

PERMEABILITY PROPERTIES AND ABRASION RESISTANCE OF COATED POLYPROPYLENE FABRICS

Sukran Kara, Sevil Yeşilpınar and Aysun Akşit

Dokuz Eylül University, Engineering Faculty, Textile Engineering Department, Turkey
sukran.kara@deu.edu.tr

Abstract: Protective garments constitute an important class of technical textiles and they serve for various application areas such as active sports, military, medicine and fire-fighting. One of the most shared properties of protective garments is providing a barrier against water or liquid penetration. Also these garments should exhibit water vapour permeability and protect from wind in order to maintain wearer comfort. These expectations for the protective garments may be provided by waterproof-water vapour permeable coatings.

In this study, polypropylene fabric was coated in order to examine its usability in protective sportswear. Effects of coating polymer type and curing temperature on the specimen permeability properties and abrasion resistances were investigated in order to reveal their usability. According to test results, waterproofness of samples did not increase to the desired levels but windproof samples were obtained from coated polypropylene samples. Polyether type polyurethane coated samples gave more preferable and consistent results when compared to polyether type polyurethane coated equivalents after washing. Coating improved the abrasion resistance of all coated samples.

Keywords: coating, polyurethane type, curing temperature, polypropylene fabrics, protective garments, permeability properties, abrasion resistance, scanning electron microscopy.

1 INTRODUCTION

Protective garments possess various functional properties such as resistance to chemicals, fire retardancy, ballistic protection etc. according to their end-uses. In addition, most of the protective garments are expected to show waterproofness at least to a certain level. For this purpose, coating or lamination is applied to protective fabrics [1, 2]. Some functional properties such as fire retardancy, liquid and dust impermeability and hand changes can also be provided by coating.

Coated fabrics can be defined as engineered flexible composite materials that are coated with a polymer layer from one or both sides. Woven, knitted or non-woven fabrics can be used as the base fabrics for coating. Coating polymers are applied to base fabric surfaces as viscous solutions or dispersions. After the application of the polymer layers, the liquid phase is removed by heat and the polymer forms a continuous layer on the fabric surface. Coating can be applied by using hot melt polymers, too [3-5].

Main polymers for textile coating are natural and synthetic rubber, polyurethane (PU), polyacrylic, polyvinyl acetate and polyvinyl chloride [6]. In addition to these main types, their variants, copolymers and terpolymers are also synthesized for coating. PU is a multipurpose coating polymer which can be used for the coating of protective garments,

upholstery, artificial leather, inflatable boats and etc. PU is not a single polymer but it consists of a polymer group with similar chemical structure. The repeating unit of PU is given in Figure 1. By changing the R, R' groups, various PU types can be obtained and desired properties can be engineered. Mostly known types of PU polymers are polyether and polyester types for textile coatings. Polyester and polyether type PUs can give different modulus, tensile strength, hardness, thermal oxidative stability or hydrolytic stability to the end product [6, 7].

PU coating polymers may be solvent-based or water-based. PU coatings are frequently done by using organic solvents. This increases problems such as flammability, toxicity, disposal and recycling. Also solvent systems are usually more expensive. Water-based PU types are more attractive as they are eco-friendly and less harmful for human health during production. Using water based coating polymers may be a good alternative for textile applications [6, 8].

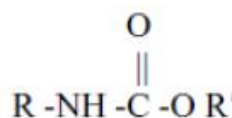


Figure 1 Urethane [5]

Polypropylene fiber (PP) consumption is increasing day by day according to its advantageous properties such as low cost, lightweight, wicking property and fast drying. However, it is not preferred for protective garments as it has some technical problems like low melting point [9].

In the literature, research works exist in which common fabrics were coated and their properties such as water resistance, water vapour permeability, mechanical properties and etc. were tested to be used in different areas. In these researches mostly cotton [10, 11], polyamide [12-17], polyester [18] and blended fabrics [15, 19, 20] were coated. Polypropylene was coated very rarely [21]. Mostly used coating polymers at these studies were PU, PU copolymers or PU blends as PU is a versatile polymer.

In this study, polypropylene fabrics were coated in order to create an alternative for protective garments. This is expected to expand the usage of polypropylene fibers.

Two PU coating polymer types and two curing temperatures were selected as the experimental variables for this study. As mentioned before, PU polymer can be engineered by using different kinds of monomers. Therefore, in this study, coatings were made by using both polyether and polyester based PU coating polymers in order to make comparisons for permeability properties [6]. Water-based PU types were selected as the coating polymers of this study due to their advantageous properties.

2 MATERIALS AND METHODS

2.1 Materials

Polypropylene base fabric, aliphatic polyether (R) based PU, polyester (W) based PU, cross-linking agent and thickener were the materials of this study. Properties of polypropylene base fabric are given in Table 1.

2 types of water-based PU dispersion were used for coatings in this study. Properties of coating polymers are given in Table 2.

An anionic, blocked isocyanate type cross-linking agent was used as the auxiliary material. Density of the cross-linker is 1.1 g/cm³ at 25°C and the pH is 7-10.

As the thickener, anionic acrylic polymer dispersion was used. Density of the thickener is 1.1 g/cm³ at 20°C and the pH is 6.

Table 1 Properties of PP base fabric

Yarn type	Weave	Warp density [warp/cm]	Weft density [weft/cm]	Unit mass [g/m ²]
100% PP multifilament	2/2 twill	56	40	76

Table 2 Properties of coating polymers

Polymer type	Polyether type PU (R)	Polyester type PU (W)
Chemical structure	Aliphatic polyether polyurethane dispersion	Polyester polyol and aliphatic isocyanate polyurethane dispersion
Appearance	White dispersion	White emulsion
Ionic structure	Anionic	Anionic
pH	7.5-8.0	7.0-9.0
Density (at 25°C)	1.0 g/cm ³	1.06 g/cm ³
Viscosity (at 25°C)	50-400 cps [centipoise]	50-400 cps

2.2 Methods

Methods of the study consist of coating of samples and analyses of the obtained samples.

2.2.1 Coating

Recipes of coating pastes are given in Table 3.

Viscosities of the coating pastes were measured by using Brookfield viscometer. Polypropylene base fabrics were coated with the above mentioned coating pastes by using laboratory type blade coating machine, as two layers of coating. Coated samples were cured at 120 and 140°C for 2 minutes.

As a result, 4 types of coated samples were obtained by changing the polymer type and curing temperature. Samples were coded as in Table 4.

Table 3 Polyether and polyester type PU coating pastes

Content	Polyether type PU paste	Polyester type PU paste
PU [parts]	100	100
Cross-linking agent [parts]	10	10
Thickener [parts]	0.3	0.7
Viscosity [cps]	9000	27800

Table 4 Codes of samples

Polymer type	Curing temperature	Sample code
Polyether type PU (R)	120°C	R120
	140°C	R140
Polyester type PU (W)	120°C	W120
	140°C	W140

2.2.2 Fabric tests

Coated samples were tested in order to reveal their usability for protective garments. As permeability properties; air permeability, water vapour permeability and waterproofness of samples were determined before washing and after 5 washing cycles. Also sample abrasion resistances were tested. Sample thicknesses and unit mass values were determined in order to detect the physical changes of samples after coating. In addition, fabric surfaces were evaluated by using scanning electron microscope (SEM).

All the tests were performed under standard atmosphere conditions (20±2°C temperature and 65±2% relative humidity).

Determination of sample thickness and unit mass

Unit mass changes of samples are related to added polymer by coating. To determine the add-on value, sample unit mass values were determined before and after coating process according to TS 251 standard [22]. Add-on [%] values were calculated according to:

$$\text{add-on [\%]} = \frac{W_s - W_i}{W_i} \times 100 \quad (1)$$

where: w_s - unit mass after coating, w_i - unit mass before coating.

Thickness values of samples were determined according to TS 7128 EN ISO 5084 standard [23] by using James Heal RxB Cloth Thickness Tester under 5 g/cm² pressure. Thickness and unit mass measurements were repeated 5 times for each sample type.

Determination of air permeability

Air permeability of samples was measured according to TS 391 EN ISO 9237 standard [24] by using Textest FX3300 air permeability tester. Air pressure was kept as 200 Pa during test. Measurements were performed on 20 cm² sample area and test was repeated for 15 times for each sample type.

Determination of water vapour permeability

Water vapour permeability is related to breathability of samples. Water vapour permeability of samples was determined by using SDL Atlas International M261 model water vapour permeability tester, according to BS 3424-34: 1992-Method 37 [25]. The amount of water vapour passed through the samples was determined after 24 h and permeability values were calculated. Test was repeated 3 times for each sample type.

Determination of waterproofness

Waterproofness values of samples were determined according to TSE 257 EN 20811 standard [26] by using Textest FX 3000 Hydrostatic Head Tester III. Pure water was used as the test liquid. Water pressure gradient was kept 60 cm/min during tests. Test area was 100 cm². Water pressures, when

the third water drops appeared on the sample surfaces, were recorded as the waterproofness values. Test was repeated 3 times for each sample type.

Determination of abrasion resistance

Coated surfaces of samples were abraded according to TS EN ISO 12947-3 standard [27] by using Nu-Martindale Abrasion and Peeling tester (James H. Heal Co. Ltd.). Test was repeated 3 times for each sample type. Samples were abraded 80000 abrasion cycles and weighed after each 2500 cycles. Test was performed by using 9 kPa pressure.

Determination of washing resistance

Samples were subjected to domestic washing cycles according to TS 5720 EN ISO 6330-2002 6A standard [28]. "A" type laundry machine was used. Main washing temperature was selected as 40°C and washing time was 24 min. 4 g/l non-phosphate ECE reference detergent without optical brightener was used. Samples were dried via straight hanging. Samples were objected to 5 washing cycles.

SEM analysis

Sample surfaces were observed by using scanning electron microscope (Jeol 6060, Tokyo, Japan). Both coated and uncoated surfaces of samples were evaluated microscopically.

3 RESULTS

3.1 Thickness, unit mass and mass change values of samples

Thickness, unit mass, add-on [%] and mass changes after washing are given in Table 5 and visualized in Figures 2-3 (with 95% confidence intervals).

As seen from Table 5, average fabric thickness is 0.223 mm for polypropylene base fabric where thickness is between 0.213-0.237 mm for coated samples. From Figure 2, it is understood that fabric thickness was increased only for R140 sample in the level of 6%. In contrary, sample thickness values decreased between 0.5% and 4.5% for R120, W120 and W140 samples. Similar thickness decrements after coating were experienced in the literature for polyester/ rayon fabrics [19].

Table 5 Thickness, unit mass, add-on % and mass changes of samples (*PPZ represents PP base fabric)

Sample code	Thickness [mm] (Standard dev.)	Unit mass [g/m ²] (St. dev.)	Add-on [%]	Mass change after 5 washing [%]
PPZ	0.223 (0.0054)	76 (0.7)	0	4.36
R120	0.213 (0.0089)	92 (1.8)	21	-1.45
R140	0.237 (0.0531)	107 (8.8)	40	0.85
W120	0.215 (0.0114)	99 (2.6)	30	-1.68
W140	0.222 (0.0054)	111 (7.7)	46	-1.34

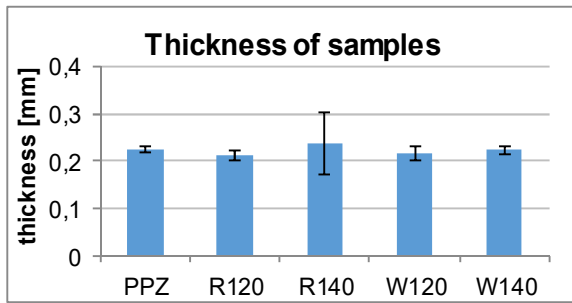


Figure 2 Thickness of coated samples

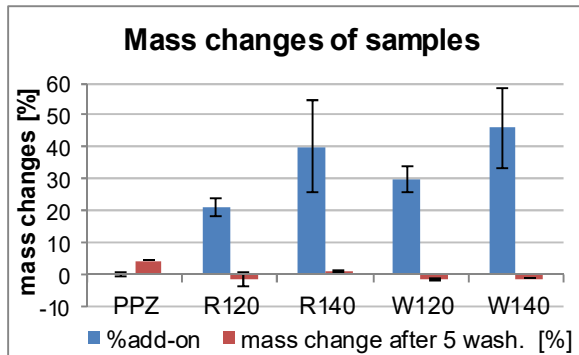


Figure 3 Add-on % and mass changes of coated samples

Add-on values and mass changes after washing are showed in Figure 3 (with 95% confidence intervals).

Coated samples showed unit mass increments between 21-46%. Add-on was higher for W coated samples which had a higher paste viscosity before coating. Also, R140 and W140 gave higher unit mass values. It was thought to be related to shrinkages of PP fabric under higher curing temperatures. After 5 washing cycles, mass changes were detected up to 2%.

In spite of unit mass increments up to 40%, sample thicknesses reduced after coating. It may be related to penetration of coating polymer to the inner parts of base fabric and stretching of samples during heat application. For further evaluation, samples were exposed to air permeability and waterproofness tests and examined microscopically by using SEM.

3.2 Waterproofness of samples

Waterproofness results of samples are given in Table 6. When the results were evaluated generally, it was concluded that both base fabric and coated samples showed very low waterproofness even before washing. Highest waterproofness was obtained from R120 sample before washing (164.3 mm water column) but it was also lower than the lowest limit of waterproofness for many application areas. According to Sen and Damewood (2005) [6], a waterproof-breathable fabric should not permit water passage until 1300 mm water column hydrostatic pressure. Similar low waterproofness results were obtained for water-based PU coated cotton fabrics in the literature [7].

Table 6 Waterproofness of samples

Sample code	Waterproofness [mm water column] (Standard Deviation)	
	Before washing	After washing
PPZ	71.5 (23.5)	35.3 (4.2)
R120	164.3 (19.2)	37 (15.4)
R140	150.7 (28.9)	24.0 (8.2)
W120	33.0 (6.1)	0.0 (0.0)
W140	61.0 (29.5)	0.0 (0.0)

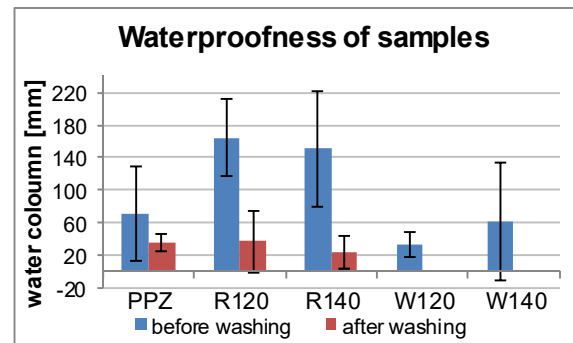


Figure 4 Waterproofness results with 95% confidence intervals

Samples coated with R (polyether) type polymer gave higher waterproofness when compared to base fabric (Figure 4). When the observations during waterproofness tests were considered, it was noticed that W (polyester) type polymer coated samples got wet before the starting time of test and many water drops appeared on the surface after starting the test. According to preliminary thermogravimetric analysis/differential thermal analysis (TGA/DTA) on the polyether and polyester type PU (with 10% cross-linking agent), it was concluded that polyester type PU might not have completed its cross-linking at 120 and 140°C during curing. TGA/DTA analysis results are given in Supplementary work. The TGA/DTA curves indicated that polyether type PU had a cross-linking temperature around 120-130°C (around exothermic peak interference) and polyester type PU had a cross-linking temperature around 120-140°C. Because of polypropylene melting and softening temperature limitations, 120 and 140°C were selected as the curing temperature. Polyester type PU had higher cross-linking temperature than polyether type PU. An insufficiency of curing procedure may have resulted with lower waterproofness of polyester type PU.

Waterproofness of all coated samples decreased after 5 times of washing. Polyester type PU coated samples did not give any water column after washing. As a result of visual inspection, it was understood that coating polymer partly removed from the sample surfaces after washing.

This was due to lower hydrolytic resistance of polyester type PU when compared to polyether type PU [6]. Also it might be related to poor adhesion between coating polymer and polypropylene or insufficient cross-linking.

3.3 Water vapour permeability of samples

Water vapour permeability of samples are tabulated in Table 7 and visualized in Figure 5 (with 95% confidence intervals).

Table 7 Water vapour permeability of samples

Sample code	Water vapour permeability [$\text{g}/\text{m}^2/24 \text{ h}$] (St. dev.)	
	Before washing	After washing
PPZ	838.0 (11.8)	800.5 (15.2)
R120	300.0 (25.9)	434.8 (26.6)
R140	445.0 (91.5)	418.7 (105.1)
W120	458.0 (5.2)	683.4 (8.5)
W140	64.0 (31.4)	646.2 (13.4)

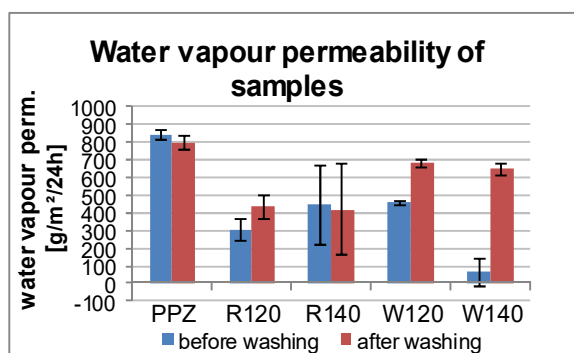


Figure 5 Water vapour permeability of samples

Highest water vapour permeability was obtained from PP base fabric with $838 \text{ g}/\text{m}^2/24 \text{ h}$ permeability value before washing. Water vapour permeability of unwashed coated samples reduced to approximately 50% of base fabric. This was due to additional PU coating layer which contributed mass transfer limitation through the fabric. Even the most breathable coating polymer was applied to the samples; it would add a resistance to the vapour flow by closing the pores and creating an additional layer [29].

When the results before washing were considered generally, any relation between the curing temperature, polyurethane type and water vapour permeability was not found. But the sample with higher add-on, namely W140, showed the lowest water vapour permeability.

After washing, water vapour permeability of coated samples increased especially for polyester type PU coated samples. It was due to removed polymer from

the sample surfaces which resulted with a more open sample structure.

3.4 Air permeability of samples

Air permeability values of samples are given in Table 8 and Figure 6 (with 95% confidence intervals).

Before washing, PP base fabric had higher air permeability when compared to coated samples as it had open pores (Table 8, Figure 6). In contrary, unwashed coated samples showed air permeability lower than $8.5 \text{ L}/\text{m}^2/\text{s}$ independent of curing temperature and coating polymer type. This is due to filling of the gaps between the fibers and yarns by coating polymer. Sample W140 with lowest water vapour permeability, also showed the lowest air permeability among all the samples, before washing.

According to Sen and Damewood (2005) [6], air permeability of fabrics should be lower than $1.5 \text{ ml}/\text{cm}^2/\text{s}$ at 1 mbar in order to provide windproofness. This corresponds to $15 \text{ L}/\text{m}^2/\text{s}$ at 100 Pa pressure. According to test results, before washing, coated samples belonged to windproof fabric class despite being measured at 200 Pa.

After washing, air permeability values of polyester type PU coated samples increased in big amounts as for water vapour permeability results. It was again due to the removed coating polymer from the sample surfaces. Air permeability of polyether type polyurethane coated samples remained almost the same after coating and they remained to be windproof after washing.

Table 8 Air permeability of samples

Sample code	Air permeability [$\text{L}/\text{m}^2/\text{s} = \text{mm}/\text{s}$] (St. dev.)	
	Before washing	After washing
PPZ	205.7 (6.7)	190.6 (10.6)
R120	8.4 (6.9)	7.3 (7.0)
R140	7.8 (4.2)	10.5 (8.7)
W120	7.1 (7.0)	142.5 (7.8)
W140	0.0 (0.0)	99.7 (24.7)

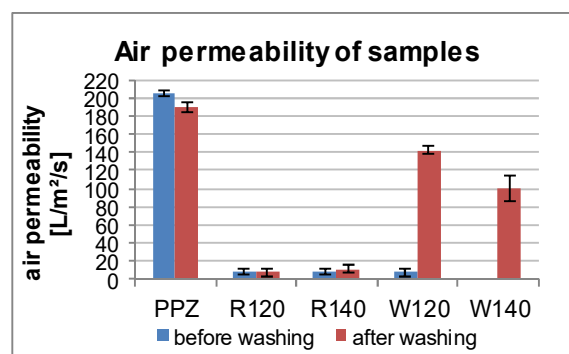


Figure 6 Air permeability of samples

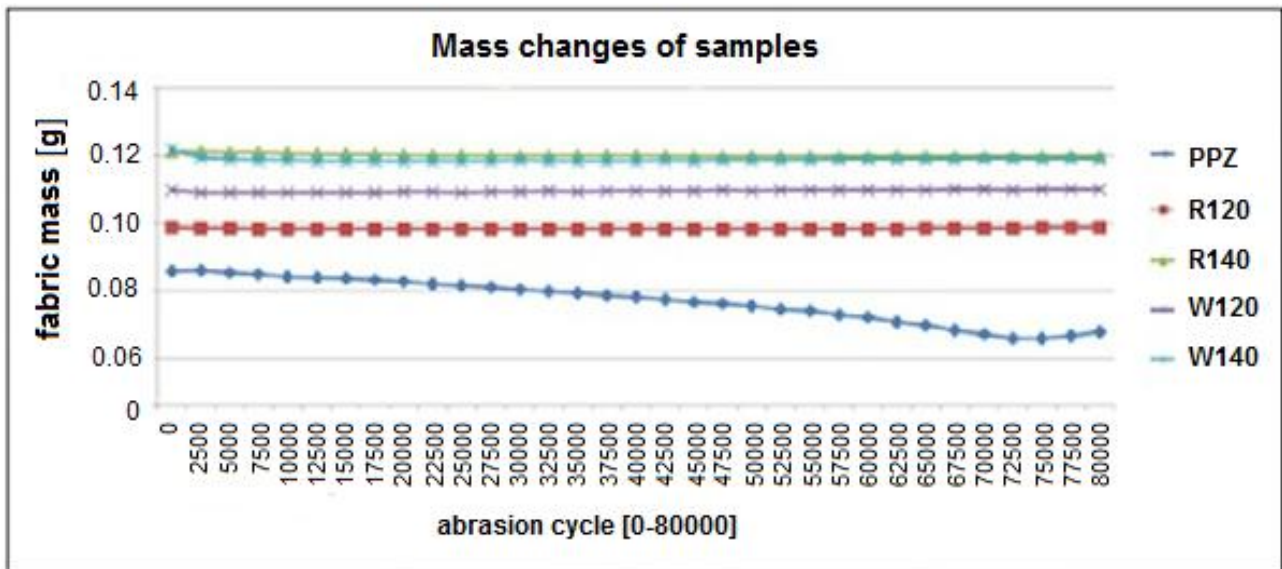


Figure 7 Mass changes of samples after abrasion cycles

3.5 Abrasion resistance results of samples

Average weight losses of samples were calculated after every 2500 abrasion cycles up to 80000 cycles. Weight losses are given in Table 9. Also results are visualized in Figure 7.

Table 9 Weight losses of samples after abrasion cycles

No. of abrasion cycles	PPZ	R120	R140	W120	W140
2500	0.2	-0.2	0.0	-0.7	-1.9
5000	-0.5	-0.2	-0.2	-0.7	-2.3
7500	-1.1	-0.3	-0.4	-0.8	-2.5
10000	-1.9	-0.4	-0.5	-0.79	-2.7
12500	-2.1	-0.4	-0.7	-0.7	-2.8
15000	-2.5	-0.4	-0.7	-0.8	-2.9
17500	-3.2	-0.5	-0.7	-0.7	-2.9
20000	-3.7	-0.5	-0.9	-0.6	-2.9
22500	-4.3	-0.4	-0.9	-0.6	-2.8
25000	-4.9	-0.4	-1.0	-0.6	-2.8
27500	-5.5	-0.5	-1.0	-0.5	-2.7
30000	-6.4	-0.5	-1.0	-0.5	-2.7
32500	-6.9	-0.5	-1.0	-0.3	-2.7
35000	-7.8	-0.5	-1.1	-0.5	-2.7
37500	-8.4	-0.5	-1.2	-0.4	-2.7
40000	-8.9	-0.5	-1.1	-0.3	-2.8
42500	-9.8	-0.5	-1.1	-0.2	-2.6
45000	-10.5	-0.4	-1.2	-0.2	-2.7
47500	-11.2	-0.4	-1.2	-0.2	-2.6
50000	-12.0	-0.4	-1.3	-0.2	-2.6
52500	-13.0	-0.4	-1.3	-0.1	-2.6
55000	-13.7	-0.4	-1.2	-0.1	-2.6
57500	-14.9	-0.3	-1.3	-0.1	-2.4
60000	-15.9	-0.4	-1.3	-0.1	-2.4
62500	-17.4	-0.4	-1.3	-0.2	-2.4
65000	-18.8	-0.3	-1.2	0.0	-2.3
67500	-20.2	-0.2	-1.3	0.1	-2.3
70000	-21.7	-0.1	-1.4	0.2	-2.2
72500	-22.9	-0.1	-1.3	0.0	-2.2
75000	-24.4	0.0	-1.4	0.2	-2.3
77500	-22.2	0.1	-1.3	0.1	-2.2
80000	-20.9	0.1	-1.4	0.1	-2.3

According to test results, abrasion did not cause important weight losses for coated samples. On the other hand, PP base fabric lost approximately 21% of its weight after 80000 abrasion cycles. Holes were formed on the base fabric after abrasion.

Highest weight loss was observed for W140 specimen after 20000 abrasion cycles, around 2.87%. Weight losses of coated samples fluctuated in a narrow range. This is related to sticking of fibers of abrasion fabric to the coated samples. Weight loss was lower than 1% for R120 and W120 samples after 80000 abrasion cycles and 1.35 % for R140 sample. Surface gloss of coated fabrics increased visibly after abrasion.

3.6 SEM evaluation of samples

SEM images of coated samples are given in Figure 8. SEM images were taken from both coated and uncoated sides of samples. As seen from the Figure 8, in the coated sides, coating polymer covered the gaps between the fibers on the surface of samples. In contrary, any polymer residue was not observed on the uncoated sides of the samples. As the coating pastes were viscous enough, coating polymers did not penetrate to the other side of the polypropylene fabrics. On the other hand, although coating the samples as two layers, all the coated surfaces of the samples were not covered by a polymer film. Coating polymer mainly filled the gaps between fibers but some gaps between the yarns can be observed especially in W120 and W140 samples. It is thought to be the reason of very low waterproofness as every unfilled point attributed to water passage at high pressures. A continuous polymer film is needed on the surface of base fabric for a very good waterproofness level.

Despite not producing a continuous coating polymer film on the surface, polymer which was deposited

between the fibers reduced the air permeability effectively.

The surface images were not enough to determine the level of penetration of coating polymer. But, as a distinct polymer film was not detected on the surface, it is understood that some amount of applied polymer penetrated to a deepness of the fabric cross-section. But it did not leak to the other side (uncoated sides) of samples as seen from Figure 8. This supports the phenomena that coated fabrics did not thicken after coating.

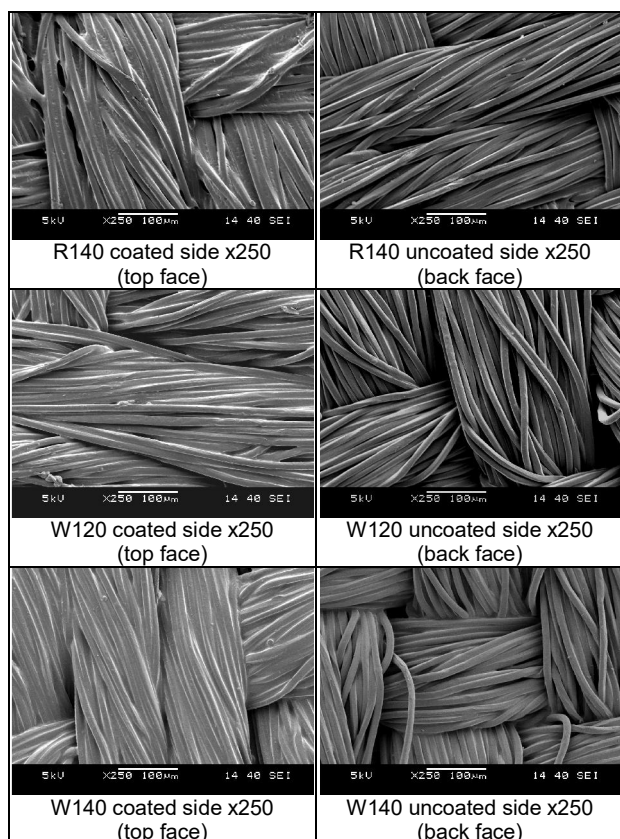


Figure 8 SEM images of coated samples

4 DISCUSSION

In this study, polypropylene fabric was coated systematically to be used in protective sportswear. Permeability properties and abrasion resistance of samples were determined in order to reveal the usability of these samples. Also physical properties such as thickness and unit mass were measured in order to observe physical changes after coating. Sample surfaces were observed by SEM in order to support test results.

When the results before washing were considered generally, add-on [%] was found higher for samples cured at 140°C and it was thought to be related to thermal shrinkages at higher temperatures. Air permeability of coated samples was found very low independent of coating polymer type and curing

temperature. It was found advantageous as the samples showed windproofness. In contrary, water vapour permeability values of samples decreased in lower amounts. This showed that coating polymer penetrated to pores of fabric but the water vapour was permitted at some amount through the coating layer. Partly coverage of pores by coating polymer was supported by SEM evaluation. Coating procedure did not increase the waterproofness of samples to the desired levels. Polyether type PU gave relatively higher waterproofness for coated samples. Coated samples showed very high abrasion resistance when compared to base fabric.

After washing cycles, it was observed that coating polymer partly removed away from polyester type polyurethane coated samples. It affected the waterproofness, water vapour permeability and air permeability results. Waterproofness of polyester type polymer coated samples decreased to zero, while air permeability and water vapour permeability increased. The increments in the water vapour permeability and air permeability were interpreted as negative related to the absence of waterproofness. Some inferiority at permeability properties was obtained for polyether type polymer coated samples too, but the degree of the inferiority was lower. It was due to higher hydrolytic stability of polyether type polyurethane when compared to polyester type polyurethane [6].

Coated samples of this study are proposed to be used as windbreaker for sportswear. To be used in intensely water contacting sports such as sailing and mountaineering, waterproofness of polypropylene fabrics should be enhanced by using different coating parameters and coating polymer types. Also, compatibility between polypropylene base fabric and coating polymer should be enhanced in order to increase waterproofness. In the literature polypropylene fibers were modified by using additives, making polymer blends or graft polymerization. By these modifications, water sorption and dyeability of polypropylene fibers were enhanced [30-32]. Similarly, polypropylene fibers hydrophilicity and polarity may be altered by fiber modifications and their compatibility to coating layer may be improved in the further studies.

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