Nr 2 (77–132) LUTY 2023 Tom LXVIII

POLIMERY

Modification of bentonite nanoclay for textile application

Muhammad Amir[1), *)] (ORCID ID: 0000-0001-5513-053X), **Syed Farhan Hasany**[2)] (0000-0003-3860-3387),
Muhammad Sajid Ali Asghar[3)] (0000-0002-4551-1299)

DOI: https://doi.org/10.14314/polimery.2023.2.1

Abstract: The influence of the bentonite content (1, 3, 5 wt%) on the mechanical properties of lightweight cotton (C), polyester (P) and polyester-cotton (P/C 50/50) fabrics was investigated. Starch was used as a water-insoluble binder for coating fabrics. Bentonite nanoparticles were obtained by repeated hydration, decantation and evaporation of the water dispersion. The bentonite particle size was determined by the XRD method using the Debye-Scherrer equation. The diffraction of the laser beam was used to determine particles size distribution. The addition of bentonite nanoclay significantly improved tensile strength (26-61% and 99–118% in the warp and weft direction, respectively) and tear strength (4–13% and 5–24% in the wrap and weft direction, respectively) of coated fabrics. Their abrasion resistance has also slightly increased. The biggest changes were noted for the cotton fabric, the smallest for the polyester fabric, which may result from the low compatibility between starch and the polyester fabric.

Key words: bentonite, textile fabrics, mechanical properties.

Modyfikacja nano bentonitu do zastosowań włókienniczych

Streszczenie: Zbadano wpływ zawartości bentonitu (1, 3, 5% mas.) na właściwości mechaniczne lekkich tkanin bawełnianych (C), poliestrowych (P) i poliestrowo-bawełnianych (P/C 50/50). Jako nierozpuszczalny w wodzie środek wiążący do powlekania tkanin zastosowano skrobię. Nanocząstki bentonitu otrzymywano poprzez kilkukrotną hydratację, dekantację i odparowanie dyspersji wodnej. Wielkość cząstek bentonitu oznaczono metodą XRD, stosując równanie Debye-Scherrera. Dyfrakcja wiązki laserowej posłużyła do określenia rozkładu wielkości cząstek. Zastosowanie nanoglinki bentonitowej wpłynęło na istotną poprawę wytrzymałości na rozciąganie (o 26–61% w kierunku osnowy i 99–118% w kierunku wątku) oraz rozdzieranie (4–13% w kierunku osnowy i 5–24% w kierunku wątku) powlekanych tkanin. Nieznacznie zwiększyła się również ich odporność na ścieranie. Największe zmiany zanotowano w przypadku tkaniny bawełnianej, najmniejsze dla tkaniny poliestrowej, co może wynikać z małej kompatybilności między skrobią a tkaniną poliestrową.

Słowa kluczowe: bentonit, tekstylia, właściwości mechaniczne.

Nanotechnology offers a variety of innovations for modern materials, including solutions for environmentally conscious treatment of interlaced fabrics [1]. It can provide high durability and improved affinity without

---

[1)] Department of Textile Engineering, NED University of Engineering and Technology, Karachi 75270, Pakistan.

[2)] Department of Chemistry, NED University of Engineering and Technology, Karachi 75270, Pakistan.

[3)] Department of Materials Engineering, NED University of Engineering and Technology, Karachi 75270, Pakistan.

[*)] Author for correspondence: qureshi@neduet.edu.pk

effecting the breathability or hand feel for textile products. This is a result of treatment with nano sized particles, which are characterized by high surface energy and large surface area-to-volume ratio [2]. Application of nanoclays on nylon, polypropylene, and polylactide improves fire retardance reducing the emission of toxic gases [3]. Bentonite clay bears notable properties, such as absorption and removal of toxins, heavy metals, impurities, odors as well as improving skin health and stain resistance [4, 5].

The interfacial bond strength between a fiber and resin influences mechanical properties of composites by altering the materials' operative load distribution. Erden et al. reported that incorporation of 3 wt% oligomeric siloxane into the polyester matrix marked an increase in tensile, flexural, and interlaminar shear strength values of a composite by 16%, 15%, and 75 %, respectively [6]. Prabhu et al. achieved better mechanical properties of glass fiber reinforced polyester containing 3 wt% clay nanoparticles. [7]. Hossen et al. reported that composites reinforced with treated jute fiber exhibited better tensile behaviors in comparison to their untreated counterparts [8]. Bozkurt et al. reported that the polyester fiber axial buckling load could be increased by 8.6% with the addition of 1 wt% clay nanoparticles [9].

Bentonite (montmorillonite) is one of the most common smectites and has been used for wide applications because of its ability to swell in presence of cationic surfactants as well as its absorption properties [10]. Milo et al. recently reported the effect of improved mixing technique and surface modification of montmorillonite on the structure and mechanical behaviors of clay and epoxy nano composites [11]. Literature review indicates an increase of fabric tensile properties in warp and weft conditions with the increment of weight percentage of nanoclay implying that nano fillers have potential to transfer stress away from examined fabrics [5, 8, 9, 11, 13, 14–18].

Nanoclay fabric coatings can be applied using numerous methods including spraying, transfer printing and padding, the ladder being most used. This is a technique where the nanoparticles are attached to the fabrics with a sponge with appropriate pressure and speed, then cured and dried until permanently fixed [13]. The large specific surface area of nanoclays, due to their nanometer size and high aspect ratio, provides an increased number of polymers–particle and particle–particle interactions compared to conventional fillers [9, 15–18]. To ensure a uniform distribution of nanoclay in coatings, a dispersant, namely binding agent, is required [12]. It has been found that clay particles, when added to the bath without such additive, do not provide satisfactory particle dispersion within the polymer matrix. Rather, the clay tends to agglomerate at the water surface and deposit upon the fabrics with poor distribution. Obtaining even nanoclay deposition, so that the clay particles do not sink or otherwise remain below the surface in the solution bath, is crucial in production of textile nano coatings [13]. The preferred binding/dispersing agents are water-soluble inorganic salts. These include sodium carbonate, sodium sulfate, potassium carbonate, potassium sulfate, magnesium sulfate, lithium sulfate, lithium carbonate, and sodium citrate, with the two first mentioned being most used [5, 6]. In this work, sodium carbonate, which is basic in character and particularly valuable in present compositions, was utilized. This inorganic salt behaves as binding agent that imparts a temporary binding force. However, importantly, since the salts are water-soluble, the binding force dissipates during washing. Thereby, they cannot facilitate even distribution of the clay upon the fabrics immersion in water [10]. There have been several reports regarding the use of starch as a binding agent for nanoclay. Starch would appear to be an excellent replacement of water-soluble salts. Substantial supplies of native starch of consistent quality are widely available, especially compared to other binders such as those mentioned hereinabove. Starch exhibits general insensitivity to water chemistry and strong binding characteristics which are desirable in dispersing agents [11].

Therefore, in this study, lightweight fabrics, such as cotton (C), polyester-cotton (P/C 50/50) and polyester (P), were coated with 6 nm bentonite nanoparticles obtained by evaporation of pre-hydrated clay nanoparticles in the aqueous supernatant. Starch was used as the water-insoluble binder. The nanoclay particles size was calculated using the Debye-Scherrer equation, and their size distribution was determined using the laser diffraction technique based on X-ray diffraction (XRD). In addition, the influence of the bentonite content (1, 3, 5 wt%) on the mechanical and tribological properties (abrasion) of fabrics was investigated.

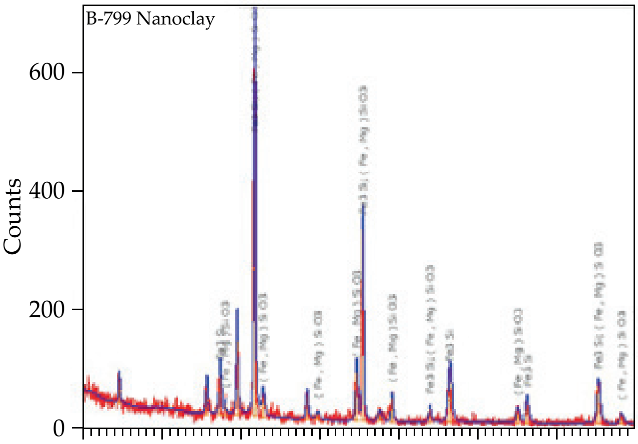

Fig. 1. X-ray diffraction of bentonite nanoclay

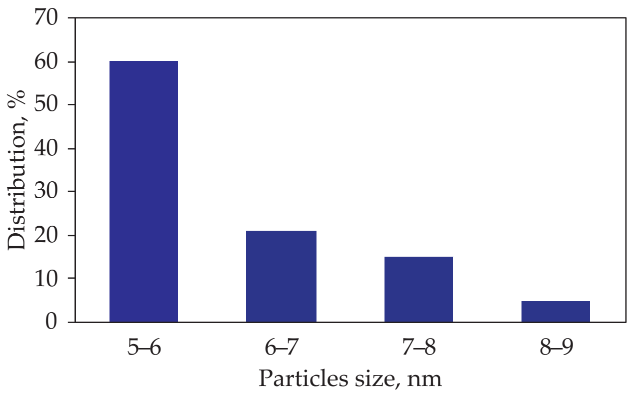

Fig. 2. Bentonite nanoparticles size distribution

EXPERIMENTAL PART

Materials

Brown bentonite clay powder and starch were purchased from Advanced Minerals and Chemicals Company Ltd., Pakistan. The nanoclay was modified by repeated hydration, decanting and evaporation of the hydrated bentonite nanoparticles. The obtained nanoclay was characterized by XRD (Fig. 1), and laser diffraction (Fig.2). The size of the obtained nanoclay particles was 6 nm. Commercially available lightweight fabrics (78–103 g/m^2), such as cotton (C), polyester (P) and polyester-cotton (P/C 50/50) were also used for testing.

Nanoclay preparation

The nanoclay was prepared according to a procedure published elsewhere [6], where the nanoclay was prepared after soaking in water for 1–180 days. The authors modified this method reducing the time to 1–90 days by repeated hydration, decantation and evaporation of hydrated bentonite nanoparticles. Briefly, 100 g of layered clay was mixed with 1 L of water and left for 24 h, then stirred for 5 min until a homogeneous mixture was obtained with some sediment. The mixture was left for 48 h, then the supernatant was separated and evaporated to give a small residue which was mixed with the same amount of water (1 L). The hydration process was repeated, after 48 h the precipitate was separated and evaporated, then after mixing with water (1L) was left for 72 h. The decanted liquid was evaporated, and the obtained residue was nanoclay. Fig. 3 shows the preparation of two batches of nanoclay. The obtained nanoclay was manually ground to reduce the agglomerates.

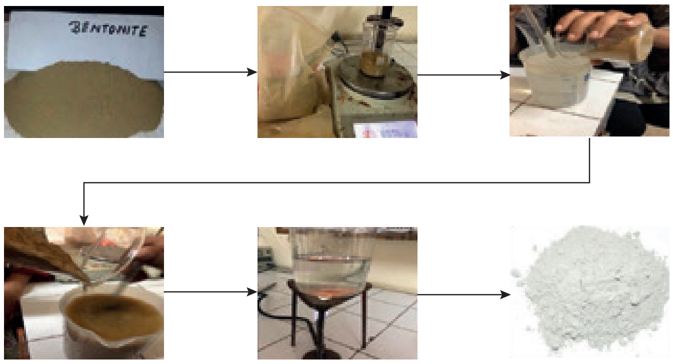

Fig. 3. Bentonite nanoclay preparation

Coating process

The literature implies that the maximum surface area will be obtained when the nanoparticles are uniformly dispersed into their individual sheets within the polymer matrix [7–9]. In this study, a padding technique was used for coating purposes. The step-by-step procedure is shown in Fig. 4.

Briefly, a mixture of water and starch (a binder) was slowly added to the nanoclay, the particles of which were subjected to mechanical mixing. A constant amount of water (100 mL) and starch (0.25 g) and a variable amount of nanoclay (1, 3, 5 mg) were used. The coated fabric samples were dried at 100°C for 10 min to achieve maximum crosslinking between the starch and the bentonite nanoclay.

Methods

X-ray diffractometer (x pert PRO; Panalytical Company, Netherlands) was used to study the crystalline phase composition of bentonite. The data were collected from 0°to 80° 2θ. The results were compared with the existing JSPDS standard and generated graphs of diffraction peaks were used to calculate the mean crystallite size. The average size of the bentonite nanoparticles was calculated based on the XRD pattern (Fig. 1) and Debye-Scherrer equation (1).

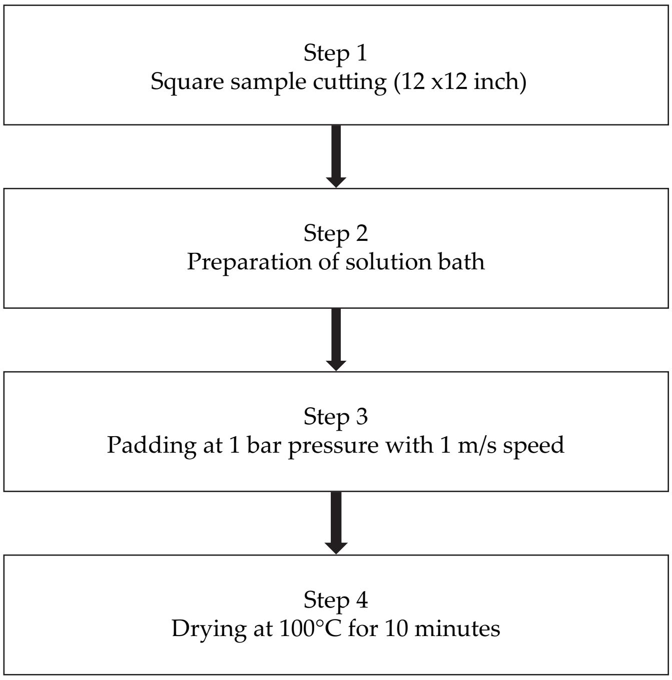

Fig. 4. Flowchart for obtaining coated fabrics

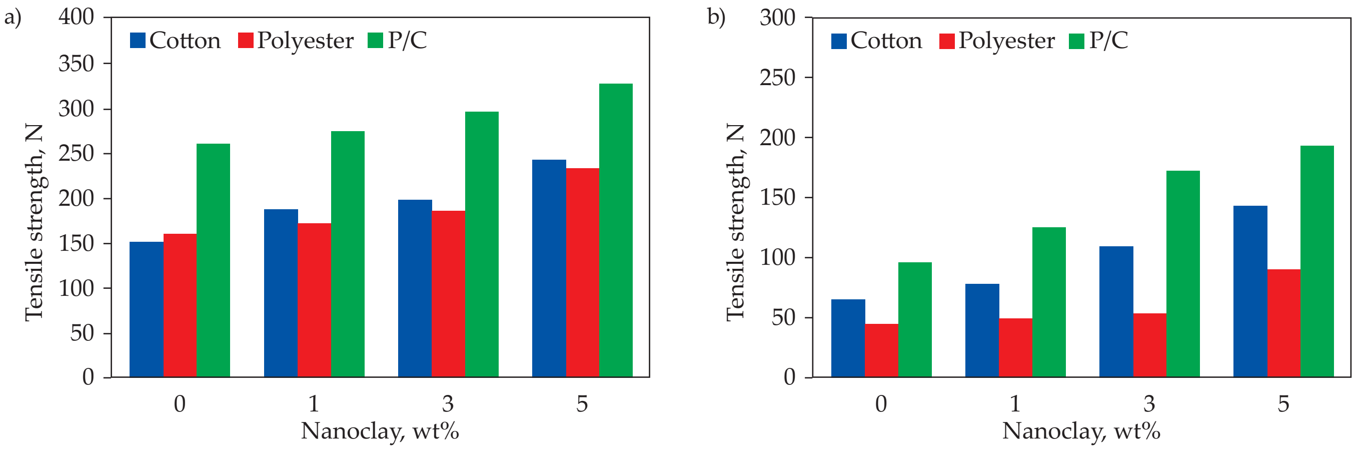

Fig. 5. Tensile strength in (a) warp and (b) weft direction of bentonite nanoclay-coated cotton, polyester, and P/C fabrics

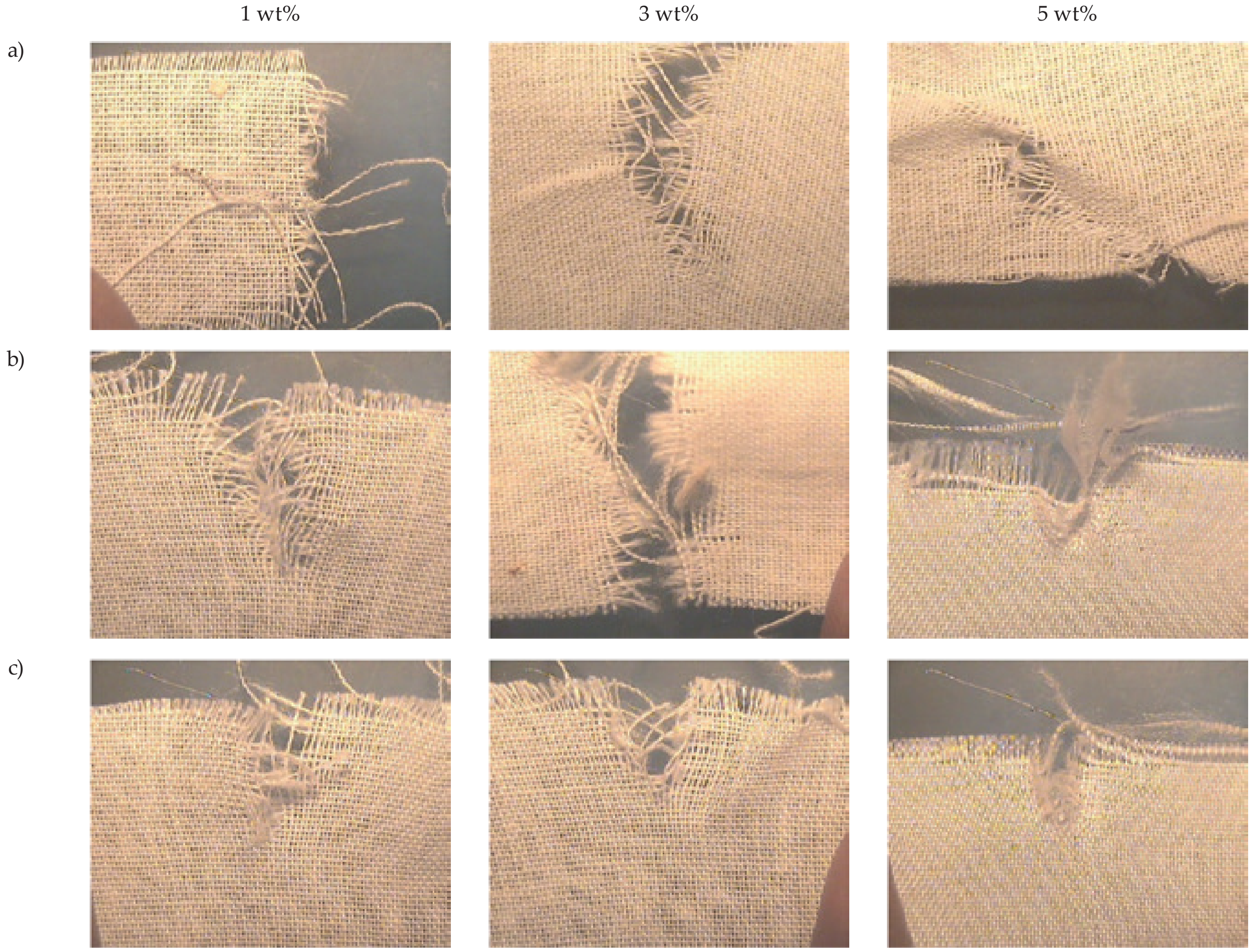

Fig. 6. Stereomicroscopy images of coated fabrics after stretching: a) cotton, b) polyester, c) P/C

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

where: K (Scherrer constant) = 0.94, λ (wave length of the X-ray beam used) = 0.154060 nm, β – full width at half maximum (FWMH) of the peak and θ – the Bragg angle [19].

The particle size distribution was evaluated in accordance with the ISO 13320 standard using the laser diffraction technique [12].

The tensile strength and tear strength of bentonite-coated fabrics were tested using a universal testing machine (710 Titan, James Heal & Co Ltd., England) with a speed of 300±10 mm/min according to EN ISO 13934-1

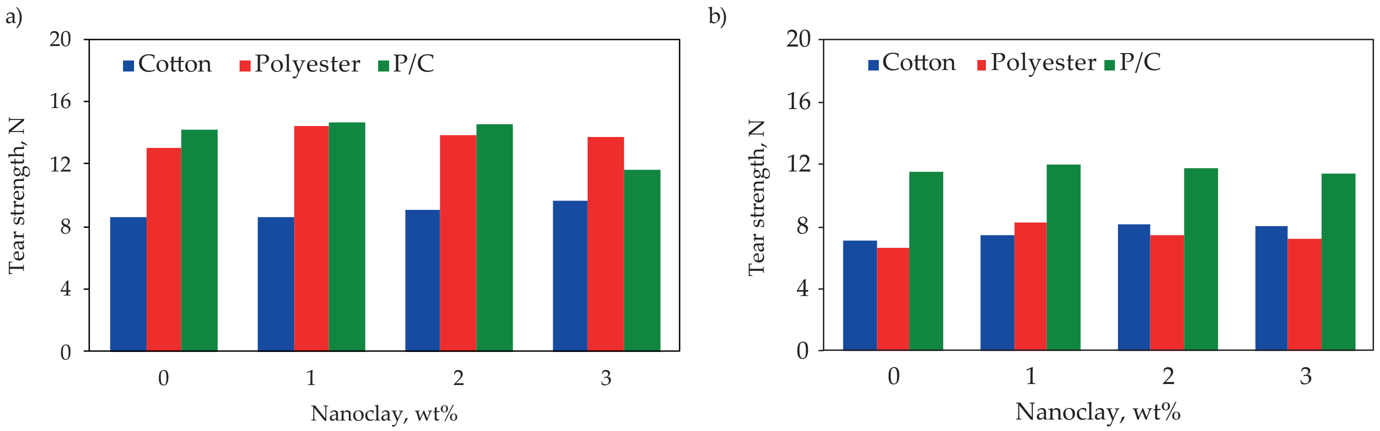

Fig. 7. Tear strength in (a) warp and (b) weft direction of nanoclay-coated cotton, polyester, and P/C fabrics

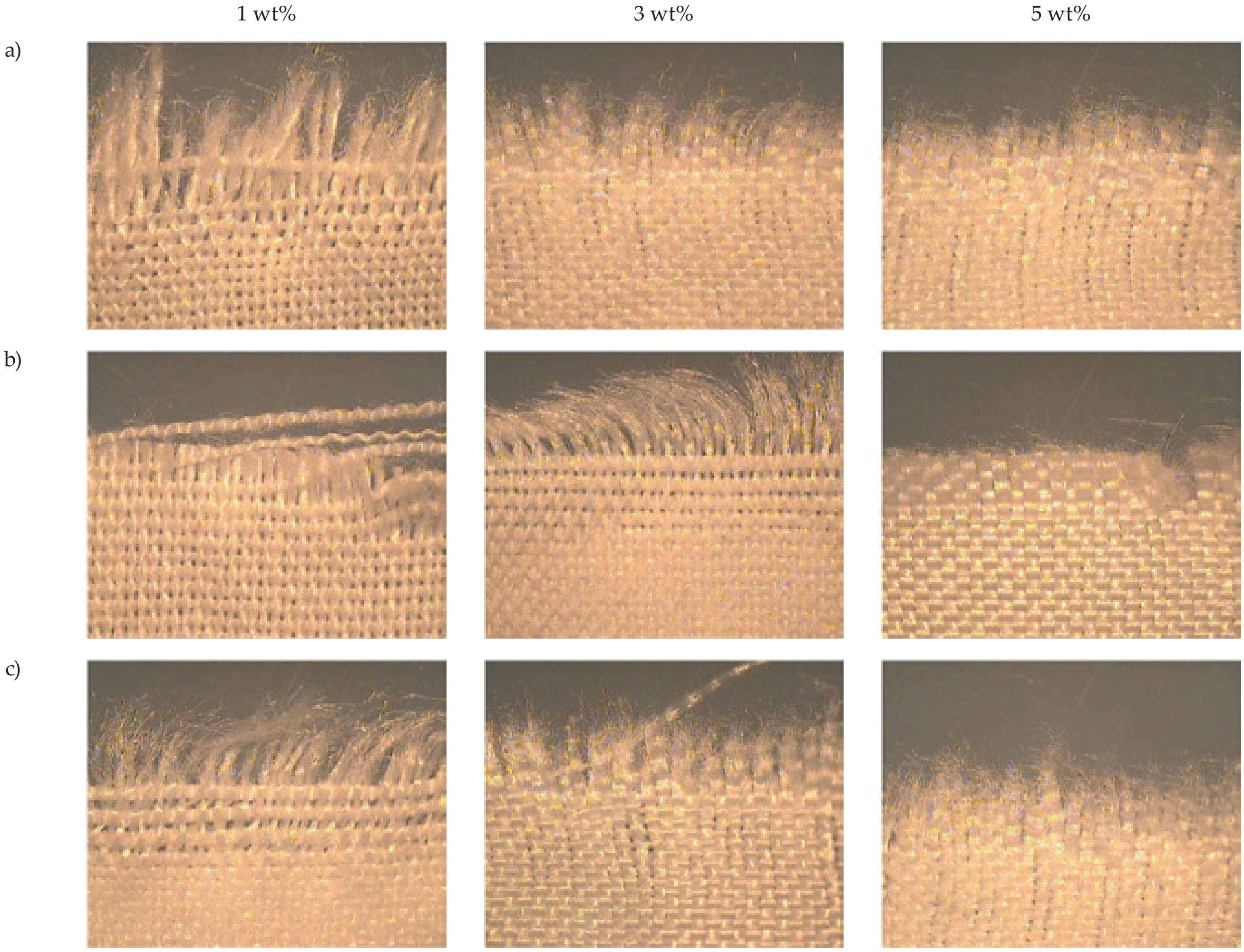

Fig. 8. Stereomicroscopy images of coated fabrics after tear test: a) cotton, b) polyester, c) P/C

and EN ISO 13937-1, respectively. The abrasion strength of bentonite-coated fabrics was evaluated according to EN ISO 12947-2 using a Martindale tester (M235/3, SDL International Ltd., England). Five specimens were tested for each fabric. The samples after tensile, tear and abrasion tests were observed using a stereo microscope (DMW-143, Motic, Hong Kong).

RESULTS AND DISCUSSION

The mechanical properties of bentonite-coated fabrics were tested in tensile, tear and abrasion modes. Fig. 5 shows that the addition of bentonite significantly improved the tensile strength depending on the fabric type and stretching direction. The tensile strength of

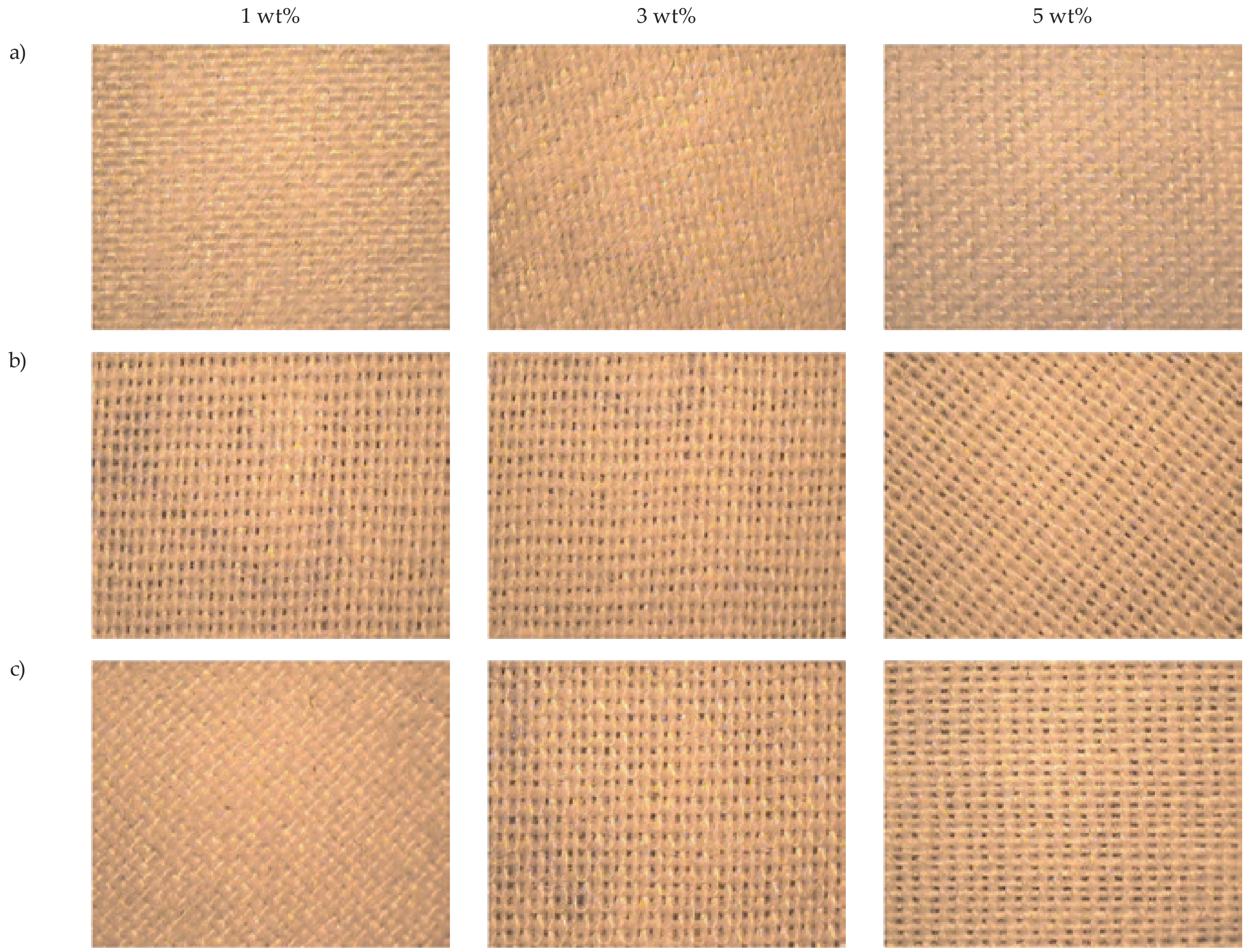

Fig. 9. Stereomicroscopy images of coated samples after abrasion test: a) cotton, b) polyester, c) P/C

cotton, polyester and P/C fabrics increased in the warp direction by 61%, 44% and 26%, respectively, and in the weft direction by 118%, 107% and 99%, respectively. The increase in tensile strength suggests improved interfacial adhesion between the nanoclay, starch and fabric substrate due to the clay good dispersion [5]. Chowdary et al. [13] obtained the highest tensile strength of a polyester fabric with a nanoclay content of 3 wt%. They found that further increasing the nanoclay load resulted in a decrease in fabric strength due to the thick coating layer.

Fig. 6 clearly shows that the tensile strength of the coated fabric strands increased with the increase in the content of bentonite nanoclay.

In the case of a cotton fabric, the tear strength increases in both directions as the nanoclay content increases (Fig. 7). However, the improvement is small both in the warp and weft directions (13%). For polyester and P/C fabrics, the highest tear strength was observed at the nanoclay content of 1 wt%. Tear strength in the warp direction increased by 11% and 4%, respectively, and in the weft direction by 25% and 5%, respectively. The decrease in tear strength with higher bentonite content can be explained by the poor compatibility of starch and polyester fabrics [7]. Fig. 8 presents microscopy images of bentonite-coated fabrics after tear tests.

Fig. 9 clearly shows that the coated fabrics were characterized by better abrasion resistance depending on the type of fabric, nanoclay content and the direction of measurement (wrap, weft). The best abrasion resistance was obtained for the cotton fabric, and the worst for the polyester fabric. Low abrasion resistance with higher content of nanoclay may result from poor compatibility between starch and polyester fabric [7].

CONCLUSIONS

Significant influence of bentonite nanoparticles on the mechanical properties of lightweight cotton, polyester-cotton and polyester fabrics was demonstrated. The tensile strength of all tested fabrics increased with the bentonite content both in the warp and weft direction. The tearing strength depended on both the type of fabric and the nanoclay content. For cotton fabric, the highest increase in tear strength was observed at the nanoclay content of 5 wt%, while for polyester and polyester-cotton fabrics at the content of 1 wt%. In contrast, the cotton fabric had the highest abrasion resistance at the nanoclay content of 5 wt%, and the polyester and polyester-cotton fabrics at the content of 1 wt%. The lower abrasion resistance of polyester fabrics with a higher content of bentonite was probably related to poor compatibility between starch and polyester fabric. Well-established knowledge provides guidelines for the industry to improve the tensile, tear and abrasion resistance of lightweight fabrics at a given content of native bentonite nanoclay.

REFERENCES

[1] Greßler S., Nentwich M.: ITA Nanotrust Dossiers **2012**, 026en. https://doi.org/10.1553/ita-nt-026en

[2] Patra J.K., Gouda S.: *Journal of Engineering and Technology Research* **2013**, *5*, 104. https://doi.org/10.5897/jetr2013.0309

[3] Coyle S., Wu Y., Lau K.-T. *et al*.: *MRS Bulletin* **2007**, *32*, 434. https://doi.org/10.1557/mrs2007.67

[4] Karnland O., Olsson S., Nilsson U. *et al.* : *Advanced Nuclear Fuel Cycles and Radioactive Waste Management* **2006**, https://doi.org/10.1787/9789264024861-7-en

[5] Adeyemo A.A., Adeoye I.O., Bello O.S.: *Applied Water Science* **2015**, *7*, 543. https://doi.org/10.1007/s13201-015-0322-y

[6] US *Pat. Appl. No.* 320 384 (2010).

[7] Le Bras M., Wilkie C.A., Bourbigot S.: *Fire Retardancy of Polymers* **2005**, https://doi.org/10.1039/9781847552396

[8] Joshi M., Bhattacharyya A., Agarwal N. *et al*.: *Bulletin of Materials Science* **2012**, *35*, 933. https://doi.org/10.1007/s12034-012-0391-6

[9] Teli M.D., Kale R.D.: *Polymer Engineering & Science* **2012**, *52*, 1148. https://doi.org/10.1002/pen.22179

[10] US Pat. No. 5 062 972 (1991).

[11] US Pat. No. 5 000 783 (1991).

[12] Eshel G., Levy G.J., Mingelgrin U., Singer, M.J.: *Soil Science Society of America Journal* **2004**, *68*, 736. https://doi.org/10.2136/sssaj2004.7360

[13] Chowdary M.S., Kumar M.S.R.N.: *International Journal of Advanced Science and Technology* **2015**, *74*, 35. https://doi.org/10.14257/ijast.2015.74.04

[14] Klug H.P., Alexander L.E..: *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials* **1974**, 992. https://doi.org/10.1002/xrs.1300040415

[15] Göcek İ.: *Journal of Polytechnic* **2019**, *22*, 509. https://doi.org/10.2339/politeknik.508592

[16] Krifa M., Prichard C.: *The Journal of The Textile Institute* **2020**, *111*, 1778. https://doi.org/10.1080/00405000.2020.1721696

[17] Fabia J., Gawłowski A., Rom M. *et al*: *Polimery* **2020**, *65*, 622. https://doi.org/10.14314/polimery.2020.9.4

[18] Rajamani D., Balasubramanian E., Dilli Babu G., Ananthakumar K.: *Journal of Industrial Textiles* **2022**, *51*, 3786S. https://doi.org/10.1177/1528083720942962

[19] Vinila V.S., Jayakumari I.: *Design, Fabrication, and Characterization of Multifunctional Nanomaterials* **2022**, *319*. https://doi.org/10.1016/B978-0-12-820558-7.00022-4

Received 10 XI 2022.