

# Effects of Machine Washing on the Chromatography Parameters of Polyester Fiber Gel Permeation

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Cite This: *ACS Omega* 2022, 7, 38789–38795



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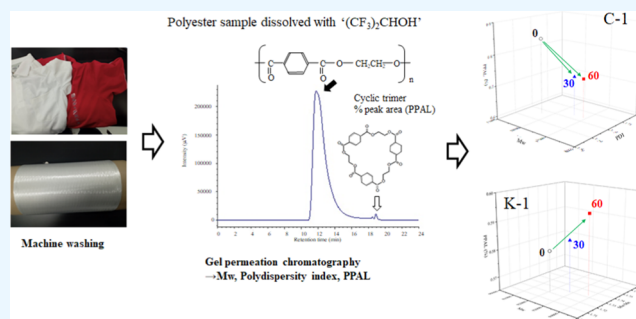
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**ABSTRACT:** Fiber examination is frequently performed in forensics, and gel permeation chromatography (GPC) is one candidate method for discriminating polyester fibers. Here, the effects of machine washing on weight-average molecular weight ( $M_w$ ), polydispersity index (PDI), and the percentage peak area of cyclic ethylene terephthalate trimer (PPAL) of commercial polyester shirts and manufactured poly(ethylene terephthalate) (PET) yarns were investigated using GPC. GPC was performed using a 1,1,1,3,3,3-hexafluoro-propan-2-ol polymer solubilizer, styrene–divinylbenzene copolymer GPC columns, a chloroform mobile phase, and a 254 nm absorbance monitor. The statistical change in the polyester fibers during machine washing was evaluated by comparing three GPC parameters of the same fiber samples before and after machine washing. Among the commercial polyester shirts examined, the GPC parameters changed significantly after machine washing with a considerable PPAL decrease. In contrast, the GPC parameters of manufactured PET yarns changed significantly with a moderate increase in  $M_w$ . This work elucidates the change on GPC parameters of polyester fibers by machine washing.



## INTRODUCTION

Fibers from clothing are left at crime scenes by perpetrators and/or victims and are also transferred between them, suggesting an association between the aforementioned individual(s) and the crime scene. The examination of this physical evidence is one of the most important and frequently performed forensic analyses, forming part of trace evidence analysis.<sup>1–3</sup> This examination is generally conducted using microscopy,<sup>4</sup> Fourier transform infrared (FTIR) spectroscopy,<sup>5</sup> and visible-light microspectrophotometry.<sup>6,7</sup> Furthermore, instrumental analyses, such as liquid chromatography–mass spectrometry (LC–MS),<sup>8</sup> Raman spectroscopy,<sup>9</sup> and inductively coupled plasma ionization MS,<sup>10</sup> have been used to detect specific minor components, such as dyes/pigments and inorganic elements. Additionally, further research has been carried out to develop new and forensically effective analytical methods.<sup>11,12</sup> Polyester, a thermoplastic polymer found in personal belongings, is the most popular material used in synthetic fibers and containers<sup>13,14</sup> and for advanced usage,<sup>14</sup> and it is routinely examined in forensic investigations.<sup>12</sup> However, it is difficult to discriminate pairs of polyester fibers with a similar additive composition because microscopic observation and FTIR spectroscopy are insufficient in differentiating between polyesters, and further instrumental analysis targeting dyes/pigments does not seem efficient for colorless polyester fibers. Polyesters are synthesized by the

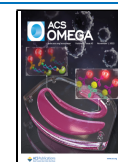
dehydrative polymerization of dialcohols and dicarboxylic acids.<sup>13</sup> The most frequently used polyester, poly(ethylene terephthalate) (PET; the structure is shown in Figure S1C), is synthesized by alternative esterification of terephthalic acid and ethylene glycol. The molecular weight (MW) of the polymer and its distribution pattern are dependent on the synthetic reaction conditions.<sup>15</sup>

Gel permeation chromatography (GPC)/size exclusion chromatography has been used to characterize synthetic polymers.<sup>16</sup> 1,1,1,3,3,3-Hexafluoro-propan-2-ol (HFIP) was adopted as a solubilizing LC solvent for polyesters, making GPC of polyesters possible,<sup>17</sup> and the GPC efficiency increased when HFIP was used in chloroform.<sup>16,18</sup> Milana analyzed polymer MW parameters for repeatedly extruded PET by solubilizing samples with HFIP and chromatographing them using the chloroform solvent.<sup>19</sup> Farah et al. recommended GPC methodologies for estimating PET polymer MWs besides polymer analytical technologies of viscosity measurement, hot-stage microscopy, atomic force microscopy, differential

Received: July 14, 2022

Accepted: October 11, 2022

Published: October 18, 2022



scanning calorimetry, and matrix-assisted laser desorption ionization MS.<sup>12,20,21</sup> Therefore, GPC appears to be a forensically effective analytical method for estimating MWs of polymers. Previously, we developed a GPC method to effectively differentiate polyester fibers by integrating three polymer parameters: polymer MW parameters of weight-average MW ( $M_w$ ), polydispersity index (PDI), and the percentage peak area of low-MW cyclic ethylene terephthalate trimer (PPAL),<sup>22</sup> where the discrimination power of polyester polymer fiber samples was 94.9%. Notably, adopting PPAL is the first trial in the forensic discrimination of polyester fibers. Cyclic ethylene terephthalate oligomers are inevitably produced from side reactions of PET synthesis, and cyclic trimers are a major component of cyclic oligomers<sup>23,24</sup> that manifest in the degeneration of fiber quality; therefore, an effort has been made to lower the cyclic oligomer levels to improve fiber quality.<sup>25</sup> Information regarding the dispersion characteristics of polyester polymers measured using GPC can play a crucial role in polyester discrimination when ordinary forensic examinations cannot provide conclusive differential identifications of polyester fiber specimens. The GPC discrimination mechanism is based on molecular characteristics of polymers that have not been forensically investigated in detail.

Polyester fibers are characterized as resistant to mechanical stress, water, and sunlight and are relatively resistant to heat and chemicals.<sup>13</sup> Since polyester fabrics show weak water absorption, they do not expand or contract after machine washing. However, polyesters can be degraded<sup>26</sup> under aqueous conditions.<sup>27</sup> Many studies have been conducted on changes in fabrics and fibers; notably, alkaline conditions,<sup>28,29</sup> ultraviolet light,<sup>30</sup> thermal treatment,<sup>31</sup> and disinfectants<sup>32</sup> are harmful to polyesters. Considering real crime situations, fiber specimens found in crime scenes are not necessarily fibers removed from unused or new fabrics but particularly from used fabrics. Fabrics deteriorate during daily usage, and regarding machine washing, polyester fibers are released from fabrics.<sup>33–35</sup> In our previous study,<sup>22</sup> samples examined using GPC were unused materials, including fabrics, and to date, there is no literature concerning the effect of machine washing on the GPC parameters of polyesters. In this paper, the change in GPC parameters after machine washing was examined to elucidate the effect on used clothes when considering actual crime cases, where unused clothes are not worn by the suspects and/or victims. As polyester samples examined for the effect of machine washing, several commercial polyester shirts having different colors have been used considering real crime situations. In addition, PET yarns manufactured from the same PET pellets by different spinning conditions have been used for speculating the effect of PET macromolecular structures.

## EXPERIMENTAL SECTION

**Materials.** HFIP, high-performance liquid chromatography (HPLC) grade chloroform and methanol, and LC–MS grade formic acid were purchased from FUJIFILM Wako Pure Chemicals (Osaka, Japan). Ultrapure water used (<18.2 M $\Omega$ ·cm) was purified using an ultrapure water system type  $\omega$  (Organo, Tokyo, Japan).

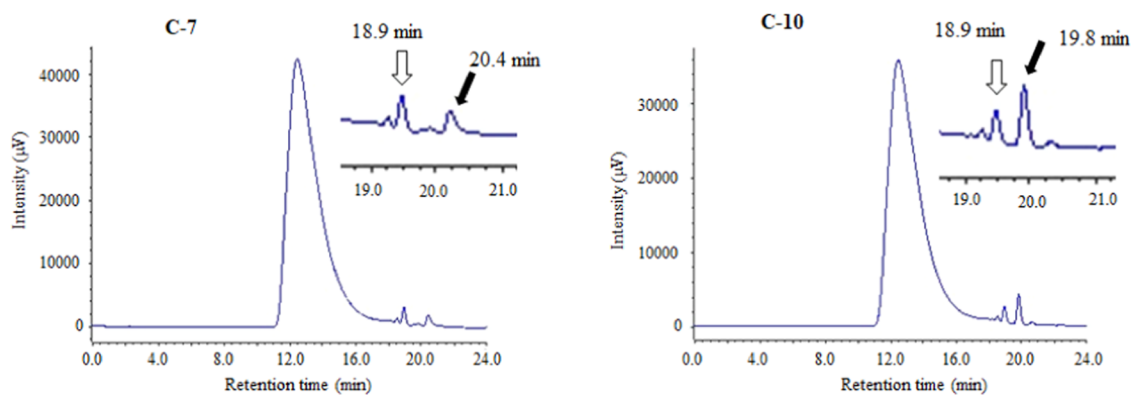
**Fiber Samples.** Fiber pieces drawn from eight different unused commercial shirts made of polyester or polyurethane-blended polyester, arbitrarily obtained from local stores, and eight PET fiber yarns manufactured in-house at TOYOBO Co.

(Shiga, Japan) from the same PET (intrinsic viscosity (IV): 1.05) pellets under different spinning conditions were examined. Detailed information on the polyester shirts and PET fiber yarns examined are shown in Supporting Information Tables S1 and S2, respectively.

**Sample Treatment.** Pieces from eight commercial shirts (chest region) and bundles of eight in-house manufactured PET yarns were placed in polyethylene mesh bags and treated to 30 or 60 cycles of machine washing (15 min wash using laundry detergent (Attack ZERO, KAO Co., Ltd., Tokyo, Japan), rinsing twice with water for 3 min, and dehydrating for 3 min) and indoor natural drying. Shirt pieces and in-house manufactured PET yarns, both machine-washed and machine-unwashed, were dissolved in HFIP (PET yarn: 1–5 cm/mL; fibers, shirt pieces, and PET bottle pieces: 0.5–40 mg/mL), diluted 10-fold with chloroform, and thereafter subjected to GPC measurement.

**Gel Permeation Chromatography.** GPC was performed using an EXTREMA HPLC system (JASCO Co., Tokyo, Japan) consisting of a PU-4180 pump, an AS-4150 autosampler, a CO-4060 column oven, and an ultraviolet–visible (UV–Vis) absorption detector (UV-4070). The styrene–divinylbenzene copolymer column, Shodex K-803L (3  $\times$  300 mm; MW exclusion limit 70,000; MW separation range 100–70,000; SHOWA DENKO K.K., Tokyo, Japan), was tandemly connected to another column, Shodex K-804L (3  $\times$  300 mm; MW exclusion limit 400,000; MW separation range 100–400,000). The column temperature was maintained at 40  $^{\circ}$ C, and the flow rate was 1 mL/min. Chloroform was delivered as the elution solvent, and the eluate was monitored using UV<sub>254</sub>. The MW standard calibration compounds for the organic solvent were Shodex Standard (SM-105, SHOWA DENKO K.K.; S-1.3 (MW: 1250); S-3.1 (3050); S-65 (6540); S-22 (22,300); S-57 (56,600); S-133 (133,000); S-317 (317,000); S-662 (662,000); S-1700 (1,700,000); S-2330 (2,330,000)). Afterward, chromatography and UV-absorbance chromatography were applied, and the  $M_w$  and PDI values were automatically calculated using EXTREMA HPLC ChromNAV GPC/SEC software. From the peak area of the low MW peak at approximately 18.9 min, PPAL was calculated. The calibration run was performed once every 2 weeks. The typical gel permeation chromatograms of PET fiber and polyethylene standards are shown in Figure S1.

The statistical comparisons of two polyester fibers in the GPC analysis were performed by evaluating the difference in the GPC parameters ( $M_w$ , PDI, and PPAL) and the standard deviation (SD). In real forensic cases, only a few fiber specimens of the same origin are subject to examination because the same fibers cannot necessarily be sampled from the crime scenes, and appropriate SD values cannot be obtained. Therefore, the configured SD values are adopted from coefficient of variation (CV) values measured using the repeated GPC measurements of the K-1 PET fiber.<sup>22</sup> The measured GPC parameters for two different fibers (fibers 1 and 2) are presented as  $M_{w1}$ , PDI<sub>1</sub>, and PPAL<sub>1</sub> for fiber 1 and  $M_{w2}$ , PDI<sub>2</sub>, and PPAL<sub>2</sub> for fiber 2. The evaluated CV values for  $M_w$ , PDI, and PPAL were 0.011, 0.02, and 0.016, respectively, shown as CV<sub>A</sub>, CV<sub>B</sub>, and CV<sub>C</sub>. For example, from the  $M_w$  the discrimination of fibers 1 and 2 was evaluated by comparing the difference “[ $M_{w1} - M_{w2}$ ]” with the converted SD, which can be calculated as the average  $M_w$  divided by CV<sub>A</sub> “[ $(M_{w1} + M_{w2}) / (2 \times CV_A)$ ]”. If the quotient of the difference divided by



**Figure 1.** GPC patterns for the colored commercial polyester shirts, C-7 and C-10. Hollow and solid arrows indicate low MW peaks assumed to be the cyclic ethylene terephthalate trimer and dyes/pigments, respectively. The magnified view for low MW components is shown in the upper right corner.

SD exceeds 2, both fibers differ significantly with the significant level of 4.55% ( $2\sigma$  criteria).

By integrating three GPC parameters into the statistical calculation, the comparison between both fibers was conducted as follows: the quotient of the difference (Euclidean distance between two fiber points) divided by the SD was squared to obtain the normalized variance “[ $4 \times CV_A^2 \times (M_{w1} - M_{w2})^2 / (M_{w1} + M_{w2})^2$ ],” designated as “ $V_A$ .” Similarly, PDI and PPAL were used to calculate  $V_B$  and  $V_C$ , respectively. Additionally, the square root of the three summed normalized variances “[ $\sqrt{(V_A + V_B + V_C)}$ ]” was calculated. If it exceeds 2, the difference in the fibers is determined to be statistically significant in the three-dimensional (3D)  $2\sigma$  criteria.

**Visual Examination.** Magnified detailed surface observation was performed using a visible-light microscope (VHX-6000, Keyence, Osaka, Japan) and a scanning electron microscope (VHX-D510, Keyence).

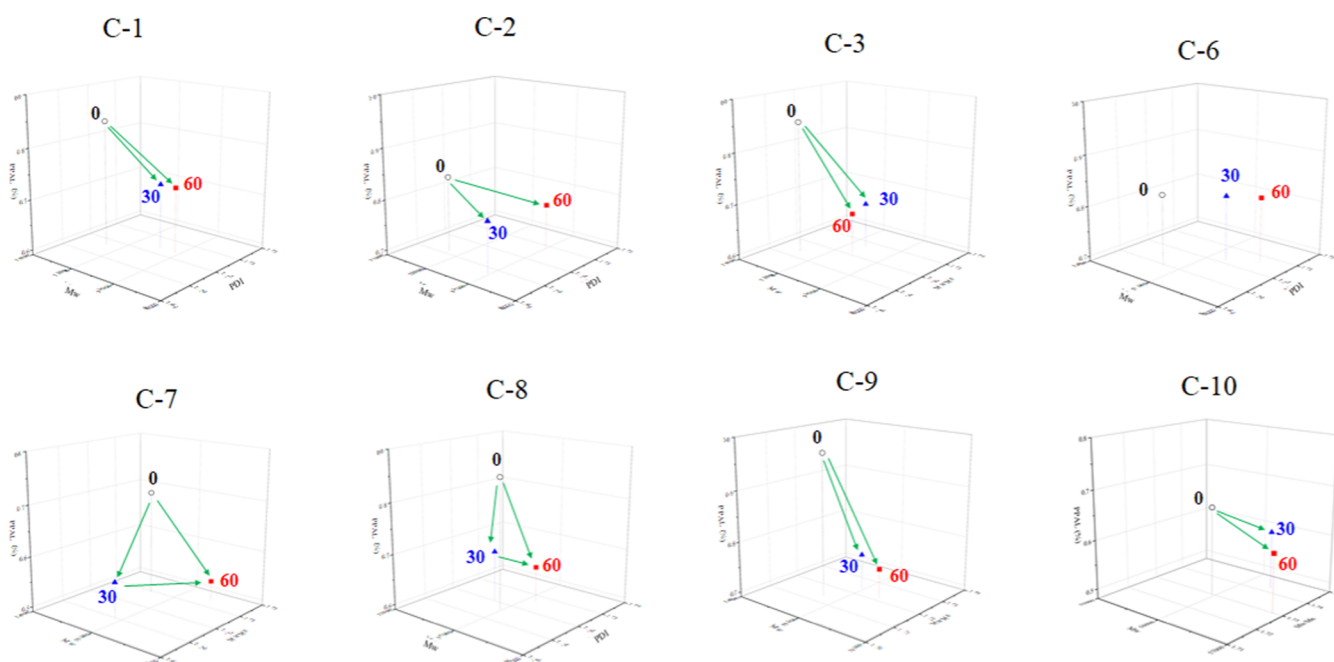
## RESULTS

**Effect of Machine Washing on Commercial Polyester Shirts.** In this study, simulated evidence fiber samples of unused commercial fabrics were used. Two T-shirts, 1 white (C-3) and 1 red (C-7); 6 Polo shirts, 2 whites (C-1, C-2, and C-6), 1 red (C-8), 1 navy (C-9), and 1 green (C-10); 7 polyesters (C-1, C-2, C-3, C-6, C-7, C-8, and C-9), and 1 blended spinning shirt of 95% polyester and 5% polyurethane (C-10) were examined. Information regarding the shirts examined are shown in Table S1. The eight shirt fibers showed similar FTIR spectra resembling the PET K-1 fiber except for polyurethane found in the C-10 shirt, as reported in a previous paper.<sup>22</sup> The GPC elution patterns were similar for all of the shirt samples, although the peak top retention times and peak dispersity profiles differed somewhat. For the colored shirts (C-7 and C-10), the low MW peaks appeared around 20 min, apart from the 18.9 min peak (Figure 1), and the assumption was that they are dye and pigment molecules. In stained polyester fabric fibers, basic dyes or dispersive dyes are included in the fibers,<sup>36</sup> and these dyes could be eluted during polyester fiber solubilization with HFIP.

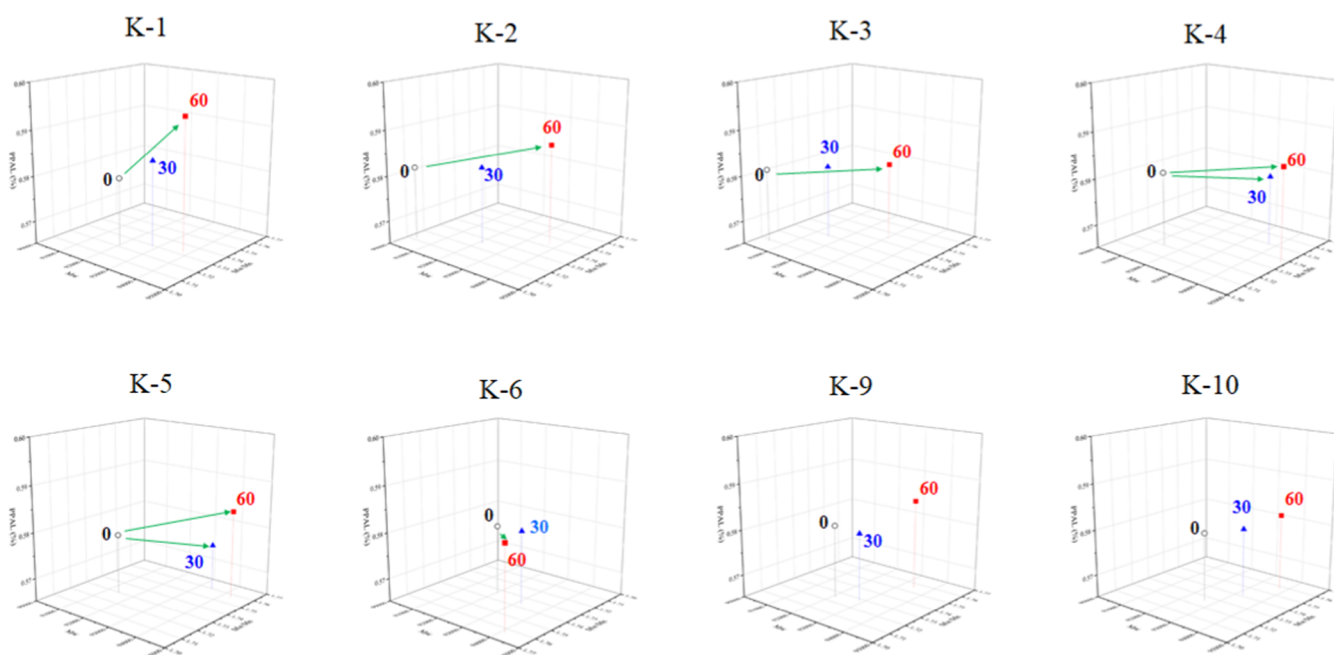
Samples taken from eight unused shirts were machine-washed for 30 or 60 cycles. FTIR spectra were almost the same for the unwashed and machine-washed fiber samples (data not shown). No significant morphological change in color or surface condition was observed microscopically, although the fibers seemed a little twisted and the fiber diameters increased

slightly for C-1 and C-2 shirt fibers (data not shown). Using scanning electron microscopy on the surfaces, approximately 10  $\mu\text{m}$  wide rising ejects were observed in the longitudinal direction compared to the flat surfaces of unwashed fibers. Figure S2A–D shows the typical examples of white and red shirts (C-1; C-7). Cionek et al. observed stretch marks and grooves in the longitudinal view for disinfectant-treated PET fabrics.<sup>32</sup> Sorensen et al. observed holes and pitting on the surface of UV-degraded PET fibers.<sup>30</sup> De Falco et al.<sup>35</sup> reported that using visible-light and scanning electron microscopes, no visible damage to the polyester fabrics during washings was observed, although considerable amounts of microfibers were released from the fabrics during washings. The cause for the absence of stretch marks/grooves and holes/pitting in our washed polyester shirts may be due to the difference in fiber degradation conditions, where neither disinfectant use nor UV irradiation was subjected to our experiment. Also, the cause for the appearance of rising ejects in our washed polyester shirts may be due to the difference in washing conditions, where few washing cycles were used for the De Falco experiment.

The result of the effects of machine washing on the GPC parameters of polyester shirts is shown in Table S3. The  $M_w$  values increased for all of the machine-washed shirts; however, only the  $M_w$  of the C-1 shirt showed a significant increase after 60 wash cycles (difference/SD = 2.03). Furthermore, changes due to machine washing were not significant in the  $2\sigma$  criteria for PDI values. Moreover, a significant decrease in PPAL values was observed (difference/SD > 3.88) for all machine-washed shirts except C-6. In addition, the percentage peak area of the other low MW peaks (20.4 min) for the colored C-7 shirt, presumed to be dye or pigment molecules, decreased significantly after machine washing in the  $2\sigma$  criteria (assuming that the CV value was the same as that of PPAL). Regarding the colored C-10 shirt, no significant decrease in the percentage peak area of the low MW peak (19.8 min) was observed after machine washing. It was speculated that low MW compounds, such as cyclic trimer, dye, and pigment, were removed from the fibers during the repeated machine washing cycles. This tendency agrees with the low PPAL values for the used white shirts C-4 and C-5 (0.503, 0.753) as reported in a previous paper.<sup>22</sup> Furthermore, the  $M_w$  increase after machine washing, especially in the C-1 shirt, can be explained by low MW polymers existing in high amounts in amorphous regions being removed from the fiber matrix. The statistical



**Figure 2.** Effect of machine washing on the 3D distribution of GPC parameters of commercial polyester shirts. Open black circles, closed blue triangles, and closed red circles indicate the points for unwashed, 30-cycle machine-washed, and 60-cycle machine-washed fabrics, respectively. The green arrows indicate significant changes between 2 points in the 3D  $2\sigma$  criteria.

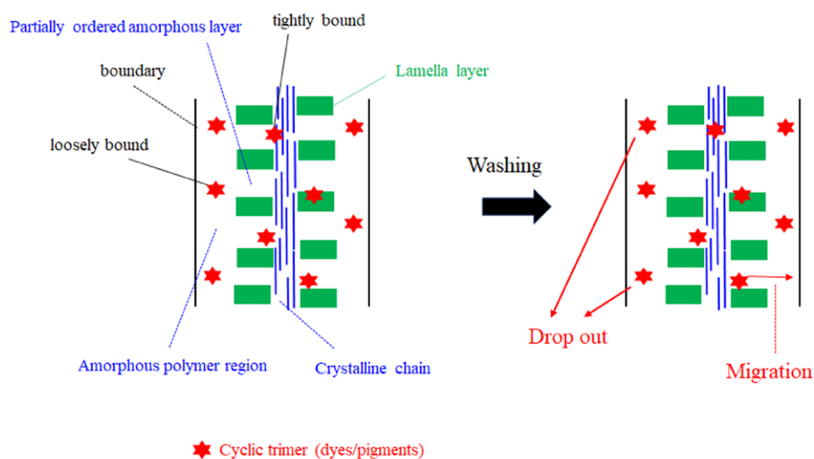


**Figure 3.** Effect of machine washing on the 3D distribution of GPC parameters of in-house manufactured PET fibers. Open black circles, closed blue triangles, and closed red circles indicate the points for unwashed, 30-cycle machine-washed, and 60-cycle machine-washed fabrics. The green arrows indicate significant changes between the 2 points in the 3D  $2\sigma$  criteria.

comparison using the three GPC parameters indicates that there is a significant change between shirts washed for 30 cycles and unwashed shirts in the  $2\sigma$  criteria (except for the C-6 shirt), and additional 30 cycles led to distinct changes in C-7 and C-8 shirts (Figure 2 and Table S3). These significant changes are attributed mainly to the significant decrease in PPAL values.

**Effect of Machine Washing on In-House Manufactured PET Yarns.** Samples taken from eight in-house

manufactured PET yarns were machine-washed for 30 or 60 cycles. Afterward, FTIR spectra were almost the same for the unwashed and machine-washed fiber samples (data not shown). Significant morphological changes in color, surface condition, and fiber diameter were not observed microscopically, although the fibers seemed a little bit twisted (data not shown), and on the surfaces, approximately  $2\ \mu\text{m}$  wide rising ejects were observed in the longitudinal direction. Figure S2E,F shows a typical example of K-1 yarn. The morphological



**Figure 4.** Schematic of the change in cyclic ethylene terephthalate trimer and dyes/pigments in polyester fiber after machine washing. The shish-kebab fiber structure proposed for the other polymers<sup>40</sup> is applied to that of the polyester polymer fibers temporarily. The fiber is composed of a crystalline chain, lamella layer, partially ordered amorphous layer sandwiched between lamella layers, and an amorphous polymer region. Cyclic ethylene terephthalate trimer and dyes/pigments are located in various fiber regions depending on the affinity of small molecules and polymers. During machine washing, small molecules near the fiber boundary of the amorphous region partially drop out, and those in the inner region partially migrate to the amorphous region.

change was significant for commercial shirts compared to the in-house manufactured PET yarns.

The result of the effect of machine washing on the GPS parameters of in-house manufactured PET yarns is shown in Table S4. The  $M_w$  values increased for all of the yarns after machine washing; significant increases were observed for K-2, K-3, K-4, K-5, and K-6 yarns after 60 cycles. Although the increase was not significantly high (difference/SD < 3.7), the tendency of the  $M_w$  to increase did not correspond with the results for commercial polyester shirts that showed an insignificant increase. There were no significant changes in the PDI and PPAL values. The small change in PPAL did not correspond with the results for commercial polyester shirts, showing highly significant decreases. The estimation for statistical comparison using the three GPC parameters indicates that the fibers machine-washed for 60 cycles underwent a significant change compared with unwashed fibers in the  $2\sigma$  criteria for all except for the K-9 and K-10 PET yarns, and after 30 wash cycles, there were significant changes in the K-4 and K-5 yarns (Figure 3).

## DISCUSSION

Some research groups<sup>33,35</sup> reported that microfibers were released from polyester fabrics during machine washing, causing serious environmental problems of seawater microplastic pollution. According to Sillanpää et al.,<sup>34</sup> 0.25–0.53% weight of polyester and related blended spinning textiles were decreased during 5 cycles of machine washing.<sup>34</sup> It is speculated that during our 30 and 60 cycles of machine washing, considerable amounts of microfibers were lost. It is reasonable that during machine washing, fabrics consisting of polyester fibers undergo various changes, such as loss of microfiber and structural change of polymer. Aging of polyesters due to hydrolysis is observed as crystallinity under hot humid conditions increases,<sup>37</sup> and mechanical strength under hot alkaline conditions decreases.<sup>38</sup> During hot alkaline aging processes, the number-average MW ( $M_n$ ) decreases in contrast with the almost constant PDI.<sup>38</sup> Under such severe hydrolytic conditions, semicrystalline polymers undergo a transition from ductile to brittle behavior when water diffuses

in the amorphous phase, and uncrystallized polymer chains were preferentially hydrolyzed, resulting in a  $M_n$  decrease and chem-crystallization.<sup>38</sup> Cionek et al. performed a simulated experiment to investigate the effect of aging on natural and synthetic microfibers by varying the temperature, time, and disinfectant concentration on melting temperature, crystallinity, onset temperature, and Young's modulus, where hydrolysis of polymers was observed using FTIR and scanning electron microscopy to observe surface degradation, such as surface stretch marks.<sup>32</sup>

In this study, FTIR spectra were not changed by machine washing for commercial shirts and in-house manufactured PET yarns. It is anticipated that no hydrolytic reaction occurs under mild machine washing conditions compared with the above-mentioned severe conditions.<sup>37,38</sup>  $M_w$  values were observed to increase significantly in 5 out of 8 in-house manufactured PET yarns but not in commercial polyester shirts except for C-1. Low-MW polyester polymers may be preferentially lost from the amorphous region of more organized polymer structures of the in-house manufactured PET fibers, compared to moderately organized polymer structures of the commercial shirts.

In addition, the absence of low MW components should also be considered. Sorensen et al. reported that under ultraviolet irradiation in 24 °C seawater conditions, PET, polyamide, and wool microfibers were degraded so as to cause surface morphological changes, such as many hole formation and fiber length shortening, and low MW additives existing originally in the fiber matrix were leached out from the deteriorated fiber surface, depending on the physicochemical properties of the additives and fibers and the extent of fiber aging.<sup>30</sup> Luongo et al. speculated from the comparison of the washing-out extent for benzothiazole, benzotriazole, and quinoline included as dyes or byproducts in clothing textiles that benzothiazoles were added to the final products and they interacted with the textiles at the fiber surface, resulting in a considerable washing-out effect. Contrarily, quinolines were included early in the manufacturing process and embedded in the fibers, resulting in a weak washing-out effect.<sup>39</sup> According to the report, 35% benzothiazole and 15% quinoline were lost

from polyester and related blended spinning textiles during 5 cycles of machine washing.

In this paper, PPAL values were observed to decrease in the commercial polyester shirts (3–21% loss estimated) but not in the in-house manufactured PET yarns. Also, the dye/pigment-like compound content for the C-7 shirt decreased (7% loss estimated). The estimated leach-out contents of the cyclic trimer (all of the shirts) and dye/pigment-like compound (C-7) are less than those of quinoline as reported by Luongo et al. This discrepancy may be due to the difference in the examined low MW compounds, polyester fibers, and machine washing conditions. As for morphological change on the fiber surface, the appearance of rising ejects was noticed considerably for commercial shirt fibers and slightly for the in-house manufactured PET yarns, in contrast to the no morphological change of polyester fabrics by several cycles of machine washing.<sup>35</sup> Surface appearance of rising ejects may be related to the decrease of PPAL values during machine washing. However, more examination is necessary to elucidate this relationship.

Low MW compounds, such as cyclic oligomers and dyes/pigments, were supposedly lost from the fiber matrix. The distribution of cyclic trimers, dyes/pigments, and their retention stability in the fiber matrix was not elucidated. It was reported that cyclic oligomers near the fiber surface were easily removed by various reagents and that they migrate partially from the inside to the surface when heated.<sup>25</sup> In in-house manufactured PET yarns, the cyclic trimer is presumably bound tightly to the PET polymers, preventing its outflow from the fibers while being machine-washed. In commercial polyester shirts, part of the cyclic trimer and dyes/pigments in colored shirts are presumably bound loosely in the amorphous region of the PET polymers, causing outflow during 30 cycles of machine washing. The rest of the cyclic trimer and dyes/pigments are presumably bound tightly to the crystalline structure of PET polymers, weakening the cyclic trimer outflow from the fibers between the 30 and 60 machine wash cycles. Figure 4 shows a schematic of the decrease in low MW compounds, such as cyclic trimer and dyes/pigments, in the polyester fiber during machine washing.

The extent of the change in GPC parameters during machine washing varied according to the polyester characteristics. Even for fabrics of the same manufacturing lot, the GPC parameters of unused fabrics differed from those of used fabrics. Forensically, it is possible to differentiate between unused and used fabric-derived fibers obtained from suspects and/or victims. From our previous report,<sup>22</sup> the minimum fiber amount necessary for GPC measurement is approximately 3 cm long fiber. Furthermore, our GPC method can expand the polymer targets besides polyester fibers, and the scope of application is not only on the effect of washing but also on the other environmental effects, such as sunlight, dirty usage, and chemical exposure.

## CONCLUSIONS

Machine washing significantly influenced the GPC parameters ( $M_w$ , PDI, and PPAL) of both commercial polyester shirts and in-house manufactured PET yarns, although considerable morphological changes were not observed. The  $M_w$  values increased in the in-house manufactured PET fibers and the relative cyclic trimer contents decreased for the commercial polyester shirts, indicating that machine washing caused structural deterioration, resulting in the removal of the cyclic

trimer, dyes/pigments, and low-MW polyester polymers. The  $M_w$ , PDI, and PPAL values are dependent on the synthetic process of producing polyester pellets and are also changeable through fiber spinning and deterioration by machine washing. Therefore, the GPC method is anticipated to provide extraordinarily high fiber discrimination power, contributing to the forensic discrimination of polyester fibers that originate from the same manufacturer but differ in usage conditions, which cannot be achieved by current forensic analyses.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c04446>.

Effect of machine washing on gel permeation chromatography parameters of polyester fibers (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by KAKENHI Grant-in-Aid for Scientific Research (B; Grant No. 22H01732) from the Japan Society for the Promotion of Science.

## REFERENCES

- (1) *Forensic Examination of Fibers*, 2nd ed.; Robertson, J.; Grieve, M., Eds.; CRC Press: New York, 1999.
- (2) European Network of Forensic Science Institute. *Best Practice Guideline for the Forensic Examination of Fibers*; The European Textile and Hair Group, 2011.
- (3) Federal Bureau of Investigation. *Forensic Fiber Examination Guideline, Introduction to Forensic Fiber Examination*; Scientific Working Group for Materials Analysis, 2011.
- (4) ASTM. *Standard Guide for Microscopical Examination of Textile Fibers*, E2228-18; ASTM, 2018.

- (5) Schmidt, P.; Raab, M.; Kolarik, J.; Eichhorn, K. J. Comparison of two modern infrared spectroscopic methods for the determination of orientation in drawn bulk polymers. *Polym. Test.* **2000**, *19*, 205–212.
- (6) Suzuki, S.; Ohta, H.; Sugita, R.; Marumo, Y. Microspectrophotometric discrimination of single fibers dyed by indigo and its derivatives using ultraviolet-visible transmittance spectra. *Sci. Justice* **2001**, *41*, 107–111.
- (7) Reichard, E. J.; Barlick, E. G.; Morgan, S. L.; Goodpaster, J. V. Microspectrophotometric analysis of yellow polyester fiber dye loadings with chemometric techniques. *Forensic Chem.* **2017**, *3*, 21–27.
- (8) Carey, A.; Rodewijk, N.; Xu, X.; van der Weerd, J. Identification of dyes on single textile fibers by HPLC-DAD-MA. *Anal. Chem.* **2013**, *85*, 11335–11343.
- (9) Watanabe, S.; Suzuki, S.; Hrynychuk, R. J. Basic study on the discrimination of poly(ethylene terephthalate) fibers by polarized confocal Raman spectroscopy. *Can. Soc. Forensic Sci. J.* **2013**, *4*, 181–196.
- (10) Gallo, J. M.; Almirall, J. R. Elemental analysis of white cotton fiber evidence using solution ICP-MS and laser ablation ICP-MS (LA-ICP-MS). *Forensic Sci. Int.* **2009**, *190*, 52–57.
- (11) Causin, V. Polymers on the crime scene: How can analytical chemistry help to exploit the information from these mute witness? critical review. *Anal. Methods* **2010**, *2*, 792–804.
- (12) Farah, S.; Kunduru, K. R.; Tsach, T.; Bentolila, A.; Domb, A. J. Forensic comparison of synthetic fibers, review. *Polym. Adv. Technol.* **2015**, *26*, 785–796.
- (13) Japan Chemical Fibers Association. Chemical Fibers, 2014. [http://www.jcfa.gr.jp/about\\_kasen/knowledge/ebook/index.html](http://www.jcfa.gr.jp/about_kasen/knowledge/ebook/index.html).
- (14) De Vos, L.; Van de Voorde, B.; Van Daele, L.; Dubruel, P.; Van Vlierberghe, S. Poly(alkylene terephthalate): From current developments in synthetic strategies towards applications. *Eur. Polym. J.* **2021**, *161*, No. 110840.
- (15) Meunier, D. M.; Wade, J. H.; Janco, M.; Cong, R.; Gao, W.; Li, Y.; Mekap, D.; Wang, G. Recent advances in separation-based techniques for synthetic polymer characterization. *Anal. Chem.* **2021**, *93*, 273–294.
- (16) Weisskopf, K. Characterization of polyethylene terephthalate by gel permeation chromatography (GPC). *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1919–1935.
- (17) Mori, S. Size exclusion chromatography of poly(ethylene terephthalate) using hexafluoro-2-propanol as the mobile phase. *Anal. Chem.* **1989**, *61*, 1321–1325.
- (18) Fox, B.; Moad, G.; van Diepen, G.; Willing, I.; Cook, W. D. Characterization of poly(ethylene terephthalate) and poly(ethylene terephthalate) blends. *Polymer* **1997**, *38*, 3035–3043.
- (19) Milana, M. R.; Denaro, M.; Arrivabene, L.; Maggio, A.; Gramiccioni, L. Gel permeation chromatography (GPC) of repeatedly extruded polyethylene terephthalate (PET). *Food Addit. Contam.* **1998**, *15*, 355–361.
- (20) Farah, S.; Tsach, T.; Bentolila, A.; Domb, A. J. Morphological, spectral, and chromatography analysis and forensic comparison of PET fibers. *Talanta* **2014**, *123*, 54–62.
- (21) Farah, S.; Kunduru, K. R.; Basu, A.; Domb, A. J. Molecular Weight Determination of Polyethylene Terephthalate. In *Poly(-Ethylene Terephthalate) Based Blends, Composites, and Nanocomposites*, Visakh, P. M.; Liang, M., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; Chapter 8, pp 143–165.
- (22) Matsushita, R.; Watanabe, S.; Iwai, T.; Nakanishi, T.; Takatsu, M.; Honda, S.; Funaki, K.; Ishikawa, T.; Seto, Y. Forensic discrimination of polyester fibers using gel permeation chromatography. *Forensic Chem.* **2022**, *30*, No. 100428.
- (23) Ross, S. D.; Coburn, E. R.; Leach, W. A.; Robinson, W. B. Isolation of a cyclic trimer from polyethylene terephthalate film. *J. Polym. Sci.* **1954**, *13*, 406–407.
- (24) Shiono, S. Separation and identification of poly(ethylene terephthalate) oligomers by gel permeation chromatography. *J. Polym. Sci., Part A: Polym. Chem.* **1979**, *17*, 4123–4127.
- (25) Kamiya, J.; Sawanoi, Y.; Hasebe, H. *Development of a Polyester Oligomer Removal Agent*; Industrial Research Institute of Ishikawa: Ishikawa, 2014; Vol. 64, pp 47–50.
- (26) Rahman, M. *Degradation of Polyesters in Medical Applications*, Saleh, H. F. M., Ed.; InTech: London, 2012; Chapter 5, pp 99–131.
- (27) Bryant, J. *Degradation of Natural and Synthetic Fibers in Various Aqueous Environments*. Honors Theses, Belmont University, 2021.
- (28) Dave, J.; Kumar, R.; Srivastava, H. C. Studies on modification of polyester fibers. I: Alkaline hydrolysis. *J. Appl. Polym. Sci.* **1987**, *33*, 455–477.
- (29) Niu, S.; Wakida, T. Effect of heat-setting temperature on alkaline hydrolysis of poly(ethylene terephthalate) fibers. *Textile Res. J.* **1993**, *63*, 346–350.
- (30) Sorensen, L.; Groven, A. S.; Hovsbakken, I. A.; Del Puerto, O.; Krause, D. F.; Sarno, A.; Booth, A. M. UV degradation of natural and synthetic microfibers caused fragmentation and release of polymer degradation products and chemical additives. *Sci. Total Environ.* **2021**, *755*, No. 143170.
- (31) Pohl, H. A. The thermal degradation of polyesters. *J. Am. Chem. Soc.* **1951**, *73*, 5660–5661.
- (32) Cionek, C. A.; Nunes, C.; Freitas, A.; Homem, N.; Muniz, E.; Amorim, T. Degradation study of polymer fiber in swimming pool water. *Textile Res. J.* **2021**, *91*, 51–61.
- (33) Hartline, N. L.; Bruce, N. J.; Karba, S. N.; Ruff, E. O.; Sonar, S. U.; Holden, P. A. Microfiber masses recovered from conventional machine washing of new or aged garments. *Environ. Sci. Technol.* **2016**, *50*, 11532–11538.
- (34) Sillanpää, M.; Sainio, P. Release of polyester and cotton fibers from textiles in machine washings. *Environ. Sci. Pollut. Res.* **2017**, *24*, 19313–19321.
- (35) De Falco, F.; Di Pace, E.; Cocca, M.; Avella, M. The contribution of washing processes of synthetic clothes to microplastic pollution. *Sci. Rep.* **2019**, *9*, No. 6633.
- (36) Goodpaster, J. V.; Liszewski, E. A. Forensic analysis of dyed textile fibers, review. *Anal. Bioanal. Chem.* **2009**, *394*, 2009–2018.
- (37) Dubelley, F.; Planes, E.; Bas, C.; Pons, E.; Yrieix, B.; Flandin, L. Predictive durability of polyethylene terephthalate toward hydrolysis over large temperature and relative humidity ranges. *Polymer* **2018**, *142*, 285–292.
- (38) Arhant, M.; Le Gall, M.; Le Gac, P. Y.; Davies, P. Impact of hydrolysis degradation on mechanical properties of PET—Towards an understanding of microplastic formation. *Polym. Degrad. Stab.* **2019**, *161*, 175–182.
- (39) Luongo, G.; Avagyan, R.; Hongyu, R.; Ostman, C. The washout effect during laundry on benzothiazole, benzotriazole, quinoline, and their derivatives in clothing textiles. *Environ. Sci. Pollut. Res.* **2016**, *23*, 2537–2548.
- (40) Somani, R. H.; Yang, L.; Zhu, L.; Hsiao, B. S. Flow-induced shish-kebab precursor structures in entangled polymer melts. *Polymer* **2005**, *46*, 8587–8623.