Studies on the Fabrication of Hydrophobic Coating Incorporating Bentonite Clay and its Effect on the Physical Properties of the Finished Leather

by

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Abstract

One of the most important properties that can be added to leather-based products is its ability to self-clean as leather cannot be washed frequently like fabrics. A simple and direct method to achieve this is to introduce a hydrophobic coating on the top of the leather, which can minimize the adhesion of foreign particles and thereby improve stain resistance. Additionally, this also increases the economic, aesthetic and functional values of the material. Generally, a hydrophobic surface on the leather is created by coating a polymer based on fluorine or silicone, which has the tendency to repel the water droplets. In this paper, the effect of hydrophobic coating on the physical properties of the leathers was studied. It was observed that the hydrophobic coating had a positive effect on the rub fastness properties improving the rating of 3 to 4. Water vapor permeability of the FCP-A alone coated leather reduced from 8.7 to 4.4 mg/cm^2/hr in comparison to crust leather, owing to the sealing of pores on the grain surface due to the film formed by these polymers. However, incorporation of bentonite clay improved the water vapor permeability of the leathers from 3.4 to 12.9% in comparison to that of the FCP-A alone coated leathers owing to the pores created in the finish film. In addition, the contact angle of the leather surface was also increased from 98° to 121° due to the introduction of roughness induced by the clay particles. Hence, the proposed work can aid in the development of easy-care and smart leathers.

Introduction

Garment and shoe industries rely to a large extent on leather for the production of footwear and clothing, which would impart good health and comfort. Leather being a heterogenous matrix with the right combination of three-dimensional structure along with required physical and chemical properties makes it a versatile material for its usage in the fashion industry. One drawback of such a breathable matrix is its poor resistance to stains and thus keeping it clean and hygienic is a challenging task.[1] Some of the methods available to overcome this problem includes a special selection of leathers that are free from the usage of non-ionic surfactants. In addition, proper selection of neutralization and dispersing agents is very critical in bringing about the washability property in leather. Moreover, use of silicone-based or fluoropolymer-based fatliquors, followed by metal capping results in washable leathers with the desired properties.

On the other hand, several researchers have focused on the production of textiles and leathers with superhydrophobicity[2–5] (i.e. those with high Water Contact Angle (CA) >150°). Owing to their unique self-cleaning, anti-contamination and anti-sticking properties, the need for washing can be reduced.[6–8] In order to realize this property, two major routes followed are i) reducing the surface free energy or ii) modifying the surface morphology of the materials. The superhydrophobic nature of lotus leaves, famously identified as the "Lotus leaf effect" confirms this phenomenon. The high surface roughness and minimal contact area between the leaf and the liquid is attributed to the unique micro-nano-binary structure on the lotus leaves. The high roughness causes a layer of air to become trapped under the water droplet, which acts as a barrier enabling the droplet to roll off from the surface.[9] Inspired by these natural structures, numerous superhydrophobic surfaces have been produced by means of a variety of techniques including plasma etching,[10] lithography,[11–13] selfassembly,[14] chemical vapor deposition (CVD),[15] electrospinning,[16] layer-by-layer deposition[17] and sol-gel processing,[18–20] generally followed by further chemical modification. The disadvantage of these techniques is that they implicate tedious and multistage processes, which restrict their large-scale application.

Recent advances in micro- and nano-fabrication techniques has diversified the fabrication methods and materials employed in leather processing varying from inorganic nanoparticles to bulk polymeric materials.[21,22] When incorporated into leather, polymeric materials improve the surface roughness and lower the surface free energy resulting in a superhydrophobic surface. Amongst the various available polymer-based materials, fluoropolymers are being increasingly employed as water repelling agents in textile industries. Water-based fluoropolymer coatings have some attractive properties, such as exceedingly low surface energy, low friction coefficients, repellency to both oil and water and relatively low permeability to

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most gases.[23–25] Even though there are several works carried out in this field, the impact of the hydrophobic or superhydrophobic coating on the physical properties of the finished leathers has not been studied in detail.

Thus, in the present work, a commercially available aqueous fluoropolymer-based binder was mixed with bentonite clay particles and used to impart hydrophobicity to the leathers. The prepared hydrophobic coating materials were then applied on the leather surface by spray coating technique. The hydrophobicity of the coated surface was measured in terms of contact angles. Eventually, the impact of polymeric coating on the leather properties such as water and air permeability, fastness and optical behavior were studied and presented in this research article.

Materials

Goat natural crust leathers were chosen as raw material. Bentonite clay with average particle size ranging between 15 to 20 microns was procured from M/S Sigma-Aldrich Pvt. Ltd. Two water-based fluorocarbon polymers (FCP-A and FCP-B), obtained from M/S ICAP leather chemicals, were chosen as waterproofing agents and used for the leather finishing trials. The chemicals procured were used as such without any further purification.

Application of fluorocarbon polymers for leather finishing trials

To initially identify the suitable fluorocarbon polymer out of the chosen, FCP-A and FCP-B, a neat coat of the polymer alone was sprayed and checked for its water repellency. Accordingly, 20% solution of the fluorocarbon polymers was directly sprayed on to the leather (crust) and the required tests were conducted based on the standard procedure as mentioned in each sub section. A 0.5 mm spray nozzle with a standard operating pressure of 50 to 70 psi was used to spray the samples from a working distance of 30 cm. Care was taken to ensure uniform spraying of the polymer in order to avoid excess deposition on the leather surface.

Preparation of water-based hydrophobic finish solution

Initially, required amount of bentonite clay (0 to 1.0 g at an interval of 0.25 g) was dispersed in deionized water and sonicated for 15 min using a Labman digital ultrasonicator with a working frequency of 20 kHz to obtain a uniform dispersion of the nanoparticles in the aqueous medium. After sonication, the chosen fluorocarbon polymer solution was added dropwise under vigorous mechanical stirring over a course of 5 min to ensure proper mixing. The obtained bentonite/fluorocarbon polymer composite BFCP-A-X (X implies the amount of bentonite used i.e. from 0 to 1.0 g) as shown in Table I. The prepared solution was then applied to the leather following the spray coating technique. The spray coated samples were then aged for 24 hours and taken up for further testing. The dry add-on of finish solution applied on the leather varied from 4.0 to 5.0 g/sq.ft depending upon the amount of bentonite used in the finish formulation.

Water contact angle (CA) measurement and surface morphology studies

Wettability characterization of the spray-deposited coating was done by measuring the contact angle values by the sessile drop method, wherein 5 µL of water were dispensed through a flat tip needle placed near the substrate. The images of the droplets were captured using a HO-IAD-CAM-01B contact angle meter from M/S Holmarc Opto-Mechatronics Ltd India. Each measurement was an average of three drops. The captured images were processed using ImageJ software along with Low-Bond Axisymmetric Drop Shape Analysis plugin for contact angle measurement.[26] To study the changes in the morphology of the leather before and after the coating process, the leather samples were visualized under a Scanning Electron Microscope (SEM). Samples from leathers were cut from the official sampling position. The surface microstructure was studied after gold sputtering using Bruker S-3400N sputter coater. All microscopic images were taken at the same magnification and compared against each other.

Air permeability and water vapor permeability (WVP) assessment

A capillary flow porometer from M/S Porous Materials Inc, USA was used to measure the pore size and distribution using leather

Table I

Solution preparation for different spray coating trials using bentonite combination with fluorocarbon polymer

Experiment	Bentonite clay added (g)	Fluorocarbon polymer (g)	Pigment (g)	Solution make up volume with water (g)
BFCP-A-1	1.00	20	5	100
BFCP-A-0.75	0.75	20	5	100
BFCP-A-0.5	0.50	20	5	100
BFCP-A-0.25	0.25	20	5	100
FCP-A alone	0 (Control)	20	5	100

samples of 20 mm diameter. Initially, a non-reacting gas was sent through the experimental samples followed by wetting with liquid of known surface tension (Calwick, surface tension 15.9 dynes cm^{-1}). The changes in flow rate were measured as a function of pressure for both dry and wet processes. WVP of the leathers were determined by following the standard method described in ISO 20344:2022-6.6. This test method was intended to determine the ability of water vapor (steam vapor) to permeate through the leather in terms of milligram per unit area and for a specified period of time. This test method works on the principle of absorption and permeation of moisture vapor between two distinct humidity levels between the grain & flesh surfaces of the leather.

Fastness properties of the finished leather

The fastness properties of the finished leather were studied by evaluating the color changes after circular rubbing action following ISO 17700:2019-Method B. This is mainly used to assess the degree of damage and transfer of a material's surface color or finish onto the rubbing felt during mild dry and wet rubbing. A specimen of finished leather is rubbed in a circular fashion using a white wool felt of 25 mm diameter under force. After a specified number of cycles of rubbing, the extent of damage to the color/finish and color transfer to the rubbing felt are assessed with grey scales.

Results and Discussion

Wetting behavior of the finished leathers

The wetting behavior of any surface plays a major role in the development of hydrophobic coatings that are capable of repelling water droplets upon contact. The hydrophobicity of any surface is generally classified based on the contact angle (CA) that a water droplet makes with the surface and is classified as hydrophilic when CA is lesser than 90° and hydrophobic if CA is 90 to 150° and superhydrophobic if CA is greater than 150°. To create a hydrophobic surface, as explained in the introduction section, a go-to system is through combination of low surface energy coatings along with micro- to nano-scale roughness. Thus, in this study, two fluorocarbon polymers (FCP-A and FCP-B) were chosen to create a non-polar low energy surface and used contact angle measurements as a tool to evaluate the fabricated surface. Though the contact angle method can help in understanding the hydrophobicity of the leather samples, the method has some drawbacks. Due to the fibers sticking out from the surface of the sample, the determination of the baseline of the water droplet is more difficult, which may in turn lead to possible underestimation of the CA data.[27–29]superhydrophobic surfaces should be able to form a composite interface with air pockets in the valleys between asperities (pillars Additionally, the protruding fibers may exhibit forces on the water droplet making it difficult to yield accurate values for advancing and receding CAs. Thus, in this work, we only measure and report static CAs for 5 µL water droplets.

The contact angle of the crust leather was at 45° which could be mainly attributed to the capillary action of the hair pore present on the grain surface and thus leading to the immediate absorption of water droplet within few seconds. The contact angle of the 20% fluorocarbon polymer only coated leather increased to 98° for FCP-A and 67° for FCP-B polymers as shown in Figure 1. This increase in the CA could be attributed to the fluorine present in the polymeric backbone, leading to a creation of low polar surface and the water droplet stayed on the surface without being absorbed in case of FCP-A coated leather while the water droplet was absorbed within 30 seconds in case of FCP-B coated leather. Thus, it can be seen that the FCP-A coated leather was in the hydrophobic region in terms of contact angle and thus improving hydrophobicity was attempted further by incorporating roughness to the polymer coated surface using bentonite clay particles. But, in case of FCP-B, there was not much improvement from the control leather and the contact angle still remained in the hydrophilic region and thus the FCP-B polymer was not further considered for this work.

Bentonite clay particles are known to improve the chemical resistance apart from introducing the roughness in polymer nanocomposites. Additionally, bentonite being an inert material can

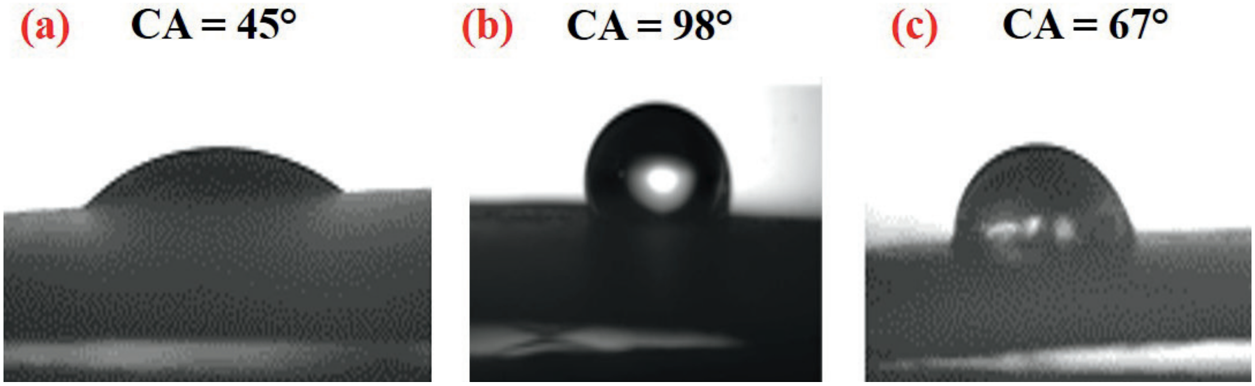

Figure 1. Water droplet contact angle images of **(a)** untreated crust leather (control), **(b)** leather coated with FCP-A polymer alone and **(C)** leather coated with FCP-B polymer alone by spray method.

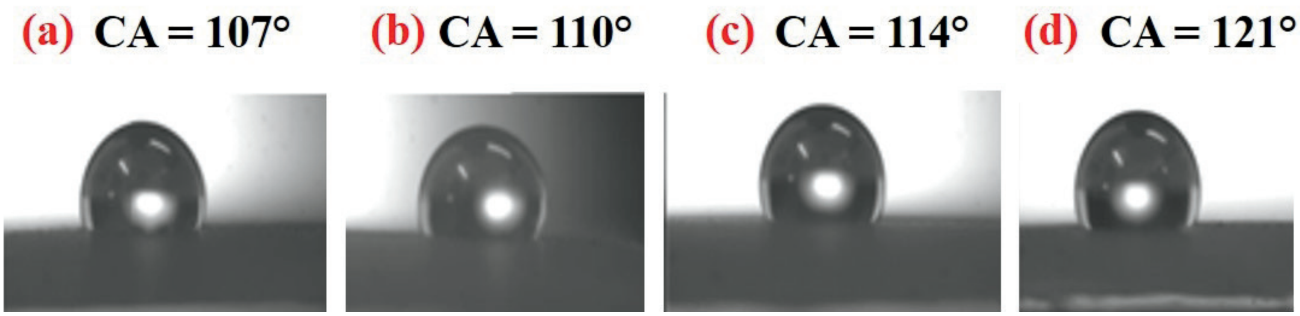

Figure 2. Contact angle of leather surfaces coated with **(a)** BFCP-A-0.25, **(b)** BFCP-A-0.50, **(c)** BFCP-A-0.75 and **(d)** BFCP-A-1.

also act as filler and its alkaline nature aids in uniform dispersion and improves its compatibility with the anionic charged binders used in leather finishing process.[30] Accordingly, the bentonite clay particles were added to the finish solution ranging from 1.25 to 5% (w/w) based on the weight of fluorocarbon polymer. It was found that the contact angle of the coated surfaces after incorporating the bentonite clay particles increased as expected, which could be attributed to the formation of micro- and nano-roughness along with the low surface energy of the fluorocarbon polymer. As a result, this synergistic effect increased the contact angle from 98° degrees of FCP-A only coated leather to 121° for BFCP-A-1 coated leather as shown in Figure 2. With respect to the BFCP-A-0.25 to 1.0, the measured contact angles were 107°, 110°, 114° and 121°, respectively as shown in Figure 2. But increasing the bentonite concentration further did not increase the contact angle and this could be attributed to the agglomeration of clay particles leading to reduction in the roughness created on the surface. This could be attributed to the larger particle size of bentonite clay leaving a very small window to achieve the maximum loading without agglomeration. But the loading efficiency without agglomeration could be maximized by using nano sized particles instead of micro particles to create the surface roughness of micro-nano scale that can even enhance the hydrophobicity of the surface.[5,31] Therefore, it can be concluded that by introducing roughness on the surface using bentonite clay particles along with the polymer of low surface energy, it is possible to drastically increase the hydrophobicity of the coated surfaces.

Surface morphology of the finished leathers

To study the influence of the morphology of the surface on the wetting behavior, SEM images of leather before and after coating with FCP-A alone and BFCP-A-1 were captured and compared. From the SEM images of uncoated crust leather, it could be seen that grain structure of the sample was fibrous and clean without any damage. Besides, the hair pores of leather were markedly large, while microstructures of leathers were denser and homogeneous in morphology. It can be seen from Figure 3 (a & b), that the surface of the uncoated leather showed grooves and cracks. In contrast, in case of the SEM micrographs of the FCP-A only coated leather, such morphological characteristics were covered by the film formed on the surface. The surface was found to be smooth due to the uniform continuous film that is formed by the fluorocarbon polymer as shown in Figure 3 (c & d). With the addition of the bentonite into the finishing solution, a uniform distribution of clay particles could be clearly seen on the surface of the leather. This deposition created the roughness required for improving the hydrophobicity of the coating on the leather surface which could be clearly seen in Figure 3 (e & f). Further, the equal distribution of bentonite particles on the leather surface was ascertained using EDAX mapping technique. In the Figure 3 (g, h & i), it can be clearly seen that the aluminum (1.486 keV) and silicon (1.740 keV) are equally distributed throughout the leather surface.

Air and water vapor permeability of the finished leathers

In order to study the effect of the finish coat on the breathability property, water vapor and air permeability tests were conducted and compared in case of polymer only coated leather along with bentonite incorporated polymer coated leather. Measurement of air permeability can be determined rapidly by Capillary flow porometry (CFP) technique.[25] In this regard, CFP measurements were carried out for crust leather, FCP-A only coated leather and BFCP-A coated leather. Generally, the permeability of leathers gets reduced after the finishing process mainly due to the formation of a continuous film on the surface, which hinders the movement of water molecules. Accordingly, as shown in Figure 4, the flow rate of the gas increased to the maximum with respect to the increase in pressure in case of crust leather (without finishing coat) in comparison to the other polymer coated leathers. Interestingly, the air flow rate was higher for the bentonite incorporated finishing system in comparison to the polymer alone coated leather. This could be attributed to the creation of pores/in-continuity in the finish film upon the addition of bentonite as shown in Figure 3 (e & f) leading to the formation of channels that can allow the air to diffuse through the finish film easier.[32] Even though the air flow rate increased for BFCP-A-1 coated leather in comparison to that of the FCP-A only coated leather, it was rather not much significant enough to be quantified and compared against the crust leather. Thus, to further quantify the breathability of the BFCP-A-1 coated leather and FCP-A only coated leather as

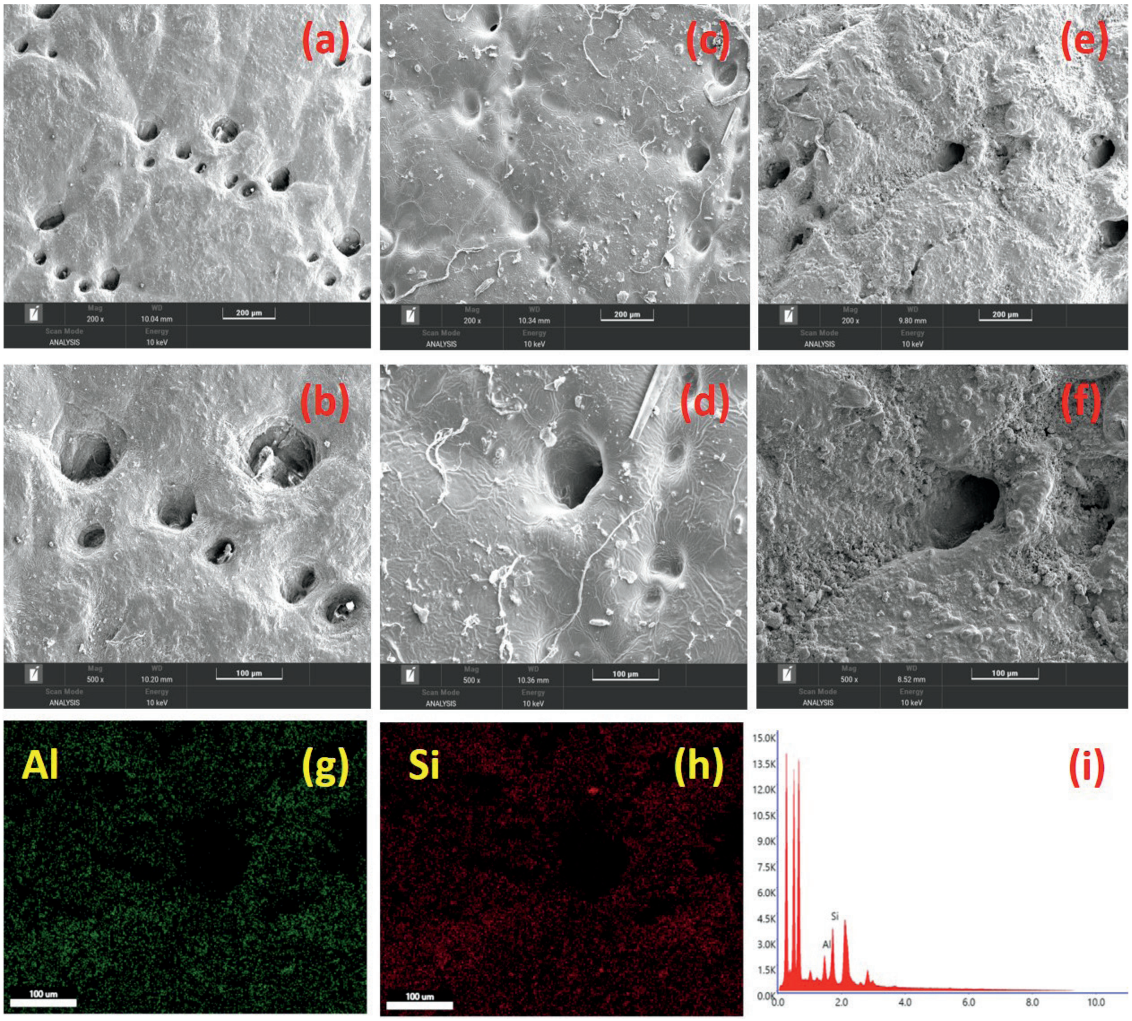

Figure 3. SEM images of untreated leather **(a & b)**, FCP-A only coated Leather **(c & d)** and BFCP-A-1 coated leather **(e & f)** at 200 µm and 100 µm respectively. EDAX - Elemental mapping and spectra of bentonite particles on leather surface **(g, h & i)**.

against the control crust leather, the water vapor permeability of the leathers was measured and compared.

The water vapor permeability of the crust leather and the polymer coated leathers were measured and the results of the measurement is tabulated in Table II. As expected, the water vapor permeability (WVP) of the crust leather was found to be highest at 8.7 mg/cm^2/hr. Meanwhile, the polymer coated leathers showed decreased WVP. It could be seen that the WVP values increased approximately from 3.4 to 12.9% in comparison to that of the FCP-A alone coated leathers. Similar to the air permeability studies, it was found that the WVP of the leathers coated with bentonite incorporated polymers were higher than the polymer alone coated leathers thus confirming the proposed hypothesis. Additionally, it was found that with the increase in the bentonite concentration, the WVP values also increased confirming that in the presence of higher amounts of clay particles, the increase in the porosity/in-continuity of film helps in increasing the movement of water vapors through the film

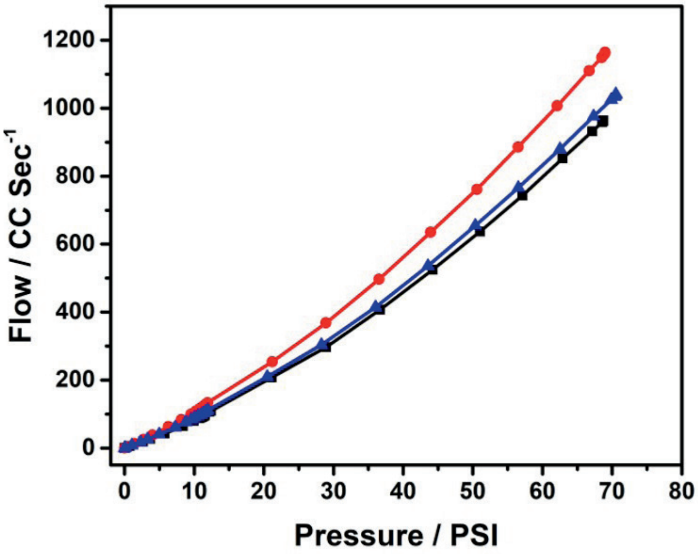

Figure 4. Capillary flow porometry analysis of crust and polymer coated leather samples - (red circles) Crust leather, (blue triangles) BFCAP-A-1 coated leather and (black squares) FCP-A only coated leather

Table II

WVP of the crust leather and polymer coated leather

Sample name	WVP (mg/cm²/hr)	% Retention in WVP as against crust leather	% Increase in WVP values as against FCP-A leather
Crust leather	8.7	-	-
FCP-A alone coated leather	4.4	50.6	-
BFCP-A-0.25	4.7	54.0	+ 3.4
BFCP-A-0.50	5.0	57.5	+ 6.9
BFCP-A-0.75	5.5	63.2	+ 12.6
BFCP-A-1.00	5.7	65.5	+ 12.9

thus enhancing the water vapor permeability values. Still, from the results, it could be seen that the WVP values were much higher than the required standard of 2.0 mg/cm^2/hr. Thus, even though a polymeric finish coat decreases the breathability of the leather due to the continuous nature of film formed, it can be improved by incorporating clay like particles which can mimic the action of pore-forming agents and in turn enhance the required properties.[33]

Fastness properties of the finished leather

In order to study the effect of the hydrophobic coating on the fastness properties of the leather, the light fastness, wet and dry rub fastness of the crust and polymer coated leather samples were assessed. It was found that the polymer coating enhanced the rub fastness values which could be attributed to the formation of a protective film by the polymeric binder. However, it was observed that as the hydrophobicity of the surface increased, the fastness properties especially the wet rub fastness improved, which could be mainly attributed to the increase in the contact angle of the leather leading to a disruption in the interaction between the water and dye molecules present in the leather.[34] Thus, the fastness characteristics of leather treated with polymer combined with bentonite clay showed an increase as compared with the leather treated with polymers alone as shown in Table III.

Optical properties of the finished leather

Though the presence of clay-incorporated hydrophobic coating on the leather surface helped enhance the permeability of air and water vapor, and fastness properties of the leather, it imparted some negative effects on the optical properties of the same. First, a mild yellow tint was observed with the addition of the bentonite clay particles upon the formation of finish film. Thus, to check this, the CIELAB L*, a* and b* values of the finished leathers coated only with the polymer and polymer-bentonite combinations were measured and compared as shown in Table IV.

Table III

Results of fastness characteristics

Sample name	Dry 512 rubs	Wet 256 rubs
Crust leather	4	3
FCP-A alone coated leather	4	3/4
BFCP-A-0.25	4	4
BFCP-A-0.50	4	4
BFCP-A-0.75	4/5	4
BFCP-A-1.00	4/5	4

Table IV

Color coordinates of crust leather and finished leathers.

Sample name	L*	a*	b*
Crust leather	79.02	-2.70	7.66
FCP-A alone coated leather	77.43	-2.53	9.56
BFCP-A-0.25	77.31	-2.02	10.25
BFCP-A-0.50	76.58	-2.11	10.87
BFCP-A-0.75	76.65	-2.05	11.64
BFCP-A-1.00	76.87	-2.00	12.38

Here, the L* represents lightness value measured from 0 to 100 wherein, the higher the number the lighter the color is, while a* represents the balance between red (positive) and green (negative) and b* represents the balance between yellow (positive) and blue (negative). Though the L* value and a* values were not much affected, the b* value increased from 7.66 for crust leather to 12.38 for BFCP-A-1 coated leather in the positive side. This could be attributed to the inherent cream-colored nature of the bentonite clay particles. Though the color is light, it could be masked with proper pigment mixtures. However, its effect on white colored leathers could be a bit challenging.

Conclusions

The treatment of leather surfaces using selected fluorocarbon polymer and bentonite clay mixture can impart hydrophobicity character to the leathers. The treatment of leather with the polymer containing relatively higher concentrations of bentonite clay showed better contact angle values than the polymer alone coated leather due to the increase in surface roughness. The hydrophobic coating increased the rub fastness, and air and water vapor permeability properties of the leather while it had a negative impact on the optical properties of the leather, mainly the color. Still, this method to impart hydrophobicity to leather surfaces is a relatively simple procedure and has venues for commercial applications in future to fine tune the properties required for a specific set of leather finishing system.

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