Investigation of the resistance to environmental stress crack of high density polyethylene parts
(Rapid Communication)

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Abstract: The research methodology for determining of the environmental stress cracking resistance (ESCR) of polymeric injection molding parts was proposed. The investigations of ESCR were carried out on the original laboratory stand. For the tests samples prepared in accordance with the standards (ISO 22088 and ISO 16770) and real objects (threaded closures) were used. The values of destruction time of samples were determined using both stable and variable loads. Studies have shown that ESCR of prepared samples depends on both their design and material properties.

Keywords: environmental stress cracking resistance, cracking of polymeric parts, packaging closures.

Badanie odporności na środowiskową korozję naprężeniową w wytworach z polietylenu dużej gęstości

Streszczenie: Zaproponowano metodologię oznaczania odporności na środowiskową korozję naprężeniową (ESCR) wytworów otrzymywanych metodą wtryskiwania. Badania ESCR przeprowadzono na oryginalnym, uniwersalnym stanowisku laboratoryjnym własnej konstrukcji. Do testów użyto próbek przygotowanych zgodnie z normami (PN-EN ISO 22088 i ISO 16770) oraz obiektów rzeczywistych (zamknięć gwintowanych). Wartości czasów zniszczenia próbek wyznaczano z zastosowaniem stałych lub zmiennych obciążeń. Badania wykazały, że ESCR przygotowanych próbek zależy zarówno od ich cech konstrukcyjnych, jak i właściwości materiałów.

Słowa kluczowe: odporność na środowiskową korozję naprężeniową, pękanie elementów polimerowych, zamknięcia opakowań.

Environmental stress cracking (ESC) is a physical phenomenon, defined as premature cracking of the polymer as a result of the combined action of stress and the liquid in which it is immersed. The crack is initiated at a craze, which is formed at the point of stress concentration. Exposure to the surface-active substances such as alcohols, oils and detergents enhances craze formation as well as accelerates the crack propagation [1, 2]. However, these phenomena result not from chemical degradation of the polymer but from plasticizing influence of the surface-active compounds [3]. Environmental stress crack resistance (ESCR) of the materials cannot be determined by conventional measurements allowing the assessment of polymer mechanical properties [4]. For this purpose it is necessary to conduct special studies according to PN-EN ISO 22088 and ISO 16770 standards, in which detergent with the trade name IGEPAL (CO-630) is usually used as a crack accelerating compound [4, 5].

Polymeric threaded closures of containers are the products in which the risk of ESC is relatively high, which is demonstrated in Fig. 1. Moreover, high requirements for polymer containers make it necessary to evaluate their utility functions, depending on the properties of the applied materials [6–9], processing parameters and environmental factors [10].

The aim of this work was the investigation of the influence of geometric features of PE-HD screw caps on their ESCR. Furthermore, ESCR of different types of PE-HD commonly used in the threaded closures production was determined. Two types of specimens were used in the measurements, namely small a dogbone specimen and a beam-shape specimen, compliant with the standards PN-EN ISO 22088 and ISO 16770, respectively.

The measurements were carried out using the original self-designed device, which allows determining boundary cracking time of the research object under defined

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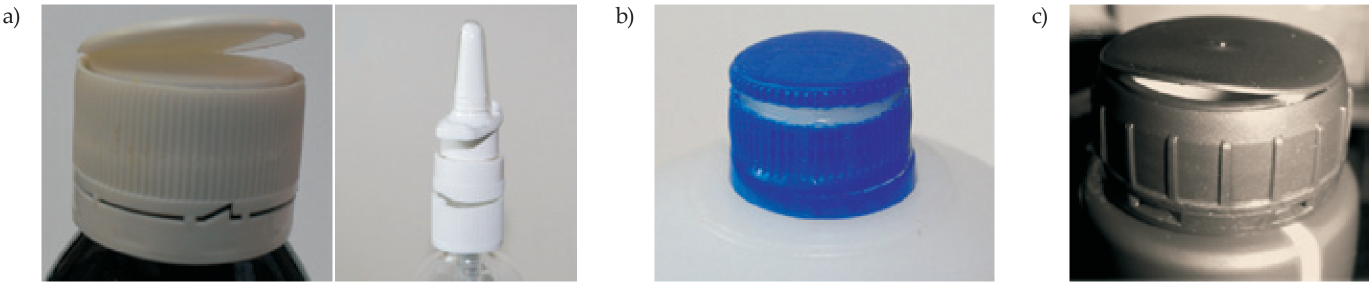

Fig. 1. Samples of environmental stress cracking in PE-HD packaging closures: a) pharmaceuticals, b) detergent, c) automotive fluid

environmental conditions and constant or variable load. The apparatus allows testing of standardized samples and real objects such as threaded closures [11, 12].

EXPERIMENTAL PART

Materials

The standard specimens have been made of PE-HD materials used for the production of threaded closures like Hostalen GC 7260 [characterized by melt mass-flow rate $MFR_{(190\,°C,\,2.16\,kg)}$ = 8 g/10 min] from Basell Orlen Company, Borealis MG 7547S [$MFR_{(190\,°C,\,2.16\,kg)}$ = 4 g/10 min] from Borealis Company and the last one named Eltex® Superstress™ CAP 508 [$MFR_{(190\,°C,\,2.16\,kg)}$ = 1.8 g/10 min) produced by INEOS Company. PE-HD Hostalen GC 7260 has been used for the production of screw caps.

Samples preparation

In order to keep the same conditions of production (process parameters) standardized specimens were produced in a rheologically balanced laboratory injection mold, presented in Fig. 2.

In the testing according to PN-EN ISO 22088, specimens of 1BA type defined by ISO 527-2:2012 standard were used. In the testing according to ISO 16770:2004, specimens of C

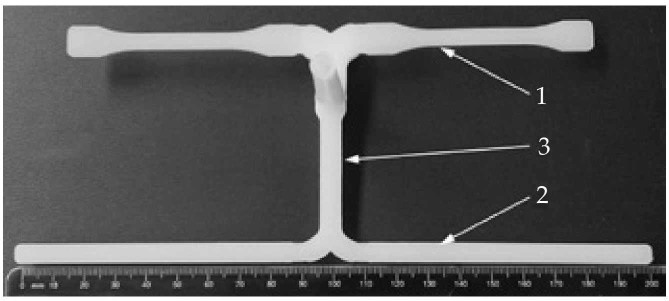

Fig. 2. Different standard samples produced in one cycle; specimens prepared according to PN-EN ISO 22088 (1) and ISO 16770 (2), balancing runner (3)

type were used. In the middle part of a specimen a 1 mm notch was cut around the section using a notch-cutting machine ZNO 2010 Zwick/Roell Company.

Screw caps were made by injection molding and have a single thread with a diameter of 52 mm and 3 mm pitch. The release of screw caps from the cavity in the injection mold during the injection process was done by pushing the plate from the male mold (mold element in cavity). Fig. 3 shows the screw cap before (A) and after the design changes (B) of the selected geometric features. Modifications concerned the geometry of the wall thickness (increase by 40 %) and introduction of the technological ribs at the location of breakage of the screw caps. The original geometry of the screw cap (A) in real conditions of use was not resistant to the ESC. The active environmental bath at 50 °C was prepared with the solution of 2 % IGEPAL CO-630 in demineralized water.

Method of testing

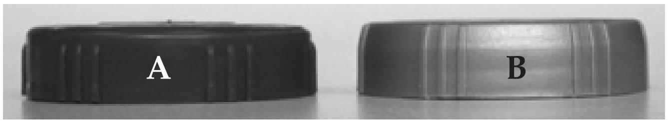

Fig. 3. Threaded closures used in comparative testing: before (A) and after (B) design changes

The tensile strength testing was carried out in the strength machine Z030 (Zwick/Roell). The test parameters were adopted in accordance with ISO 527-2:2012 standard. The basis of the universal stand for testing of ESCR, shown in Fig. 4, is a frame (1), in which a tank guide unit was mounted (2). The guide unit allowed to displace the tank (4) with the working bath up and down. The specimen (13) is fixed with grips (12) to a frame of the testing stand. Force is generated by a weight (3) or strength unit (14) and then it is transmitted by the operating lever (10). The failure of a test piece makes the mechanical sensor send the signal (5) to time-meter (7) (stop counting) and lits cracking signal light (6). The control system is equipped with a switch-key supply and a switch-key heater (9) and it controls the heaters (11) by the thermoregulator (8).

In the study performed on standard specimens and threaded closures ESCR was expressed by measuring of the time to rupture (failure) of a specimen or cracking of the screw cap. The load of the screw cap was performed by a force working perpendicularly to the bottom surface,

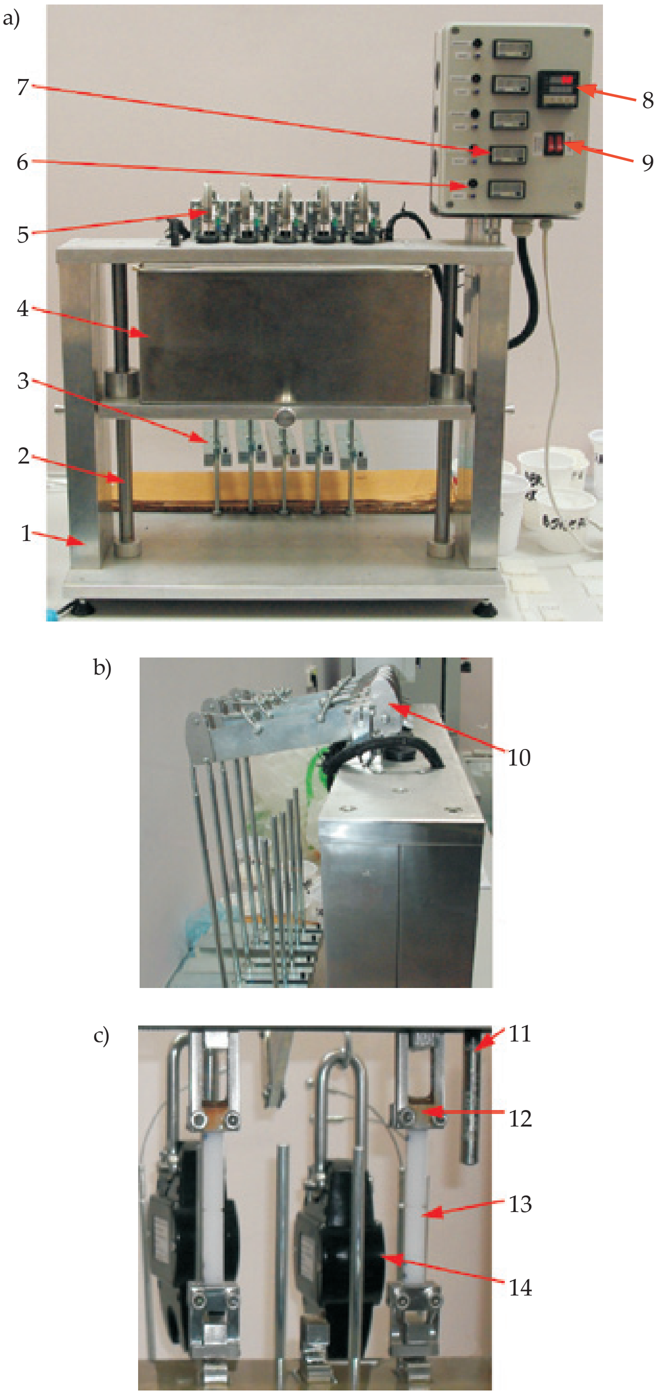

Fig. 4. Universal stand to test (ESCR): a) working state, b) operating levers, c) gripping specimens in operating area (1 – frame, 2 – tank guide unit, 3 – weight, 4 – tank with working bath, 5 – unit with mechanical sensor, 6 – cracking signal light, 7 – time-meter, 8 – thermoregulator, 9 – supply and heater switch-keys, 10 – operating lever, 11 – working bath heater, 12 – grips, 13 – specimen, 14 – strength unit)

the latter of which was responsible for the tightness of the package.

RESULTS AND DISCUSSION

The results of tensile strength for test specimens for selected types of PE-HD are collected in Table 1. Differences in tensile strength in each geometry of the test specimen do not exceed 1 MPa. In the case of strain, differences between the results do not exceed 1 mm. In the case of a specimen according to ISO 16770 with the application of the notch on each face of the specimen resulted in tensile strength by approx. 40 % higher as compared to the specimen according to PN-EN ISO 22088, and in shortening of the strain by approx. 33 % for each test material. The results of the tensile strength measurements are proportionate and they stem from a greater cross-section area of the specimen in accordance with ISO 16770 (cross-section area of 16 mm^2) in relation to the specimen in accordance with EN ISO 22088 (cross-section area of 10 mm^2). Cutting of a notch in the beam-shaped specimen (removal of an outer skin-layer with an amorphous structure) does not significantly affect the change in tensile strength, but it has an influence on reducing the strain. An example of stress-strain curves for Hostalen sample stretching is shown in Fig. 5. The impact of the notch on reducing the strain can be seen.

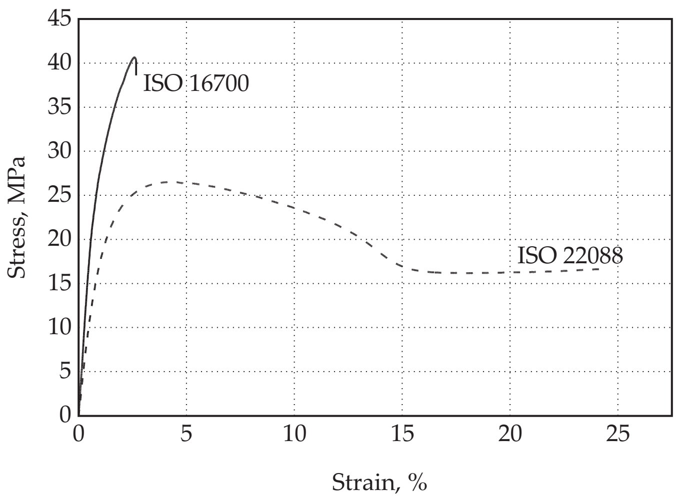

Fig. 5. Comparison of stress-strain curves for the specimens prepared according to PN-EN ISO 22088 and ISO 16770 (sample runs) for Hostalen

Fig. 6 shows the results of the ESCR, given by the cracking time, under increasing stress for the selected materials used

T a b l e 1. The results of tensile strength tests for selected types of PE-HD

Material	Standard defining specimen type			
	ISO 22088		ISO 16770	
	stress, MPa	strain, mm	stress, MPa	strain, mm
Hostalen	26.33	4.33	40.55	2.64
Borealis	25.40	4.77	41.08	3.34
Eltex®	23.46	4.60	41.50	3.29

T a b l e 2. The results of the research of the impact of the design changes in a real plastic part (threaded closure) on ESCR A – screw cap before the design changes, B – screw cap after the design changes

Load, kg	Cross-section of the closure mm^2		Closure tensile stress MPa		Cracking time h	
	A	B	A	B	A	B
2	194.9	329.1	0.101	0.060	19	669
4			0.201	0.119	17	101
6			0.302	0.179	2	24
8			0.403	0.238	1	18
10			0.503	0.298	0.25	8

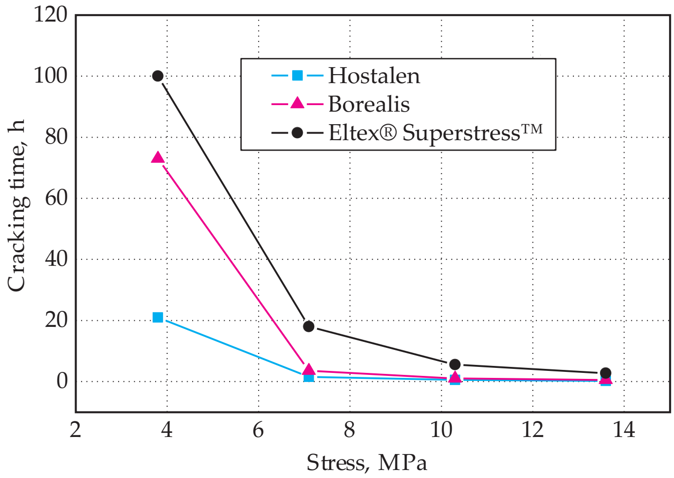

Fig. 6. Results of ESCR for increasing stress in various materials used to produce container closures (bath fluid: 2 % solution of IGEPAL CO-630, bath temp. 50 °C)

in the manufacture of threaded closures of packages. In the case of Hostalen for each stress value, the results obtained are lower than for Eltex by several times. With the increase of the cracking stress, the difference in resistance between the ESCR for Hostalen and Borealis samples are getting smaller. The differences between the selected materials decrease along with the increase in stress cracking values.

ESCR research carried out according to ISO 16770 and research according to PN-EN ISO 22088 are not interchangeable. This is due to the difference between the geometry of the samples (cross-section area and thickness of the specimen), specimen preparation to the test (making of the notch) and the conditions of the study (temperature and stress). The comparison of the results of the ESCR investigation according to both standards for Hostalen is shown in Fig. 7.

Summary of all input and output variables showing the effects of design changes in the screw cap in order to increase ESCR was presented in Table 2. Changes in geometrical features of nuts allowed to increase the cross-section area of the nut most exposed to the presence of ESC by more than 1/3. This resulted in a drop in stress by 41 % in relation to the screw cap before the changes in geometry. Table 2 summarizes the results of comparative tests of a screw cap before and after the design changes made in order to increase ESCR of the threaded connection in the entire package. Modification in the design features of the screw cap has allowed a 16--fold increase in ESCR for the load to be applied with a

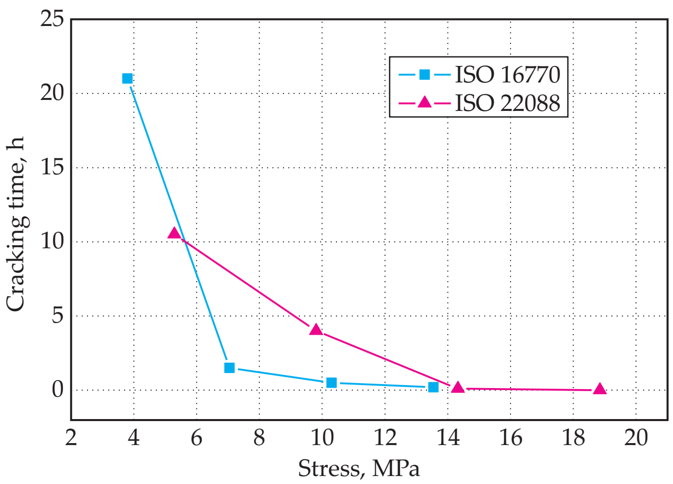

Fig. 7. Comparison of ESCR researches conducted in accordance with ISO 16770 and PN-EN ISO 22088 for Hostalen

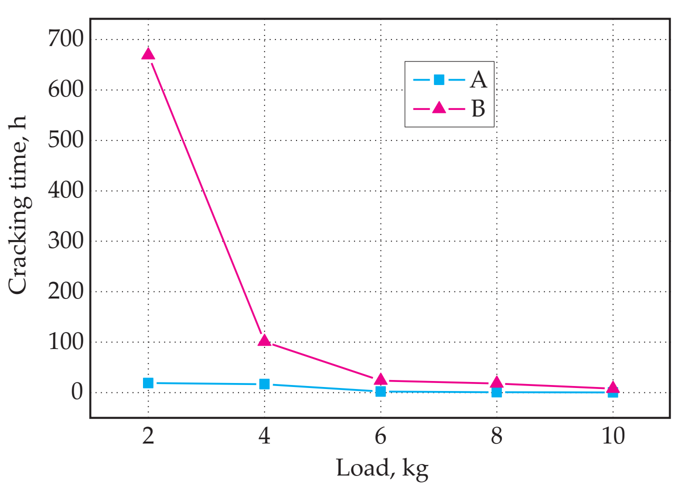

Fig. 8. Results of ESCR tests for the first closure geometry (A) and the second, corrected closure geometry (B) (bath fluid: 2 % solution of IGEPAL, bath temp. 50 °C)

force of 98.07 N. At the force of 19.61 N ESCR increased more than 35-fold. The effect of applying a load on the cracking time before and after the screw cap design changes can be observed in Fig. 8.

CONCLUSION

The universal test stand used in the research enables the assessment of the impact of environmental stress cracking (for varying active substances-fluids) on specimens prepared according to standards (PN-EN, ISO and ASTM) and the real objects (*e.g.*, threaded closures). It was stated that ESCR is affected by both the design features of the threaded containers and properties of the materials. These studies revealed no direct correlation between the results of tests for determining ESCR according to ISO 16770 and PN-EN ISO 22088.

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