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Evaluation of the Elastomeric Composite Self-repair Process for the Construction of Protective Gloves

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Abstract
Preliminary results of the implementation of self-healing polymers in all-rubber protective gloves are presented. The aim of the study was to evaluate the self-healing process of the elastomeric composite in PPE (personal protective equipment). Tests were performed for two types of materials based on methyl vinyl silicone rubber with and without a textile carrier. Assessment of the surface morphology of the materials was performed before and after the self-healing process. The protective properties, including tear, deformation and chemical permeation resistance were determined. Surface damage was simulated to reflect real changes that might occur during work. The materials were damaged by simulated puncture, cutting and abrasion. All tests were performed for samples without damage, with micro damage as well as after self-repair. The results obtained confirm the possibility of using the elastomeric composite tested in the construction of protective gloves and showed the effectiveness of the self-healing process.

Key words: *self-healing polymers, methyl vinyl silicone rubber, protective gloves.*

Introduction

At the beginning of the 21st century, new polymeric materials with properties that allowed them to autonomically repair were developed. Self-healing leads to the recovery of these materials of the same or similar properties to the original ones and thus to its regeneration [1]. It is not difficult to imagine a variety of applications of self-healing materials, from bridges and buildings that repair their own cracks, to car bumpers made of shape memory polymers that automatically go back to their original shape after collisions at low speed.

Over the last decade, scientists in the field of materials engineering have intensively designed and developed so-called "intelligent" materials that support our daily lives.

A topic of particular interest has been the extension of the end of the service life of polymeric and composite materials. Researchers are constantly striving to make the mechanism of self-healing of materials as similar as possible to analogous situations in nature (eg healing of the skin, the growth of broken bones). In addition, the speed of reaction with a minimal contribution of external factors is also very important.

There is a considerable amount of literature on the design and development of materials containing in their structure systems capable of eliminating occurring damage, so-called "self-healing materials" [2-10].

Self-healing can be defined as the ability of a material to heal (recover/repair) damage automatically and autonomously, that is, without any external intervention [11].

Many common terms such as self-healing, self-repairing, autonomic-healing, and autonomic-repairing are used to define such a property in materials. Incorporation of self-healing properties in polymer materials very often cannot perform the self-healing action without an external trigger. Hence we distinguished two types of self-healing mechanism: autonomically self-healing materials and non-autonomic systems. Non-autonomic systems require some type of externally applied stimulus (such as heat or light) to enable a healing function. However, it needs to be underlined that this case allows the healing process to be performed in a controlled way. Autonomic systems, on the other hand, require no stimulus (other than the formation of damage) for operation. These mechanisms do not require human intervention and are entirely self-contained. They resemble biological systems very closely, which deliver healing agents to compromised regions as soon as damage is inflicted.

Until now, the self-repairing of material has been based on three conceptual approaches: the use of micro-encapsulated systems, micro-channels and internal mechanisms [12-16].

Most literature reports the application of self-healing materials in the electronics, automotive, aerospace, and building industries [17-19]. These polymer materials are susceptible to both: mechanical, chemical, thermal and radiation factors. Consequently the direct impact of the factors above leads to the occurrence of micro-damage in the structure of the materials that, as already mentioned, is invisible and difficult to identify organoleptically at the initial stage.

Recently works aimed at designing elastomeric materials with self-healing properties have been carried out. These materials could potentially be used in the construction of personal protective equipment, e.g gloves [20-22].

On the basis of literature data and requirements for gloves protecting against chemical agents, five criteria were defined related to the selection of proper polymeric materials for use in elastomeric protective gloves [23-28].

The first criterion was to define of the types of hazards that cause the micro-damage of protective materials in various work environments. Due to the existence of various types of mechanical hazards occurring in the work environment, the material was micro-damaged by simulated: puncture, cutting and abrasion.

The second criterion was the characteristics of physicochemical parameters of the glove material, such as flexibility and good mechanical parameters. These parameters eliminate the use of materials with self-healing properties

based on micro-capsules, because the necessary amount of the healing agent which provides good effectiveness of the self-healing process results in an increase in rigidity and low deformation ability. Therefore for the pilot study an internal (intrinsic) mechanism of self-repairing which allows to create a flexible polymer foil was selected.

The third criterion was the compatibility of the repair agent with the matrix of the barrier material. To ensure full safety, protective materials should fulfil their role over the entire surface. The substance responsible for the self-repair process should be evenly spread throughout the material. Local aggregation of the healing agent should be avoided, which is a common problem in the case of microencapsulated healing agents (usually monomer). This is not a problem in the case of self-healing polymers based on internal mechanisms, because the substance responsible for self-healing is introduced in the manufacturing process together with the elastomeric mixture.

The fourth criterion was the repeatability of the self-healing process in relation to the intrinsic self-healing mechanism. This mechanism allows for a multiple self-healing process in the same place. Materials dedicated for PPE should increase safety and, at the same time, minimise the amount of materials used.

The fifth criterion was economic and ecological considerations. Interest in the subject of self-healing polymers in protective materials is related to ensuring greater work safety during their use as well as extending their service life. This is of great importance not only in economic terms, but also ecological, translating into reductions of waste of polymer destroyed in the course of exploitation.

On the basis of previous studies on the safe use of protective gloves (the end of service life), the authors observed that such gloves can be affected by various factors which reduce their mechanical properties, and a quick loss of protective properties can be observed. These factors originate from the conditions at the workplace as well as from the interaction between the user and glove, and mechanical stress or multiple contact with one or several substances of different concentrations. It should be emphasised that changes in glove properties cause a reduction in the time of safe use of protective barrier materials, which are not easily identified by workers due to their micro-size, as confirmed by the structure. In an environment where glove material is exposed to harmful chemicals, micro-damage may result in hazards related to faster penetration of dangerous substances into the glove interior [29].

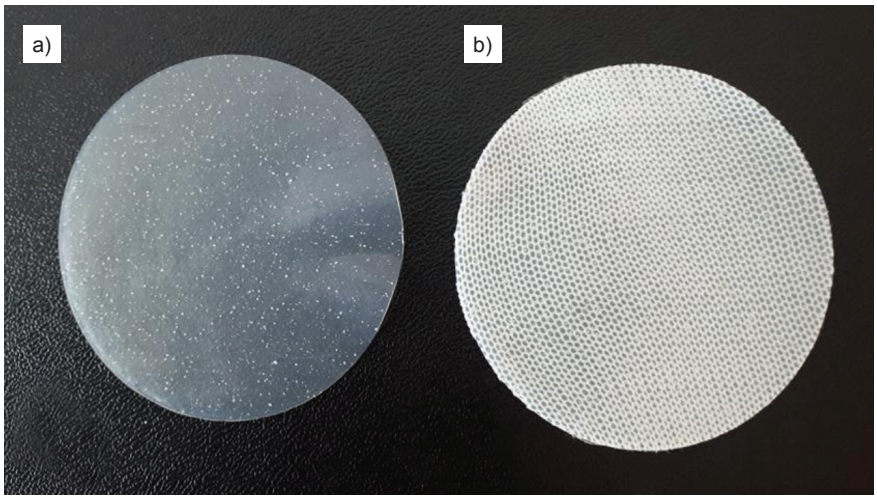

Figure 1. *Elastomer composition with self-healing properties: aminopropylisobutyl-POSS (AP-POSS), aminoethylaminopropylisobutyl-POSS (AEAP-POSS) and amic acid-isobutyl-POSS (AA-POSS): a) film polymer sample, b) polymer sample with textile carrier (100% cotton).*

Currently self-healing polymer materials are examined to minimise economic loss and accidents in the work environment. One of the promising solutions may be the use of self-healing polymeric materials to produce protective gloves. Self-healing materials display the unique ability of self-repair when subjected to failure through fracture/fatigue.

Contemporary research on self-healing polymer applications for protective gloves should be conducted towards obtaining appropriate physicochemical properties of these materials, such as good chemical resistance, adequate flexibility and mechanical strength, and the ability of multiple self-healing.

Experimental

Materials

The object of this study was methylvinylsilicone rubber MVQ polymer 0.07 containing 0.07% of vinyl groups (produced by the chemical Plant 'Silikony Polskie' in Nowa Sarzyna, Poland). The elastomer was cross-linked with dicumyl peroxide (DCP) (Sigma-Aldrich), and the filler was fumed silica Aerosil 380 (Degussa, Germany). Next aminopropyl (isobutyl) -POSS (AP-POSS), a hybrid molecule with an inorganic silsesquioxane at the core, organic isobutyl groups attached to seven corners of the cage, and an aminopropyl group attached to the eighth were added. Three types of POSS : aminopropylisobutyl-POSS (AP-POSS), aminoethylaminopropylisobutyl-POSS (AEAP-POSS) and amic acid-isobutyl-POSS (AA-POSS) containing 5 parts by weight (Hybrid Plastics Company, Fountain Valley, California) were used in this study (***Table 1***).

Variant B is identical to A, with the exception that a textile carrier in the form of cotton fabric is additionally applied. The same relates to the labelling of samples C and D.

The samples were made in the form of a polymer film or composite of polymer and a textile carrier (***Figure 1***). Detailed information of the elastomer composition is described in patent number PL218804(B1) [30].

Table 1. *Shows the composition of self- healing composites of methyl vinyl silicone rubber.*

L.p.	MVQ, phr	DCP, phr	Aerosil A380, phr	AP – POSS, phr	AEAP – POSS, phr	AA – POSS, phr	Textile carier
A	+	+	+	+	0	+	–
B	+	+	+	+	0	+	+
C	+	+	+	0	+	+	–
D	+	+	+	0	+	+	+

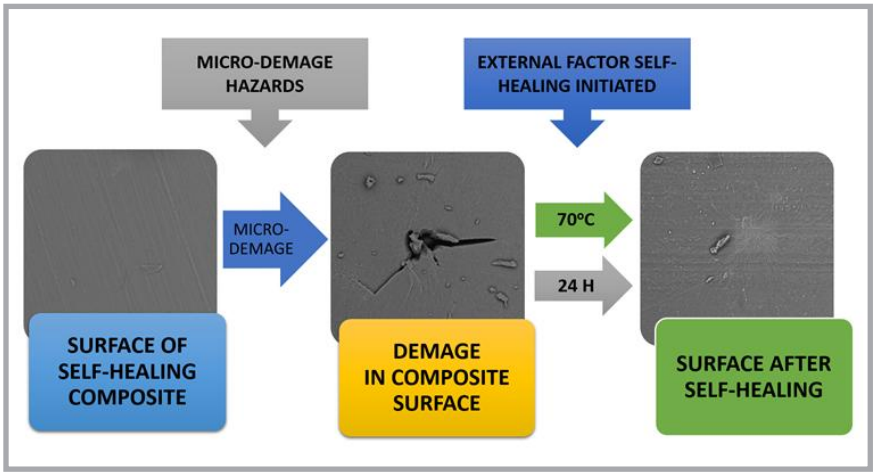

Figure 2. *Scheme showing the operation of the self-repair process with the use of an external stimulus such as temperature.*

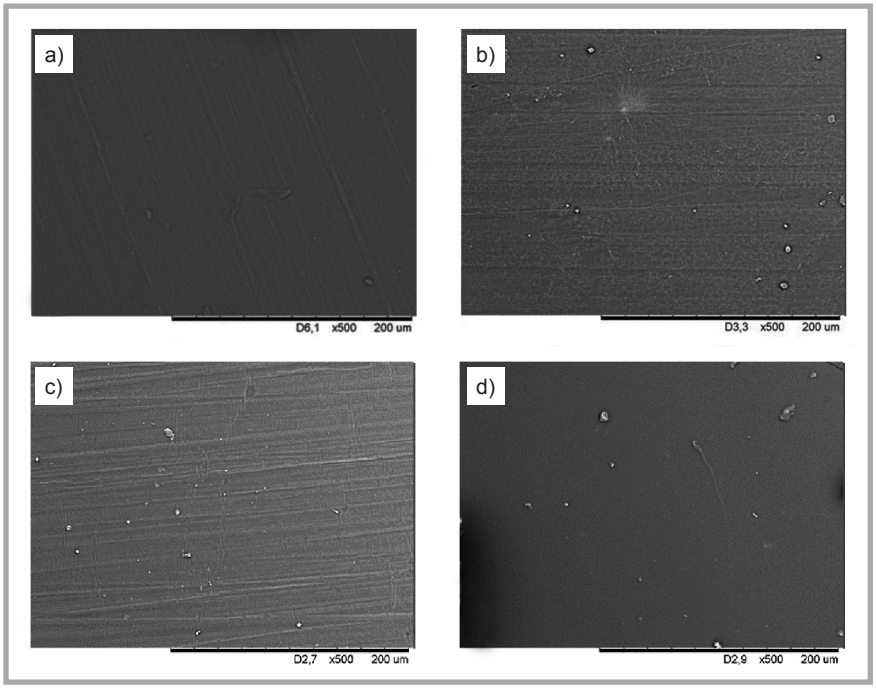

Figure 3. *Surface morphology of elastomeric composites with self-healing properties – samples a), b), c), d) described in* ***Table 1****).*

Methods

Self-healing process

Intrinsic self-healing polymers are materials capable of repairing molecular and microscale damage via a temporary local increase in mobility of the polymeric chains. Such behaviour is based on specific molecular structures of the polymers that allow an effective restoration of the chemical or physical bond strength upon stimulus removal. The external trigger used in this research was elevated temperature. For this purpose, damaged materials were placed in an oven at 70° C. Samples at this temperature were conditioned for 24 hours.

A diagram showing the operation of the self-healing process using temperature as the external stimulus is shown in ***Figure 2***.

Simulation of mechanical hazards

Due to the occurrence of various types of mechanical hazards in the work environment, the material was micro-damaged by simulated puncture, cutting and abrasion.

For the tests, samples of commercial gloves and prepared self-healing polymer samples were used. The samples of commercial gloves were taken from areas representative of the construction of protective surfaces. The samples should be prepared in such a way that the micro-damage is performed exactly in the middle of the prepared sample through its entire thickness. Cutting and abrasion simulation are carried out exactly in the middle of the prepared sample; the sample size should not be less than 5 cm × 5 cm, and puncture was performed using a 0.45 mm diameter needle. In the case of the cut, it should be made at an angle of (45 ± 10) o to the longitudinal direction of the sample using a scalpel and should have a length of (2 ± 0,5) mm, which should be assessed using a magnifying glass.

Abrasions occurring on gloves caused by their use during work were simulated using sandpaper with a grain thickness of 250 microns. The simulation of abrasion was carried out exactly in the middle of the prepared sample. All samples were rubbed manually until the surface layer was damaged.

Visualisation of the surface – Scanning electron microscopy (SEM)

The samples were assessed with scanning electron microscopy (SEM; TM-1000 Tabletop Microscope, Hitachi, Japan). The samples were placed on carbon plasters and sputtered with Au (Cressington Sputter Coater 108 auto, UK) for 60 s.

In the first stage of the work, the morphology of the entire surface was observed. Further tests were aimed at illustrating the damage and changes occurring during the self-healing process. Observation was made of the surface at a magnification of x 90-2500.

Tensile tests

Mechanical measurements were made on an INSTRON testing machine. For strength measurements, paddle-shaped samples were prepared. The dimensions of the specimen to be tested were 50 × 5 × 1 mm . The tensile test speed was 1 mm*min-1, and the maximum value of the force at rupture was 1000 N. The measurement was repeated for 3 samples, carried out in accordance with the guidelines of the standard "Textiles – Tensile Properties Of Fabrics – Part 1: Determination Of Maximum Force And Elongation At Maximum Force Using The Strip Method (ISO 13934-1:2013)"

Resistance to penetration of chemical substances

Chemical permeation tests were carried out in accordance with the test method-

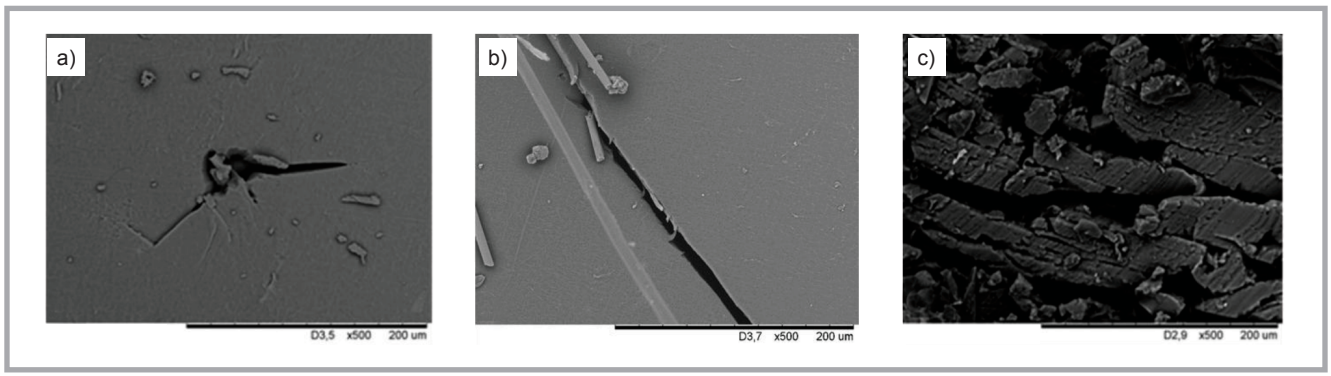

Figure 4. *Surface morphology of elastomeric composites with self-healing properties subjected to simulated micro-damage.*

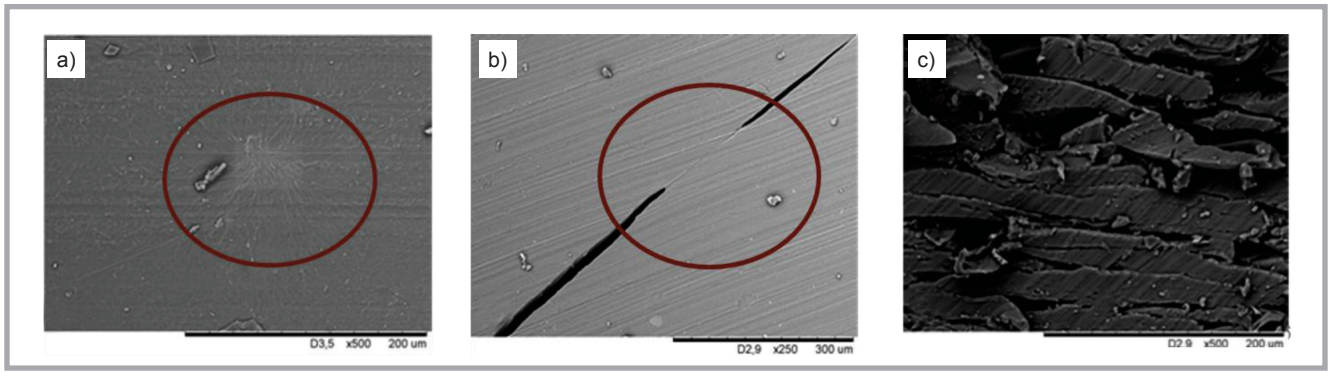

Figure 5. *Surface morphology of elastomer composites with self-healing properties subjected to simulated micro-damage after the self-repair process.*

ology described in the revised European standard PN-EN 16523-1: 2015-05 "Determination of material resistance to permeation by chemicals – Part 1: Permeation by liquid chemical under conditions of continuous contact" (EN 16523-1 : 2015, using two open systems – gas chromatography coupled with a flame ionization detector, GC-FID.

Results and discussion

Evaluation of the surface morphology of elastomeric composites

Figure 3 presents SEM images of the surface of elastomeric self-healing composites without a textile carrier – A, C and with – B, D.

A smooth surface was observed regardless of the type of functional group used. In ***Figure 3*** the surface of a thin polymer film with longitudinal lines that could have been formed during vulcanisation is seen. In the case of the composition with knitted fabric, the area analysed is more homogeneous. We can also see that the fabric has been completely embedded in the elastomeric layer and is not visible in the SEM images.

Figure 4 shows the surface morphology for exemplary samples subjected to simulated damage conditions: A-puncture, B-cut and C-abrasion.

On the basis of the SEM images obtained for all samples tested with and without atextiles carrier, it was found that no differences were observed between the composites of different composition and that the knitted fabric had no influence on surface properties.

Samples with micro-damage were subjected to a self-healing process by conditioning at 70 °C for 24 hours. After this time, in order to confirm the effectiveness of the process, surface visualisation was performed again. Results of the SEM analysis are shown in ***Figure 5***.

The results obtained confirm the occurance of the self-healing phenomenon, however, its effectiveness depends on the size of the damage.

Figure 4.a shows the damage resulting from the puncture (loss of size 200 mm) after the self-repair process. We observe a complete capping of the cavity. In ***Figure 4.b***, we can see the partial capping of the defect resulting from the scalpel cut (***Figure 5.b***). This is due to the difference in the size of the damage. In samples damaged by a scalpel, an incision of approximetly 2 mm was formed. Regeneration oof the whole surface was not observed . In the majority of such damaged samples, the healing process was observed at a length of about 200 mm. In the case of the samples with a textile carrier, the same relations were observed.

For samples whose external surface was damaged by abrasive paper (***Figure 4.c***), surface morphology images (***Figure 5.c***) do not indicate that the self-repair process had occurred. There were no visible differences in the pictures presented.

Based on an analysis of the morphology, we can conclude that the degree of self-healing largely depends on the size of the damage. In the case of slight damage caused by cutting, a material regeneration process was observed. In the case of major damage as a result of the cut, partial self-healing was observed.

Moreover for samples damaged as a result of abrasion, no visible changes in the morphology indicating the self-repair process were observed, which is related

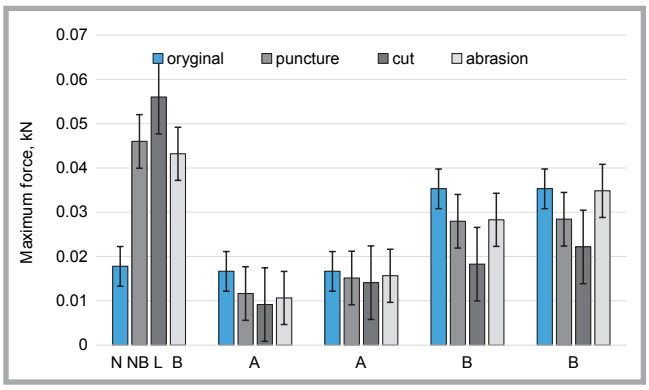

Figure 6. *Maximum force A at rupture during the tensile test of non-damaged commercial glove samples (N-nitrile glove, NB-nitrile glove with cotton carrier, L-latex glove and B-butyl glove) and elastomeric composites samples with self-healing properties subjected to various micro-damage.*

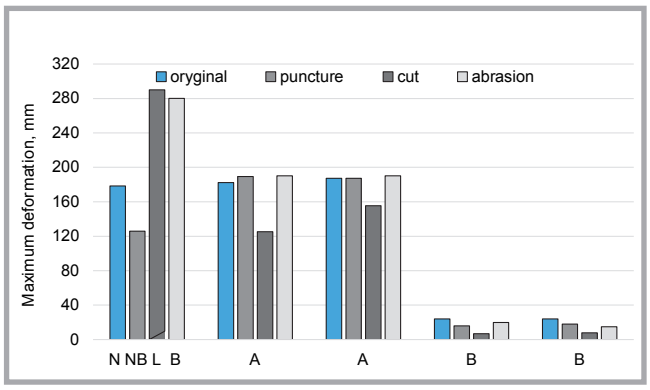

Figure 7. *Maximum deformation during the tensile test of non-damaged commercial glove samples (N-nitrile glove, NB-nitrile glove with cotton carrier, L-latex glove and B-butyl glove) and elastomeric composite samples with self-healing properties subjected to various micro-damage.*

to the loss of material in the surface part, not only to its damage. Analysis of the surface morphology confirmed the effectiveness of the self-repair process in certain cases.

Analysis of the results of protective parameters

Assessment of tensile strength

Protective parameters were also tested for both damaged and self-healed samples (conditioning 24 h at 70° C) and compared to the mechanical properties of samples acquired from commercial gloves. The results obtained for commercially available samples are shown in ***Figures 5*** and ***6***.

Figure 6 shows the maximum force at rupture [kN].

The elastomeric composite with self-healing properties reached a value of about 0.02 kN of the maximum force at break, close to the value for a nitrile glove. Conditioning of the damaged samples resulted in an increase in the maximum force value at break, which indicates that the process of self-healing and regeneration of damaged bonds occurred (***Figure 6***). Damaged chains were able to reconnect, which resulted in the recovery of mechanical parameters close to the initial parameters.

During the tensile tests, the maximum deformation of the samples was also evaluated. ***Figure 7*** shows the maximum strain [mm].

Composites of silicone rubber applied to knitted fabric achieved very low deformation values of about 20 mm. Polymer films made of silicone rubber in both variants reached a higher deformation value – about 200 mm. Micro-damage reduced the mechanical properties of the materials tested. The weakest mechanical parameters were obtained for materials cut with a scalpel.

On the basis of the pilot mechanical tests, we can conclude that the material proposed can be used for the production of protective materials, including protective gloves. The mechanical parameters are promising and their values are at the level of materials currently available on the market. The use of knitted fabric in polymer composites allow to obtain a material of better mechanical properties but lower deformation value.

Assessment of resistance to penetration of chemical substances

Assessment of the resistance to permeation of chemical substances was carried out for the samples: before damage, damaged and subjected to the self-healing process (24 hours at 70 °C).

Table 2. *Results of tests relevant to the NBT value, min – testing the resistance of the silicone rubber composite to the penetration of n-propanol.*

Sample type	Measurement, min		
	Before damage	Damaged	After self-healing
A	5	0	5
B	8	0	6
C	3	0	3
D	6	0	3

The damaged samples did not provide any protection against the selected solvent. Breakthrough occurred immediately after contact of the polymer with isopropanol.

The study of the resistance of chemical substances to the original, non-damaged samples shows a short time of resistance to breakthrough – approximately 3-8 min. However, it should be noted that these times for samples subjected to the process of self-repair returned to the initial values.

According to the standard EN 16523-1:2015 – entitled "Determination of material resistance to permeation by chemicals", only the first level of effectiveness was achieved. The results obtained are presented in ***Table 2***.

Effectiveness of the self-healing process.

In order to check the correctness of the self-healing process, a series of micro-damage was performed in acomposite containing methyl vinyl silicone rubber and silesxanes: isobutyl-POSS functionalized with amine and aminopropyl (isobutyl)-POSS (A) or aminoethyl-propyl (isobutyl)-POSS (C) derivatives.

Afterwards an analysis of micro-damage in the form of a simulated puncture and cut using a statistical distribution of the amount of micro-damage repaired in relation to all damage performed was carried out.

In ***Figure 8*** a schematic distribution of micro-damage on the sample is presented.

The data collected was subjected to statistical analysis in SPSS Statistics 23.0. Student's t-test was applied using the the posteriori bootstrap method (sampling 1000). A 95% confidence interval (± 2 SD) was determined for mean variable values.

Table 3 presents a summary of test statistics for the effect of the micro-damage type on the effectiveness of self-repairing composites.

Significantly higher efficiency of self-healing of the composite was found in the case of micro-damage caused by a puncture than by cutting (by 29.67%). The effectiveness of self-healing, expressed by the ratio of damage repaired to all that caused by the cut and puncture, is shown in ***Figure 9***.

On the basis of the results presented in ***Figure 9***, we can conclude that the process of self-repair for test composites damaged as a result of puncture takes place effectively and repeatedly. However, in the case of cuts, the self-healing process occurs only in 50% of damage.

Conslusions

Interest in the subject of self-healing polymers in protective materials is related to ensuring better work safety during their use as well as extending their service life. This is of great importance not only in economic terms, but also ecological, translating into reductions of polymer waste.

However, selected materials intended for the production of all-rubber protective gloves should be characterised by very good flexibility and proper mechanical parameters. In addition, they should guarantee safety on all their surface. To obtain such material with self-healing properties, the choice of polymeric materials based on an intrinsic mechanism is a good solution. Therefore we chose an elastomer composite with Silsesquioxanes (POSS), which contains functional groups that enable self-healing of the polymer.

Based on microscopic examination of the self-repair process, we concluded that the self-healing process takes place in various places, indicating evenly distributed POSS in the polymeric material. There is no aggregation of the self-healing agent here, as is often the case in microencapsulated materials, because the substance responsible for self-healing is introduced in the manufacturing process together with the elastomeric mixture.

Selected materials are characterised by repeatability of the self-repair process in the case of micro-damage (puncture), due to the possibility of re-reacting the current bonds via a temporary local increase in mobility of the polymeric chains. Such behaviour is based on specific molecular structures of polymers that allow an effective restoration of the chemical or physical bond strength upon stimulus removal.

Moreover the composites tested were characterised by good mechanical factors and met the requirements of the subject standards. Unfortunately the study of the resistance to permeation of chemical substances shows a very short time of resistance to breakthrough. However, it should be noted that permeation times for samples subjected to the process of self-repair return to the initial values. It seems, therefore, that these preliminary studies are promising and should be continued.

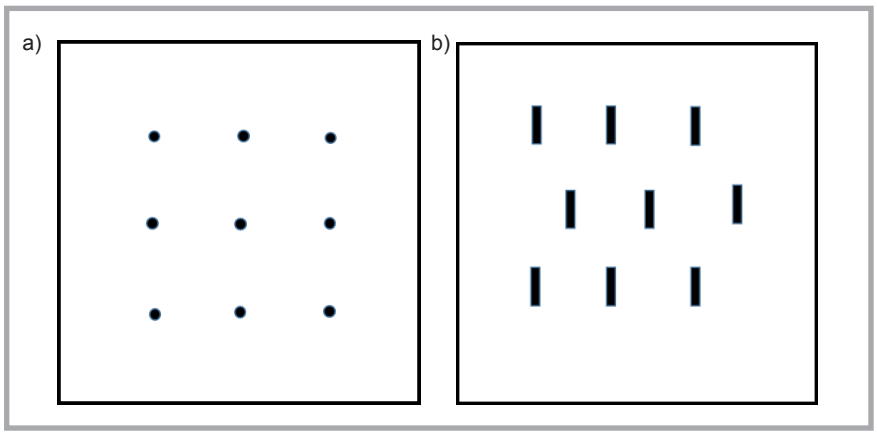

Figure 8. *Schematic distribution of micro-damage on the sample for a) punctures and b) cuts.*

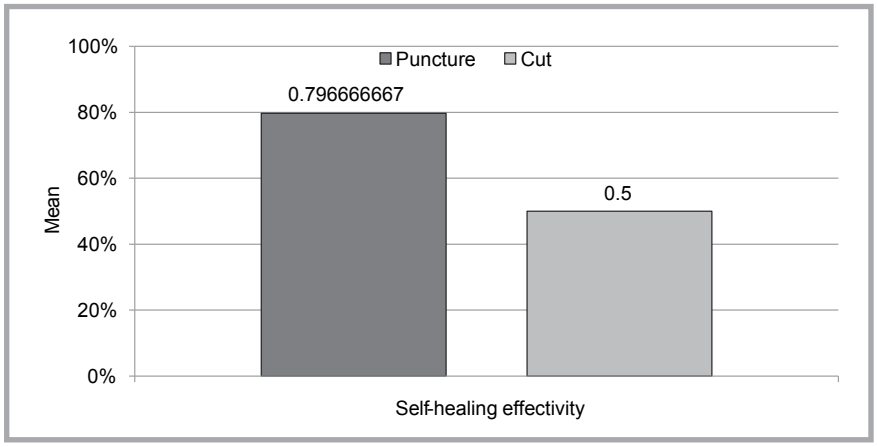

Figure 9. *Efficiency of self-repairing of micro-damage caused by a puncture or cutting.*

Table 3. *Test T statistics for the effect of the type of micro-damage on the effectiveness of the self-repairing process.*

		Puncture	Cut	*t*(5)	*p*
Self-healing effectiveness	M	7.17	4.50	6.68	$p < 0.001$
	SD	0.75	0.00		

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