Characteristics of microstructural phenomena occurring on the surface of protective gloves by the action of mechanical and chemical factors

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Abstract: The aim of this study was to evaluate the microstructural changes on the surface of glove materials used in the workplace — new and subject to mechanical and chemical interactions in both simulated conditions in a laboratory and on actual jobs. The introductory part presents a brief review concerning application of the scanning electron microscope technique to characterize the microstructural phenomena occurring on the surface of textiles used to construct protective gloves. Research has indicated that a scanning electron microscope can be used to characterize the microstructural phenomena occurring on the surface of the materials exposed to mechanical and chemical harmful factors. Based on the results, it was found that the impact of the proposed conditions has a different influence on the morphology of the rubber surface: acrylonitrile-butadiene and chloroprene. In both cases there are different morphological features characterizing particular types of changes observed on the surface.

Keywords: protective gloves, scanning electron microscope, acrylonitrile-butadiene rubber, chloroprene rubber, microstructural phenomena.

Charakterystyka zjawisk mikrostrukturalnych zachodzących na powierzchni rękawic ochronnych w wyniku oddziaływania czynników mechanicznych i chemicznych

Streszczenie: W badaniach prowadzonych przy użyciu skaningowego mikroskopu elektronowego oceniano zmiany strukturalne na powierzchni materiałów rękawic ochronnych stosowanych na stanowiskach pracy — nowych oraz poddanych oddziaływaniu różnych czynników mechanicznych i chemicznych, zarówno w warunkach symulowanych w laboratorium, jak i rzeczywistych, na stanowiskach pracy. Scharakteryzowano uszkodzenia powierzchniowe, powstałe w wyniku oddziaływań zewnętrznych,wpływających na szybszą utratę właściwości ochronnych badanych materiałów, niezauważalnych nieuzbrojonym okiem pracownika. Dowiedziono, że wymienione czynniki powodują charakterystyczne zmiany morfologii powierzchni badanych materiałów rękawic ochronnych, zależnie od typu oddziaływania.

Słowa kluczowe: rękawice ochronne, skaningowy mikroskop elektronowy, kauczuk butadienowo-akrylonitrylowy, kauczuk chloroprenowy, zjawiska mikrostrukturalne.

Protective gloves made of polymer films and coated textiles are widely used in various industries due to the possibility to use them in many workplaces where there is a risk associated with the combination of several dangerous factors [1]. Materials used for gloves to be used in mechanical workshops act as multifunctional protection as they protect the employee's hands from both selected mechanical (cuts, punctures and abrasion) and chemical factors (mineral oils, grease).

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During the simultaneous impact of mechanical and chemical factors on the protective glove materials, a gradual loss of their protective properties could be seen. No doubt, this is related to the occurrence of microstructural phenomena occurring on the surface of the gloves (cavities, cracks, or gradual degradation of materials) under the influence of external factors.

Although in many cases the surface morphology changes in the micro scale it translates into a deterioration of the protective properties what is very important for the hands of the employee.

It should be noted that the effectiveness of protective gloves is assessed on the basis of standardized test methods, but the efficiency of telling the extent of protection of the tested products refers to the new units and does not include multiple use. Little is known about the duration of the service life of gloves, because the degree of wear and tear, or loss of protective properties depends on many factors occurring in the workplace. The impact of these factors is the subject of the analysis conducted in accordance with the standards, the feed roller methods of testing and evaluation of these measures. Therefore, it is important to advance our knowledge of microstructural phenomena occurring on the surface of protective gloves in the context of the loss of the protective properties during their use.

The most common technique used to evaluate the morphology of the materials is a scanning electron microscope (SEM). A large depth of field scanning microscope makes it particularly useful to study the surface morphology, especially concerning the surface quality and damage to the surface layer [2—4]. Microscopic examination also allows verifying the changes in the structure of textiles, polymers and coated textile materials [5, 6].

The first reports on the use of a scanning electron microscope to study the surface morphology of textiles come from 1970s. These tests involved evaluation of the morphology of the treated cotton fibers, exposed to swell factors, such as morphine, piperidine, piperazine, ethylenediamine and zinc chloride. The results indicated a significant gradation in recrystallized swollen and non-swollen cotton fibers, which have been used to develop a visual scale of microfibers useful in assessment of recrystallized cotton [7].

Subsequent reports on the use of scanning electron microscope for morphology studies related to the testing of textile cotton fibers [8]. Studies using scanning electron microscope to evaluate the morphology of the surface were also used in the preparation of composite fabric, where polyacrylonitrile (PAN) was deposited on nylon and polyethylene (PE) fibers. The scanning electron microscope study clearly showed that the composites thus obtained were characterized by much better conductive properties and adhesion. It was caused, according to the authors, by an increase in the interaction of macromolecules by diffusion of polyacrylonitrile (PAN) chains into layers of fibers, which was confirmed by images obtained by scanning electron microscope [9].

Currently, as it is often used to control scanning electron microscope imaging and surface morphology of fibers and textiles, in which the deposited polymer layer in order to impart high mechanical and chemical resistance of the output fiber [10—12] or drainage of excess electrical charge through the use of conductive polymers [13, 14]. The above mentioned technique was quickly used to evaluate the surface morphology of textiles, which were incorporated in the nanoparticles in order to obtain functional products — silver nanoparticles in textile fibers [15] or chitosan nanoparticles with essential oils [16].

Scanning electron microscope studies confirmed the incorporation of the nanoparticles of chitosan in the fiber structure, and the gas chromatography coupled with mass spectrometry (GC-MS) studies confirmed sustained release of fragrance from their interior [16]. The zinc oxide nanoparticles layer on the surface of cotton fibers, applied by immersing and then drying the fibers, was designed to enhance their antibacterial properties. Scanning electron microscope examination of the structures thus obtained showed that nanoparticles were uniformly distributed on the fiber surface, and the physical characteristics showed no significant differences in mechanical strength while increasing the bactericidal properties [17]. Studied the morphology of the surface-modified silver metallic fibers using a novel wet-chemical technology — scanning electron microscope images obtained confirmed that the fibers are properly coated with a silver layer [18].

The scanning electron microscope technique was also used to assess the structure and morphology of the polymer-modified fibers, including many compounds, *e.g.* boronic acid [19], and ferric chloride [20].

From the point of view presented in this paper interesting was the study on the use of nanoparticles using electrospray incorporated in the surface of fabrics in order to increase their resistance against water and mineral oils. The resulting scanning electron microscope images confirmed that the application of nanoparticles using the above techniques prevents the electrostatic interactions by formation of agglomerates, which significantly increases the oil resistant properties of textiles [21].

In the literature there is no study on the evaluation of microstructural phenomena occurring on the surface of the protective gloves due to mechanical and chemical factors that occur in the workplace. The work carried out so far on the impact of individual factors (most of selected chemicals such as acids and bases or mechanical actions) only on the standards defined in the protection of materials [22—28]. They did not relate to assessment of changes in the surface structure of materials created as a result of use in the real world, and during or after the process of use. One study on the effects of mineral oil on the protective properties of the materials indicated the need for such analyzes to enable accurate interpretation of the results of safety parameters [29, 30].

In this paper, a scanning electron microscope technique to evaluate the microstructure of the surface layer of the polymer-coated textile in the protective gloves was used. The materials were subjected to single and complex interactions — mechanical stresses (tensile, bending and abrasion), chemical (mineral oil) and microclimatic — taking place in the space between the user's hand and the glove material (sweat, temperature, humidity). The aim of this study was to evaluate the microstructural changes on the surface of glove materials used in the workplace — new and subjected to the above mentioned influences in both simulated conditions in a laboratory and in real workplaces. Particular emphasis is placed on the surface characteristics of microdamage resulting from external influences that could translate into more rapid loss of the protective properties of the tested materials, imperceptible from the perspective of the employee. A scanning electron microscope which is a device designed to study the material structure was used in this study.

EXPERIMENTAL PART

Materials

Two types of materials commonly used for protective gloves at work in mechanical workshops were chosen — knitted gloves coated with acrylonitrile-butadiene rubber (NBR) and chloroprene (CR) all-rubber gloves flocked with cotton fibers inside. Chloroprene rubber and acrylonitrile-butadiene rubber, depending on the thickness, processing conditions, the additives used and other factors, have different resistance to the penetration of mineral oils, usually at a high level. The gloves selected for testing were manufactured by two leading manufacturers and suppliers of gloves of this type in the world, according to manufacturers' declarations — gloves showed high resistance to the penetration of mineral oils — 6 levels of performance (EN 374-3:2003, EN 374-3:2005, EN 374-3:2005/AC:2006] gives the classification scale 6 — gradual, according to procedure described in [31]). This means that the penetration of the compounds takes place at an average of more than 8 hours of continuous contact with the glove samples was therefore influence factor by simulations and actual cycle of 8 hours corresponding to a working shift at work.

Method of testing

The tests included the following options:

— a new one (as reference material); subjected to mechanical loads only (tensile, abrasion) during a simulated test work performed in the gloves;

— subjected to the artificial sweat, only a basic pH (pH = 8,0 ± 0,2);

— subjected to the combined action of mechanical loads, artificial sweat and mineral oil under certain conditions, temperature (36 °C) and humidity (60 %) the device simulated research work performed in the gloves;

— exposed to the real conditions in the workplace.

Studies described in this work were done according to the previously described test procedure by the authors in [31, 32]. A characteristics of the variants is shown in Table 1. A scanning electron microscope was used to assess the surface morphology of two types of polymer gloves. The scanning electron microscope experiments were performed on a HITACHI S-3500N at the accelerating voltage of 10 and 15 kV and magnifications in the range between 40 and 2000 times.

The samples for microscopic examination were cut from the palms of the gloves. Chloroprene rubber films and acrylonitrile-butadiene rubber connected to the fabric layer, with the dimensions 10 × 10 mm, were glued to the microscope table with a conductive adhesive. Samples were coated with a gold layer 5 nm thick.

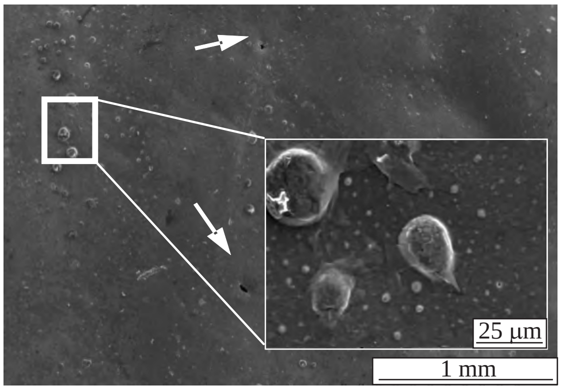
RESULTS AND DISCUSSION

Microscopic analysis shows differences in surface morphology of polymer protective gloves. Figures 1 to 10 show the surface microstructure of the tested samples.

Figure 1 shows the surface morphology of knitted gloves coated with acrylonitrile-butadiene rubber. The surface of the initial gloves has characteristic elements of structure. Typical micropores have size in the range of 8 to 40 microns (the places indicated by arrows) (Fig. 1A). The similar topography has been observed by numerous researchers [33]. Rubber surface of gloves is weakly developed. Figure 1A shows the scanning electron microscope photograph of typical structures of investigated polymer materials. Spherical elements of structure on Fig. 1A are molecules of the dispersed phase, characteristic for acrylonitrile-butadiene copolymers. Fig. 1B shows regions of melted rubber which are formed as a result of joining the fabric and polymer.

Figs 2 to 5 show the surface morphology of the knitted materials after an exposure to external factors. The surface observed had different morphology. Figs 2 and 3 show the surface morphology of materials treated with single agents, mechanical interactions and activity of artificial sweat, respectively. Characteristic of these surfaces is the presence of spherical structural elements that occur on the material surface not influenced by external impacts.

A)



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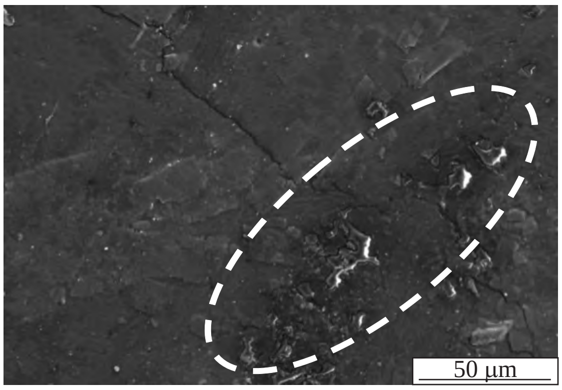

Fig. 1. SEM micrographs of reference knitted fabric acrylonitrile-butadiene rubber (NBR) gloves (1N)

T a b l e 1. Characteristics of the tested materials

Protective gloves	Knitted gloves coated with rubber	All-rubber gloves
Symbol	1	2
Characteristic	Fabric of polyamide yarns, coated with acrylonitrile-butadiene rubber (NBR) in the palm	Chloroprene (CR) all-rubber gloves flocked with cotton fibers inside
Tested variants		
Samples from a new gloves	1 N	2 N
Samples subjected to mechanical loads only (tensile, abrasion) to the test simulated work performed in the laboratory — 8 h	1M	2M
Samples subjected to the artificial sweat in laboratory — 8 h	1S	2S
Samples subjected to the combined action of mechanical loads, artificial sweat and mineral oil under certain conditions, temperature and humidity in the device simulated real work — 8 h	1L	2L
Samples exposed to the real conditions in the workplace in mechanical workshop — 8 h	1MW	2MW

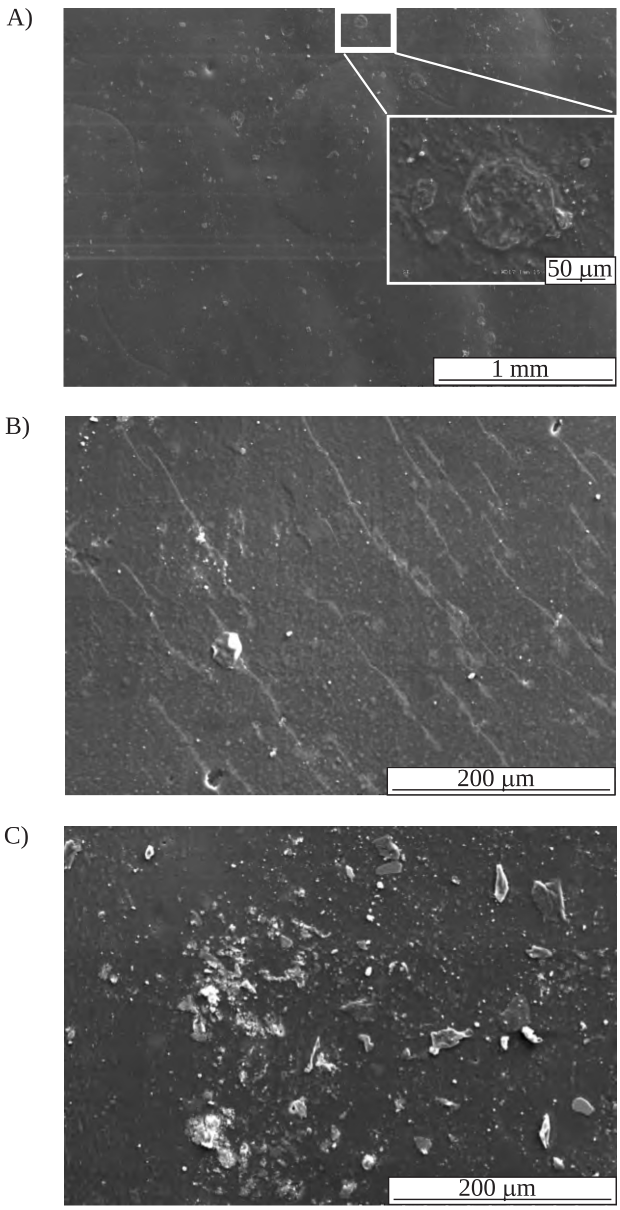

Fig. 2. SEM surface morphology of knitted fabric acrylonitrile-butadiene rubber (NBR) gloves after mechanical impact (1M)

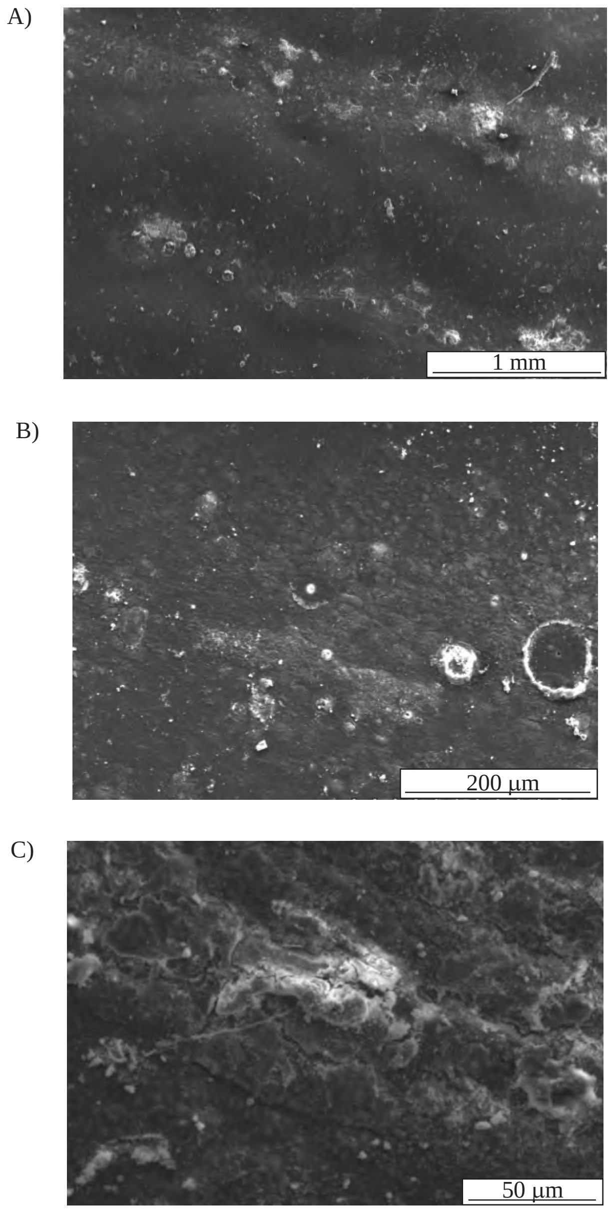

Fig. 3. SEM surface morphology of knitted fabric acrylonitrile-butadiene rubber (NBR) gloves after the chemical reactions (artificial sweat) (1S)

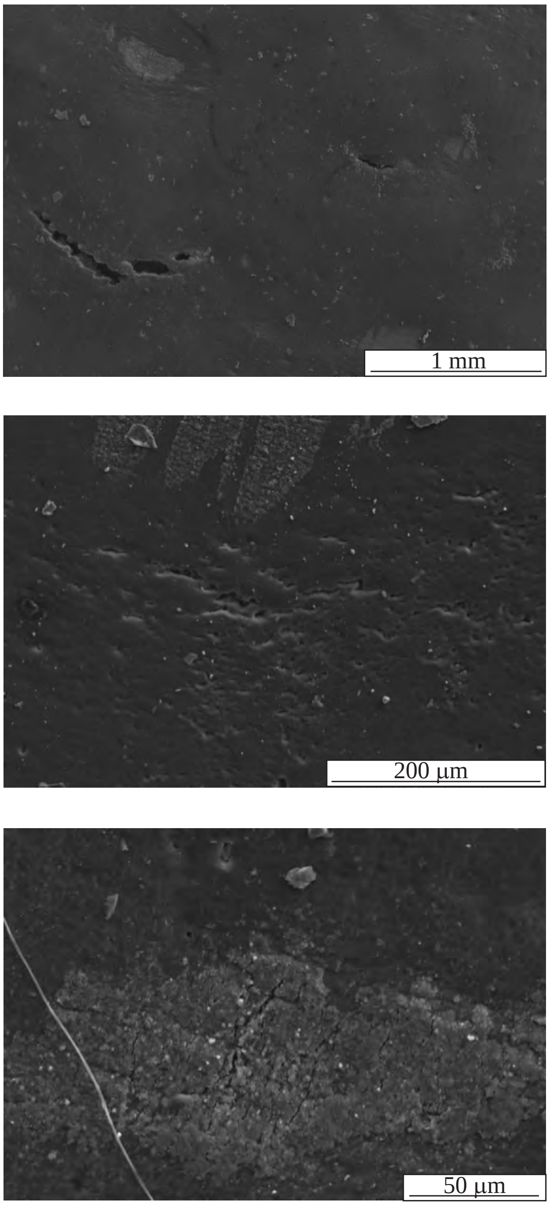

Fig. 4. SEM surface morphology of knitted fabric acrylonitrile--butadiene rubber (NBR) gloves after work in simulation conditions in laboratory (1L)

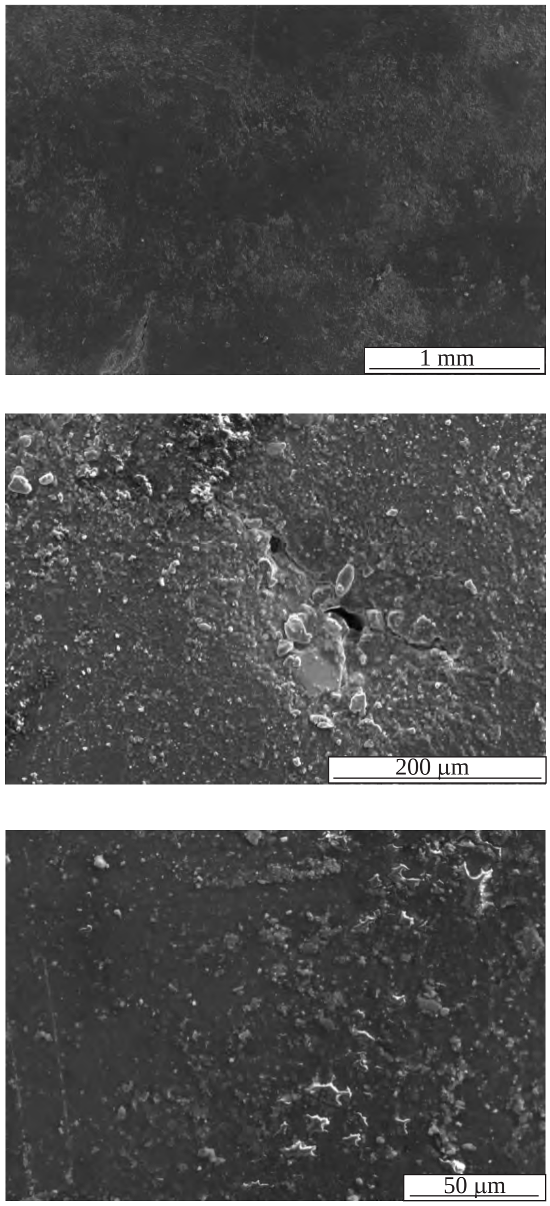

Fig. 5. SEM surface morphology of knitted fabric acrylonitrile--butadiene rubber (NBR) gloves after usage in car repair shop (1MW)

Occurring in the form of spherical precipitates dispersed phase morphology has changed compared to the initial state. For the 1M material (Fig. 2A) dispersed phase in the form of spherical elements of the structure is more flat in comparison to the starting material (Fig. 1), whereas for the material 1S (Fig. 3) on the periphery of the dispersed phase separation (light line) related to the impact of artificial sweat to the surface occurs. In addition, the mechanical interaction causes formation of characteristic bands associated with mechanical damage to the surface (Fig. 2B). There are also crumbled filler particles and/or contamination on the surface (Fig. 2C).

Artificial sweat has a different impact on the rubber surface. Figure 3 shows light cracked areas on the surface, which testify to aggressive impact of this factor on the acrylonitrile-butadiene rubber. Cracking and swelling of the material found on the surface are in the form of bands (Fig. 3A), which may be associated with the occurrence of agglomerates fillers in these areas. So you can say that these areas which are weakly resistant to the artificial sweat in consequence lead to loss of continuity of the material surface. Changes on the surface of the protective gloves are typical to the processes of chemical degradation of rubber, which may consequently lead to reduction in a number of properties of the material, including protective properties [34].

Study of the effect of artificial sweat on polymeric materials in the context of the loss of their protective properties has not been intensified. There are reports confirming that the artificial sweat has hydrolytic properties in regard to polymer and causes the degradation. Studies were carried out on the special device to allow dispensing of the artificial sweat solution which was thermostated. The results clearly confirm that the artificial sweat considerably increases the weight loss of polymers in terms of exposure to visible light. It should also be noted that designed sweat dosing device made sweat application in temperature conditions similar to human body temperature, since the dosing container was placed in a thermostatic vessel [34].

Despite results of investigations by Korinth *et al.* [35] stating that sweat does not have any effect on chemicals penetration through gloves material, it was observed that during the contact of artificial sweat with plastics, chemicals which were added to polymer compositions in order to improve their properties, were often released.

The additives: dithiocarbamates [36] or thiurams [37], are carcinogenic and can lead to allergic reactions, what impacts the comfort and safety of the finished products' users.

Based on microscopic analysis it can therefore be concluded that the mechanical impact and the impact of artificial sweat, despite the fact that they have different effects on the morphology of the rubber surface, lead to a decrease in protective properties of the tested gloves. Both factors lead to significant development of surface damages in comparison to the initial material. In the first case, surface damage is visible due to the tension acting, in the second case there is a chemical surface degradation.

Figures 4 and 5 show surfaces of materials subjected to the combined effect of exposure factors. In both cases of materials tested in simulated and real working conditions changes in the surface morphology of the gloves are affected by many factors. In both samples a considerable surface degradation was observed. Spherical elements of the structure were not found, what testifies to intensive wear of the rubber's surface layer. Presented results show that mechanical impacts have complex character in case of simulated researches and real working conditions.

Simulated conditions in a laboratory have led to significant damage to the surface of the glove (see Fig. 4). Damage to the surface indicates that simulated operating conditions during the experiment produce complex mechanical influences. Voids formed as a result of stresses are visible on the material surface. As a result, there are frictional forces acting to remove the layer from the surface of the elastomer and disclose filler agglomerates. Note that in the initial material a thin layer of elastomer was protecting filler, since filler was not observed on the surface. Cracks and microcracks in both elastomer (Fig. 4B) and in the filler (Fig. 4C), which can affect the barrier properties of the test materials against mineral oils are present. The resulting damage to the rubber surface (cracks, delaminations, voids) is the cause of weakening of the protective properties — resulting mainly in accelerated penetration of substances present in the workplace to the skin of the hands.

The surface of gloves used in a car repair shop were very impure. As a result of the real use of the fillers agglomerates were revealed on the rubber surface. There were empty spaces (cracks) observed on the border between elastomer and fillers.

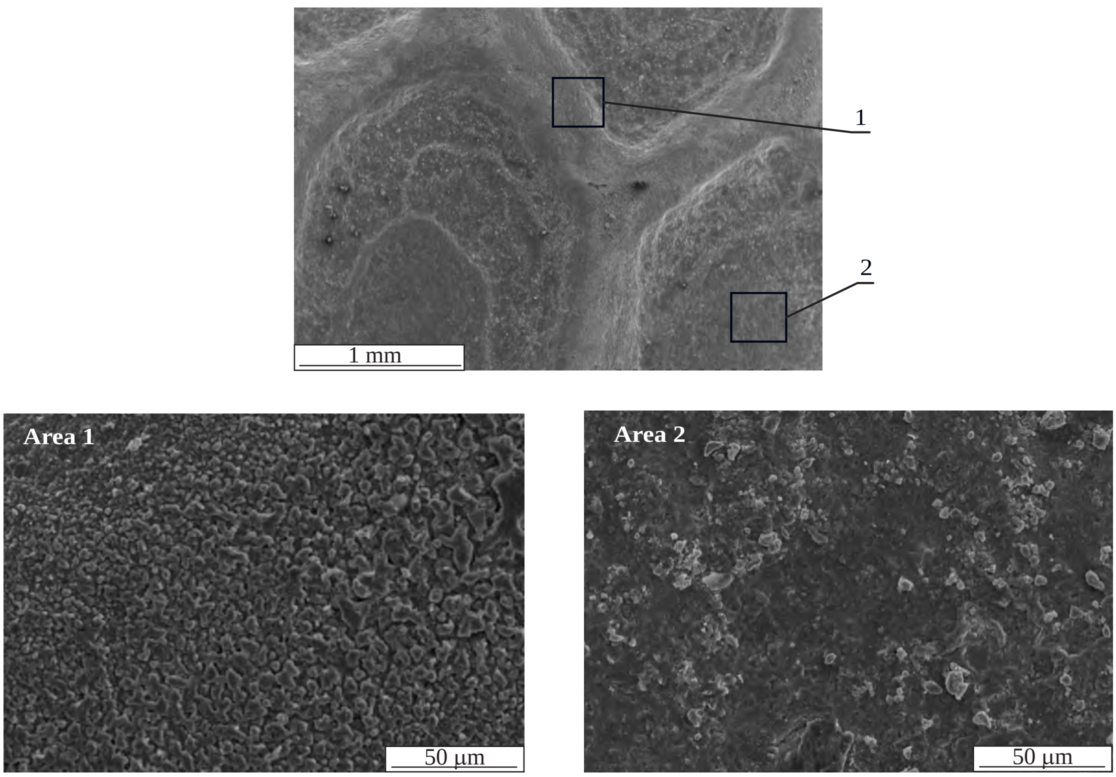

Fig. 6. SEM surface morphology of chloroprene rubber (CR) gloves, flocked cotton fibers from the inside (reference samples) (2N)

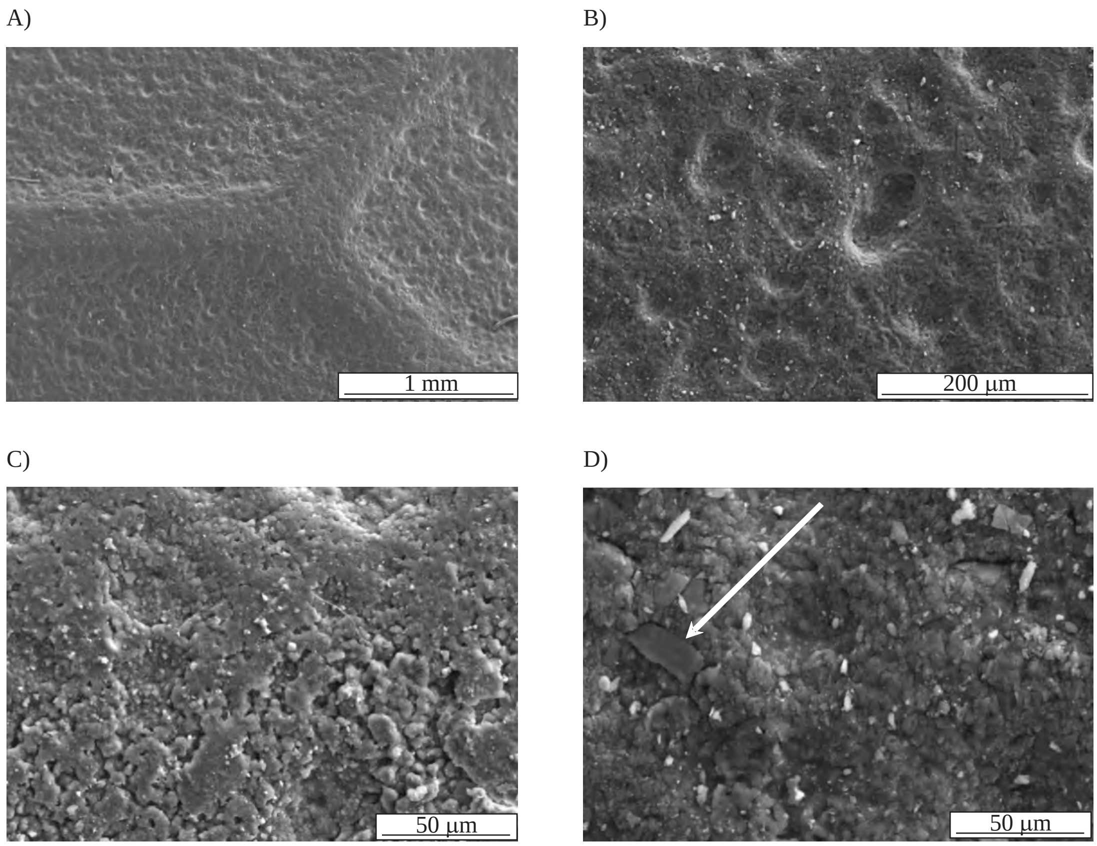

Fig. 7. SEM surface morphology of chloroprene rubber (CR) gloves after mechanical affect (2M)

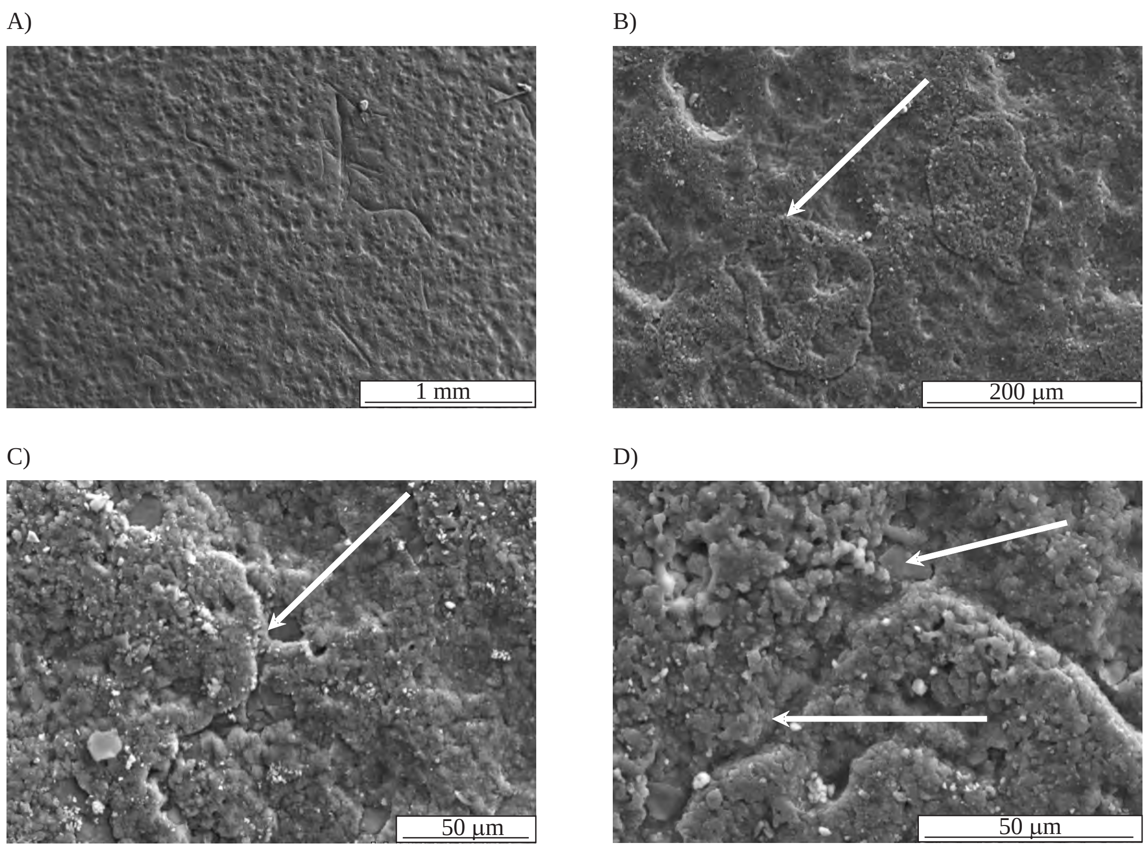

Fig. 8. SEM surface morphology of chloroprene rubber (CR) gloves after the chemical interactions (artificial sweat) (2S)

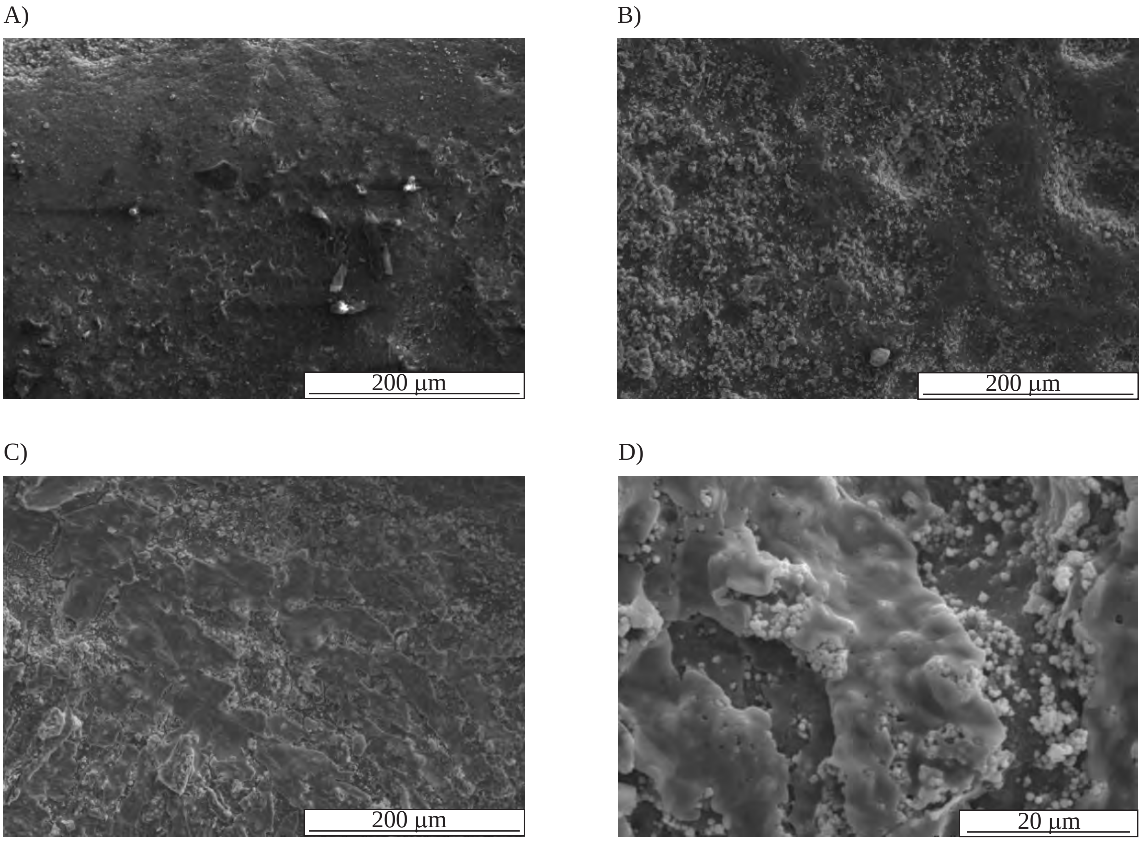

Fig. 9. SEM surface morphology of chloroprene rubber (CR) gloves after work in simulation conditions in laboratory (2L)

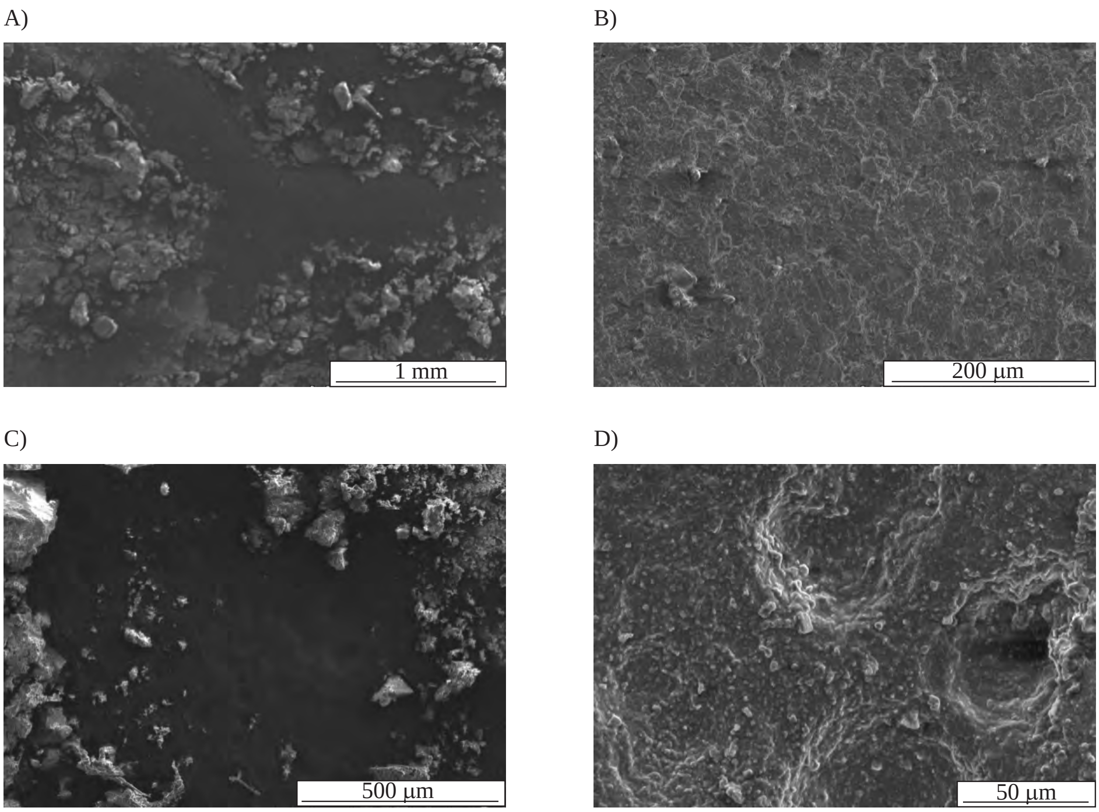

Fig. 10. SEM surface morphology of chloroprene rubber (CR) gloves after usage in car repair shop (2MW)

Another group of test materials were chloroprene rubber gloves. The morphology of the initial state and the impact of external factors (Table 1) are shown in Figs 6—10.

Figure 6 shows the surface morphology of chloroprene rubber gloves, flocked with cotton fibers from the inside. The influence of the specified conditions on the surface layers of CR rubber was analyzed. On the inner surface of gloves two characteristic microstructural areas were observed due to the presence of the textured non-slip structures. The area 1 (Fig. 1) has a developed surface. Area 2 between the edges of the non-slip structure has a morphology characteristic of filled elastomers [6]. This figure shows the aggregates and agglomerates of fillers on the rubber surface.

The analysis showed that used factors in different ways affect the changes to the surface of chloroprene rubber gloves. Figures 7 and 8 show the surface morphology of gloves after mechanical and artificial sweat interactions, respectively. For both materials, between the edges of the anti slip structure an increase in the degree of surface development compared to the initial material was observed. This is mainly due to the presence of characteristic microcraters on the rubber surface (Fig. 8B and 7B). In both cases presence of individual filler particles on the surface was found. On the surface of the samples treated with artificial sweat pits and etched areas were present (Fig. 8B—D). Surface discontinuities being a result of contact with artificial sweat can lead to deterioration of surface density of the rubber and the loss of their protective properties during use. In this case chemical degradation on the anti-slip structure was not observed.

Significant changes in the surface morphology were observed in rubber samples tested in a laboratory simulation. Figure 9 shows scanning electron microscope photograph of the morphology of structure of anti-slip edges which became fractured due to intensive friction. Anti-slip edges are the most abrasion hazard during work conditions simulated in the laboratory [6]. The area between the edges has numerous pits (Fig. 9B) and is largely covered with a coating (precipitates) (Fig. 9C and D). Precipitates on the rubber surface are in the form of a fractured layer and spherical particles.

Due to large surface contamination of gloves used in the car repair shop it was very difficult to identify surface changes. It was clearly stated that non-slip surfaces of the edge of the structure has been significantly damaged as a result of real usage. Fig. 10B shows the cracks and crumbled pieces of elastomer on the surface. For all samples of chloroprene rubber gloves which were tested in variable environments different morphology of the pits was observed, what can be identified by comparison of the following images: 7B, 8B, 9B, 10D. This demonstrates clearly the different impact of investigated factors on the chloroprene rubber surfaces.

Similarly, conditions simulated in the laboratory have an effect on the chloroprene rubber surfaces. In this case there were observed changes in surface morphology which are cause of mechanical cracks and under the chemical environmental influence. It can be unambiguously stated that as a result of these interactions there is both mechanical and chemical degradation of tested surfaces.

T a b l e 2. Mean values of the tested protection parameters and performance levels for the studied protective gloves according to current standards for personal protective equipment evaluation [32]

Sample designation	Mean values of blade cut resistance [i_n] [x±SD]	Blade cut resistance performance levels *)	Mean values of abrasion resistance [number of cycles]	Abrasion resistance performance levels *)	Mean values of tear resistance; tearing force [N] x±SD	Tear resistance performance levels *)	Mean values of oil permeation rate during 8 h continuous exposure [μg/cm²·min] [x±SD] **)
1N	1.8 ± 0.1	**1**	2000	**3**	87 ± 2	**4**	171 ± 9
1L	1.6 ± 0.1	**1**	500	**2**	52 ± 3	**3**	1266 ± 39
1MW	1.7 ± 0.1	**1**	500	**2**	54 ± 3	**3**	1126 ± 38
2N	1.7 ± 0.0	**1**	2000	**3**	25 ± 2	**2**	18 ± 1
2L	1.5 ± 0.1	**1**	500	**2**	15 ± 1	**1**	94 ± 3
2MW	1.5 ± 0.0	**1**	500	**2**	15 ± 2	**1**	76 ± 2

Notes: x — mean value, SD — standard deviation, number of tested samples: n = 6.

*) Tests for cutting, abrasion and tearing were conducted according to the standards EN 388:2003 and EN 420+A1:2010; in case of cut resistance there was no differences for new and used samples of gloves; in case of abrasion resistance there was reduction of performance level for used samples of gloves in comparison to the new one (reported one point decreasing in protective level); tear resistance — there was decreasing of performance level of used gloves samples in comparison to the new one (reported one point decreasing in protective level from 4 to 3 for knitted gloves coated with rubber and from 2 to 1 for all-rubber gloves).

**) The test for mineral oil permeation was conducted according to the standards EN 374-3:2005, EN 374-3:2005/AC:2006. In this studies a huge amount of mineral oil permeating thru the gloves during 8 h testing in used samples in comparison to the new one was observed (the amount of permeated mineral oil thru the gloves was about 100 % higher for knitted gloves coated and also all-rubber gloves in comparison to the new one).

In Table 2 mean values of the tested protection parameters and performance levels for the studied protective gloves are shown.

The conducted study shows that the conditions under which gloves are used and the harmful factors they are exposed to exert a substantial impact on their effectiveness as a barrier against harmful chemical substances including mineral oils. Measurement of the concurrent effects of material degradation (decreased mechanical strength) changes in the permeation rate and changes in their surface morphology enables a comprehensive assessment of glove usefulness for repeated use.

CONCLUSIONS

— The research has indicated that the scanning electron microscope technique can be used to characterize the microstructural phenomena occurring on the surface of the materials barrier exposed to mechanical and chemical harmful factors. Scanning electron microscope technique allows accurate assessment of the morphology of the glove surface impacted by a single and combined action of harmful factors and shows that the simultaneous impact of risk factors on the gloves can negatively affect protection performance. Obtained scanning electron microscope observations allow claiming that for this purpose the device simulating usage processes in laboratory achied similar results in comparison to materials used in the workplace.

— Presented studies using a scanning electron microscope reveal changes in the microscopic scale on the protective gloves surface. Based on the results, it was found that the impact of the proposed conditions has a different influence on the morphology of the surface of both acrylonitrile-butadiene and chloroprene rubbers. In both cases there are different morphological features characterizing particular types of changes observed on the surface.

— In the case of the impact of individual factors on polyacrylonitryle rubber: mechanical factors and artificial sweat, there can be seen a different kind of damage to the surface, respectively, delaminations and voids. They confirm lack of rubber continuity, triggered by stress, swelling and cracking of the material, typical of the chemical surface degradation. In the case of complex impacts, the mechanical one has the most considerable influence on the impenetrability of the rubber. It is proven by the damage of the surface which is typical for mechanical degradation.

— The nature of the surface damage of the neoprene rubber is mainly influenced by the presence of a non-slip structure on the tested surface that is exposed to mechanical damage to a greater extent than other areas of the glove surface, which was proven on the basis of the research carried out in a workplace. In the case of the artificial sweat impact, some etched areas on the surface of the glove were found. Other surface changes resulting from the influence of the aggressive environment were observed in the case of application of the group of factors in simulated conditions in the laboratory. In the second case there was observed the cracked surface layer and the presence of light spherical particles, which may be products of chemical degradation of the surface.

— Scanning electron microscope technique could be used as an auxiliary tool which helps to predict the end of the service life of protective gloves and protective properties after the loss. Using SEM together with the protection parameters tests gives a full view of investigated gloves samples and it helps to conclude that the penetration of chemicals through protective material of the glove, that is its contact with human skin, may occur as soon as after 8 hours of work, despite the fact that the glove does not display any visible signs of damage. Defining the end of the use period of the protective gloves in workplaces after they were used for a few days or a few weeks may eliminate the situations where the user is exposed to uncontrolled impact of mainly harmful chemicals on his skin and the whole organism.

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REFERENCES

[1] Krzemińska S., Irzmańska E.: *Occupational Medicine* **2011**, *62(4)*, 435.

[2] He S., Scott C., De Luise M., Edwards B., Higham P.: *Biomaterials* **2003**, *24*, 235.

[3] Gomes A. P., J. F. Mano A. P., Queiroz J. A., Gouveia I. C.: "Microscopy: Science, Technology, Applications and Education" (Eds.: Mendez-Vilas A., Diaz J.), Formatex Research Center 2010, pp. 286—292.

[4] Goldstein J., Newbury D., Echlin P., Joy D., Romig A., Lyman C., Fiori C., Lifshin E.: "A text for biologists, materials scentists, and geologists", Plenum Press, New York 1992.

[5] Výchopňová J., Čermák R., Obadal M.: "Modern Research and Educational Topics in Microscopy" (Eds., Mendez-Vilas A., Diaz J.), No. 3, Vol. 2, FORMATEX, Badajoz, Spain 2007, pp. 704—712.

[6] Pandey K. N., Setua D. K., Mathur G. N.: *Polym. Test.* **2003**, *22*, 353.

[7] Betrabet S. M., Rollins M. L.: *Text. Res. J.* **1970**, *40(10)*, 917.

[8] Peterlin A., Ingram P.: *Text. Res. J.* 1970, *40(4)*, 345.

[9] Jin X., Gong K.: *J. Ind. Text.* **1996**, *26(1)*, 36.

[10] Monteiro V. F., Duboc Natal A. M., BastosSoledade L. E., Longo E.: *Mater. Res.* **2003**, *6(4)*, 501.

[11] Stawski D., Połowiński S., Herczyńska L., Sarna E., Rabiej S.: *J. Appl. Polym. Sci.* **2012**, *123(3)*, 1340.

[12] Hanumansetty S., Maity J., Foster R., O'Rear E. A.: *Appl. Sci.* **2012**, *2*, 192. doi:10.3390/app2010192

[13] Bidoki S. M., McGorman D., Lewis D. M., Clark M., Horler G., Miles R. E.: available on line: www.instrumentel.com/

documents/ink-jet-printing-of-conductive-patterns-on--textile-fabrics.pdf (01.09.2012).
[14] Bashir T., Skrifvars M., Persson N.-K.: *Polym. Advan. Technol.* **2011**, *22(12)*, 2214.
[15] Lee H. J., Jeong S. H.: *Text. Res. J.* 2005, *75(7)*, 551.
[16] Hu J., Xiao Z. -B., Zhou R. -J., Ma S. -S., Li Z., Wang M.-X.: *Text. Res. J.* **2011**, *81(19)*, 2056.
[17] Anita S., Ramachandran T., Ramaswamy R., Koushik C. V., Mahalakshmi M.: *JTATM* **2010**, *6(4)*, 1, available on-line: http://ojs.cnr.ncsu.edu/index.php/JTATM/article/viewFile/899/723 (01.09.2012).
[18] Onggar T., Cheng T., Hund H., Hund R.-D., Cherif C.: *Text. Res. J.* **2011**, *81(19)*, 2017.
[19] Wu G. P., Lu C. X., Wang Y. Y., Ling L. C.: *Fiber. Polym.* **2011,** *12*(7), 979.
[20] Cai Y., Gao D., Wei Q., Gu H., Zhou S., Huang F., Song L., Hu Y., Gao W.: *Fiber. Polym.* **2011**, *12(1)*, 145.
[21] Güneşoglu C., Kut D., Orhan M.: *Text. Res. J.* **2010**, *80(2)*, 106.
[22] Kingner T. D., Boeiniger M. F.: *JOEH* **2002**, *5*, 360.
[23] Harrabi L., Dolez P., Vu-Khanh T., Lara J.: *JOSE* **2008**, *14*, 1.
[24] Larivière C., Tremblay G., Nadeau S., Harrabi L., Dolez P., Vu-Khanh T., Lara J.: *Appl. Ergon.* **2010**, *41(2)*, 326.
[25] Vu Thi B. N., Vu-Khanh T., Lara J.: *Theor. Appl. Fract. Mec.* **2009**, *52(1)*, 7.
[26] Harrabi L., Dolez P., Vu-Khanh T., Lara J., Tremblay G., Nadeau S., Larivière C.: *Safety Sci.* **2008**, *46(7)*, 1025.
[27] Dolez P. *et al*.: "Effect of industrial contaminants on the resistance of protective gloves to mechanical risks", Proceedings of the 4th European Conference on Protective Clothing (ECPC) Performance and Protection, The Netherlands, Papendal, Arnhem, 10—12 June 2009.
[28] Krzemińska S., Rzymski W. M.: *Mater. Sci.* **2011**, *29(4)*, 285.
[29] Dolez P., Gauvin Ch., Lara J., Vu-Khanh T.: *JOSE* **2010**, *16*, 169.
[30] Vu-Khanh T., NgaVu T. B., Nguyen C. T., Lara J.: "Gants de protection: Étudesur la résistance des gants aux agresseurs mécaniques multiples. Études et recherché", R-424, IRSST 2005, 86.
[31] Irzmańska E., Dyńska-Kukulska K.: *Rev. Anal. Chem.* **2012**, *31(2)*,113.
[32] Irzmańska E., Stefko A., Dyńska-Kukulska K.: *Arch. Environ. Occup. H.* DOI: 10.1080/19338244.2013.787963.
[33] Dolez P., Vinches L., Plamondon P., Wilkinson K., Vu-Khan T.: *J. Phys. Conf. Ser.* **2011**, *304*, 012066.
[34] Dubois C., Vebrel J., Rigny-Bourgeois V.: *Macromol. Symp.* **2003**, *203*, 325.
[35] Korinth G., Schmid K., Midasch O., Boettcher M. I., Anderer J., Drexler H.: *Ann. Occup. Hyg.* **2007**, *51(7)*, 593.
[36] Abraham E. K., Ramesh P., Joseph R., Mohanan P. V., Remakumari V. M.: *Rubber Chem. Technol.* **2005**, *78(4)*, 674.
[37] Knudsen B. B., Larsen E., Egsgaard H., Menné T.: *Contact Dermatitis* 1993, *28(2)*, 63.

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— *J. Kucińska-Lipka, I. Gubańska, H. Janik* — Poliuretany modyfikowane polimerami naturalnymi do zastosowań medycznych. Cz. II. Poliuretan/żelatyna, poliuretan/skrobia, poliuretan/celuloza (*j. ang.*)

— *S. Firlik, Z. Wielgosz, S. Pawlowski, L. Tokarz, J. Stasinski, K. Suwala* — Wpływ 2,4,6-trimetylofenolu na wydajność syntezy i właściwości poli(tlenku fenylenu) (*j. ang.*)

— *U. Cabulis, I. Sevastyanova, J. Andersons, I. Beverte* — Pianki poliizocyjanurowe z udziałem poliolu z oleju rzepakowego modyfikowane różnego typu nanocząstkami (*j. ang.*)

— *I. Jacukowicz-Sobala, A. Ciechanowska, E. Kociołek-Balawejder* — Polimer hybrydowy zawierający tlenki żelaza otrzymany z wykorzystaniem polimeru redoksowego. Cz. II. Badanie właściwości sorpcyjnych wobec chromianów (*j. ang.*)

— *M. Stepczyńska, M. Żenkiewicz* — Wpływ wyładowań koronowych na właściwości warstwy wierzchniej polilaktydu

— *H. Żakowska* — Oznaczanie udziału surowców odnawialnych w polimerowych materiałach opakowaniowych

— *K. Formela, M. Cysewska* — Efektywność procesów termomechanicznej regeneracji miału gumowego, prowadzonych w przeciwbieżnej lub współbieżnej wytłaczarce dwuślimakowej (*j. ang.*)

— *A. Węglowska* — Wpływ parametrów zgrzewania wibracyjnego na jakość złączy z poliamidu 66

— *R. Koźmińska, I. Oleksiewicz, A. Pinar, W. Dominikowski* — Ocena wpływu biochemicznej modyfikacji powierzchni włókien poliestrowych na wskaźniki komfortu higienicznego wyrobów