Impact of Chitosan Pretreatment to Reduce Microfibers Released From Synthetic Garments During Laundering

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Research Article

Keywords: microplastics, microfiber, laundering, plastic pollution, chitosan pretreatment, solutions

Posted Date: May 17th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-482018/v1

Abstract

Sewage treatment is known to be able to remove more than 90% of microplastics; nevertheless, a considerable amount of microplastics is eventually discharged into the ocean. Given that microfibers (MFs) primarily generated from the washing of synthetic clothes are the most abundant type of microplastics among various microplastics detected in the sewage treatment, it is necessary to reduce the amount of MFs entering these plants. This study aimed to reduce the amount of MFs released from the washing process by applying a chitosan pretreatment to the garments before the washing. In this study, before the chitosan pretreatment, the polyester clothes released 148 MFs/L, whereas a 95% MFs generation reduction was observed after the chitosan pretreatment using a 0.7% of chitosan solution. Other types of garments, such as polyamide and acrylic garments, were treated with a 0.7% of chitosan solution, and this resulted in the reduction of MFs generation by 48% and 49%, respectively. Therefore of the morphology analysis after the washing, chitosan coating on polyamide and acrylic were more damaged than on polyester. It suggests that the binding strength of polyamide and acrylic with chitosan were weaker than of polyester coated with chitosan. Thus, the results of this study suggest that chitosan pretreatment is a promising solution for reducing the amount of MFs generated in the laundering process.

1. Introduction

Since its invention, plastic has been incorporated into many products due to its convenience, however, its use has dramatically increased (Depledge et al. 2013). The generation of plastic waste has increased in recent years leading to 4.8–12.7 million tons of plastic being discharged into oceans every year because of improper waste mismanagement (Jambeck et al. 2015). Microplastics are less than 5 mm in size and can be generated by plastic wastes introduced into the environment, which undergo pyrolysis and physical and chemical transformations, due to which they are decomposed and fragmented into smaller particles (Singh and Sharma 2008; Browne et al. 2010). Such microplastics have been detected in the form of films, flakes, and fibers, and of these, microplastic fibers (MFs) are the most commonly detected in all aquatic environments, such as lakes, rivers, oceans, and marine sediments (Browne et al. 2011; Dris et al. 2015; Nel and Froneman 2015; Gallagher et al. 2016; Murphy et al. 2016; Koelmans et al. 2019).

MFs are typically released when synthetic textiles are laundered in washing machines (Napper and Thompson 2016; Pirc et al. 2016); therefore, ongoing research has focused on MFs released during the washing process. Considering that approximately 162 ± 52 MFs/g can be generated from a single washing, it is estimated that up to 6 million MF particles can be released from a 5 kg load of polyester (PE) textiles (De Falco et al. 2018b). Once MF enters the aqueous environment, it is difficult to remove them; thus, it would be essential to mitigate the amount of MFs entering the waterbodies (McIlwraith et al. 2019).

De Falco et al. (De Falco et al. 2018a) reported that the pectin pretreatment of polyamide garments can reduce the amount of MFs released by up to 90% compared to untreated cloth. Despite a good efficiency

in reducing MFs generated by applying the pectin pretreatment, this required an additional crosslinking agent (glycidyl methacrylate) to increase the bonding strength of pectin with garments.

Koo et al. (Koo et al. 2005) showed that the addition of chitosan film foam to PE fabric led to increasing the stiffness by approximately 63%. Considering that most of MFs are released by physical damage in the process of laundering (Goynes and Rollins 1971; Cai et al. 2020). We hypothesized that the chitosan film covered PEs garments strengthens the stiffness of PE fabrics thus reducing the amount of MFs generated during physical damage. Therefore, in this study, we explore if the chitosan pretreatment of PE garments can reduce the amount of MFs generated during the washing process. The amount and length of MFs released from the chitosan pretreated PE clothes and untreated ones were compared, and their characteristics were also analyzed. In addition, the main cause of MFs generation during the washing process was examined. Finally, to compare the applicability of chitosan solution to other polymer garments (Acrylic, Polyamide), the characteristics of the pretreated garments and the amount of MFs reduction were analyzed.

2. Materials And Methods

2.1. Reagents and polyester (PES) garment samples

Acetic acid (CH_3COOH, extra pure reagent) was obtained from Daejung (Seoul, Korea) and chitosan ($C_6H_{11}NO_4$) was purchased from Showa (Tokyo, Japan). The material used for the experiments consists of 100% PEs obtained from fitness vests (Table 1). To effectively discern MFs from garments, fluorescent colored garments were used.

2.2. Grafting of chitosan solution on PEs garments and washing process

Predetermined amount of chitosan powder was added to 1 L of 1% (v/v) aqueous acetic acid (Daejung, Korea) and its final concentrations were 0.1%, 0.4%, 0.7%, and 1% (w/v) (Jeon et al. 2003). Each solution was stirred for 24 h until completely dissolved. The PE garments were immersed in the chitosan solution for 1 h at 24°C, and to completely dry the cloth, they were placed in a drying oven at 120°C for 2 h, this was done for each experiment.

To measure the amount of MFs generated while domestic washing, a top-loading household washing machine (TR138K, LG, Korea) was used. The top-loading machine had a built-in sieve of 330-μm pore size to remove dust generated during the washing process. In terms of washing condition, 40 mL of detergent was used for each washing (40 L of water used per each washing). The wash cycle was performed at 135 rpm for 10 min. To avoid any extraneous MFs entering the washing machine, the washing machine was cleaned twice with distilled water before and after washing in each experiment. The collected washing drainage (40 L) was filtered using 100-μm sieve, and the sieved MFs were transferred to a beaker using distilled water. The sieved MFs were re-filtered using a track-etched polycarbonate (PCTE) filter (20-

μm pore size and 47-mm diameter) (GVS, Sanford, ME, USA) and then dried in a desiccator prior to analysis to minimize air contamination. To prevent additional contamination, all glassware was rinsed at least three times with distilled water, and the researchers wore black gowns to distinguish the MFs released from the researchers' clothes from the garments used in the washing experiment.

2.3 Application of chitosan pretreatment on other polymer types

For the applicability of the chitosan pretreatment method, we used two different types of polymer garments: polyamide (PA) and acrylic (AC). PA garments were 150 g, 50*55 cm and AC garments were 156 g and 50*52 cm. Both garments were pretreated with chitosan solution and washed the same way as PEs garment.

2.4 Instrumental MFs analyses

To easily recognize the MFs generated, MFs were stained with Nile red (NR) following the Nile red plate (NR-P) method proposed by Kang et al. (Kang et al. 2020), and they were observed using a stereoscopic microscope (Discovery V8, Carl Zeiss, Oberkochen, Germany). UV light with a wavelength of 365 nm was applied, and the luminescent the MFs were counted. Length of the MFs generated were recorded by an IMT cam 6.3 camera (IMT i-Solution Inc., Canada) and their length was measured using i-Solution software. We randomly selected 100 MFs from washed PE clothes to sort size distribution.

The morphology of PE garments before and after the chitosan pretreatment were analyzed by scanning electron microscopy (SEM, S-4800, Hitachi, Ltd., Japan) in 3.0 kV with ~ 1,000–3,000 times magnification. PE samples were cut into 1 × 1 cm and coated with platinum. To measure the coating degree of untreated and chitosan treated garments, stiffness test was conducted by a drape tester. The garment samples were cut into 5 × 5 cm, and each sample was measured five times using a drape tester (James H. Heal, UK).

3. Results And Discussion

3.1 The characteristics of untreated MFs generated in the washing process

The amount of untreated MFs released in the washing drainage was 148 ± 21 MFs/L which was equal to 85 ± 12 MFs/g as a weight basis; this value was similar to previous studies (Napper and Thompson 2016; De Falco et al. 2018b). We expected that the length of MFs contained in the drainage would be less than 300 μm owing to the 300-μm sieve built-in the washing machine filtered the drainage. However, 97% of MFs detected were over 300 μm. This is likely that the flexible MFs can easily pass through the 300 μm sieve screen. The most frequently detected MF size was in the range of 500–1,000 μm in length with a median value of 957 μm and a maximum MF length of 2,114 μm (Fig. 1). Thus, this indicates that the

MFs generated during laundering in a real environment may have various lengths regardless of sieve size built-in the washing machine.

In terms of the morphology of MFs generated, as we expected, most of MFs detected were curved shapes due to their weaving in the garment manufacturing process (Fig. 2). And no tangled MFs were observed; thus, individual MFs were released from the weaving fibers by the washing process.

To determine the main cause of MF generation during the washing process, the morphology of MFs produced in the drainage and MFs intentionally cut by scissors were compared by SEM analysis. According to SEM analysis, the morphology of MFs in the drainage was different from the MFs cut using scissor (Figs. 3c,d). The cross-section of MFs cut using scissors were very clear with no fragment generation. However, the cut edge of the generated MFs in the laundering was not as clear as the intentionally cut MFs; thus, it might generate nano- and/or micro-sized fragmented fibers (Fig. 3a). It is speculated that the MFs generated during the washing process may be broken by physical damage owing to the repeated twisting motion (Hearle et al. 1998; Morton et al. 1962) In addition, nano-sized fragment generation was observed on the cross-section of MFs where the fiber was broken (Fig. 3b), indicating a possible risk of secondary pollution such as secondary MF generation.

3.2 Reduction of MFs amounts generated after the chitosan pretreatment

The amount of untreated MFs released during laundering was 148 ± 21 MFs/L. Despite pretreating with 0.1% chitosan solution, no reduction in the amount of MFs generated was observed (Fig. 4). This indicated that the 0.1% chitosan concentration may not be strong enough to form a coating owing to its low dosage and fails to prevent physical damage during washing.

In the case of pretreatment with 0.4%, 0.7%, and 1% chitosan solutions, 63(± 36), 7(± 3), and 72(± 2) MFs/L were generated from the PE garments, respectively. Thus, the highest percent reduction was achieved with the 0.7% chitosan solution pretreatment showing a 95% reduction in the amount of MFs released after the washing.

Compared to control samples not pretreated with the chitosan, the fibers with chitosan pretreatment looks well-connected (Fig. 5). Thus, it indicated that the application of chitosan solution may function as a link/bridge between each fiber by reducing the MFs generated. To be more specific, chitosan particles adhere to the fabric surface through linear bonding with the carboxyl group of chitosan and the terminal group of PE fabric leading to an increased tensile strength between each fiber (Park et al. 2005). When the samples were pretreated with a 0.7% chitosan solution, the coating was most uniformly formed on the MFs (Fig. 5b), whereas the films on the MFs of the sample treated with 1% chitosan solution were not uniform because of film sagging (Fig. 5c). Thus, it appeared as a non-uniform and thick-layered coating due to excessive chitosan concentration used. Therefore, it was confirmed that the chitosan coating was more uniform at a moderate concentration (0.7%) than at the highest concentration (1.0%); further, it was observed that the chitosan coating formed evenly with the 0.7% chitosan solution. Thus, the uniformity of

the chitosan coating may be a key factor in reducing the MF generation during the laundry process. Optimal chitosan concentration may highly depend on the area/weight of garments; thus, it requires further research about optimal conditions for the case of various areas and weight of garments.

To examine the changes in physical properties of MFs before and after chitosan pretreatment, the tensile strength was determined by measuring the drape index of the garment pretreated with 0.7% chitosan and untreated MFs (Table 2). The results showed that the application of 0.7% chitosan pretreatment increased the garment stiffness up to 58%. The increase in stiffness was due to the penetration of chitosan into the PE fabric, which promotes film formation on the fabric's surface and reduces the degree of freedom of the MFs (Park et al. 2005).

3.3 Application of chitosan pretreatment on other polymer types

For the untreated samples, 85 ± 12, 160 ± 45, and 239 ± 37 of MF particles/g were released from the PE, AC, and PA garments, respectively (Fig. 6). Considering that the density of each polymer type was 1.38, 1.2, and 1.14 g/cm^3 for PE, AC, and PA, respectively, it seems that the garments with high density released less amount of MFs than low density garments (AC and PA). Similarly, Napper (2016) showed that the amount of MFs generated from the PE garments was lesser than the AC garments during washing, with 82.6 MFs/g from PE and 121.4 MFs/g from AC (Napper and Thompson 2016). Yang et al. (2019) also reported that PE garment released 2,012 MFs/m^2 and PA generated 50,686 MFs/m^2. Therefore, both observations support our hypothesis that the high density of garments reduced the amount of MFs generation.

After the chitosan pretreatment, the amount of MFs generated from a PE garment reduced to about 95 ± 1.9%; and there was a reduction of about 48 ± 10.45% and 49 ± 14.2% in MF generation for chitosan pretreated PA and AC, respectively. To explore the possible reason for the different amount of MFs generated depending on the type of garments, the morphology of coating on each garment was analyzed using SEM. Figure 7 shows that while PES and AC are well-coated with chitosan solution before washing (Fig. 7a,b), the coating between the fibers on PA is not perfect (Fig. 7c). After washing, SEM images of PE garments showed that chitosan coating did still stick tightly, whereas a part of chitosan coating had peeled off in AC (Fig. 7d,e). Thus, it indicates that the degree of chitosan coating was affected by the type of polymer in the garments. Therefore, optimal conditions for each type of clothes, such as a chitosan concentration, soaking time, and appropriate solutions, are required for further research.

4. Conclusion

This study demonstrated that chitosan pretreatment can reduce the amount of MFs generated during laundering. We found that the optimal concentration of chitosan solution for pretreatment is 0.7% for PE garments, and the amount of MFs generated before and after the chitosan pretreatment was compared. The amount of MFs generated from the untreated PE garments during the washing process was 148 ± 21

MFs/L with a median length of 957 μm. After the chitosan pretreatment, the number of MFs generated after washing was reduced by 95 ± 1.9% compared to the untreated ones. To confirm the applicability of chitosan pretreatment, other synthetic garments (PA and AC) were pretreated, and MF generation was reduced by 48 ± 10.45% and 49 ± 14.2% for PA and AC, respectively. The lower reduction rate compared to PE was due to chitosan's poor binding strength with PA and AC.

Laundry is a major source of MFs generation, and it is estimated that 6 million MFs can be released from 5 kg of synthetic textiles and flow into the waterbodies through the sewage treatment plant (Napper and Thompson 2016; Carney Almroth et al. 2018; De Falco et al. 2018b). Therefore, research has focused on methods for reducing microplastics generated during the washing process. The study for reducing the generation of MFs during laundry can be categorized into in-drum and external device approaches (McIlwraith et al. 2019; Napper et al. 2020). In-drum devices are placed inside the washing machine along with the garments to capture MFs and reduce friction, and external devices use a membrane to reduce MFs contained in the washing drainage. MFs were reduced by 21–78% in in-drum and external device studies, and the highest reduction rate was 87% when using the membrane.

Our study has shown a method to reduce the MFs generation from garments. However, the coating process in the chitosan pretreatment used in this study requires a relatively long time to be completed, resulting in its low efficiency. Therefore, further research is required to develop a pretreatment method that improves the coating process time. In addition, further investigation into the reduced amount of MFs from several types of synthetic fabrics is planned using the same pretreatment method.

Declarations

Authors' contributions

HK: methodology, writing, analysis. SP: review, editing, supervision. BL: data analysis, editing. JA: review. SK: supervision, methodology.

Funding

This research was funded by the Korea Institute of Civil Engineering and Building Technology (KICT), Project No. 20190186-001.

Data availability

Not applicable

Ethical approval

Not applicable

Consent to participate

Not applicable

Consent to publish

Not applicable

Competing interests

The authors declare no conflict of interest

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Tables

Due to technical limitations, table 1 is only available as a download in the Supplemental Files section.

Table 2
Result of drape index before and after chitosan pretreatment.

	Control	0.7% chitosan solution	% increase
Drape index	0.337 (± 0.014)	0.572 (± 0.009)	58 (± 1)

Figures

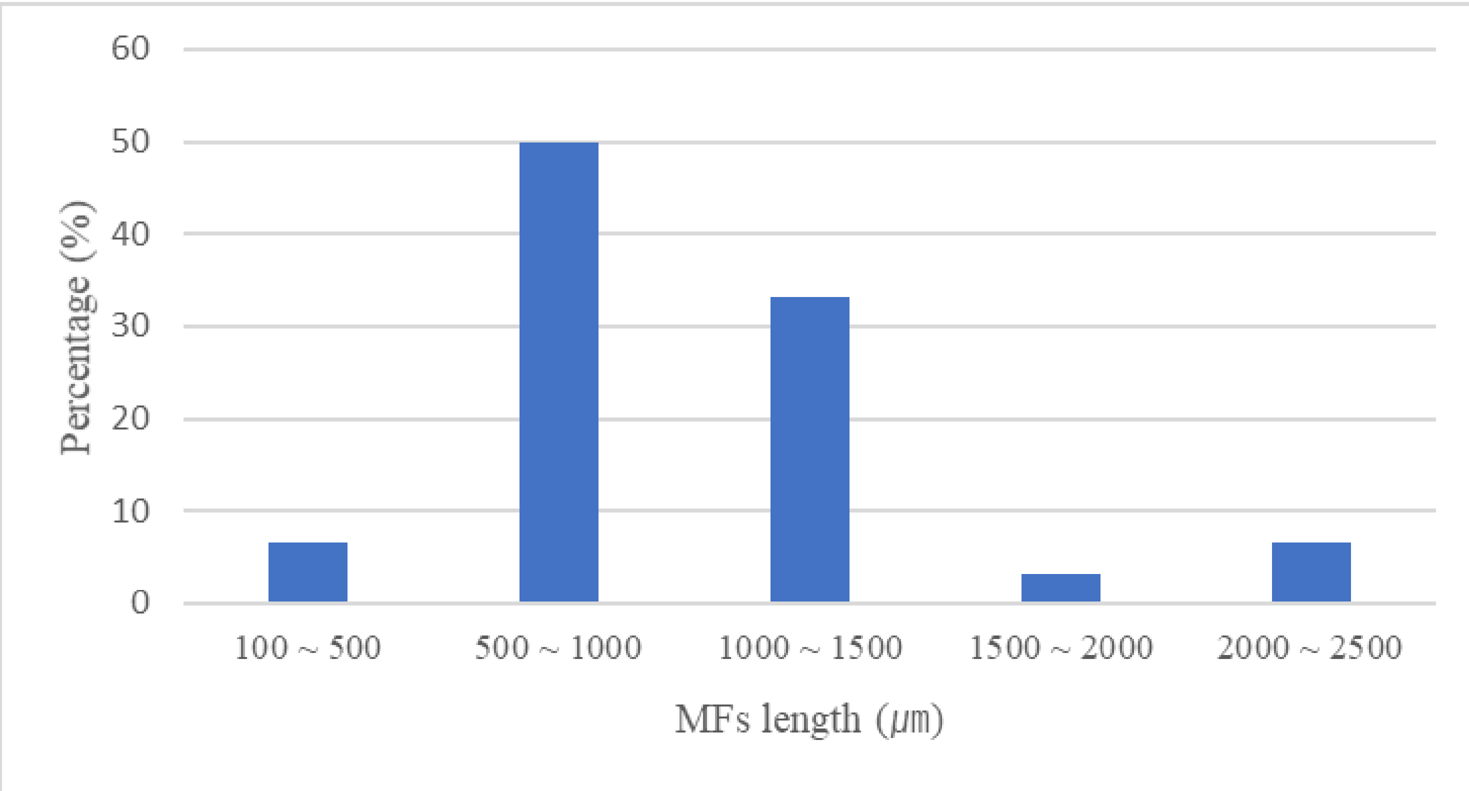

Figure 1

Length distribution of MFs released in the process of washing.

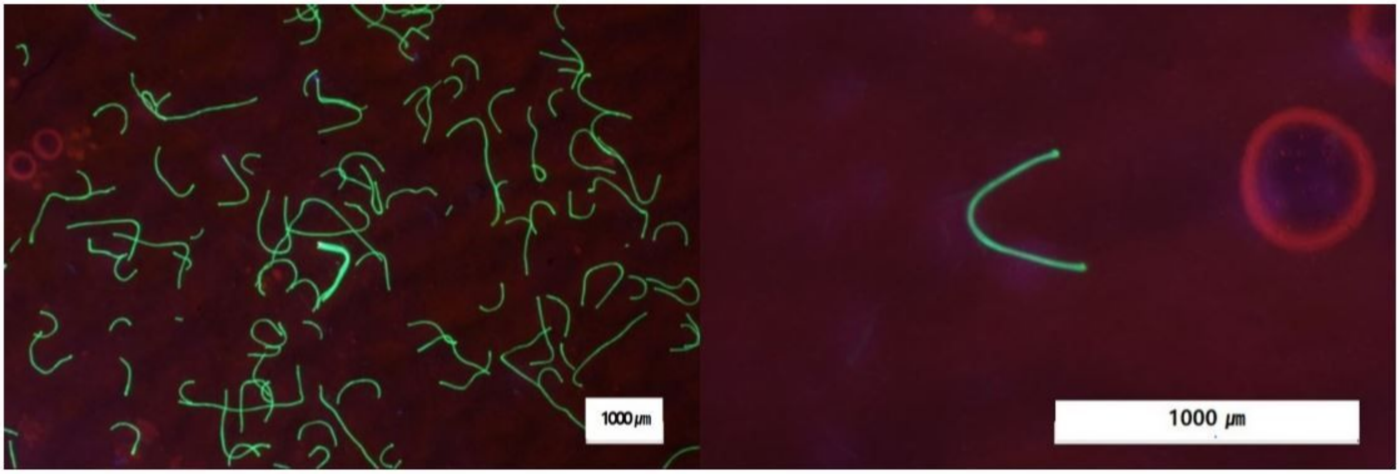

Figure 2

Identification of MFs contained in washing drainage by the NR-P method.

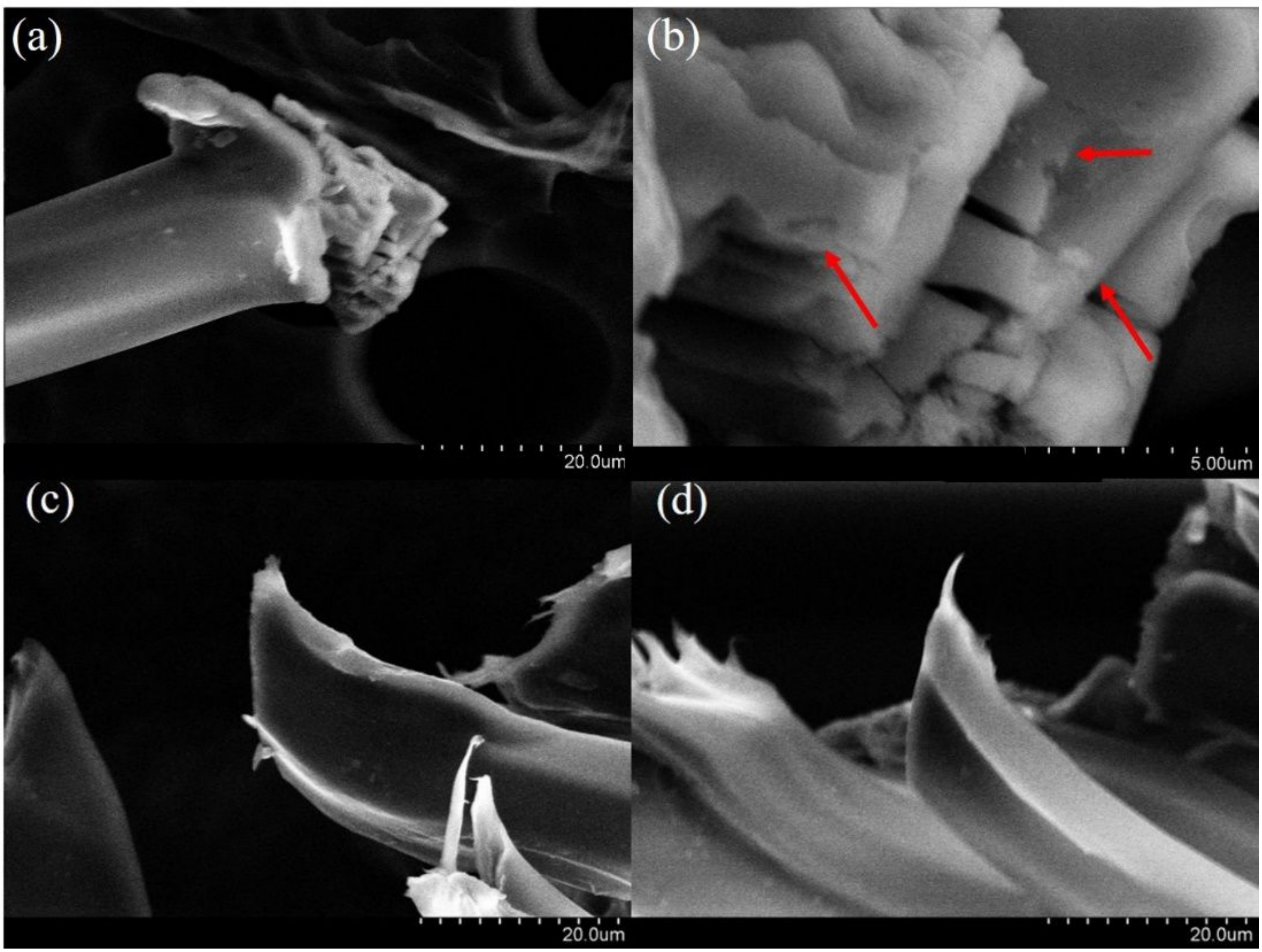

Figure 3

SEM images of the cut edge of the PE garments: (a, b) Fibers broken by physical forces after washing; (c, d) cut by scissor.

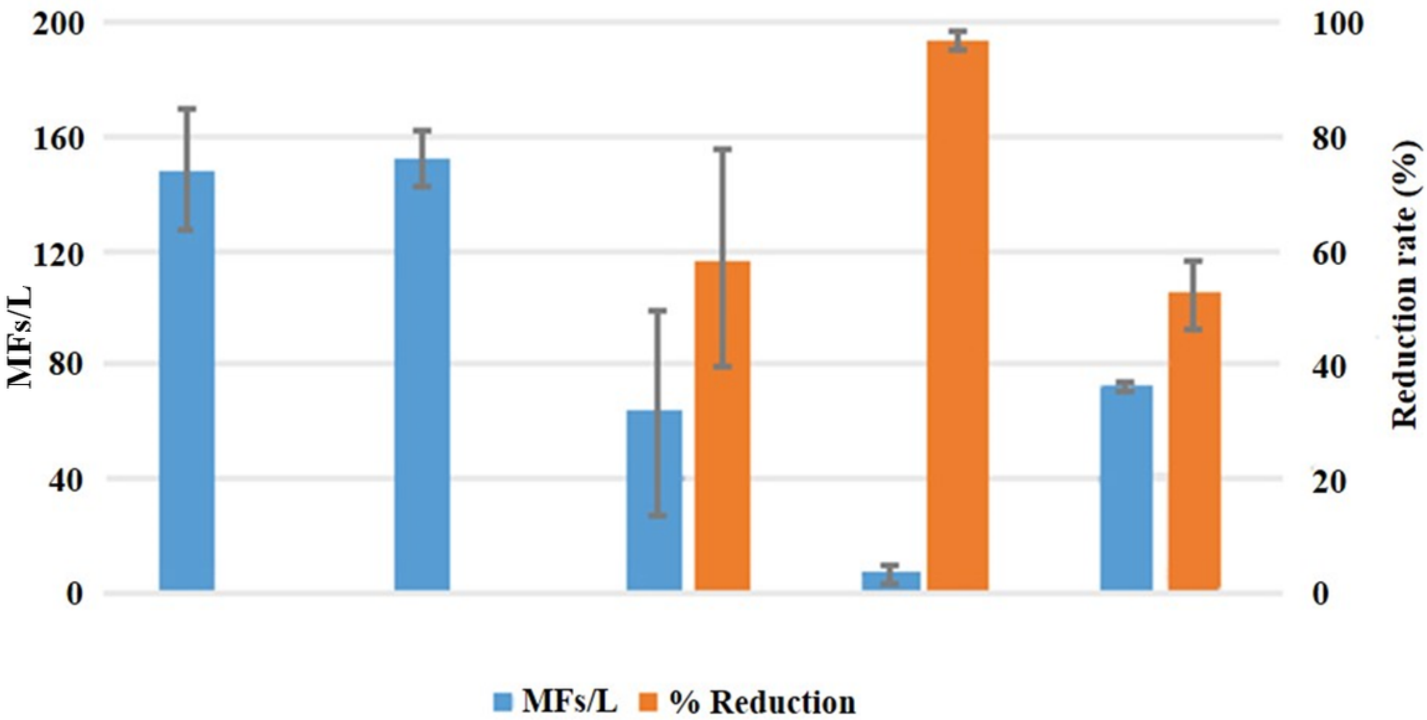

Figure 4

Number of MFs from the untreated control and percent reduction with chitosan pretreatments at various concentrations.

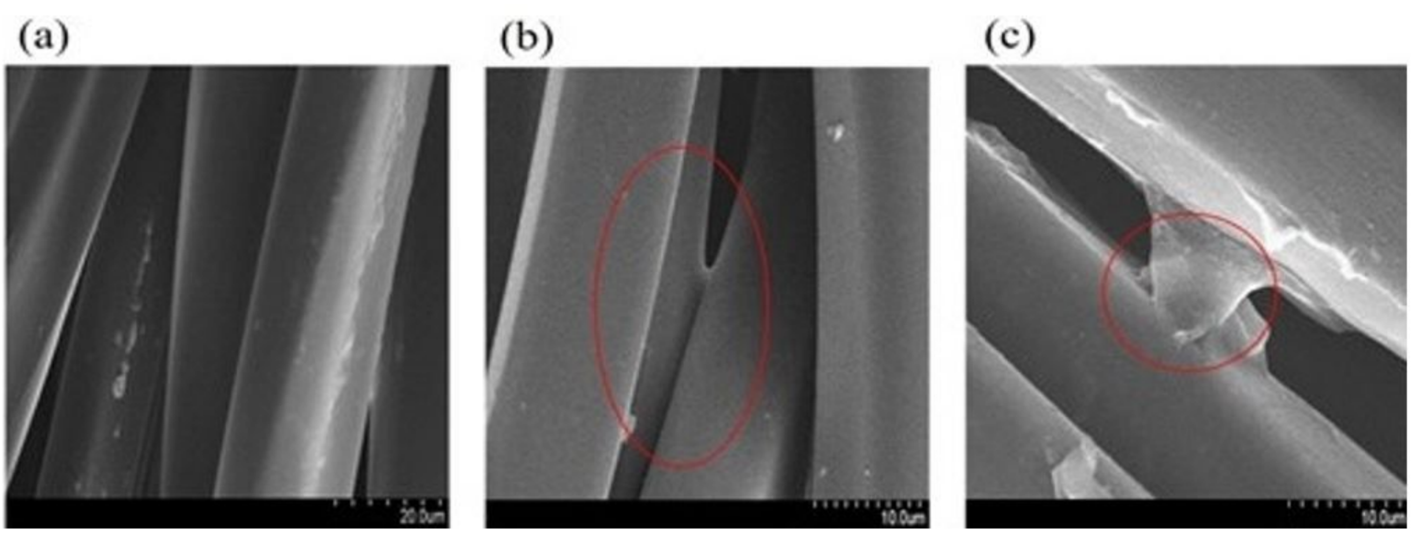

Figure 5

SEM images of cloth surfaces: (a) without pretreatment (control); and with pretreatment using (b) 0.7% chitosan solution, and (c) 1% chitosan solution.

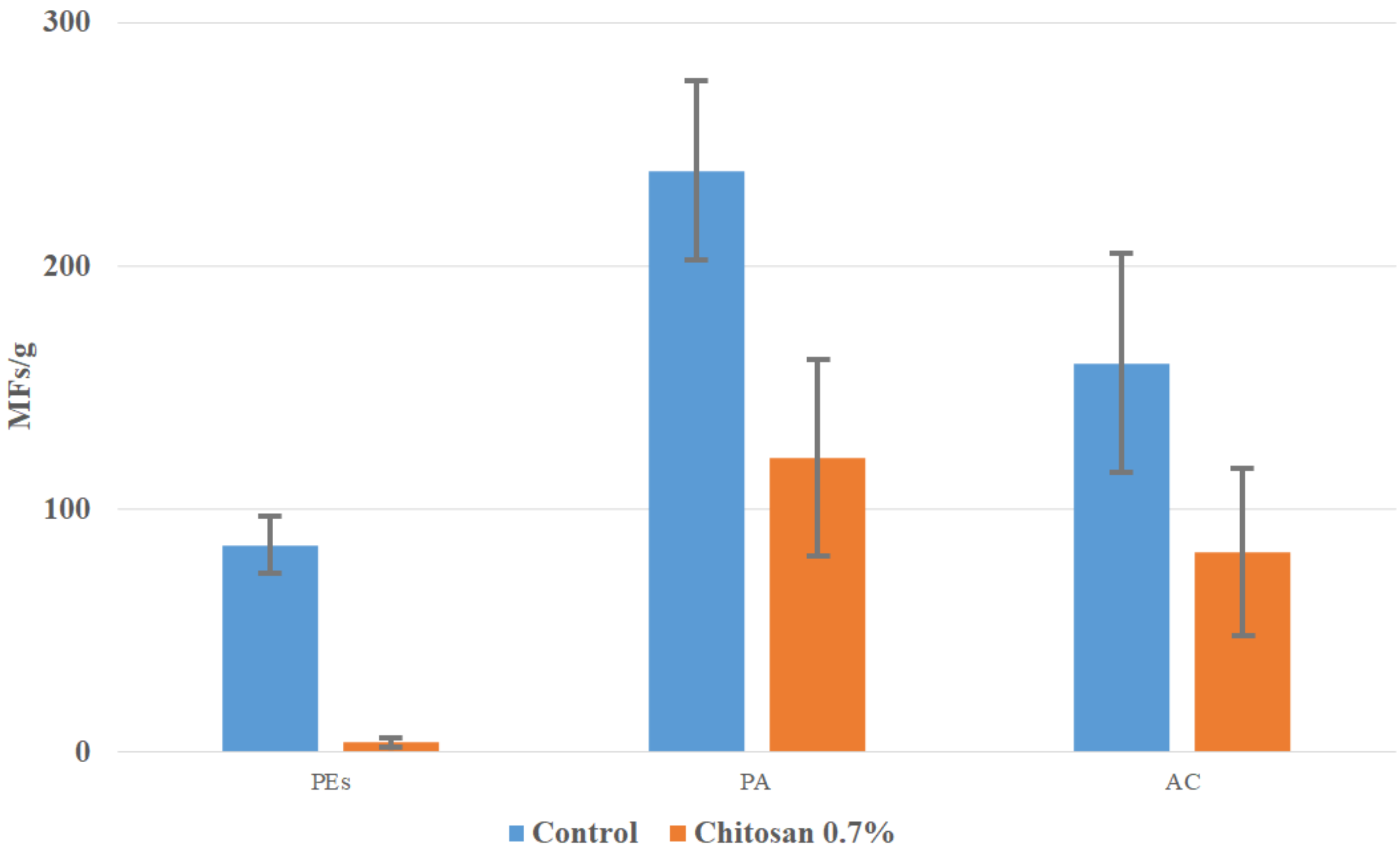

Figure 6

Amount of released (PES, PA, AC) MFs before and after chitosan treatment.

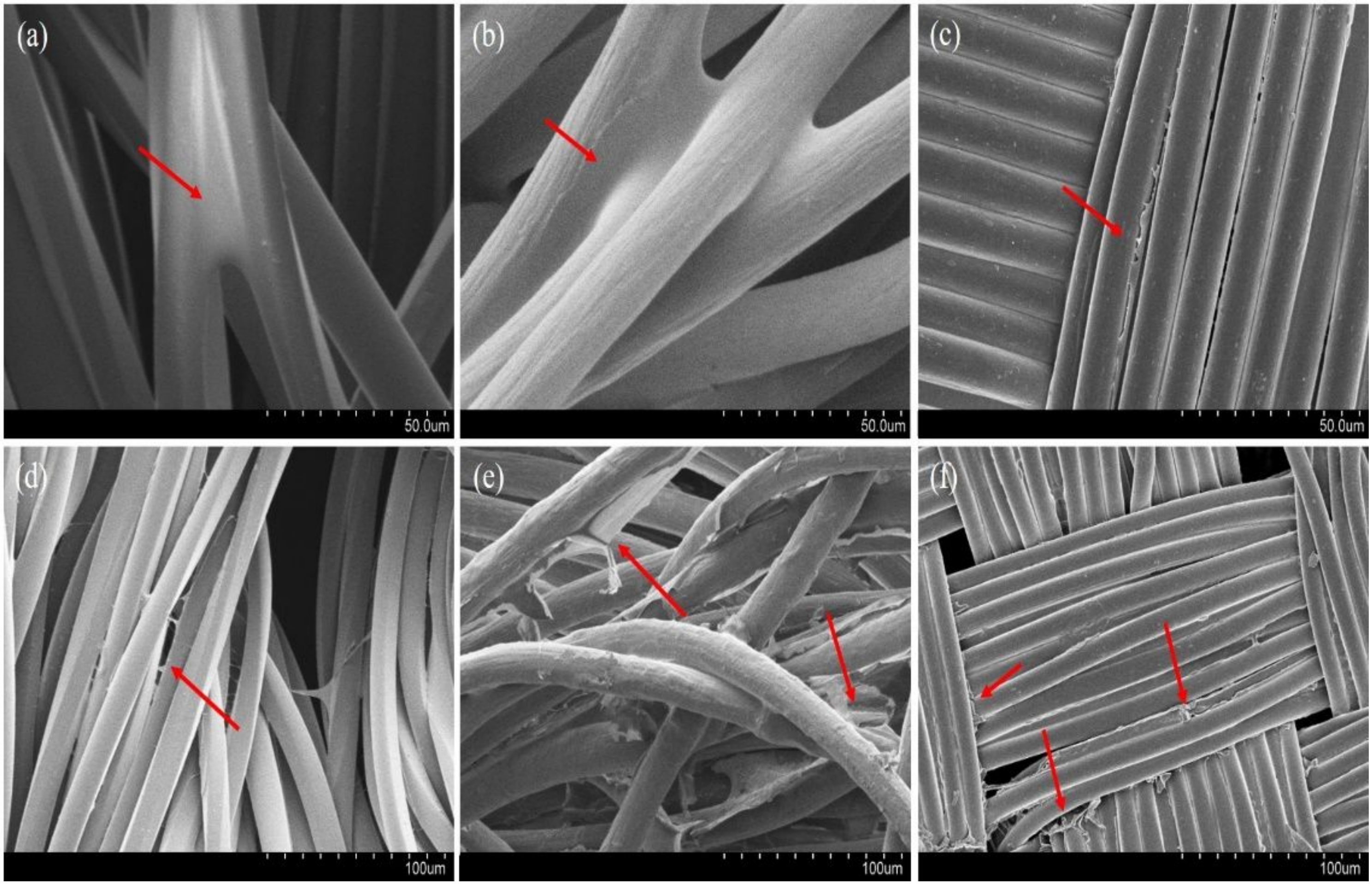

Figure 7

Before chitosan treated ((a) PES, (b) AC, (c) PA) garment and after washing ((d) PES, (e) AC, (f) PA).

Supplementary Files

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- Table1.jpg