TEKSTİL VE KONFEKSİYON

VOL: 35, NO. 1
DOI: 10.32710/tekstilvekonfeksiyon.1424993

Investigation of Performance Properties of Wool Fabrics Treated with Bromelain from Pineapple Peel Wastes

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ABSTRACT

The pilling and shrinkage of wool fabrics are major problems in the textile industry. Chemical treatments are used to improve the performance properties of wool fabrics. These processes severely pollute the ecosystem. This study is aimed to use bromelain isolated from pineapple peel waste instead of toxic chemicals used during pretreatments to prevent shrinkage and minimize pilling in the woolen textile industry. Bromelain was isolated from pineapple peels using different techniques and isolated bromelain to be used was also encapsulated. Encapsulation was preferred to increase enzyme stability and reusability and to reduce cost. Area shrinkage, pilling, tensile strength, elongation, and weight loss tests were performed on the treated fabrics. According to the findings of this study, the isolated and encapsulated bromelain from pineapple peel wastes improved the washability of the wool fabric and eliminated the pilling problem. This developed method is sustainable, low cost, high added value, innovative, and environmentally friendly.

ARTICLE HISTORY
Received: 27.01.2024
Accepted: 05.06.2024

KEYWORDS

Bromelain, Waste management, Wool fabric, Pilling, Pineapple peel waste

1. INTRODUCTION

The amount of waste generated as a result of the rise in pineapple production and consumption increased in recent years [1, 2]. While 30% of the total mass of pineapple is consumed as fresh fruit, 70% of pineapple is thrown away as waste in the form of stem, core, crown, and peel. Bromelain is abundantly found in the peel and core of the pineapple fruit, which are removed as waste after being processed industrially. This processing waste can be used as a cheap, renewable, sustainable, green raw material source in the production of bromelain with new processes. Thus, it can contribute to the prevention of environmental problems caused by fruit waste, the use of waste as a cheap raw material source, and its conversion into high value-added products [3, 4].

Bromelain (E.C 3.4.22.4) is a cysteine protease class enzyme and its known single source is pineapple (*Ananas comosus*), the most common member of the *Bromeliaceae* plant family. Bromelain is a combination of proteolytic enzymes as well as different components such as thiol endopeptidases, phosphatases, glycosidases, peroxidases, cellulases, ribonucleases, glycoproteins, carbohydrates and some protease inhibitors [5–8]. Bromelain is present in different amounts in all parts of the pineapple, including the root, stem, leaf, fruit, peel, and seed. The commercially available bromelain enzyme is obtained from pineapple stems[5, 6, 9, 10]. Stem bromelain (E.C 3.4.22.32) has an isoelectric point of 9.5, a molecular weight of 26–37 kDa, an optimum pH range of 6-7, and an optimum temperature range of 50–60 °C. Fruit bromelain (E.C 3.4.22.33) has an isoelectric point of 4.6, a molecular weight of 24.5-32 kDa, an optimum pH range of 3-8, and an optimum temperature range of 37-70 °C. The optimum pH and temperature range of fruit bromelain are wider compared to stem bromelain [8, 10–13]. Thus, fruit bromelain obtained from pineapple peel waste was used in this study.

Enzymes are one of the alternative methods for reducing the use of toxic and harmful chemicals in the textile industry. Enzymes can be used in textile finishing methods to provide eco-friendly textile products with a high level of added value by producing clean technology, sensitive processing techniques, reactions on substrate-specific bonds, and biodegradability. Various enzyme groups are used in textile finishing processes, such as lipase, amidase, cutinase,

To cite this article: Açıkgöz S, Özgen Keleş B, Okutucu B. 2025. Investigation of Performance Properties of Wool Fabrics Treated with Bromelain from Pineapple Peel Wastes. *Tekstil ve Konfeksiyon*, 35(1), 54-63.

laccase, transglutaminase, cellulases, and proteases [14–17].

Wool, the most commonly used animal fiber, has many features that make it superior to other natural and synthetic fibers, such as good wrinkle resistance, flexibility, high moisture absorption capacity, durability, heat insulation properties, stain resistance, warmth, antistatic, flame-retarding, and wrinkle resistance. Wool is an important fiber consisting of polysaccharides, 82 keratin proteins, 17 non-keratin proteins, and lipids [18–22]. The most important disadvantage of wool fabric is the irreversible shrinkage problem that occurs due to washing and mechanical agitation. Chemical processes are used in the industry to prevent wool fibers from shrinking and make them machine washable. Chemical methods commonly used in wool fabric finishing processes to increase shrinkage resistance are chlorine-Hercoset, peroxymonosulfuric acid treatment, ozone oxidation, resin treatment, UV radiation, plasma irradiation, etc. However, these processes negatively affect other physicochemical properties of wool fiber and increase the tendency to stain. Furthermore, the gases and wastewater produced by these chemical processes severely pollute the entire ecosystem. Therefore, anti-shrinking treatment should be carried out by biodegradable, renewable, and sustainable chemicals [19, 23–25].

The wool fiber surface can be modified by oxidative or reductive method, the application of polymer resin or enzymatic treatments [26, 27]. Different enzymes can be used in the wool fiber surface modification and in the improvement of performance properties of woolen garments like anti-shinking, descaling [28-30]. The proteins present in the surface cuticles of the wool are hydrolysed by the enzyme, thus wool garment gain better handle and shrink resistance [31]. The most commonly used enzyme class in woolen products is proteases. Protease enzymes hydrolyze peptide bonds. Cortez et.al [32] applied a microbial transglutaminase to wool fabric either alone or following a protease treatment in order to increase the strength of woolen fabric. Levene et. al. [27] and Silva et. al. [33] used proteases to effectively achieve shrink-resist finishing to wool fabrics. Both the cuticle and the cortex layer of the fiber are modified by proteolytic enzymes. Thus, protease enzyme is used to increase the smoothness and softness of wool fibers, as well as to provide better dyeability and tensile strength [34].

Pilling is another common fabric defect that causes serious problems during usage of wool garments. The formation of pills is usually caused by wear, friction during washing, external pressure, and fiber friction against each other. As a result of mechanical stress on the fabric surface, small pills are formed by the dynamic process of entangling loose fibers [35–38]. Fabric surface pilling causes an unpleasant appearance, makes the fabric feel poor, degrades the quality of the fabric and it also shortens its service life [14, 38–40].The anti-pilling finish is performed using various chemical methods to reduce the pilling tendency of fabrics. The most used chemical methods to solve the pilling problem are resin finishing, liquid acrylic polymers, and commercial chlorination modification methods. These methods cause the formation of high amounts of toxic waste and the release of toxic gases into nature. Therefore, research has been conducted on effective, eco-friendly, and sustainable methods for preventing pilling [38, 41].

The major problems observed in wool fabrics are shrinkage and pilling. In a previous study, commercially obtained bromelain was used to minimum weight and tensile strength loss of wool fabrics [42]. Kaur and Chakraborty [43] also achieved a reduction in shrinkage, weight loss, and pilling in wool fabrics by pH optimization of commercial bromelain treatment. Koh et al. [44] showed that bromelain enhanced the dyeing properties of wool although it wasn't enough to decrease remarkably its tensile strength in the wool fiber. Unlike other studies, bromelain isolated from pineapple peel waste procured from local markets was encapsulated in widely used chitosan and utilized for the first time in wool fabric treatment to improve its performance properties in this study. Area shrinkage, pilling, tensile strength, and elongation of wool fabrics treated with fruit bromelain isolated from pineapple peel waste was examined. The results of wool fabrics treated with both commercial (stem) and isolated (fruit) bromelain were compared. The present study investigated whether the isolated enzyme is as effective as the commercial enzyme. Thus, it is aimed to develop a sustainable, low-cost, eco-friendly and innovative waste management method to improve the performance properties of wool fabric and to prolong its service life in this study.

2. MATERIAL AND METHOD

2.1 Material

The wool woven fabric (warp: Nm64/2, weft: Nm37/1, ends per cm: 23, picks per cm: 24,5) was used for the experiments. Wool fabric for experimentation was kindly provided by Yünsa. Bromelain from pineapple stem (E.C 3.4.22.32), ammonium sulphate ≥99%, casein from bovine milk, chitosan with molecular weight 310000-375000 Da and deacetylation degree >75% (CAS No. 9012-76-4), sodium tripolyphosphate 90-95%, carboxymethylcellulose sodium salt, glutaraldehyde 25% were purchased from Sigma-Aldrich Chemical Co. Ltd. Ethanol 99.9%, Acetic acid 100% were procured from Isolab Chemicals and Rucowet ® ALC was kindly provided by Ekoten.

2.2 Isolation of bromelain from pineapple peel waste

Pineapple peel waste used in this study was obtained from the local market in İzmir (free of charge). The waste was homogenized with cold Na-Pi buffer (0.1 M, pH 7) in a ratio of 1:0.5 in a homogenizer (Silverson). The homogenate was filtered through cheesecloth to separate the fibrous material and solid residue. The solution was centrifuged at 9000 rpm at 4 °C for 30 min to remove insoluble materials. The bromelain was isolated using two different methods by ethanol precipitation and gradient

ammonium sulfate precipitation from the supernatant. In the first method, ethanol cooled to 0 °C was added to the supernatant in drops until concentrations of 30%, 70%, and 30–70% (w/w) were reached [45]. In the second method, 0-20%, 20-40%, 40-60% gradient ammonium sulfate precipitation was carried out in the supernatant at 4 °C [46]. The precipitates were dissolved in Na-Pi buffer (0.1 M pH 7) and dialyzed against distilled water at 4 °C for 36 hours. The protein content of isolated bromelain was determined by Lowry method [47]. The proteolytic activity of isolated/commercial bromelain was determined using casein as the substrate according to the modified Kunitz method [48]. 0.625 ml of casein (0.65%) was added to 0.15 ml of enzyme solution and incubated for 30 minutes at 37 °C. Subsequently, the reaction was stopped by the addition of 1.25 ml of trichloroacetic acid (5%) solution, and the mixture was maintained for 5 min at room temperature. The mixture was centrifuged at 5000 rpm for 15 min. The supernatant was measured at 280 nm using a UV/visible spectrophotometer (Perkin Elmer Lambda 35).

2.3 Bromelain encapsulation

Chitosan (CS), which is a polysaccharide obtained by alkaline deacetylation of chitin, has polyamine character. This character makes the polymer water soluble and brings in bio-adhesive properties [49]. Chitosan can be used to improve antimicrobial activity, antifelting, and dyeability properties of wool materials [49, 50]. By the help of good film-forming property and hydrophilicity, chitosan has the ability to overcome the problems of wool being easily felting. In this study chitosan was used as an encapsulation material for enzymes. This encapsulation process helps to protect enzyme against degradation promoted by the external conditions (multiple usage) and the controlled release of enzyme [50-52]. The chitosan-enzyme beads were applied to wool by covalent grafting with glutaraldehyde as a crosslinker.

CS has the ability to create gels when interacting with tripolyphosphate (TPP), a non-toxic polyanionic ion. Ionic interactions occur between the negatively charged polyanion groups of the multivalent crosslinker TPP and the positively charged amino groups of CS. This physical crosslinking process is termed the ionotropic gelation technique [53, 54].

Encapsulation of the enzyme into CS was carried out for both commercial and pineapple peel waste bromelain. The CS at a concentration of 3% was dissolved in a 2% acetic acid solution. CS solutions were prepared with bromelain at different ratios (3:0.5 /3:1 /3:2 /4:1 / 4:2/ 5:1/ 5:2) and mixed at room temperature for 1 hour at 40 rpm on a rotator (Stuart). The CS-enzyme solutions were added dropwise into TPP solutions at different concentrations (0.5% -10%) with the help of a 10 ml blunt-ended injector and mixed for 30 minutes at 250 rpm [55]. The beads were separated by filtration after staying in TPP solution for 2 hours at room temperature and washed twice with distilled water. It was kept in a 1% carboxymethyl cellulose (CMC) solution at room temperature overnight [56]. The beads were separated by filtration (Buhner funnel) and washed twice with distilled water. Subsequently, it was portioned into falcon tubes for further use and stored at 4 °C.

2.4 Enzymatic treatment of wool fabrics

Wool fabric is highly hydrophobic by nature. It was observed that the wetting time of the wool fabric was 1 hour and 17 minutes before any washing process was applied. Therefore, the fabric was treated with 2 g/L Rucowet® ALC wetting agent at room temperature for 1 hour to increase the hydrophilicity of the wool fabric and the fabric's wetting time was observed to decrease to 25 minutes. Half of the fabrics were mixed with 0.2% glutaraldehyde (GA) for 4 hours at room temperature [57]. Glutaraldehyde is a bifunctional cross-linking agent which react with amine groups in wool and produce new bonding groups with chitosan-enzyme beads and enzyme molecules, respectively. Fabrics that are untreated and treated with GA were shaken with commercial bromelain and bromelain isolated from pineapple peel waste at room temperature for 1 hour. Fabrics that are untreated and treated with GA were also added to distilled water containing encapsulated commercial bromelain and encapsulated isolated bromelain prepared with 3% TPP and mixed with an orbital shaker (IKA® KS 260 basic 2) for 1 hour at room temperature.

2.5 Scanning electron microscopy

The surface morphology of the untreated and treated fabric samples was studied using Zeiss Evo HD15 Scanning electron microscopy (SEM). The fabric samples were mounted on aluminium stubs and sputter-coated with gold palladium mixture for preparation of SEM examination. The SEM images were taken at a working distance of 2.9 mm with an accelerating voltage of 3 kV, and a magnification of 2000x.

2.6 Performance tests of wool fabric

Tests were carried out to examine the performance properties of the prepared samples and to compare the effect of using isolated and commercial bromelain for the fabric treatment. Weight loss percentages were calculated according to the TS 251 Method 6 standard, tensile strength and elongation tests were performed in the Zwick Z010 Strength Tester according to the TS EN ISO 13934-1 standard, and the pilling test was performed with a Martindale device at 2000 cycles according to the TS EN ISO 12945-2 standard. Wool fabrics were washed in a CLS brand Wascator FOM71 washing machine at 40 °C according to the ISO 5A standard (TS 5720 EN ISO 6330) in order to determine the effect of washing on the area shrinkage of wool fabrics. The performance tests were statistically evaluated with the SPSS-25 program. Treated wool fabrics were coded as shown in Table 1 in the interest of easy expression.

Table 1. The codes of treated wool fabrics

Treatment of wool fabric	Treated without GA	Treated with GA
Commercial enzyme	A1	A2
Encapsulated commercial enzyme	B1	B2
Isolated enzyme	C1	C2
Encapsulated isolated enzyme	D1	D2

3. RESULTS AND DISCUSSION

3.1 The isolation of Bromelain from pineapple peel waste

The protein contents of bromelain isolated by the first method (ethanol precipitation) were found 0.08 mg/ml (30% ethanol), 0.32 mg/ml (70% ethanol) and 0.25 mg/ml (30–70% ethanol) respectively. Soares et al. [45] reported the protein content of bromelain isolated from pineapple stems and peels as 0.2 mg/mL at 70% ethanol precipitation. The protein contents of bromelain isolated by the second method (gradient ammonium sulfate precipitation) were found 1.13 mg/ml (0-20%), 4.42 mg/ml (20-40%) and 1.70 mg/ml (40-60%) respectively. Soares et al. [46] determined the protein amount of bromelain isolated from pineapple stem, bark and leaves as 0.089 mg/ml at 20-40% ammonium sulfate precipitation. Silvestre et al. [58] reported that 2.8 mg/ml protein was obtained in bromelain isolation from pineapple peel with 0–40% ammonium sulfate precipitation. Because pineapple contains high concentrations of bromelain in the ripe stage [6, 7]. The aim of this study is to use only the waste part of pineapple that is the reason of environmental pollution.

Specific activities of isolated bromelain with the first method were determined as 1.39 U/mg (30% ethanol precipitation) and 2.57 U/mg (70% ethanol precipitation). Besides, the highest enzyme activity was found to be 3.14 U/mg (30–70% ethanol precipitation) with the first method. Even though the protein content with 70% ethanol precipitation was higher than 30-70% ethanol precipitation, comparing the results, higher proteolytic activity was determined for 30–70% ethanol precipitation. The reason can be the addition of 70% ethanol in a single step, because it causes denaturation and a decrease in activity. Thus, ethanol was added in two steps (30–70%) to prevent protein denaturation. The specific activities of isolated bromelain with the second method were obtained as 0.76 U/mg (0-20% ammonium sulfate precipitation), 2.84 U/mg (20–40% ammonium sulfate precipitation) and 1.09 U/mg (40-60% ammonium sulfate precipitation) in this study. Silvestre et al. [58] found 3.4 U/mg activity with 0–40% ammonium sulfate precipitation from pineapple peels. The specific activity of commercial bromelain was determined as 13.38 U/mg. Reason of the difference in results may be use of different pineapple parts, the ripeness of the fruit, and the protein content. The bromelain protein content and activity in pineapple may vary depending on the soil type, climatic conditions, cultivation method, and irrigation water content.

The highest protein and activity values were obtained with 20-40% ammonium sulfate precipitation when the results of two different precipitation methods were analyzed. Accordingly, encapsulation studies were continued with bromelain obtained by 20-40% ammonium sulfate precipitation.

3.2 Bromelain Encapsulation

Fabric weight loss and fiber surface damage may occur if enzymes are treated directly to fabrics. Therefore, a pre-treatment step including polymeric surface modifications can usually be added in order to reduce wool damage. Thus, the enzymatic treatment steps can be made more uniform and regular, and fiber damage can be reduced to minimum levels [17, 59].

The formed beads were kept in 1% CMC overnight to increase their stability. It was observed that the beads' hardness increased, their tendency to disperse decreased, and the loss of beads during washing decreased when the outer surface of the beads was coated with CMC. Beads formed with both commercial bromelain and isolated bromelain at a ratio of 3:0.5 in 3% TPP had the highest stability. These beads were selected for use in the next steps.

3.3 Performance test results

3.3.1 Pilling

The pilling degrees of wool fabric before and after fabric treatment with isolated enzyme and commercial enzyme were investigated (Table 2). The pilling degree was measured on a scale ranging from 5 meaning no pilling to 1 meaning very severe pilling. The pilling degree of the untreated fabric (blank) was determined as 4.

Table 2. Pilling degree of treated wool fabrics

Treated wool fabrics	Pilling Degree
Blank	4
A1	4-5
A2	5
B1	4
B2	4-5
C1	4
C2	4-5
D1	4-5
D2	5

When fabrics treated without GA were examined, the pilling degree of A1 and D1 were found higher than blank fabric. However, the pilling degree of B1 and C1 didn't show any improvement compared to the untreated fabric. The pilling degrees of B1 and C1 were determined as 4 as well.

When all the results were taken into account, a considerable increase in pilling degrees was observed in all fabrics treated with GA. The pilling degree of B2 and C2 increased compared to blank. The pilling test conducted on fabrics showed that A2 and D2 had no pilling after 2000 cycles. Thus, the pilling degrees of A2 and D2 were determined as 5. These results are in accordance with the study of Levene et. al. [27]. In his study, wool yarns treated with protease enzyme gave less neps, low hairiness and the knitted wool fabric also had soft feel with good pilling performance and dimensional stability.

Based on these results, it was shown that encapsulated isolated enzyme could obtain the same satisfying pilling results as commercial enzyme. Consequently, it was shown that encapsulated bromelain isolated from pineapple peel waste could be used instead of commercial bromelain to eliminate the pilling problem in the textile industry.

3.3.2 Tensile strength and elongation

One of the major problems due to enzymatic treatment of wool materials is the strength loss [31]. This problem is associated with the high reactivity of enzyme that causes enzyme to penetrate into the cortex of the wool and damage the fiber during the treatment. When the results were compared with the untreated fabrics, the tensile strength of the fabrics treated with GA decreased, as shown in Figure 1. However, this decrease in tensile strength is within the acceptable range. Fabric A1 showed higher increase in tensile strength than others. The fabric A2 showed an increase in tensile strength of 2.3%. The reason for this is that the commercial enzyme alone has greatly increased the tensile strength. Moreover, the tensile strength of the fabrics treated without GA also increased. The fabric with the highest tensile strength is A1, and its calculated change percentage in tensile strength is 6.29%. After A1, the highest tensile strength increases of 2.53% was observed in C1 fabric treated with an isolated enzyme. Thus, it can be said that both commercial and isolated bromelain enzyme treated wool fabric showed good shrink resistance without loss of strength. These results are consistent with the previous study of Ammayappan [61].

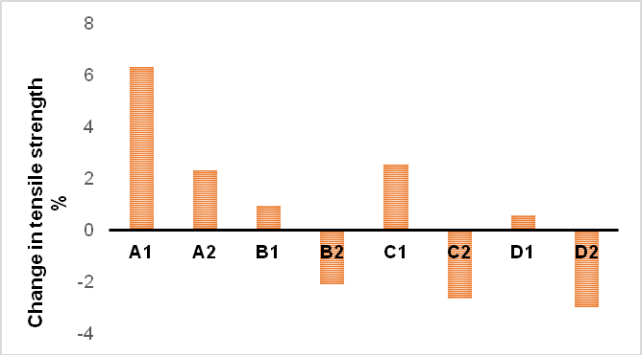


Figure 1. Results of percentage change in tensile strength of treated fabrics

According to the results of the Shapiro Wilk test, it was determined that the data was in a normal distribution. Therefore, t tests and Bonferroni post hoc were used for statistical evaluation of tensile strength (Table 3) and elongation (Table 4) and for pairwise comparisons, respectively.

From the results, it was found that there was a statistically significant difference between tensile strength values of wool fabrics treated with commercial enzyme and those treated with other groups. No statistically significant difference was observed between wool fabrics treated with isolated enzyme and those treated with both encapsulated enzyme groups. It was also found that there wasn't a statistically significant difference between tensile strength results of wool fabrics treated with encapsulated commercial enzyme and those treated with encapsulated isolated enzyme.

Table 3. Bonferroni Post. Hoc. results of the effect of enzyme treatments on tensile strength

(I)Enzyme_Treatment	(J) Enzyme_Treatment	Mean Difference (I-J)	Std. Error	Sig.
Commercial Enzyme	Isolated Enzyme	4.36036*	1.26261	0.009
	Encapsulated Commercial Enzyme	5.07541*	1.26261	0.002
	Encapsulated Isolated Enzyme	5.51899*	1.26261	0.001
Isolated Enzyme	Commercial Enzyme	-4.36036*	1.26261	0.009
	Encapsulated Commercial Enzyme	0.71505	1.26261	1.000
	Encapsulated Isolated Enzyme	1.15862	1.26261	1.000
Encapsulated Commercial Enzyme	Commercial Enzyme	-5.07541*	1.26261	0.002
	Isolated Enzyme	-0.71505	1.26261	1.000
	Encapsulated Isolated Enzyme	0.44358	1.26261	1.000
Encapsulated Isolated Enzyme	Commercial Enzyme	-5.51899*	1.26261	0.001
	Isolated Enzyme	-1.15862	1.26261	1.000
	Encapsulated Commercial Enzyme	-0.44358	1.26261	1.000

* The mean difference significance level is 0.05.

When elongation results of treated fabrics were compared with blank fabric, it showed an increase in all treated fabrics. It was observed that the elongation amount increased more in fabrics untreated with GA as shown in Figure 2. The fabric with the highest increase in elongation is A1 and its percentage change was 17.30% compared to blank fabric. The fabric with the lowest elongation increase is C2, and it was measured at 1.04 %.

The effects of the various enzymatic treatments on the fabrics were statistically evaluated, the difference between wool fabrics treated with commercial enzyme and those treated by other enzyme groups was proven to be statistically significant. The results of treated wool fabrics with isolated enzyme and those treated with both encapsulated enzyme groups did not show any statistically significant difference. Furthermore, post hoc tests showed that no significant difference existed between wool fabrics treated with encapsulated commercial enzyme and those treated with encapsulated isolated enzyme.

3.3.3 Weight loss of fabrics

Enzymes can be used as an alternative to chemicals in the textile industry. However, direct application of enzymes to fabrics causes weight loss and damage to the fibers. Due to the penetration of the enzyme into the internal layer of the wool, it may lose weight after enzymatic hydrolysis. Also increasing concentration of enzymes and longer time of treatment increases weight loss. A pre-treatment process that includes various surface modifications was added in an attempt to prevent fiber damage [60].

In this study, wool fabrics were initially treated with GA to prevent weight loss and fiber damage. It has been observed that all treatments have increased the weight of the fabrics, as shown in Table 5. Weight increase is higher in fabrics treated with GA. It was seen from the results that the enzyme concentration and treatment time had been properly controlled during treatment.

The outputs of statistical analyses also supported the data that enzyme type has an important effect on fabric weight loss. Weight loss results were also evaluated by Bonferroni post hoc comparisons for different fabric treatments (Table 6). A statistically significant difference between wool fabrics treated with commercial enzyme and those treated with enzyme from other groups was found. Nevertheless, no significant difference was observed between weight loss results of fabrics treated with isolated enzyme, encapsulated isolated enzyme and encapsulated commercial enzyme.

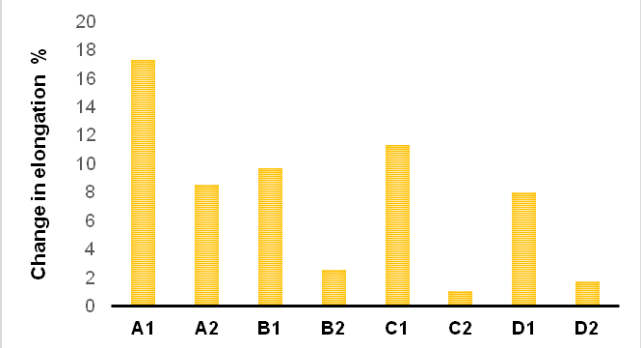


Figure 2. Results of percentage change in elongation of treated fabrics

Table 4. Bonferroni Post. Hoc. results of the effect of enzyme treatments on elongation

(I)Enzyme_Treatment	(J) Enzyme_Treatment	Mean Difference (I-J)	Std. Error	Sig.
Commercial Enzyme	Isolated Enzyme	6.76227*	2.24886	0.029
	Encapsulated Commercial Enzyme	6.80730*	2.24886	0.027
	Encapsulated Isolated Enzyme	8.05167*	2.24886	0.006
Isolated Enzyme	Commercial Enzyme	-6.76227*	2.24886	0.029
	Encapsulated Commercial Enzyme	0.04503	2.24886	1.000
	Encapsulated Isolated Enzyme	1.28941	2.24886	1.000
Encapsulated Commercial Enzyme	Commercial Enzyme	-6.80730*	2.24886	0.027
	Isolated Enzyme	-0.04503	2.24886	1.000
	Encapsulated Isolated Enzyme	1.24437	2.24886	1.000
Encapsulated Isolated Enzyme	Commercial Enzyme	-8.05167*	2.24886	0.006
	Isolated Enzyme	-1.28941	2.24886	1.000
	Encapsulated Commercial Enzyme	-1.24437	2.24886	1.000

* The mean difference significance level is 0.05.

Table 5. Weight loss % result of treated wool fabrics

Treated wool fabrics	A1	A2	B1	B2	C1	C2	D1	D2
Weight Loss %	4.92	6.75	2.13	4.49	2.44	4.08	2.03	3.55

Table 6. Bonferroni Post. Hoc. results of the effect of enzyme treatments on weight loss

(I)Enzyme_Treatment	(J) Enzyme_Treatment	Mean Difference (I-J)	Std. Error	Sig.
Commercial Enzyme	Isolated Enzyme	2.52400*	0.52436	0.000
	Encapsulated Commercial Enzyme	2.57800*	0.52436	0.000
	Encapsulated Isolated Enzyme	3.04600*	0.52436	0.000
Isolated Enzyme	Commercial Enzyme	-2.52400*	0.52436	0.000
	Encapsulated Commercial Enzyme	0.05400	0.52436	1.000
	Encapsulated Isolated Enzyme	0.52200	0.52436	1.000
Encapsulated Commercial Enzyme	Commercial Enzyme	-2.57800*	0.52436	0.000
	Isolated Enzyme	-0.05400	0.52436	1.000
	Encapsulated Isolated Enzyme	0.46800	0.52436	1.000
Encapsulated Isolated Enzyme	Commercial Enzyme	-3.04600*	0.52436	0.000
	Isolated Enzyme	-0.52200	0.52436	1.000
	Encapsulated Commercial Enzyme	-0.46800	0.52436	1.000

* The mean difference significance level is 0.05.

3.3.4 Area shrinkage of fabrics

According to the results, 20.8% area shrinkage was observed in the blank fabric after 15 washings. Area shrinkage was only observed in fabric B1 and C1 among all treated fabrics as 2.83% and 1.42% after 15 washings, respectively. In the samples coded B2 and C2, the effect of cross-linking with the presence of glutaraldehyde completely eliminated the shrinkage. When evaluated in general, area shrinkage stability of wool fabrics increased after bromelain enzyme treatment. The enzymatically treated wool fabrics were observed to have extremely high area shrinkage stability (Figure 3) and have successfully solved the area shrinkage problem, which is a major issue with wool fabrics. In addition, the results obtained reveal that a product produced from samples treated with enzymes is in a machine-washable form. Compared with untreated wool fabric, encapsulation of isolated bromelain also eliminated shrinkage completely and improved the dimensional stability to felting even after 15 washings.

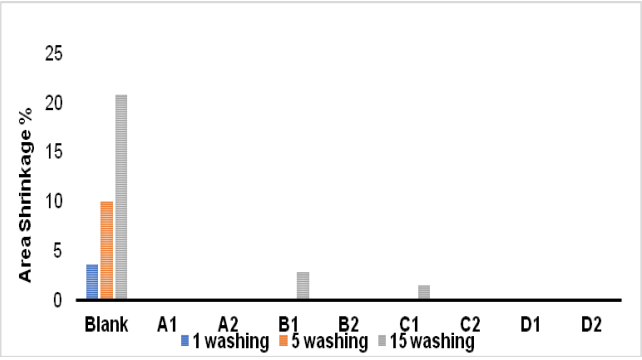


Figure 3. Area shrinkage results of treated wool fabrics

The control of the enzyme catalytic activity on the fiber surface is complicated due to the composite nature and ease of accessibility of wool fiber and thus processes of protease enzyme processes still may not meet with commercial acceptability because of excessive losses of weight and strength [61]. However, in this study, although some shrinkage was detected when the isolated enzyme was applied directly, after the application of the encapsulated isolated enzyme, no shrinkage was achieved in the wool fabric with less weight loss.

3.3.5 Surface Morphology

Micrographs of woven wool fabrics were taken using SEM of untreated (blank) and treated fabric samples. The SEM image of untreated wool fabric (Figure 4) shows the presence of wool fibers identified by a rough texture composed of overlapping scales.

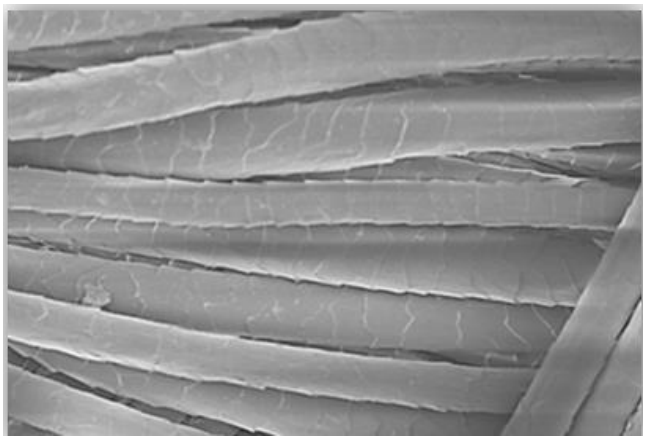


Figure 4. SEM image of blank fabric

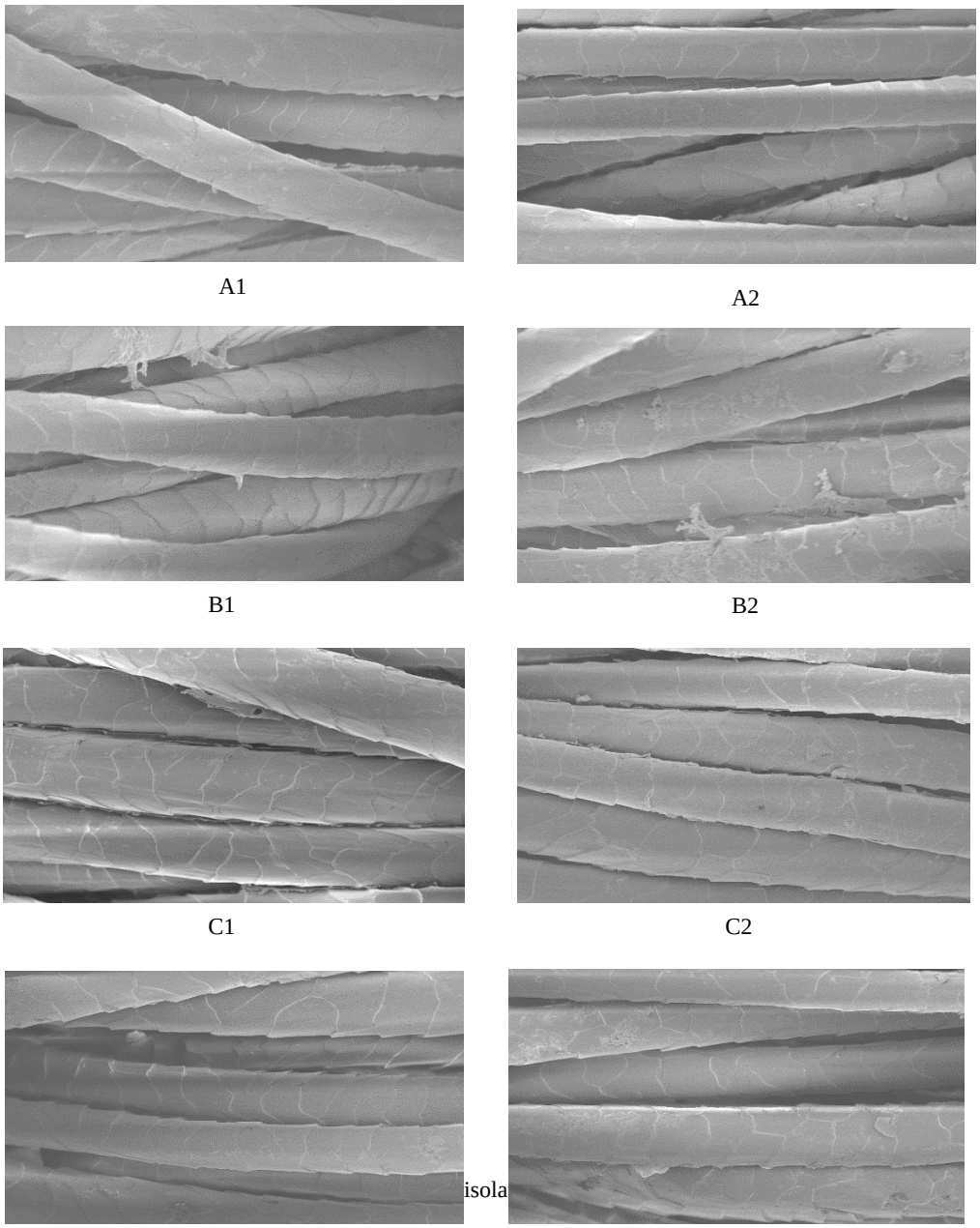
The fiber surface morphology after enzyme treatments is shown in Figure 5. In this study, it could be observed from the SEM images that the bromelain enzyme has slimmed down the surface cuticles of the wool partially, such as rounding scales and microcracks [49]. This is evident from the SEM images of enzyme treated sample that both isolated and encapsulated isolated bromelain induced

partial removal of the scales of wool, which resulted in improved area shrinkage of wool fabrics. When images of fabrics treated with glutaraldehyde were examined, it was seen that some grainy substances on the surface of the wool fibers were formed. That might be attributed to the immobilization of protein molecules. This result is consistent with the study of Wang et. al. [57]

When chitosan is considered, it can be observed that chitosan covers the scaly surface of the fiber and provides smoother appearance without any damage [49]. As shown in Figure 5, the chitosan-encapsulated fibers are relatively smoother than the untreated fibers. This could be attribute to oxidation and scission of the large number of disulfide bonds in the exocuticle of wool [51].

4. CONCLUSION

In the last decades, the use of enzymes instead of toxic chemicals during production and processing has increased. However, commercially providing these enzymes significantly raises the costs. Furthermore, millions of tons of vegetable and fruit waste accumulate in the garbage and cause environmental pollution every year. Pineapple waste that is disposed of as garbage contains an important enzyme, bromelain. Bromelain isolated from these wastes can be evaluated in many industries such as health, food, pharmaceutical, and textile. Bromelain is utilized to improve the performance properties (dyeing, felting, pilling, tensile strength, weight loss) of fabrics in the textile industry.



In this study, bromelain isolated from pineapple peel waste procured free of charge was encapsulated in widely used chitosan, and this application improved the area shrinkage and pilling problems of wool fabric considerably. Wool

fabric pilling is eliminated by commercial bromelain and encapsulated isolated bromelain to the same degree. After treatment with bromelain and glutaraldehyde, area shrinkage, which is the most important problem of wool fabric, has also been eliminated. As a result, a low-cost, high-value-added, and eco-friendly method was developed by using pineapple peel waste to prevent pilling and area shrinkage problems in wool fabrics. In future studies, the bromelain enzyme can be isolated from different parts of pineapple waste, and it can be investigated whether it has the same effect on wool fabrics.

Acknowledgements

The authors acknowledge the financial support from the Ege University Science Research Project (FYL 23009).

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