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Article

The Influence of Mechanical, Physical and Chemical Influences on Protective Clothing

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Abstract: The article is focused on testing the mechanical, physical and chemical characteristics of the selected protective clothing. Old anti-chemical protective clothing formerly used in tactical exercises (but never during a real intervention) was selected. Protective clothing has an expected lifespan when used correctly. When in use, external influences can negatively affect and function of these garments. The article describes the preparation of individual samples of protective clothing which were exposed to the effects of selected inorganic and organic chemicals, water vapor, UV radiation and long-term exposure to elevated temperatures. The prepared samples were subsequently torn on the tearing device, and the change of mechanical and physical properties was monitored. The stress at which the samples broke and the length they reached at the moment of breaking were measured. The exposure to individual chemicals, UV radiation and elevated temperature resulted in decreases in the modulus of elasticity in each case. The largest decrease was recorded in samples treated with hydrogen peroxide and the smallest in samples exposed to long-term thermal load.

Keywords: chemical-resistant clothing; civil protection; occupational exposure; occupational health; occupational safety; protective clothing; quality of life

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1. Introduction

Contrary to popular belief, firefighters are occupationally exposed not only to thermal but also biological, chemical and physical hazards resulting from fire. Thus, their clothing, including its material, fabric types, layers and properties, must withstand these challenges in order to provide sufficient protection. Firefighters' protective clothing undergoes continuous modifications in terms of improve air/liquid impermeability, thermal insulation capacity and integrity, thus increasing the protection provided. To avoid injury and provide sufficient protection of the garment and the equipment, the International Organization for Standardization (ISO), the European Committee for Standardization (EN) and the National Fire Protection Association of the USA (NFPA) work constantly on certified firefighter products. However, the clothing may be damaged during individual interventions, and its properties may change as a result of this damage. Therefore, the aim of our work was to investigate the changes in the properties of protective clothing due to various external factors. Some authors have already pointed to the importance of focusing on this type of danger [1,2].

Officers of the Fire and Rescue Service (F&R Service) in Slovakia enter into various situations during their service in which they must go to great efforts in order to help others, including putting their own lives on the line. However, there are also cases where, in addition to normal equipment, various special apparatus, clothing and means are used in order to protect the life and health of the intervening firefighter in accordance with EU

Standards. For this purpose, anti-gas services are used in the F&R Service. Their use is approved by the Presidium of the F&R Service, and their means, use, control and testing are described in Instruction No. 70/2003 (instruction of the President of the Fire and Rescue Corps) [3,4]. In particular, this instruction describes the organization of work involved in the use, testing, maintenance and repair of anti-gas services, as well as the theoretical and practical training of the F&R Service officer in the use of these services during fire incidences or other hazards.

Individual emergencies include situations associated with chemical, technological or ecological accidents where the release of hazardous substances occurs or is expected to occur; these substances not only endanger the life and health of people present but also cause environmental pollution. Anti-gas services are used by members of the F&R Service during interventions in hazardous environments and are intended for use in searching for hazardous substances in the intervention area and in capturing and collecting hazardous, neutralizing, decontaminating or sorption substances. There are also means intended for reviving the vital functions of various filling, control, measuring and testing devices, as well and firefighting equipment intended for carrying out chemical-technical, epidemiological–hygienic and ecological activities [3].

In various hazardous interventions, it is important that firefighters protect their lives and thus their health. To this end, protective clothing is used to protect the surface of the body. There is protective clothing used for protection against chemical agents and biological materials, protective clothing for protection against thermal radiation and protective clothing for protection against radioactive fallout, as well as combined protective clothing. All types of protective clothing must be used according to the instructions specified by the manufacturer. Therefore, in order for protective clothing to be deployed in an intervention, an order is needed from the intervention commander, who considers the situation at the exposed articular site and subsequently issues an instruction for the use of each type of protective clothing [4–8].

Moreover, protective clothing for firefighters should meet special requirements concerning materials, layers and physicochemical properties, which are described in the European Standards: EN 469:2020, which concerns basic clothing for firefighting, referring in the text to so-called "structure fires" [9]. The EN 15384:2020 document sets out new laboratory methods and requirements by which to protect the firefighter's body—except for the head, feet and hands—using clothing that is worn during wildland firefighting [10]. Firefighters are also exposed to other harmful occupational conditions besides high temperature, e.g., during rescue operations. The EN 16689:2017 standard covers protective clothing for technical rescue [11]. The EN 1486:2007, which is available in the English language, is the standard indicating personal protective reflecting clothing for specialized firefighting [12]; however, in the Polish language, there is the newer PN-EN 1486:2009 standard, wherein the requirements for reflecting thermal radiation clothing for special firefighting action have been reported [13]. These two standards consider the use of whole-body protection, including protection of the respiratory tract, head, hands and feet. There are also special European Standards concerning firefighters' head protection (EN 13911:2017; EN 443:2008; EN 16471:2014; EN 16473:2014 [14–17]), hands protection (EN 659:2003+A1:2008 [18]), feet protection: (EN 15090:2012 [19]) and eyes protection: (EN 14458:2018 [20]).

Protective clothing must meet the required criteria and standards. Moreover, its expected lifespan is dependent on the proper storage and care of the suits. There are several studies that emphasize the need to address external influences that can negatively affect the life and quality of protective suits and thus reduce their protective properties [21,22]. The studies mainly deal with the structures of substances themselves and their disruption after use and the influence of various conditions. The problems pertain to repeatability and difficulties in interpreting the results. For this reason, it was necessary to carry out testing which can be repeated under certain conditions without the need to examine the very structure of the tested substance. The test results can be verified for other protective items of clothing made of similar material and will enable the crisis manager to assess the suitability of used protective clothing for use. Based on the obtained results, it will then be possible to achieve sufficient protection of persons who are directly involved in managing crisis phenomena. They will not have to worry that the material used does not meet the required protective properties.

MSA Auer Vautex Elite chemical-resistant clothing was used for testing in these experiments. The tested chemical-resistant garments were classified as category III personal protective equipment. This category includes personal protective equipment that is designed to protect life and health and to protect against hazards that cannot be detected in time. Personal protective equipment provides a degree of protection against biological and chemical contamination and ionizing radiation. The personal protective equipment in this category is also designed to protect against hazardous gases, liquids or solid particles. This equipment is also used in high- or very low-temperature environments, in work where contact with electricity may occur or in work at heights or depths [23–25].

Protective clothing can be classified within the group of pressurized chemical protective suits. The entire protective suit is covered by a layer of elastomer and laminate foil. The suit consists of a suit body, a replaceable visor, a replaceable glove system, boots and the sealed seams of the protective garment. The total weight is approximately 9 kg. It provides protection not only against solid, liquid and gaseous chemicals but also from radioactive contamination. Simultaneously, it provides high protection against flames with a temperature of up to 800 °C for 5 s. It can also be used in conditions where the ambient temperature ranges from −30 °C to +60 °C. This type of protective clothing must be stored within the temperature range 15–25 °C [26,27]. With regard to the service life of the suit, a time interval of approximately 10 years can be discussed [28]. Due to the initial purchase price, these materials are usually used even after this period. Therefore, it is necessary to test how external influences may affect the quality of protective clothing.

The aim of this study was to use the described experiments to verify the suitability of protective chemical-resistant clothing over its repeated use.

2. Materials and Methods

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods were used simultaneously for the thermal analysis of the filaments on a Mettler Toledo TGA/DSC 2 instrument in the temperature range 25–750 °C, with a temperature rise rate of 20.00 K/min and an air flow rate of 50.0 mL/min in an alumina crucible with a volume of 70 μL.

The experiment aimed to monitor the mechanical, physical and chemical properties of chemical-resistant clothing meeting the criteria of the EN and ISO standards to protect firefighters against harmful occupational conditions. All tests were performed on a suit that had been reused multiple times in exercises. It was not contaminated with any chemical substance, but had been mechanically stressed during repeated donning, decontamination, drying and storage. A control sample was collected from this protective clothing. The firefighters' protective clothing was decommissioned and was provided to the Occupational Safety Research Institute by an unnamed firefighting unit from the Žilina region of Slovakia. The protective clothing was used in tactical exercises and had never been used in an intervention. The samples that were cut from the suit were observed for changes.

2.1. Preparation of Chemical-Resistant Garment Samples for Chemical Application

The protective clothing tested was cut into squares measuring approximately 13 × 13 cm. For testing, the most common chemicals that firefighters come into contact with were chosen. These chemicals were selected after consultation with the clothing provider and with regard to the most probable chemicals used in the given location during interventions. Subsequently, on one square, part of the suit was exposed to H_2SO_4 (sulfuric acid) 96%; on another square, HNO_3 (nitric acid) 65% was dropped. Hydrogen peroxide (H_2O_2) (30%) and dimethyl sulfoxide (C_2H_6OS, p.a.) were added to parts of the garment. Subsequently, another part of the suit was exposed to UV radiation and long-term (18 h) temperature elevation. Petri dishes were not used for tests. The areas of the garment were straight and taut.

For exposure of protective clothing to the effects of the selected chemicals, adding the inorganic and organic chemicals to the individual samples was completed in accordance with the mock-up presented in Figure 1.

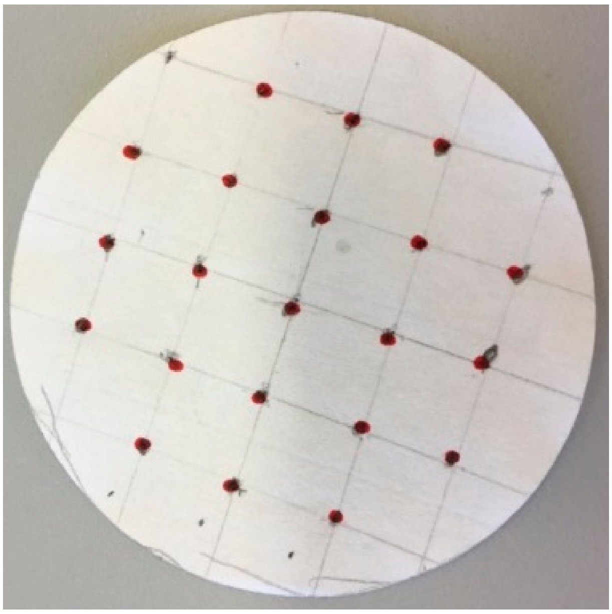

Figure 1. Mock-up of dropping of the selected chemicals onto protective clothing.

The first substance dropped onto the test protective clothing was sulfuric acid (H_2SO_4). The droplets spread over the suit and their color changed from brown to black, as shown in Figure 2a. The second chemical dropped was the inorganic compound nitric acid (HNO_3). After application, the drops spread over the clothing and created patterns of various shapes and change color to black. The edges of the figures were dark black, and the interior of the figures were a faint shade of black, as shown in Figure 2b. The third substance used was hydrogen peroxide (H_2O_2). The droplets spread but did not cause any staining of the garment and no changes were visible, as shown in Figure 2c. The last substance used was the organic chemical dimethyl sulfoxide (C_2H_6OS). In this case, the drops also spread but did not cause any coloration of the garment and no changes were visible, as shown in Figure 2d.

All chemicals were left on the samples for 60 min. After this time, they were rinsed: each inorganic chemical sample was rinsed with 50 mL of distilled water, and each organic chemical sample was first rinsed with 10 mL of ethanol and then with 50 mL of distilled water.

The rinsed samples were placed in a MEMMERT ULE 400 electric drying oven with the temperature set at 35 °C. The samples were left in the oven for 2 h. All samples were completely dried in that time. The parts of the protective clothing to which sulfuric acid was applied were still wet and could not be dried completely.

(**a**) Effect of H_2SO_4 (sulfuric acid) on protective clothing after 60 minutes

(**b**) Effect of HNO_3 (nitric acid) on protective clothing after 60 minutes

(**c**) Effect of H_2O_2 (hydrogen peroxide) on protective clothing after 60 minutes

(**d**) Effect of C_2H_6OS (dimethyl sulfoxide) on protective clothing after 60 minutes

Figure 2. Effect of various applied substances on protective clothing after 60 minutes.

2.2. Preparation of Samples for Exposure of Protective Clothing to UV Radiation and Prolonged Exposure to Elevated Temperature

The protective suit was exposed to UV radiation at temperatures of up to 100 °C for approximately 20 min. Visually, no mechanical or other damage could be observed (see Figure 3).

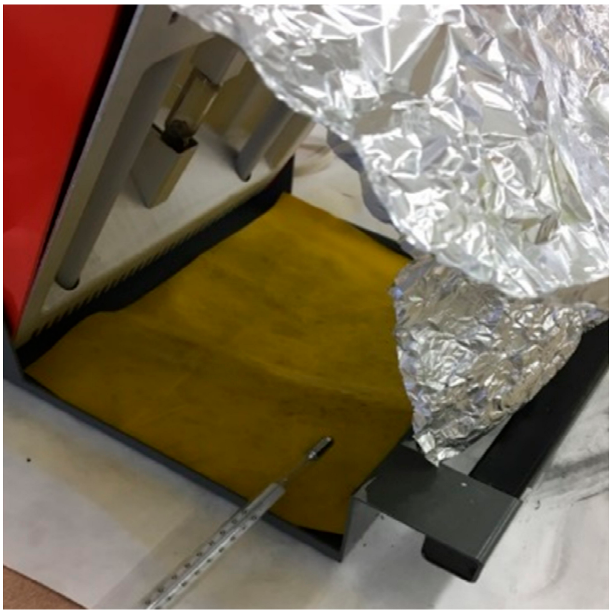

Figure 3. Effect of UV radiation on the tested part of the protective clothing.

In cases of intervention by firefighters, the protective suit is often exposed to elevated temperatures. Therefore, the testing also focused on the influence of increased temperature for a certain period of time. For 24 h, the suit was placed in a dryer where the temperature was 65 °C. After removal, no damage could be observed.

TGA (thermogravimetric analysis, thermogravimetry) and DSC (differential scanning calorimetry) were performed on the protective clothing samples that were exposed to UV radiation and to prolonged elevated temperature.

2.3. Testing Methodology

The specimens prepared as described were tested in accordance with the standard for static and mechanical tensile testing for plastics: CSN EN ISO 527 Plastics—Determination of tensile properties. The specimens were supplemented with a control specimen (C) to which neither chemical nor physical influences were applied.

For the tests, a tearing machine was used, which is a testing machine for the determination of the strength of materials, manufactured by VEB TIW (Thüringer Industriewerk) Rauenstein, mechanical type, year of manufacture 1987; the machine meets the requirements of EN OSO 7500-1 for accuracy class 1. The distance between the upper and lower jaws of the tearing machine was set to a distance of 40 mm.

The principle of the mechanical test used in the measurement is the short-term loading of the test specimen with a defined load. The behavior of individual elastic materials in the small strain region can be described by Hooke's law, which defines a directly proportional relationship between stress and strain. From the obtained values of F and Δl using mathematical relations, the mechanical stress (1), the relative strain (2), and the tensile modulus (3) were calculated.

$$\sigma = F/S \quad (1)$$

σ—Mechanical stress (MPa);
F—Power (N);
S—Area (m^2).

$$\varepsilon = \Delta l/l \quad (2)$$

ε—Relative deformation (−);

Δl—Length increment after loading (m);
l—Length increment before loading (m).

$$E = \sigma/\varepsilon \quad (3)$$

E—Tensile modulus of elasticity, also Young's modulus (MPa);
σ—Mechanical stress (MPa);
ε—Stress-induced deformation (−).

The main evaluation criterion is the change in the modulus of elasticity (E) after chemical exposure and physicochemical action.

To test the influence of physical conditions on the samples, UV radiation was used. For the long-term exposure and elevated temperature, a MEMMERT ULE 400 electric dryer was used. The samples thus exposed were also subjected to DTA and DSC. A METTLER TOLEDO TGA/DSC 2 HT/1600/101 was used for this analysis. The samples were weighed to an accuracy of 1 µg. The temperature range for organic compounds was set to 25–750 °C with a heating rate, i.e., temperature rise, of 20 K/min. The volume of the cup was 70 microliters, and the composition of the cup was alumina (AlO_3). Data logging was performed at 1 s intervals. The air flow rate was 50 l/min. The measurement was carried out in an atmosphere of 80% nitrogen and 20% oxygen. For subsequent analysis, the results were evaluated in the appropriate software.

The tests were performed on a small scale. Before measurement, the test materials were placed in a climate chamber for two days, in which the temperature was set at 23 °C and the humidity at 60%.

3. Results and Discussion

The measured values from the experiments (averages of five measurements) are shown in Figures 4–6 for the chemical loading of the suit samples and in Figures 7–9 for the physical loading of the suit samples.

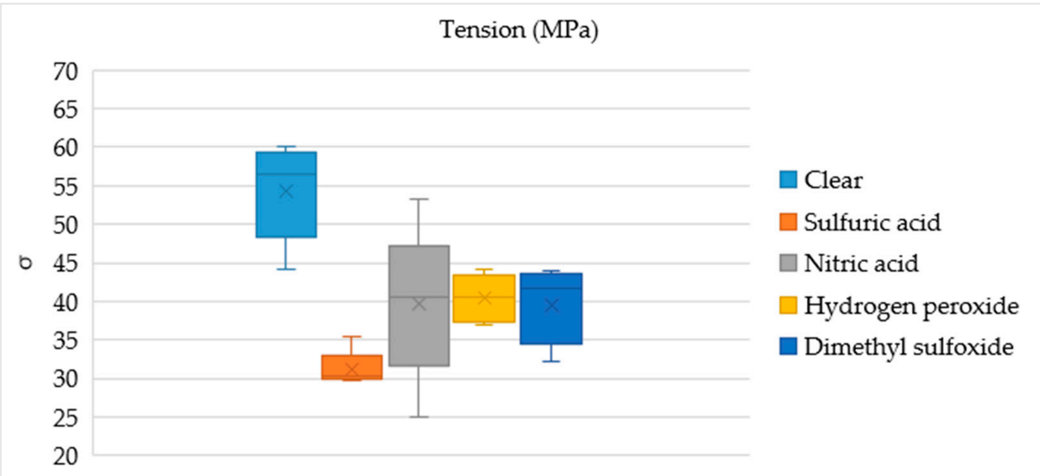

Figure 4. Average values of the mechanical stresses under the action of the studied/selected chemicals.

As shown in Figure 8, the biggest decrease in mechanical stress was observed for sulfuric acid; it reached −23.17 MPa, which was 42.61%. More moderate decreases of −27.05 and −25.70 MPa were recorded for nitric acid and hydrogen peroxide, which were equivalent to 14.71 and 13.98%, respectively. The smallest decrease in mechanical stress was recorded for dimethyl sulfoxide (−19.86 MPa), which was equivalent to 10.80%. All the applied chemicals caused a decrease in mechanical stress, but not to the same extent [29,30]. As was expected, the greatest decrease in mechanical stress was caused by sulfuric acid.

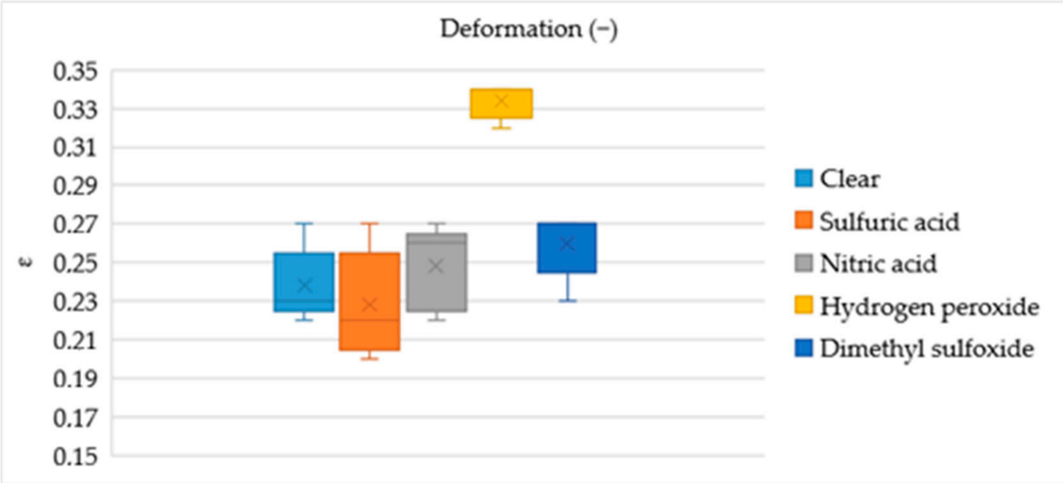

Figure 5. Average strain values on exposure to the studied/selected chemicals.

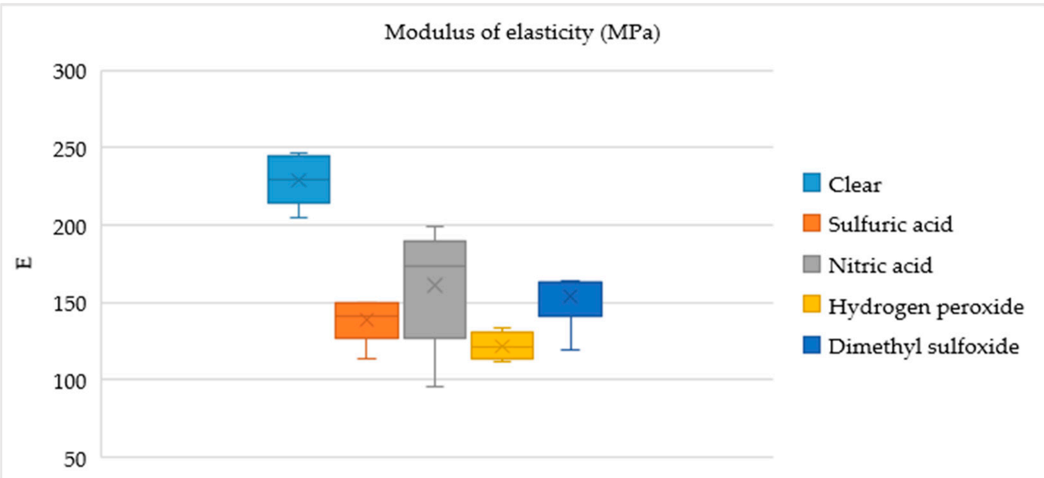

Figure 6. Average values of the tensile modulus of elasticity under the action of the above chemicals.

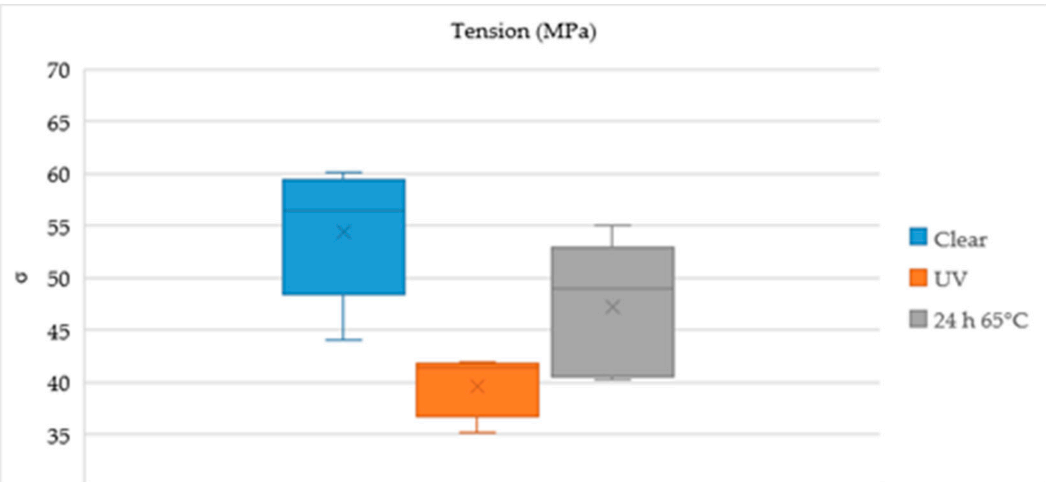

Figure 7. Average values of mechanical stress under physical influences.

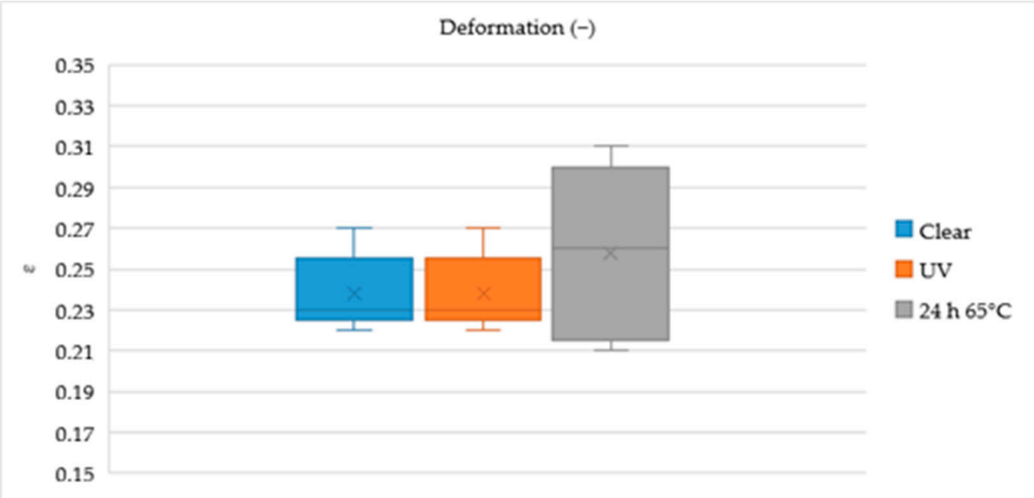

Figure 8. Average values of deformation under physical influences.

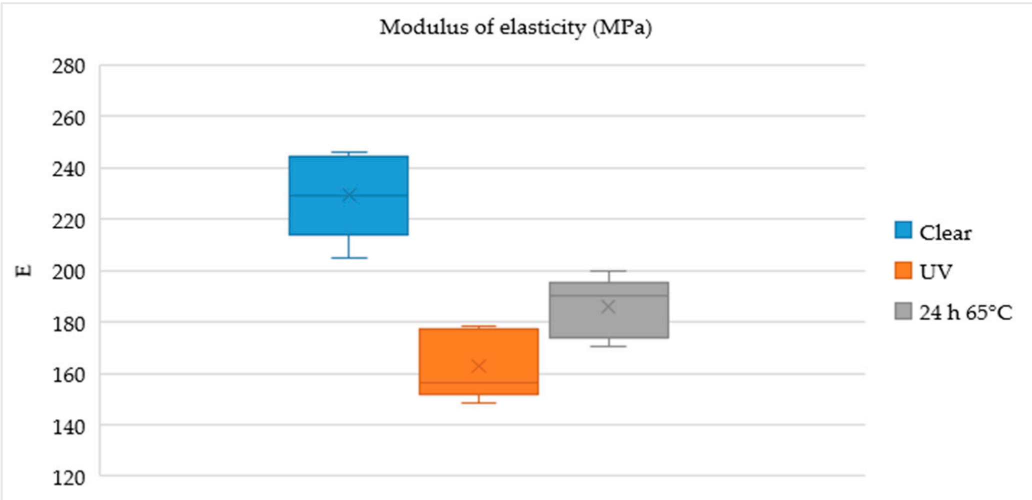

Figure 9. Average values of tensile modulus of elasticity under physical influences.

In the deformation evaluation, the applied chemicals caused different changes [31,32]. If, in the previous evaluation criterion, the measured values of mechanical stress were observed to decrease in all cases, for deformation, we observe a decrease (not statistically significant) of only −0.01, which amounts to 4.2%; for the other chemicals, we observe an increase in deformation. For nitric acid, an equally small increase of +0.01 (4.2%) was observed. Moreover, for hydrogen peroxide, an increase of +0.08, which amounts to 37.5%, was reported. An increase of +0.02, which amounts to 8.33%, was observed for dimethyl sulfoxide (see Figure 5).

For the tensile modulus of elasticity, as for the mechanical stress, a decrease was observed for all the studied chemicals, but it did not follow the same order or have the same values [32,33]. As can be seen from Figure 9, a decrease of −90.58 MPa in tensile modulus was recorded for sulfuric acid, which was 39.52%. A milder decrease was recorded for nitric acid, of −68.12 MPa, which was 29.71%. For hydrogen peroxide, the largest decrease of −107.56 MPa was recorded, which was 46.92%. For dimethyl sulfoxide, a decrease of −75.1 MPa was observed, which was 32.76%. All the applied chemicals caused a decrease in mechanical stress, but not to the same extent [34]. As we expected, the greatest decrease in mechanical stress was caused by sulfuric acid, because sulfuric acid is a strong inorganic acid with hygroscopic and oxidizing properties.

The physical effect on the chemical-resistant suit material was measured using the same evaluation criteria and then expressed in terms of changes in mechanical stress, strain and tensile modulus of elasticity [35,36].

When evaluating the change in mechanical stress, a decrease in the values for both physical effects compared to the control sample was observed. For UV exposure, the decrease was 14.74 MPa, which was 27.1%, and for conditions of 65 °C for 24 h, the decrease was 7.2 MPa, which was 13.24% (see Figure 7).

In terms of physical effects, UV radiation had no effect on the deformation, with the same average value measured as for the control sample [37–39]. In addition, the exposure to heat at 65 °C for 24 h had very little effect for the change; it increased the deformation by only +0.02, which was 8.33% (see Figure 8).

When evaluating the change in tensile modulus, a decrease in values compared to the control sample was observed for both physical effects. For UV exposure, the decrease was 59.32 MPa, which was 25.88%, and for exposure to 65 °C for 24 h, the decrease was 43.47 MPa, which was 18.96% (see Figure 9).

During the study, the following question emerged: would there be a change in thermal stability in comparison to the original material? The sample was exposed to 65 °C for 24 h in a drying oven or 2 h of UV irradiation equivalent to the level of "mountain sun". TGA and DSC were performed. The weight decay occurred at about 240 °C and was associated with a mild exoeffect, which peaked and was terminated by an intense exoeffect with a maximum at 560 °C. It is important to test protective materials to meet safety requirements in companies [40].

Civil protection focuses on the prevention of crisis phenomena, the preparedness for crisis phenomena, the response to crisis phenomena and the return to the original state after the crisis [41]. Every organization tries to prevent the occurrence of a negative event through prevention [42,43]. Despite this, it is not possible to completely eliminate the risk of a crisis phenomenon, which is why it is necessary to pay sufficient attention to preparedness for possible crisis phenomena [44,45]. This will enable a more effective response and a smoother return to the pre-crisis state [46,47]. In the case of an event where a dangerous substance is leaked, it is necessary for the responding firefighters or civil protection units to have clothing that provides the necessary protection. After an intervention involving a hazardous substance, protective clothing must be decontamination, cleaned, dried and then stored [46]. A previously used suit may have lower durability and protection even though the expected lifespan has not passed [48,49]. Some authors have investigated the properties of protective clothing used by firefighters based on available data and evaluations [50]. In the case of firefighters' protective clothing, the focus of testing is mainly related to the effect of heat on the protective clothing [51]. The studies focus on the resistance of the material in the case of prolonged exposure to a certain factor and on the duration of damage to the material. Protective clothing may come into contact with various physical and chemical factors during use. Individual factors affect the properties of the garment and will damage it to a certain extent when they act on it. Within this study, we wanted to indicate the need to focus on this issue by taking these influences into account. Based on the results, it is possible to assess the extent to which the protective suit may be degraded and subsequently become unsuitable for further use. In the case of underestimating these factors, the health or life of the person involved could be endangered during an intervention with the used protective suit [52]. The importance of examining external influences on the quality of protective clothing is also emphasized in the research of He et al. (2023) [53]. As part of our studies, we focused on certain types of influences with which it was assumed that the interventionist might come into contact. In the event that, in some areas, the responding units come into contact with other substances, a similar study should be carried out that performs these same procedures but with substances that are typical or expected for the given environment.

4. Conclusions

The results of tests on the chemical-resistant garment samples show that exposure to chemicals (sulfuric acid, nitric acid, dimethyl sulfoxide, hydrogen peroxide), UV radiation and elevated temperature (~65 °C), in all cases, was associated with a decrease in the modulus of elasticity. The highest decrease was reported in the sample with hydrogen peroxide and the smallest in the sample exposed to long-term thermal load.

Nevertheless, the TGA and DSC curves were identical for the original garment sample and for the samples exposed to UV radiation and long-term thermal stress. Protective clothing decomposes at or above a temperature of 240 °C with a slightly elongated exoeffect, which changes to the main exoeffect at 560 °C. The values obtained from the measurements can be used by fire protection units in practice during interventions. It will also serve as useful information for the International Organization for Standardization, the European Committee for Standardization, the National Fire Protection Association of the USA and the National Standards Body in Poland, which ensures the protection of life, health, environment and work safety, demonstrating that the suit meets their criteria and protects firefighters' health. The importance of this issue is also emphasized in the European environment because, in the case of serious accidents associated with the release of hazardous substances, intervention by firefighters or civil protection units is necessary. Therefore, it is necessary that their clothing meets all requirements and is not damaged by hazardous substances. This is important because a safety culture should include the knowledge of all risks that may occur.

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