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Analysis of Variations in Porosity of Metal Crosslinked Collagen Matrix

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ABSTRACT: The fundamental knowledge of the porous nature of crosslinked collagen matrix such as tanned leather is an aid to design appropriate chemicals for leather making. It would also help to target a particular area of matrix to improve its uniformity and other functional properties. The purpose of this study is to analyze the variations in pore sizes of chromium crosslinked collagen matrix, chrome tanned leather, from different animal species and different areas of the same species. In this study, chrome tanned leather from goat and sheep were investigated for surface area, pore size, and distribution. Thermoporometry results show that average pore radius of goat leather is around 2–30 nm and that of sheep is 2–20 nm. Nitrogen adsorption result shows that average surface area of goat (8.24 m^2/g) leather is higher than sheep (6.73 m^2/g), but the average pore diameter of goat (289 nm) is smaller than sheep (385 nm) leather. It has been found that more numbers of smaller pores are present in goat than sheep leather and all the leather samples including goat and sheep obeyed type-III adsorption isotherm. Capillary flow porometry analysis gives the smallest, largest, and mean-flow-diameter of through-pores. The average size of largest throat pore diameter of sheep (1313 nm) is smaller than that of goat (1385 nm) leather. In general, the pore volume distribution of sheep leather is higher than that of goat leather. Morphological analysis using scanning electron microscopy shows that pore mouth of goat is deeper than that of sheep. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40835.

KEYWORDS: biomaterials; crosslinking; porous materials

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INTRODUCTION

Animal hides/skins serve as the main raw material for leather manufacturing. Type-1 collagen is the predominant protein present in skin matrix. The architectural marvel of collagen present in skin matrix has been investigated and reported earlier.[1–3] The chemical composition and structural organization of collagen in the supramolecular level is same for different types and different areas of skin. However, the macromolecular structure viz., packing arrangement of fiber, fiber density, and angle of weave, and other physiochemical properties are not uniform throughout the matrix and are different for different types of skin matrix.[4–6] The irregular pattern of macromolecular structure makes the skin matrix heterogenic. Due to this, skin contains different types of pores, with size ranging from micro (< 2 nm), meso (2–50 nm) to macro (> 50 nm), and different nature of pores such as blind pore, open pore, closed pore, and through-pore.

Leather processing mainly involves three different steps, namely, pretanning, tanning, and post-tanning. Noncollagenous protein and fat are removed during the pretanning operation, whereas enzymatic and thermal stability are imparted during tanning process. The heterogeneity of matrix is further increased during pretanning and tanning processes.[7,8] The main objective of the post-tanning process is to increase the homogeneity of matrix and also to impart color and lubrication to the fibers. Diffusion of post-tanning chemicals and the efficiency of post-tanning process are strongly influenced by the pore sizes, pore size distribution, pore connectivity, charge of tanned leather, size, and the charge of post-tanning chemicals.

Zettlemoyer et al. estimated the internal surface area of untanned hide and formaldehyde tanned leather using water and nitrogen adsorption technique.[9] Later on, Kanagy estimated the macro pores in leather matrix using mercury intrusion porosimeter.[10] Fathima et al. studied the effect of hydrothermal shrinkage on internal surface area and porous nature of untanned leather.[11] The changes in pore structure of skin during leather processing and the effect of crosslinking agents on pore structure of skin matrix have been investigated.[12,13] Recently Gil et al. analyzed the variations in porous nature and water vapor permeability of the skin by using mercury intrusion porosimeter, nitrogen adsorption, and water-vapor sorption isotherm, after it has been subjected to various treatment process such as dehydration, pickling, crosslinked with chromium, and vegetable tannins.[14] However, thorough investigation on the

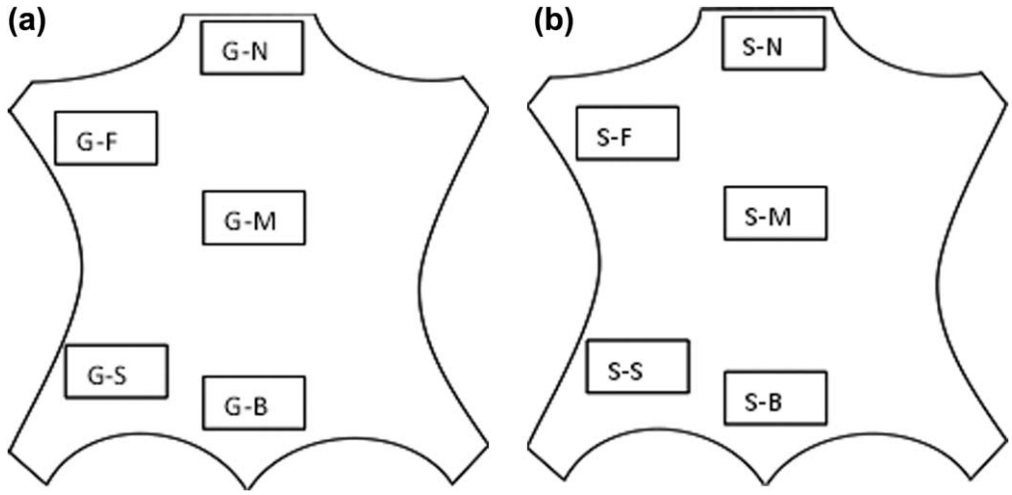


Figure 1. (a) Goat sampling position. (b) Sheep sampling position.

porosity of tanned leather of different species of animals, and mapping of pores in different areas of same leather has not yet been carried out.

The focus of this study is to analyze the pore size and distribution of pores in different areas of the of goat and sheep chrome-tanned leather (wet-blue). This is the first attempt to compare the variations in porous structure of leathers made from goat and sheep and also to compare the variations in different areas of the same. It is well known that to understand the porous nature of a material like skin one porometry technique will not suffice. Hence, in this study, we have investigated the porous nature by using thermoporometry, nitrogen adsorption, capillary flow porometry, and scanning electron microscopy on different areas of goat and sheep chrome-tanned leather.

MATERIALS AND METHODS

Chromium crosslinked collagen matrix (wet-blue) of goat and sheep were made as per standard procedures.[15] The sampling was done at different areas of goat and sheep wet-blue leather as represented in Figure 1(a,b), respectively. The samples from each area were subjected to thermoporometry, nitrogen adsorption, capillary flow porometry, and scanning electron microscopy analysis.

Thermoporometry Analysis

Differential scanning calorimeter (Q-Series 200 TA Instruments) was employed for thermoporometry analysis. The samples from different areas of goat and sheep wet-blue (3–5 mg), having moisture content about 65%, were blotted uniformly to remove surface water and then hermetically encapsulated in aluminum pans. The sample was immediately cooled to −40°C and held for 15 min at this temperature to ensure that water inside all pores were frozen. Heating was performed from −40 to 5°C at the heating rate of 1°C min^{-1}. The pore radii and pore volume distribution was calculated from thermogram details as reported earlier.[16]

Nitrogen Adsorption Measurements

The samples from different areas of both goat and sheep wet-blue leathers were dehydrated as per the standard procedure.[17] The samples were uniformly cut into small pieces in order to avoid the sampling error. The nitrogen adsorption-desorption isotherms were recorded at 77 K using Sorptomatic 1990 analyzer. The samples were outgassed in the analyzer degas port for 16 h at 298 K prior to use. The surface area was calculated from the Brunauer-Emmet-Teller (BET) method. The average pore size and pore size distribution curve were determined from desorption isotherm using the model proposed by Barrett, Joyner, and Halenda (BJH). The total pore volume (Vp) was obtained from the amount of vapor adsorbed at a relative pressure of about 0.99.

Capillary Flow Porometry Analysis

PMI capillary flow porometer (Porous Material) was used in this study to analyze the pore size and its distribution. The dehydrated samples from different areas of goat and sheep wet-blue leathers were cut into pieces 20 mm diameter and the thickness was noted. Calwick with a defined surface tension of 15.9 dynes cm^{-1} (Porous Material) was used as wetting liquid for porometry measurements. In this technique, at first a non-reacting gas was sent through a dry sample. Second, the same sample was wetted with liquid of known surface tension, through which the above mentioned gas was sent. The changes in flow rate were measured as a function of pressure for both dry and wet processes. For every sample, wet and dry profiles (pressure vs. gas flow rate) were measured. From these plots, the pore size was calculated by the software from Porous Materials using the following equation:

$$D = \frac{4\gamma \cos\theta}{p} \quad (1)$$

where, D is pore diameter; γ is surface tension of the wetting liquid (15.9 dynes cm^{-1}); θ is contact angle of the wetting liquid; p is differential pressure. By using dry flow and wet flow curve, we can also determine largest pore diameter, mean flow pore diameter, and pore size distribution.[18–20]

Scanning Electron Microscopy Analysis

Surface and cross-section morphology of the samples were studied using scanning electron microscope (A JEOL JSM−5300).

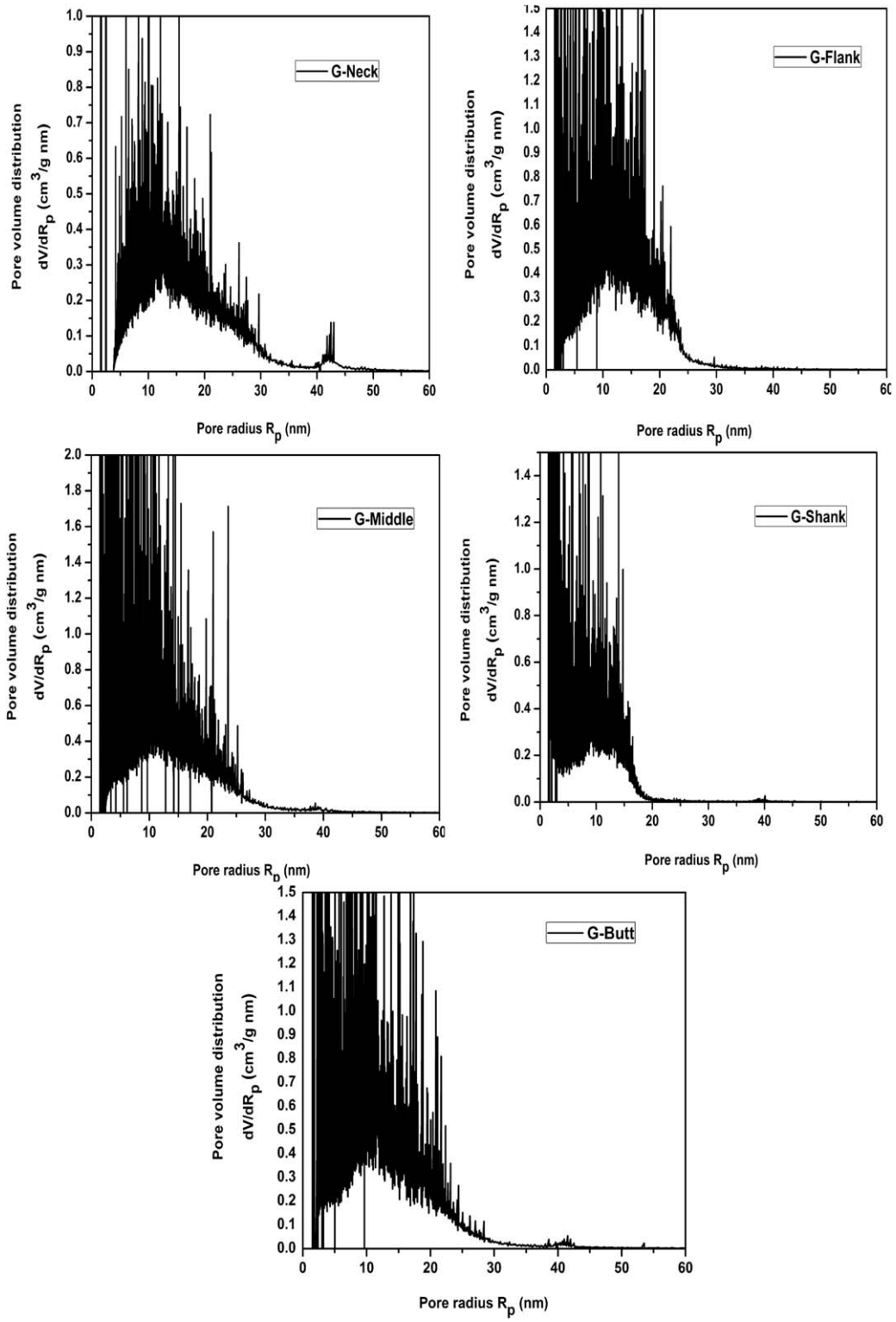


Figure 2. (a) Thermoporometric investigation on different areas of goat wet-blue leather. (b) Thermoporometric investigation of different areas of sheep wet-blue leather.

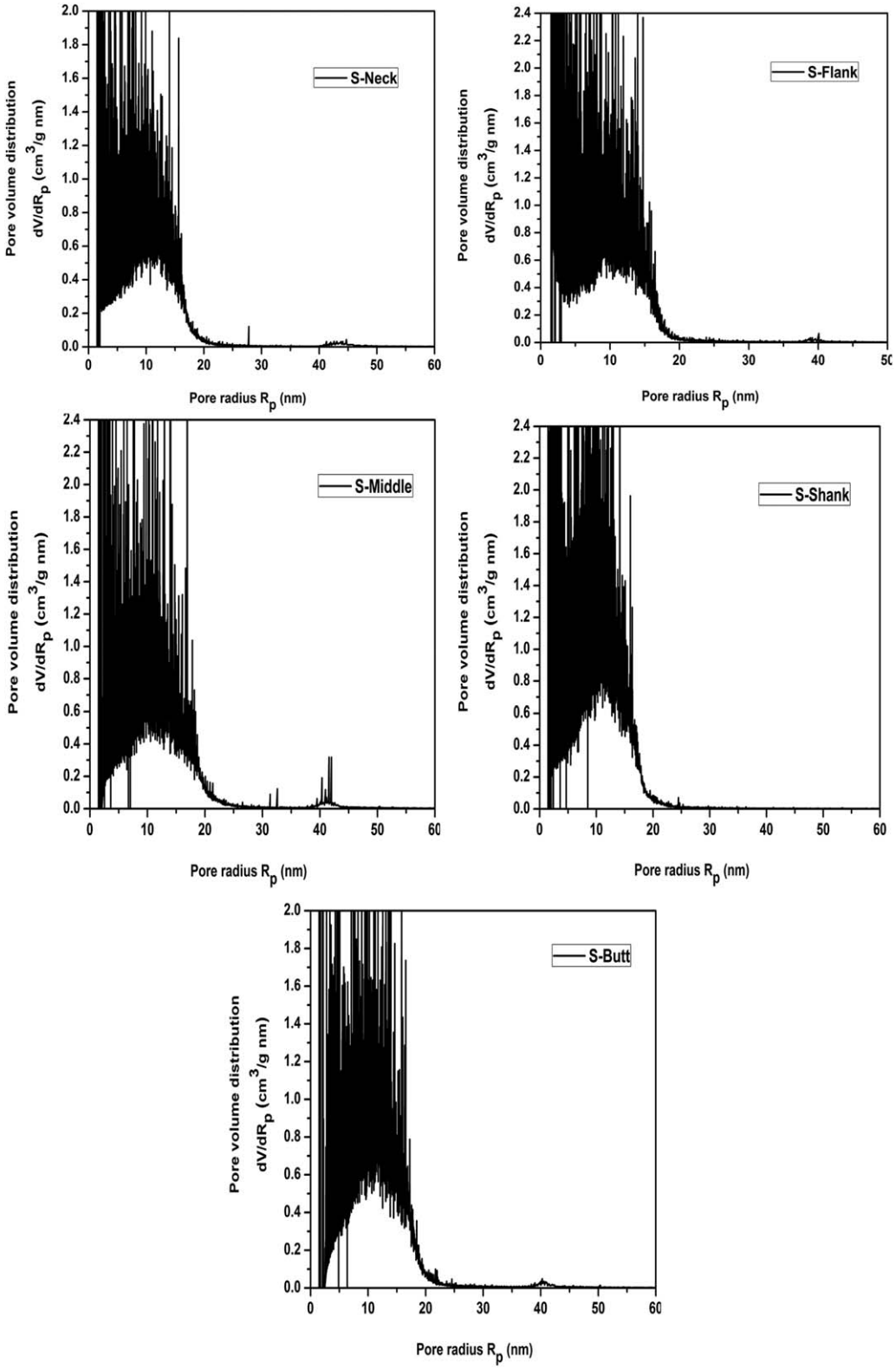


Figure 2. (Continued).

Table I. BET Surface Area, Total Pore Volume and Pore Size of Different Areas of Goat and Sheep Wet-Blue Leather

	BET surface area (m^2/g)		Total Pore volume (cm^3/g)		Pore size (A°)[a]	
Area	Goat	Sheep	Goat	Sheep	Goat	Sheep
Neck	6.98	9.29	0.042	0.068	279.14	297.30
Flank	12.16	5.04	0.074	0.054	276.32	429.01
Middle	5.61	6.25	0.040	0.068	359.13	446.16
Shank	9.14	7.26	0.053	0.066	249.43	372.10
Butt	7.29	5.79	0.046	0.050	282.45	384.42
Average	8.24 ± 2.5	6.73 ± 1.6	0.051 ± 0.013	0.061 ± 0.010	289.3 ± 41	385.8 ± 58

[a] BJH desorption average pore diameter.

All specimens were coated with gold using a JEOL JFC−1100E ion−sputtering device before analysis.

RESULT AND DISCUSSION

Thermoporometry Analysis

Thermoporometry is a suitable tool for studying the porous nature of solid in wet condition. It is based on the thermodynamic relationship between pore size and melting temperature of frozen solvent present in the pore, the pore size, the pore volume, the pore shape, and the internal surface area of a wet solid are determined.[21–25] The principle of thermoporometry is based on Gibbs-Thomson effect (A small crystal of a liquid melts at lower temperature than bulk liquid crystal). Brun et al. described the full thermodynamic relationship involved in thermoporometry technique.[26] Differential scanning calorimetry technique is generally used to trace the melting temperature of ice crystals embedded in porous materials. The relationship between pore radius (Rp) and melting temperature of ice crystals present in difference pore size is given by the eq. (2):

$$Rp = \frac{-32.33}{T - T_0} + 0.68 \quad (2)$$

where, R_p: pore radius, T_0: melting temperature of pure solvent (Water: 0°C), and T: melting temperature of frozen solvent in different pore size. The pore volume distribution is estimated by using eq. (3):

$$\frac{dV}{dR_p} = \frac{\Delta V}{T_i - T_{i+1}} \quad (3)$$

where, ΔV: pore volume.

The obtained calorimetric information has been substituted in eqs. (2) and (3) to get the pore size and pore volume distribution, respectively. A graph has been plotted for pore size versus pore volume to compare the porous nature of goat and sheep wet-blue leather at different areas. The results of thermoporometric investigation on different areas of goat and sheep wet-blue leather are shown in Figure 2(a,b), respectively. It is evident from Figure 2(a) that neck area of goat wet-blue has pore radius in the range of 5–45 nm, but the pore population is low when compared with other areas of goat wet-blue.

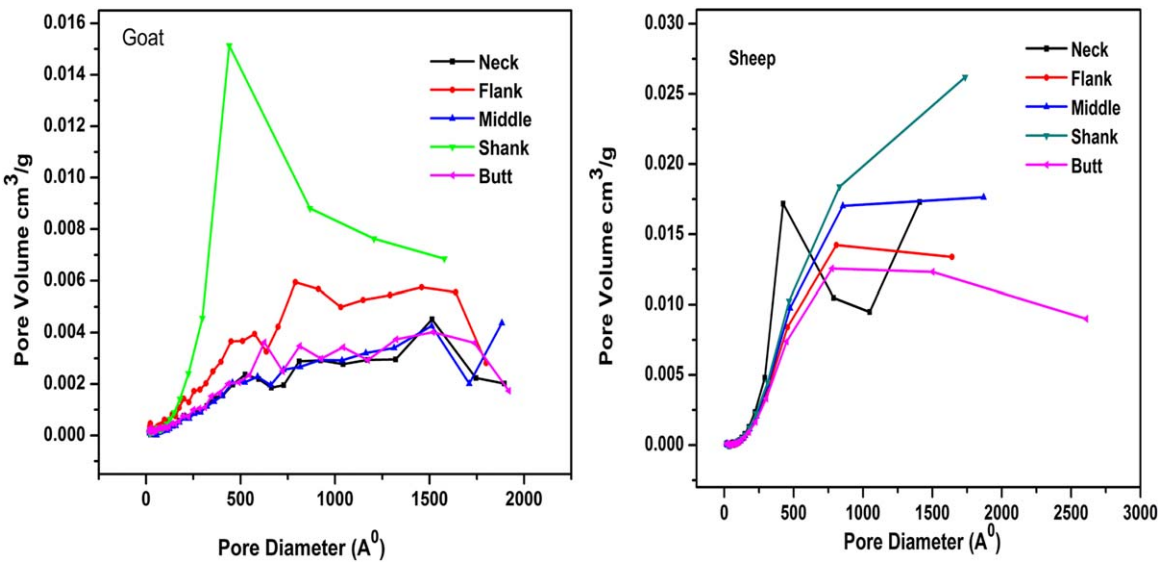


Figure 3. BJH desorption pore distribution of goat and sheep wet-blue. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Capillary Flow Porometry Results Obtained from Different Areas of Goat Wet-Blue

Area (Goat)	Pore diameter (nm) S.D*	M.D*	L.D*	Analysis of the results
Neck	106	397	1154	• In the case of neck area, the pore diameter ranges between 106 and 397 nm permeates 50% of the air flow although the pore size is small. Even when the pore size is larger (between 397 and 1154 nm) only 50% of the air flows through that pore range. • This result clearly indicates that the pore intensity (distribution) is higher and narrower in the pore diameter range of 106–397 nm. • This helps us to conclude that the uniformity of pore size below the size of mean flow pore diameter (M.D), which is 397 nm, is relatively higher when compared with the pore size above mean flow pore of 397 nm. A similar phenomenon has been observed in flank and shank areas. • Whereas in the case of middle and butt areas, wide range of pores are present below the M.D than above the M.D. • This leads us to conclude that the uniformity of pore size above the M.D is relatively higher as compared with the pore size below the M.D. • It is also observed from the results that the largest throat pore diameter is bigger for flank and shank area as compared with other areas of goat wet-blue.
Flank	158	456	1980	
Middle	108	767	974	
Shank	149	327	1432	
Butt	132	881	1387	
Average	130 ± 23	565 ± 243	1385 ± 380	

S.D*: Smallest throat pore diameter; M.D*: Mean flow pore diameter; L.D*: Largest throat pore diameter.
Note: Pores smaller than M.D* permeates 50% of the air flow and the other 50% of the air flow is through pores larger than the M.D*.

It is also evident from Figure 2(a) that flank area has pore radius ranging from 2 to 25 nm and has uniformity in pore population throughout the range. From these results, it can be concluded that flank area has more number of pores than other areas. The pore size (2–30 nm) and pore intensity is almost similar for middle and butt areas. The shank area has pore size distribution in the range 2–20 nm. The pore size and pore size distribution of different areas of sheep wet-blue leather is shown in Figure 2(b). It can be seen from the figure that all the areas of sheep have pore size around 2–20 nm but the pore population and pore volume distribution is not same. Flank and shank areas have more pore intensity and pore volume than other areas. There is no considerable difference has been observed between neck, middle, and butt areas. It has been observed from Figure 2(a,b) that pore volume of sheep leather is higher than that of goat leather.

Table III. Capillary Flow Porometry Results Obtained from Different Areas of Sheep Wet-Blue

Area (Sheep)	centerPore diameter (nm) S.D*	M.D*	L.D*	Observation
Neck	153	269	1191	• In the case of neck area, the pore diameter range between 153 and 269 nm permeates 50% of the air flow though the pore size is small. Even when the pore size is larger (between 269 and 1191 nm) only 50% of the air flows through that pore range. • This result clearly indicates that the pore intensity (distribution) is higher and narrower in the pore diameter range of 153–269 nm. • This helps us to conclude that the uniformity of pore size below the size of mean flow pore diameter (M.D), which is 269 nm is relatively higher as compared with the pore size above mean flow pore of 269 nm. The similar phenomenon has been observed in all the areas of sheep wet-blue. • It is also observed from results that the largest throat pore diameter is smaller for shank and neck areas than the other area of sheep wet-blue.
Flank	263	617	1318	
Middle	108	433	1566	
Shank	149	390	1126	
Butt	132	421	1364	
Average	161 ± 59	426 ± 125	1313 ± 170	

S.D*: Smallest throat pore diameter; M.D*: Mean flow pore diameter; L.D*: Largest throat pore diameter.
Note: Pores smaller than M.D* permeates 50% of the air flow and the other 50% of the air flow is through pores larger than the M.D*.

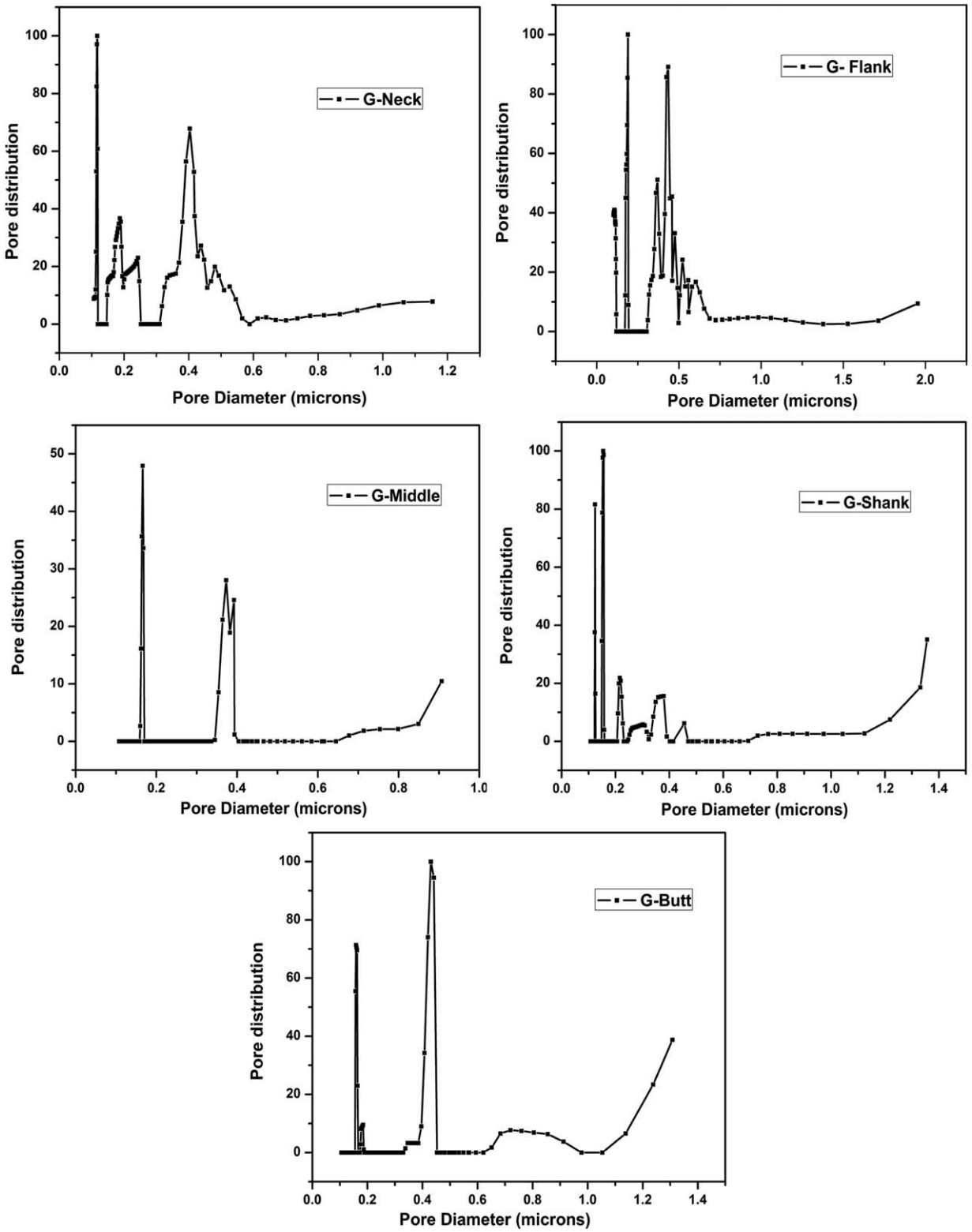


Figure 4. (a) Pore size distribution of different areas of goat wet-blue leather measured by capillary flow porometry analysis. (b) Pore size distribution of different areas of sheep wet-blue leather measured by capillary flow porometry analysis.

Nitrogen Adsorption Measurements

Thermoporometry analyzes the pore size by tracing the melting temperature of water crystals present in the pore. The melting temperature depends on size of water crystal present in the pore and not on the nature of pore. Nitrogen adsorption technique (BET) is generally used to determine the surface area as well as size and volume of small-size through-pores and blind pores present in the porous matrix.[27–29] Hence, nitrogen adsorption

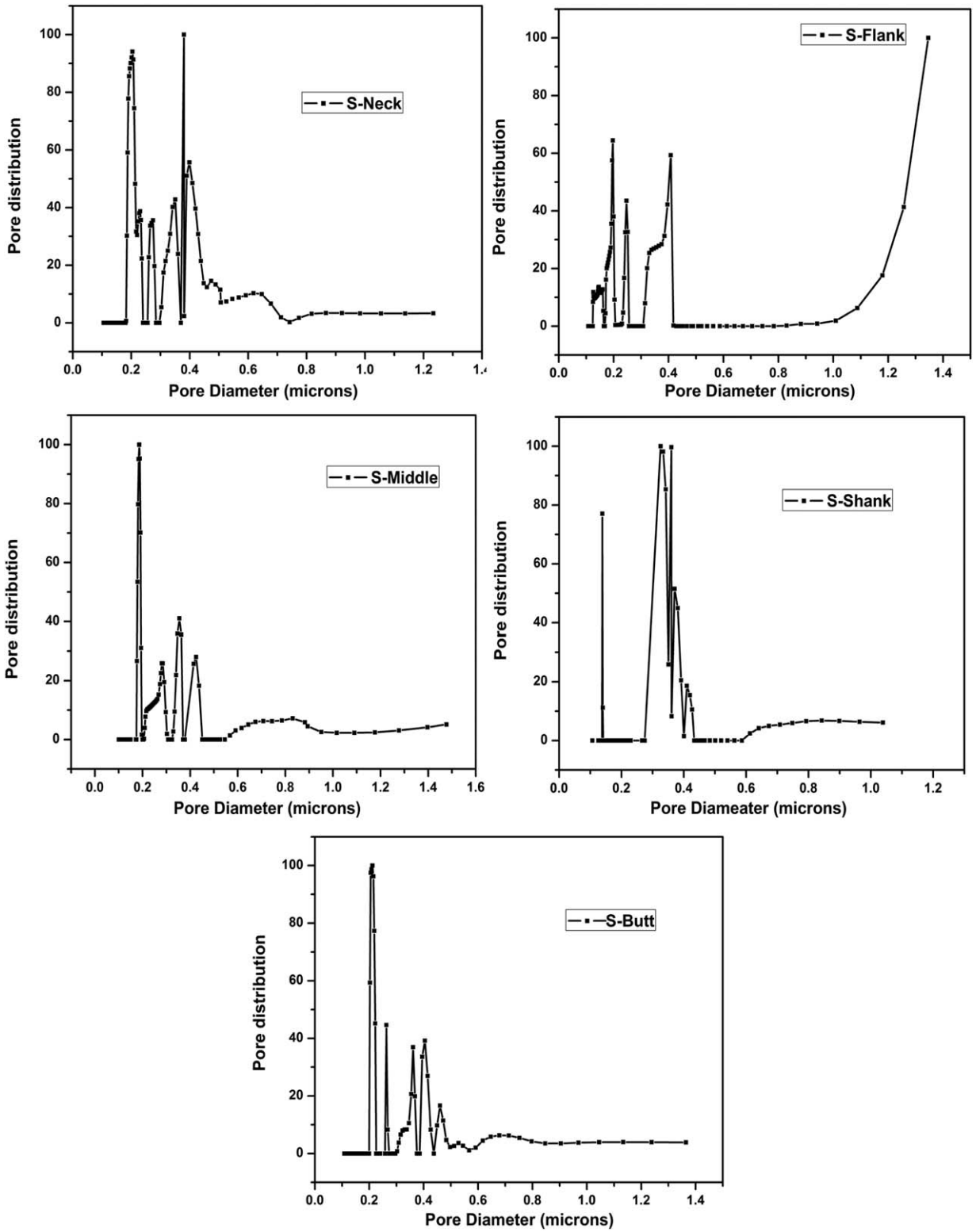


Figure 4. (Continued).

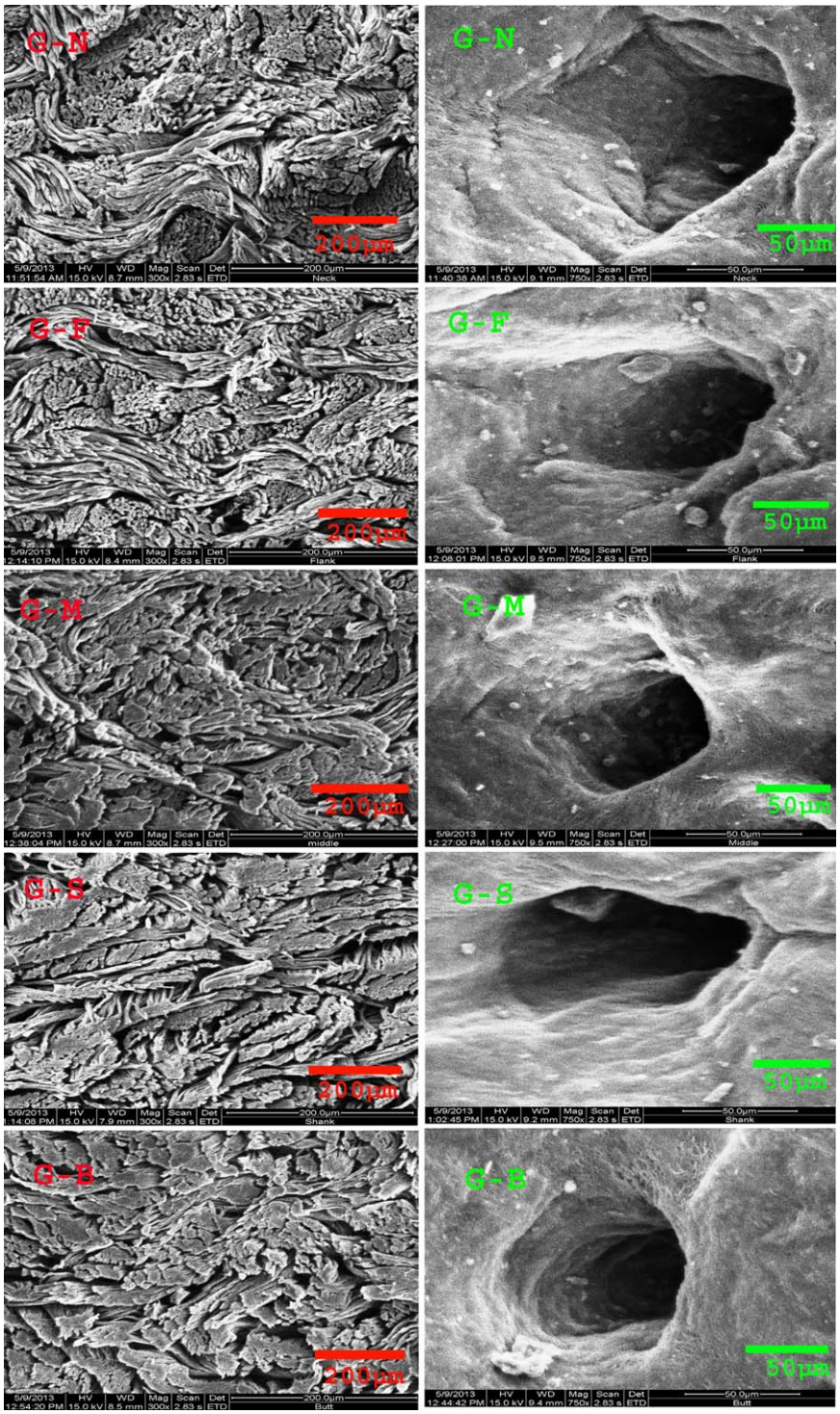


Figure 5. (a) Scanning electron micrographs of cross-section (300× magnification, 200 µm scale) and grain surface (750× magnification, 50 µm scale) of different areas of goat wet-blue leather. (b) Scanning electron micrographs of cross-section (300× magnification, 200 µm scale) and grain surface (500× magnification, 100 µm scale) of different areas of sheep wet-blue leather. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

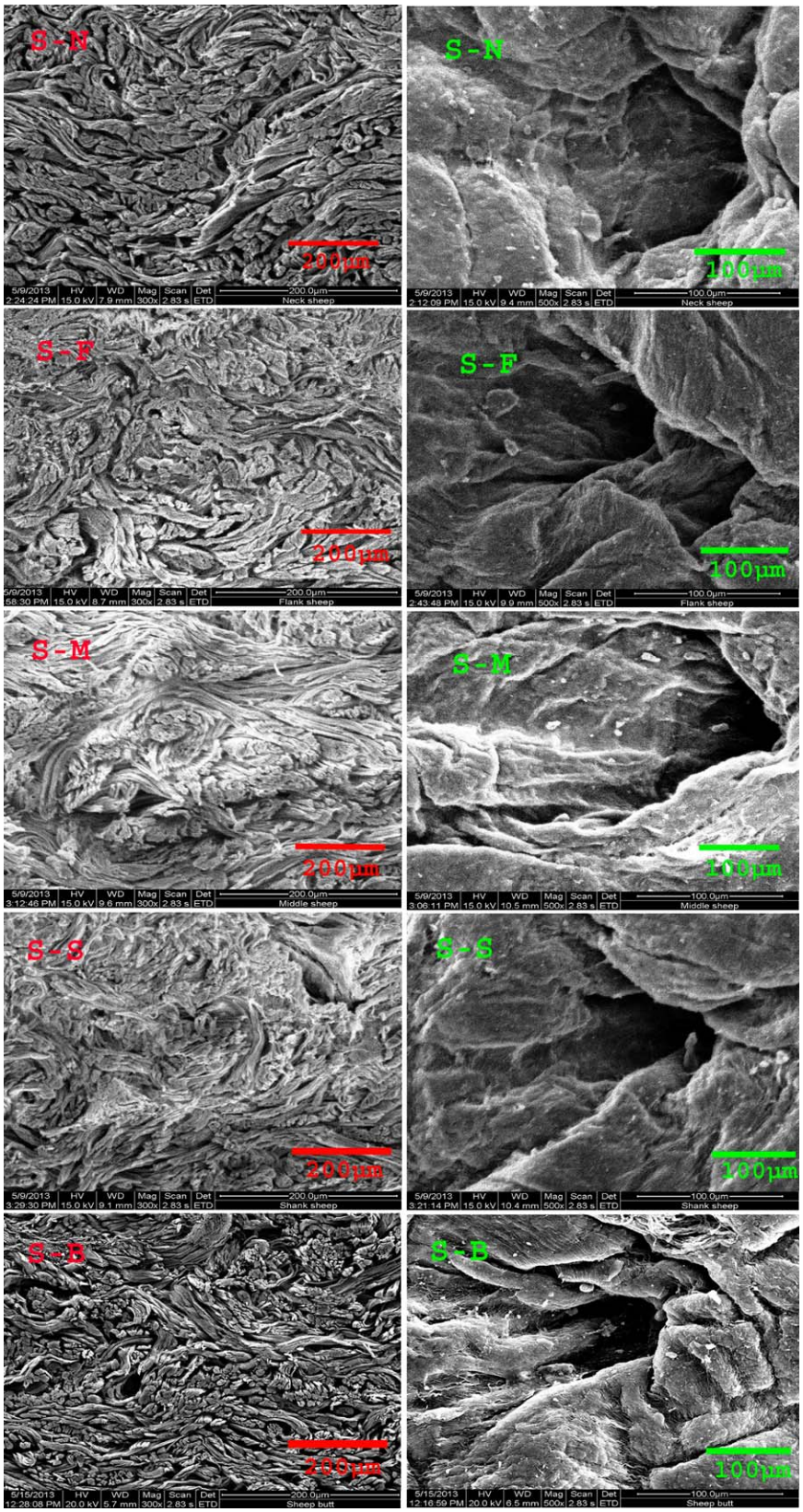
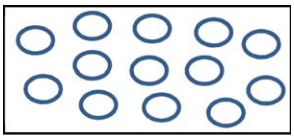
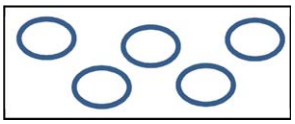
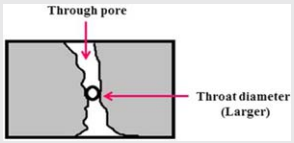
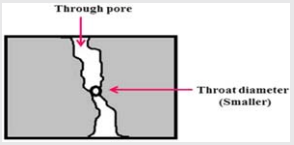


Figure 5. (Continued).

Table IV. Comparison of Salient Features of Goat and Sheep Wet-Blue Leather

	Features	
Technique Name	Goat	Sheep
Thermoporometry	• Average pore radius range from 2 to 30 nm but pore volume distribution is lesser than sheep.	• Average pore radius range from 2 to 20 nm and pore volume distribution is higher than goat.
Nitrogen adsorption	• BET surface area is high (8.24 m^2/g). • Lesser pore volume (0.051 cm^3/g) than sheep. • Average pore diameter is smaller (289.3 nm) than sheep.  • It is evident from the above results that goat wet-blue leather has more surface area with smaller pore diameter. • Therefore, more numbers of smaller pores are present in goat wet-blue.	• BET surface area (6.73 m^2/g) is smaller than goat. • Pore volume (0.0612 cm^3/g) is higher than goat. • Average pore diameter (385.8 nm) is bigger.  • In the case of sheep wet-blue, leather pore diameter is larger with smaller surface area. • From the above results, we can conclude that sheep wet-blue leather have lesser numbers of pores with larger diameter.
Capillary flow porometry	• It measures only the throat diameter of through pore. • Average diameter of largest throat pore (1385 nm) is bigger than sheep. 	• In the case of sheep, largest throat pore diameter is 1313 nm. 
Scanning electron microscopy	• Pore mouth is deeper than sheep.	• Pore mouth is not deeper than goat.

measurements have been carried out on different areas of both goat and sheep wet-blue leathers. It has been observed that all the samples exhibit type-III adsorption isotherms (IUPAC classification). The BET surface area, total pore volume, and BJH desorption average pore diameter, of different areas of goat and sheep wet-blue leather are summarized in Table I.

It can be observed from the Table I that the flank and shank areas of goat have more surface area and total pore volume than other areas. But, the average pore diameter is smaller than that of other areas. From this observation, we can conclude that a higher number of small through-pores and blind pores are present in the shank and flank areas of goat. Middle area has less surface area (5.6132 $m^2\ g^{-1}$) and large pore size (359 Å). In the case of sheep, the observation is slightly different from goat. Flank area has less surface area (5.0498 $m^2\ g^{-1}$) and larger pore size (446 Å). In both the cases, goat and sheep, middle area has larger pore size than any other area. The BJH pore size distribution of different areas of goat and sheep is presented in Figure 3. It is observed that shank areas of goat and sheep wet-blue leather have pore size distribution in the range of 500–1500 Å and 750–2000 Å, respectively. Other areas of goat and sheep leather have pores up to 2500 Å.

Capillary Flow Porometry Analysis

Capillary flow porometry is a simple and nondestructive technique that allows rapid measurement of pore size and distribution by tracing the gas pressure and flow rates through dry and wet samples. As we know, the skin matrix contains different types of pores having irregular cross-sections and pore diameters along the pore path. In capillary flow porometry, the presence of throat pore is detected by increasing the pressure of gas, which removes the liquid from the pore and allows the gas to flow through.[30,31] Throat (or) constricted pore plays an important role in leather manufacture. The complete diffusion of leather chemicals into the skin matrix depends on the size of throat-pore and the size of leather chemicals. In principle, the size of the chemical should be smaller than the throat-pore diameter for complete diffusion. The knowledge on the throat-pore diameter of different areas of two different raw materials would help in designing completely diffusible molecules. This may enhance the process efficiency and reduce the process time. In this regard, capillary flow porometry measurements have been carried out for different areas of goat and sheep wet-blue leather. The smallest throat pore diameter is obtained from the pressure at which the wet and dry curves meet. The largest throat diameter of through-pore is obtained from the

pressure needed to initiate flow through a wet sample. The largest throat pore is also called as bubble point pore and the corresponding pressure is called as bubble point pressure.

The mean flow pore diameter is computed from the mean flow pressure: the pressure at which wet-flow curve and half-dry flow curve intersect is called mean flow pressure. Pores smaller than the mean flow pores permit 50% of the flow and the other 50% of the flow is through pores larger than the mean flow pore. Tables II and III contain the results of capillary flow porometry of different areas of goat and sheep wet-blue leather, respectively. Figure 4(a,b) show the measured pore size distribution function V_s pore diameter of different areas of goat and sheep wet-blue leather, respectively.

It is evident from Figure 4(a) that neck area of goat has pore size in the range of 0.2–0.6 μm, whereas in case of middle and butt areas, most of the pores are around 0.4 μm, whereas in flank area it is around 0.3–0.7 μm. It is seen from Figure 4(b) that flank area of sheep wet-blue has wide range of pore size (0.2–1.2 μm) distribution than other areas. Middle and butt area of sheep wet-blue are found to have similar pore size distribution in the range of 0.3–0.5 μm. Around 80% of pores are present in the range between 0.3 and 0.5 μm in the shank area of sheep.

Scanning Electron Microscopy Analysis

Surface morphology (grain surface of the leather) and cross-sectional view of different areas of goat and sheep wet-blue leather have been investigated through scanning electron microscopy analysis and the results are presented in Figure 5. It can be seen from Figure 5(a) that pore-mouth of neck, middle and butt areas of goat wet-blue are deeper than flank and shank area. Fiber diameter of neck and flank area is almost similar but the fibers are compact in the case of neck area. Middle and butt areas are showing cemented fiber than other areas of goat wet-blue leather. Fibers are loosely packed in the case of shank area. Figure 5(b) shows the cross-section and grain surface of different areas of sheep wet-blue leather. When compared with goat wet-blue leather, it was observed that sheep wet-blue leather has lower pore-mouth depth and the pores are interconnected. The splitting of fiber in case of sheep is more when compare to goat wet-blue leather, which indirectly states that porosity of sheep is more than goat wet-blue. Comparison of salient features of goat and sheep wet-blue leather is given in Table IV.

CONCLUSION

Pore size and pore size distribution are known to be strongly interrelated with heat and mass transfer of leather matrix. The bulk and other physical strength properties of final leather are greatly improved in post-tanning process. The nature of raw materials and post-tanning chemicals influence the final properties of leather. In this study, a thorough investigation on the pore size and distribution, and the surface area, of goat and sheep wet-blue leather has been made. The porosity of different areas of goat and sheep wet-blue leather has been studied using thermoporometry, nitrogen adsorption, capillary flow porometry, and scanning electron microscopy. Each technique has measured the different pore size and nature of pore present in sheep and goat wet-blue leather. Thermoporometry results show considerable difference in pore size and pore population in different area of goat and sheep wet-blue leather. It has been observed that the average pore radius of goat wet-blue is around 2–30 nm, whereas in case of sheep it is around 2–20 nm. It has also been found that pore volume distribution of sheep leather is more than that of goat leather. From the BET analysis as referred above goat wet-blue has smaller pore size and more BET surface area than sheep wet-blue leather. But, the pore volume of sheep wet-blue is more than that of goat wet-blue. The results from capillary flow porometry show that the smallest throat diameter of goat wet-blue ranges from 100 to 150 nm, whereas sheep range from 150 to 325 nm. Goat wet-blue has largest throat diameter of around 1100–1450 nm, whereas sheep wet-blue has 1200–1560 nm. It has been observed from the scanning electron micrographs that pore-mouth of goat wet-blue is relatively deeper than that of sheep wet-blue. This study may give an opportunity to leather technologists to design appropriate post-tanning molecules for targeting a particular area or type of skin matrix, which may enhance the process efficiency and conserve the processing time and chemical usage.

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GLOSSARY

G-N: Goat Neck area

G-F: Goat Flank area

G-M: Goat Middle area

G-S: Goat Shank area

G-B: Goat Butt area

S-N: Sheep Neck area

S-F: Sheep Flank area

S-M: Sheep Middle area

S-S: Sheep Shank area

S-B: Sheep Butt area

BET: Brunauer-Emmett-Teller isotherm

Throat diameter: Size at the most constricted part of the through-pore

S.D: Smallest throat pore diameter is obtained from the pressure at which the dry and wet curve meet

M.D: The mean flow pore diameter is computed from the mean flow pressure-the pressure at which wet-flow curve and half-dry flow curve intersects is called mean flow pressure.

L.D: The largest throat diameter of through pore is obtained from the pressure needed to initiate flow through wet sample.

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