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Article

Moisture and Surface Properties of Radically Photo-Grafted Poly-(Ethylene Terephthalate) Woven Fabric

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Abstract: This study aims at the modification of the surface properties of twill-5 polyethylene terephthalate (PET) fabric, in particular to improve its hydrophilicity. It compares the hydrophilic potential and efficacy of two vinyl monomers radically grafted onto the fabric by photoinduced processes. Poly(ethylene glycol) diacrylate (PEGDA) and [2-(methacryloyloxy)-ethyl]-trimethylammonium chloride (METAC) affected the wettability of the fabric towards water, significantly reducing the water contact angle (WCA). As a consequence, the treated fabrics showed a good improvement of dynamic moisture management. Adopting specific conditions (e.g., type of monomer and grafting monomer concentration), the grafted PET fabrics remained hydrophilic after washing, laudering, dry cleaning, and rubbing tests; thus, the surface treatment modification resulted to be durable overall.

Keywords: polyester; photo-grafting; wettability; contact angle; moisture management; hydrophilicity

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1. Introduction

Global fiber production and consumption are currently dominated by poly(ethylene terephthalate) (PET); the market share is currently far exceeding other types of textiles, namely, cotton and polyamides [1]. The market dominance of PET is partly due to its versatility in application and its commendable properties such as high mechanical strength, abrasion resistance, chemical stability, excellent wash and wear, good dimensional stability, anti-wrinkle, and quick-drying properties.

However, due to its chemical structure and its high crystallinity (which guarantees good mechanical performance), PET is hydrophobic [2] and has a moisture absorption of only 0.6–0.8%, i.e., much lower than cotton and other natural fibers [3]. For these reasons, it has poor moisture management, which means that in clothing, the transport of moisture vapor and liquid away from the body is unsatisfactory. As a consequence, the sensory properties and comfort of the wearer are considered rather low [4]. Research to make PET hydrophilic has therefore attracted wide attention in both the industrial and the academic sectors, and many processes have been developed with the objective of obtaining a fabric with better comfort [5]. Copolymerization with hydrophilic monomer [6,7] and melt blending with hydrophilic additives before fiber extrusion [8] have been proposed. An alternative approach is the modification of fiber or fabric with different finishing treatments. On an industrial scale, alkaline treatment of PET has been used for decades to improve the wettability and wicking of PET fabrics [9]. Recently, a more sustainable, energy-efficient process of hydrolysis has been proposed [10]. However, the alkali hydrolysis of polyesters promotes degradation of the polymer, which is accompanied by a loss of strength of the fabric [11]. Another widely used technique is the Denier reduction by aminolysis [12], which introduces hydrophilic groups like the alkali hydrolysis, but has similar drawbacks. PET can also be modified by other wet treatments, such as oxidation with $KMnO_4$ [13] in acidic conditions.

Alternative treatments with less profound effects on the mechanical properties of PET are enzymatic treatment and plasma treatments; they are also accepted as environmentally friendly techniques for improving moisture absorption of PET fibers [14–17].

Few papers have reported on the use of ozone, ofter under UV and eventually followed by further chemical modifications; this oxidative treatment causes a change not only on the surface of PET, but also in its internal morphological structure, enhancing water absorption overall [18,19].

Coatings can also be applied to change surfaces, and several works describe the use of complex nanostructured layers containing silica and titania nanoparticles on top of PET fabrics [20–22]. Coating is often combined with a process able to modify surface topography. This approach is explored for the development of durable PET superwicking surfaces, whose water contact angle is 0°, and the liquid spread area is larger than that of a superhydrophilic surface. By creating surface microgrooves using sandpaper and then applying a nanocomposite coating of TiO_2-SiO_2, a robust modification was achieved, obtaining self-cleaning and self-repairing capabilities at the same time [23].

Finally, grafting offers an approach to functionalize polymers such as PET using different chemistries [24] and light sources such as electron beams [25]. In particular, photo-grafting with UV is popular and offers several advantages over conventional thermal methods; it is well known that photoinduced processes have lower overall costs, assure high productivity, increase safety by eliminating volatiles, and have low energy requirements and environmental sustainability [26]. The most common photo-initiated grafting reactions follow a radical mechanism first discussed by Ranby at a molecular level [27]: Under UV radiation, in the presence of photoinitiators, and on the surface of polymers, active macroradicals are formed. The polymerization of unsaturated monomers present at the surface can be initiated, and the resulting chains grow from the surface itself. Free polymerization can also take place at the same time: While its products can interact with the substrate via secondary bonds, the grafted chains grown from the surface macroradicals are covalently bonded to the surface itself. UV grafting has been applied for the purpose of modifying a variety of polymers, making their surfaces functional [28]. In the case of PET fabrics, photografting has been performed in several research works, and the purposes were manyfold, such as improving adhesion, promoting flame retardancy, and imparting antistatic properties and antibacterial response to the fabric [29–34]. The different properties obtained are mainly ruled by the type of chain grafted, and thus depend on the choice of the monomer.

In this work, to improve the wetting and the moisture management of PET fabric, photoinduced grafting is attempted using two hydrophilic acrylic monomers, and the robustness of the finishes obtained using different washing procedures and rubbing tests is assessed.

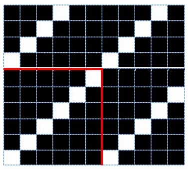
2. Materials and Methods

2.1. Materials

2.1.1. Fabrics and Grafting Reagents

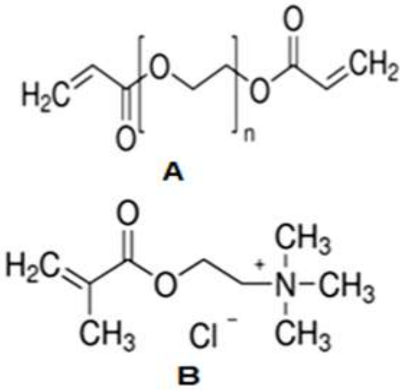
Mill-bleached polyester twill-5/1 fabric with a weight of 230 g/m^2 and a 0.325 mm thickness was supplied by Atmosphere Tissus (59800 Lille, France). The warp and weft count were 38 yarns cm^{-1}. The yarn density was 34 tex. Further characterization of the polyester fabric is reported in [35].

The graphical representation of the fabric is given in Scheme 1.



Scheme 1. Twill 5/1 PET fabric construction.

METAC (75 wt% in water, Mn 207.7) and PEGDA (Mn 700) were supplied by Sigma-Aldrich S.r.l. (Milano, Italy). The photo initiator, 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) 99%, was supplied by BASF Kaisten AG (Hardmatt, Kaisten, Switzerland), in liquid form. Ethanol (99.5%) (Sigma-Aldrich S.r.l., Milano, Italy) was used as the solvent. The chemical structures of the monomers and the photo-initiator are reported in Scheme 2.



Scheme 2. Structure of: (**A**) PEGDA; (**B**) METAC.

2.1.2. Dyeing Materials for PET

The following materials were used in the dyeing process: a commercial acid-stable red disperse dye, Anocron Rubine S-2GL (Shanghai Anoky Group Co., Ltd., Shanghai, China); acetic acid 99.5% (Guangzhou Congzhongxiao Chemical Technology Co., Ltd., Guangzhou, China); high-temperature leveling agent 100% (Suzhou Eastion New Material & Technology Co., Ltd.); and dispersant (Guangzhou Congzhongxiao Chemical Technology Co., Ltd., Suzhou, China). The reducing agent sodium hydrosulfite ($Na_2S_2O_4$) and NaOH were used for washing.

2.2. Methods

2.2.1. Fabric Preparation

To eliminate any surface active agents and prior spinning and weaving oils, the polyester fabric under study was Soxhlet-extracted using a Soxhlet apparatus (Carlo Erba, Milan, Italy) for 4 h in petroleum ether at a weight ratio of 1:5 (fabric:petroleum ether). After extraction and drying, the fabric was then conditioned (according to ISO 139:2005 Textiles—standard atmospheres for conditioning and testing) at 20 °C (±2 °C) and 65% RH (±4%) for 24 h.

2.2.2. UV-Radical Grafting

Ultraviolet initiating light for all UV treatments was provided by a 400 W metal halide lamp (Dymax ECE 5000-Dymax Corporation, Torrington, CT, USA). The UV intensity was measured using an irradiance meter—UV Power Puck II (EIT Inc., Sterling, VA, USA).

The working distance between the UV lamp and the fabric platform was set at 6 cm for all UV treatments, delivering irradiances (intensities) of 280 $mWcm^{-2}$, 145 $mWcm^{-2}$ (UVA), and 135 $mWcm^{-2}$ (UVB). Firstly, the effect of UV irradiation (without any chemicals) on the untreated PET fabric was evaluated to assess any change in PET hydrophilicity after exposure to UV light. Five fabric samples with dimensions of 5 × 5 cm were exposed to the UV lamp for different durations (5, 10, 15, 20, and 25 min).

The grafting treatment of PET with PEGDA or METAC in the presence of the photo-initiator and UV irradiation was carried out according to the following procedure. In one experiment, PEGDA was dissolved in ethanol at concentrations between 0.1 and 5% v/v. Then, the HMPP photoinitiator was added at a concentration of 0.1% with respect to the solvent. After thorough agitation, 5 × 5 cm PET fabric specimens were soaked in the bath for 10 min and then padded to squeeze out excess solution before air-drying under room conditions. The two sides of the monomer-soaked fabrics were then irradiated for one minute under gaseous nitrogen to assure an inert atmosphere, avoid oxygen inhibition, and prevent ozone formation. In a second set of experiments, the PET fabric specimens were treated with METAC following the same procedure as for PEGDA.

To remove unreacted monomer, Soxhlet extraction of the PET grafted fabrics was carried out in a Soxhlet apparatus (Carlo Erba, Milan, Italy) in petroleum ether for 4 h.

2.2.3. Dyeing

The following equipment was used during dyeing and colour assessment: a precision electronic balance BL-500F (Tianjin Danaher Sensors & Controls Engineering Co., Ltd., Tianjin, China) with an accuracy of 0.001 g for weighting dyestuff and auxiliaries, a pH meter PHS-3E (Shanghai Leici Co., Ltd., Shanghai, China) to check the dyeing liquor pH, and a Mathis Labomat IR lab dyeing machine (Wuxi Yangbo Textile Equipment Co., Ltd., Wuxi, China).

A dyebath consisting of 2% (w.o.f) dye, a fabric to liquor ratio of 1:20 w/v, 1 g/L of leveling agent, and 1 g/L of dispersant was prepared. Using acetic acid, the pH of the dyebath was adjusted to 5. A washing bath consisting of 2 g/L of $Na_2S_2O_4$ and 2 g/L of NaOH was also prepared. Grafted and ungrafted PET fabric samples of 5 g each were then introduced into beakers containing the dye bath and later mounted onto the dyeing machine. With the temperature rising at a rate of 2 °C/min, dyeing was carried out at 130 °C for 60 min, followed by cooling at 4 °C/min. The dyed PET fabrics were then washed in the washing bath with a fabric to liquor ratio of 1:30 w/v at 80 °C for 15 min. The washed fabrics were then rinsed in distilled water before drying at room temperature.

2.2.4. Fabric Characterization

The add-on, which can reflect the percentage of monomer grafted on the fabric, was computed using the following equation:

$$\%add - on = \frac{W_{Grafted} - W_{Pristine}}{W_{Pristine}} \times 100 \tag{1}$$

where $W_{Grafted}$ and $W_{Pristine}$ are the weights of the pristine and grafted PET fabrics, respectively. The weight of the PET samples was measured with an accuracy of 0.001 g on an analytical balance (ME104-Mettler Toledo, Milan, Italy).

A wetting test was carried out on the fabric before and after grafting according to the test method AATCC 79, 2007—absorbency of textiles, which estimates the time taken for a water drop of 0.2 mL to be fully absorbed by a fabric. Sixteen samples of the PET fabric were then obtained and characterized for static water contact angles recorded over a period of time by the sessile drop technique using a KRUSS drop shape analyzer, DSA100 (KRUSS, Hamburg, Germany).

The fabric was also tested for dynamic liquid transport properties (AATCC Test Method 195-2011-Moisture management properties of textile fabrics) using a moisture management test (MMT) device (SDL Atlas LLC, Charlotte, NC, USA).

To ascertain the grafting robustness towards washing and rubbing, ad hoc testing using standard rubbing with a Crockmeter (AATCC Test Method 08, 2005) and the washing fastness test (AATCC Test Method 61–Test No. 2A) were carried out. Washing fastness was carried out using a 4 g/L water solution of ECE non-phosphate detergent (A) at 60 °C, with a fabric to liquor ratio of 1:50, for 35 min.

The appearance and hand of grafted fabrics after laundering and drycleaning were measured. Washing was carried out twice for each sample, following the standard home laundering conditions described in ISO 6330—domestic washing and drying procedures for textile testing (similar to AATCC Monograph (M) 6135—standardization of home laundering conditions) using 4 g/L distilled water solution of ECE non-phosphate detergent without optical brighteners (SDL Atlas, Stockport UK), with a modification in the equipment: a high-temperature laboratory machine (Labomat) was used, with stainless steel balls added in the washing beakers. The washing beakers rotated during washing. Washing was performed at a temperature of 40 °C (rising at a 1.5 °C per sec) with a fabric to liquor ratio of 1:20 for 30 min. Dry-cleaning was carried out once on each fabric sample, following AATCC 86-2013-Durability of Applied Designs and Finishes, with a modification; petroleum ether was used as the solvent in a Soxhlet apparatus (Carlo Erba, Milan, Italy). The changes in hand and appearance after washing were evaluated using the rating scale described in AATCC 86-2013.

The surface morphology of treated and untreated samples was studied using a ZEISS Merlin field emission scanning electron microscope (ZEISS, Oberkochen, Germany) operating at a voltage of 5 kV, a pressure of 200 Pa, and a working distance of 5.8 mm.

X-ray photoelectron spectroscopy (XPS analysis) was carried out by a PHI 5000 Versaprobe (Physical Electronics, Chanhassen, MN, USA) of a monochromatic Al K-α X-ray source with a power of 25.2 W. A scan area of 100 μm^2 was used to collect the photoelectron signal while it was placed between the gold electrodes. A pass energy value of 187.85 eV was used for the survey spectra.

Colorimetric measurements of the dyed PET fabrics were performed with the UltraScan PRO UV/VIS reflectance spectrophotometer D65 (HunterLab, Reston, VA, USA) with a 10° standard observer using the CIE L*abh space [36]. Mean values from six measurements were recorded for each colour parameter on each fabric sample.

3. Results

3.1. PET Wettability and Moisture Management by Photografting

The wetting behavior of untreated PET fabric was first evaluated by water contact angle (WCA) measurements after thorough removal of all contaminants by Soxlet extraction, followed by careful drying and conditioning. The results are reported in Figure 1 as a function of the contact time of the water droplet onto the untreated fabric. The average static WCA was 110° in the first 5 s (T0). It decreased to 100°, 95°, and 88° after 30, 60, and 90 s, respectively (T30, T60, and T90). With the hydrophobic threshold being 90°, the untreated PET fabric could be deemed hydrophobic [37]. The average WCA of polyester fabrics recorded in the literature is between 72° and 140° depending on the morphology of PET, its roughness, and the fabric structure [2,38]: The high WCAs measured in this work can be partly attributed to the tight packing of the twill-5 configuration, which also increases fabric roughness.

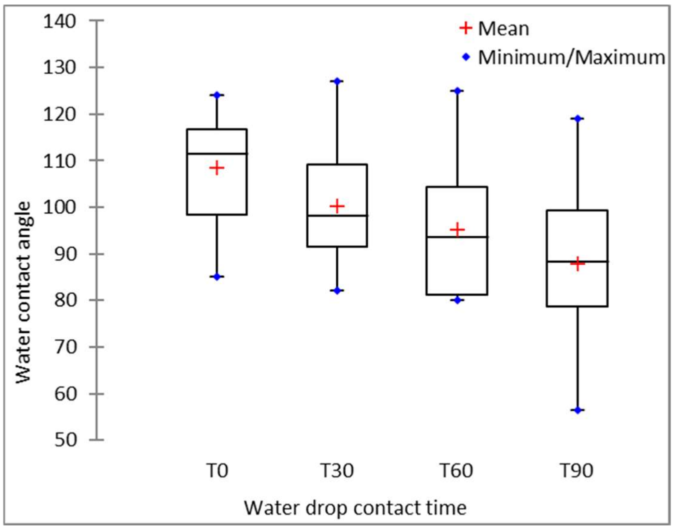


Figure 1. Static WCAs measured against water drop contact time on 16 untreated PET fabrics.

Wettability was also estimated by the liquid drop test AATCC Test Method 79-2007. The water drop took an average of 56 s for total spreading on the untreated PET fabric surface; thus, the material was defined as non-absorbent.

Before investigating the finishing of the fabric by photografting, PET samples were exposed to UV irradiation without any other chemicals. Table 1 shows the change in WCAs as a function of irradiation time. When the irradiation time was shorter than 5 min, samples were mostly unchanged; for longer times of exposure to UV light, WCAs were found to be lower than those of the untreated sample due to photo-degradation and photo-oxidation of PET. Nevertheless, the WCAs remained above 70° for any UV exposure duration.

Table 1. Static WCAs of PET fabrics for different UV exposure times.

Water Drop Contact Time (s)	**UV Irradiation Time (min) and WCA ± Standard Deviation**					
	0	**5**	**10**	**15**	**20**	**25**
T0	110 ± 5	100 ± 3	100 ± 9	98 ± 4	90 ± 8	86 ± 6
T30	100 ± 8	97 ± 7	95 ± 7	89 ± 9	82 ± 9	84 ± 5
T60	95 ± 4	90 ± 5	89 ± 4	87 ± 8	71 ± 6	73 ± 9
T90	88 ± 5	89 ± 6	87 ± 7	86 ± 8	70 ± 8	70 ± 7

PET was then modified by photografting: After soaking the fabric samples in the acrylic monomer solutions, padding them to remove the excess of solution, and air-drying them, the samples were irradiated under nitrogen for 1 min, i.e., avoiding photo-degradation and photo-oxidation, as assessed by the previous experiment.

The acrylic monomers selected were hydrophilic: PEGDA700, which contains acrylic end groups and has a linear polyether chain made of 16 ethoxy units, while METAC is a quaternary ammonium salt with a reactive acrylic function that is commonly used as an intermediate in the production of polymers such as polyelectrolytes.

The add-on and the WCA of the PET fabrics grafted with PEGDA (PEGDA-g-PET) and METAC (METAC-g-PET) were measured and are shown in Table 2 as a function of the photoreactive monomer concentration.

Table 2. Add-on and static WCAs of PEGDA-g-PET fabric and METAC-g-PET fabric.

PEGDA Conc. (% *v*/*v*)	**Add-on (%)**	**WCA at T0**	
5	2.7	0	
3	2.4	0	
2	1.6	0	
1	0.9	0	
0.5	0.9	0	
0.2	0.3	0	
0.1	0.2	0	
METAC conc. (% *v*/*v*)	Add-on (%)	WCA at T0	WCA at T30
5	2.1	0	0
3	0.89	5	0
2	0.62	7	0
1	0.45	10	0
0.5	0.15	36	0
0.2	0.08	34	10
0.1	0.05	45	15

When PET was grafted with PEGDA, even at the lowest monomer concentration, 0.1% *w*/*v*, there was complete wetting of the PEGDA-g-PET fabrics even at T0, the shortest contact time with the water droplet, i.e., in less than 5 sec. As expected, the monomer add-on increased when using higher PEGDA concentrations.

Similarly, the METAC monomer add-on increased with the concentration, but complete wetting (WCA = 0° for T0) was achieved only for the highest concentration of METAC.

While examining the wettability at T30 (i.e., 30 s of contact time of the water droplet), WCA was found equal to 0° at a concentration as low as 0.5%.

The results clearly show that the UV-grafting of a hydrophilic acrylate is a suitable finish for the PET fabric to guarantee complete hydrophilicity (WCA = 0°). It can be interesting to make a comparison with other treatments reported in the literature in terms of enhancement of wettability, although the treated fabrics are different and wettability depends on fabric structure and roughness [37]—moreover, measurement methods should be the same [39]: one can observe that the approach used in this work is as efficient as oxygen plasma treatments [17] and definetively more successful than treatments with oxidants (e.g., $KMnO_4$), alkali (NaOH) or ozone, for which the best results are WCA = 60°, 50°, and 83°, respectively [9,13,40].

The treatments applied to PET changed the surface properties of the fabric, but did not alter the fiber diameter: as assessed by SEM, for the pristine PET used in this work, values ranged between 17 µm and 23 µm, with an average of 19 µm, while for METAC-g-PET, the range was 15–19 µm with an average of 18 µm, and for PEDGA-g-PET, the range was 14–20 µm with an average of 18 µm. The aspect of the textile was unmodified at the naked-eye inspection, and this result was confirmed by the SEM images that can be seen in the Supplementary Materials (Figure S1).

XPS analysis was carried out on PET fabrics before and after grafting to explore the composition at the outermost surface. Given that PET has similar characteristic carbons and oxygens as PEGDA, the spectra profiles and the experimental ratio of carbon atoms to oxygen atoms of the samples before and after PEGDA grafting were found to be equal, with a value around 2.8, which is very close to the theoretical value of 2.5 for PET. It was of interest to examine the spectrum of the fabric after grafting of METAC (Supplementary Materials Figure S2). There, a peak at a binding energy 401.8 eV represented N1s, identifying the presence of the ammonium salt, usually falling between binding energy 400.4–403.2 eV. Moreover, a Cl2p signal appeared at 198.7 eV, which was attributable to the chloride counterion. Thus, the XPS results confirmed the grafting of METAC on the PET fabric to be responsible for the relative changes in PET wettability, as already discussed.

It has been demonstrated that grafting of PEGDA or METAC on PET can make PET hydrophilic. The hydrophilic finishing is expected to affect the moisture management ability of the fabrics [3,5,24], i.e., the ability to regulate moisture moving the liquid from the skin surface to the environment through the fabric, thus optimizing comfort, regulating the body temperature, and maintaining heat balance.

To provide objective measurements, MTT tests were performed according to AATCC Test Method 195-2011. During the test, a predetermined amount of aqueous conductive solution was automatically dropped onto the surface of the fabric specimen held flat between upper and lower arrays of concentric electric sensing pins; changes in the electrical resistance of the specimen were used to calculate changes in the fabric liquid moisture content and to quantify dynamic liquid moisture transport characteristics in the three directions of the specimen. The standard test duration is usually 120 s after dosing the 2 mL water drop on the fabric top surface. Predetermined indices were used to grade the fabric moisture management behaviour as shown in Table 3. TW is the time taken for the fabric to become wet after the supply of liquid moisture; BW is the time the water takes to penetrate through the fabric thickness and wet the bottom surface. TA and BA refer to the rates of absorption of liquid moisture by the fabric sample at the top and at the bottom, respectively. The maximum spread values of liquid along the surface of the fabric in radial direction from the source of liquid input, calculated for the top surface and bottom surface separately, are labeled TM and BM; TS and BS are the spreading speeds along the surface of the fabric to reach the maximum wetted radius. Finally, AOT is the accumulative one-way transport index measuring the difference in the moisture accumulated at the top and bottom surface of the fabric.

Table 3. Dynamic moisture management properties of pristine and selected grafted PET fabric.

Fabric	TW (s)	BW (s)	TA (%/s)	BA (%/s)	TM (mm)	BM (mm)	TS (mm/s)	BS (mm/s)	AOT
PET	3.5	120	29.2	0.0	5.0	0.0	1.4	0.0	−834
PET irradiated 5 min	2.5	120	40.9	0.0	5.0	0.0	1.8	0.0	−893
PET irradiated 10 min	2.9	120	41.3	0.0	5.0	0.0	1.6	0.0	−828
PEGDA-g-PET 0.2%	3.0	5.8	39.5	25.0	13.8	22.5	3.0	3.6	−43.9
PEGDA-g-PET 1%	2.6	2.3	46.5	37.3	17.5	27.5	4.5	6.5	214
METAC-g-PET 1%	3.5	5.6	32.2	19.7	10.0	15.0	1.9	2.0	−242
METAC-g-PET 5%	3.0	4.5	36.7	23.8	15.0	17.0	2.3	2.1	−136

TW—top wetting time, BW—bottom wetting time, TA—top absorption rate, BA—bottom absorption rate, TM—top maximum wetted radius, BM—bottom maximum wetted radius, TS—top spreading speed, BS—bottom spreading speed, AOT—accumulative one-way transport index.

The results of TW and TA show that the upper sides of the irradiated samples, as well as the PEGDA-grafted ones, had improved wetting and absorption abilities compared to the pristine fabric, while the effect of METAC was rather limited, and only the top absorption rate slightly improved. An interesting comparison was made among the results related to the bottom BW and BA: It suggested that the test liquid was not absorbed through the bottom by the untreated PET fabric nor by the PET fabrics exposed to UV only, while a very short wetting time and a high absorption rate were measured for the grafted fabrics. In order words, the grafting of PEGDA and METAC enhanced the moisture absorption and spreading rates of the PET fabric. Particularly, PEGDA had the most significant impact on the bottom wetting properties, with a higher monomer concentration (1%) imparting a pronounced hydrophilic effect. This means that the transfer of moisture from the top to the bottom of the fabric was efficient. In a clothing application, the PET fabric would transfer moisture from the wearer to the outer part of the apparel. This would result in enhancement of the wearing comfort. Based on standard MTT scaling, the 1% PEGDA-g-PET fabrics showed a very good grade (4/5), and the best grade for one-way transport ability. TM and BM data, together with the top and bottom spreading speeds, confirm the previous conclusions on the effect of grafting on moisture management, with reference to in-plane performance.

Figure 2 is a visual presentation of the MMT results. The light blue areas indicate the wetted areas on the top and bottom surfaces of the fabric at the end of the test. Taking the untreated fabric as a reference in Figure 2A, it is clear that PEGDA grafting is the treatment assuring complete wetting of both sides, while METAC imparted partial wetting of the top and bottom sides of the PET fabric. The effect of UV irradiation visualized in Figure 2B showed that a slight absorption was achieved. The effect of the monomer concentration is also reflected by the depth and area of the absorbed liquid; higher monomer concentrations showed deeper and wider absorption. Overall, the moisture management data are consistent with the earlier result from the WCA measurements.

AOT data (Table 3) can give a direct overall evaluation of and result for the liquid moisture management properties. Each of the fabrics can be classified. According to the following scale:

AOT < −50: poor; −50 to 100: fair; 100–200: good; 200–400: very good; >400: excellent

Thus, pristine PET with an AOT value of −834 clearly has a very poor moisture management capacity; simple irradiation of the fabric has no effect, while grafting is very effective and fabrics after treatment are classified as fair/good. Grafting of PEGDA is especially promising, as the AOT value can overcome 200, i.e., a very good grade is reached.

As the multidirectional nature of the MMT evaluation can depict aspects of moisture movement in clothing, such as the ease of drying, management during sweating and perspiration, and the wicking properties of a fabric, overall, the grafting of hydrophilic monomers seems to be a valuable method for improving PET quality and obtaining a fabric with better performance in terms of comfort.

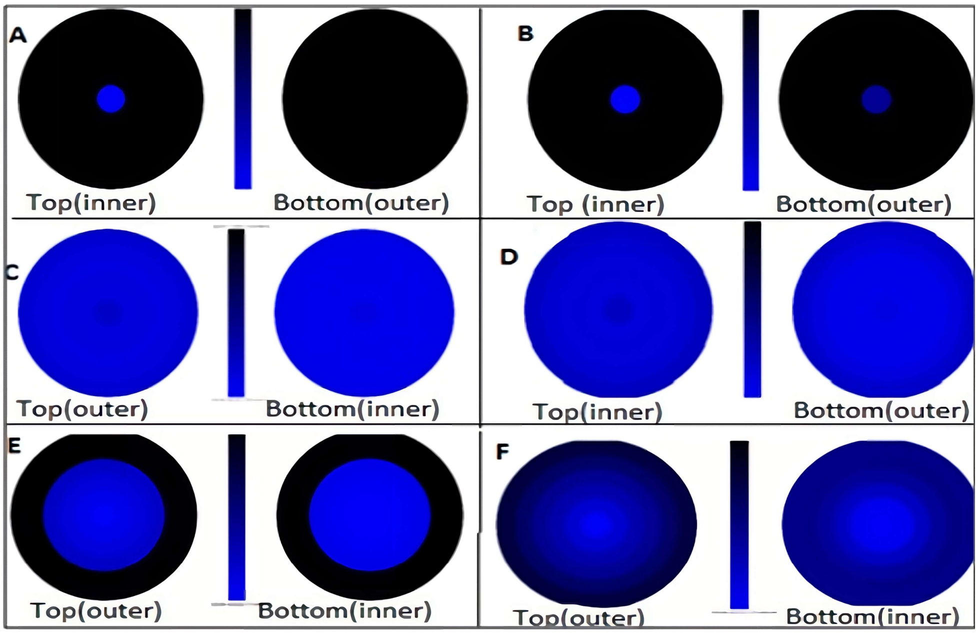


Figure 2. Schemes of top and bottom wetted radii for the tested fabrics: (**A**)-Pristine PET; (**B**)-UV-treated 5 min; (**C**)-1% PEGDA-g-PET; (**D**)-0.2% PEGDA-g-PET; (**E**)-5% METAC-g-PET; (**F**)-1% METAC-g-PET.

3.2. Durability of UV-Grafting Treatment and Compatibility with Dying

The durability of the photografting treatment was assessed by a washing fastness test (AATCC Test Method 61—Test No. 2A) and by Soxhlet extraction in petroleum ether. WCA measurements were repeated, and the data are reported in Table 4. To note the changes in WCAs, reference should be made to Table 2, which shows the WCAs of fabrics before any washing or rubbing treatment.

Table 4. Static WCAs of PEGDA-g-PET and META-g-PET after washing and Soxhlet extraction.

PEGDA Conc.	**After Washing**			**After Soxhlet Extraction**	
(% *v*/*v*)	**WCA T0**	**WCA T30**	**WCA T0**	**WCA T30**	**WCA T60**
5	0	0	31	0	0
3	0	0	12	0	0
2	0	0	19	0	0
1	0	0	32	0	0
0.5	5	0	28	0	0
0.2	33	5	25	5	0
0.1	43	0	64	21	0

METAC conc.	after washing			after Soxhlet extraction		
(% *v*/*v*)	WCA T0	WCA T30	WCA T60	WCA T0	WCA T30	WCA T60
5	103	42	0	27	15	0
3	103	61	0	18	0	0
2	100	55	0	22	5	0
1	83	30	0	55	37	0
0.5	101	20	0	85	35	30
0.2	98	51	22	89	56	27
0.1	88	50	28	80	30	25

Washing with the detergent solution affected fabrics grafted with the lowest PEGDA concentrations of 0.1% and 0.2%; however, the grafted fabric remained hydrophilic, with the highest contact angle value at T0 being 43°. For a longer contact time, T30, complete hydrophilicity was found. WCAs at T0 for PEGDA-g-PET samples increased after Soxhlet extraction for all concentrations of PEGDA, albeit maintaining wetting thresholds. For longer contact times, T30 and T60, complete hydrophilicity was regained. WCAs measured on METAC-g-PET fabrics after washing increased: at T0, the washing fastness was very poor and the hydrophilicity was completely lost. However, wetting was re-attained within 30 s of the drop deposition for any monomer concentrations. Relatively lower increases in WCAs were noted after Soxhlet extraction, and hydrophilicity was maintained overall. The robustness of the grafting treatment was also confirmed by controlling wettabilities after rubbing the fabrics in either a wet or in a dry state. As reported in Table 5, the changes in wettability were negligible. The durability of the treatment was overall satisfactory and comparable to the results reported for other finishing treatments, e.g., the newest plasma etching treatments [17].

Table 5. Static WCAs of PEGDA-g-PET and of METAC-g-PET after the rubbing test.

PEGDA Conc. (% *v*/*v*)	**After Dry Rubbing**		**After Wet Rubbing**	
	WCA T0	**WCA T30**	**WCA T0**	**WCA T30**
5	0	0	0	0
3	0	0	0	0
2	0	0	5	0
1	7	0	0	0
0.5	0	0	0	0
0.2	10	0	15	5
0.1	0	0	10	0

METAC conc. (% *v*/*v*)	after dry rubbing			after wet rubbing		
	WCA T0	WCA T30	WCA T60	WCA T0	WCA T30	WCA T60
5	0	0	0	5	0	0
3	5	5	0	5	0	0
2	7	0	0	11	0	0
1	16	0	0	13	0	0
0.5	41	20	0	31	5	0
0.2	26	11	0	39	15	0
0.1	30	15	0	45	25	10

The untreated PET and the modified fabrics were dyed as described in the experimental section using a disperse dye. As reported in Appendix A (Table A1), colorimetric measurements showed no relevant differences between the fabric as it was and the grafted fabrics [31]. These results are relevant; the photografting did not affect the dyeability of the fabric.

The durability of the dyed fabric was also evaluated after washing, laundering, dry cleaning, and rubbing by performing standard tests. Table A2 shows the results of the appearance, color fastness, and hand of grafted fabrics (i.e., the subjective assessment of a fabric by the sense of touch) after different processes, mimicking the practical daily use by the consumer. No difference between the original PET fabric and the grafted samples was found.

Rubbing fastness, which refers to the degree of color fading of dyed fabrics after rubbing and can be from either dry rubbing or wet rubbing, was also satisfactory for both the treated and untreated fabrics.

4. Conclusions

This study explored the surface grafting onto PET of two reactive acrylic monomers bearing polar moieties using an efficient process, i.e., irratiating the textile soaked in the acrylate solution. The add-on, which represents the grafting yield and was estimated after extraction, together with the robustness of the modification, which was resistant to washing, rubbing, and dry cleaning, confirmed that the acrylic modifiers are covalently linked to PET. With either of the two monomers, lowering of the contact angle could be achieved depending on the irradiation time and soaking solution concentration. However, PEGDA guaranteed complete hydrophilicity with a water contact angle as low as zero, as measured on plasma-treated textiles. An important result was the improvement of the moisture management properties of the treated fabric, while the grafting did not change its hand, appearance, or color fastness (even after cleaning and rubbing). With the efficient transfer of moisture from the top to the bottom of the fabric, the treated PET can assure better comfort of clothing and be suitable for applications requiring an efficient transfer of moisture from the wearer to the outer part of the apparel.

Thus, photografting is an attractive method for PET finishing. It is a good alternative to other finishing processes as the grafting time is short (no more than 1 min of irradiation was necessary) and the energy cost is only related to the irradiating lamp. Further research can be conducted to improve the sustainability of the process, namely, substituting organic solvents for the soaking and washing steps before and after irradiation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/fib12100090/s1, Figure S1: SEM images (1000×) of pristine PET (left), grafted PET with METAC (center), and PEGDA (right).; Figure S2: XPS spectrum of METAC-g-PET fabric (1% v/v concentration).

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Appendix A

Table A1. Colorimetric measurements of dyed PET fabrics (dye: red Anocron Rubine disperse dye).

Fabric	L*	a*	b*	C*	h
PET	40.52	51.53	8.53	53.22	9.22
PEGDA-g-PET 0.2%	38.46	51.97	8.27	53.66	8.79
PEGDA-g-PET 1%	37.64	52.21	7.77	53.79	8.46
METAC-g-PET 1%	38.61	52.60	7.71	53.47	8.34
METAC-g-PET 5%	37.77	52.32	6.64	54.76	7.35

Table A2. Hand, appearance, and color fastness.

Fabric	Hand/Appearance after Laundering	Hand/Appearance after Drycleaning	Color Fastness Dry/Wet Rubbing	Color Fastness Washing/Washing Staining
PET	B5/A5	B5/A5	4/3.5	4/4
PEGDA-g-PET 0.2%	B5/A5	B4/A4	4/3.5	4.5/4.5
PEGDA-g-PET 1%	B5/A5	B5/A5	4.5/4	4.5/4.5
METAC-g-PET 1%	B5/A5	B5/A5	4.5/4	4.5/4
METAC-g-PET 5%	B5/A5	B5/A5	5/4.5	5/4.5

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