of each component of the packet.

Conclusions

1. The present research proves the significant impact of ageing conditions (temperature, humidity) on the rate of proceeding the ageing processes.
2. The conditions of the Central European climate, where anti-blow vests are actually used, feature a humidity within a range of 40 - 60%, whereas, considering the temperature, are softer than those assumed for the programme of accelerated ageing research.
3. Degradation processes occur much more slowly in natural conditions of use than in laboratory conditions, as the results of tests on a vest after 10-years of exploitation prove.
4. The arrangement of the 3 materials selected, applied in the protective packet of anti-blow vests, provides a high level of protection throughout a long period of usage.
5. The research described in the article confirms the correctness of the method chosen for the laboratory simulation of the ageing of anti-blow packet.

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