

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 chemical 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 in the treatment of fabrics was 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.

Novelty Statement

Bromelain was isolated from pineapple waste using various techniques and isolated and commercial bromelain were comparatively applied to wool fabrics to improve the selected properties of the fabrics.

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, 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, shrinkage treatment should be carried out by biodegradable, renewable, and sustainable chemicals [19, 23–25].

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 [26–29]. Fabric surface pilling not only causes an unpleasant appearance, makes the fabric feel poor, wear on the fabric, and degrades the quality of the fabric; but also shortens its service life, and causes a decrease in added value [14, 29–31]. 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, traditional resin finishing, 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 [29, 32].

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 [33]. Kaur and Chakraborty [34] also achieved a reduction in shrinkage, weight loss, and pilling in wool fabrics by pH optimization of commercial bromelain treatment. Koh et al. [35] showed that the bromelain was enhance 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 Methods

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 $\geq 99\%$, 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 [36]. In the second method, 0–20%, 20–40%, 40–60% gradient ammonium sulfate precipitation was carried out in the supernatant at 4°C [37]. 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 [38]. The proteolytic activity of isolated/commercial bromelain was determined using casein as the substrate according to the modified Kunitz method [39]. 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) 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 [40, 41].

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 [42]. 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 [43]. 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 [44]. 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. 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. [36] reported the protein content of bromelain isolated from pineapple stems and peels as 0,2 mg/mL at 70% ethanol precipitation. The result of this study is better than Soares [36] depending on the chemical characteristics of pineapple peel waste.

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. [37] 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. [45] reported that 2,8 mg/ml protein was obtained in bromelain isolation from pineapple peel with 0–40% ammonium sulfate precipitation. In the studies of Soares [37] and Silvestre [45], it was found effective to use different parts of the pineapple and different ripening levels of pineapple on the protein content. 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 was 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 adding 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. Soares et al. [36] reported that the highest specific activity in bromelain isolation was obtained at 28.2 U/mg with 30–70% ethanol precipitation. The enzyme activity using different parts of the pineapple or waste was determined in Soares' study. However, enzymatic activity was measured using only pineapple peel waste in this study.

The enzyme activities may be different from the results of Soares [36] since different parts of the pineapple were studied.

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. [45] found 3.4 U/mg activity with 0–40% ammonium sulfate precipitation from pineapple peels. Soares et al. [37] obtained a specific activity of 359.28 U/mg with 20–40% ammonium sulfate precipitation from pineapple waste. The specific activity of commercial bromelain was determined as 13.38 U/ml. 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, 46].

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 were 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 degree of A2 and D2 were determined as 5.

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

When the results were compared with the untreated fabrics, the tensile strength of the fabrics treated with GA decreased, as shown in Fig. 1. However, this decrease in tensile strength is within the acceptable range. Only one fabric showed an increase in tensile strength. 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 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.

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	-,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 Fig. 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.

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.

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 be losing 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 [47].

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.

Table 5
Weight loss % result of treated wool fabrics

Treated wool fabrics	Weight Loss %
A1	4,92
A2	6,75
B1	2,13
B2	4,49
C1	2,44
C2	4,08
D1	2,03
D2	3,55

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.

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 A1 and C1 among all treated fabrics as 1.42% and 2.83%, respectively. When A1 and C1 fabrics were compared with A2 and C2 fabrics, it was seen that crosslinking completely eliminated the area shrinkage. 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 (Fig. 3). Enzymatically treated fabrics have successfully solved the area shrinkage problem, which is a major issue with wool fabrics. Also, results showed that the enzyme-treated fabrics could be machine washable.

4. Conclusions

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.

Declarations

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Author contributions

Sena Açıkgöz: Methodology, Preparation, Investigation, Writing – analysis, Writing – review and editing, Validation. **Banu Özgen Keleş:** Supervision, Conceptualization, Investigation, Analysis, Writing – original draft, Writing – editing, Validation, **Burcu Okutucu:** Supervision, Conceptualization, Investigation, Writing – editing, Validation.

Data availability

The data that support the findings of this study are available in this paper and on a request from the corresponding author.

Conflict of interest

The authors declare that they have no known competing financial interests of personal relationships that could have appeared to influence the work reported in the paper.

Ethical approval

Not applicable.

References

1. Sarangi PK, Anand Singh T, Joykumar Singh N, et al (2022) Sustainable utilization of pineapple wastes for production of bioenergy, biochemicals and value-added products: A review. *Bioresour Technol* 351:127085. <https://doi.org/10.1016/j.biortech.2022.127085>
2. Tran T Van, Nguyen DTC, Nguyen TTT, et al (2023) A critical review on pineapple (*Ananas comosus*) wastes for water treatment, challenges and future prospects towards circular economy. *Sci Total Environ* 856:158817. <https://doi.org/10.1016/j.scitotenv.2022.158817>
3. Sukri SAM, Andu Y, Tuan Harith Z, et al (2022) Effect of feeding pineapple waste on growth performance, texture quality and flesh colour of Nile tilapia (*Oreochromis niloticus*) fingerlings. *Saudi J Biol Sci* 29:2514–2519. <https://doi.org/10.1016/j.sjbs.2021.12.027>
4. Polanía AM, Londoño L, Ramírez C, et al (2022) Valorization of pineapple waste as novel source of nutraceuticals and biofunctional compounds. *Biomass Convers Biorefinery*. <https://doi.org/10.1007/s13399-022-02811-8>
5. de Lencastre Novaes LC, Jozala AF, Lopes AM, et al (2016) Stability, purification, and applications of bromelain: A review. *Biotechnol Prog* 32:5–13. <https://doi.org/10.1002/btpr.2190>
6. Ramli ANM, Manas NHA, Hamid AAA, et al (2018) Comparative structural analysis of fruit and stem bromelain from *Ananas comosus*. *Food Chem* 266:183–191. <https://doi.org/10.1016/j.foodchem.2018.05.125>
7. Ramli ANM, Aznan TNT, Illias RM (2017) Bromelain: from production to commercialisation. *J Sci Food Agric* 97:1386–1395. <https://doi.org/10.1002/jsfa.8122>
8. Chaurasiya RS, Umesh Hebbar H (2013) Extraction of bromelain from pineapple core and purification by RME and precipitation methods. *Sep Purif Technol* 111:90–97. <https://doi.org/10.1016/j.seppur.2013.03.029>
9. Arshad ZIM, Amid A, Yusof F, et al (2014) Bromelain: An overview of industrial application and purification strategies. *Appl Microbiol Biotechnol* 98:7283–7297
10. Manzoor Z, Nawaz A, Mukhtar H, et al (2016) BRAZILIAN ARCHIVES OF BIOLOGY AND TECHNOLOGY Bromelain: Methods of Extraction, Purification and Therapeutic Applications Human and Animal Health. *Brazilian Arch Biol Technol Biol Technol v* 59:1–16
11. Agrawal P, Nikhade P, Patel A, et al (2022) Bromelain: A Potent Phytomedicine. *Cureus* 14:1–8. <https://doi.org/10.7759/cureus.27876>
12. Hikisz P, Bernasinska-Slomczewska J (2021) Beneficial properties of bromelain. *Nutrients* 13:. <https://doi.org/10.3390/nu13124313>
13. Varilla C, Marcone M, Paiva L, Baptista J (2021) Bromelain, a group of pineapple proteolytic complex enzymes (*Ananas comosus*) and their possible therapeutic and clinical effects. a summary. *Foods* 10:. <https://doi.org/10.3390/foods10102249>

14. Dalbaşı ES, Özçelik Kayseri G (2015) A research about the effect of the anti-pilling treatments on different structured cotton knitted fabrics. *Tekst ve Konfeksiyon* 25:54–60
15. Fu J, Su J, Wang P, et al (2015) Enzymatic processing of protein-based fibers. 10387–10397. <https://doi.org/10.1007/s00253-015-6970-x>
16. Song AR, Kim HR, Song WS (2012) Optimization of enzymatic treatment of polyamide fabrics by bromelain. *Fibers Polym* 13:282–288. <https://doi.org/10.1007/s12221-012-0282-x>
17. Vélchez S, Manich AM, Jovancic P, Erra P (2008) Chitosan contribution on wool treatments with enzyme. *Carbohydr Polym* 71:515–523. <https://doi.org/10.1016/j.carbpol.2007.06.024>
18. Hassan MM, Leighs SJ (2017) Applied Surface Science Effect of surface treatments on physicomechanical, stain-resist, and UV protection properties of wool fabrics. *Appl Surf Sci* 419:348–356. <https://doi.org/10.1016/j.apsusc.2017.05.046>
19. Hassan MM, Carr CM (2019) A review of the sustainable methods in imparting shrink resistance to wool fabrics. *J Adv Res* 18:39–60
20. An F, Fang K, Liu X, et al (2020) Protease and sodium alginate combined treatment of wool fabric for enhancing inkjet printing performance of reactive dyes. *Int J Biol Macromol* 146:959–964. <https://doi.org/10.1016/j.ijbiomac.2019.09.220>
21. Bakker C, Ghosh A, Tandon S, Ranford S (2018) Surface Modification of Wool Fabric with POSS® Nanomaterial. 19:2127–2133. <https://doi.org/10.1007/s12221-018-1169-2>
22. Bulut MO, Sana NH (2018) Modification of Woolen Fabric with Plasma for a Sustainable Production. 19:1887–1897. <https://doi.org/10.1007/s12221-018-8488-1>
23. Kadam V, Rani S, Jose S, et al (2021) Biomaterial based shrink resist treatment of wool fabric: A sustainable technology. *Sustain Mater Technol* 29:e00298. <https://doi.org/10.1016/j.susmat.2021.e00298>
24. Li Y, Noro J, Li J, et al (2021) Grafting of Poly(tyrosine) by Laccase Improves the Tensile Strength and Anti-shrinkage of Wool. *J Nat Fibers*. <https://doi.org/10.1080/15440478.2021.2002785>
25. Rani S, Kadam V, Rose NM, et al (2020) Wheat starch, gum arabic and chitosan biopolymer treatment of wool fabric for improved shrink resistance finishing. *Int J Biol Macromol* 163:1044–1052. <https://doi.org/10.1016/j.ijbiomac.2020.07.061>
26. Elmastaş Gültekin Ö, Kılıç A, Özçelik Kayseri G (2022) Stochastic Modelling of Pilling Degree Changes During the Pilling Process of Wool Fabrics. *Tekst ve Konfeksiyon* 32:65–76. <https://doi.org/10.32710/tekstilvekonfeksiyon.974026>
27. Yap PH, Wang X, Wang L, Ong KL (2010) Prediction of Wool Knitwear Pilling Propensity using Support Vector Machines. *Text Res J* 80:77–83. <https://doi.org/10.1177/0040517509102226>
28. Tusief MQ, Mahmood N, Saleem M (2012) Effect of different anti pilling agents to reduce pilling on polyester/ cotton fabric. *J Chem Soc Pakistan* 34:53–57
29. Zhu L, Ding X, Wu X (2020) A novel method for improving the anti-pilling property of knitted wool fabric with engineered water nanostructures. *J Mater Res Technol* 9:3649–3658.

- <https://doi.org/10.1016/j.jmrt.2020.01.102>
30. Ukponmwan JO, Mukhopadhyay A, Chatterjee KN (1998) Pilling. *Text Prog* 28:1–57.
<https://doi.org/10.1080/00405169808688874>
 31. Wu J, Wang L, Xiao Z, et al (2021) Wool knitted fabric pilling objective evaluation based on double-branch convolutional neural network. *J Text Inst* 112:1037–1045.
<https://doi.org/10.1080/00405000.2020.1821984>
 32. Korzeniewska E, Sekulska-Nalewajko J, Goclowski J, Walczak M (2018) Assessment of pilling effect on the laser modified textile substrates. *2018 Appl Electromagn Mod Tech Med PTZE 2018* 129–132.
<https://doi.org/10.1109/PTZE.2018.8503229>
 33. Kaur A, Chakraborty JN (2015) Optimization of Bromelain Treatment pH with Wool for Antifelting and Reduced Pilling Behaviour: Objective Assessment Approach. *J Text* 2015:1–7.
<https://doi.org/10.1155/2015/230879>
 34. Kaur A, Chakraborty JN (2015) Controlled eco-friendly shrink-resist finishing of wool using bromelain. *J Clean Prod* 108:503–513. <https://doi.org/10.1016/j.jclepro.2015.07.147>
 35. Koh J, Kang S, Kim S, et al (2006) Effect of Pineapple Protease on the Characteristics of Protein Fibers. *Fibers Polym* 7:180–185
 36. Soares PAG, Vaz AFM, Correia MTS, et al (2012) Purification of bromelain from pineapple wastes by ethanol precipitation. *Sep Purif Technol* 98:389–395. <https://doi.org/10.1016/j.seppur.2012.06.042>
 37. Soares P, Coelho D, Mazzola P, et al (2011) Studies on bromelain precipitation by Ethanol, poly (Ethylene Glycol) and Ammonium Sulphate. *Chem Eng Trans* 24:979–984.
<https://doi.org/10.3303/CET1124164>
 38. Lowry OH, ROSEBROUGH NJ, FARR AL, RANDALL RJ (1951) Protein measurement with the Folin phenol reagent. *J Biol Chem* 193:265–275. [https://doi.org/10.1016/s0021-9258\(19\)52451-6](https://doi.org/10.1016/s0021-9258(19)52451-6)
 39. Kunitz M (1946) Crystalline soybean trypsin inhibitor. *J Gen Physiol* 29:149–154.
<https://doi.org/10.1085/jgp.29.3.149>
 40. Fan W, Yan W, Xu Z, Ni H (2012) Formation mechanism of monodisperse, low molecular weight chitosan nanoparticles by ionic gelation technique. *Colloids Surfaces B Biointerfaces* 90:21–27.
<https://doi.org/10.1016/j.colsurfb.2011.09.042>
 41. Sacco P, Paoletti S, Cok M, et al (2016) Insight into the ionotropic gelation of chitosan using tripolyphosphate and pyrophosphate as cross-linkers. *Int J Biol Macromol* 92:476–483.
<https://doi.org/10.1016/j.ijbiomac.2016.07.056>
 42. Jeong D, Choi KY (2020) Biodegradation of Tetracycline Antibiotic by Laccase Biocatalyst Immobilized on Chitosan-Tripolyphosphate Beads. *Appl Biochem Microbiol* 56:306–312.
<https://doi.org/10.1134/S0003683820030047>
 43. Yan M, Chen T, Zhang S, et al (2021) A core-shell structured alginate hydrogel beads with tunable thickness of carboxymethyl cellulose coating for pH responsive drug delivery. *J Biomater Sci Polym Ed* 32:763–778. <https://doi.org/10.1080/09205063.2020.1866350>

44. Wang Q, Fan X, Hu Y, et al (2009) Antibacterial functionalization of wool fabric via immobilizing lysozymes. *Bioprocess Biosyst Eng* 32:633–639. <https://doi.org/10.1007/s00449-008-0286-5>
45. Silvestre MPC, Carreira RL, Silva MR, et al (2012) Effect of pH and Temperature on the Activity of Enzymatic Extracts from Pineapple Peel. *Food Bioprocess Technol* 5:1824–1831
46. Vílchez S, Jovančić P, Erra P (2010) Influence of chitosan on the effects of proteases on wool fibers. *Fibers Polym* 11:28–35. <https://doi.org/10.1007/s12221-010-0028-6>
47. Demirkan E, Kut D, Sevgi T, et al (2020) Investigation of effects of protease enzyme produced by *Bacillus subtilis* 168 E6-5 and commercial enzyme on physical properties of woolen fabric. *J Text Inst* 111:26–35. <https://doi.org/10.1080/00405000.2019.1624069>

Figures

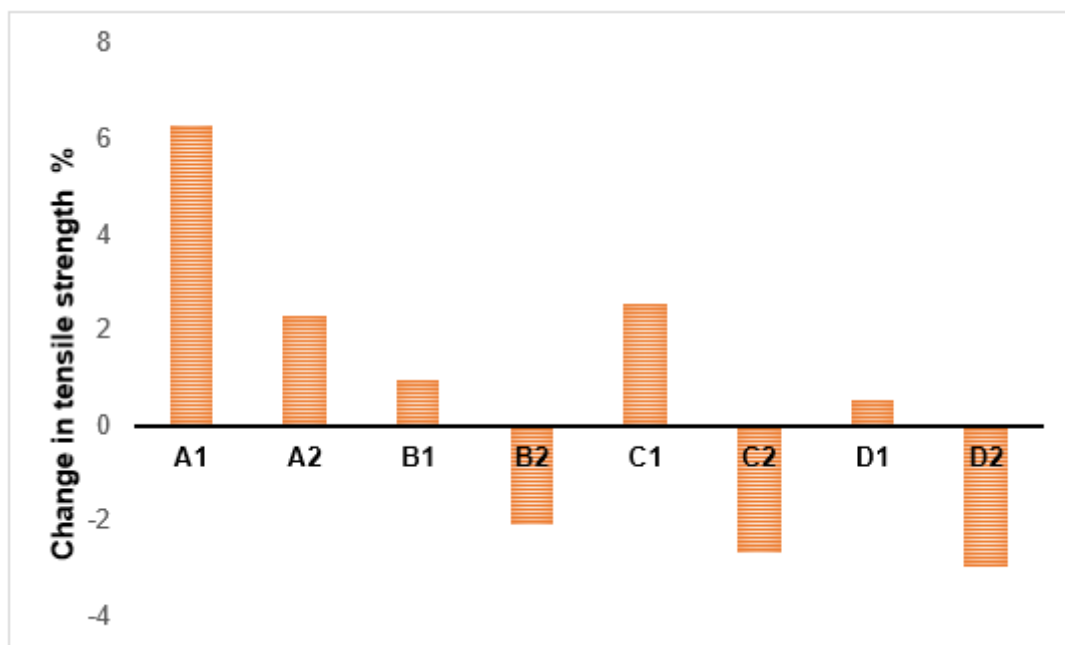


Figure 1

Results of percentage change in tensile strength of treated fabrics

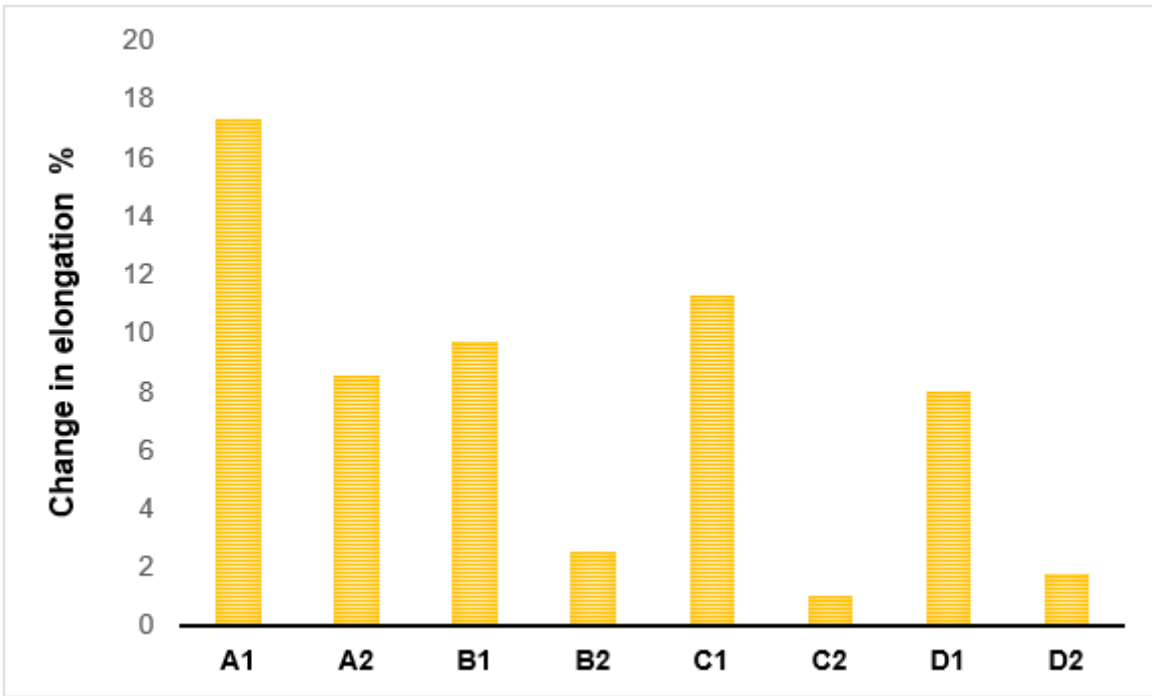


Figure 2

Results of percentage change in elongation of treated fabrics

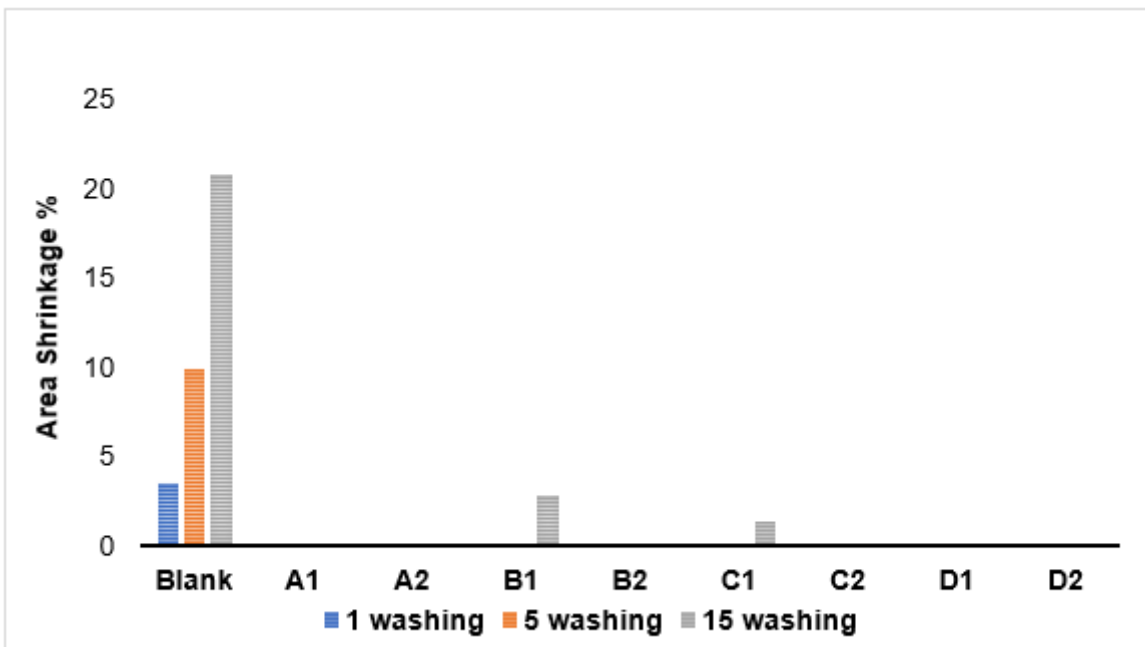


Figure 3

Area shrinkage results of treated wool fabrics

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