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A SELF-HEALING SYSTEM FOR THE SOLES OF ALL RUBBER PROTECTIVE FOOTWEAR

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ABSTRACT

The objective of work was to improve the safety performance of protective footwear by increasing its service time using next-generation polymeric materials featuring autonomous self-healing mechanisms capable of repairing mechanical defects in a sole structure without an external intervention. The project innovation consists of using autonomous self-healing mechanisms in protective footwear to increase its service time and improve its safety performance in the workplace. Some mechanical defects naturally occur in the structure of personal protective equipment in the course of its normal use. While initially those defects are often not visible and difficult to detect, they may compromise polymeric materials and over time lead to permanent damage and shorter service times. The applied autonomous self-healing mechanisms (ASMs) have the capacity of immediate material regeneration without the external intervention. The first ASM involves a micro-encapsulated monomer released in the case of damage to fill the resulting defect in the sole. The other ASM involves the implementation of a network of channels supplying the monomer to the damaged area.

KEYWORDS

Protective footwear, self-healing materials.

INTRODUCTION

New achievements in the field of materials engineering now allow the production of innovative polymer materials with the ability to self-repair and the application of these solutions to the personal protective equipment used in the work environment, e.g. polymer elements used for the soles of safety shoes or protective gloves and clothing to increase its service time and improve its safety performance in the workplace.

Existing knowledge about the end of service life of protective footwear is very limited, because the degree of their wear (loss of their protective properties) depends on multiple factors associated with workplaces. The actual level of protection conferred by the sole is affected by many determinants, which are not evaluated in laboratories for methodological reasons, but which may have a significant impact on their performance [1].

Laboratory tests conducted according to standards harmonized with Directive 89/656/EEC supply basic information about the degree of protection provided by footwear, which may be used, e.g., for comparing products available in the market in terms of their suitability for specific workplace condition [2].

Unfortunately, this information, addressed to workers and employers alike, does not reflect the actual levels of protection as it does not take into account in a comprehensive manner the effects of external factors on the footwear or the time of its use in the workplace. Some mechanical defects naturally occur in the structure of personal protective equipment in the course of its normal use. While initially those defects are often not visible and difficult to detect, they may compromise polymeric materials and over time lead to the permanent damage and shorter service times. Products may be affected by various factors reducing their mechanical or protective properties. These factors originate from the conditions at the workplace as well as from the interaction between the user and gloves or footwear and mechanical or chemical stress. Moreover, self-healing polymer materials can minimize economic loss and accidents in the workplace.

In the literature, there is a division of polymer composites with the ability to self-repair due to the method of its initiation defined by the chemical structure and the self-healing mechanism: autonomous self-healing materials (AMS), where the self-healing mechanism starts automatically in response to damage / fracture in the material and non-automatic self-healing materials (NMS) requiring an external stimulus, e.g. temperature, pressure [3–4].

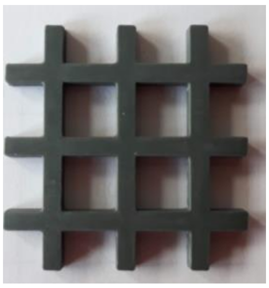
The paper shows innovative research on self- healing materials. The CIOP-PIB conducted exploratory research on the use of polymers with self-healing properties based on a non-autonomous self-healing mechanism occurring as a result of an external stimulus, i.e., the temperature in elastomeric personal protective equipment. Promising results were obtained for self-healing polymeric materials based on methylvinylsilicone rubber containing hybrid molecules with an inorganic silsesquioxane in the protective gloves. Evaluation of self-healing process of the elastomeric composite predicted to the personal protective equipment was performed. For this purpose the assessment of the surface morphology of materials have been performed before and after the self-healing process. The protective properties were also confirmed by analysis of permeation resistance before and after the healing process. The obtained results confirm the possibility of using tested elastomeric composite in the construction of protective gloves and showed an effectivity of the self-healing process [5–6].

Currently underway work concerning the development of products containing materials characterized by the ability to immediately regenerate them without any human intervention - i.e., polymers based on autonomous mechanisms in the safety footwear.

The first ASM involves a micro-encapsulated monomer released in the case of damage to fill the resulting defect in the sole. The other ASM involves the implementation of a network of channels supplying the monomer to the damaged area [7–8].

MATERIALS AND METHODS

The study involved soles made of materials widely used in commercially available protective footwear, namely, poly (ethylene-co-vinyl acetate) (EVA), poly (vinyl chloride) (PVC), and polyurethane (PU). Then the test results were compared to the results with a sole made of polyurethane with self-healing mechanisms applied, containing microcapsules (Figure 1a) and polymer microchannels (Figure 1b).

a) 

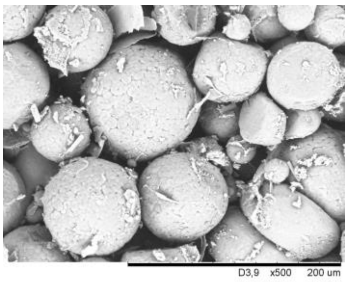
b) 

Figure 1. Visualization of polymeric microchannels and microcapsules responsible for the self-repair process.

The studied commercially available soles were evaluated in terms of protective parameters (bending strength and abrasion resistance) as well as physical parameters (density, hardness, morphology of surface). Samples with self-healing properties were tested before and after the simulated puncture failure. Samples were acclimatized at (23 ± 2)°C and a relative humidity of (50 ± 5)% for 48 h.

RESULTS AND DISCUSSION

The presented preliminary study focused on the abrasion resistance and bending strength of three commercially available sole materials. Changes in the density and hardness of the examined materials were evaluated by the following exposure to cyclical factors. Statistical analysis was performed to identify significant differences between the three types of polymers in terms of abrasion resistance, density, and hardness. The surface morphology (Figure 2) of the sole materials was examined by means of scanning electron microscopy.

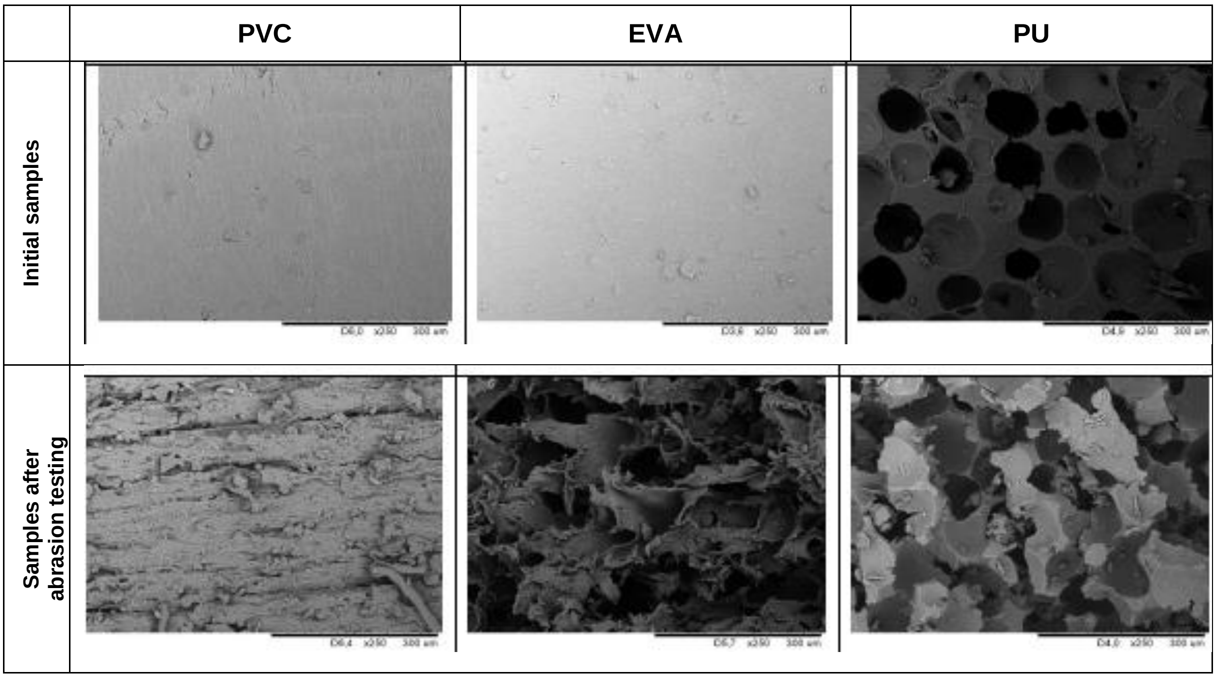


Figure 2. Photomicrographs of the surface morphology of sole samples.

In the case of dry workplaces, the soles are mainly affected by friction processes leading to the abrasion of the sole surface. The abrasion resistance of sole materials depends on their density and porosity. The porous structure affects a number of material properties, such as sorption capacity as well as mechanical, thermal, and electric characteristics. The properties of porous materials depend on the content of open and closed pores. Other important factors are pore shape (ranging from narrow slits to spherical cavities), size fractionation, and spatial distribution. In the present study, the lowest density was found for EVA soles (0.22 g/cm^3). Following the abrasion of the external surface, the revealed structure was highly porous (with open pores). The highest density was recorded for non-porous PVC soles (1.21 g/cm^3); their surface displayed scratches, irregularities, and detaching fragments.

Then influence of self-healing mechanisms in the polyurethane matrix was investigated. Studies on commercial soles have shown that polyurethane soles have the greatest tendency to crack and wear. The use of polymeric microchannels and microcapsules filled with a repair agent is aimed at releasing the repair agent as a result of damage and preventing the material degradation, lowering protective parameters and extending the end of service life.

CONCLUSION

Conducted research confirmed the possibility of applying self-healing mechanisms to the construction of protective gloves and footwear. The self-healing process was also proven effective with gloves and safety shoes in response to damage. The new approach applied in this work may be a useful tool in improving the safety of workers using the polymeric protective footwear in the context of sole wear. Our results constitute the first step towards a better understanding of the effects of self-heling systems on estimating the service life of soles in all-rubber footwear.

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