Kirk-Othmer Encyclopedia of Chemical Technology.

LEATHER-LIKE MATERIALS

Leather (qv) has been employed for many uses since ancient time on account of the convertibility of an easily decomposed substance into one which resists putrefaction. Leather is still an important material with its unique structure; it is so dense in texture that it resists wind and water while retaining breathability and flexibility, which makes the resulting goods comfortable. Early attempts to imitate leather included application of oil, rubber, or soluble cotton onto paper or fabrics. However, very little progress had been made until the era of synthetic resins began in the twentieth century.

In the second quarter of the twentieth century, with the development of poly(vinyl chloride), nylon, polyurethane, and other polymers, many new and improved leather-like materials, so-called coated fabrics (qv), were placed on the market. Shortages of leather after World War II led to the expansion of these leather-like materials ("man-made" leathers) to replace leather in shoes, clothing, bags, upholstery, and other items. Durability and waterproof qualities superior to leather made coated fabrics advantageous, in spite of imperfection in breathability and flexibility. Demands for shoes, clothing, and other items are still increasing due to growing world population and urbanization.

During the third quarter of the twentieth century, with improved nonwoven fabrics, man-made leathers finally succeeded in simulating leather to such an extent that they are nearly identical in appearance, physical properties, and structure. These leathers have enjoyed success in all leather-use areas. With the technology of microfibers, they continue to evolve both in quality and quantity.

1. Types of Leather-Like Materials

Leather-like materials now important in the market are of three main classes: (*1*) vinyl-coated fabrics, (*2*) urethane-coated (synthetic) fabrics, and (*3*) man-made leathers. To appreciate their leather-replacement capabilities it is necessary to know the structure of natural leather.

1.1. Leather

Natural leather is made from hides, which are salted and cured, then tanned. Through the preparing process, useless matter which cannot be tanned, such as outerskin (epidermis) and flesh, are removed, leaving the true skin (corium). In the tanning process, the fluid matter which maintains the skin in a flexible and moist condition is removed, and there remains nothing but the fibrous portion to be acted on by the tanning chemicals (1–3).

As a result, leather is made up of interlaced bundles of collagen fibers (Fig. 1). A schematic model of collagen bundles in leather is shown in Figure 2 (4). A collagen bundle (about 80 μm in diameter) is made up of collagen fibers (1–4 μm), composed of microfibrils (0.08–0.1 μm). Furthermore, a microfibril consists of many protofibrils (about 1.5 nm), which consist of several bundles of polypeptide chains.

Fig. 1. Cross-sectional view of natural leather.

Such a unique hierarchical structure gives leather several advantages: (*1*) transformability into any desired shape, (*2*) resistance to penetration of wind, water, and other materials, (*3*) breathability (water vapor and air permeability, and water absorption), (*4*) flexibility, and (*5*) processibility into finished forms having a grain or suede surface.

1.2. Vinyl-Coated Fabrics

Leather substitutes are designed to imitate the appearance of leather with its grain surface. This requirement has been accomplished by coating substances that are capable of forming a uniform film, and was first met by plasticized poly(vinyl chloride) (PVC). A leather-like material termed vinyl-coated fabric was developed in the 1930s in the United States and Germany. Shortages of leather after World War II spurred the expansion of this material.

The construction of vinyl-coated fabrics varies according to its application. A vinyl-coated fabric used for automobile seat covers is shown in Figure 3; a woven fabric is the substrate. The material is durable but stiff and heavy. Incorporating an expanded foam structure into the coating layer reduces the weight (Fig. 4), and replacing the woven substrate fabric with a soft knit fabric improves flexibility.

Vinyl-coated fabrics exhibit high density, extremely low water vapor and air permeability, cold touch, poor flex endurance, and plasticizer migration. However, they have good scratch resistance and colorability and are inexpensive.

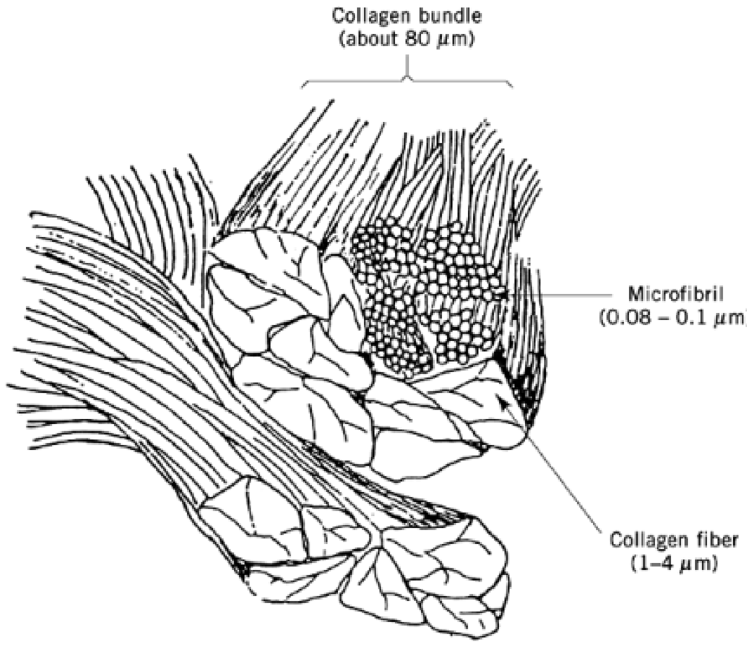

Fig. 2. Schematic model of collagen fiber bundle in natural leather.

1.3. Urethane-Coated Fabrics

Urethane-coated fabrics, termed synthetic leather, were developed in the 1960s by applying a coat of polyurethane (PU) onto a woven or knit fabric. Polyurethane is flexible at room temperature without a plasticizer due to its low glass-transition point ($<0°C$). Urethane-coated fabrics are manufactured by drying a cast polyurethane solution to form a film which is laminated onto a substrate. An improvement in appearance, feel, and resistance to grain break is achieved by using a brushed fabric as the substrate, which is laminated with a cast polyurethane film. Further improvement in flexibility is achieved by the introduction of poromerics, which provide polyurethane with a porous structure by using a solvent that permits coagulation with a nonsolvent. Thus poromeric urethane-coated fabrics are produced by applying an organic solvent solution of polyurethane to a brushed woven fabric and then immersing the fabric in a nonsolvent bath for coagulation, followed by coating with a cast polyurethane film (Fig. 5). With poromerics, urethane-coated fabrics can be employed for many uses. On the other hand, woven or knit fabric substrates still limit their application, due to low conformability. In making three-dimensional shaped goods, such as shoes, the material must conform to the shape of a last (shoe form) and maintain it after the last has been removed.

1.4. Man-Made Leathers

These materials were developed in the 1960s by combining the technologies of poromerics and nonwoven fabrics. Substitution of nonwoven fabric for knit or woven fabric increased conformability, and eliminated this limitation in application (5, 6). Most early man-made leathers, such as Du Pont's Corfam, had a three-layer structure containing a thin woven fabric inserted between a nonwoven fabric and a coating layer to compensate for the unevenness of the nonwoven fabric. However, this woven fabric stiffens the resulting three-layer products, which were hence not widely accepted. Clarino (Kuraray Co., Ltd.) has a two-layer structure utilizing a novel

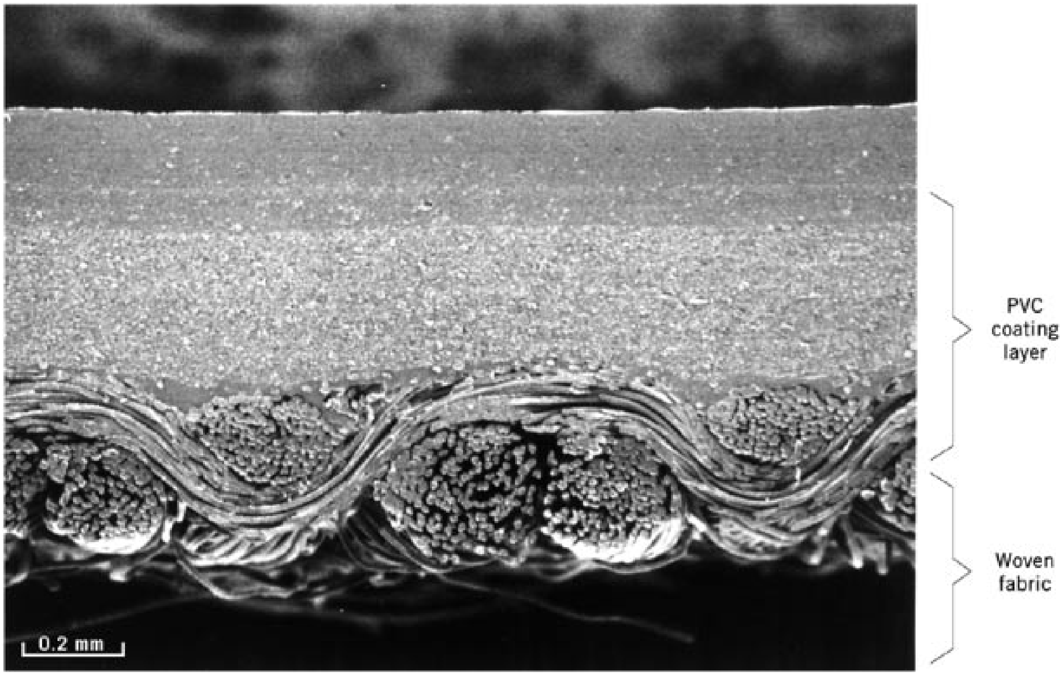

Fig. 3. Cross-sectional view of vinyl-coated fabric with PVC coating layer.

nonwoven fabric impregnated with polyurethane and coated with a layer of continuous micro-pores (Fig. 6). Grain-type man-made leathers are mostly of this two-layer structure.

Significant improvement in the fiber structure of leather is finally achieved by using microfibers as fine as 0.001–0.0001 tex (0.01–0.001 den). With this microfiber, a man-made grain leather Sofrina (Kuraray Co., Ltd.) with a thin surface layer (Fig. 7), and a man-made suede Suedemark (Kuraray Co., Ltd.) with a fine nap (Fig. 8) were first developed for clothing, and have expanded their uses. Ultrasuede (Toray Industries, Inc.) also uses microfibers with a rather thick fineness of 0.01 tex (0.1 den). Contemporary (1995) man-made leathers employ microfibers of not more than 0.03 tex (0.3 den) to obtain excellent properties and appearance resembling leather.

2. Physical and Chemical Properties

The properties of leather-like materials depend on the polymer used for substrate and coating layer. Feel, hand, and resistance to grain break are affected by the construction. The polymers and constructions of leather-like materials are shown in Table 1. Physical properties of leather and leather-like materials are shown in Table 2.

2.1. Weight, Thickness, and Density

The thickness differs according to application. Vinyl-coated fabrics are very heavy and dense. Urethane-coated fabrics and man-made leather are very light and two-thirds to one-half leather in density.

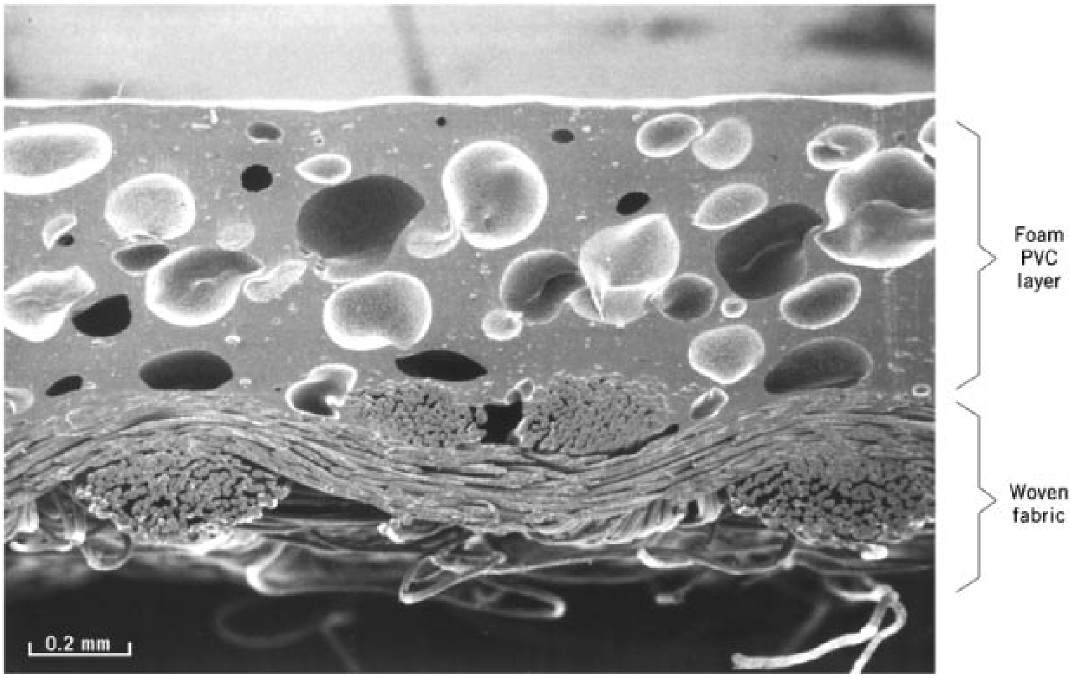

Fig. 4. Cross-sectional view of vinyl-coated fabric with PVC foam layer.

Table 1. Constructions of Leather-Like Materials

		Substrate	
Material	Coating[a] layer polymer	Structure	Polymer
man-made leather	polyurethane (segmented)	nonwoven	nylon, polyester, acrylics
urethane-coated	polyurethane (segmented)	knit or woven	cotton, rayon, nylon, acrylics, polyester, and others
vinyl-coated	PVC	knit or woven	cotton, rayon, acrylics, nylon, polyester, and others

[a] Structure is solid and/or porous.

2.2. Strength and Elongation

The tensile strength and elongation depend mostly on the substrates. Woven fabric substrates give a steep slope in the stress–strain (S–S) curve with a small elongation at break, and knit and nonwoven fabric substrates give a gentle slope with large elongation. In making shoes which need lasting, a good balance of strength and stretch and a high conformability is desirable. Nonwoven fabrics, especially those comprising poromerics with microfibers, are the best for these shoes.

2.3. Water-Vapor Permeability

Water-vapor permeability depends on the polymer used for the coating layer and its structure. Vinyl-coated fabrics have little water-vapor permeability due to the coating layer. Although polyurethane polymer is water-vapor permeable, urethane-coated fabrics also have low permeability values due to their solid layer structure.

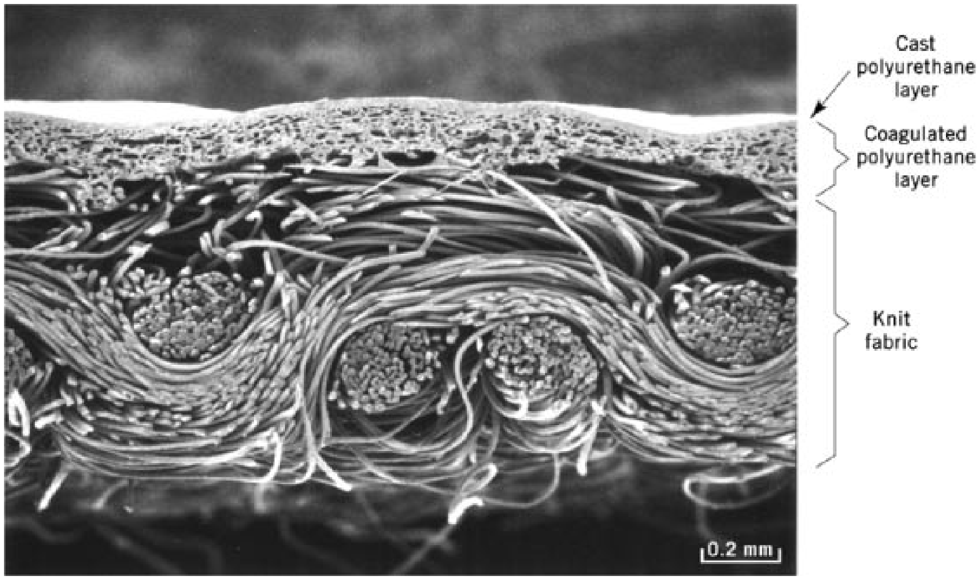

Fig. 5. Cross-sectional view of urethane-coated fabric with coagulated polyurethane layer.

On the other hand, man-made leathers have good permeability values as high as that of leather due to their porous layer structure. The permeability of grain-type is lower than that of suede-type, influenced by finishing method.

2.4. Durability

Flex endurance is correlated with water-vapor permeability, s vand man-made leathers have the best durability. Scratch resistance is inversely correlated with water-vapor permeability, and vinyl-coated fabric has the best performance. Durability for aging depends on the polymer used for the coating layer, because the polymer of the substrate fabric is generally more durable than that of the layer. Vinyl-coated fabrics are sufficiently durable. The durabilities of urethane-coated fabrics and man-made leathers vary to a large extent depending on the polyurethanes used because the physical and chemical properties of segmented polyurethanes markedly vary according to the segment type (see Urethane polymers). Polyurethanes degrade because of water, oxygen, NO_x, SO_x, and other chemical substances. Hydrolysis, degradation by H_2O, is the most important factor in the durability of polyurethanes, and it depends on the soft segments used. Soft segments are classified into three groups: polycarbonates, polyethers, and polyesters, and have better resistance to hydrolysis in this order. The components of a polyurethane can be selected according to the end use. Polyesters and polyethers are mainly used; polycarbonates are used for items especially requiring durability, such as in automobiles.

2.5. Other Properties

With respect to dry-cleanability, vinyl-coated fabrics are worse than the others due to dissolution of plasticizer in the cleaning solvent. Only man-made leathers with poromeric nonwoven can be skived, split, and cut in the same manner as leather.

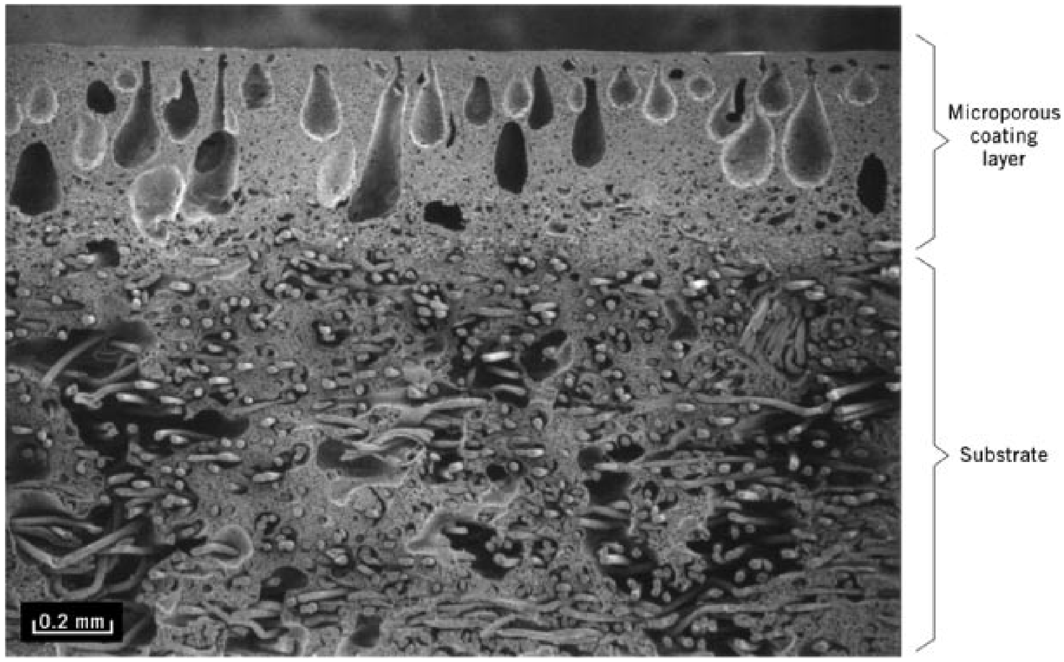

Fig. 6. Cross-sectional view of Clarino.

3. Manufacture and Processing

3.1. Vinyl-Coated Fabrics

Manufacturing methods for vinyl-coated fabrics now available are calendering and extrusion for thick layer, and paste coating for thin layer. Both solid and foam vinyl-coating layers are used.

In the calendering method, a PVC compound which contains plasticizers (qv) (60–120 phr), pigments (qv) (0–10 phr), fillers (qv) (20–60 phr), stabilizers (10–30 phr), and other additives, is kneaded with calender rolls at 150–200°C, followed by extrusion between clearance-adjusted rolls for bonding onto the substrate. This method is employed for products with thick PVC layers, ie, of 0.05–0.75 mm thickness. The main plasticizer used is di-2-ethylhexyl phthalate (DOP). For filler to reduce cost, calcium carbonate is mainly used. A woven or knit fabric made of cotton, rayon, nylon, polyester, and their blend fiber is used as substrate. For foamed vinyl-coated fabrics, the bonded materials are heated in an oven to decompose the foam-blowing chemicals. Most foam-blown vinyl-coated fabrics are finished to have a solid coating layer to improve scratch resistance.

Another method is extrusion; the PVC compound is kneaded in an extruder, and then extruded through a T-die for bonding onto a substrate.

In the paste coating method, a PVC paste, which contains emulsion-polymerized PVC and additives, is applied onto a substrate and heated to gelation before fusion to produce a coating layer. This method is employed for products with a thin layer, ie, of 0.007–0.05 mm thickness. For foamed vinyl-coated fabrics, a substrate is laminated onto a transfer paper on which a PVC paste containing a foam-blowing agent has been applied and gelled. After removal of the transfer paper, the paste is blown.

These processes may be followed by heat treatment and pressing with engraved rolls to produce the desired grain surface.

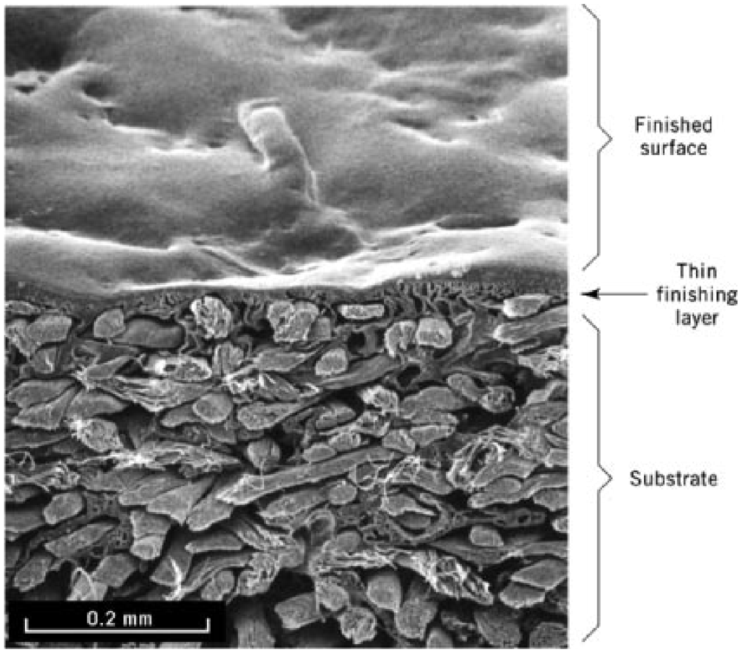

Fig. 7. Cross section of Sofrina 45° diagonally cut.

3.2. Urethane-Coated Fabrics

Manufacturing methods for urethane-coated fabrics are the dry system and the wet system.

In the dry system, the coating layer consists of two or three layers, for which a solvent-soluble linear polyurethane and a two-component cross-linkable polyurethane are employed. The former is used for the top and/or middle layers, and the latter for the bottom layer, ie, adhesive layer. The solvent contains dimethylformamide (DMF), methyl ethyl ketone (MEK), 2-propanol, toluene, or other solvents, to accelerate drying. Manufacture proceeds by the following sequence: (*1*) 100 g/m^2 of a 10% polyurethane solution is applied onto a transfer paper which carries a grain pattern, and dried in an oven; (*2*) 100 g/m^2 of a 40% two-component polyurethane solution which is composed of a polymer diol and a polyisocyanate, is applied on the first layer and then slightly dried to a tacky state, to form an adhesive layer; (*3*) a substrate is laminated onto the adhesive layer thus formed and passed through an oven and rolled up, and the roll is cured at 40–60°C for 2–3 days; and (*4*) after completion of the cross-linking, the transfer paper is removed from the finished urethane-coated fabric. There are several modifications: (*1*) the first operation is repeated for a middle layer before the second operation; (*2*) drying is omitted in the second operation; (*3*) a linear polyurethane solution is used for second operation; and (*4*) the fourth operation is followed by a finishing process if required, such as color shading. For the substrate, a woven or knit fabric made of cotton (qv), rayon, nylon, polyester, or their blends is used.

In the wet system, manufacture proceeds as follows: (*1*) a 7–20% polyurethane solution of DMF is applied onto a fabric and immersed in water containing 0–10% of DMF for coagulation; (*2*) the coated fabric is washed and dried; (*3*) the surface is finished by the dry system. For the substrate, a woven or knit fabric which has been brushed on its surface is often used to improve appearance, resistance to grain break, and feel.

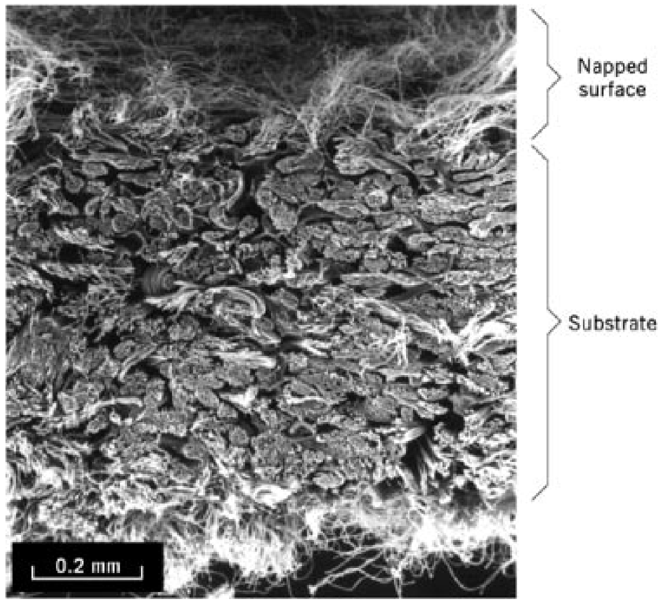

Fig. 8. Cross section of Suedemark 45° diagonally cut.

3.3. Man-Made Leathers

These materials contain a nonwoven fabric which is impregnated with a polyurethane to improve flexibility, processibility, and conformability (Fig. 9). Advanced man-made leathers contain microfibers as fine as 0.03 tex (0.3 den) or less to imitate collagen fiber bundles, thereby attaining the soft feel and appearance essential for soft leather use. Polyurethane in the substrate is usually provided with porous structure by poromeric technology. The coating layer is also porous in the two-layer type man-made leathers (5–10).

A special fiber has been developed for Clarino (5, 7, 8). Two polymers of different solubility are mixed for spinning. In the resulting fiber, the two polymers are separated by an islands-in-the-sea structure. The islands-in-the-sea structure is controlled by the polymers, their proportion, and spinning conditions (5, 7, 8, 13). Solvent extraction of either component gives a porous fiber or a microfiber bundle (Fig. 10). The islands component ranges in fineness from about 0.01 tex (0.1 den) to about 0.0001 tex (0.001 den), or less, and in the number of islands from 100 to 1000 or more (5). Porous fibers reduce the weight of products (Fig. 11). As seen in Figure 11**b**, fine fibers obtained by this method show a thickness distribution most suited to simulate the collagen fiber of leather. Another method is used for Ultrasuede; a special nozzle is used to produce a multi-islands-conjugate fiber (5, 14). The fiber fineness is limited to about 0.01 tex (0.1 den) and the number of islands to about 50, due to the structural limit of the nozzle.

In the method shown in Figure 9, manufacture proceeds by the following steps. (*1*) A special fiber is made by melt spinning and cut into 25–60 mm length. (*2*) The fibers are carded and cross-lapped (15) to form a batt. (*3*) The batt is needle-punched (16) with a barbed needle (17) and entangled to improve physical strength (18); the batt is then subjected to sizing and pressing (19) to become a nonwoven fabric with adequate thickness. (*4*) The nonwoven fabric is impregnated with polyurethane and immersed in a DMF–water bath for coagulation to create a substrate with porous polyurethane structure. For the two-layer substrate, a polyurethane coating process must come between impregnation and coagulation. (*5*) The substrate is prefinished by coating or sanding for grain or suede surface, followed by, as required, embossing, dyeing, and other finishings.

Table 2. Physical Properties of Leather and Leather-Like Materials

Product	Substrate/fiber[a]	Coating layer	Weight, g/m^2	Thick-ness, mm	Density, g/mL	Tensile strength, N/mm^2[b], [c]	Elongation at break, %[c]	Tear strength, kN/m[c], [d]	Water-vapor permea-bility,[e] mg/(cm·h)	Flex endurance,[e] 10^3 cycles
					Man-made leather					
Clarino[f]	nonwoven/porous	thick foam	580	1.50	0.39	8 (5)	45 (85)	30 (33)	2.6	>1000
	nonwoven/micro	thin solid	550	1.30	0.42	15 (13)	80 (115)	69 (68)	3.8	>1000
Sofrina[f]	nonwoven/micro	thin solid	220	0.50	0.44	12 (14)	115 (120)	100 (80)	5.0	>1000
Suedemark[f]	nonwoven/micro	suede	120	0.35	0.34	9 (7)	70 (106)	43 (43)	12.4	>1000
					Urethane-coated fabrics					
solid-type	woven/regular	thin solid	393	0.90	0.44	12 (7)	20 (28)	45 (66)	1.5	300
foamed-type	woven/regular	thick foam	404	1.13	0.36	11 (8)	7 (29)	30 (22)	1.5	400
					Vinyl-coated fabrics					
solid-type	knit/regular	thick solid	912	0.91	1.00	9 (7)	33 (229)	31 (35)	0.3	50
foamed-type	knit/regular	thick foam	839	1.03	0.81	6 (4)	31 (200)	24 (27)	0.4	150
					Leather					
carf		grain	450	0.80	0.56	11 (10)	55 (75)	25 (25)	10.1	>1000
side		grain	1000	1.50	0.67	23 (13)	70 (96)	73 (93)	7.5	500

[a] Product is nylon in man-made leathers; cotton in urethane- and vinyl-coated fabrics.
[b] To convert N/mm^2 to kgf/cm^2, multiply by 10.2; to psi, multiply by 145.
[c] Numbers in parentheses are crosswise.
[d] To convert kN/m to ppi, multiply by 5.71.
[e] At 20°C.
[f] Registered trademark of Kuraray Co., Ltd.

Most manufacturing methods now available are similar to this but with the following modifications: in the first step, the polymers for fibers are mainly made of polyester, nylon, or their blends. Acrylics and polypropylene are also sometimes employed. A regular fiber as thick as 0.01–0.4 tex (0.1–4 den) may sometimes be used instead of the special fiber to imitate the hard leather.

In the second step, a papermaking method is also used for the fine fibers, less than 0.1 tex (1 den). This process is usually followed by a high pressure water jet process instead of the third step. In the fourth step, to obtain the required properties in specific applications, a polyurethane is selected out of the segmented polyurethanes, which comprises a polymer diol, a diisocyanate, and a chain extender (see Urethane polymers). A DMF–water bath for coagulation is also controlled to create the adequate pore structure in combination with fibers.

In the fifth step for man-made leathers, a grain surface is given by embossing with heated rolls engraved with the desired leather pattern, color-printing with gravure rolls or color spraying, and dyeing. For the grain type with thin layer, such as Sofrina, the finishing includes application of a polyurethane thin layer before embossing. For suede type, finishing includes napping before dyeing.

4. Economic Aspects and Application

The demand for leather products is expected to increase steadily due to growing world population and urbanization. On the other hand, leather has a limit in its supply because it is a by-product of the meat industry.

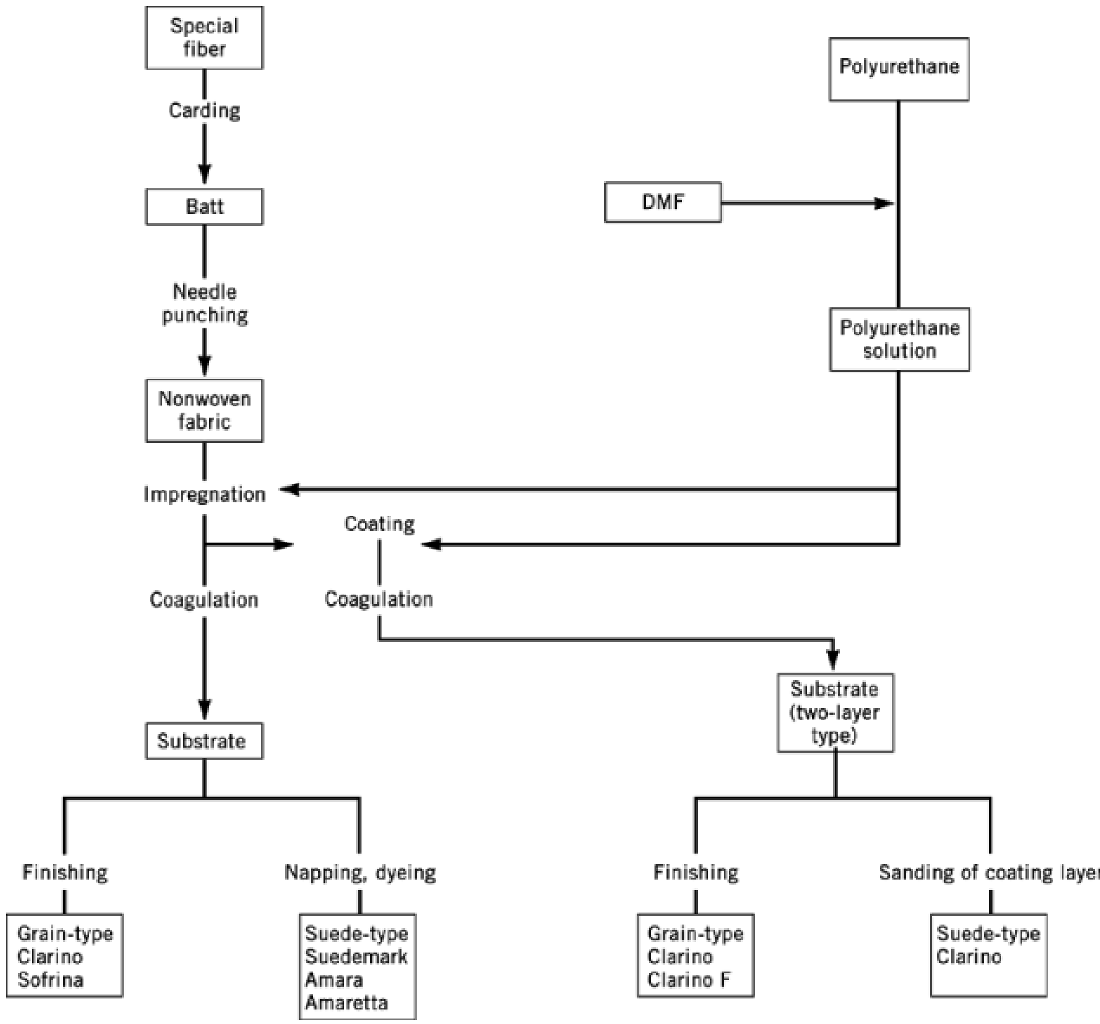

Fig. 9. Manufacturing process of Kuraray man-made leather.

The production of coated fabrics including vinyl- and urethane-coated in the early 1980s is shown in Table 3 (4). Only production in the Far East showed an increase. The increase of urethane-coated fabrics mainly supports this tendency (Table 4).

The production of man-made leather has increased rapidly due to its high quality (Table 5). Production was first started in Japan, and is expanding to the world. Up to 90% is produced in the Far East, and approximately 50% is exported to the United States and European countries.

The big three applications of vinyl-coated fabrics are (*1*) automotive (36%), (*2*) bags (17%), and (*3*) interiors (10%). Those of urethane-coated fabrics are (*1*) clothing (18%), (*2*) shoes (18%), and (*3*) accessories of shoes (11%). Those of synthetic leathers are (*1*) shoes (46%), (*2*) clothing (13%), and (*3*) bags (10%) (18).

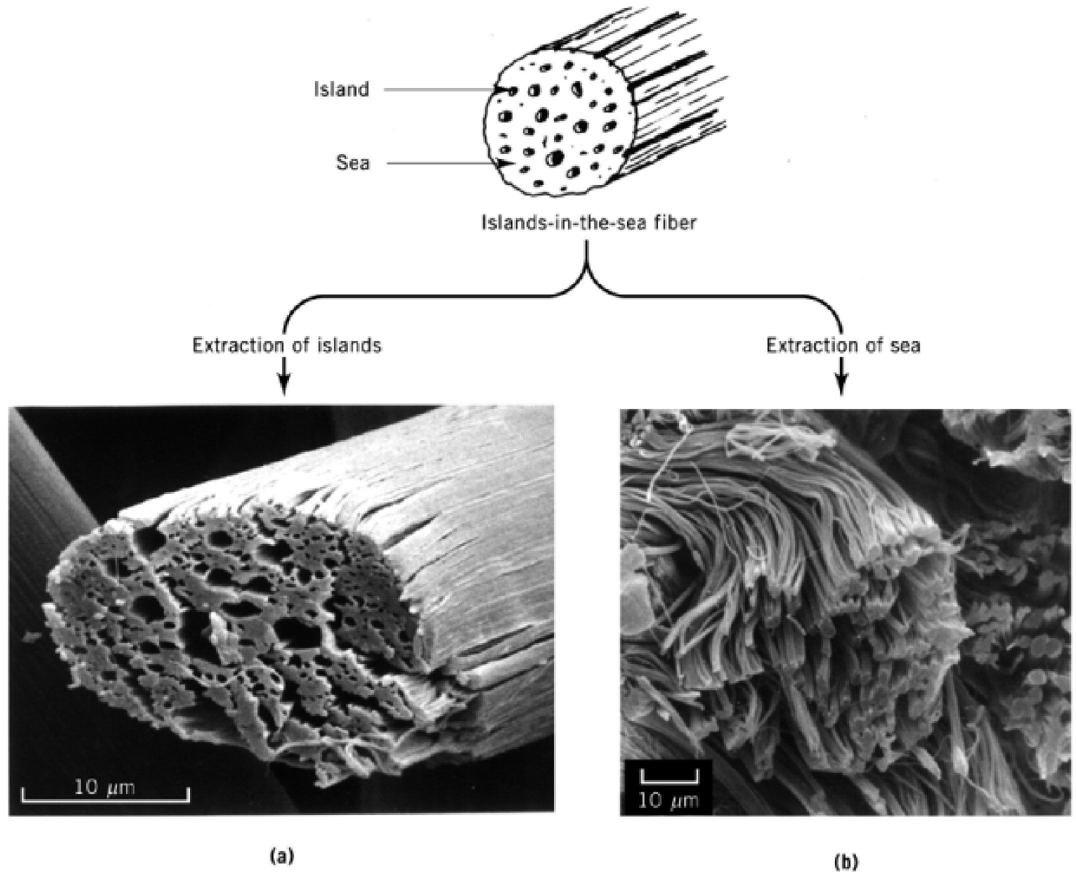

Fig. 10. Formation of fibers used in Kuraray man-made leather: (**a**) porous fiber, and (**b**) a bundle of microfibers.

Table 3. Worldwide Production of Coated Fabrics[a]

	10^6 m^2/year	
Location	1978	1983
Far East	480	700
Eastern Europe	330	330
Western Europe	700	700
North America	505	505
South America	115	115
Africa	35	35
Total	*2165*	*2385*

[a] Ref. 5.

5. Test Methods

Test methods vary from maker to maker. In the United States, test methods for the physical properties of coated fabrics are given in ASTM D751-79. Flex endurance can be measured by ASTM D813-52T. ASTM for fabrics, such as D1683-78, and ASTM for leather, such as D2346-68, can also be used. In Japan JIS for fabrics, such as

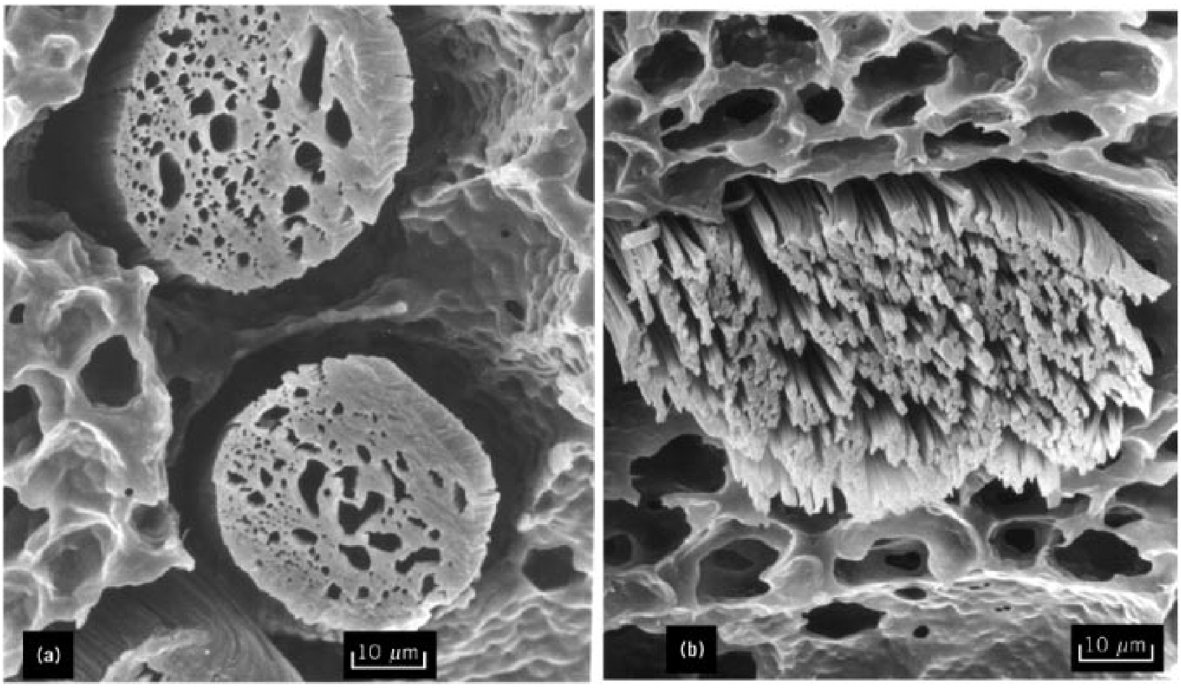

Fig. 11. (**a**) Cross-sectional view of substrate with porous fibers and polyurethane sponge. (**b**) Cross-sectional view of substrate with bundle of microfibers and polyurethane sponge.

Table 4. Urethane-Coated Fabrics Production in the Far East[a]

	10^6 m^2/year		
Country	1982	1987	1992
China (Taiwan)	71	113	166
Japan	46	49	46
Korea (South)	36	64	71
Thailand	8	7	15
China			25
others	10	8	12
Total	*171*	*241*	*335*

[a] Ref. 20.

L1096, and for leather, such as K6545, are available. In Europe BS and DIN, such as D75202 for automobile, are available.

Table 5. Worldwide Production of Man-Made Leather[a]

Location	Company	Product	10^6 m^2/yr 1982	1992
Far East			18	51
Japan	Kuraray	Clarino, Sofrina, Suedemark, Amara, Amaretta	18	33
	Toray	Ultrasuede		
	Teijin	Cordley		
	Kanebo	Bellace		
	Asahi	Lamous		
	Mitsubishi	Glore		
others				16
Europe	Iganto	Alcantara	4	6
	Porvair	Porvair		
Total			*22*	*55*

[a] Ref. 20.

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