

Cut-resistant functional coated aramid knitted textiles

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Abstract: The effect of SiO₂ (0.5–2.5 wt%) with a particle size of 1–5 μm on the rheological and tensile properties as well as cut resistance of aramid fabrics coated with a thin layer of silica-containing latex was investigated. The rheological properties of the latex were assessed based on the dependence of viscosity on shear rate. The developed polymer coatings belong to the group of nonlinear, shear-thinning viscoelastic fluids, since their viscosity decreases with increasing shear rate. A 40% increase in cut resistance was obtained with increasing SiO₂ content in the latex.

Keywords: polymer coatings; cut resistance materials; silica.

Funkcjonalne powlekanie tkaniny aramidowe odporne na przecięcia

Streszczenie: Zbadano wpływ SiO₂ (0,5–2,5% mas.) o wielkości cząstek 1–5 μm na właściwości reologiczne i mechaniczne przy rozciąganiu oraz odporność na przecięcie tkanin aramidowych pokrytych cienką warstwą lateksu zawierającego krzemionkę. Właściwości reologiczne lateksu oceniono na podstawie zależności lepkości od szybkości ścinania. Opracowane powłoki polimerowe należą do grupy nieliniowych, rozrzedzanych ścinaniem płynów lepkosprężystych, ze względu na to, że ich lepkość zmniejsza się wraz ze wzrostem szybkości ścinania. Uzyskano 40% wzrost odporności na przecięcie wraz ze wzrostem zawartości SiO₂ w lateksie.

Słowa kluczowe: powłoki polimerowe, materiały odporne na cięcie, krzemionka.

The functionalization of textile materials, including those intended for personal protective equipment, can be done by physical or chemical surface modifications as well as by the application of nanoparticles to obtain certain protective and functional properties [1–5]. The extensive research efforts in this respect have included the development of extensible elastomeric fibers, such as polyester-based elastic fibers and shape memory coatings [6–8], the functionalization of high-performance polymer fibers by nanoscale modifications [9–11], as well as the fabrication of 3D textiles, nanoporous structures, and specially designed textile-based composite structures for improved protection against mechanical hazards [12–14]. Notably, the mechanical strength (including cut resistance) of textile materials can be enhanced by the application of polymer coatings which add to its thickness and alter its surface structure [15–17]. Such coatings are typically made of poly(vinyl chloride), latex, polyurethane, and nitrile [18, 19]. Of the essence of the technology of coated textile production are the rheological parameters of the applied polymers [20].

The polymers used for coating textile materials primarily belong to the group of thermoplastic polymers [21]. In the process of coating textile materials, of particular importance are thickness, continuity, and uniformity of the coating. These parameters directly impact the homogeneity of material properties across its entire surface. The viscosity of the polymer layer during the coating process has a major influence on the uniformity of coating distribution [22–24]. Moreover, the rheological properties of polymers are important to the functionalization of textiles in that they impact the plastic deformation of the surface layer under loading [24].

The basic rheological parameters of polymers include viscosity (η , mPa · s), stress (τ , Pa), melt flow rate (MFR) or melt volume rate (MVR), as well as the relationship between viscosity and shear rate ($\dot{\gamma}$, s⁻¹) [20, 25]. The rheological behavior of a polymeric material depends, amongst other factors, on its particle orientation and aggregation, ability to form phases over various temperature ranges, degree of crystallinity, and chemical composition (including any additives or fillers) [26].

The addition of fillers changes the physical and chemical properties of polymers. The size, shape, and chemical structure of the introduced filler particles significantly influence the formation of the porous structure of the polymer [27–29]. Depending on parameters such as particle size, morphology, and surface area, three main groups of fillers can be identified – reinforcing, semi-reinforcing,

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and non-reinforcing [30]. Fillers influence the viscosity of polymers by altering their physical and chemical properties through filler-polymer interfacial interactions [31, 32].

Due to their structure, the most used reinforcing fillers are inorganic ones: they not only fill the polymer matrix, but also enhance its mechanical properties [33]. The most widely used reinforcing filler is amorphous silicon dioxide (silica, SiO_2). In terms of mechanical properties, silica leads to superior strength parameters as compared to carbon-based fillers due to their high adhesive properties in the polymer matrix [34, 35]. Siloxane groups on the surface of silica increase their surface activity, while the presence of hydroxyl groups leads to strong interactions between filler particles and the formation of strong intermolecular bonds. This increases the affinity of the filler for the polymeric material, resulting in good dispersion of the filler in polymer matrices [36].

The size of filler particles used is also crucial. Unlike microparticles, nanoscale particles tend to rapidly aggregate due to their large specific surface area and high surface free energy [37]. On the other hand, a large diameter of filler particles can lead to weaker interactions with the polymer and an uneven distribution of particles throughout the composite volume, resulting in its decreased resistance to mechanical forces [30].

Mechanical properties are also influenced by the amount of filler per unit volume of polymer. Exceeding the optimal filler concentration may cause particle agglomeration and reduce the mechanical properties of the composite [38, 39]. Importantly, rheological properties can be used to qualitatively assess changes in molecular parameters under the influence of external factors, including mechanical deformation [40].

Resistance to cutting is a particularly important protective parameter in the context of mechanical hazards [41]. The protective parameters of personal protective equipment (PPE) are subject to the requirements of the Regulation of the European Parliament and of the Council (EU) 2016/425 [42]. The primary test method for materials protecting against mechanical factors is described in the standards EN 388 [43] and EN ISO 13997 [44]. In terms of improving the mechanical properties of protective materials by the application of thin polymer coatings, researchers have studied the impact of polyurethane coatings on tensile strength and elongation [21, 45], as well as on stab and puncture resistance [19].

In the available literature the influence of the viscosity of the polymeric material which is subsequently applied

to the textile carrier in terms of its effect on cut resistance has not yet been assessed.

In this study, thin polymer coatings made from latex paste containing silica (0.5–2.5 wt%) were investigated. The rheological properties were evaluated to determine the viscosity-shear rate relationship, followed by the tensile properties, and cut resistance. The aim of the study was to determine the effect of the rheological and tensile properties of the latex paste used to produce thin coatings on the cut resistance of the resulting composite materials.

EXPERIMENTAL PART

Materials

Latex paste (Texchem Ltd., Latchorzew, Poland) with five different contents of SiO_2 (purity: 99%, specific surface area: ca. $150 \text{ m}^2/\text{g}$; 3D-nano, Cracow, Poland) with a particle size of 1–5 μm were used (Table 1). The maximum filler content allowing homogeneous integration with the polymer paste was 2.5 wt%, therefore higher content was not used in this study. The filler was combined with the latex paste by mixing in a laboratory stirrer at 1200 rpm for 5 min. Rheological properties were evaluated on samples in liquid form.


Table 1. Composition of examined samples

Sample	Silica content, wt%
W0	0.0
W1	0.5
W2	1.0
W3	1.5
W4	2.0
W5	2.5

Samples preparation

Latex paste, with different concentrations of SiO_2 , was spread in a template to obtain with the dimensions in accordance with the standard EN ISO 527-1. The paste was cured at 120°C for 10 min in a laboratory dryer (Adverti Ltd., Łódź, Poland). Thickness of the polymer samples after drying were $0.9 \pm 0.05 \text{ mm}$. The test material for the evaluation of cut resistance consisted of thin polymer coatings with different silica concentrations applied to a textile carrier, i.e., aramid knitted fabric (Opta-tech,

Table 2. Characteristics of the textile carrier

Image of textile carrier	Nn	Weave	Surface density, g/m^2	Thickness, mm
	28/2	left-right	234.1	0.25

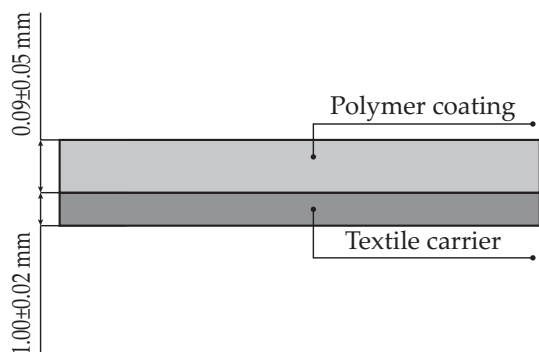


Fig. 1. Scheme of the aramid knitted fabric with a polymer coating

Warsaw, Poland) (Table 2). The coatings were evenly distributed by moving the trowel twice over the textile carrier. The coatings were cured in a laboratory dryer (POL-EKO, Wodzisław Śląski, Poland) at a temperature above 110°C for 10 min to fix them on the textile carrier. The scheme of the aramid knitted fabric with a polymer coating is shown in Fig. 1. The reference sample consisted of a textile carrier with a thin polymer coating without a filler (W0).

Methods

The dynamic viscosity of latex with different silica contents as a function of shear rate was determined using a Physica MCR-301 cone-and-plate rheometer (Anton Paar, Graz, Austria) with a diameter of 25 mm and a cone angle of 1° (CP 25) at a temperature of 25°C. Tensile properties were evaluated according to ISO 527-1 using an Instron universal testing machine (High Wycombe, UK) at a crosshead speed of 500 mm/min. The cut resistance was measured using a tomodynamometer (P.I. Kontech Ltd, Łódź, Poland) according to EN ISO 13997 [44]. The load applied to the blade ranged from 1.0 N to 30.0 N (Fig.

Table 3. Performance levels for cut resistance [43]

Performance level	A	B	C	D	E	F
Cutting force, N	2	5	10	15	22	30

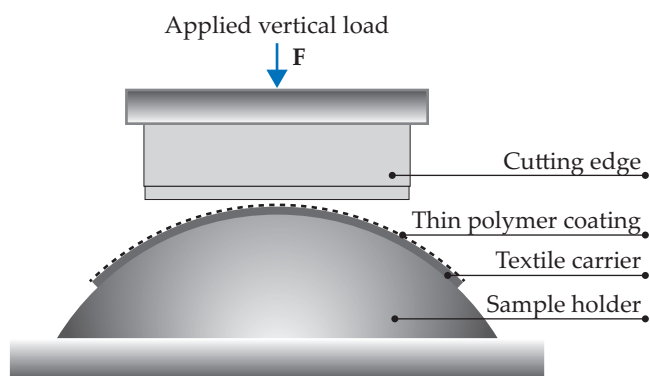


Fig. 2. Diagram of the cutting process

2). The cutting speed was 2.5 ± 0.5 cm/s. Prior to mechanical tests specimens were conditioned at $23 \pm 2^\circ\text{C}$ and a relative humidity of $50 \pm 5\%$ for 24 h. The results were interpreted according to the standard requirements given in Table 3.

RESULTS AND DISCUSSION

Rheological properties

Polymers used for thin coatings belong to the group of thermoplastic polymers, which makes them suitable for application on textile carriers. In the process of applying polymers to textile materials, the essence is the uniformity of the coating, and therefore the rheological properties of the latex have a decisive influence under certain process conditions [24].

Rheological properties assessed by parameters such as shear rate and viscosity depend on the integrity and interactions between the polymer coatings and fillers [46]. Silica was used in the current study due to the presence of hydroxyl groups that induce the formation of hydrogen bonds between the filler molecules and the polymer components. Consequently, silica exhibits affinity for the polymer, resulting in good dispersion in the matrix [37]. The interactions between the matrix components are also dependent on the filler content and particle size [47]. The silica used in the present study had a particle size distribution in the range of 1–5 μm and was used in different amounts (Table 1) to obtain thin polymer coatings with different rheological properties.

Figure 3 shows the shear rate curves of the latex paste for both the reference sample (Fig. 3a) and the samples containing silica (Fig. 3b–3f). With the increase of filler content, the viscosity of the polymer paste increased even twice (W5) compared to the reference sample (W0). Rheological studies indicate that the obtained polymer paste is a nonlinearly shear-thinning viscoelastic fluid. Moreover, the viscosity of the tested pastes decreases with an increasing shear rate. Shear thinning is believed to be caused by the rearrangement of previously chaotic particles in the flow direction under the influence of shear force, which reduces friction and results in a decrease in viscosity [48–49].

Tensile properties

The number of fillers in polymer materials and the tendency of particles to agglomerate under shear affect the strength of the polymer, leading to chipping and degradation [30–49]. Figure 4 presents tensile properties of thin polymer coatings in terms of elongation at break (Figure 4a), force at break (Figure 4b), and strength at break (Figure 4c).

Thin polymer coatings showed elongation at break ranging from 31% (W0) to 57% (W2). The highest elongation was obtained with a filler content of 1 wt%.

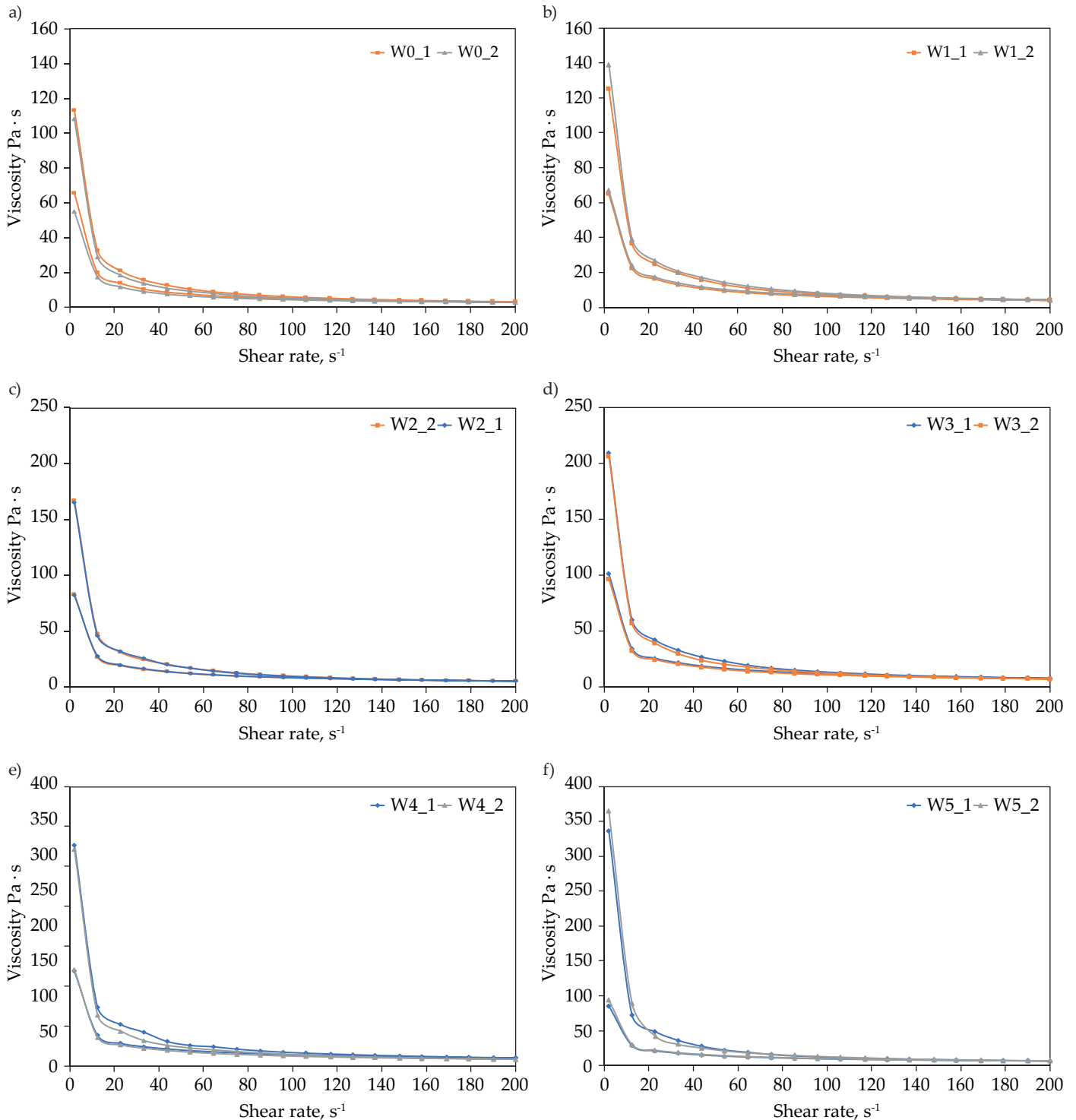


Fig. 3. Viscosity-shear rate curves: a) reference sample, b) W1, c) W2, d) W3, e) W4, f) W5

Similar elongation at break was noted for W3 (54%) and W4 (51%). Lower elongation was obtained for W1 (48%) and W5 (44%) samples. The highest break force (10.1 N) was also observed for the sample with 1 wt% silica (W2). Samples containing 0.5 wt.% (W1) and 1.5 wt.% (W3) filler showed lower break force, 9.3 N and 8.9 N, respectively. Three samples, including the reference sample, had similar break force (7.42–7.11 N); the filler content was 2.0 wt.% (W4), 2.5 wt.% (W5) and 0 wt.% (W0). The high-

est strength at break (3.4 MPa) was found for W2 sample. The sample containing 0.5 wt% filler (W1) had a slightly lower strength (3.3 MPa). In addition, W3–W5 and the reference sample (W0) exhibited similar force at break, ranging from 2.70 MPa to 2.38 MPa.

Exceeding the optimum silica content, which in the presented study was 1 wt%, resulted in a decrease in tensile strength. Excessive filler amount led to a 30% reduction in strength of thin polymer coatings, which is

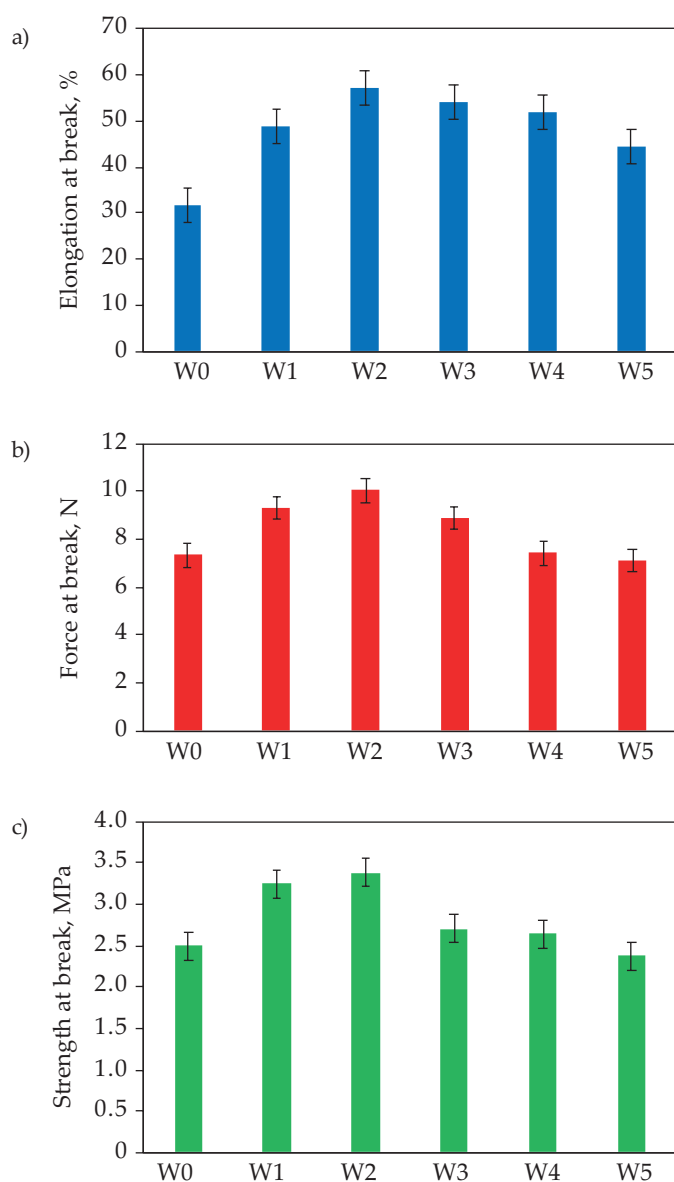


Fig. 4. Tensile properties: a) elongation at break, b) force at break, c) strength at break

caused by weakening the interactions with the polymer matrix [48, 50]. Applying polymer coatings to textiles increases their mechanical resistance. In the study by Matković et al., it was found that the presence of a polymer coating increases the breaking force by 24% compared to uncoated materials [21]. Mechanical strength can be further improved by adding fillers to the polymer matrix [51, 52]. In the case of materials coated with coatings containing boron carbide, a fourfold increase in puncture resistance was observed compared to uncoated materials [53].

Cut resistance

In the current study, samples were evaluated for cut resistance using a method dedicated to assessing protective gloves [44]. The application of polymer coatings has been reported to improve the mechanical proper-

ties of fabric carriers, including cut resistance [21, 51, 53]. However, no previous research has evaluated the effects of latex parameters, and in particular rheological properties, on the cut resistance of textiles coated with thin polymer coatings, even though these properties play an important role in the functionalization of such materials [54]. Finally, it should be noted that cutting force, or the amount of energy needed for cutting polymer materials, consists of two components: one of them is the energy expended on cleaving molecular chains, and the other one causes the plastic deformation of materials [55].

Figure 5 shows the effect of silica content on the cut resistance of aramid fabric with a thin polymer coating. The tested samples exhibited cut resistance ranging from 17.6 to 24.6 N. The highest cut resistance (24.6 N) was obtained for W5 with 2.5 wt% silica content, which translates into performance level E. Samples with 2 wt% (W4) and 1.5 wt% (W3) silica contents exhibited similar cut resistance, at 21.37 and 20.07 N, respectively, and were both classified at performance level D. Lower cut resistance (18.64 N and 17.90 N) were obtained for W2 (1 wt%) and W1 (0.5 wt%), also putting them at performance level D. The lowest cut resistance was observed for the reference sample without filler (W0). Furthermore, it was found that the increase in cut resistance due to the application of thin polymer coatings with varying silica content was of a linear nature.

To illustrate the effect of silica content on properties of coated textiles dependence between tensile and rheological properties as a function of cut resistance were evaluated.

Figure 6 shows the relationship between tensile properties and cut resistance for samples W0–W5. Based on this relationship, the influence of the former on the latter can be determined. The lowest cut resistance, obtained for W0, is associated with the lowest strength parameters. For samples containing 0.5 wt% (W1) and 1.0 wt% (W2) of silica, the increased filler content in the thin polymer coating coincides with improved mechanical properties and enhanced cut resistance. Filler content above 1 wt% (W3, W4, and W5) result in superior cut resistance expressed in terms of cutting force despite decreased elongation, force, and stress at break.

The dependence of the viscosity at a shear rate of 20 s^{-1} as a function of cut resistance shown in Fig. 7 indicates that the viscosity increases with increasing silica content

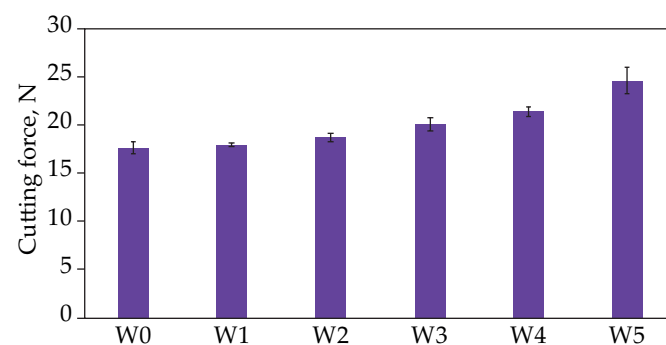


Fig. 5. Cut resistance of the tested samples

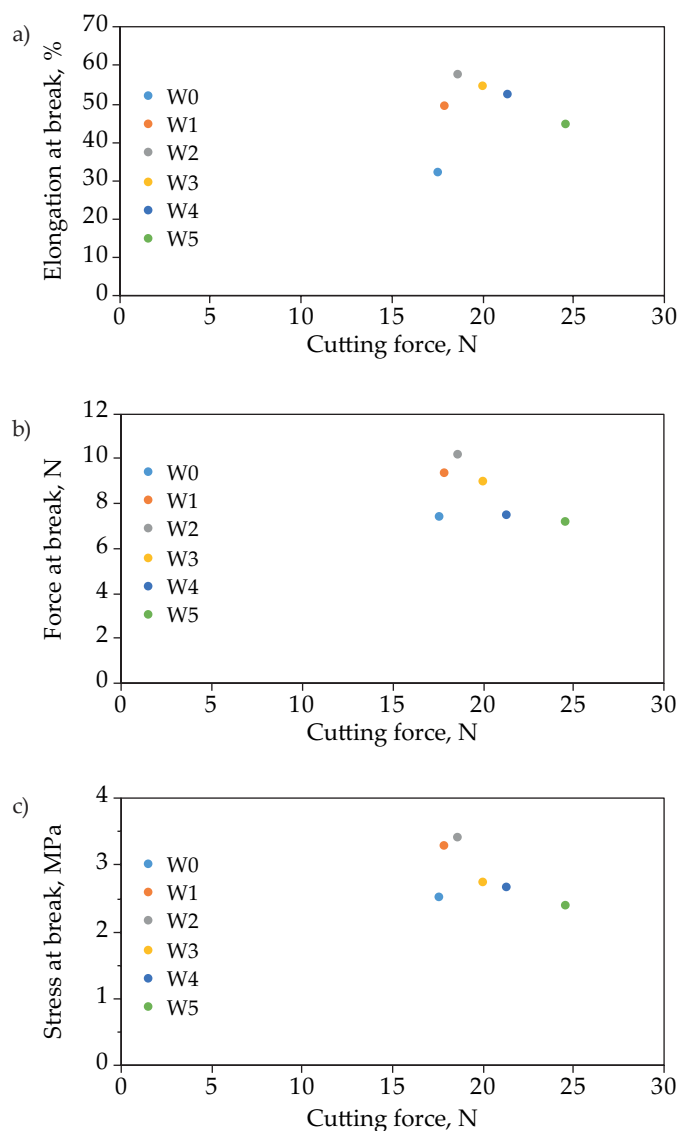


Fig. 6. Tensile properties as a function of cut resistance: a) elongation at break, b) force at break, c) strength at break

and the cut resistance increases with the viscosity of coatings containing inorganic filler.

CONCLUSIONS

The research presented in this article indicates that adding an inorganic filler (SiO_2) to a polymer matrix (latex) improves its protective properties. It has been shown that the technological process involving the application of thin polymer coatings with different amounts of silica improves the anti-cut properties. Compared to fabric carriers with a thin polymer coating without filler, the increase in cut resistance was 40%. However, the presence of inorganic fillers alone is not the only factor influencing cut resistance; another important issue is its content in the polymer matrix. It was found that the elongation at break of the coated material increased by as much as 57% at a filler content of 1 wt.%. From the point of view of the research, it is important that cut resistance increases with the viscosity of coatings containing inorganic filler.

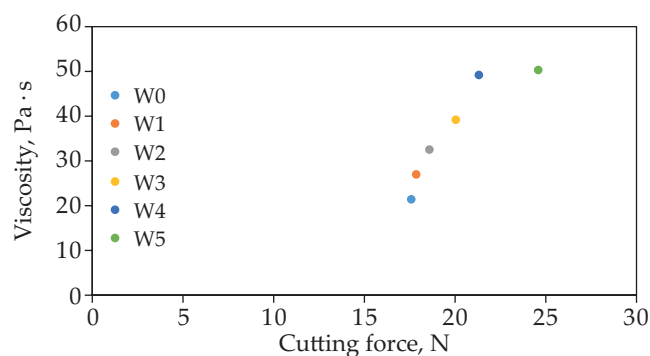


Fig. 7. Dependence between rheological properties as a function of cut resistance for viscosity at a shear rate of 20 s^{-1}

The paper presents preliminary studies aimed at assessing the effect of polymer viscosity used as a coating layer on protective materials on cut-resistant properties. In the future, the authors plan to conduct studies aimed at determining how the use of inorganic fillers affects the tribological properties of materials, including the degree of their cross-linking, mechanical strength, and cut resistance. Investigation of these phenomena is crucial for the use of the proposed materials coated with thin polymer films in cut-resistant gloves.

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Authors contribution

P.K. – conceptualization, methodology, validation, investigation, writing-original draft, writing-review and editing, visualization; E.I. – methodology, validation, writing-review and editing.

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Conflict of interest

The authors declare no conflict of interest.

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