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Effect of Viscosity on the Characteristic Properties of Solvent Free Patent Finished Leathers

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ABSTRACT

Patent leather is a well-known leather type having a mirror-bright gloss finish and is produced from goat, calf, cattle, and corrected grain crust leathers by the use of patent finishing technique. Due to the emission limitations of volatile organic compounds, now water-based finishing applications are used in leather industry instead of solvent-based systems and still there has been no information in literature to reveal the effect of viscosity on the characteristic properties of patent leathers. Therefore, in the present study, water-based patent leathers differentiated in viscosity were investigated in terms of surface reflectance, tensile strength and elongation at break, to and fro rubbing fastness, distension and strength of surface, heat resistance, flexing resistance, air permeability, colorfastness to water spotting tests and scanning electron microscopy displays prior and subsequent to ageing process. The results of the study revealed that the patent film with 194.46cSt viscosity (S2) viscosity provided comparatively better results.

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KEYWORDS

Patent leather, water-based finishing, solvent-based finishing, viscosity

1. INTRODUCTION

The leather industry is subject to pressures of globalization, environmental legislations, regulations, and changing consumer behaviors [1,2]. The use of chemicals containing hazardous substances have been prohibited or restricted according to environmental regulations [2]. Thus, to reduce the pollution load of the leather industry, natural, environmentally friendly, and biodegradable substances have been widely used and adapted to processing technology since many years [3-12]. Among these methods, solvent free finishing is one of the well adapted techniques to the manufacturing of leathers and has been widely used recently in leather industry [13-16].

Finishing process plays an important role for ensuring the desired appearance and surface characteristics to final leather products such as color, feel touch, gloss including fastness properties and durability and is described as a serious of operations performed for the coating treatment of leathers [17,18]. By this process, broad range of leather articles can be produced depending on different finishing chemicals, techniques and mechanical operations [18] and patent leathers are one of the leather types differentiated in afore-mentioned conditions and substances. Generally patent finishing technique is applied to upper leathers produced from mostly goat and calf skins and protects the wearing materials from external effects [19]. Patent leathers are manufactured from a corrected grain of buffed leathers by coating the leather surface and have a high gloss finish [1,18,19]. For the traditional patent finishing, coating substances are linseed oil, pigments, fillers, binders, resins, polyurethanes, crosslinkers and solvents [19,20].

In mid of the century, patent finish was applied to leathers by the use of linseed oil and the leathers were allowed to air dry. Until fifties, nitrocellulose binders were used for the patent finish. Later nitrocellulose-based patent finish technique was superseded by solvent based polyurethane finishing [19,21,22] and polyurethane products were firstly

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used in this type of leather production [18,19,23].

After the legal stringent regulations on the usage of solvents during finishing, water-based chemicals have been started to use instead of organic solvents to reduce pollution in environment [13]. But, although varied studies were performed for improving the finishing application on leathers by using different cross-linkers and organic solvents [1,18,24-31], no scientific study has been reported on the characterization and performance tests of patent leathers manufactured by the use of different viscosity up to date.

Viscosity, the measurement of flow characteristics of the substance by time or temperature, should always be tested prior to patent finishing application due to the formation of track and non-homogenous distribution of the finishing films. Therefore, viscosity has a great importance on finishing application and film quality [32].

Thus, this study deals with the effect of viscosity on solvent free patent finishing system to reveal the characteristic properties of the patent leathers. For this purpose, goat crust leathers were manufactured by the use of water-based patent finishing technique differentiated only in the value of viscosity. The characteristic properties of the patent leathers were determined prior and subsequent to ageing process in terms of surface reflectance, tensile strength and elongation at break, to and fro rubbing fastness, distension and strength of surface, heat resistance, flexing resistance, air permeability, colorfastness to water spotting tests and scanning electron microscopy displays.

2. MATERIALS AND METHODS

2.1. Materials

Twelve chromium tanned crust goat leathers were used in order to perform the water and solvent based finishing applications for the study. An aziridene based substance was used as the cross-linker. The chemicals used in leather finishing process were those conventionally used in patent finishing applications.

2.2. Methods

2.2.1. Viscosity adjustment of finishing films

In the present study, DIN ford type viscometer (Viscometer no 4), which is generally used for the viscosity determination of varnishes, lacquers, and related liquids and found in manufacturing plants [33-35], was used at room temperature 25±0.2ºC (77±0.4ºF) in accordance with Alonso et al., 2005 and ASTM D1200-10 2018 respectively [36,37].

The samples were entitled as BC for the base coat as a blank, S_1 for the sample having 136.71 centistokes (cSt) (40 seconds), S_2 for the sample having 194.46 (55 seconds), and S_3 for the sample having 252.21 cSt (70 seconds) finishing film viscosities.

2.2.2. Finishing applications of patent leathers

Water and solvent based patent finishing techniques were performed for the finishing applications. For the water-based finishing trials, the leather samples entitled as S_1, S_2, and S_3 were subjected to the same water-based finishing formulation differentiated only in the viscosity of the films. After mixing the substances of the basecoat layer (Table 1), the mixture was applied to leathers with roller-coating machine for three times, and subsequently the leathers were ironed using rotopress. Later the leathers were processed with roller coating again for three times to transfer the finishing formula and dried using a drying cabinet and hot plate at 80ºC for 3 minutes and at 100ºC and 100bar respectively. The surfaces of the leathers were controlled for the dust remaining and if there was any, on the surface, it was removed.

Solvent based (conventional) patent finish was applied to leathers as a control group to compare the characteristic properties of the water-based patent finished leathers. The formulation of this technique is given in Table 2. All leathers used for the finishing applications were the same type of leather and each finishing trial was performed in triplicates.

Table 1. Water-based patent finishing formulation

Chemicals	Basecoat A	Topcoat B	Application
Compound Binder (31% w/w)[1]	690		
Compound Binder (30% w/w)[2]	50		Three times roller coat
Fuller (26% w/w)	25		Roto press
Penetrator	55		Three times roller coat
Leveling Aid[3]	30		
Anionic Pigment (20 w/w)	150		
Polyurethane Lacquer (35% w/w)		980	
Aziridine Based Crosslinker (70% w/w)		20	Three times roller coat for topcoat film application

1 Compound binder consists of polyurethane and other polymer
2 Compound binder consists of polyurethane and other polymer is used for giving better adhesion and flexible performance to the leather.
3 Leveling Aid is surfactant used for minimizing the problems and improving the viscosity originated from surface tension.

Table 2. Solvent-based patent finishing formulation

	Base coat A	Rugan B	Application
Compound Binder (30% w/w)	805		A) 3 times roller coat and roto-press
Black anionic pigment (20% w/w)	160		
Fuller (26% w/w)	35		3 times roller coat
Rugan Lacquer (%50 w/w) Polyester dispersion in solvent		635	B) Only one film application performed on leather surface.
Hardener (%60 w/w)		295	
Black aniline solution solved in solvent		70	

2.2.3. Accelerated ageing process

Accelerated ageing process was performed with climate chamber device (Angelantoni Challenge 340) following the related standard of TS EN ISO 17228, 2015 using the conditions of 70ºC±2ºC for 12 hours ±1 hour with 90% relative humidity (RH) ± 5% RH. Each sample was assessed by grayscale under the daylight in the light cabin [38].

Each group of patent leather was divided into two and half of the leathers were aged as described above and the other half was remained as it was. Subsequent to ageing process, all leather samples were conditioned and prepared in accordance with the standards TS EN ISO 2419, 2012 and TS EN ISO 2418, 2017 respectively prior to the physical tests [39,40].

2.2.4. Determination of surface reflectance

The reflectance measurements of patent leathers were performed at two different wavelengths. The diffuse reflectance of the patent leathers was measured at 900 nm whether the patent leather was reflected the 55% of radiation following the standard of ISO 17502, 2013 [41]. Additionally, the reflectance of the leather surfaces was measured in the visible wavelength using Hunterlab Ultra Scan XE spectrophotometer (350-700 nm).

2.2.5. Determination of tensile strength and elongation at break

The tensile strength (N/mm^2) and elongation at break (%) values of the patent leathers were tested according to TS 4119 EN ISO 3376 standard [42].

2.2.6. To and fro rubbing fastness test

The artificial corrosion of finishing films was performed with Bally Finish Tester 9029 to determine the rubbing fastness properties of the patent finished leathers. Dry and wet rubbing fastness characteristics of leathers were determined with wet and dry felts (100 rubs dry and 25 rubs wet) under the conditions of 10% stretch [43]. After the test, samples were evaluated by using grayscale in accordance with the standards ISO 105-A05 and ISO 105-A04 [44,45].

2.2.7. Determination of distension and strength of surface

The distension and strength of patent leathers surface (Ball Burst Method) was determined according to the standard of ISO 3379, 2015 [46].

2.2.8. Heat resistance test of the finishing films

The heat resistance test was applied to patent finished leathers using a modified ball burst test. The metal hemisphere (2.1mm diameter) was adapted to the sphere of lastometer. Then the samples were placed into the non-metallic dome. The lasting was controlled by measuring the height of the formed dome of material with a micrometer inside the testing device. When the dome area is calculated, the proportion of the area increase retained is the set of the material (Satra STD 449).

2.2.9. Determination of flexing resistance

Flexometer test was applied in accordance with the standard of EN ISO 5402 to determine the flex resistance of the patent leathers [47]. After 35.000 cycles, the flexing endurance of patent leathers was measured and controlled by naked eye and optic microscope to observe the changes on the leather surface. The damage in the flexed area was noted as in the standard; cracks visible with naked eyes, fine cracks visible by the magnifier, or micro cracks visible by microscope.

2.2.10. Air permeability test

Air permeability of the leather samples were tested with the brand of Devotrans, DVT-HG model device [17]. Leather samples were prepared following the standard of TS EN ISO 2419 [39] and bonded with metal rings having different surface areas. For the pretreatment test, the area 100 cm^2, the pressure 200 pA, and the time 5 minutes were selected, and the amount of air passed through the samples was measured. Depending on the results of pretreatment tests for air permeation; pressure, test area, and duration of testing were chosen as 200Pa, 100 cm^2, and 10 minutes, respectively.

2.2.11. Colorfastness of patent leathers to water spotting

The effect of water spotting on the patent finished leathers was determined with the standard of TS EN ISO 15700

[48]. Two drops of distilled water were placed upon the suede sides of the leathers due to the impervious surface of the finishing films. After 30 minutes, one of the drops was removed and the physical change was observed. The second drop was allowed to stay overnight and the same observation was performed. Color changes were assessed according to the grayscale [38].

2.2.12. Scanning electron microscopy images of the leathers

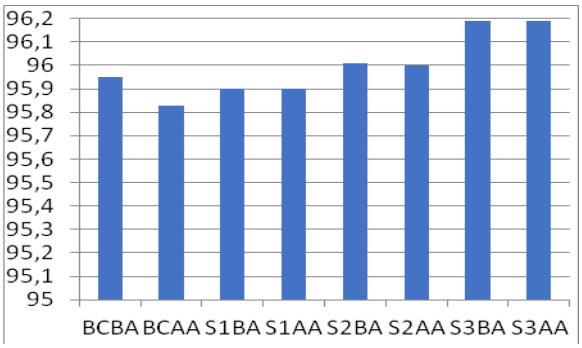
Finishing layers of the patent leathers applied in different viscosities were displayed by scanning electron microscopy (Hitachi TM1000) [49,50]. Cross-sections of the leathers were magnified 100 times to compare the morphology of the films.

3. RESULTS AND DISCUSSION

3.1. Reflectance values of the patent leathers

The reflectance results of the patent leathers obtained from the measurements performed prior and subsequent to ageing process are given in Figure 1 and Table 3. The results showed that the reflectance values of the patent leathers were obtained above the value of 95%. The reflection of light from the leather surface gives the glossy effect to patent leathers and this is because of the polyurethane binders that are used in patent leather finishing process [13,51]. Although Bacardit et al., 2009 presented that solvent-based patent finish resulted a higher degree of gloss than the water-based patent finishing application [18], in our study no significant difference was found between the patent leathers. This result showed that the reflectance of the leather surfaces has not seemed to be affected by increasing the viscosity of the finishing films (Figure 1).

The maximum reflectance values of the leather samples measured under the visible wavelength (350-700 nm) with the increase of 20 nm is shown in Table 3 and no significant difference was observed between the leather samples and control group (Table 3).



*BA; before ageing *AA; after ageing

Figure 1. Diffuse reflectance values of the patent leathers at 900nm

3.2. Tensile strength and elongation at break values

Tensile strength and elongation at break values of patent finished leathers are given at Table 4. According to the results, increasing the viscosity of the finishing films led to an increased tensile strength and elongation at break values of the patent leathers. After the accelerated ageing process, a decrease in tensile strength values were observed for all leather samples but this decrease was not seemed significant. However, the rate of decrease occurred in the elongation at breaks values (%) of the leathers after the accelerated ageing were found higher than the tensile strength values. The highest tensile strength and percentage of elongation at break values were obtained from the patent leathers finished with the viscosity of 252.21cSt (S_3). It is well known that the binder used in finishing formula increase the tensile strength of the leathers [24]. In addition to this finding, we also determined in our study that the viscosity of the finishing film has a positive effect on the increase of the tensile strength and elongation at break values. The patent leathers entitled as S_2 and S_3 meet the quality requirements for shoe uppers in terms of tensile strength similarly with the literatures of [13,52].

Table 3. Reflectance of the patent leathers (%) in visible wavelength

Wavelength	Reflectance (%) of Patent Leather Surfaces							
nm	**BC_{BA}**	**BC_{AA}**	**S_{1BA}**	**S_{1AA}**	**S_{2BA}**	**S_{2AA}**	**S_{3BA}**	**S_{3AA}**
350	4.84	4.73	4.87	4.81	4.66	4.65	4.90	4.80

Table 4. Tensile strength and elongation at break values of the patent leathers

	Before Ageing		After Ageing	
	Tensile Strength ($N.mm^{-2}$)	**Elongation at break (%)**	**Tensile Strength ($N.mm^{-2}$)**	**Elongation at break (%)**
BC	12.15	21.79	11.89	20.27
S_1	13.93	22.56	13.26	20.94
S_2	15.45	25.63	15.10	23.75
S_3	16.41	32.46	15.93	28.06

3.3. To and fro rubbing fastness results

To and fro rubbing fastness values of the patent leathers obtained before and after the accelerated ageing process are shown in Table 5. Prior to ageing, similar dry and wet rubbing fastness values were obtained from the patent finished leathers. The effect of viscosity could be seen for the leather samples of S_2 and S_3 due to the determination of higher rubber fastness results compared to S_1. Dry and wet rubbing fastness evaluations of control leathers (BC) presented the lowest rubbing fastness results compared to patent leathers finished with different viscosities.

After ageing process, no significant change was occurred for the dry fastness values of control and patent finished leathers when it was evaluated according to felt. However, the dry fastness values of the leathers were decreased. The patent leathers finished with the highest viscosity (S_3; 252.21cSt viscosity) gave similar dry rubbing fastness values with the control leathers, although S_1 and S_2 gave higher results than the S_3 leathers. Besides, same results were determined from the wet rubbing fastness values of felt. However, the decrease occurred in wet fastness values of leathers were found higher than the dry fastness values. Similar to dry fastness evaluation, S_3 gave the lowest wet rubbing fastness value compared to S_1 and S_2. Control leathers had minimum wet rubbing fastness values before and after ageing process. However, the most affected fastness results were found for wet rubbing fastness values of leathers after ageing. It was revealed from the results that accelerated ageing conditions were found affected on the patent leathers finished with different viscosities and the best results were provided from the leathers finished with S_1 (136.71cSt) and S_2 (194.46 cSt). The dry and wet rubbing fastness values obtained by our study were found similar to the results obtained by Bacardit et al., 2009b [13]. However, after ageing process, a decrease has occurred as it is expected.

3.4. The distension and surface strength of the patent leathers

The effect of the increase in viscosity led to a decrease in distension (mm) directly proportional to the viscosity increase despite the increase occurred in the grain strength for the patent finished leathers. The leathers only have the base coat (BC; control group) had the lowest grain load in contrast to highest distension. But for the patent leathers, this effect was found vice versa. Subsequent to ageing, the distension and grain strength values of the leather samples were decreased. Patent finished leathers gave higher values compared to control leathers after ageing and the minimum decrease was observed from the sample of S_3 keeping the distension and grain load values nearly constant. But if the distension was considered primarily, the best result could be obtained from the leather sample of S_2 (194.46cSt viscosity) after the accelerated ageing process (Table 6).

According to CEN/TC 309/WG1 standard, the lowest admissible value of the extension is accepted as 7 mm. Also, the suppliers guarantee this value as 6.7-7.0 mm against imperfection. The values of distension and surface strength of the patent leathers obtained in our study were found above these recommended values (Table 6) [52,53].

3.5. Heat resistance of the patent leathers

The separations and deformations of the finishing films were observed after the heat resistance test of the patent leathers only for the control leathers and the leathers finished with minimum viscosity (S_1) (Figure 2). This may be caused due to the pressure and heat applied during the test as well as inadequate binding of finishing film onto leather. Unlike the results mentioned above, no deformation was observed on the grain surface of the leather samples with S_2 and S_3 having the viscosities of 194.46cSt and 252.21cSt respectively.

Table 5. To and fro rubbing fastness values of the patent leathers

	Before Ageing							
	Dry Rubbing		**Wet rubbing**		**Dry Rubbing**		**Wet Rubbing**	
	Felt	Leather	Felt	Leather	Felt	Leather	Felt	Leather
BC	5	2/3	1	1	5	3	1	1
S_1	5	5	5	4/5	5	4/5	5	3
S_2	5	5	5	5	5	4/5	5	3
S_3	5	5	5	5	5	3	5	2

Table 6. Determination of distension and grain strength of the patent finished leathers (Ball Burst Test)

Samples	**Before Ageing**		**After Ageing**	
	Load at Grain Crack (kgf)	**Distension (mm)**	**Load at Grain Crack (kgf)**	**Distension (mm)**
BC	16.00	11.12	13.50	9.74
S_1	16.88	10.99	14.50	8.70
S_2	19.67	10.15	17.17	11.91
S_3	17.33	9.18	17.33	9.79

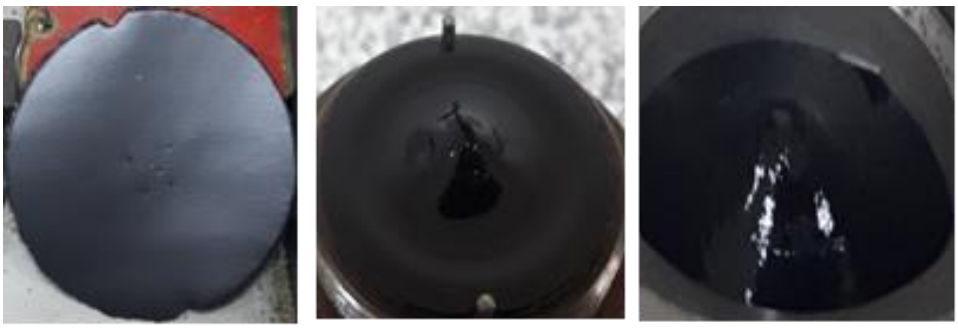


Figure 2. Displays of the patent leather surfaces after heat resistance test (a; S_2 and S_3 leathers without any damage; b; patent leather with the lowest viscosity (S_1); c; control leather

3.6. Flexing resistance of the patent leathers

The flexing resistance of the patent leathers showed that the samples of S_1, S_2 and control leathers provided good flexing resistance properties (Table 7). However, macro cracks were observed from the patent leathers entitled as S_3. It was thought that these cracks could be occurred due to the breakdown of bonds between the finishing film and leather by the effect of flexing movements depending on the increase in the viscosity of the finishing film. Additionally, no change was observed after the accelerated ageing in terms of flexometer results. It is reported that the use of cross-linker and the type of polyurethane have increased the flex resistance of the leathers including patent leathers [13,54]. Likewise, it is determined that the water-based polyurethane has increased the flex resistance values compared to solvent based ones and only the topcoat cracking has occurred after the flex resistance test as the same that we observed in the study [13].

3.7. Air permeability of the patent leathers

Air permeability of a leather is a very important characteristics for determining the ability of the air to transmit [55]. It is reported that air permeability of the leather could be changed depending on the type of the finishing [17]. The air permeability of finished buffalo calf leather was found almost four times lower than the unfinished leathers [56]. Lixin et al., 2014 specified that patent leather had the lowest air permeability value and the results ranking from the best to the worst; nubuck, unfinished garment leather, full-grain garment leather, and garment patent leather respectively [57]. In a similar manner with the previous literatures, it was clearly seen that the control group had the highest air permeability values (Figure 3). Increasing the viscosity of the finishing film caused a reduction in air permeability. Ageing process affected the air permeation of leather negatively except the control leathers. After ageing process, the air permeation results of the patent finished leathers were decreased in the ratio of 62.01%, 59.87%, and 18.00% for the finishing applications of S_1, S_2, and S_3 respectively. It was determined that the air permeability of the leathers having only the base coat (BC; control leathers) had 15.70% higher proportion after accelerated ageing process compared to prior.

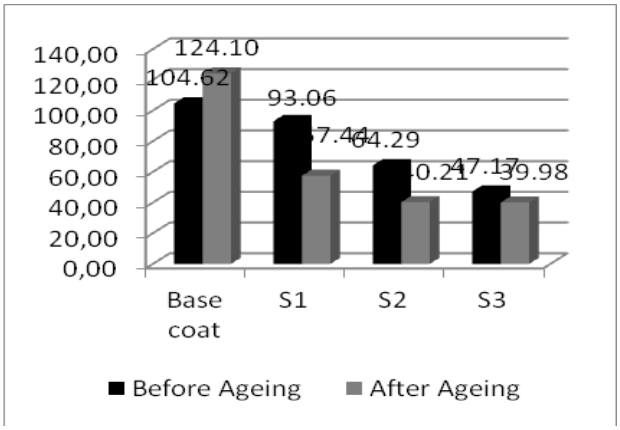


Figure 3. Air permeability values of the patent finished leathers

3.8. Color fastness properties to water spotting

After 30 minutes and 16 hours of the water spotting test, swelling of the films was observed only from the control leathers. The swelling and partition of water spotting rate was decreased by increasing the viscosity of the finishing films (Figure 4). No color changes and damages on the topcoats were observed for the patent finished leathers same as the study performed by Olle et al., 2009 [51]. Also, Bacardit et al., 2009 reported that the topcoat applications improved the physical properties of leathers such as wet rubbing fastness and water spotting test [18].

3.9. Scanning electron microscopy images of the patent leathers

The scanning electron microscopy images of the finishing layers were shown in Figure 4. The thicknesses of the patent films applied to leathers were found 80-100µm, 100-120 µm, and 250-300 µm for 136.71cSt (40 seconds), 194.46cSt (55 second), and 252.21cSt (70 second), respectively. It can be easily seen that increasing the viscosity of the finishing films led to an increase in the thickness of the patent film. When kinematic viscosity of the finishing film was increased from 136.71cSt (40 seconds) to 194.46cSt (55second), the thickness of the finishing film was obtained 20% higher. However, increasing the kinematic viscosity of the finishing film from 136.71cSt to 252.21cSt, the film thickness was increased

more than three times. It was thought that these differences were caused due to the viscosity of the finishing films and pressure applied by the cylinder for spreading the finishing film on the leather surface.

4. CONCLUSION

The results of the study revealed that required limit values from patent finished leathers were provided by water-based patent finishing applications. Higher viscosity values of the finishing films were found affected on the comfort properties of the patent leathers. Although increasing the finishing film viscosity has resulted high tensile strength, elongation at break, crack resistance and distension values, some fastness properties such as flexing resistance, air permeability and water spotting values were decreased. Besides, no significant difference was found in color and reflectance values of the patent leathers. It was determined that the finishing film having 194.46cSt viscosity (S2) gave the best result among the other viscosity values. Even though some tracks on the leather surface was generated due to the cylinder for the finishing films having high viscosity, the films having low viscosity gave irregular distribution on the leather surface because of the vibration effect occurred between the finishing film and cylinder. In view of these findings, this study is considered as remarkable in terms of revealing the effect of patent finishing film viscosity on the final patent leather properties.

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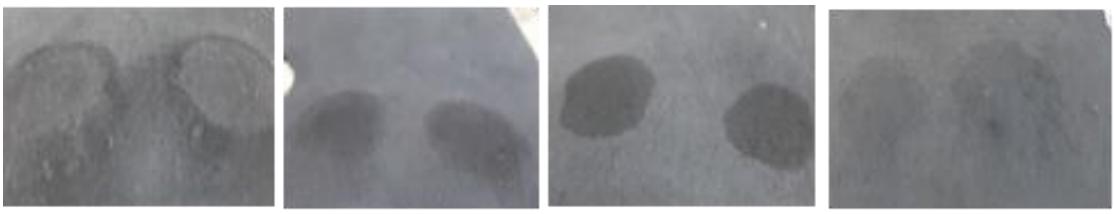

Figure 4. Visual displays of water spotting test for the patent leathers (a; BC, b; S_1, c; S_2, d; S_3)

Table 7. Flexing resistance of the patent leathers

Samples	Evaluation	
	Before Accelerated Ageing	**After Accelerated Ageing**
BC	No cracks observed	Micro cracks observed
S_1	Micro cracks observed	Micro cracks observed
S_2	Micro cracks observed	Micro cracks observed
S_3	Macro cracks	Macro cracks

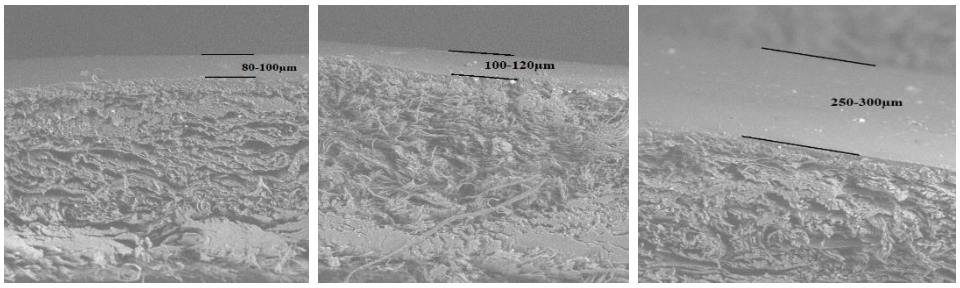

Figure 5. Cross-section displays of the water-based patent leathers with magnification 100x

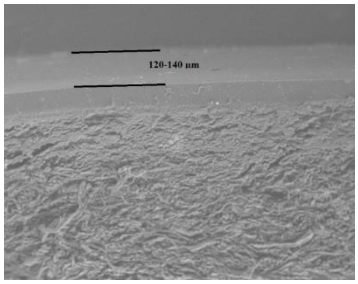

Figure 6. Cross-section display of the solvent-based patent leather with magnification 100x

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