ABSTRACT

SCHENK, ANNETTE KERSTIN. Study of the Impact of the Nonwoven Substrate Formation on Artificial Leather. (Under the direction of Dr. Behnam Pourdeyhimi.)

Since 30 years, the artificial leather industry is mainly located in Asian countries, as common production processes faced little or no restrictions and regulations in terms of hazardous chemical usage over there. Nowadays available water based polyurethane coatings allow an environment-friendly approach without known health risks, resulting in a great interest to get the artificial leather market back to the US. The first step in this approach is an in depth study of prior art and an investigation of artificial leather manufacturing key factors.

Processability is mainly ruled by the base substrate, which represents the most important part for artificial leather production, as it also governs future qualities such as appearance, haptic and mechanical properties. In this study various nonwoven substrates are created, characterized and compared after several stages throughout the formation process, with the help of solid volume fraction, apparent density, air permeability, flexural rigidity, burst strength, abrasion resistance, water vapor permeability and scanning electron microscopy.

To further investigate the performance and impact of the different nonwoven substrates on artificial leather, a technique for creating a three-layer transfer coating grain finish topcoat, based on water-soluble polyurethane, has successfully been established and optimized. Appearance and mechanical properties of coated samples were analyzed and compared by testing the orange peel effect, flexural rigidity, burst strength and water vapor permeability.

A direct comparison of mechanical properties of uncoated and coated substrates is done to study the impact of various nonwoven substrates during different formation stages on
artificial leather. It has been shown that dense and even substrates are essential to obtain desired mechanical properties and enhance coatability. Increase in flexural rigidity could be observed for all coated fabrics, while there was no significant change in burst strength. In terms of competitiveness, water vapor permeability of created samples is compared to genuine leather and commercial available samples. More than half of produced artificial leather sample have a higher water vapor transmission rate than real leather and can also keep up with commercially available artificial leather samples.

Finally, it has been shown that bicomponent fibers, which are capable of splitting or fibrillating into ultrafine fibers showed best performance in appearance, sensual and mechanical properties. This was especially true for coated nonwoven fabrics, which have been created of 51 island in the sea or 24 segmented pie fibers. Apart from good abrasion resistance, 4 segmented pie mixed media fabric, consisting of less fine fibers, also showed very good performance in terms of appearance haptic and mechanical properties.
Study of the Impact of the Nonwoven Substrate Formation on Artificial Leather

by
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_______________________________  ________________________________
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______________________________
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DEDICATION

To all the innocent animals used for human cravings
BIOGRAPHY

Annette Kerstin Schenk was born on February 8, 1988 in Schwäbisch Hall, Baden-Württemberg, Germany. In 2012, she received her Bachelor of Engineering degree in Textile- and Clothing Technology at Albstadt-Sigmaringen University in Albstadt, Germany. In the course of her studies she spent the compulsory internship semester at the Nonwovens Institute (NC State) in 2010. During her Bachelor’s Thesis research in 2011, she was working on the drapability of various non-impregnated carbon fiber reinforcements at São Paulo State University in Guaratinguetá, Brazil. In order to acquire her Master’s degree she returned to NC State and entered the Textile Engineering program in 2012.
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1 Introduction

Early evidences, like for example Egyptian wall paintings, prove that leather is a material which is as old as humanity and consequently leather tanning represents one of the eldest human activities [1, p. 5, 2].

Looking at the hide, the outermost thin layer known as epidermis, hair and the bottommost layer, which is attached to the underlying fat and flesh, are discarded. The thick middle layer, known as the dermis, is used for generating leather [1, pp. 54-55]. It consists of two sublayers, the reticularic layer and the papillary layer. The reticularic layer comprises entangled coarser fibers which are made up of bundles of collagen fibrils. On the way to the surface, the structure of the reticularic layer becomes finer and finer and more consolidated, ending in the fine fibered densely entangled papillary layer, which becomes the grain side. The grain side is responsible for the characteristic skin pattern and closely related to surface quality of the final product [1, pp. 54-55, 3, 4].

After the tanning process, the hide is transformed into leather, which is available in multiple colors and shapes, made of different skins (e.g. horsehide, sheepskin, sharkskin etc.). Its unique smell and touch beautifully stimulate the senses. As leather ages gracefully, it provides a long-lasting pleasure [1, p. 5].

Next to its unique beauty, leather comprises far more advantages, like for example its mechanical properties. It shows good tensile and tear strength in both longitudinal and lateral directions. Due to its pliability, it has very good drapability and flexibility in shape. It is easily dyeable and the cutting operation of the compact uniformly packed tissue is effortless.
Properties like appropriate moisture absorbency, water vapor permeability and temperature stability or rather heat insulation significantly enhance wearer’s comfort [5]. Therefore, leather represents a great material for the production of comfortable shoes, which should be permeable to water vapor, absorb normal foot moisture and show flexibility as well as shape retention properties [1, p. 9].

Nevertheless, this special natural product also has its drawbacks. As leather is made from hides of individual animals, its properties considerably differ from one animal to another. Hides also vary from one race to another or even sex and age play a role. Next to the difference between several hides, there are also variations in thickness from part to part in one and the same piece. The quality of leather moreover depends on the circumstances the animal was living in and the part of the animal’s body, the leather comes from. Malnourished animals for example have thin skin which will result in leathers lacking in elasticity. Furthermore there are imperfections like scars, wrinkles insect bites or fungal infections, which are often played down as “natural markings” [1, p. 47, 6]. Following figures show examples of typical blemishes.

![Figure 1: Veins](image1.png)

![Figure 2: Neck-Wrinkles](image2.png)
Of course leather is not available in yard good but in restricted differing sizes, of which not every part is usable as desired. Last but not least, the inevitable tanning process is a time consuming hardly controllable technique. All those disadvantages impede industrialization of leather manufacturing. Besides high costs of being handled manually, the price of leather, as a byproduct of meat, further suffers from fluctuations of meat production [5].

As has been shown, leather provides numerous advantages which are at first glance not too special with regard to each single property. It is the combination of all its individual benefits, which has made leather very desirable for centuries [1, p. 194]. Therefore the urge arose of creating synthetic leather having the same beneficial properties, or even improved ones, as the natural product without the found demerits [5]. In producing artificial leather as a roll good, greater quantities are available at a lower price, making the luxurious material affordable for the general public.

Nowadays, artificial leather is not only known under multiple names as leather like material, synthetic leather, imitation leather, fake leather, pleather, faux leather, man-made leather or leather replacement, there are also numerous approaches and advancements in creating this material. In the following chapter, there will be a review of the historical background as well
as different techniques for creating this special material. A closer look is taken at the substrate, with regard on different fiber shapes and processing methods, before covering the impregnation and/or coating used to create the leather-like surface layer.
2 Literature Review

2.1 Historical Background

People already started to imitate leather in the 14th century by treating fabrics with special oils to achieve a similar appearance as leather [1, p. 18].

In the 17th century, Japan’s artificial leather tradition started. Inspired by Spanish leather or gilt leather which was introduced by the Dutch, Japanese used “washi” a traditional long-fibered handmade paper to imitate it. Washi was in contrast to known Western paper softer, tougher and more flexible. Leather paper, named “Kinkarakawa”, was achieved by treating washi in a special press inducing light crinkles before coating it with a mixture of rice paste and lampblack onto its smooth side. After drying, a paste dye was applied and in the end, it was finished with an impregnation of lacquer [1, p. 179].

In 1839 Charles Goodyear accidentally discovered vulcanization as a way to treat natural rubber with a respective proportion of sulfur and heat to prevent it from cracking in sun or cold ambient temperature [1, p. 26+27]. Rubber is based on long coiled molecular chains, which are able to disentangle move and slip past each other in temperatures above the glass transition temperature. Although entropy urge the chains to return into a randomly entangled configuration as soon as applied force is removed, excessive stretching separates the material, as unbound molecular chains untangle and completely slide past each other. Goodyear’s vulcanization describes an irreversible cross-linking reaction of sulfur and rubber molecular chains. This new state of controlled freedom of movement results in a greater resistance of swelling and improved elastic properties [7]. This improved performance by vulcanization was the initiation of a growing rubber industry, leading to numerous new
products, inter alia artificial leather. Multiple patents were published with imitation leathers comprising rubber combined with all sorts of materials, as cloth, cork or scrap leather [1, p. 26+27]. About 1850, Storey Brothers produced “Leathercloth” in England, which was firstly used for lining coaches of small English railways and further for horse-drawn carriages. By 1862, Storey expanded business and was soon producing “Leathercloth” in three different colors and different substrate cloths. Primarily it was produced manually, by stretching a cloth over a wooden platform and treating it with several rubbers oils and pigments. The distinct surface grain was gained with the help of an embossing roller. “Leathercloth” also found its way to India where it was sold for rickshaw covers. There it however had to face a hot humid ambient which led to a big solid lump when it has been stored for some time [1, p. 28+29]. In 1872 Harrington & Co. patented Leatherette, which was often used for bookbinding and was sold for an eighth the prize of leather. It consisted of a pressed, long-fiber felt, which has been varnished and had a grained surface drawn from real leather hide. As it was thoroughly dyed, vivid colors appeared instead of white patches at upcoming worn areas (e.g. corners). However, bookbinders complained about its little suppleness and elasticity making it difficult to handle [1, p. 18+25]. In 1884 the patent “Improvements in the Production of Compounds Containing Nitrocellulose Suitable as Varnishes and for Making Leather Cloth”, by Joseph Storey and William Virgo Wilson was published. According to this patent, nitrocellulose could be dissolved in amyl acetate (volatile and flammable) to produce a viscous liquid or paste which was used to produce artificial leather after subsequent mixing above mentioned solution with
pigments and castor oil. This nitrocellulose was not explosive as the one which was commonly known as guncotton because of less degree of nitration. In England, this produced imitation leathercloth was sold under the name “Queen’s Leathers” and was used for book binding, seat covers and baby carriages. Similar artificial leather products in Europe were Rexine and Pegamoid; the US representative was Moroccoline by the Boston Artificial Leather Company [1, pp. 31-34].

1896 the American Pegamoid Company was established in New Jersey, changing to the New York Leather & Paint Company two years later before finally being known as the Fabrikoid Company. In 1908, this company successfully produced artificial leather, of which almost thousand kilometers were shipped each year for shoe linings, baseballs etc. The start of Du Pont’s business in artificial leather was set when they bought the Fabrikoid Company and soon produced kilometers of artificial leather daily. This Fabrikoid of the early 20th century could be found as seat covers of many Ford Ts and was produced by a mixture of cellulose nitrate, castor oil, amyl acetate, pigments plus other solvents to get a viscous honey like consistency. The achieved coating was directly applied by a doctor blade, whereby the skin layer had a higher amount of castor oil to provide desired suppleness. In large ovens at approximately 85°C the assembly was dried by evaporating the solvents. Subsequently, the coated fabric was calendered to smooth pitted surface. In the end steam-heated rollers or flat-bed presses having an imprint of leather grain, were used to emboss the coated fabric and present leather-like appearance. However Fabrikoid was not as good as leather, it peeled off easily, was not water vapor permeable, had hard and brittle coating and it often had a distinct unpleasant odor, especially when the used castor oil turned rancid [1, pp. 18+34-38].
In 1914 Du Pont started a campaign against one of its competitors, split leather, in asking how many hides a cow has. This provocative question came from the fact that tanners split one cow hide into at least two, up to four layers; a top grain layer and other weak inferior layers, which were coated with a similar coating as Fabrikoid and embossed to imitate the grained surface of leather [1, p. 42].

In 1926, Kurashiki, later renamed to Kurashiki Rayon Company and nowadays known as Kuraray as well as Toyo Rayon which was changed to Toray in 1970, was founded. In the beginning these were giants in Japanese chemical industry before concentrating on synthetic leathers afterwards [1, p. 180].

In the beginning of 1944, Goodyear announced Neolite, which was well established by the end of World War II. In 1960, 400 million pairs of shoe soles were produced per year leading to bankruptcy of old-established tanners specialized in sole leather [1, p. 6+108]. Neolite, a styrene-butadiene rubber, showed multiple benefits; it was flexible and durable without transmitting a rubber like feeling [8].

In the 1950s vinyl fabrics arose in the marked, as for example Naugahyde by the U.S. Rubber Company. Naugahyde was leather like but showed plastic characteristics. In hot ambient temperature it feels hot and tacky, squeaking as soon as it is moved. Nevertheless it shows advantages like being mildew and oil resistant, it is available in any imaginable color, highly abrasion resistant and cheap. It has for example been utilized for upholstery and bookbinding. Vinyl-imitation leather was either made by casting, resembling transfer coating, in pouring vinyl having a syrup-like consistency, between rollers onto a release paper. After curing in an oven, a second layer, comprising a blowing agent, was applied onto
the gained film. During subsequent curing process in an oven, a foam layer was formed by the heat-sensitive blowing agent. In the end, vinyl and release paper are separated and both are wound up respectively. The vinyl sheet can later be combined with a textile substrate, the release paper is reusable. Another approach is melting PVC together with plasticizers and pigments to get a highly viscous paste which is deposited onto a conveyor belt leading to hot calender rolls, which convert said paste into a solid colorful vinyl sheet, that is subsequently laminated to a textile substrate in an oven [1, pp. 18+69-75].

The final steps usually included printing and embossing to achieve an attractive leather-like finish. Next to having a nice appearance, the plastic coating was responsible for good wearing properties, i.e. withstanding flexing and abrasion. The stretch properties of the composite highly depend on used substrate fabric, which also contributed most tensile and almost all tear strength of resulting product [6].

Figure 5 shows one of the simplest ways of creating a vinyl fabric. The slight penetration of the coating into the upper part of the woven substrate indicates that the PVC was applied by
direct coating. Care must be taken to not deeply penetrate the fabric, as this would lead to an unwanted rigid material, exhibiting inferior properties [6].

A great problem of polyvinyl coated fabric materials was its impermeability to water vapor, preventing sweat to escape. The sweat gathered at the interface of coating and cloth often inducing delamination. Further investigations led to microporous vinyl coatings which were water vapor permeable, but unfavorably suffered from poor physical properties as little abrasion resistance [6].

1963, after more than 25 years of research, Du Pont announced their new product called Corfam, which was supposed to replace leather. In 1937, Du Pont researchers already identified shoe upper material as the biggest market for the conception of synthetic leather alternatives. In contrast to vinyl, Corfam is water vapor permeable, meaning in other words “breathable” like leather. This poromeric should not only combine the appearance but also the properties of leather. Utilizing Corfam as shoe upper material freed leather from its monopoly in shoe industry [1, pp. 4-5+9-12]. In looking up “shoe” in the oxford dictionaries, the strong interrelation between shoes and leather becomes obvious; a shoe therein is defined as “a covering for the foot, typically made of leather […]” [9].

In contrast to previous leather imitations, not only the appearance of leather (i.e. its grain surface) was imitated but also other intrinsic qualities. As can be seen in following three images (Figure 6, Figure 7 and Figure 8), Corfam alluded to the structure of leather: Comparing the cross-section of leather on the left hand side and the one of Corfam right next to it, parallels can be drawn, as for example the flesh side of the leather resembling the
nonwoven substrate of the imitation. To mimic the tightly entangled structure of the quasi void free reticular structure, Corfam is impregnated with an elastomeric binder. The microporous coating resembles the very fine fibered papillary layer, known as the grain side. In contrast to the natural product, the nonwoven fibrous structure of Corfam does not show a smooth transition from coarse to very fine fibers, in contrast to that there is a woven interlayer between nonwoven structure and microporous coating, which acts as a support for increased tensile and tear strength, but also leads to less elongation at break [6].

Figure 6: Cross-section Leather, SEM 25x Magnification [6]

Figure 7: Cross-section Corfam, SEM 35x Magnification [6]

Figure 8: Sketch of Poromeric Structure [6]
In 1949, John Piccard set the development process of Corfam in motion by his studies on nonwoven material, which were promising to be a great substrate for artificial leather. In his work he primarily was focused on porosity, in the beginning he started with polyester, polyethylene and cellulose acetate fibers, bonded these to a nonwoven structure in a hot press and afterwards washed out the cellulose acetate fibers with acetone, leading to a fabric containing multiple “wormholes”. The softness of gained fabric raised proportional to its porosity. However the gained pores were too big, meaning that not only water vapor was able to pass through but also water could enter. This problem was solved in using cellulose acetate fibers which were small enough to leave after washing them out tiny pores, not big enough for water to enter [1, pp. 114-118]. A couple of years later, in 1955, Du Pont engineer James Rushton White looked at a process to create nonwovens as a basis for artificial leather. He was inspired by ordinary felt, which is made by washing, spreading and beating a wool fleece, before it is shrunk into a mat. In contrast to the smooth polyester fibers to be used, wool fibers inhibit tiny scales which automatically strongly interconnect. To entangle the polyester fibers, Hollow and his group fell back on needlepunching technology to form the mat. In order to intimidate wool shrinkage, they used drawn polyester fibers which shrank as soon as they were heated. An air-laid web was entangled via needlepunching and subsequently passed through three warm water baths with increasing heat to induce web shrinkage. The result closely resembled the fleshy bottom of leather. 1956, Hollowell ordered some polyurethane to study, which was delivered dissolved in DMF (dimethyl formamide). Its property of forming microporous structures via coagulation was detected by accident: Robert Johnston, a member of Hollow’s team, prepared a film of the sent Polyurethane DMF
solution, in order to dry it out overnight. Due to the highly humid air and the hygroscopy of DMF, the polyurethane coagulated and turned into a smooth elastic white structure of interconnected micro pores, being permeable to water vapor [1, pp. 122-125].

After releasing Corfam as a final product on the shoe market disadvantages soon appeared concerning the wearing comfort. Although breathability of Corfam has always been emphasized, it still was less water vapor permeable than genuine leather and did not absorb as much water, to be more specific 13 times less than leather, leading to hot feet of Corfam shoe wearers. Moreover, Corfam did not stretch at all, and thereby never molded itself to flatter the foot, in other words, a Corfam shoe had to fit from the very first time as it would never conform to the shape of the foot as leather did [1, pp. 133-138+158].

In 1969, everything, which was soft, comfortable and conformable, was in trend. Corfam shoes did not resemble anything of that kind; furthermore vinyl shoe upper material entered the market, representing a material which was not water vapor permeable at all but so cheap that people buying vinyl shoes were not concerned of breathability. These disturbing factors led to production stoppage of Corfam in 1971 [1, p. 143+146].

Not only Du Pont manufactured poromerics in the 1960s but also companies in Japan did so. Toray for example produced Hitelac, consisting of an impregnated nonwoven substrate, moreover had a woven interlayer and a microporous coating. 1970, they introduced a synthetic suede material which is known under different names in different parts of the world. In Japan it was first called Ecsaine, Ultrasuede in the United States and Alcantara in Europe after Toray and an Italian company collaborated to produce it in a factory in Terni,
Italy. It was soft and strong, drapy without wrinkling and machine washable [1, pp. 169+180-182].

The Kuraray Co., Ltd. went through the whole process of imitating leather beginning with crushed leather scraps which were transformed to so-called “regenerated leather” followed by “imitation leather” closely resembling predecessor products with nitrocellulose, rubber or vinyl coatings. These imitations were similar in appearance to genuine leather. Its strength however only depended on the used woven base substrate. This was not the case for its successor “synthetic leather”, the first generation of the brand Clarino, which was made of plastics providing good strength and chemical resistant properties. Furthermore, the previously woven substrate was replaced by a nonwoven fabric, which was topped by microporous foam [5].

In comparing Corfam with this first version of Clarino (see Figure 9 and Figure 10) a certain similarity can be observed. Both consist of a nonwoven substrate coated with a microporous top layer. Clarino does not comprise a woven interlayer but shows larger voids in the top layer than Corfam. Furthermore it can be seen that the fibers of Clarino are embedded in a matrix of polyurethane foam. The fibers however do not tightly adhere to the foam, but rather freely pass through a “tunnel systems”. Therefore, Clarino’s fibers have greater freedom of movement, leading to a more flexible material. The absence of adhesion therefore can be linked to the relatively good workability of Clarino [6].
However, not only the structure and appearance resembled Corfam, it also possessed similar demerits. To fulfill industrial demands for artificial leather not only with a similar appearance but also with equal or even superior qualities than the natural product, further research was done of which results were published in US Patent 3,424,604 by Osamu Fukushima et al. in 1969. A process of creating an air and moisture-permeable synthetic leather is described as follows. Mixed spun fibers, consisting of two polymers in different ratios (e.g. 40% nylon 6 and 60% polystyrene) are cut in staples, formed into a web by a random webber, before being entangled to a nonwoven by needlepunching. The created fabric subsequently is impregnated in a solution of high molecular weight material comprising a polymer having rubber-like elasticity and another polymer not being elastic like a rubber, as for example 6% solution of polyurethane in dimethyl formamide (DMF). After a padding process, A top coat, also consisting of a high molecular weight material solution (polyurethane in DMF), is applied via spraying or coating, before the whole assembly is coagulated in several water baths. Then, the sheet material is pressed in a hot press where one of the two polymers, the mixed spun fibers consist of, is removed by a solvent. In the case of nylon and polystyrene, the latter one is removed with toluene at a temperature of 70°C. Thereby multiple micropores are formed.
between nylon fibers, entailing less adhesion to the coagulated polyurethane elastomer. The increased mobility of the fibers finally leads to enhanced pliability of the resulting artificial leather. It has been shown, that the higher the porosity, in other words the greater the amount of the subsequently removed polymer, the more flexible gets the created material [5].

Kuraray’s Clarino was popular in the Japanese market for their shoe upper material. Both, Alcantara and Clarino were based on microfibers, a brand new technology at that time, which was responsible for their special properties and performance [1, pp. 180-182].

Fiber fineness of conventional spinning processes on the one hand depend on the hole size, the polymers are drawn through with a respective spinning speed; on the other hand fibers will break as soon as they are drawn too fast or the holes are too tiny, as they become too fragile due to extreme fineness during spinning process. Polyester was limited to circa 0.3 denier until Miyoshi Okamoto developed a new technology. Among other things, commonly utilized extraction processes to gain light delicate values of natural materials raised his idea of a novel fiber forming process. Silk, which comprises fibroin fibers embedded by the, to be removed, sericin; or leather, where everything beside the middle layer, consisting of the fine fibered grain layer and the corium, is separated from the hide. Okamoto’s first approach on nowadays well known island-in-the-sea fibers was in 1965. For this, he used a simple glass test tube, having a diameter of 1 inch and a funnel at one end, of which tip acted like a spinning nozzle. Numerous polyester and nylon fibers were randomly arranged inside the tube, before heating the apparatus in a silicone bath to 300°C to induce melting of both polymers. After carefully extruding the molten fiber mix by pushing with a piston, the quenched new fiber was stretched under heat to three or four times its original
length. Last but not least, the extraction step followed, wherein nylon was dissolved by formic acid, leading to a remaining bundle of ultrafine soft and supple polyester fibers. To further mature this technology, Toray acquired a special designed spinneret [1, pp. 184-188].

1967, Miyoshi Okamoto filed the US Patent 3,531,368, which was published in 1970, representing the origin of the nowadays well known island in the sea fibers. The technique for creating island in the sea fibers as well as the used apparatus is introduced. It is proposed that these synthetic fibers can on the one hand eliminate drawbacks of an individual polymer by combining it with a polymer having different properties to compensate demerits in the resulting fiber. For instance, in combining polyester and polyamide, the low Young’s modulus of latter polymer is offset by the higher modulus of polyester. On the other hand island in the sea fibers are perfectly capable for creating microfibers, involving a big step up the ladder for creating pliable artificial leather [10].

In 1966, Okamoto had the idea of improving Hitelac, having similar problems as Corfam, i.e. too rigid and an unappealing hand, in using previously described supple soft microfibers to create the substrate. Three years later, 1969, Okamoto was announced to the head of a new group, having the mission of revive Toray’s artificial leather business [1, p. 190].

In contrast to Toray’s Alcantara, comprising 60% polyester, Kuraray’s later suede version called Amaretta consists of 60% nylon. Amaretta furthermore was available as smooth-grained synthetic leather garment, having the same formulation as Clarino but thinner leading to greater pliability [1, p. 193+196].

In 1982 Kuraray handed samples of Clarino over to Giorgio Poletto, the R&D director of one of the largest Italian tanneries – “Conceria Italiana Reunite” (CIR), to ask for improving their
After years of experiments, CIR tanners developed a way to “retan” Kuraray’s artificial leather and thereby gained a remarkable softer product, they called Lorica [1, pp. 174-177]. US Patent 4,766,014 gives a closer insight into their work:

To increase appearance, suppleness, hand and flammability of given microporous leather imitation, it is treated similarly to real leather during its tanning process. First the material is placed into rotary tanning drums, in which it is soaked in a mixture of water and surface-activator, before it is treated with a metal salt solution, resembling traditionally used tanning salt solution, until the whole material is impregnated. The subsequently added caustic soda solution elevates the pH level up to 7.5 and causes, in combination of heat, the salt to precipitate as hydroxides in a gel-like manner. These hydroxides fill the pores of treated microporous material and thereby increase its weight, regularity and diminish flammability. After washing off excess gel, greasing is conducted. Hereby, utilized esters or oils penetrate the pores and act like lubricants, in other words help to improve fiber flow, with the result of increased flexibility of the processed product. In the end, the synthetic leather is treated with a solution of a fireproofing combined with a softening substance, before finishing with a dyeing procedure. [11] Lorica quickly found its use in traditional leather goods as upholstery, gloves, handbags and sport shoes. Furthermore, Doc Martens filled a niche in utilized Lorica for “vegetarian” shoes in America, which are free of ethical concerns [1, p. 177].

Du Pont, Toray and Kuraray established the basis for producing leather-like material, of which principles were refined and further developed over the years. With the appearance of new technologies, further approaches were made in the manufacturing process. In the following sections, used technologies and developments will be examined.
2.2 Substrate

The substrate builds the centerpiece of synthetic leather. Although there are products using woven or knitted fabrics as basis, this thesis will concentrate on nonwoven material, which is commonly used for high end imitation leather, as its structure closest resembles the entangled collagen fibers of the natural product. When Fukushima pointed out the essential basic principles for manufacturing artificial leather, he addressed the importance of the substrate, which governs future quality aspects of the created product. Not only hand and processability are ruled by this layer but, as has been seen in history, changes in the substrate also considerably altered appearance and mechanical properties [12]. Corfam, Hitelac as well as the first version of Clarino, which still consisted of regular fibers, struggled with stiffness and little pliability. In using microfibers, Clarino established a softer hand and desired suppleness. Therefore, it is obviously important to focus on utilized fibers, prior to concentrating on different manufacturing technique.
2.2.1 Bicomponent Fibers

Monocomponent fibers, spun by a common spinneret, can have excellent dynamic properties, they are however limited in fineness and usually have a simple cross sectional shape. This leads to demerits in appearance and haptic as for example less gloss and texture [13]. As previously shown, microfibers represent a key factor for producing a supple leather-like product, i.e. fiber fineness should be less than 0.5 dtex to get a flexible and soft substrate and not end up with rough touch and feel [14]. Bicomponent fibers are fibers with two immiscible polymer types distributed along the axis of one single fiber. They are therefore also known under composite, conjugate or hetero fibers [15, 16]. In splitting them into their components, of which at least one has a cross-section in microsize, or removal of one polymer type, desired microfibers can be gained [16]. Next to creating ultrafine fibers, bicomponent fibers offer further benefits, depending on arrangement of components and cross-sectional shape. Thereby, they can be tailored for application-specific needs [17]. In the following typical bicomponent fibers will be introduced.

Starting with a look at Figure 11, a schematic cross-section of a side-by-side fiber can be seen. The two components are arranged next to each other, each filling one half of the cross-sectional area. Side-by-side fibers were the first developed bicomponent fibers and are commonly used in self-crimping applications. Fiber crimping is created by different shrinkage or expansion properties of the two components. Typically used polymers are polyethylene/polypropylene and co-polyester/polyester [18].
Figure 12 and Figure 13 both depict schematic cross-sections of sheath-core fibers. As their name already implies, sheath-core fibers consist of a core, surrounded by a sheath. In comparing Figure 12 and Figure 13, it can be detected, that the location of the core may vary depending on desired application. If the core is placed centrally, it is called a concentric sheath-core fiber (Figure 14), whereas the core in an eccentric sheath-core fiber is located decentrally [18]. Most commonly, sheath-core fibers are used for self-bonding binder fibers. Hereby a polymer having lower melting temperature is used as sheath component, while the core component shows a higher melting temperature. Therefore the sheath fuses prior to the core to realize bonding without affecting the core component, leading to higher stability and strength of the final product. Common used polymers are polyethylene/polyester, co-polyester/polyester and polypropylene/polyester. Next to its self-binding properties, sheath-core fibers can further be used to save costs in reducing the amount of expensive materials, such as for example specialty additives, in only incorporate them into the sheath and fill the
core with a cheaper component. Due to the specifically application desired functionality is still given without filling the whole bulk of fiber with the expensive material [17].

In contrast to introduced sheath core fiber, which only has one core surrounded by a sheath, the Island in the sea fiber represents a multicore fiber, consisting of the islands, which are isolated from each other, surrounded by the sea (see Figure 15 and Figure 16). The island component is selected from melt-spinnable polymers; having a high melt viscosity and surface tension under spinning condition, like for example PA6 and PET. The sea component (e.g. PE, PP, PS, or PVA) on the other hand shows a lower melt viscosity than the island polymer. If later dissolution is desired, used polymers for the island and the sea must have different solubility to the solvent used to remove one of the two components (usually the sea component) [14].

Figure 15: Island in the Sea

Figure 16: 37 I/S Cross-Section [19]

Figure 17: 600 I/S, Sea Dissolution [19]
Island in the sea fibers, used to create substrates for artificial leather, should not have too little or too much sea component. Depending on the used polymer it is suggested to have it in a range of less than 25% or more than 75%, or respectively 15 to 50% [14, 20]. If the sea percentage of the fiber is too small, it is hard to completely remove the whole amount by dissolution, resulting in a substrate showing insufficient flexibility and softness. In contrast, an exceeding amount of sea component in the bicomponent fiber will result in a deficient amount of fibers left after sea removal. This does not only imply lower mechanical properties but is also environmentally and economically undesirable from a cost and productivity point of view [14].

Next to island in the sea fibers, bicomponent fibers consisting of alternating segments are commonly used to create microfibers in using two immiscible polymers, which allow subsequent fiber splitting by physical and/or mechanical agitation, such as differential swelling or shrinking, shear forces or hydroentangling [21]. As can be observed in the following, there are various types of alternating segmented fiber. Starting with segmented pie, of which cross-section resembles a pie diagram. The amount of segments is engineerable. There are segmented pie fibers comprising only 4 segments, or also the ones having 16 segments, shown in Figure 18, used to get fine fibers. Evolon® is produced by a web of PET/PA6 16 segmented pie fibers which is subsequently bond by hydroentangling. High pressure water jets hereby not only tightly entangle but also split segments to gain microfilaments of 0.15dtex (see Figure 20) [22].
Figure 18: Cross-Section 16 Segmented Pie

Figure 19: Split 16 Segmented Pie

Figure 20: Evolon®, NW: seg. pie fibers split and entangled by hydroentangling [22]

Figure 21 depicts a hollow pie fiber, which has in contrast to segmented pie fibers a hollow center core [17]. Due to its shape it is also referred to citrus type bicomponent fiber [18]. In contrast to segmented pie fibers, it has the advantage to make splitting easier in preventing inner tips of wedges from joining [23]. In the European patent EP 0624676 B1 this type of bicomponent fiber is exemplary used to partially thermally bond a nonwoven web before fiber splitting is initiated by rubbing and wrinkling to separate components of the fibers in between the bonded regions [24].

Segmented ribbon fibers represent the most readily splittable cross-section [17]. Although this fact is desirable after web formation, fiber splitting during web formation is highly unwanted. If fibers split and become microfibers during carding process, clogging of card clothing or nep formation possibly occurs [21].
To prevent this spectacle, Takeda et al. investigated in a bicomponent staple fiber, consisting of two polymer components which are arranged like segmented ribbons in a round fiber. Furthermore one polymer is completely surrounding the other and thereby building the periphery to increase resistance to prematurely peeling or splitting during nonwoven manufacturing process [25].
Figure 24 depicts a schematic diagram of silk before and after the so-called degumming process, during which the outer layer (Sericin) is removed from the trilobal shaped cores. Released Fibroin shows excellent mechanical properties plus remarkable luster, smoothness and comfort [26]. In comparing Figure 24 with Figure 25, it can be detected that the shape of tipped trilobal fibers was copied from nature to profit from its benefits. Trilobal fibers provide rigidity and resilience. Its numerous reflecting surfaces lead to pleasant appearance and are able to hide dirt [23]. In Figure 25 and Figure 26, two types of bicomponent trilobal fibers are shown. A tipped trilobal fiber is a three sided core fiber, of which tips consist of another polymer [18]. In contrast to a modified tipped trilobal fiber, both components are exposed on the surface. In forming a nonwoven while splitting the modified tipped trilobal fibers into four separate fibrils, a curly and crimpy structure is obtained (see Figure 27). The gained fabric provides a soft hand and excellent dyeability [27]. Whereas numerous splittable fibers have the demerit of the so-called “velcro-effect”, describing the sticky behavior of the surface, i.e. it easily hangs on to other surfaces. This effect can result from extreme fiber fineness. Modified tipped trilobal fibers do not show velcro effect, as the tips are grown to the major component, facilitating fiber splitting [28].
2.2.2 Needlepunching

After opening, blending and web formation, a subsequent bonding process is carried out in order to convert the loose web into a strong well-bonded nonwoven fabric. There are three main technologies, named mechanical, thermal and chemical bonding. In this section the needlepunching process is examined, which represents one of the most dominant mechanical bonding technologies [29].

The main task of the needling process is to reorient fiber tufts with the help of barbed needles from in-plane to out-of-plane direction in order to achieve a highly consolidated well-bonded coherent structure, having improved mechanical properties [30, 31]. The first step to reach this goal is the pre-needling process. The incoming bulky batt initially is compressed via a batt feeding system, for example in the form of a pair of aprons or rolls, to provide a uniformly continuous transport into and through the needling zone without uncontrolled drafting [32, 29]. The needling zone is characterized by the gap between a perforated bed and stripper plate. The holes of these plates are assigned to the position and number of potential needles fixed in the needleboard. Depending on needle type and used process settings, spacing of the needles relative to another may differ, to not for example simultaneously penetrate one and the same fiber bundle during one stroke with several needles [31]. Figure 28 depicts a stage of the down-punching movement of the pre-needling loom. It is shown that after passing the stripper plate, the needles make their way through the horizontally oriented fiber web before they finally go through the holes of the bed plate. During this down stroke movement, bunches of fibers are caught by the needle barbs, thereby transported and reoriented in z-direction [29]. The fibrous web is held back in place by the stripper plate.
when needles subsequently return and the fabric moves along horizontally before needles repeatedly penetrate [30].

![Diagram of needle penetration](image)

**Figure 28: Down Stroke [30, p. 271]**

The greater the penetration, i.e. the higher the punching density and the deeper the penetration depth are, the denser and stronger becomes the resulting nonwoven. Excessive penetration may however end in fiber damage and thereby diminish fabric strength. Penetration depth is described by the distance of the needle point of the penetrating needle in its down stroke position to the bed plate, including the whole bed plate thickness. The punching density is the density of needle punches per unit area. The value is derived of several machine- and process parameters and may be calculated as follows [29].

\[
PD = \frac{s \times n}{v} \times 10^{-4},
\]

where the punching density (PD, in punches per square centimeter) is calculated by multiplying the strokes per minute (s) times the number of acting needles (needles per meter) and dividing this amount by the web feed rate (v, in meters per minute). Finally everything is multiplied by \(10^{-4}\) to convert punches per square meter to the desired punches per square centimeter [29, 30]. From introduced equation it can be deduced that the
punching density can be increased by raising the amount of penetrating needles per stroke (n), elevating the stroke frequency (s) and/or slowing down the web feed rate (v).

Total punching density can further be increased by introducing another simultaneously acting needle board or having several needle looms in line. In this case, needling densities of each acting board can be added to get an approximate total punching density [29].

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**Figure 29:** Penetration either from top or bottom [30, p. 275]

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**Figure 30:** Penetration from top and bottom [30, p. 275]

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Acting needle boards can hereby be arranged in different ways in the needle loom, as shown in Figure 29 and Figure 30. Needles may either punch downwards or upwards and vice versa or a combination of both, whereby the punching needle boards can be arranged alternately or in the same vertical plane. If latter arrangement is the case, only half of the needles are used in each board to not set the needles vis-à-vis and thereby prevent crashing [30, 29].

Penetration direction and intensity influence product appearance and performance. If for example only down stroking needle boards are used, fibers from the fabric face as well as some of its center are caught and reoriented in vertical direction towards the back of the fabric. This results in a fabric having a smooth face surface with clearly visible needle holes and a fuzzy back. In using multiple needle boards from both directions, fuzziness is
neutralized by a following upstroke, leading to a symmetrical texture [29]. Although needle board arrangement, punching density and penetration depth impact the consolidation and later performance of the final product, bonding efficiency and product quality are moreover highly influenced by the used needles. Needle design and fineness determine degree of consolidation, which is dependent on the number of fibers being reoriented by each needle stroke [30]. In the following a typical needle design including its engineerable parts will be described. Figure 31 schematically shows the design starting with the crank and shank, which are used to fix the needles in the board, followed by a reduced shank (in case of a double reduced needle) and the shoulder that leads to the centerpiece of the needle, referred to as working blade. The tip of the needle is called point and can be sharp or rounded. During the needling process, the point enters the felt first and pushes away the fibers which are subsequently seized by the barbs [30].

![Figure 31: Drawing of Double Reduced Needle](image-url)
The barbs are integrated into the working blade at one or more edges in equal distances, which can be big to small, such as 6.3 mm for regular barb needles or 3.3 mm for close barb ones [29, 30]. Figure 32 depicts relevant parts of a typical barb, like throat depth, length and angle, kickup, total barb depth and barb angle. Product quality is dependent on all named parts, which can be customized to achieve desired performance [29].

![Figure 32: Barb Specifications [33]](image)

Fiber transport efficiency is mainly dictated by barb depth and length [30]. The total barb depth is defined by the distance between the top and the deepest portion of the barb, or more particular the sum of the throat depth and the kick up [14]. Depending on desired performance, there are furthermore different blade shapes available, of which cross-sections can be observed in Figure 33 and Figure 34.

![Figure 33: Cross-section Triangular and Tear Drop Blade Shape [34]](image)

![Figure 34: Cross-section Tri Star and Cross Star Blade Shape [34]](image)
The triangular shape represents the standard working part, in which barbs can be placed on all three edges, or also only on one or two edges. In contrast to previous three barbed edges, tear drop shape represents a rounded working blade that only has one barbed edge. Due to its mostly rounded working part, tear drop needles are highly suitable for joining a woven scrim to a nonwoven as weft and warp yarns are protected while needling performance still is present due to the barbed edge. Just like the triangular working part, the tri star shows three barbed edges with the special feature of concave sides, which present a higher fiber holding efficiency. Cross star working blades provide four edges barbs can be forged in, and are used for achieving even needling results with heavy weights [34].

In the end it is important to emphasize that an immense number of factors play a role in the needling process. Appearance and performance of the final product already depend on the web characteristics. Each type of fiber has distinct physical properties influencing later needling procedure and fabric behavior. Specific attributes result from polymer type as well as fiber fineness, length and geometry. Moreover the way the web is formed by, such as bale opening, carding and cross-lapping, influences fiber orientation, basis weight and thickness. A web, consisting of only parallel arranged fibers - or of too little fibers that are available throughout the web thickness, will not generate enough frictional resistance for satisfying dimensional stability after the needling procedure [29]. Furthermore, process values, i.e. needles having specific parameters, such as form and number of barbs, working blade geometry and gauge, their arrangement in the needle board and needling parameters such as direction of penetration (from top and/or bottom), stitching density and penetration depth, used during the manufacturing process itself affect nonwoven quality [30].
2.2.3 Spunbond

The spunbond process represents a “direct laydown” technique, in which a nonwoven fabric is directly produced from polymer materials in combining fiber and web formation followed by bonding in a continuous process [35]. In 1959 the first spunbond polyester nonwoven product was commercialized by DuPont under the name REEMAY® [36]. Fibers, spun by common spunbond processes, spinning monocomponent filaments, show excellent mechanical properties, the nonwoven itself however has demerits due to the large fiber diameter as for example poor flexibility [37]. Therefore, spinning multicomponent fibers is preferable for artificial leather to be able to get ultrafine fibers. Figure 35 shows an exemplary spunbond device capable of spinning bicomponent fibers (e.g. island in the sea or segmented pie fibers).

Figure 35: Spunbond (Multicomponent Filaments) [36]
There are two hoppers, each loaded with one respective polymer type. From the hoppers, the polymers are fed to screw extruders, where the initial pellets are melted. Through heated pipes, the molten polymers flow separately into the metering pump and spin pack. The bicomponent fibers are subsequently extruded through the orifices of the spinneret, which is directly located downstream of the spin pack. The formed curtain of filaments is quenched and pneumatically drawn and attenuated by an aspirator before they are deposited on a conveyor belt to form a fibrous web [38, 36]. Underneath this belt a vacuum is preferably applied to ensure pinning the web onto it. Depending on the speed of the forming belt, the basis weight of the gained fabric can be adjusted [35]. Spunbond fibers generally have a diameter of 10 to 30 microns. In the end, the spunbond web is bond, for example thermally by calendering or mechanically by hydroentangling to form a nonwoven fabric [38, 36].
2.2.4 Hydroentangling

Hydroentangling represents a fast growing bonding technique and is especially suitable to thoroughly entangle ultra-fine fibers [39, 40]. The process can basically be described as a curtain of fine high speed water jets penetrating a spunbond or a staple fiber web to thoroughly rearrange and entangle fibers of which the web is composed of. The web is transported on a perforated conveyor belt into the working zone. Here it passes underneath several manifolds into which jet strips, comprising one to three rows of orifices, are inserted. The manifolds are arranged across the machine direction and water is pressed into them, first penetrating the web before it is immediately sucked by the suction boxes, which are installed opposite to each manifold, under the conveyor belt. As soon as the web arrives in the working zone, it is pre-wetted and slightly entangled by the first manifold, having less pressure than upcoming ones, to prepare the web for following high speed water jets and prevent web tattering [41]. To now get the highest energy per unit area it is critical to produce a needle-like stream and not allow very fine jets to break up into droplets and thereby spaciously spread their energy [42]. This is commonly achieved in using cone down nozzles. The way of the fabric can either be horizontally, with horizontally arranged manifolds only penetrating one surface of the fabric, or circumferentially, during which the fabric is lead around a circular drum and consequently penetrated from both sides to achieve symmetrical surfaces [41].

Hydroentangling has the great merit of continuously applying enormous force, and thereby makes it possible to split/fibrillate bicomponent fibers while bonding them via entangling at the same time [39].
2.2.5 Fiber Splitting/Fibrillation

Splitting bicomponent fibers involves mechanical action, such as twisting, carding, needling or hydroentangling. It is desired to have a relatively weak bonding between the polymers of a bicomponent fiber to facilitate splitting process. The bonding must however be strong enough to allow bicomponent fiber spinning [16]. Bicomponent configurations such as segmented pie, segmented ribbon and tipped trilobal are splittable as surfaces of both polymers are exposed [43].

Polymers of sheath core or island in the sea fibers do also share a common interface but in contrast to previous named configurations, not all components are exposed. Both, core as well as the islands are completely surrounded by the sheath or the sea respectively. Therefore, microfibers are usually gained by removing the sea of the island in the sea fibers, but it has been shown that higher surface area webs can be gained by fracturing them [43].

The process of peeling and dividing island in the sea fibers is called fibrillation. This has for instance been realized for island in the sea fibers consisting of Nylon 6 and polyethylene terephthalate, by shrinking the Nylon component with the help of a solution containing benzyl alcohol or in using an aqueous alkali solution to slightly dissolve the part of the PET component, to weaken their interface and start separation. Multiple wet heat plus drying treatments as well as physical action, like rubbing, was utilized to fulfill fibrillation [25]. Another technique is spinning island in the sea fibers and forming a web by spunbond technology and subsequently fibrillate and simultaneously entangle the web by hydroentangling [21].
2.2.6 Fiber Washing

Next to fiber splitting or fibrillation, ultrafine fibers are commonly achieved by fiber washing. Island in the sea fibers are favorably used to gain ultrafine fibers by treating them after fabric formation with suitable chemicals to remove the sea component [21]. Fibers consisting of at least two kinds of incompatible polymers with different dissolving properties, i.e. a removable one and an ultrafine fiber forming polymer, are laid to a web and bonded to get a nonwoven fabric. After impregnation with an elastic polymer followed by coagulation, starting bi–or multi component fibers are converted to superfine microfibers by removing one polymer [20]. Dependent on the removable polymer type, different solvents are used. The soluble polymer can inter alia be dissolved in hot water or alkali solution [16]. Polyester is for example removed by sodium hydroxide, polyamide by formic acid and polystyrene and polyethylene can be dissolved by trichloroethylene as well as toluene [20].
2.2.7 Nonwoven Substrates based on Staple Fibers

Miyoshi Okamoto et al. introduced a technique for manufacturing synthetic leather comprising a substrate of multiple entangled bundles of ultrafine fibers. Prior developments struggled with producing a fibrous substrate similar to the collagen structure of natural leather. They had no technique to process microfibers, although fine fibers were achieved, further steps necessary for nonwoven development (e.g. needlepunching) were problematic. In US Patent 3,562,374, which has been further developed to US Patent 3,932,687, a solution is provided for producing ultrafine fiber bundles by using island in the sea fibers, of which the sea component is subsequently dissolved. There have also been approaches on developing a synthetic leather substrate from island in the sea fibers, where the islands were dissolved to gain multi-hollow-fibers resulted in flexible soft cloth but did not resemble the natural collagen structure. This is why the patent at hand concentrates on removing the sea component. The introduced procedure starts with forming a web of the spun island in the sea fibers which is thereupon needled to gain a nonwoven fabric. The entangled fibers are bonded at their junction points by an elastic material; a suggested technique is impregnation followed by coagulation.

Figure 36: Bonded Ultrafine Fiber Bundles [45]  
Figure 37: Single Junction Point [45]
After described treatment, the matrix is dissolved of the bicomponent fibers to remain with ultrafine fiber bundles (see Figure 36), which are slightly fixed to each other at their contact points to provide three-dimensional stability. Figure 37 shows the longitudinal freedom of mobility of adjacent fibers in fiber bundles, which results in a flexible material [44, 45].

US patent 3,705,226 deals with increasing free fiber movement upon reception of external load by additionally applying a water soluble high-elastic polymeric substance prior to the polyurethane impregnation. After washing out the water soluble temporary binder, inter fiber slippage is increased which is important for softness and drapability. Moreover comfortable touch is provided in having a surface with suede touch or grain finish opposed to a velour touch surface. To achieve set goals, the inventors followed following procedure.

Island in the sea fibers are carded and cross-lapped to a web before it is needlepunched with at least 200 punches per square centimeter using needles with up to three acting barbs. After shrinking the resultant nonwoven fabric by more than 25%, it is impregnated with a water soluble high-polymeric substance, like for example polyvinyl alcohol, carboxylic methyl cellulose or starch. Subsequently, the sea component is removed to end up with bundles of ultrafine fibers of 0.001 to 0.5 denier loosely connected by the previously applied water soluble high-polymeric substance. If the fibers would be finer than 0.001 denier, the fabric would not be strong enough to withstand practical usage and dyeability would be reduced. Coarser fibers than 0.5 denier would lead to a rough, unpleasant touch and poor flexibility.

Next, this fibrous sheet is sliced in parallel direction to its surface. The sliced fibrous assembly is then impregnated with polyurethane to fill the spaces between fibrous bundles to increase dimensional stability. After solidifying the applied polyurethane, the water soluble
high-polymeric substance is removed to create basic fibrous sheet layers. Fibers which have previously been reoriented by needling in z-direction, stick out as fiber ends after slicing operation. After buffing, these extremely fine fiber ends are raised and uniformly cover the surface, resembling a velour type touch. The opposite surface is coated by a high-polymeric substance layer, which is either embossed to get a grain finished artificial leather or grinded to end up with a suede touch [4].

Another way to increase flexibility is given by Taguchi et al. in European patent EP 0176181 A2. In the beginning, the manufacturing process resembles previously introduced US patent 3,705,226. A fibrous web, consisting of island in the sea fibers, is needled to a nonwoven fabric which is shrunk and impregnated with PVA before the sea component is removed. After immersing the sheet into polyurethane dimethyl formamide solution, EP 0176181 A2 takes a different path than conventional artificial leather processes in just partly coagulating the impregnated polyurethane before the substrate is subjected to a hydroentangling treatment. The high speed water jets hereby brake weak adhesion structure and increase entanglement of the not yet solidified composite sheet to end up with a dense soft fragmentary structure. As strong adhesion structures remain unbroken, there is no great loss in strength. After fracturing, the sheet is introduced in water to complete coagulation before washed in hot water to remove DMF residues and PVA. In the end, the gained substratum is sliced in and buffed to form naps if suede type artificial leather is desired. Grained surface can also be achieved in applying a polyurethane topcoat. The final product shows good drapeability, softness and strength. Grain finished synthetic leather form dense
creases while bending. As can be seen in Figure 38, drapeability is directly related to the water pressure.

![Figure 38: Drape Coefficient vs. Water Pressure](image)

The higher the water pressure, the greater is the penetration and consequently deeper the fragmentary structure, which leads to more flexibility. Examples 1 to 4 are manufactured in the same way, only differing in the water pressure applied during hydroentangling. The water pressure increased from example 1 (25 Kg/cm²) till example 4 (150 Kg/cm²). Comparative example 1 was not subjected to high pressure water jets at all and thereby shows a continuous binder structure [46].
The plot in Figure 38 shows that the drape coefficient exponentially decreases the more pressure is applied. Considering that the lower the drape coefficient the better is the drapeability, a more flexible material is achieved by Taguchi’s et al. technique [47].

Kato et al also took advantage of using high pressure water jets in the European patent EP 0090397 B1. A closer look at their invention is taken hereinafter. The created artificial leather comprises entangled fiber bundles consisting of ultrafine fibers with a fineness of less than 0.5 denier. Branched fiber bundles form entangled ultrafine fibers, which are anchored into previous described portion. It is desirable to have the combination of branched ultrafine entangled fibers that cover entangled fiber bundles. A sheet solely consisting of entangled fiber bundles cannot be entangled densely, resulting in a nonwoven, which is likely to undergo deformation. While a sheet entirely consisting of branched ultrafine fibers would lead to exaggerated entanglement, ending in insufficient flexibility, as mutual fiber movement is restricted. In the following an exemplary process is described to manufacture previously specified nonwoven fabric. Island in the sea fibers with PET islands in a PA6 sea are treated with formic acid to remove the sea component. Large tows of resultant island fibers are bundled and bond with PVA, before bundles are cut and crimped to staple fibers. Subsequently a fibrous web is formed which is entangled by needlepunching with a punching density of 2500 needles per square centimeter to create a nonwoven fabric with an apparent density of 0.19 g/cm³. The apparent density is then increased by heat pressing via calendar to 0.21 g/cm³, followed by the key step – hydroentangling. In subjecting the fabric through high pressure water jets (700 Pa) for three successive times, PVA is dissolved while upper fibers,
i.e. portion of ¼ thickness from surface, are branched and entangled. In the end, the surface is pressed and a resin (e.g. polyurethane) is applied to achieve a grain type artificial leather [48].

Similar to previous patent EP 0090397 B1, a nonwoven, consisting of ultrafine fiber bundles or island in the sea fibers capable of forming microfiber bundles, is created by needling a formed web before at least one surface is subjected to high speed fluid jets to branch and highly entangled fibrous bundles at the surface region. The main goal of Kato et al. thereby is to create a mélange-colored sheet, in using at least two types of ultrafine fibers having different dyeing properties. As can be seen in Figure 39, the degree of branching increases from the inner portion to the surface until it ends in super-entangled fibrils at the top. The entanglement density of the fibers should hereby be not greater than 200 microns and is measured as follows. Looking at Figure 40, a magnified portion of a representative sample is schematically depicted. The abbreviations $f_1$, $f_2$, $f_3$ and so on stand for the fibers, whereas $a_1$, $a_2$, $a_3$ … show the junction points from which the linear distances $a_1a_2$, $a_2a_3$ etc. are measured, added and divided by the number of measurements. $f_2$, for example is entangled with $f_1$ in $a_1$. After going over $f_1$, the next time fiber $f_2$ represents the lower one, in other word is overlapped by another fiber, in this case $f_3$ will be the subsequent entangling point $a_2$. 
The higher the resultant entangling density, meaning the smaller the distance between adjacent junction points, the more stable is the surface against fluff and cracks. In using needlepunching as mechanical bonding technique, it is not possible to create a desired entanglement density of less than 200 microns. In their invention, Kato et al. propose two methods to create desired super-entangled surface. Multicomponent fibers or different staple fibers, for example two kinds of island in the sea fibers, that have the same sea component but differ in their island polymer, are mixed to get a web of ultrafine fiber forming fibers having different dyeing properties. This web is needled, before one, or both surfaces in case of a thick fabric, is hydroentangled to branch and entangle fibrous bundles at the surface. Hydroentangling can either take place before sea removal or after sea removal. In first case, water jets must penetrate the surface with a higher pressure (70 to 300 kg/cm²), to ensure both, breaking or peeling off the sea component to set free island fibrils for instantaneously entangling. The gained fabric is subsequently dyed with different dye stuff to create a mélange-colored surface, which can furthermore be coated with transparent or semitransparent resin followed by embossing to end up with grained pattern artificial leather. If the ultrafine fibers have already been formed by sea removal, less energy (5 to 200 kg/cm²)
is required to super-entangle the surface, as water jets do not have to fibrillate the fibers first. A temporary binder, such as PVA may be applied prior to sea removal, which will be washed out after the hydroentangled fabric is impregnated with polyurethane to ensure fiber mobility. In the end this fabric is also dyed to get the mélange-colored surface. There are principally two methods to dye the substrate, single-bath and multi-bath dyeing. Although single-bath dyeing shortens the dyeing period, as only one bath is used, and not multiple cycles are necessary, the presence of different dye stuff in one bath oftentimes result in unwanted color contamination [49].

In contrast to the flexible material in previously introduced US patents, Kusunose et al. pursue the target of producing an artificial leather substratum, which has a relatively high flexural rigidity. It is stated that although very soft artificial leathers work well for clothing, where a high degree of softness and flexibility is required, shoe leather needs to have a high dimensional stability and a certain degree of stiffness. These features may be achieved by adding a high amount of elastic polymer to a conventional nonwoven fabric, as spaces between the fibers would be filled. This is however not recommendable as the resultant material will have an undesired rubbery hand. US patent 1,107,374, deals with creating a web of fibrous bundles which consists of numerous extremely fine fibers having a fineness of 0.005 to 0.5 denier. The filaments of the fibers hereby are spontaneously adhered to each other without using an adhesive, before the web is entangled to a nonwoven fabric which is subsequently impregnated by an elastic polymer to end up with a synthetic leather substratum. To better understand this theory a brief example is provided in the following. Cellulose dissolved in a cuprammonium solution is extruded by multiple orifices into a
coagulation bath to form filamentary solution streams. These streams are bundled before coagulation is completed to use inherent tackiness for spontaneous adhesion. The earlier stage of coagulation, the higher is the adhering strength of the filamentary solution streams. After completely coagulation, withdrawing and up winding, each fiber bundle is sized with 3% polyvinyl alcohol, before crimped cut into staple fibers. Subsequently a fibrous web is produced by carding and cross-lapping, which is entangled to a nonwoven fabric by needlepunching. Then created fabric is immersed into a 5% PVA solution and squeezed with a mangle to achieve an impregnation of 150% PVA based on the fabric weight. After drying, the fabric is impregnated with a polyurethane solution and coagulation is started in a dimethyl formamide-water bath. After repeatedly squeezing by mangle, the fabric is introduced in a pure water bath to complete coagulation process. Before drying, the substrate is sliced to end up with a basis weight of 280 g/m². Finally, the PVA is removed in boiling water before, before a grain layer is applied by knife coating. Hereby, 25% of polyurethane, solved in DMF is applied and coagulated in a water bath. The final product has a relatively high flexural rigidity of 15 mm but nevertheless shows proper suppleness, as fibers are able to move relative to each other [50].

While the inventors of US patent 1,107,374 emphasize to not work with extra adhesive to bind fibers, Wang et al. build their invention up on enhancing strength in using adhesion fibers. They claim to produce high strength imitation leather in mixing adhesion fibers, comprising TPU, with regular fibers or microfibers, before forming a web which is subsequently needle punched to a nonwoven. This base fabric is impregnated with a
polyurethane-dimethyl formamide solution and coagulated to form a synthetic leather substrate. Finally a transfer coated skin layer is laminated to gain grain finished artificial leather. The tested samples have burst strength of up to 30 kg/cm² [51].

As most nonwoven based synthetic leather cloths fail to achieve high shape stability, which is for example required in shoes or seat upholstery, the US patent 7,484,277 B2 discloses a way to reinforce the nonwoven with a scrim. Generally, there are two methods for this reinforcement, in particular by adhesive or by fiber entanglement. The adhering process hereby is the easier controllable one, but problems as a tendency to delamination or excessive stiffness may occur afterwards. Mechanically entangling the nonwoven and the woven scrim in thickness direction leads on the one hand to a strong bonding, but the difference in their fibrous structure might on the other hand end in unwanted changes in the structure of the nonwoven and the scrim. Moreover, fiber damage can occur during strong entangling. Using the needlepunching process to join the nonwoven and the scrim, there are multiple factors influencing the procedure. Usually, the needles penetrate the fabrics from the side of the nonwoven. Nevertheless, the structure of the woven scrim must receive attention. The twist of the yarns for instance plays a key role. The lower the twist, the “fluffier” the yarns and the easier they are caught on the barbs, which causes significant damage. Highly twisted yarns are stronger and difficult to break even though they are caught on barbs, but exhibit a hard hand feel, affecting the touch of the final product. Regarding the problem of yarns which are accidently caught by the barbs, there have been approaches to solve this problem in using needles having a barb depth of half or less of the diameter of the yarns of the scrim. Due to
the resulting relatively small barb depth however, insufficient entangling efficiency is achieved. This could be enhanced by increasing the punching density which would unfortunately increase fabric damage due to higher penetration. To break this vicious circle Tanaka et al. developed following formulas helping to control this process of joining a nonwoven web with a scrim by needling [14].

\[
S_1 < 2P \leq S_1/\cos(D_1 \times \frac{\pi}{180})
\]

\[
S_2 < 2P \leq S_2/\cos(D_2 \times \frac{\pi}{180})
\]

where \( P \) stands for the total barb depth, describing the distance from the top to the deepest portion of the barb or in other words the sum of the throat depth and the kick up. To get the best result, \( P \) should be in a range of 50µm to150µm. If \( P \) is smaller than 50µm, fibers to be entangled become difficult to be caught, leading to no or little entanglement of the web itself and with the underlying scrim. Exceeding a depth of 150µm would deteriorate smoothness and evenness of the nonwoven, furthermore noticeable pores would emerge due to the penetrating needles. \( S_1 \) and \( S_2 \) are the diameters of the warp (\( S_1 \)) and weft yarns (\( S_2 \)) and \( D_1 \) and \( D_2 \) describe the angle of the penetration angle of the barb to the scrim. This angle should be in the range of 35° to 55° to insure that fewer yarns are caught by the barbs during needling.

After setting these base conditions, a fibrous web comprising superfine fiber-forming fibers is superposed on a woven cloth and united by needling. The maximum punching density hereby should not be higher than 2000 punches per square centimeter to prevent immense scrim damage. In case that the web on top of the scrim has already been entangled before, a punching density of less than 1000 punches per square centimeter is sufficient to not
excessively entangle the fibrous web. After joining the fabrics, the whole assembly is impregnated by an elastic polymer (e.g. PUR) followed by coagulation to create a substrate for artificial leather. By impregnating the fabric assembly, superfine fibers, i.e. in this case finer than 0.5dtex, are secured and cannot be pulled out of the substrate, furthermore, the later adhesion to a surface coating layer is enhanced. Hand feel is also controlled by this impregnation step. It is hereby important to not exceed 150% by the mass based on the nonwoven after sea removal, to prevent a rubbery touch. After impregnation and coagulation, the sea component is washed out of the substrate to get ultrafine flexible fibers, before one side of the substrate is buffed to get suede artificial leather [14].

Intertwining a nonwoven with a reinforcing woven or knitted fabric by needling, to create a strong and soft assembly is also the target of Fujii et al. in US patent US 5112421 A. In contrast to the previous patent, a strong focus is set on the number of twists instead of the total barb depth. As has already been shown, higher twist lead to less fiber breakage, because firmly twisted yarns act as a thick fiber which is not likely to break easily by small needle barbs. Exaggerated turns however lead to unwanted stiffness. Therefore Fujii et al. set a rule of thumb of using yarns for the woven or knitted fabric having 700 up to 4000 turns per meter. Yarns with less than 700 turns per meter are easily damaged by penetrating needle barbs, ending in a weak fabric of which broken fibers may stick out. These broken fibers can also stiffen the assembly by undesired extra entangling with staple fibers. If a reinforcing fabric is used, of which one part of the constituents consists of less twisted yarns, needle barbs should be oriented parallel to these yarns to not been able to hook fibers and prevent
damage. Before superposing the fibrous web, consisting of ultrafine fiber forming composite fibers, and the reinforcement fabric, the web is slightly preneedled to prevent creasing of the fabric in later entangling process. Different superposing combinations are suggested, such as web-fabric, web-fabric-web or web-fabric-fabric-web. After intertwining, the sea component is removed and the assembly is impregnated with PVA, dried and impregnated with a PUR DMF solution, which is subsequently coagulated in water. In the end PVA is removed by hot water before naps are formed by buffing. In comparing artificial leather consisting of a woven plain weave, sandwiched in between ultrafine fiber nonwovens to an artificial leather created exactly as previous one except of not inserting the high twist yarn woven fabric, Fujii et al. underline the success of their technique to produce a soft strong highly wear resistant and relatively low elongation suede, which would be for example suitable for sport shoes [52]. Following table shows a comparison of the given example.

<table>
<thead>
<tr>
<th></th>
<th>Sample w/ Woven Fabric</th>
<th>Sample w/o Woven Fabric</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basis Weight</strong></td>
<td>446 g/m²</td>
<td>438 g/m²</td>
</tr>
<tr>
<td><strong>Tensile Strength</strong></td>
<td>15.2 kg/cm</td>
<td>10.5 kg/cm</td>
</tr>
<tr>
<td><strong>Tensile Elongation</strong></td>
<td>48% (length)</td>
<td>101% (length)</td>
</tr>
<tr>
<td></td>
<td>51% (width)</td>
<td>112% (width)</td>
</tr>
<tr>
<td><strong>Custom Abrasion</strong></td>
<td>18500 cycles</td>
<td>4200 cycles</td>
</tr>
</tbody>
</table>
Hwang et al. also investigated in reinforcing a nonwoven to create a stronger form stable final product. As a reinforcing material either woven or knitted material is proposed. In contrast to US patent 7,484,277 B2, the focus is not on perfect uniting the fabrics by needling but on strength and elongation, to not only improve durability and form stability but also facilitate later mounting process and workability. The constant load elongation hereby represents a key factor. In their US patent US 2008/0293316 A1, it is claimed that a constant load elongation of 10 to 30% is desirable in longitudinal as well as lateral direction to achieve best results. If the constant load elongation of a fabric was higher than previous range, the form stability of artificial leather is poor as extension would continue during usage. An elongation of less than 10% increases the possibility of product damage during the mounting process. Next focus is the strength, which is set to be in the range of preferably 35 to 60 kilogram force per 50 millimeters. Not only little elongation but also a weaker fabric diminishes workability as there is a higher risk of damage during mounting. A higher strength than 60 kilogram force per 60 millimeters is not possible as elongation would become too little. To achieve desired strength and elongation properties, a woven or knitted fabric, having a warp/weft density up to 100 yarns per inch, is entangled with a nonwoven base material by needlepunching. The reinforcing fabric must have a minimum of 20 yarns per inch to provide sufficient strength, more than 100 yarns per inch are however not possible, as the probability of damaging the yarns by needling is too high. A damaged fabric would lead to deteriorated elongation properties of the final product. In contrast to US patent 7,484,277 B2, needles having one or no barbs are recommended to prevent damaging reinforcing material moving with a punching density from 1500 to 3000 punches per square
centimeter. After joining the reinforcement to the nonwoven, a 3 to 15% concentration of a water soluble solution, like for example polyvinyl alcohol, is padded onto and dried. Subsequently, the sheet is dipped in a polyurethane solution before it is coagulated and washed in hot water (50 to 80°C) to also remove the temporary filled water soluble polymer. After drying, there should be a polyurethane content of 10 to 50% by weight with respect to the weight of the composite sheet on the fabric. The PVA impregnation prior to the polyurethane wet impregnation helps to prevent a hard hand feeling as the polyurethane resin is hindered to excessively bind with fine fiber bundles. In the end, the sea component of the bicomponent fibers forming the nonwoven is dissolved to produce fibers finer than 0.3 denier. Thereby, the thickness of the composite sheet decreases while improving the apparent density (describing the mass per unit volume). The structure of the joined reinforcing woven or knitted cloth hereby helps to maintain the form of the composite sheet. Finally, the surface is napped to raise fibers to get suede like artificial leather [53].

Takeda et al. investigated in a bicomponent staple fiber, which provides among other things interesting structural advantages for artificial leather substrates. The invention, including its merits, will be explained in the following. Figure 41 depicts the cross-section of the developed composite staple fiber. As can be seen, it consists of two polymer components which are arranged like segmented ribbons in a round fiber. Furthermore it can be detected that one polymer is completely surrounding the other and thereby building the periphery. This encapsulation has to meet the requirement of being thicker than 0.05 µm to entail on the one hand the desired higher resistance to prematurely
peeling or splitting during nonwoven manufacturing process. Undesired fluff can be prevented when fibers will not already start splitting during web formation, i.e. carding process, and web entangling through needling. On the other hand, the surrounding should not be thicker than \(1.5 \, \mu \text{m}\) to not hinder but allow fiber splitting during hydroentangling to form ultrafine fibers in the end. In contrast to ultrafine fibers gained by dissolving, fiber splitting results in considerable higher production efficiency, because no component is lost during microfiber formation. As can be seen in Figure 42, Figure 43 and Figure 44, the individual filaments have a flat shape, resulting in a characteristic luster.

![Figure 41: Bico Fiber [25]](image1)

![Figure 42: Split Bico Fiber](image2)

![Figure 43: Polymer A [25]](image3)

![Figure 44: Polymer B [25]](image4)

To get good dyeability, the ratio of length “L” and thickness “D”, describing the flatness, should be at least 2. A flatness ratio less than 2 would result in poor dyeability, meaning that a high amount of dye would be necessary to achieve satisfying color development. Moreover,
it must be taken into account that, hand feeling is related to the fiber thickness. The finer the fiber, the better is the touch of the final product. In this example, the thickness “D” of the individual fibers (see Figure 43 and Figure 44) may not exceed 3 µm to ensure soft hand feeling. To get a compromise of acceptable dyeability and good touch, individual fiber thickness must be adjusted. Preferably it is suggested to set fiber fineness to at least 0.02 dtex up to 0.6dtex [25].

As has been shown by Takeda et al. in previous introduced US patent 6,335,092 B1, fiber size and shape play a significant role in dyeability and surface gloss. Looking at conventional island in the sea fibers, there is a problem of either extremly fine islands, showing poor dyeability combined with little dye fastness and fabric tenacity, or easy dyable coarser islands which will only lead to low surface gloss and oftentimes poor feel. Wang et al. concentrated on mitigating and obviating these problems in creating artificial leather of island in the sea fibers comprising different island sizes (see Figure 45) to obtain excellent dyeability and fluff-like properties. There are two conventionally used techniques of spinning island in the sea fibers, named conjugated and mixed spinning [54]. Conjugated melt spinning can be described as two or more components, which are combined in a predefined arrangement at the back of a spinning nozzle and elongate before extrusion [55]. Numerous core streams are injected into a matrix stream by multiple tiny tubes to converge in the spinneret hole and form a conjugated island in the sea stream. Mix spinning differs from conjugated spinning in already mixing the respective polymer amounts, e.g. 30% sea component and 70% island component, in the extruder before the molten assembly passes a
static mixer, which over and over divides the multicomponent stream to form a matrix with hundreds of cores inside [56].

![Figure 45: Schematic Cross-Sections Mix-Spun I/S Fiber [54]](image1)

![Figure 46: Cross-Section Mix-Spun I/S Fiber [54]](image2)

In their invention the mixed spun polymers are a polyamide for the island component and for example a polyolefin, polyester containing sulfonic salt or polyvinyl alcohol for the sea component. It is important that the polymers have different dissolving properties and have a ratio of melt flow index (MI) divided by relative viscosity (RV) of used polymers is in the range of 2.7 to 3.5 [54]. The melt flow Index is used to indicate the rheological behavior of a polymer and can be described as the amount of a molten polymer passing through capillary equipment with standardized shape and length at a defined temperature under a predetermined weight [57].

The relative viscosity is the ratio of the viscosity of the polymer solution to the viscosity of the used solvent. It is determined by dividing the flow time of a polymer solution by the flow time of the pure solvent to travel through a capillary viscometer [58].
After mix spinning the island in the sea fibers, they are stretched, crimped and cut to obtain staple fibers, which are subsequently formed to a web by carding and cross-lapping before a nonwoven is created by needling. To increase tenacity, an additional nonwoven fabric or coarser (1 to 6 denier) monocomponent fibers, for example nylon, polyester or polyolefin staple fibers, can be incorporated. Next, the created fabric is impregnated with solvent soluble polyurethane, solidified and washed before the sea component is removed to remain with island fibers having different sizes from 0.01 to 0.5 denier [54]. The obtained artificial leather is tested with standard AATCC-8, during which the test specimen is rubbed with a white crock test cloth to measure color transfer for later comparison with a gray scale. The achieved wet abrasion fastness in dying is grad 3.5, furthermore it is stated that similar properties to genuine leather were gained [54, 59].

In contrast to engineering the shape of single components of a composite fiber, US Patent 6,299,977 B1 concentrates on deforming the whole bicomponent fiber in order to draw advantages for the appearance and properties of the final product. Takeyama et al. introduce a method for manufacturing a nonwoven substrate especially suitable for creating different types of artificial leather, in particular nubuck-like man-made leather, having short naps, grain type nubuck-like man-made leather, partially showing short naps, and full grain man made leathers which do not comprise any naps. The achieved leather like material should meet main characteristics of natural leather, which are stated as an extremely smooth surface implying a soft hand and fine wrinkling on bending [60]. Fine bent wrinkles represent the so called “leather-like grain break”, standing for the behavior of well finished leathers during
folding and crumpling. In contrast to the fine wrinkles on the smooth curved contour of a leather piece, paper and films form sharp creases and big wrinkles when folded. This undesired effect is called “pin wrinkling” [61]. To reach their goal, Takeyama et al. started with island in the sea staple fibers, of which fibrils will be finer than 0.2 denier after sea removal. A nonwoven fabric was established by web formation followed by needlepunching with a punching density of at least 500 punches per square centimeter, to obtain sufficient entanglement, which is necessary for adequate strength. However it is recommended not to exceed 3000 punches per square centimeter, as excessive punching would lead to fiber damage and breakage. Next, the nonwoven is softened by heat before passing it through calender rolls to get desired apparent density of about 0.25 to 0.45 g/cm³, which equals basis weight divided by thickness. Afterwards, the gained nonwoven fabric is impregnated in a solution of a high molecular elastomeric dissolved in an organic solvent, such as polyurethane in dimethyl formamide, followed by a coagulation process to form a microporous sheet. After drying the assembly, the composite is pressed under heat by smooth calendar rolls, in order to form the upper island in the sea fibers into ellipses. Their shape has to comply with following equation: \(0.1 \leq a/b \leq 0.6\), where \(b\) describes the width, representing the major diameter, and \(a\), as minor diameter, describes the height (see Figure 47).
The relevance of this rule is depicted in Figure 48 through Figure 51. As can be observed in Figure 48 and Figure 50, a/b ≤ 0.6 results in a smooth evenly covered surface in contrast to Figure 49 and Figure 51. If the fibers, appearing at the surface have a width (b) and height (a) resulting in a/b>0.6, the gained artificial leather shows considerable big gaps in between the fibers. This will lead to an unfavorably low nap density in a nubuck like synthetic leather (see Figure 49) or respectively an unsmooth grain surface (see Figure 51) [60].
Furthermore, orange peel effect occurred for latter described imitation leathers when bending. This means that an initial relatively smooth appearing surface will form large wrinkles when flexing the material, resembling the bumpy skin of an orange peel [60, 62]. In the end, the material is subjected to a solvent bath to dissolve the sea component and remain with ultrafine island fibers, before the surface is treated with a solvent for the high molecular elastomeric polymer, for example DMF as a solvent for polyurethane. This removing treatment is repeated several times, followed by drying steps, to get a nice even homogenous surface after subsequent buffing step. To end up with a grain type artificial leather (like Figure 50: a/b ≤ 0.6) a film of high elastomeric polymer material is placed on top of the coagulated material before pressing the whole assembly to achieve elliptical shaped fibers, following previously described rule 0.1 ≤ a/b ≤ 0.6, at the surface of the leather imitate. In the end, the sea component of the island in the sea fibers is dissolved to convert these to ultrafine fibers [60].

Previously introduced staple fiber artificial leather substrates have in common that they are usually combined with an elastomeric material, i.e. polyurethane to achieve desired leather-like properties. Horiguchi et al. addresses the demerits of these composite materials as for example the use of hazardous organic solvents, such as dimethyl formamide, negatively impacting the working environment. Moreover recyclability is difficult as the elastomer is permanently integrated into the fibrous structure. Different decomposition methods or highly expensive separation into individual components would be necessary. To overcome inter alia named problems; in their European patent EP 1647620 A1 they introduce a technique to
produce a leather-like sheet comprising no or at most very little elastomer. A highly compact nonwoven fabric is produced by following steps:

Bicomponent staple fibers of different lengths are mixed and formed to a web. Short fibers having a length in the range of 0.1 to 0.5 cm and long fibers in the range of 1 to 10 cm are combined to gain high density and better appearance by shorter fibers, whereas longer fibers enhance physical properties of final product. Formed web is needled with a punching density of at least 1000 punches per square centimeter to gain an apparent density of at least 0.12 grams per cubic centimeter, before bicomponent fibers are converted to ultrafine fibers of a fineness of 0.0001 to 0.5 decitex. The nonwoven consisting of ultrafine fiber bundles is now impregnated with a water soluble temporary binder resin, such as polyvinyl alcohol, and dried before the fabric is sliced perpendicular to its thickness to gain two or more separate sheets. Integrated PVA is either removed before or during hydroentangling with a pressure of at least 10 MPa, to be able to strongly entangle ultrafine fibers among themselves. To further increase apparent density to at least 0.28 grams per cubic centimeter and thereby improve dense hand and later abrasion resistance, the thickness of the created nonwoven is reduced to 0.1 to 0.8 times by hot calender rolls after water jet treatment. Prior calendaring, jet dyeing can be conducted to end up with a semi-grain leather-like surface. A suede-like substrate with raised fibers can be created by buffing the calendered fabric.

To further increase material properties, additives, such as fine particles or chemical substances can be added. In for example integrating fine particles, abrasion resistance can be increased. In further adding softening agents, soft hand and smooth surface touch are obtained but abrasion resistance decreases at the same time. Therefore a balance between
different additives must be figured out to meet desired product properties. Claimed abrasion resistance of invention at hand is a weight loss of at most 20 mg and not more than 5 pills after 20,000 turns in the Martindale testing device with a weight of 12 kPa [40].

As it has already been stated that longer staple fibers are likely to increase physical properties it is interesting to get to know further merits and/or demerits and other processing methods. Therefore, following paragraphs investigate in artificial leather substrates made of continuous fibers.
2.2.8 Nonwoven Substrates based on Continuous Fibers

In contrast to described artificial leather substrates based on staple fibers, using continuous filaments forgoes numerous devices like bale opener, raw fiber feeder, carding and crosslapper. Continuous filaments are not limited by named apparatus. Staple fibers are restricted in length, degree of crimp and fineness. In view of stability, staple fibers should generally have 3 to 6 dtex, whereas multicomponent continuous fibers may be selected from 1 to 5 dtex to obtain desired fineness, hand and properties after conversion [20]. Furthermore, the strength of a nonwoven fabric is enhanced due to the continuity of the fibers [20, 37]. As has previously been shown, island in the sea fibers are preferably used to get a nonwoven fabric comprising ultrafine fibers. Commonly, the sea component is hereby released by dissolving, to end up with the tiny islands. Nevertheless, there are also techniques using splittable multicomponent starting fibers.

In the European patent EP 0624676 B1 a technique is introduced to create a nonwoven base fabric for artificial leather, comprising microfibers gained by fiber splitting. Starting with a spunlace process, bicomponent fibers are spun, attenuated and instantly laid to a web. Gained web forming fibers (see Figure 52) consist of two polymers having significant difference in melting temperature and are not soluble in each other to reduce their affinity and facilitate later splitting process. Subsequently, the web is subjected to point calendaring to soften the polymer having a lower melting point and thereby fuse the filaments partially together. After this bonding step, the nonwoven is rubbed and wrinkled to separate components of the fibers in between the bonded regions (see Figure 53). The degree of splitting in the non-heat bonded areas should be at least 70% [24].
In contrast to splitting fibers by hydroentangling, there are no crushed elements, which may on the one hand not be suitable to form a nonwoven fabric, or on the other hand result in dust. Furthermore, the nonwoven fabric is not tightly bond three dimensionally, leading to increased softness [24]. Although this technique seems to be promising in respect of degree of splitting, it is questionable whether the fabric shows sufficient strength as fibers are not entangled three dimensionally and only partially bonded. Moreover, as can be clearly seen in Figure 53, the final base material is not uniform with regard to its thickness. This fact complicates later coating process and increases the tendency of delamination.

Although it has been argued that converting fibers into microfibers by splitting, and thereby dividing the polymers through their interfaces in longitudinal direction, is hardly uniform and therefore not recommended for creating a substrate for suede type artificial leather, Wagner et al. introduced a technique to produce such a nubuck like synthetic leather [20, 63]. In the US patent 6,838,043 B1 they concentrate on creating a strong nonwoven fabric, consisting of supermicro endless filaments (having a diameter of less than 0.2 dtex), as a base material to be impregnated and/or coated to result in a synthetic leather. It is disclosed that a spunlaid web, consisting of bicomponent fibers is bonded and simultaneously split by hydroentangling. Hereby it is important that the produced bico fibers consist of two
incompatible polymers, such as polyamide and polyester, to allow good splittability into ultrafine endless filaments. The polymers are arranged in an orange like segmented pie structure and it is claimed to add dyeing pigments among other additives to the polymers to strongly bind the dye into the fiber and prevent future fading. In contrast to European patent EP 0624676 B1, the spunlaid fabric is strongly bonded by high pressure fluid jets alternately from both sides to gain a very uniform nonwoven fabric with isotropic filament distribution. Furthermore a fiber splitting amount of more than 90% should be achieved by this technique. To produce desired artificial leather, the created base fabric is either impregnated with a polyurethane dimethyl formamide solution, followed by coagulation or an aqueous polyurethane latex dispersion is used as an eco-friendly version, which is coagulated by hot water and subsequently dried and cross-linked without having solvent residues left. In the end, the nubuck-like synthetic leather is polished or buffed, to raise microfiber ends at the surface to improve feel and surface properties and get the so called "writing effect”, which describes the possibility of visibly orienting exposed fiber ends [63]. Creating a spunbond nonwoven with improved strength is also the target of Krishnamurthy in the patent US 2012/0156461 A1. A spunbond web is formed of sheath core fibers, having polyethylene terephthalate as core and polytrimethylene terephthalate as sheath, with an average fiber diameter in the range of 2 to 20 microns. After spinning and lay down process, the spunbond web is intermittently bonded to provide a more breathable web. By point calendaring, the PTT component of the fibers is partially melted to create fusion bonds between the spunbond fibers, whereas the PET core component is due to its greater thermal stability, not melted and will therefore further contribute to the nonwoven strength. The
gained fabric shows higher strength than comparable pure PET or pure PTT spunbond nonwovens. To show some numbers, the gained tensile strength in both, machine and cross direction is up to 5 N/m² and the Mullen burst per unit basis weight is in the range of 3.5 to 10 KPa/m² [35].

Creating a substrate for grain-finished artificial leather, having softness without resistance, hand with stiffness and high peeling strength is the objective of Fujisawa et al. in their European Patent EP 2025806 B1. Similar to US Patent 6,299,977 B1 an important criteria of the final product furthermore is fine bent wrinkles. Moreover, it is remarkable that the substrate is produced without using hazardous solvents to protect the global environment. Spunlaid multicomponent fibers, which consist of at least two different polymers having different chemical and/or physical behavior, build the nonwoven base layer. Preferably, the fibers are spun as island in the sea, to end up with uniform microfine fibers and prevent damages during needling. By removing the sea component, the filaments are converted to the ultrafine fibers. To facilitate removing and meanwhile protecting environmental pollution, thermoplastic polyvinyl alkolohol, having a low degree of polymerization (less than 500) to increase solubility in hot water, is chosen to form the sea component. PVA is not only water-soluble but also biodegradable. Waste water containing PVA can be decomposed by activated sludge. For the islands component, an easy heat shrinkable polymer like polyamide, polyoelfines or polyesters is chosen. The multiple spunlaid webs are superposed and three dimensionally entangled by needle punching to obtain an apparent density of 0.13 to 0.2 g/cm³. Next, the fabric is heat shrunk to get a higher densification. Hereby, the fabric is first wetted and then shrunk at an ambient temperature of 60 to 95°C and relative humidity of
75 to 95%. By adding the water, the PVA sea polymer is sufficiently plasticized to allow the islands to shrink. The high relative humidity prevents hardening of the PVA throughout the shrinking process due to evaporation of water to ensure sufficient contraction to an apparent density of 0.3 to 0.7 g/cm$^3$. Subsequently the nonwoven fabric is hot pressed to smoothen the surface and adjust the apparent density to 0.4 up to 0.8 g/cm$^3$. During this step it is important that the fabric is still wet to remain the plastiziced state of the PVA. The fabric now has a smooth surface, a sufficient high apparent density and a good shape retention resulting in a soft product having enough stiffness. This is the reason why little amount of binder resin (elastic polymer) is ample. Usually, as a subsequent step, the nonwoven substrate is impregnated with a binder resin and coagulated to obtain a natural leather-like softness. Preferably, a crosslinked elastic polymer is used to increase water resistance after coagulation and drying process, but, crosslinked elastic polymers have poor adhesive properties. This resembles a big problem for producing grain-finished artificial leather, as the adhesiveness of the used adhesive is decreased by the crosslinked elastomer on the surface of the nonwoven substrate. Therefore the laminated grain layer (skin layer) will not adhere properly and peels off easily. To solve this problem, Fujisawa et al. claim that the created substrate should have one densified surface, comprising microfibers, which is free of a binder resin, whereas the remaining part and opposite surface should be impregnated with an elastic polymer to fix microfine fibers sufficiently and get good shape retention, surface smoothness and fine bent wrinkles. To reach this claim, the sea component PVA plays a key role. Water is purposefully applied on one surface of the nonwoven fabric to locally plasticize the PVA sea components. Next, the fabric is put under a hot press, where the moist surface will turn to
a very densified layer or a film. As the surface portion has been pre-wetted, a quite low
temperature (110 to 130°C) is enough to evaporate the water and fix the PVA based resin in a
shrunk state. Without water, or in using another sea component (e.g. PE), a higher
temperature would be necessary, making it impossible to only densify the surface portion
without increasing the apparent density of the whole fabric.

After creating the desired PVA film at one surface, the fabric is impregnated with an aqueous
emulsion of an elastic polymer. The aqueous emulsion is hereby hindered to migrate into the
densified surface, leading to one surface which is free from elastic polymer. Subsequently the
emulsion is coagulated and dried, before the sea component is removed in a dying machine,
i.e. jet dying machine, to end up with ultrafine fibers of 0.0003 to 0.5 dtex. Finer fibers than
0.0003 dtex would collapse, leading to undesired immense densification, whereas. After
dissolving the sea component, the densified surface portion is buffed by sandpaper to remove
possible binder resin remnants, before laminating the skin layer. As there is no elastic
polymer left on the substrate surface to be laminated to the grain layer, the adhesion strength
between the respective layers is high [20].

As it has been shown, high strength combined with a very pleasant hand are two important
aspects of artificial leather. In their US patent 5,652,051 Shawver et al. introduce their “hand
enhanceing polymers”, they use to create a spunlaid fabric fullfilling previous named aspects.
To measure the softness of their nonwoven fabrics, they use a “cup crush test”, which
evaluates the stiffness in measuring the peak load required to crush a fabric, which is shaped
into an inverted cup. The cup shaped fabric is surrounded by a cylinder to ensure a uniform
deformation. A hemispherically shaped foot constantly descends until the fabric is crushed.
The lower the crush value, the softer the sample. In incorporating hand enhancing polymers, the tested crush value should diminish at least 25% in comparison to similar fabrics produced without them. Said polymers are either copolymers containing polypropylene and ethylene, 1-butylene or 1-hexylene in a specific weight percentage or a teropolymer comprising propylene, ethylene and 1-butylene [38]. Although it is stated that a fabric with pleasant hand is produced, it is questionable whether this can be verified by only using a cup crush test.
2.3 Coating

The main objective of coating a polymeric layer on a textile base fabric is to impart new characteristics in respect of appearance and functional properties. Depending on the substrate as well as the coating material (i.e. paste, solution, solid powder or film), the respective coating method is chosen [64]. During the production of artificial leather impregnation direct or transfer coating are the most common application techniques.

2.3.1 Impregnation

Impregnation, or dip coating generally means full immersion of the material into the fluid, before excess is removed either by squeeze rolls or doctor blades. The time the substrate is in the tank of coating material is known as dwell time. To ensure higher penetration, a prewet station is added to remove air from fiber interstices prior to actual impregnation [64]. Dip coating is used in artificial leather manufacturing process for impregnating the nonwoven substrate with a binder resin and further coagulate it to obtain a natural leather-like softness [20]. Moreover impregnation is also used for polyvinyl alcohol saturation. Polyvinyl alcohol is commonly used as temporary binder to enhance product quality. It is not only water-soluble but also biodegradable. Waste water containing PVA can be decomposed by activated sludge [20]. PVA impregnation prior to polyurethane wet impregnation helps to prevent a hard hand feeling as the polyurethane resin is hindered to excessively bind with fine fiber bundles [53]. Next to ensuring fiber mobility, PVA is used to temporarily fix fiber bundles for slicing a nonwoven substrate prior to further production steps [40].
2.3.2 Direct coating

During the direct coating process (see Figure 54), an even amount of coating material is directly coated onto a dry smooth fabric. This is commonly achieved by knife coating, which is also known as spread coating [65, p. 13, 64].

![Diagram of Direct Coating](image)

Figure 54: Direct Coating [66]

Generally, the fabric is kept under tension and simultaneously fed over the bearer rolls under a knife, where the coating process takes place. There are three different arrangements of the doctor blade, i.e. knife on air, knife over blanket and knife over roll. Figure 55 depicts where the knife is located during a knife on air coating process. This arrangement is also known as floating knife. As the doctor blade is positioned directly after a support table, the knife completely rests on the fabric. This is the reason why a higher compression is applied on the coating material leading to greater penetration and forces the coating compound to enter interstices of the fabric. With this technique very thin, lightweight impermeable coatings may be achieved. As the knife directly rests on the fabric, the amount of add-on is not determined by the gap size but by the viscosity and fabric tension. The higher the viscosity of the
coating, the more is added on the substrate. In contrast, a tauter fabric will lead to a lower coating weight [64].

In comparison to the previous arrangement, Figure 56 shows that in the knife over blanket type, a short conveyor endless rubber blanket, mounted and stretched on two rolls, acts as support for the knife. Therefore, it is possible to coat easy damageable unstable fabrics. The add-on amount is regulated by the tension of the rubber blanket [64].

Knife over roll is the most simple and accurate technique. As can be seen in Figure 57, the doctor blade is directly placed on top of a roll. The gap between knife and roll, or more precisely between knife and fabric which is passing over the roll, is adjustable and controls the coating weight [64].
To coat a fabric, the compound is applied in front of the knife. The knife is fixed and acts like a barrier as soon as the fabric moves forward. Due to the motion, the viscous coating reservoir in front of the doctor blade starts to rotate. This rolling bank subjects pressure on the web and is able to influence the coating weight. The higher the rolling bank, the greater the pressure and the heavier is the coating. This phenomenon can however lead to unevenness, as soon as the coating material is not poured equally in front of the knife and rolling bank is for example higher at the center than at the sides, resulting in a heavier coating at the center. Next to the arrangement of the knife and the evenly applied coating material, the shape of the knife itself and its operation angle play a great roll [64].
In Figure 58 and Figure 59 two commonly used knifes are shown. The knife type (see Figure 58) with its small base of about 0.5 to 4 mm is suitable for lightweight coatings. In contrast, the shoe type knife, which can be observed in Figure 59, exhibits a large base of approximately 2 to 30 mm, allowing a heavier add-on. Moreover, the penetration can be altered by elevating the heel of the knife. As the toe is closest to the fabric, the higher the heel is lifted, the greater is the wedge formed between heel and substrate. As more coating material may enter a larger wedge, more pressure is on the fabric leading to increased penetration. This “wedge effect” is also used by the V type knife.

\[
\text{Figure 60: V Type [64]}
\]

Due to the pressure on the coating material, higher penetration is achieved as the compounds are forced into interstices of the fabric. This entails good mechanical adhesion. Due to its sharp base however, multiple passes may be required to end with desired coating weight. As has already been mentioned, the angle the knife is mounted affects the penetration. If the knife is not horizontal to the axis of the roll below, a wedge appears. If the knife is on the one hand in an acute angle to the moving fabric, a wedge is formed, leading to higher pressure on the coating material and therefore more penetration and heavier add-on. On the other hand, an obtuse angle will result in a low coating weight [64].
2.3.3 Transfer Coating

In contrast to direct coating, during the indirect coating process, which is commonly known as transfer coating, the layers are applied the other way round. First a hard and abrasion resistant topcoat, then the intermediate layer, usually made of a softer polymer, before the adhesive coat is applied to finally laminate the substrate to the produced film. Between each application step, it is important to thoroughly dry applied layer prior to coat the subsequent one on top of it [47, pp. 13,14].

Figure 61: Transfer Coating [66]

Figure 61 depicts that the coatings are applied to a paper which is able to release the whole assembly after drying. This release paper is coated by silicone or polypropylene to provide desired releasing properties and oftentimes comprise engravings, gloss or matting degrees, of which the negative structure is transferred to the applied coating [65, pp. 13,14].

To prevent release paper damage while applying the coating, the combination knife over rubber backing roll is typically chosen. In regard of polyurethane topcoats, it is favorable to use a three-coat operation, meaning applying two top layers prior to the adhesive (tie coat)
followed by lamination. The two top layers have the benefit of impeding pinholes and the possibility of applying two different polyurethanes types for special performance [64].
2.3.4 Polyurethane

Polyurethanes were developed in 1937, when Otto Bayer developed diisocyanate polyaddition and Heinrich Rinke created 1,6-hexamethylene diisocyanate (HDI). Initially, fiber forming was the focus of polyurethane development in order to compete with DuPont’s Nylon fiber. Later on research was broadened to polyurethane foams and coatings [67]. Polyurethanes are esters of carbamic acids and are generally formed by a reaction of organic isocyanates and a compound having hydroxyl functionality. Figure 62 depicts the reaction of an isocyanate group with a hydroxyfunctional coreactant, resulting in a urethane linkage [68, pp. 1-3].

\[
-N=C=O + H-O- \rightarrow -N-C-O-H
\]

(Isocyanate Group + Hydroxyl Group = Urethane Unit)

Figure 62: Formation of Urethane Repeating Unit [68, p. 2]

All polymers, containing multiple urethane groups in their backbone are classified as polyurethane. It hereby does not matter of what chemical groups the rest of the chain is made of. Therefore, common polyurethane may comprise aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea and isocyanurate next to its urethane groups [68, pp. 1,2]. Depending on the selection of polyisocyanate and suitable coreactant, key characteristics, such as solid content, gloss, elasticity, tensile strength, hardness, solubility, resistance to chemicals and costs can be controlled [69]. As it is schematically shown in Figure 63, polyurethane consists of hard and soft segments, whereby the coreactants, such as polyl
represent the soft and the urethane and urea groups the hard segments. Latter ones are able to build hydrogen bonds between themselves. Depending on the soft or hard segments concentration, polyurethane characteristics change. The hard segments with secondary bonds are in crystalline form and responsible for high melting point, tear and tensile strength and influence solubility in polar solvents like water and alcohol. In contrast, the soft segments are responsible for elasticity, the solubility in unpolar organic solvents and influence glass transition temperature [65, pp. 237,238]. Soft segments allow water vapor transmission leading to breathability, while hard segments repel water droplet penetration [70].

Figure 63: Hard and Soft Segments of Polyurethane [65, p. 237]

Polyurethanes are popular as a coating or impregnation material due to advantageous physical and chemical properties such as flexibility, high brittleness temperature, high abrasion resistance, high tensile and tear strength and chemical resistance. Already thin coats fulfill previous named functions, which compensates price difference to lower performing more cost effective PVC [61, 66, 70].
2.3.4.1 Water Vapor Permeability

Water vapor permeability, which is often also referred to as breathability, is a key factor of comfort in the clothing industry. It can be defined as the time rate during which water vapor passes through a flat permeable material having a unit thickness. Water vapor transmission is hereby induced by vapor pressure difference between the two respective surfaces [71]. For the human body, it is desirable to maintain a constant core temperature in different environmental as well as activity conditions [70]. It loses approximately 30 grams of water per hour through the skin during rest and even 1000 grams per hour during physical activity [65, p. 3]. Body heat balance is maintained by cooling down with the help of evaporating sweat from the skin. If worn clothing is barely breathable and consequently builds a barrier that hinders evaporated sweat from passing, water vapor condensation occurs, leading to discomfort and clammy feeling [70]. This is especially problematic in case of artificial leather, as Hole and Whittaker showed in their paper that impermeable coatings easily lead to sweat accumulation at the junction between fabric and film, having a negative effect on adhesion and thereby possibly end up in delamination, especially during flexing in wear [6].

Breathable coated fabrics are microporous and/or monolithic. Microporous coatings have, as the name already implies, multiple open micro pores, which are 2-3 µm small, allowing water vapor molecules having a size of $40 \times 10^{-6}$ µm to pass through, but resist water penetration as water droplets are too big with a size of 100 µm to pass through fine interconnected channels. Non-porous monolithic coatings let water vapor pass molecularly through hydrophilic hydrogen groups in the polymer chain. First, water vapor is absorbed by the exposed polymer surface and subsequently migrates under concentration gradient to the
opposite surface. As previously been mentioned, water vapor transmission takes place in the soft segments of the polymer (see Figure 63). To better describe this mechanism, Figure 64 depicts a magnified soft segment section and the way absorbed water vapor molecules take.

![Figure 64: Mechanism of Water Vapor Molecule Migration](image)

Soft segments show enough space for water vapor molecules to jump stepwise along the molecular chain in forming temporary hydrogen bonds with its functional hydrophilic groups. Hydrogen bonds only last until a succeeding water vapor molecule displaces previous one and thereby induces traveling motion through the film.

Most highly hydrophilic polymers are however not suitable to use as permanent fabric coatings as they either easily swell heavily when brought in contact with water or are too stiff and not flexible. To get a strong film with adequate swelling, it is recommended to use polymers having a nice balance of hydrophobic and hydrophilic groups. As a rule of thumb, the rate of water vapor transmission through a fabric decreases the lower the amount of pores and the thicker the assembly (fabric and coating) is. When fabric thickness and amount of pores is kept constant, a surface with finer pores will show higher water vapor permeability [72].
2.3.5 Solvent-based

Solvent based polyurethane coatings result in high performance products having a pleasant hand and are used to coat more than 500 million square meters of textiles every year to achieve leather like characteristics. They however impart the great disadvantage of using toxic solvents [73]. Most commonly, solventborne polyurethane coatings are two-component systems, of which polyisocyanate acts like one component and polyol as the other. As components would immediately start crosslinking upon mixing, they are blended in a solvent, in order to dilute the concentration of reactive groups and thereby suppress crosslinking reaction until coating is applied. As soon as solvent evaporates, the concentration of reactive functional groups increases proportional to reaction rate [74]. As it is easily dissolved in water and most organic chemicals, in this case polyurethane, dimethyl formamide (DMF) is the most commonly used solvent. About 50% of used solvents are directly discharged in the surrounding air, and DMF residues usually remain in the material, leading to environmental pollution and enormous health hazard to humans working and or living in surrounding areas [75, 73].
2.3.5.1 Coagulation

Traditionally, artificial leather is typically formed by coagulation (also often referred to as wet process), as a first step to increase structural density and get leather like pleasant hand, before buffing or grain finish is applied to enhance appearance [66, 65, p. 21]. High performance solvent borne polyurethanes require relatively toxic and high boiling solvents (such as DMF), thus, for the coagulation process, the substrate is coated or impregnated with a polyurethane dimethyl formamide solution, before it is passed through several DMF-water baths, with decreasing DMF concentrations until it is immersed into pure water. Hereby, the water penetrates into the layer and displaces the DMF solvent. This leads to a slow precipitation of polyurethane in the substrate from its outside to the center. The described phase transfer results in sponge-like cellular structure of interconnected micropores, similar to the characteristic microporosity of natural leather [61, 73]. Created micropores are fine enough to keep water droplets from entering but fortunately do not hinder tiny water vapor molecules from passing through [70]. Khorasani et al. investigated in factors affecting the coagulation process and consequently the resulting porous structure. To get best performance, a uniform microporous structure of polyurethane is desired, in which macrovoids would represent weak points. The effect of different polyurethane concentrations, various coagulants and temperatures was examined to end up with the result that a higher polyurethane concentration favorably suppresses macrovoid formation, but also decreases the number of pores. Highest porosity value was achieved in using water as coagulant and playing around with different temperatures showed that higher temperatures increase porosity but also easily lead to macrovoids, as more water is allowed to inflow and
thereby raise the solvent/nonsolvent exchange [76]. Therefore, coagulation is more than just passing polyurethane-DMF treated fabric through water baths, i.e. balancing the different influencing parameters is essential to get desired highly microporous final product.

Although polyurethane represents the polymer, which is most often used for the coagulation process, other polymers, like polyamide can also be processed. The polyamide is first dissolved in an appropriate solvent, like for example formic acid. Next, a textile substrate is impregnated or coated with gained solution before it is immersed into a water bath to coagulate the polyamide. During this slow coagulation process, the water penetrates the polymer solution, leading to polyamide precipitation with fine water droplets which will later on result in a microporous structure after drying [65, p. 45].
2.3.6 Waterborne

Although traditional synthetic leather is still produced in countries, like for example China, that have little or no regulations in regard to environmental pollution and workers’ health, laws and regulations formulated by the United States and Europe, restricting the import of solvent borne artificial leathers, leading to an inevitable trend of replacing solvent-based polyurethanes by waterborne ones. [75]. Conventional polyurethane solutions contain an approximate proportion of volatile organic solvent (VOC) of about 40 to 60% by weight. This does not fulfill the desire of low organic solvent content to meet increasing health, safety and environmental concerns [77]. Government regulations, as the Clean Air Act in the US and the German “Technische Anleitung zur Reinhaltung der Luft”, abbreviated as “TA Luft” moreover underpin environmental consciousness [78, 79, 80]. Water-borne polyurethane systems are created by aqueous polyol dispersion with a suitable polyisocyanate. There are either conventional hydrophobic polyisocyanates, which are known from two-component solventborne coatings, or specially developed hydrophilic modified polyisocyanates. Previous ones can only be incorporated in aqueous dispersions by high shear in combination with external emulsifier. This technique usually leads to large particle sizes susceptible to instabilities. Hydrophilic modified polyisocyanates can be formed of hydrophobic polyisocyanates in introducing hydrophilic ionic or non-ionic groups acting as highly active internal emulsifiers within the polyisocyanate mixture, which facilitate emulsifying gained hydrophilic polyisocyanate in water without enormous stirring [69, 78]. There are mainly three suitable types of hydrophilic monomers, two of ionic and one of non-ionic nature. The most common ones are anionic waterborne polyurethanes, which are
prepared of polyols containing carboxylic acid or sulfonic acid groups. The reaction of carboxylic acid with isocyanate during preparation is inhibited by steric hindrance. To obtain water solubility, the acid groups are neutralized with base compounds, such as tertiary amines. Cationic polyurethanes represent the second ionic group, which are however not as commonly used as anionic polyurethanes. For cationic polyurethanes, quaternary ammonium compounds, which are derived from tertiary amines that reacted with protonic acid or alkylating agent, are responsible for its water solubility [78]. Protonic acids build positive hydrogen ions in aqueous solutions, whereas alkylating agents form alkyl groups in the compounds they are reacting with, in removing one hydrogen atom from an alkane [81, 82]. Building blocks, containing previously described compounds are reacted with isocyanates to build cationic polyurethanes. Next to ionic type hydrophilic groups, there are the non-ionic types, of which building blocks (e.g. water-soluble polyethers based on ethylene oxide) are incorporated to gain water-emulsifiable polyurethane. Ionic and non-ionic water-soluble polyurethanes have distinct merits and demerits, ionic type polyurethane dispersions are for example stable in temperatures above 70°C and only partly resistant to high shear forces, whereby non-ionic dispersion types are unstable in temperatures above 70°C but in exchange have good stability to strong shear forces. Therefore, it is desirable to have both ionic and non-ionic emulsifiers integrated in the same polymer to achieve highest stability. To get high performance water-soluble polyurethane, it is recommended to include urea (-NH-CO-NH-) in addition to the urethane (-NH-CO-O-) groups. This is done by several steps. First polyurethane polymers are formed by polyaddition, in reacting polyols with an excess of polyisocyanate. As this reaction will take place in water, there is a reaction of isocyanates
and water at the same time. Hereby, the isocyanate is hydrolyzed to form amines which will subsequently react with remaining isocyanate groups to form ureas [78, 83]. In the following, the chemical equations of described hydrolysis to form amines, followed by aminolysis (see Figure 65) to gain desired urea groups are shown.

1) \[ RNCO + H_2O \rightarrow RNHCO_2H \]

2) \[ RNHCO_2^- + H^+ \rightarrow RNH_2 + CO_2 \]

The hydrolysis of isocyanates takes place in two steps, first reacting to the unstable carbamic acid (RCH\(_2\)NO\(_2\)), that quickly decomposes to finally end up with amine and undesirable carbon dioxide emission. Product amine can now react with reactant, i.e. isocyanate. This reaction is a so called aminolysis.

![Figure 65: Aminolysis to form Polyurea](image)

As can be seen in Figure 65, the reaction of diisocyanate and diamine will result in polyurea [84, 85, 86]. This aminolysis thereby contributes to the extension of the macromolecular chain. To get desired high performance polyurethane system, it is desirable to integrate a high concentration of urea groups in the polyurethane chain. Therefore, on the one hand a high amount of amine is necessary, which, as previously shown, can be derived by hydrolysis. Hereby however carbon dioxide evolves, leading to unwanted severe foaming,
which results in the desire of minimizing this isocyanate/water reaction. Therefore, it is preferred to produce polyurea by directly adding polyamines to the system. Due to the higher reactivity of amine/isocyanate than water/isocyanate, it is possible to complete an amine chain extension of polyisocyanate in water and thereby reduce foaming [83].

US patent 4,171,391 discloses a method of producing leather like composite sheet in impregnating a porous sheet, such as a needlepunched nonwoven fabric, with an aqueous polyurethane dispersion, of which the polyurethane is subsequently ionically coagulated to end up with the final product after drying. The patentee firstly describes the preparation of the used ionic aqueous polyurethane dispersion. Polymers, having free carboxylic acid groups, which are covalently bond to the backbone ends, are prepared. First, polyurethane is formed by reacting molar excess of diisocyanate with polyol to obtain isocyanate-terminated polymers, with which dihydroxy acid is reacted to provide pendant carboxyl groups. The diisocyanates are chosen by final end use. Aromatic diisocyanate tend in contrast to aliphatic diisocyanates to yellow when exposed to UV radiation, if they have not been stabilized by UV stabilizers. Therefore, aliphatic diisocyanates are beneficial for exterior application. Furthermore, the usage of long chain polyol increases elongation and elasticity of final product. To hinder undesired potential reaction of pendant carboxylic group with remaining isocyanates, 2,2-hydroxymethyl-substituted carboxylic acids are used.
As can be seen in Figure 66, adjacent alkyl groups (hydroxymethyl) prevent carboxylic acid and isocyanate groups from reacting due to steric hindrance [61]. This hindered, undesired isocyanate/carboxylic acid reaction would consume potential ionic groups and branch polyurethane, resulting in high viscosity [83]. To obtain water solubility, the carboxylic acid groups are neutralized with tertiary amines. Next, the polymer chain is extended and dispersed by adding water while stirring. To end up with dispersed polyurethane, having a concentration of about 10 to 40% by weight solids, sufficient water must be added. Remaining isocyanate groups hereby react with water to form urea groups by hydrolysis and aminolysis. This process continues until all isocyanate groups are reacted. The relatively low viscosity (10 to 1000 centipoise) of the produced dispersion helps to subsequently penetrate the porous substrate. As substrate permeation is controlled by viscosity of the dispersion and the hydrophilic characteristics of the substrate, less penetration can be achieved by adding thickeners (e.g. carboxymethyl cellulose) or by increasing solid concentration, if desired. After impregnating the substrate with polyurethane in a range of 15 to 50% of the total composite weight, coagulation is initiated by dipping the assembly in an aqueous acetic acid bath, having a concentration of 0.5 to 5%. Hereby, the amine, which has been neutralizing the carboxylic acid pendant, is replaced by a hydrogen ion and consequently restoring the
polyurethane polymer to initial not dilutable condition causing coagulation. In the end, the sheet is buffed to gain suede-like effect, or to adjust thickness for later transfer coating [61].

Instead of starting coagulation by dipping the impregnated fabric into an aqueous acid bath, Vogt introduces an elastomer composition of which coagulation is initiated by heat. In the US patent 5,916,636, he claims a method of producing a suede-like elastomer composite with the help of an elastomer composition comprising waterborne polyurethane latex with a solid content of at least 40%, heat-activated acid-generating chemical, meaning that the chemical is not an acid at room temperature but produces an acid as soon as it is exposed to heat and a cloud point surfactant. The cloud point surfactant represents any surfactant that becomes less water soluble upon heat exposure. It easily binds to polyurethane latex upon gelling and thereby facilitates uniform coagulation of polyurethane over entire substrate. It is critical to have adequate amounts of acid-generating chemical and surfactant to end up with ideal final product. Too much of both ingredients results in a hard texture, whereby too little only leads to partial coagulation. If one component is missing, there would be no coagulation process. The introduced eco-friendly mixture further has the great advantage of providing a relatively long shelf life of at least 2 weeks. After impregnating textile substrate with elastomeric composition, the assembly is heated to start reaction. To achieve a proper uniform coagulation and prevent formation of continuous film, it is important to remain polyurethane latex moist. Therefore, steam application at a temperature of around 100°C is the preferred heat treatment. After coagulation, the fabric is dried in a high convective oven at low
temperatures of less than 120°C. If drying temperatures would be too high or too long, a potential undesired film could form on the surface [87].
2.3.6.1 Foam Coating

In plain words, polymeric foams can be described as a polymeric material which consists of a solid and a gas phase [88]. To create foam of polyurethane dispersions, air is either mechanically incorporated or a blowing agent is added to the polymer solution [66, 65, p. 109]. The mechanical incorporation is done by whipping air into the polymer dispersion, whereas blowing is induced by raising the temperature, to liberate gas which creates pores [65, p. 109]. Depending on the amount of air entrapped, foams of various densities can be produced. Conventionally, characteristic water vapor permeable microporosity of natural leather is imitated by coagulating a polyurethane dimethyl formamide solution in water (see 2.3.5.1 Coagulation). The frothed foam process can be used to produce similar porous layers. Figure 67 shows a direct comparison of artificial leather produced by solvent-borne coagulation with transfer coated topcoat and waterborne foam with transfer coating.

![Figure 67: Solventborne Coagulation vs. Waterborne Foam](image)

For the foaming process, it is essential to use polyurethane dispersions with high solid content of up to 60%, in combination with stabilizers, thickeners, crosslinking agents and optional pigments to achieve thick layers having a relative high density [73]. A mixture of
PU and PU/polyacrylic acid ester is dispersed in water. Furthermore, additives are added to stabilize the structure after foaming. The created foam is coated on one fabric surface and dried to gain a porous direct coat. As the pores are relatively large, the fabric is subsequently calendered and a topcoat is applied to improve water resistance [70]. In comparison to conventional coagulation, the frothed foam process furthermore offers next to its ecological advantages economic benefits in reducing energy costs as less water has to be evaporated [73]. In contrast to using the polymeric foam as a substitute for coagulation, a foamed layer is also frequently used as intermediate coat to compensate substrate irregularities and furthermore provides soft touch and a “full” feeling [65, pp. 21, 113]. Chinese patent CN 202227185 U discloses a transfer coating process, during which the polymeric foam is applied as intermediate layer, after an aqueous polyurethane resin has been applied on the release paper. In the end an adhesive is used to laminate the assembly to a nonwoven [75].
2.3.7 Suede

Natural suede represents an attractive raw material for the apparel industry. However, it is susceptible to dirt and other spots on its surface and therefore requires care like constant cleaning and brushing to provide long lasting joy. As natural suede is relatively expensive and stains often are not removable without damaging its feel and appearance the desire arose of imitating this pleasant material [89]. In previous subchapters, techniques of producing suede type artificial leather have been introduced. Creating surface with comfortable suede touch was for example achieved by coating the surface before grinding [4]. Oftentimes, a textile substrate is impregnated with a polyurethane solution which is coagulated before it is sliced in half and buffed to form naps, or just one surface is buffed or napped to raise fibers for the suede like touch [46, 14, 53]. Not only solventborne but also water soluble polyurethanes are used to create suede-like artificial leather in impregnating a fabric followed by coagulation and buffing (see subchapter 2.3.6 Waterborne) [61, 87]. It is thereby important to have evenly distributed microfine fibers which are raised to get a uniform suede surface. Therefore it is highly recommended to gain microfibers by for example sea extraction and not fiber splitting along their longitudinal axis [63]. In contrast to previous named techniques, Norman Forrest explains a technique of producing synthetic suede from a sandwich structure comprising at least three layers of non-fibrous materials. Figure 68 depicts the continuous process disclosed in US patent 4,044,183. Three non-fibrous materials are fed into a nip formed by two heated rotating cylinders, each carrying an endless silicone rubber molding band, having multiple fine molding cavities, into which molten polyurethane outer film materials flow to later form raised fibers on both surfaces (see Figure 69). It is
important to not use soft polyurethane films as outer material, because fibers would not stand up and have a rubbery hand. Moreover, there is a higher tendency to pill. On the other hand, too stiff polyurethane films would lead to undesired roughness. Next to flowing into the mold cavities, the remaining molten outer layer parts weld together with the inner layer. The composite assembly remains compressed during the cooling process in a cold water bath, before the molding bands pass over a pair of rotating cylinders with internal vacuum. The sandwich structure is now continuously stripped of the molding bands and perforated by a pair of cylinders, which are covered with card clothing. Finally the surfaces are brushed before the gained synthetic suede is wound up [89].

Figure 68: Continuous Suede Manufacturing Process [89]

Figure 69: Cross-Section of Endless Synthetic Suede [89]

It is remarkable, that there are no chemical or solvent treatments necessary to produce described synthetic suede [89].
2.4 Testing Methods

Important properties of artificial shoe leather are tear and tensile strength on finished sheets in terms of degradation and gross wrinkling [61]. In the following, standards and testing methods are introduced to examine named properties. To pursue the target of imitating or even improving leather, it is reasonable, that furthermore, a look is taken at several standards designed for testing genuine leather.

Tearing resistance of artificial leather and similar sheets can be determined by the tongue tear test. Hereby a specimen is cut perpendicular to its shorter side (see Figure 70) and the two gained tongues (or strips) are clamped to form a “T” in the testing device (see Figure 71). During testing the clamps uniformly pull apart the legs and induce tearing at the set cut.

The force to continue described tearing is recorded for five samples in machine and five samples in cross-machine direction [91].

Regarding tensile strength, the grab test method represents the recommended breaking strength test for coated fabrics [92]. Breaking strength and elongation are tested in centrally mounting the test specimen in the clamps of a constant rate of extension (CRE) tensile testing
machine. For this purpose, five samples in machine direction as well as cross-machine direction are cut to a distinct size which is wider than the clamping area. After installing the specimen, the clamps continuously extend until breakage occurs. Breaking force as well as elongation at break is measured [93].

Total and irreversible elongation of artificial leather can be determined by constantly loading a test specimen with a respective weight for a specific time. The achieved elongation is measured before the sample is released and laid down flatly to allow shortening. A total of six specimens, there in machine direction and three in cross-machine direction are tested. In relating the original length with the total elongation and the remaining elongation after straining, the total elongation and irreversible elongation can be calculated [94].

In contrast to testing tensile strength, during which mainly one direction (most commonly machine or cross-machine direction) is stressed, bursting strength measures all directions simultaneously. As most products are stressed from multiple directions during service, bursting strength can provide insight into future performance.

To conduct ball burst test, a constant-rate-of-traverse (CRT) tensile testing machine is used in combination with a ball burst attachment (see Figure 72 and Figure 73) [95].
Five specimens are cut from different areas of the material [95]. Each sample is subsequently tested one after another in placing it in the ring clamp without tension, so that the steel ball will not touch the coated surface [96]. As soon as the CRE tensile-testing machine is started, the steel ball is continuously lowered to exert force against the sample until it ruptures. Required burst strength is reported before next specimen is mounted for testing [95].

Figure 74 shows the testing assembly used to determine bagginess, creep and relaxation of genuine leather. Soft leather, which is commonly used for shoe uppers, furniture and garments, can be tested. Due to its viscoelasticity the material only partially relaxes after induced stress, which will remain as bagginess [97].
To carry out the process, three samples are cut and tested one after another. Depending on future use, either the flesh or the grain side faces the cylindrical sensor. For garments and shoes, stress should be applied to the flesh side, whereas for furniture force should act on the grain side. As soon as the specimen is mounted in the ring clamp with the respective side facing down, the sensor moves towards the sample and stays in a specific position to hold applied stress for a distinct time until it returns. This procedure will be repeated five times before the specimen is allowed to relax. The remaining elongation is subsequently recorded and the degree of bagginess is determined. Creep and relaxation is deduced by recording for each cycle the elongation induced by applied force and the velocity it declines as long the sensor stays in position [97].

Material flexibility and related pliability play a significant role in workability and feasibility of the prospective product. One way to test stiffness properties is the so-called cantilever test method, during which the materiel bends under its own weight. After cutting, weighing and labeling five samples from machine as well as cross-machine direction, the testing procedure takes place as illustrated in Figure 75 to Figure 78.
The sample is first placed, faceside up, on the horizontal plate, before the moveable slide is carefully placed on top of it. Subsequently, the clamped specimen is continuously moved by hand in a nice and even manner until the edge of the specimen touches the knife edge (see Figure 77). The overhang length can now be read and recorded as shown in Figure 78.

Described procedure is repeated for both ends of specimen of face as well as back side. In other words, each sample is tested in four respective ways before the following specimen will be examined. In the end the average overhang length of each specimen, the bending length and the flexural rigidity is calculated by measured data [98]. If the tested material however is too stiff and consequently does not bend under its own weigh, the cantilever test method is not suitable. In the following, a standard for such cases will be introduced.
DIN 53350 is based on ASTM D747 and is used to determine bending rigidity of coated textiles. As depicted in Figure 79 and Figure 80 the sample to be tested is fixed on one side in a clamp, at which edge a pointer is attached and the center of rotation is located. The other sample side loosely lies on a bending plate. The clamp is able to rotate clockwisely around the center of rotation and thereby induces bending of the mounted specimen (see Figure 81). During the rotation, the pointer shows the bending angle on a scale which is attached to the pendulum disc that has a common center of rotation with the clamp [99].

![Figure 79: Schematic Bending Rigidity Testing Device [99]](image1)

![Figure 80: Mounted Specimen, Starting Position [100]](image2)

![Figure 81: Position of Test Specimen During Test [100]](image3)
To carry out testing, five samples in both machine and cross-direction are cut, followed by thickness measurements. One coated sample is subsequently clamped into the apparatus (coated surface down), necessary weight is added to the pendulum and load cell is adjusted to zero if needed [99, 100]. The clamp is then rotate with a velocity of 1.5 degrees per second and bending moment is recorded at desired bending angle. In the end bending rigidity and bending modulus are calculated [99].

Bending leather concavely, i.e. the grain surface is located on the inside of the bend, leads to the so-called break. Break of leather describes the pattern of fine wrinkles, which are formed on the grain surface of leather during previously mentioned bending. It depends on the fibrous structure and the relation of grain and other strata of the leather. Break is mostly detected in the vamp of shoe upper leather during walking. Talking about break of leather, it has to be distinguished between fine break and coarse break. Fine break describes a grain pattern showing many fine wrinkles during bending, whereas coarse break reveals only few coarse wrinkles. Latter one is undesirable not only in terms of beauty, but also serviceability, as few coarse wrinkles are an indicator for a separating layer [101]. The same effect can be observed when bending artificial leather. A fine wrinkle pattern is hereby deserved to on the one hand imitate the appearance of high quality leather. On the other hand, buckling wrinkles are a sign of delamination or a fiber structure consisting of relatively coarse fibers, resulting in diminished pliability.

Fujisawa et al. introduce a technique to test for buckling wrinkles in the European patent EP 2 025 806 B1 [20].
As can be seen in Figure 82, a 4 cm x 4 cm sample is bent, so that the grained surface is inside and clipped at two ends, 1 cm inside from the edges. The clipped portion is further narrowed to diminish previous 2 cm interspace to 1 cm. Finally, the formed wrinkles are count and evaluated with the help of Table 2 [20].

<table>
<thead>
<tr>
<th>A</th>
<th>0-2 buckling wrinkles</th>
<th>Best</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3-4 buckling wrinkles</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5-7 buckling wrinkles</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8 or more buckling wrinkles</td>
<td>Worst</td>
</tr>
</tbody>
</table>

Bending the material in opposite direction, i.e. with the grain surface on the outside of the bend, is used to test cracking resistance [102]. Good resistance to flex-cracking is a key factor for shoe upper material, as the vamp is subjected to flexing and folding by foot.
bending during walking [103]. Lighter leather, which can for example be used for shoe upper material, is tested for cracking resistance in creating a sharp crosswise fold, with the grain surface of the leather facing out. Subsequently, the area around this double fold bend is examined for cracks in finish and/or grain, which may extend deeper into the material [102]. DIN 53359 represents a standard for a flex cracking test for artificial leather and similar sheets. Five specimens in machine as well as cross-direction are cut and thickness is measured. Each sample is mounted without tension, as shown in Figure 83.

![Mounted Specimen](image1)

![Folded Specimen](image2)

Figure 83: Mounted Specimen [104]  
Figure 84: Folded Specimen [104]

The testing device is capable of performing 200 folds per minute. The amount of folds is either predetermined by customer or can be chosen sample-dependent from 1,250 up to 500,000 folds per testing. The specimens are assessed with the help of magnifying glasses, and thoroughly checked for damages (e.g. crazes, cracks and/or blistering) and alterations (e.g. stress whitening) [104].

Imitated creases, which are usually formed at the vamp during walking, can be examined in Figure 86. Both, inward as well as outward creasing, develop while wearing shoes. Therefore, the SATRSA vamp flexing test resembles a good method of examining the durability of the material in wear [6, 105, 103]. Hereby, shoe upper material should at least withstand one million flexes without any damage [6].
Average quality leather can be flexed several million times, before cracks appear. Figure 87 and Figure 88 show a grained natural leather surface and cross-section, which has been finished with a thin pigmented polymer film, after 20,000 flexes.

Hairline cracks can be observed on the surface and delamination is clearly visible when looking at the cross-section. Figure 89 is the result of flexing a poromeric 500,000 times. This SEM picture depicts that a crack is formed within the microporous layer, propagating to the surface [6].
Flex resistance is further described in DIN EN ISO 32100. A coated textile is clamped into an apparatus, that folds and flexes the specimen for specified times to examine and evaluate its behavior. Three samples in both machine, as well as cross direction are cut and stored under standard atmosphere at 23°C and 50% relative humidity.
Figure 90-Figure 93 show the procedure, during which a sample is first folded along its longitudinal axis, so that the coated layer is on the inside before it is clamped at one side (see Figure 90). Subsequently, the clamped sample is folded over the edge and further clamp the second side straight below without tension. Hereby, the coated layer is turned inside out (see Figure 91 and Figure 92). The second clamp is fixed, while the first one is able to swing. During testing, the upper clamp repeatedly swings out 22.5° and back in, to generate a continuous pleat within the sample (see Figure 93). After several periods, the specimen is checked for damage and/or visible alterations [106].

Delamination during flexing and wear may further be supported by accumulated sweat at the junction between fabric and film that negatively affects adhesion strength. This especially applies to impermeable coatings [6]. There are two ways of testing water vapor transmission of a material, the desiccant method and the water method. The method is selected dependent on later conditions of use. For the desiccant method, a desiccant is used to create vapor pressure difference between the two sample surfaces, whereas for the water method distilled water is used instead of desiccant. Both methods have in common, that the assembly is
weight periodically to determine the rate of water vapor movement through the tested specimen [71]. Genuine Leather is tested for water vapor permeability by sealing the sample, having the surface, which will be exposed to damper environment in future application, facing up, to the open mouth of a test dish containing a desiccant. The whole assembly is placed hereby in standard atmosphere with circulating air. In continuously rotating the test dish, the desiccant stays in motion. The test dish is weight in the beginning and in the end of testing, weight difference represents water vapor absorption of desiccant [107].

Although leather represents a water vapor permeable material, shoe upper leather still has to fight with sweaty feet. To determine the effect of perspiration on shoe upper leather, ASTM D2322 – 10 examines its behavior when subjected to a treatment with artificial perspiration, specifically designed for breakdown of leather. Two test specimens are cut, of which one is marked and will later be exposed to the artificial sweat solution and the other serves as control sample. The area of the specimen is measured before and after the treatment to calculate area loss. Furthermore, resistance to grain cracking is tested and compared to the grain crack strength of an adjacent specimen to deduce deterioration [108].

Next to water vapor permeability helping to keep feet dry from the inside, it is moreover important to keep feet dry from the outside. Dynamic water resistance of shoe upper leather therefore plays a considerable role for shoe wearing comfort. With the help of the Dow Corning Tester, the dynamic water resistance of shoe upper leather is examined. For the procedure, the specimen is weight before it is mounted into the holder, consisting of two vertical clamps, of which one is fixed and the other one moveable. Stainless steel balls are
put into the created specimen pocket and an electrode is inserted into the steel balls. The assembly is placed in a water tank, in which a salt solution is poured and another electrode placed that is in constant contact with the sample. During the testing procedure, flex is imparted to the leather to imitate vamp flexing of a shoe during walking. Each flex is counted until water penetrates the inside of the specimen. This initial water penetration leads to a current leakage which results in a relay to operate, inducing immediate counter stop. To determine initial water penetration, the number of flexes until, counter stopped are recorded. Water absorption can furthermore be calculated in weighing the sample after flexing, and correlating it to the weight prior to testing [109].
3 Objectives and Approach

In looking at the patents dealing with artificial leather, it is striking, that most inventors are from Asia. The shift of the artificial leather industry to Asian countries mainly happened due to little or no restrictions and regulations in regard to hazardous chemicals used in common production processes. Consequently extensive experience and knowledge has been developed over there the last 30 years. Nowadays, available water based polyurethane coatings allow an environment-friendly approach without known health risks, resulting in a great interest to get the artificial leather market back to the US. Foremost the military is interested in getting artificial leather for military shoes from a local source to increase its independence. Therefore, the first aim of this research is to get the knowledge of creating artificial leather back. The thorough study and analysis of numerous patents, starting from the very first till recent publications provides necessary basic knowledge which is subsequently deepened by experimental approaches.

It has been shown in the literature review, that the substrate represents the most important part for manufacturing artificial leather. It governs future qualities such as appearance and mechanical properties. Moreover hand and processability are ruled by this layer. Therefore the next main focus of this study is to form and compare various nonwovens as base fabric for artificial leather. Nonwoven substrates are formed of diverse fiber types using various manufacturing techniques; fibrous webs are created by carding and cross-lapping or spunbond process, which are mechanically bond to nonwoven fabrics by needlepunching and/or hydroentangling. Used fiber types range from simple monocomponent to bicomponents in different shapes and compositions. In addition to commonly used island in
the sea fibers, less widely or never utilized fiber structures, such as segmented pie and trilobal bicomponents are chosen for artificial leather base formation.

Created substrates are characterized and compared with the help of solid volume fraction, apparent density, air permeability, flexural rigidity, burst strength, abrasion resistance and scanning electron microscopy.

To further investigate in the performance and impact of the different nonwoven substrates on artificial leather, a grain finish topcoat must be established. Favorably, water based polyurethane systems are used for topcoat formation to work in accordance with environmental as well as workplace health and safety standards.

Coatability and resulting performance is characterized with the help of cross-sectional SEM pictures, orange peel effect, burst strength, flexural rigidity and water vapor permeability before and after coating.
4 Substrate

Various nonwoven substrates are created of staple fibers or filaments, tested and characterized for comparison in terms of performance and suitability as base layer for artificial leather manufacturing.

The trials to produce staple fiber nonwoven fabrics are conducted in the Staple Nonwoven Laboratory located at NC State, using a Trützschler bale opening, blending and feeding system, a Trützschler High-Speed Nonwoven Card EWK 413 and the Asselin "Profile 415-FD" cross-lapper to prepare the fibrous webs which are subsequently mechanically bonded by a Trützschler pre-needler single board needle loom followed by the Asselin A.50-RL needle loom, DF-4 version, including 4-boards, two up and two down stroke [110]. Continuous fibrous webs are produced by a single-beam bicomponent spunbond device and subsequently bond by hydroentangling on an Aquajet line from Fleissner, Inc. There are five high pressure manifolds included, allowing hydroentangling pressure of up to 230 bar. Water jet bonding is possible on front and backside by the combination of belt and drum fabric transportation.

4.1 Monocomponent Fiber Nonwoven Fabrics

Starting from scratch, the first approach is done with monocomponent polyester staple fibers to get familiar with and optimize the procedure to draw conclusion for subsequently processing bicomponent fibers.
Available needles for planned needlepunching procedure are listed in Table 3. 40 gauge conical is used for pre-needling, while 40 gauge intermediate needles, 36 gauge twisted needles and 42 gauge finish needles are meant for subsequent bonding procedures.

<table>
<thead>
<tr>
<th>Needles</th>
<th>Dimensions</th>
<th>Manufacturer</th>
<th>Code Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Needle</td>
<td>15x17x40x3.5</td>
<td>RBA F 20</td>
<td>6-2/3B/CON</td>
</tr>
<tr>
<td>Intermediate</td>
<td>15x18x40x3</td>
<td>C 222 G3037</td>
<td>/ 609901</td>
</tr>
<tr>
<td>Twisted</td>
<td>15x18x36x3.5</td>
<td>PBA F 20</td>
<td>6-4B</td>
</tr>
<tr>
<td>Finish</td>
<td>15x18x42x3</td>
<td>R111 G 3017</td>
<td>/ 610791</td>
</tr>
</tbody>
</table>

Taking a closer look at the needles, there are 6 barbs milled into the working blade of the 40 gauge conical needle, with a point to first barb distance of 3 mm and 13 mm to the last one. The 6 barbs are placed in turn on all three edges having a spacing of 2 mm to each other. The intermediate needle has 6 barbs in total starting at 3 mm from the point and ending at 8 mm. Again the barbs are placed on all three edges, but in a closer distance of 1 mm to each other. As its name already implies, the twisted needle has a twisted working blade, into which three edges 8 barbs are milled, starting 3 mm from the point and ending at 9 mm. Due to its shape, the twisted needle is promising for high consolidation and possible splitting for later used bicomponent fibers. The finishing needle has 3 barbs on its working blade, starting after 3 mm from the point and ending at a distance of 7 mm.

Depending on set penetration depth, a certain amount of barbs interacts with the web and vertically reorients the caught fibers. Each needle works in a distinct manner and changes the structure of the fibrous web prior to next penetration. As every needle sequence, change in
penetration depth and punching density will result in different fiber orientation and nonwoven structure, there are too many factors influencing the resulting nonwoven to cover all possible cases in a design of experiment.

This is the reason why a first trial is done of which results will be learned and knowledge is built up for further refinements.

4.1.1 First Approach

It has been shown in the literature, that artificial leather substrate is highly consolidated to obtain a very dense structure, just like its natural counterpart. For good coatability an even and uniform surface is furthermore necessary. The first approach is set as shown in Table 4, where intermediate and twisted needles penetrate from both sides to highly entangle the staple fiber web before the finish needles take care of diminishing surface fuzz.

<table>
<thead>
<tr>
<th>PET I</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Pass</td>
<td>Pre-Needle 100 punches/cm² 9 mm penetration</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
</tr>
<tr>
<td>2nd Pass</td>
<td>Twisted 100 punches/cm² 6 mm penetration</td>
<td>Twisted 100 punches/cm² 6 mm penetration</td>
</tr>
<tr>
<td>3rd Pass</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
</tr>
</tbody>
</table>

With a penetration depth of 9 mm, all 6 barbs on the working blade of the intermediate needle are in action. The twisted needles are set to a penetration depth of 6 mm, so that 4 of
its 8 barbs stressed. The finish needles just penetrate 3 mm, so that only one barb is acting, enough to take care of cleaning and evening out the surface.

Samples are kept at each stage to evaluate and examine consolidation.

4.1.2 Testing and Characterization Methods

- **Solid Volume Fraction**

The solid volume fraction, abbreviated as SVF, describes the percentage of fibers in a volume element [111]. It is defined by the ratio of the solid volume of all fibers to the total fabric volume [112], and is calculated as follows.

\[
\alpha = \frac{m}{\rho_{Fiber} \cdot t} \times 100, \quad \text{where } \alpha \text{ is the solid volume fraction, } m \text{ the basis weight of the fabric, } \\
\rho_{Fiber} \text{ represents the fiber density and } t \text{ is the thickness of the fabric.}
\]

Basis weight and thickness are measured and recorded for each sampling unit as follows.

- **Basis Weight**

Ten specimens are cut from different locations of the sampling unit, each having an area of 100 cm². One sample after another is weighed with the help of a XL-3100D toploading balance from Denver Instrument Company, with a sensitivity of 0.01 grams (see Figure 94). Measured weight is multiplied by 100 to end up with the unit g/m². Finally average and standard deviation for each sampling unit are calculated.
Thickness

According to ASTM standard D1777, the thickness of ten specimens per sampling unit is determined by a dead-weight thickness gauge, with an applied pressure of 0.6 psi (see Figure 95). In the end average thickness and standard deviation are calculated for each sampling unit.

Results and Discussion

In plotting the solid volume fraction after each pass, it is observed that the twisted needles (2\textsuperscript{nd} Pass) did not significantly further consolidate the nonwoven structure, i.e. not increase its solidity.
This is the reason why the second approach will skip the twisted needle and concentrate on the combination of intermediate and finish needling.

### 4.1.4 Second Approach

PET II skips the twisted needle, to see if there is a difference when the finish needle directly penetrates the web after the 1\textsuperscript{st} pass of intermediate needles, while PET III and PET IV replace the twisted needle in the second pass with another finish or intermediate pass respectively.

<table>
<thead>
<tr>
<th></th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PET II</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1\textsuperscript{st} Pass</td>
<td>Pre-Needle 100 punches/cm(^2), 9 mm penetration</td>
<td>Intermediate 100 punches/cm(^2), 9 mm penetration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.5 Testing and Characterization Methods

- **Basis Weight**

  The basis weight is determined, as described in 4.1.2 Testing and Characterization Methods.

- **Thickness**

  The thickness is determined as described in 4.1.2 Testing and Characterization Methods.

- **SVF**

  The SVF is determined as described in 4.1.2 Testing and Characterization Methods.
4.1.6 Results and Discussion

Again, the change in solid volume fraction at each stage is plotted. It can be seen that there is no noticeable improvement in skipping the twisted needle. As all barbs of the intermediate needle are already acting and the main task of the finish needle is not to consolidate the structure but to improve the surface quality, it is reverted to the twisted needle in the subsequent approach.

![SVF PET II, PET III & PET IV](image)

Figure 97: SVF PET II, PET III, PET IV

4.1.7 Third Approach

To further consolidate the fabric, the twisted needle is used again and set as first pass with a higher penetration depth of 11 mm. As can be seen in Table 6, this deep penetration is followed by two passes of the intermediate needle (PET V) or one pass intermediate (PET VI), until the fabric is finished in the end. All barbs of both, twisted and intermediate
needles are acting during this trial to catch and reorient numerous fibers to obtain high entanglement and density.

<table>
<thead>
<tr>
<th>PET V</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm² 9 mm penetration</td>
<td>Twisted 100 punches/cm² 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; Pass</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PET VI</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm² 9 mm penetration</td>
<td>Twisted 100 punches/cm² 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Pass</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
<td>Finish 200 punches/cm² 3 mm penetration</td>
</tr>
</tbody>
</table>

4.1.8 Testing and Characterization Methods

- **Basis Weight**

  The basis weight is determined, as described in 4.1.2 Testing and Characterization Methods.

- **Thickness**

  The thickness is determined as described in 4.1.2 Testing and Characterization Methods.
• **SVF**

The SVF is determined as described in 4.1.2 Testing and Characterization Methods.

4.1.9 Results and Discussion

Looking at the solid volume fraction of PET V and PET VI, it can be seen that both will end with a solidity of approximately 12%, which is higher than previous trials. Both PET V and PET VI are deeply consolidated after the first pass and are further solidified by the intermediate needles in the second pass. The intermediate needles of the third pass of PET V needling condition however do not noticeably change the solid volume fraction of the obtained structure.

![Graph showing SVF PET V + PET VI](image)

Figure 98: SVF PET V + PET VI
Best structure in terms of solidity is created by PETVI needle conditions. But it has also been shown that it was not possible to get a higher solid volume fraction than 12% with used technique.

4.1.10 Refinement

To increase the solid volume fraction beyond 12%, the idea is to consider additional bonding techniques such as thermal bonding with the help of high shrinkage fibers and hydroentangling. First tests are done with high shrinkage fibers in combination with heat treatment to shrink the whole fabric and consequently increase its density, before a look is taken at additional water jet bonding.

4.1.10.1 High Shrinkage Fibers and Heat Treatment

10% high shrinkage PET fibers are mixed to the web for processing PET VIII & PET IX with the same needling conditions as PET VI combined with an additional heat treatment at the end. PET VIII and PET IX only differ in their heat treatment temperature.

Table 7: Needling and Through-Air-Bonding Conditions PET VII

<table>
<thead>
<tr>
<th>PET VII</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
<th>Fleissner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Pass</td>
<td>Pre-Needle</td>
<td>Twisted 100 punches/cm²</td>
<td>Twisted 100 punches/cm²</td>
</tr>
<tr>
<td></td>
<td>100 punches/cm²</td>
<td>11 mm penetration</td>
<td>11 mm penetration</td>
</tr>
<tr>
<td>2nd Pass</td>
<td>Intermediate</td>
<td>Intermediate 100 punches/cm²</td>
<td>Intermediate 100 punches/cm²</td>
</tr>
<tr>
<td></td>
<td>100 punches/cm²</td>
<td>9 mm penetration</td>
<td>9 mm penetration</td>
</tr>
<tr>
<td>3rd Pass</td>
<td>Finish</td>
<td>Finish 200 punches/cm²</td>
<td>Finish 200 punches/cm²</td>
</tr>
<tr>
<td></td>
<td>200 punches/cm²</td>
<td>3 mm penetration</td>
<td>3 mm penetration</td>
</tr>
<tr>
<td>4th Pass</td>
<td></td>
<td></td>
<td>260°F (≈127°C), 2 m/min</td>
</tr>
</tbody>
</table>
Moreover, trials are run with a changed fiber mixture, comprising 50% 6 denier 2 inch PET and 50% 3 denier 1 inch high shrinkage PET. This web is mechanically bonded by needlepunching using the needling conditions of previous approaches, which resulted in highest solidities, and finally thermally bonded by through air bonding. PET IX is the counterpart of PET III, PETX of PET V and PET XI of PET VI.
Table 8 Continued

<table>
<thead>
<tr>
<th>PET X</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
<th>Fleissner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td>Twisted 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 11 mm penetration</td>
<td>Twisted 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; Pass</td>
<td>Finish 200 punches/cm&lt;sup&gt;2&lt;/sup&gt; 3 mm penetration</td>
<td>Finish 200 punches/cm&lt;sup&gt;2&lt;/sup&gt; 3 mm penetration</td>
<td></td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt; Pass</td>
<td></td>
<td></td>
<td>310°F (≈154°C), 2 m/min</td>
</tr>
</tbody>
</table>

PET XI

<table>
<thead>
<tr>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
<th>Fleissner</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td>Twisted 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
<td>Intermediate 100 punches/cm&lt;sup&gt;2&lt;/sup&gt; 9 mm penetration</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Pass</td>
<td>Finish 200 punches/cm&lt;sup&gt;2&lt;/sup&gt; 3 mm penetration</td>
<td>Finish 200 punches/cm&lt;sup&gt;2&lt;/sup&gt; 3 mm penetration</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; Pass</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.10.2 Hydroentangling

Next attempt increase solidity is to incorporate hydroentangling as additional bonding technique. The idea is to replace the finishing pass of the PET VI trial with high pressure water jet bonding, having the conditions shown in Table 9.
Table 9: Hydroentangling Conditions PET VI w/o Finish + Hydro

<table>
<thead>
<tr>
<th>PET VI w/o Finish + Hydro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
</tbody>
</table>

To get a better understanding of the performance of so far created nonwovens, not only the solid volume fraction but also further testing and characterization methods are applied to compare and evaluated the obtained fabrics.

4.1.10.3 Testing and Characterization Methods

- **Basis Weight**
  
The basis weight is determined, as described in 4.1.2 Testing and Characterization Methods

- **Thickness**
  
The thickness is determined as described in 4.1.2 Testing and Characterization Methods

- **SVF**
  
The SVF is determined as described in 4.1.2 Testing and Characterization Methods

- **Air Permeability**
  
Air Permeability of nonwoven fabrics was determined according to ASTM standard D737 with the help of a TEXTEST FX 3300 apparatus. Ten specimens of each sample unit are one after another tested using pressure differentials of 125 Pa. Individual test results are recorded as m$^3$/m$^2$/min. Finally, average and standard deviation for each sampling unit are calculated.
• Dent’s Theory

In his paper “The Air-permeability of Nonwoven Fabrics”, R. W. Dent correlates the air permeability with fabric thickness and density to successfully set fabrics of a wide weight range in correlation.

\[ \ln \frac{1}{A_p l} = r + s \rho_f, \]

where \( A_p \) is the air permeability, \( l \) the fabric thickness and \( \rho_f \) the web density. \( r \) is further described as \( 1 - v_f \ln R_a \) and \( s \) as \( \frac{1}{\rho_f} \ln R_f \), where \( v_f \) describes the fiber volume fraction, \( \rho_f \) the fiber density, \( R_a \) is the resistance of the air and \( R_f \) the resistance of the fiber.

As can be seen in Figure 99, intact structures formed by needle punching having different basis weights form an overlapping linear rising graph.
Figure 99: Dent’s Theory for 45 needled fabrics, weight range of 190 - 330 g/m2 [112]

- **Flexural Rigidity**

Stiffness of nonwoven fabrics was determined in using the cantilever test as directed in ASTM standard D 5732. Five specimens in machine as well as 5 specimens in cross direction, each having a size of 1 by 6 inch are cut from every sample unit. Each specimen is weight with a XL-3100D toploading balance from Denver Instrument Company, with a sensitivity of 0.01 grams (see Figure 94) and subsequently tested 4 times, i.e. in front right and left end, plus back right and left end respectively. Overhang length is read and recorded and average is taken for further calculations (see Figure 77 and Figure 78).
Bending length is calculated by dividing average overhang length by two and the value of flexural rigidity is gained by following equation:

\[ G = 9.809 \times 10^6 M c^3, \]

where \( G \) is the flexural rigidity [\( \mu \text{Nm} \)], \( M \) the fabric mass per unit area [\( \text{g/m}^2 \)] and \( c \) represents the bending length [\( \text{mm} \)] [98]. Finally, average flexural rigidity and standard deviation are calculated for each sampling unit in machine and cross-machine direction.

- **Burst Strength**

  Bursting strength of nonwoven fabrics was determined according to ASTM standard D6797 via constant-rate-of-extension (CRE) ball burst test (see Figure 72 and Figure 73). Five specimens of each sampling unit are cut and the force required to rupture the fabric by the steel ball is recorded. Finally average and standard deviation of each sampling unit are calculated. Furthermore, data is normalized to a nominal basis weight of 200 g/m\(^2\) to allow comparison of different fabrics varying in weight. This is done with the help of following equation:

\[ S_{nB} = S_B \times \left( \frac{n_m}{m} \right), \]

where \( S_{nB} \) is the normalized burst strength, \( S_B \) the measured burst strength, \( n_m \) the chosen nominal basis weight and \( m \) represents the basis weight of the tested fabric.

**Apparent Density**

The apparent density describes the mass per unit volume of a material [113], and is calculated as follows:

\[ \text{Apparent Density} \ [\text{g/cm}^3] = \frac{m}{\ell}, \]
where \( m \) is the basis weight of the fabric and \( t \) represents the thickness of the fabric. As has previously been shown in the literature review, Horiguchi et al. offered a good basis for comparison in stating that nonwoven substrates for artificial leather should at least show an apparent density of 0.12 grams per cubic centimeter after needling and preferably rise to 0.28 grams per cubic centimeter after subsequent processing steps, like hydroentangling, to achieve desired properties such as dense hand and excellent abrasion resistance.

- **Abrasion Resistance**

Abrasion resistance is determined using the Martindale abrasion tester. Six specimens of each sampling unit of interest are tested, three specimens are subjected to 5,000 rubs and remaining three ones to 20,000 turns. Samples are mounted into the specimen holder and placed onto the abradant, of which data can be observed in Table 10. During testing, a pressure of 12 kPa is applied to the specimen, a weight which is suitable for testing abrasion resistance of heavier material such as upholstery and consequently also shoe upper material.

<table>
<thead>
<tr>
<th>Yarn Specifications</th>
<th>Warp</th>
<th>Weft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber Diameter</td>
<td>25.7 ( \mu )m</td>
<td>28.5 ( \mu )m</td>
</tr>
<tr>
<td>Yarn Linear Density</td>
<td>62.1 tex</td>
<td>73.2 tex</td>
</tr>
<tr>
<td>Yarn Singles Twist</td>
<td>541.1 tpm</td>
<td>506 tpm</td>
</tr>
<tr>
<td>Yarn Folded Twist</td>
<td>431.2 tpm</td>
<td>330 tpm</td>
</tr>
</tbody>
</table>

### Woven Fabric Specifications

<table>
<thead>
<tr>
<th>Material</th>
<th>100% Wool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warp End</td>
<td>174 per 10 cm</td>
</tr>
</tbody>
</table>
Table 10 Continued

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Weft Pick</td>
<td>130.6 per 10 cm</td>
</tr>
<tr>
<td>Basis Weight</td>
<td>212.4 g/m²</td>
</tr>
<tr>
<td>Oil Content</td>
<td>0.5 %</td>
</tr>
</tbody>
</table>

The effect of abrasion is determined in observing the change in appearance and calculating the mass loss difference as percentage by \( \frac{A-B}{A} \times 100 \), where A is the weight before and B the weight after abrasion [115].

![Figure 100: Martindale Abrasion and Pilling Tester](image1)

![Figure 101: VeriVide](image2)

Resistance to surface changes and pill formation on textile fabrics is usually determined as directed in ASTM Standard D4970. Usually, degree of pilling is evaluated by comparing tested samples with visual standards. This method works fine for most woven and knitted fabrics, however is not applicable for nonwoven fabrics [116]. In this study, tested specimen are mounted on a VeriVide viewing apparatus to visually compare surface change and pilling formation under same lighting conditions.
4.1.10.4 Results and Discussion

First of all a look is taken at the obtained solid volume fraction in incorporating high shrinkage fibers and thermally bonding the final product.

![SVF Comparison w/ or w/o H.S. Fibers](image)

Figure 102: SVF Comparison w/ or w/o H.S. Fibers

In directly comparing the created nonwovens with and without heat treatment, it is obvious that incorporating high shrinkage fibers plus thermally bonding did not increase the solidity. Except for PET X, all additionally thermally bonded nonwovens show lower solid volume fraction than their counterparts. Although PET X has a slight higher solidity than PET V, the aim of increasing the solidity to more than 12% was not achieved by high shrinkage fibers.
To further see, whether the formed fabrics show defects, like pinholes, the air permeability is measured and correlated to the solid volume fraction. Usually the air permeability decreases the higher the solidity gets. The graph below shows the trend of decreasing air permeability the higher the higher the solidity gets. At first glance, three sample units seem to be outliers, which are identified as PET IX, PET X and PET XI, the trials that have a different fiber mixture and consequently behave differently. Setting the focus on just these three samples, it can be observed that the air permeability linearly decreases with increasing solidity.

![SVF vs. Air Perm](image)

**Figure 103: SVF vs. Air Perm PET**

Comparing the flexural rigidity of all needled 3 denier PET as well as high shrinkage PET fabrics, it can be seen that for the pure PET fabrics (PET I-PET VI) rigidity is constant in
machine as well as cross-machine direction, indicating that fibers are randomly oriented. Differences in stiffness can be explained by varying fabric basis weights. Due to the discontinuous process, it was impossible to get a constant basis weight. This is the reason why PET III, having the highest basis weight of 337 g/m², is the stiffest sample unit.

High shrinkage fibers are stiffer in machine than in cross-machine direction. This possibly results from the through air bonding process after needling, during which the fabric is transported through an oven, where hot air is blown through the fabric to induce fiber shrinkage and increase fabric density.

![Flexural Rigidity](image)

**Figure 104: Flexural Rigidity PET**

Strength of the fabrics in all directions is tested by ball burst and directly compared in following diagram.
To be able to compare fabrics with different basis weights, the values are normalized prior to plotting to a nominal weight of 200 g/m². Highest burst strength is obtained with PET III and PET VI. Although the high shrinkage samples have similar or even slightly greater SVF values, they are significantly weaker regarding their burst strength.

As previously mentioned, it was not possible to obtain constant basis weights for the created needlepunched fabrics. To nevertheless correlate fabrics of a wide weight range, dent’s theory is applied. Intact structures should form an overlapping linear rising graph. As can be seen this hypothesis is true for needled 3 denier monocomponent fibers, which linearly rise in an overlapping manner. Nonwoven fabrics incorporating different fiber mixture, i.e. PET IX,
PET X and PET XI, are also in line but show a differentiated slope from. It can be deduced that intact nonwoven structures without irregularities have been produced.

![Correlation Air Perm, Thickness and Solidity](image)

Figure 106: Correlation Air Perm, Thickness and Solidity PET

Replacing the finishing step by hydroentangling resulted in a great improvement of solid volume fraction. Air permeability constantly decreases with this increase.
Hydroentangling results in higher consolidation leading to thickness reduction. As can be seen in the following, the hydroentangled sample also shows higher flexibility than the original needled PET VI fabric.
Figure 108: Flexural Rigidity PET VI, PET VI w/o Finish + Hydro

Figure 109: Burst Strength PET VI, PET VI w/o Finish + Hydro
Although hydroentangling changed solidity and flexural rigidity, burst strength stays constant for PET VI and PET VI w/o Finish + Hydro.

To achieve desired properties like dense hand and excellent abrasion resistance, Horiguchi et al. stated that nonwoven substrates for artificial leather should at least show an apparent density of 0.12 grams per cubic centimeter after needling and preferably rise to 0.28 grams per cubic centimeter after subsequent processing steps, like hydroentangling.

As can be seen in the bar chart, almost all needled sample unit have a greater apparent density than 0.12 grams per cubic centimeter. Subsequent steps like thermally bonding or hydroentangling could however not increase this value to as high as 0.28 grams per cubic centimeters. Best performance of needled substrate is governed by PET VI, followed by hydroentangled PET VI w/o Finish having an apparent density of 20 g/cm³.
In the following the abrasion resistance of these fabrics (PET VI and PET VI w/o Finish + Hydro) is evaluated. Both fabrics did not suffer from weight loss after 500 or 20000 rubs, but surface changes can be observed. As can be seen in Table 11 numerous tiny nep can already be seen on the surface of PET VI after 5000 rubs, which will form out to big pills after 20,000 rubs. PET VI w/o Finish + Hydro has a better abrasion resistance. The fabric is roughened after 5000 turns and only shows few tiny pills after 20,000 rubs.

<table>
<thead>
<tr>
<th>Table 11: PET VI Surface Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET VI after 5000 rubs</td>
</tr>
<tr>
<td>PET VI w/o Finish + Hydro after 5000 rubs</td>
</tr>
</tbody>
</table>
4.2 Bicomponent Fiber Nonwoven Fabrics

Needling conditions of PET VI are chosen for processing following bicomponent staple fibers. Three different bicomponent staple fibers will be observed, starting with trilobal sheath core, followed by 51 island in the sea and 24 segmented pie. After focusing on staple fibers, a closer look is also taken at bicomponent filaments.

4.2.1 Trilobal Sheath Core Staple Fibers

The initial idea was to use modified tipped trilobal staple fibers consisting of 75% Pet and 25% PA6, which are consolidated by needling and simultaneously split extended tips from the center body to obtain a soft and supple nonwoven fabric. Customized staple fibers were especially ordered, which however turned out to be trilobal sheath core fibers (see Figure 111). Splitting consequently represented an impossible task.

Nevertheless a great interest arose in peeling the sheath from the trilobal core to obtain silk like trilobal fibers having soft and curly sheath parts wriggling around the core fiber axis. To fulfill this task, a combination of needling followed by hydroentangling is used in order to exert enough force for at least partially peeling the sheath of the core.
4.2.1.1 Neeldepunching

Based on optimized needling conditions, which were figured out in 4.1 Monocomponent Fiber, TT1 is produced following the example of PET VI. Exact needling conditions are shown in Table 12.

### Table 12: Needling Conditions TT1

<table>
<thead>
<tr>
<th>TT1</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st}) Pass</td>
<td>Pre-Needle 100 punches/cm(^2) 9 mm penetration</td>
<td>Twisted 100 punches/cm(^2) 11 mm penetration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Twisted 100 punches/cm(^2) 11 mm penetration</td>
</tr>
<tr>
<td>2(^{nd}) Pass</td>
<td>Intermediate 100 punches/cm(^2) 9 mm penetration</td>
<td>Intermediate 100 punches/cm(^2) 9 mm penetration</td>
</tr>
<tr>
<td>3(^{rd}) Pass</td>
<td>Finish 200 punches/cm(^2) 3 mm penetration</td>
<td>Finish 200 punches/cm(^2) 3 mm penetration</td>
</tr>
</tbody>
</table>

During the first pass a lot of fiber fuzz is observed, indicating fiber breakage due to twisted needles. To prevent possible fiber damage, a gentler approach is done in skipping the relatively coarse twisted needles. As can further been seen in Table 13, the intermediate needles are set to a punching density of 200 punches per square centimeter to nevertheless obtain desired high consolidation.

### Table 13: Needling Conditions TT2

<table>
<thead>
<tr>
<th>TT2</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st}) Pass</td>
<td>Pre-Needle 100 punches/cm(^2) 9 mm penetration</td>
<td>Intermediate 200 punches/cm(^2) 9 mm penetration</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Intermediate 200 punches/cm(^2) 9 mm penetration</td>
</tr>
<tr>
<td>2(^{nd}) Pass</td>
<td>Finish 200 punches/cm(^2) 3 mm penetration</td>
<td>Finish 200 punches/cm(^2) 3 mm penetration</td>
</tr>
</tbody>
</table>
4.2.1.2 Testing and Characterization Methods

- **Basis Weight**
  The basis weight is determined, as described in 4.1.2 Testing and Characterization Methods

- **Thickness**
  The thickness is determined as described in 4.1.2 Testing and Characterization Methods

- **SVF**
  The SVF is determined as described in 4.1.2 Testing and Characterization Methods

- **Air Permeability**
  The air permeability is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Flexural Rigidity**
  The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Burst Strength**
  The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods

4.2.1.3 Results and Discussion

Previously made assumption of fiber and fabric damage is proven by obtained testing results. In correlating solid volume fraction and air permeability, it can be seen that TT1 and TT2 do not differ in solidity; TT1 however has significantly higher air permeability. The greater air permeability reveals fabric damage like broken fibers or pinholes.
SVF vs. Air Permeability

![SVF vs. Air Permeability Graph](image)

Figure 112: SVF vs. Air Perm TT1, TT2

Next to higher air permeability, TT1 is far more flexible than TT2. An intact structure has greater intrinsic cohesion increasing stiffness, while a damaged fabric is not able to immensely withstand gravity.
Flexural Rigidity - MD [Nm]

Obtained burst strengths also fit in line with previous results. TT1 is weaker than TT2.

Normalized Burst Strength

Figure 113: Flexural Rigidity TT1, TT2

Figure 114: Normalized Burst Strength TT1, TT2
All discussed results support the assumption that TT1 is damaged during production. Therefore further consolidation steps will be done utilizing TT2 as basic material.

4.2.1.4 Hydroentangling

Created TT2 fabric is exposed to high pressure water jets to further consolidate the fabric and induce peeling of the sheath from the trilobal shaped core. Samples are kept at each stage to evaluate and compare structural development. Used hydroentangling conditions are shown in Table 14.

<table>
<thead>
<tr>
<th></th>
<th>1st Pass</th>
<th>2nd Pass</th>
<th>3rd Pass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jet Head</td>
<td>Pressure</td>
<td>Strip Type</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>20 bar</td>
<td>GB - 130 Micron Strips 600 Spacing</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>200 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>200 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>200 bar</td>
<td></td>
</tr>
</tbody>
</table>

4.2.1.5 Testing and Characterization Methods

- **Scanning Electron Microscope**

A phenom G2 pro desktop scanning electron microscope (see Figure 115) is used to examine and analyze surface and cross-section of nonwoven fabrics. Particular attention is paid to degree of fiber splitting.
- **Basis Weight**

The basis weight is determined, as described in 4.1.2 Testing and Characterization Methods.

- **Thickness**

The thickness is determined as described in 4.1.2 Testing and Characterization Methods.

- **SVF**

The SVF is determined as described in 4.1.2 Testing and Characterization Methods.

- **Air Permeability**

The air permeability is determined as described in 4.1.10.3 Testing and Characterization Methods.

- **Flexural Rigidity**

The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods.

- **Burst Strength**

The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods.
- **Apparent Density**

The apparent density is determined as described in 4.1.10.3 Testing and Characterization Methods.

- **Abrasion Resistance**

The abrasion resistance is determined as described in 4.1.10.3 Testing and Characterization Methods.

4.2.1.6 Results and Discussion

Figure 116 to Figure 120 depict scanning electron microscope pictures of TT2 after needling and each pass through the Aquajet line. It can be seen that after needling, the structure is still relatively open and few sheath parts peeled off. After the first hydro pass, the structure is denser, but no significant peeling occurred. After the second and third pass, peeled sheath parts can be observed which wriggled around adjacent fiber axes.

![Figure 116: SEM TT2](image1)

![Figure 117: SEM TT2 Cross-Section](image2)
Figure 118: SEM TT2+1st Pass Hydro

Figure 119: SEM TT2+2nd Pass Hydro

Figure 120: SEM TT2+3rd Pass Hydro
The graph above shows the burst strength of TT2 in different stages. As can be seen, hydroentangling noticeably increases burst strength due to greater entanglement. There is however no significant improvement in burst strength from two to three hydroentangling passes.
In correlating solid volume fraction to air permeability of TT2 as well as TT2 after 2 and 3 hydro passes, it is obvious that hydroentangling significantly consolidated the nonwoven fabric starting from TT2 to TT2 + 2*Hydro. TT2 + 3*Hydro however has almost the same solidity and air permeability as TT2+Hydro, pointing out that a plateau has been reached and the nonwoven structure is stable.

This assumption is confirmed by the bending behavior. As can be seen below, the nonwoven first got stiffer after hydroentangling due to increased entangling and consolidation and does not significantly change after the third hydro pass.
Comparing obtained apparent densities of created trilobal sheath core nonwoven fabrics shows that after needling an apparent density of 0.12 grams per cubic centimeter is achieved, which was further increased by hydroentangling. The apparent density however did not rise up to 0.28 grams per cubic centimeter, which is according to Horiguchi et al. necessary to obtain excellent abrasion resistance.
Table 15 depicts the surface changes of TT2 fabrics after 5000 ad 20,000 turns on the Martindale abrasion tester. First pills as well as a roughened surface can be observed for TT2 after 5000 rubs. After 20,000 turns the surface of TT2 shows numerous big pills and significant wear. No noticeable change in surface appearance is found for TT2 + 2*Hydro as well as TT2 + 3*Hydro after 5000 turns. TT2 + 2*Hydro even increased in softness after 20,000 rubs without showing wear or ugly surface changes. TT2 + 3*Hydro however developed nips after 20,000 turns.
<table>
<thead>
<tr>
<th>Table 15: TT2 Surface Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT2 after 5000 rubs</td>
</tr>
<tr>
<td>TT2 + 2*Hydro after 5000 rubs</td>
</tr>
<tr>
<td>TT2 + 3*Hydro after 5000 rubs</td>
</tr>
</tbody>
</table>

Taking a look the weight loss after 5000 as well as 20,000 rubs, it can be seen that TT2 showed no weight loss, while TT2 + 2*Hydro as well as TT2 + 3*Hydro lost a little weight after 5000 turns. Little surface wear readily rubbed off these fabrics leading to a remaining nice and even surface appearance. After 20,000 rubs, TT2 lost as much weight as TT2 + 2*Hydro, while TT2+3* Hydro shows twice the weight loss than TT2+2*Hydro.
Figure 125: Weight Loss TT2, TT2+2*Hydro, TT2+3*Hydro

Worse performance of TT2 + 3*Hydro can be explained by possible slight fabric damage due to exaggerated hydroentangling. As fabric is already defective, possible broken fibers are easily rubbed out of the fabric structure as well as pill formation is supported.

Although the apparent density of TT2 + 2*Hydro did not conform to requirements stated by Horiguchi et al., the nonwoven fabric nevertheless showed excellent abrasion resistance. The reason for its soft surface after 20,000 rubs, are the trilobal sheath core fibers.
As can be seen in Figure 126, the sheath peeled of the cores due to the rubbing action, resulting in a soft hand feeling.
4.2.2 51 Island in the Sea Fibers

Island in the sea fibers at hand consist of 60% PA6 and 40% co-polyester. PA6 islands are surrounded by co-polyester sea.

Figure 127 depicts the cross-sectional few of 51 island in the sea fibers.

![Figure 127: SEM Cross-section 51 Island in the Sea Fibers](image)

To be able to create a nonwoven fabric having microfibers, the web is needled prior to sea removal. Needling conditions are based on optimized conditions figured out in 4.1 Monocomponent Fiber for PET VI.

4.2.2.1 Needlepunching

<table>
<thead>
<tr>
<th>51 I/S</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm², 9 mm penetration</td>
<td>Twisted 100 punches/cm², 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td></td>
<td>Intermediate 100 punches/cm², 9 mm penetration</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Pass</td>
<td></td>
<td>Finish 200 punches/cm², 3 mm penetration</td>
</tr>
</tbody>
</table>
4.2.2.2 Co-Polyester Removal

After creating the needlepunched nonwoven fabric, a caustic treatment in a Mathis overflow jet dyeing system type “JFO” (see Figure 128) is used to remove the co-polyester sea component.

Figure 128: Jet Dyeing Apparatus

4.2.2.3 Hydroentangling

After sea removal, a hydroentangling step is added to further consolidate the nonwoven structure. Less pressure is used than for trilobal sheath core fibers, as the sea has already been removed and consequently no energy-sapping fibrillation was necessary.

Table 17: Hydroentangling Conditions 51 I/S

<table>
<thead>
<tr>
<th>51 I/S Removed + Hydro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
</tbody>
</table>
4.2.2.4 Testing and Characterization Methods

- **Basis Weight**
  The basis weight is determined as described in 4.1.2 Testing and Characterization Methods

- **Thickness**
  The thickness is determined as described in 4.1.2 Testing and Characterization Methods

- **SVF**
  The SVF is determined as described in 4.1.2 Testing and Characterization Methods

- **Air Permeability**
  The air permeability is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Flexural Rigidity**
  The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Burst Strength**
  The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Apparent Density**
  The apparent density is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Abrasion Resistance**
  The abrasion resistance is determined as described in 4.1.10.3 Testing and Characterization Methods.
4.2.2.5 Results and Discussion

In correlating the air permeability with the solid volume fraction, it can be seen that the nonwoven structure is nicely consolidated after hydroentangling, showing a solidity of almost 24% and very little air permeability.

![SVF vs. Air Permeability](image)

**Figure 129: SVF vs. Air Perm 51 I/S**
Fiber size and shape plays a great roll in bending rigidity. Generally it can be presumed that the finer the fibers are the lower is the bending rigidity of the tested fabric [39]. Therefore nonwoven stiffness considerably decreases after sea removal. Subsequent hydroentangling step highly entangled fiber bundles. Greater entanglement of microfibers leads to less fiber mobility and consequently increases the stiffness of the nonwoven fabric.

Burst strength is on the one hand an indicator of entanglement but is also greatly influenced by fiber elongation. A fabric will fail as soon as maximum elongation of the fiber is reached. Therefore extremely entangled fabrics tend to fail earlier as fibers cannot extent far due to little freedom of movement. The other extreme, a not yet bonded web, will promptly fail as the ball can move through it without any hindrance. Burst strength of 51 I/S needled, after
sea removal as well as after hydroentangling can be observed below. After sea removal, burst strength increased as island fibers show more freedom of movement. In contrast to previous entangled bundles, consolidation and entanglement of microfine fibers increases leading to less fiber mobility.

![Fig. 131: Burst Strength 51 I/S](image)

In plotting the apparent density, it can be seen below that a higher apparent density than 0.12 grams per cubic centimeter is achieved. Further water jet treatment dramatically increased the apparent density so that some of the tested specimen had an apparent density of as much as 0.28 grams per cubic centimeter, which is according to Horiguchi et al. necessary to obtain excellent abrasion resistance.
Both fabric sides are tested for abrasion resistance, the surface onto which the water jets directly penetrated and the bottom. Both sides did not suffer from weight loss. Table 18 depicts the surface changes after 5000 and 20,000 rubs. As can be seen no nips or pills formed even after 20,000 turns. The only results are soft buffed surfaces.

Table 18: 51 Island in the Sea Surface Change

<table>
<thead>
<tr>
<th></th>
<th>51 IS Hydro Top after 5000 turns</th>
<th>51 IS Hydro Top after 20,000 turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 5000 turns</td>
<td><img src="image1.png" alt="Image of fabric top after 5000 turns" /></td>
<td><img src="image2.png" alt="Image of fabric top after 20,000 turns" /></td>
</tr>
<tr>
<td>After 20,000 turns</td>
<td><img src="image3.png" alt="Image of fabric top after 20,000 turns" /></td>
<td><img src="image4.png" alt="Image of fabric top after 20,000 turns" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>51 IS Hydro Bottom after 5000 turns</th>
<th>51 IS Hydro Bottom after 20,000 turns</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 5000 turns</td>
<td><img src="image5.png" alt="Image of fabric bottom after 5000 turns" /></td>
<td><img src="image6.png" alt="Image of fabric bottom after 20,000 turns" /></td>
</tr>
<tr>
<td>After 20,000 turns</td>
<td><img src="image7.png" alt="Image of fabric bottom after 20,000 turns" /></td>
<td><img src="image8.png" alt="Image of fabric bottom after 20,000 turns" /></td>
</tr>
</tbody>
</table>
4.2.3 24 Segmented Pie

The idea is to highly consolidate and split 24 segmented pie fibers, consisting of 50% PA6 and 50% PET, with a combination of needling followed by hydroentangling in order to exert enough force to fulfill this task to obtain a dense, soft and supple nonwoven fabric.

![SEM Cross-Section 24 Segmented Pie Fiber](image)

Needling conditions are based on optimized conditions figured out in in 4.1 Monocomponent Fiber for PET VI and hydroentangling conditions are like the ones used in 4.2.1.4 Hydroentangling. Samples are kept at each stage to evaluate and compare structural development as well as mechanical properties.

4.2.3.1 Needlepunching

<table>
<thead>
<tr>
<th>24 Segm. Pie</th>
<th>Trützschler</th>
<th>Asselin – One Up, One Down</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Pass</td>
<td>Pre-Needle 100 punches/cm² 9 mm penetration</td>
<td>Twisted 100 punches/cm² 11 mm penetration</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Pass</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
<td>Intermediate 100 punches/cm² 9 mm penetration</td>
</tr>
</tbody>
</table>
Table 19 Continued

<table>
<thead>
<tr>
<th>3rd Pass</th>
<th>Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>200 punches/cm²</td>
</tr>
<tr>
<td></td>
<td>3 mm penetration</td>
</tr>
<tr>
<td></td>
<td>Finish</td>
</tr>
<tr>
<td></td>
<td>200 punches/cm²</td>
</tr>
<tr>
<td></td>
<td>3 mm penetration</td>
</tr>
</tbody>
</table>

4.2.3.2 Hydroentangling

Table 20: Hydroentangling Conditions 24 Segmented Pie

<table>
<thead>
<tr>
<th>24 Segmented Pie</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Pass Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
<tr>
<td>2nd Pass Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
<tr>
<td>3rd Pass Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
</tbody>
</table>

4.2.3.3 Testing and Characterization Methods

- **SEM**

The Scanning Electron Microscope is used as described in 0. Testing and Characterization Methods

- **Basis Weight**

The basis weight is determined as described in 4.1.2 Testing and Characterization Methods

- **Thickness**

The thickness is determined as described in 4.1.2 Testing and Characterization Methods
- **SVF**
  The SVF is determined as described in 4.1.2 Testing and Characterization Methods

- **Air Permeability**
  The air permeability is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Flexural Rigidity**
  The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Burst Strength**
  The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Apparent Density**
  The apparent density is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Abrasion Resistance**
  The abrasion resistance is determined as described in 4.1.10.3 Testing and Characterization Methods

4.2.3.4 Results and Discussion

As can be seen in Figure 134 and Figure 135, no fiber splitting occurred during needling process.
After the first hydroentangling pass fiber splitting already started. Nevertheless, there is still a high amount of not split fibers visible (see Figure 136 and Figure 137).

After two (see Figure 138 and Figure 139) and three passes (see Figure 140 and Figure 141) very good fiber splitting results were obtained. As can be seen fibers on the surface are all split and only view whole bicomponent fibers remain throughout the structure.
In correlating solidity with air permeability, it can be seen that after the first pass, solid volume fraction enormously increased and air permeability decreased due to higher consolidation and start of fiber splitting. As more and more fibers are split during the second hydroentangling pass, the air permeability further decreased and stayed constant. The solid volume fraction however also decreased. This phenomenon can be explained by fiber slipping. Short staple fibers are more susceptible to move around during water jet penetration. This movement leads to weight loss, which affects obtained solidity. Especially the third pass is showing a great loss in solidity, because the surface has already been closed.
by completely split 24 segmented pie fibers after the second pass and penetrating high pressure water jets therefore bounce off the surface. This force possibly results in further fiber slipping.

![SVF vs. Airperm](image)

Figure 142: SVF vs. Air Perm 24 Seg. Pie

The assumption of fiber moving and reorientation is supported by the flexural rigidity. As can be seen below, stiffness first increased after the first hydroentangling pass because the nonwoven is more entangled and consolidated. Following decrease in flexural rigidity can be explained by fiber splitting, because finer fibers show higher flexibility. It would also be reasonable that the flexural rigidity increases during the third pass as split fibers are more entangled; however exaggerated increase in machine direction is indicative of fiber slippage and reorientation into machine direction.
Taking a look at the burst strength it can be seen that the strength first increases due to higher consolidation and entanglement, before it decreases after the second hydro pass. Completely split and distributed fibers at the surface possibly is a smaller barrier for the descending ball. After the third pass, burst strength slightly increases again which may result of further entanglement.
After needling, an apparent density of more than 0.12 grams cubic centimeters is obtained, which is further treated by hydroentangling. After the first and second pass a higher apparent density than 0.28 grams per cubic centimeter is achieved, which should be promising in terms of abrasion resistance.
Surface changes of hydroentangled 24 segmented pie fabrics are shown in Table 21. All fabrics do not show any pills after 5000 or 20,000 rubs. The samples after two and three hydroentangling passes moreover have a smooth surface without significant changes, while the specimens of the sample unit after one hydro pass have a buffed surface.

Table 21: 24 Segmented Pie Surface Change

<table>
<thead>
<tr>
<th>24 Segmented Pie 1 Hydro Pass</th>
<th>24 Segmented Pie 1 Hydro Pass</th>
</tr>
</thead>
<tbody>
<tr>
<td>after 5000 rubs</td>
<td>after 20,000 rubs</td>
</tr>
</tbody>
</table>
Looking at the weight loss in the following chart, it can be observed that the nonwovens after one hydroentangling pass have only little weight loss. 24 segmented pie after two and three hydroentangling passes show noticeable higher weight loss than previous samples. It must however been considered that even the highest weight loss is below 0.5%.
Figure 146: Weight Loss 24 Seg. Pie
4.2.4 Mixed Media

Mixed media represents a hybrid system, containing different bico and/or homo-components, which are spun by the same spin pack. Next to combining different fiber types, rows can also be designed as for example two or three layers and alternating designs (see Figure 147, Figure 148 and Figure 149). Depending on the desired final application, benefits can be drawn, if for example microfibers are only needed on the surface. Mixed media not only improves tensile strength but also tear strength in creating rip-stops due to the mixture of different fiber types in the system [27].

![Figure 147: 8 Segmented Pie / Monocomponent 2 Layers [27, p. 28]](image1)

![Figure 148: 8 Segmented Pie / Monocomponent 3 Layers [27, p. 28]](image2)

![Figure 149: 8 Segmented Pie / Monocomponent – Alternate Design [27, p. 28]](image3)

Figure 150 depicts the structure of the created 75/25 PET/PA6 alternating 4 segmented pie mixed media fabrics. Mixed Media I & II are produced the same way only varying in weight.
Mixed Media II is formed of three, while Mixed Media I is formed of two spunbond web layers.

![Figure 150: Schematic Diagram](image1)

![Figure 151: SEM Mixed Media (4800x)](image2)

4.2.4.1 Hydroentangling

<table>
<thead>
<tr>
<th>Table 22: Hydroentangling Conditions Mixed Media</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mixed Media I &amp; II</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>1&lt;sup&gt;st&lt;/sup&gt; Pass</strong></td>
</tr>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
<tr>
<td><strong>2&lt;sup&gt;nd&lt;/sup&gt; Pass</strong></td>
</tr>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
<tr>
<td><strong>3&lt;sup&gt;rd&lt;/sup&gt; Pass</strong></td>
</tr>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
<tr>
<td><strong>4&lt;sup&gt;th&lt;/sup&gt; Pass</strong></td>
</tr>
<tr>
<td>Jet Head</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Strip Type</td>
</tr>
</tbody>
</table>
4.2.4.2  Jet Dyeing

Mixed Media I & II are dyed with a jet dyeing system type “JFO” to get an impression of the impact on structural properties. Based on the weight of the fabric to be dyed, the dye is mixed of disperse and acid dyes with a ratio based on Table 23.

Table 23: Disperse and Acid Dyes

<table>
<thead>
<tr>
<th>Disperse Dye</th>
<th>Acid Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount</td>
<td>Color Type</td>
</tr>
<tr>
<td>3%</td>
<td>Foron Black E-DC</td>
</tr>
<tr>
<td>3%</td>
<td>Dianix Black CCR</td>
</tr>
<tr>
<td>1%</td>
<td>Foron Yellow AS-FL</td>
</tr>
</tbody>
</table>

As most blacks turn out navy, the yellow pigments are added to obtain a more “blackish” result. Next to the disperse and acid dyes, the dye bath consists of water, in a ratio of 15:1 to the fabric weight, 1 gram of leveling agent and acetic acid per liter plus 1 milliliter defoamer per dye bath liter.

As the Mixed Media fabrics, especially Mixed Media II, are quite stiff, the water in the Jet Dye is first heated up to 80°C to soften it and the nozzle is wide open to ensure good fabric transport. This however entails higher abrasion and massaging force acting on the fabric. To complete the dyeing procedure, the whole system is heated up to 130°C with a heating rate of 2°C per minute. The system then stays for 60 minutes at 130°C before it is cooled down.
4.2.4.3 Testing and Characterization Methods

- **SEM**
The Scanning Electron Microscope is used as described in 0 Testing and Characterization Methods

- **Basis Weight**
The basis weight is determined as described in 4.1.2 Testing and Characterization Methods

- **Thickness**
The thickness is determined as described in 4.1.2 Testing and Characterization Methods

- **SVF**
The SVF is determined as described in 4.1.2 Testing and Characterization Methods

- **Air Permeability**
The air permeability is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Flexural Rigidity**
The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Burst Strength**
The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods

- **Apparent Density**
The apparent density is determined as described in 4.1.10.3 Testing and Characterization Methods
• Abrasion Resistance

The abrasion resistance is determined as described in 4.1.10.3 Testing and Characterization Methods.

4.2.4.4 Results and Discussion

Looking at the SEM pictures of Mixed Media I before and after dyeing, it can be seen that the structure is more open. This can also be seen in the graph below, in which solidity and air permeability is correlated.

Heavier Mixed Media II is less air permeable than Mixed Media I. Less solidity and higher air permeability of dyed fabric can be explained in looking at the thickness. The dyed versions increased in thickness; due to the mechanical action in the jet dye, the structures became fluffier and more open.
As can be seen in the bar chart below, structural changes also significantly affect bending behavior. Flexural rigidity of heavier Mixed Media II is not determinable with the cantilever method, as it is too stiff and consequently never touches the knife to record the overhang length. After jet dying the fabric it becomes far more flexible due to the structural changes.
Although flexural rigidity decreased for the fluffier dyed mixed media fabrics, burst strength continuously increased.
The apparent density of the mixed media fabric does not reach 0.28 grams per square centimeters, which are recommended for good abrasion resistance. The open structures of the dyed mixed media result in a significant decrease of apparent density.
The change in apparent density already predicted that the open structure will show less abrasion resistance. As can be seen below, the dyed mixed media lose more weight after 20,000 turns.

![Abrasión Resistance Graph](image)

**Figure 158: Weight Loss Mixed Media**

Table 24 depicts the surface change of mixed media and dyed mixed media fabrics after 5000 and 20,000 rubs. After 5000 turns, there are already numerous nips visible on the surfaces, which are increased to big pills surrounded by a roughened surface.
Table 24: Mixed Media Surface Change

<table>
<thead>
<tr>
<th>Mixed Media I after 5000 rubs</th>
<th>Mixed Media I after 20,000 rubs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyed Mixed Media I after 5000 rubs</td>
<td>Dyed Mixed Media I after 20,000 rubs</td>
</tr>
<tr>
<td>Mixed Media II after 5000 rubs</td>
<td>Mixed Media II after 20,000 rubs</td>
</tr>
<tr>
<td>Dyed Mixed Media II after 5000 rubs</td>
<td>Dyed Mixed Media after 20,000 rubs</td>
</tr>
</tbody>
</table>
4.2.5 Modified Tipped Trilobal Fibers

A spunbond hydroentangled dyed modified tipped trilobal fabric is taken into account to have a look at the performance of modified tipped trilobal fibers in an artificial leather base fabric. Although the available fabric has a considerably lower basis weight, affecting mechanical properties, such as flexural rigidity and burst strength, its surface can be observed in terms of coatability and softness.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Dyed Modified Tipped Trilobal Fabric 50% PA6 50% PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis Weight [g/m²]</td>
<td>150</td>
</tr>
<tr>
<td>Thickness [mm]</td>
<td>0.78</td>
</tr>
<tr>
<td>SVF [%]</td>
<td>15.46</td>
</tr>
<tr>
<td>Apparent Density [g/cm³]</td>
<td>0.19</td>
</tr>
<tr>
<td>Air Permeability [cfm]</td>
<td>21</td>
</tr>
<tr>
<td>Burst Strength [lbf]</td>
<td>59.47</td>
</tr>
<tr>
<td>Flexural Rigidity MD [µNm]</td>
<td>0.031</td>
</tr>
<tr>
<td>Flexural Rigidity CD [µNm]</td>
<td>0.006</td>
</tr>
</tbody>
</table>

After 5000 rubs the surface of the modified tipped trilobal fabric is still smooth and even. After 20,000 pilling is visible on the fabric surface.
Some specimens only show few pills, while others have numerous pills all over the surface. This can be explained by the weight loss shown below. The increased weight loss after 20,000 turns indicates that pills are rubbed off the surface. The high standard deviation explains that some specimen show more pills than others.

![Abrasion Resistance](image_url)
5 Impregnation and Coating

5.1 Impregnation and Direct Coating

Impregnation and direct coating experiments are done with HST 4292A & B provided by Lubrizol Corporation to enhance abrasion resistance and textile hand. HST 4292A & B are water-based polymer systems of aliphatic polyether urethane and acrylic latex, whereas the HST 4292B is a pad version of sample A. Mixed Media is chosen as the fabric to enhance abrasion resistance, as especially the dyed fabric shows a very open structure, susceptible to HST 4292B being directly poured into the padder nip of a Werner Mathis Padder HVF 24489 before the dyed mixed media is inserted. Due the relatively high viscosity, it was problematic to guide the fabric through the rolls. Two initial trials were done with a pressure of 1 and 6 bar. Both fabrics were dried in the Werner Mathis Labcoater LTF 134489 for 5 minutes at 160°C. The results however were very stiff and had an unpleasant hand.

Figure 160: Padder

Figure 161: Labcoater
To reduce the applied amount, HST 4292B is diluted with water. A 50/50 HST 4292B/water solution is subsequently padded into the dyed mixed media fabrics with a pressure of 6 bar and dried for 4 minutes at 160°C.

An EZ-Coater EC 100 (see Figure 162: EZ-Coater) is chosen to apply the highly viscous HST 4292A. The topcoat is directly applied onto mixed media as well as dyed mixed media fabrics.

![Figure 162: EZ-Coater](image)

5.1.1 Testing and Characterization Methods

- **Abrasion Resistance**

  The abrasion resistance is determined as described in 4.1.10.3 Testing and Characterization Methods, with the only difference that all tested specimen were subjected to 20,000 rubs.

5.1.2 Results and Discussion

Table 27 shows the surface change of the dyed mixed media fabrics which have been impregnated with HST4292 B. It can be seen that big pills formed on some parts of the surface. This effect can be explained by the fact that the padded solution did not uniformly
penetrate throughout the whole fabric. As further can be seen in the bar chart below, some pills were rubbed off during the process resulting in weight loss.

Table 27: Dyed Mixed Media + HST4292 B Surface Change

<table>
<thead>
<tr>
<th>Dyed MM I + HST4292 B after 20,000 rubs</th>
<th>Dyed MM II + HST4292 B after 20,000 rubs</th>
</tr>
</thead>
</table>

Weight Loss

Figure 163: Weight Loss Coated Mixed Media

The directly coated mixed media fabrics show a constant weight loss of around 2%. The lost weight however does not affect the fabric itself. As can be seen in Table 28 only the topcoat was slightly rubbed off. The coated samples therefore show a high abrasion resistance and even have a surface appearance like an aged leather couch.
Table 28: Mixed Media + HST4292 A surface change

| MM I + HST4292 A after 20,000 rubs | Dyed MM I + HST4292 A after 20,000 rubs |
| MM II + HST4292 A after 20,000 rubs | Dyed MM II + HST4292 A after 20,000 rubs |

5.2 Water-Soluble Polyurethane Transfer Coating

Transfer coating process is chosen to create an even, uniform and thin topcoat having a leather-like grain finish. Bayer MaterialScience provided a basic formulation for a three-coat application, which is shown in Table 29.

Table 29: Basic Water Based Formulation

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impranil DLC-F</td>
<td>1000</td>
</tr>
<tr>
<td>BYK 333</td>
<td>3</td>
</tr>
<tr>
<td>Pigment Paste</td>
<td>50</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>150</td>
</tr>
<tr>
<td>Borchi Gel A La</td>
<td>35</td>
</tr>
</tbody>
</table>

1st Coat
Moreover, it is optional to use Bayhydur 302 as cross-linker in each layer to further improve mechanical properties.

Impranil DLC-F is an anionic polycarbonate ester polyurethane dispersion in water, showing high resistance to hydrolysis, aging and scratching. It is suitable for technical articles, outerwear and shoe uppers [118]. BYK333 is a polyether modified polydimethylsiloxane used as surface additive to strongly reduce surface tension and thereby improve substrate wetting [119, 120]. Borchi Gel A LA is a polyacrylate-based thickener, utilized to improve the rheology of aqueous coatings [121]. Impranil DLU represents an anionic aliphatic polyether/polycarbonate polyurethane dispersion, known for its good flexibility and hydrolytic stability. It is crosslinkable and suitable for high-quality coatings for upholstery, automobile seats and sport goods [122]. Dispercoll U42 is an aqueous anionic high molecular weight polyurethane dispersion, suitable for forming adhesives used for wet bonding processes of textile substrates [123].
5.2.1 Preliminary Trials

To get to know the behavior of the coating on the release paper and figure out best suitable application method, preliminary tests were made with the first layer. Following the amounts listed in Table 30 Impranil DLC-F, Byk 333, pigment paste and distilled water are mixed before Borchigel AL A is added as thickener to obtain a solution with desired viscosity.

Table 30: Topcoat Formula 1st Layer

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>1/20 Amount</th>
<th>Wet Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Coat</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impranil DLC-F</td>
<td>50 g</td>
<td>0.04 mm</td>
</tr>
<tr>
<td>Byk 333</td>
<td>0.15 g</td>
<td>(= 1.6 mil)</td>
</tr>
<tr>
<td>Pigment Paste</td>
<td>2.5 g</td>
<td></td>
</tr>
<tr>
<td>Distilled Water</td>
<td>7.5 g</td>
<td></td>
</tr>
<tr>
<td>Borchigel AL A</td>
<td>1.75 g</td>
<td></td>
</tr>
</tbody>
</table>

First coating tests are done with the Werner Mathis Labcoater LTF 134489, located in the Dyeing and Finishing Laboratory in the College of Textiles at NC State University. Figure 164 summarizes conducted experiments using knife over roll and knife over blanket setting.
5.2.1.1 First Preliminary Results and Discussion

It was not possible to achieve an even uniform coating result, neither with the knife over roll nor, the knife over blanket setting. The knife angle did not matter, as the main problem is the stiffness and little pliability of the release paper, which consequently readily bent, as soon as the knife moved along.

5.2.1.2 Refinement

To prevent unwanted paper movement during coating and curing process, a staple even heat resistant support is necessary. For this task a tile was customized to fit onto the tenter frame holder. To secure the release paper from sliding around during the coating process, a heat resistant tape was chosen to secure the edges to the tile.
5.2.1.3 Second Preliminary Results and Discussion

Significant improvement was achieved in providing the tile as paper support throughout the whole procedure. Nevertheless, the result was not satisfying as applied film still varied in thickness and some areas of the release paper remained uncoated. Minimal thickness deviations of the tile itself may be the reason for accomplished irregular results.

5.2.1.4 Refinement

Instead of using a tile, which can slightly vary in uniformity due to baking during manufacturing process, a glass plate is customized as a substitution.

5.2.1.5 Third Preliminary Results and Discussion

In using the glass plate as base for the coating procedure, the paper lies perfectly flat, secured by heat resistant tape at its edges. Although the paper support problem was solved, the knife represents a remaining issue. Accurately adjusting the gap size to as little as 0.04 millimeters practically is an impossible task at the used device. Furthermore, the coated solution uncontrollable leaks out at the sides, impeding constant film width.

5.2.1.6 Refinement

U-shaped drawdown bars (see Figure 165), each having two clearances in one unit, are customized to desired gap choices.
Due to its u-shape, the drawdown bar prevents leakage and results in sharp edges and forms hand sheets with a constant film width of 6 inches.

5.2.2 U-Shaped Drawdown Bars

Table 31 lists base fabrics to be coated, from produced and characterized nonwovens in chapter 4 Substrate.

Table 31: Selected Nonwoven Base Fabrics

<table>
<thead>
<tr>
<th>Monocomponent Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 denier PET</td>
</tr>
<tr>
<td>PET VI</td>
</tr>
<tr>
<td>PET VI w/o Finish + Hydro</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bicomponent Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trilobal Sheath Core</td>
</tr>
<tr>
<td>TT2</td>
</tr>
<tr>
<td>TT2+2*Hydro</td>
</tr>
<tr>
<td>TT2+3*Hydro</td>
</tr>
</tbody>
</table>

| 51 Island in the Sea          |
| 51 I/S Removed + Hydroentangled|
Table 31 Continued

<table>
<thead>
<tr>
<th>24 Segmented Pie</th>
<th>24 Segmented Pie 1&lt;sup&gt;st&lt;/sup&gt; Pass Hydro</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24 Segmented Pie 2&lt;sup&gt;nd&lt;/sup&gt; Pass Hydro</td>
</tr>
<tr>
<td></td>
<td>24 Segmented Pie 3&lt;sup&gt;rd&lt;/sup&gt; Pass Hydro</td>
</tr>
<tr>
<td>Mixed Media</td>
<td>Mixed Media I</td>
</tr>
<tr>
<td>Modified Tipped Trilobal</td>
<td></td>
</tr>
</tbody>
</table>

For laboratory size coating procedure one-twentieth of the recipe Bayer MaterialScience provided is mixed. Used amounts can be observed in Table 32.

Table 32: Reduced Water Based Formulation

<table>
<thead>
<tr>
<th></th>
<th>Raw Material</th>
<th>1/20 Amount</th>
<th>Wet Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; Coat</td>
<td>Impranil DLC-F</td>
<td>50 g</td>
<td>0.04 mm (= 1.6 mil)</td>
</tr>
<tr>
<td></td>
<td>Byk 333</td>
<td>0.15 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pigment Paste</td>
<td>2.5 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>7.5 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Borchigel AL A</td>
<td>1.75 g</td>
<td></td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Coat</td>
<td>Impranil DLU</td>
<td>50 g</td>
<td>0.07 mm (= 2.8 mil)</td>
</tr>
<tr>
<td></td>
<td>Pigment Paste</td>
<td>1.75 g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Borchigel AL A</td>
<td>1.5 g</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; Coat</td>
<td>Dispercoll U42</td>
<td>50 g</td>
<td>0.14 mm (= 5.5 mil)</td>
</tr>
<tr>
<td></td>
<td>Borchigel AL A</td>
<td>1.25 g</td>
<td></td>
</tr>
</tbody>
</table>
Release paper is secured on the glass plate with a heat resistant tape before the first film is applied with the help of a u-shaped drawdown bar, having a gap clearance of 1.6 mil. After curing the first layer at 90°C for 6 minutes, the second coat is applied with a u-shaped drawdown bar having a gap size of 2.8 mil. The second layer is also cured at 90°C for minutes before the adhesive layer is applied as third coat with a gap clearance of 5.5 mil. The nonwoven fabric is placed on to the adhesive layer and constantly pressed with the customized tile on top during the curing procedure for 10 minutes at 90°C.

5.2.2.1 Results and Discussion

While applying the topcoat onto the release paper, the coating immediately converged to droplets instead of remaining as a continuous thin film. The second layer could also not cover all gaps and pinholes. Furthermore, the release paper lost its planarity and started curling as soon as the coating touched its surface.

After curing the whole assembly, it was hard to completely remove the release paper as the water based polyurethane topcoat interacted with it.

The gained artificial leather has a beautiful grain finish at the parts, where the transfer paper was removable, however big wrinkles and unwanted orange peel effect and delamination are observed while bending.

5.2.2.2 Refinements

Flow and leveling of coating is paper dependent. The described coating converging issue is a wetting problem, which can be solved by adding more leveling agent. To control the flow of the second layer and facilitate closing of possible pinholes, more thickener is added.
Table 33: Topcoat Recipe Refinements

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>1/20 Amount</th>
<th>Adjustments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1st Coat</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impranil DLC-F</td>
<td>50 g</td>
<td></td>
</tr>
<tr>
<td>Byk 333</td>
<td>0.15 g</td>
<td>0.3 g, 0.6 g</td>
</tr>
<tr>
<td>Pigment Paste</td>
<td>2.5 g</td>
<td></td>
</tr>
<tr>
<td>Distilled Water</td>
<td>7.5 g</td>
<td></td>
</tr>
<tr>
<td>Borchigel AL A</td>
<td>1.75 g</td>
<td></td>
</tr>
<tr>
<td><strong>2nd Coat</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impranil DLU</td>
<td>50 g</td>
<td></td>
</tr>
<tr>
<td>Pigment Paste</td>
<td>1.75 g</td>
<td></td>
</tr>
<tr>
<td>Borchigel AL A</td>
<td>1.5 g</td>
<td>2 g</td>
</tr>
</tbody>
</table>

Table 33 depicts proposed improvements; the leveling agent BYK 333 in the first coat is increased twice and four times to observe its effect on wetting and to obtain an even continuous film. One third more of the thickener Borchigel AL A is used in the second coat to adjust its flow and improve coverage.

To help the release paper to resist the attack of water and consequently prevent loss of planarity and release problems, if coating stayed too long onto it, advantage is taken of the so-called “dry sponge effect”. A dried kitchen sponge does not absorb water readily. This effect is used for the release paper in drying them for 2 minutes at 90°C prior to applying the topcoat. Ambient moisture is drawn out on the one hand and moisture is prevented to enter up to a certain extent.
To enhance lamination, a Stork laminator, shown in Figure 166, is used with and without pressure to join the nonwoven fabric to the wet adhesive layer. The device is not heated up for this process and runs with a speed of 2.5 m/min.

Figure 166: Laminator

5.2.2.3 Testing and Characterization Methods

- **Appearance and Haptic**

Evaluation of hand feeling and appearance is done subjectively by bending and folding the whole fabric plus touching the surface while stroking in various direction.

- **SEM**

The Scanning Electron Microscope is used as described in 0 Testing and Characterization Methods, whereas particular attention is paid to the created foam structure, its penetration and void size.
5.2.2.4 Results and Discussion

The converging issue was improved by adding more leveling agent to the first layer. Twice the amount of BYK333 results in a satisfying continuous film. The thickened second coat evenly covered the first layer.

Pre-drying the release paper helps to prevent the water from attacking its structure, i.e. the coated assembly peels off easily after curing and curling during application is diminished. Using the Stork laminator for joining the coated film to the nonwoven fabric improves lamination. A pressure of 50psi was necessary to obtained soft and supple hand sheets not showing huge wrinkles while bending and no signs of delamination.

Although the coated fabrics look good to the naked eye, a closer look with the scanning electron microscope reveals that there are big voids in between the fabric surface and the laminated film. The reason for these gaps is that the topcoat is held by some buckling fibers and does not attach to the actual fabric surface. This effect is best seen in Figure 167. Scanning the remaining coated nonwovens, depicted in Figure 168 to Figure 177 it becomes that this effect is reduced the finer and even the coated surface is. The 51 Island in the Sea fabric (see Figure 175), of which the sea has been removed and the surface been subsequently hydroentangled, does not have coarse buckling fibers and consequently shows no voids and better adhesion to the laminated topcoat.
Figure 167: PET VI + Topcoat

Figure 168: PET VI w/o Finish + Hydro + Topcoat

Figure 169: TT2 + Topcoat

Figure 170: TT2+2*Hydro + Topcoat

Figure 171: TT2+3*Hydro + Topcoat

Figure 172: 24 Seg. Pie 1st Pass Hydro + Topcoat
5.2.2.5 Refinements

There are two approaches to close the unwanted voids between fabric surface and laminated film. The first is to create a foam layer, which penetrates the fabric on the one hand, and
evens its surface on the other to chemically close the undesired gap and improve topcoat-substrate bonding. The second attempt is to iron the nonwoven prior to the transfer coating process with a heated laminator to smoothen the surface.

The first focus is set on the frothed foam process before a closer look is taken at the ironing process.

(I) Frothed Foam Process

To avoid time, water and energy consuming coagulation process, including its hazardous solvent dimethyl formamide, the idea was to use solvent free Impranil polyurethane dispersions to create a foam layer as a qualitative alternative. Their high solid content of 60 percent is engineered by mixing large with very small polyurethane particles, which are capable of filling the gaps between the bigger particles (see Figure 178).

![Bimodal Polyurethane Particle Distribution](image)

The high solid content entails less application times, i.e. one time is sufficient, and shorter drying times as less water is incorporated [125].
Bayer MaterialScience provided a recipe for creating frothed foam lab bench samples. All chemicals listed in Table 34 are one after another (starting from the top) poured into a beaker and thoroughly mixed under agitation. The recommended procedure is hereby to primarily stir everything with a bench top mixer under 700 RPMs for 3 minutes before subsequently using a hand blender with a wire mixing blade on high for another 3 minutes. Enough air should now be incorporated in the achieved foam which is subsequently applied. Drying should ideally take place in a 3 stage oven having three respective heating zones of 50, 70 and 140°C in which the coated assembly should stay for 1-2 minutes per zone. If such an oven however is not available, it is suggested to dry the coated substrate at 100°C for 5 minutes.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Weight [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impranil DLU</td>
<td>324.00</td>
</tr>
<tr>
<td>Stokal STA</td>
<td>4.86</td>
</tr>
<tr>
<td>Stokal SR</td>
<td>6.48</td>
</tr>
<tr>
<td>Acrafix ML</td>
<td>6.48</td>
</tr>
<tr>
<td>Borchi Gel A LA</td>
<td>9.40</td>
</tr>
</tbody>
</table>

Impranil DLU is an anionic aliphatic polyether/polycarbonate polyurethane dispersion, known for its good foamability, flexibility and hydrolytic stability. It is crosslinkable and suitable for high-quality coatings for upholstery, automobile seats and sport goods [122]. Stokal STA and SR are foam stabilizers helping to maintain the created foam and prevent
collapsing [126]. Acrafix ML is a melamine resin, used as crosslinking agent and Borchi Gel A LA is a polyacrylate-based thickener, utilized to improve the rheology of aqueous coatings [127, 121].

To complete the frothed foam process at lab-scale, the recipe is adjusted as shown in Table 35. Besides the adjusted amount of raw material, pigment paste is added to better track foam penetration on the white base nonwoven substrate.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>1/2 Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impranil DLU</td>
<td>162 g</td>
</tr>
<tr>
<td>Stokal STA</td>
<td>2.43 g</td>
</tr>
<tr>
<td>Stokal SR</td>
<td>3.24 g</td>
</tr>
<tr>
<td>Acrafix ML</td>
<td>3.24 g</td>
</tr>
<tr>
<td>Pigment Paste</td>
<td>5 g</td>
</tr>
<tr>
<td>Borchi Gel A LA</td>
<td>4.7 g</td>
</tr>
</tbody>
</table>

To process the small amount, usual benchtop mixer are however not suitable. Therefore in this study a Norpro cordless mini mixer (see Figure 179) is used to thoroughly incorporate air and create the foam structure. The cordless mini mixer is delivered with four attachments of which the froth and whip are used to fulfill the job.
Stokal STA, Stokal SR, Acrafix ML, pigment paste and BorchiGel ALA are mixed to Impranil DLU under stir, using the froth attachment for 3 minutes. Next, the composition is beaten with the wire mixing blade (whip attachment) for another 3 minutes. The created foam is directly applied on the nonwoven substrate with the help of a draw down bar having a gap size of 5.5 mil (= 0.14 mm) and dried in an oven for 5 minutes at 100°C. Subsequently the created substrate is coated by the previously described three-layer transfer coating process.

5.2.2.6 Testing and Characterization Methods

- **SEM**
  
The Scanning Electron Microscope is used as described in Testing and Characterization Methods, whereas particular attention is paid to the created foam structure, its penetration and void size.

- **Appearance and Haptic**
  
  Evaluation of hand feeling and appearance is done subjectively by bending and folding the whole fabric plus touching the surface while stroking in various direction.
5.2.2.7 Results and Discussion

During application, the foam is readily absorbed by the base fabric. Covered fibers at the surface are very stiff and stick out of plane, leading to a very rough hand feeling. These fibers were also visible as numerous tiny dents and hills through the laminated transfer coat. Furthermore, the topcoat did not stick well to the surface layer, which might be due to the rough, stiff and uneven surface.

![Figure 180: Varying Foam Pore Sizes](image)
![Figure 181: SEM Foam Pores](image)

Another issue is shown in Figure 181. Looking at the foam structure via SEM, it can be seen that there are numerous large pores, which are not desirable, as huge voids diminish mechanical properties and negatively impact coating uniformity.

5.2.2.8 Refinements

To improve frothed foam process, two approaches were done. As can be seen in Figure 182, one is focusing on modifying the foam structure itself and the other concentrates on modifying the way of applying the created foam. The goal of depicted approaches is to reduce foam pore size and prevent the foam from fully flowing into the nonwoven substrate.
To modify the foam structure, the mixing time is increased from 3 to 5 minutes with the froth attachment as well as from 3 to 5 minutes for the whip attachment to end up with a total mixing time of 10 minutes. Another attempt to prevent foam from fully flowing into the substrate is in thickening it by adding a higher amount of Borchigel AL A.

For the foam application three new approaches are considered. The first is to pre-impregnate the nonwoven fabric with polyvinyl alcohol solution to fill some voids in the nonwoven structure and thereby prevent the foam from entering the fabric up to a certain extent. A Werner Mathis Padder HVF 24489 is used to dip the nonwoven fabric into a 5 % PVA solution, followed by padding with a pressure of 6 bar and drying in the Werner Mathis Labcoater LTF 134489 at a temperature of 135°C for 2 minutes. The gained PVA-impregnated substrate is directly coated with the polyurethane foam and cured in at a
temperature of 100°C for 5 minutes. Obtained foam coated sheet is subsequently washed in a kettle for 10 minutes at 60°C to remove the PVA.

The second approach is to apply multiple layers with and without intermittent curing.

The third application modification is to use bigger gap sizes. The chosen gap sizes are 8 mil (= 0.2 mm), 16 mil (= 0.41 mm), 40 mil (= 1.02 mm).

A topcoat is laminated to created foam coated substrates.

5.2.2.9 Testing and Characterization Method

- **SEM**

The Scanning Electron Microscope is used as described in 0 Testing and Characterization Methods, whereas particular attention is paid to the created foam structure, its penetration and void size.

5.2.2.10 Results and Discussion

Increasing the mixing time did not significantly influence pore size and a higher amount of thickener could also not stop the foam from completely drifting into the fabric. The PVA impregnation led to a very stiff substrate, having hard fibers sticking out of the surface, which made continuous and even sliding of the drawdown bar on top of the surface difficult. Again, the foam was highly absorbed by the substrate. During the washing process, the applied dried foam layer degraded, indicating that crosslinks have not been formed yet. A higher curing temperature of approximately 140°C for 2 minutes should be added to start and complete crosslinking action of added melamine resin Acrafix ML.
Applying multiple layers with a drying step after each layer was problematic and unsatisfactory, as stiff fibers, which were sticking out of the surface after first applied layer, inhibited smooth and even coating of the second layer, because it was impossible to evenly slide the drawdown bar on top of it. Moreover buckling fibers were still visible and tangible after second coat. Applying multiple coats without curing led to more promising results. While the first foam layer completely drifted inside the nonwoven structure, the second and especially third application mostly remained on the surface.

The third modification method of use bigger gap sizes, i.e. 8 mil (= 0.2 mm), 16 mil (= 0.41 mm), 40 mil (= 1.02 mm) showed no noticeable improvement for 8 mil and 16 mil gap clearances. Foam layers applied with a 40 mil gap drifted inside the nonwoven structure but also sufficiently remained on the surface to cover buckling fibers. The created handsheets are however super stiff and have a rubbery touch.

Although, a smooth foam surface without disturbing buckling fibers has been achieved by using a bigger gap size or multiple applications without intermittent drying, the laminated transfer coat did not bond well to the foam substrate. Figure 183 shows the gap between the topcoat and the foam layer.

![Figure 183: SEM Intersection Topcoat – Foam](image1)

![Figure 184: Foam-Topcoat Interface](image2)
The reason for only partially bonding can be a wavy foam layer, resulting from different pore sizes. During the lamination process, the relatively stiff foam layer is not adaptable enough to completely join with the transfer coat at all heights.

Consequently, the problem of closing the voids in between the topcoat and the substrate to increase inter alia delamination resistance could not be solved by the frothed foam process.

(II) Fabric Ironing

To smooth the surface and get rid of disturbing buckling fibers, the nonwoven fabric is ironed prior coating with a Klieverik LFC 101-1000 laminator. The device is heated up to 130°C, the fabric runs through with a speed of 5 m/min and a constant pressure of 50 psi is applied from both the belt and the rubber roll. Ironed fabric is subsequently coated by previously described optimized transfer coating process.

5.2.3 Testing and Characterization Methods

- **SEM**

The Scanning Electron Microscope is used as described in 0 Testing and Characterization Methods. Particular attention is paid to the cross-section of the coated specimens to examine and analyze the respective layers.

- **Orange Peel**

The technique, introduced by Fujisawa et al. in the European patent EP 2 025 806 B1 is used to evaluate the orange peel effect, emerging while bending created artificial leather samples. Cut specimen (4 cm x 4 cm) squares, are bent, so that the grained surface is inside and clipped at two ends, 1 cm inside from the edges. The clipped portion is further narrowed to
diminish previous 2 cm interspace to 1 cm (see also Figure 82). Finally, the formed wrinkles are count and orange peel effect is evaluated with the help of Table 2 [20].

- **Flexural Rigidity**
  The flexural rigidity is determined as described in 4.1.10.3 Testing and Characterization Methods. To reduce friction and make sliding of the coated surface possible, a Teflon tape is installed.

- **Burst Strength**
  The burst strength is determined as described in 4.1.10.3 Testing and Characterization Methods. The coated test specimens are mounted with the coated side down, so that the steel ball will not primarily touch the coating when descending during testing procedure.

- **Water Vapor Permeability**
  The water vapor permeability of produced specimens was tested with Mocon’s apparatus Permatran-W 100k according to ASTM standard D 6701-01. Water vapor transmission rate of 5 samples at a time is tested. This standard is capable of determining water vapor transmission rate ranging from 500 to 100 000 g/m²day [129]. To further be able to define the impact of coating on water vapor transmission, both raw as well as coated substrates are tested and compared. The non-symmetrical coated samples are mounted with the fabric side facing high humidity as water vapor transmission in real life application will also be from inside (fabric) out (topcoat).
5.2.4 Results and Discussion

Figure 185 to Figure 196 depict the result of the transfer coating process onto the “pre-ironed” nonwoven substrate. As can be seen, buckling fibers were successfully lowered resulting in a smoother surface. Huge voids between topcoat film and fabric surface could be eliminated or at least reduced. Nonwoven fabrics, having coarser fibers such as PET VI still show voids between the topcoat and the fabric due to their more open structure.

Figure 185: Ironed PET VI + Topcoat
Figure 186: Ironed PET VI w/o Finish + Hydro + Topcoat
Figure 187: Ironed TT2 + Topcoat
Figure 188: Ironed TT2+ 2*Hydro + Topcoat
Figure 189: Ironed TT2 + 3*Hydro + Topcoat

Figure 190: Ironed 51 I/S Removed + Hydro + Topcoat

Figure 191: Ironed 51 I/S Removed + Hydro (Coarse Side Up) + Topcoat

Figure 192: Ironed 24 Seg. Pie 1st Pass + Topcoat

Figure 193: Ironed 24 Seg. Pie 2nd Pass + Topcoat

Figure 194: Ironed 24 Seg. Pie 3rd Pass + Topcoat
Table 36 shows the results of the orange peel tests. The specimens are evaluated with the help of a ranking ranging from A to D, with A as best result having 2 or less buckling wrinkles and D as worst result showing 8 or more buckling wrinkles (see also Table 2). As can be seen, best results are governed by nonwoven fabrics comprising bicomponent fibers and were produced by a mixture of needling and hydroentangling or only hydroentangling. Pure needled fabrics were however more susceptible to orange peel, especially nonwovens consisting of monocomponent fibers showed bad results.

<table>
<thead>
<tr>
<th>Coated Fabric</th>
<th>PET VI</th>
<th>PET VI w/o F. + Hydro</th>
<th>TT2</th>
<th>TT2+2H</th>
<th>TT2+3H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rating</td>
<td>C</td>
<td>D</td>
<td>C</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Coated Fabric</td>
<td>51I/S+Hydro</td>
<td>51I/S+Hydro (Coarse)</td>
<td>24 SegP. 1st Pass</td>
<td>24 Seg.P. 2nd Pass</td>
<td>24 Seg.P. 3rd Pass</td>
</tr>
<tr>
<td>Rating</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Coated Fabric</td>
<td>Mixed Media I</td>
<td>Modified Tipped Trilobal</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Rating</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>
In the following, the effect of coating on flexural rigidity and burst strength will be observed. All coated fabrics of each fiber type are set into comparison.

Starting with the monocomponent polyester fibers, it can be seen that the topcoat immensely increased the flexural rigidity for both PET VI and PET VI w/o Finish + Hydro in machine and cross-machine direction. PET VI + topcoat was too stiff to be measured on the cantilever test in both directions and consequently is only depicted as an endless red bars.

![Flexural Rigidity w/o and w/ Topcoat](image)

The burst strength slightly decreased after coating PET VI and PET VI w/o Finish + Hydro. The reason for this probably is that the fibers partially stuck together due to the adhesive, impairing their freedom of movement.
Coated trilobal sheath core fabrics also show greater stiffness after coating. Interestingly especially TT2+3*Hydro is even too stiff to be tested on the cantilever after coating. The reason for this possibly is previously discovered fabric damage due to exaggerated hydroentangling. Adhesive can easier enter into the partially broken structure and consequently increase its flexural rigidity.
Looking at the burst strength of coated and not coated trilobal sheath core nonwoven fabrics it can be seen that previous assumption that adhesive deeply penetrated into the structure of TT2+3*Hydro is also true for the burst results. As a result fibers stuck together leading to less mobility and burst strength. The increase of burst strength of TT2 can be explained by its greater thickness. Fibrous structure is first compressed and backed up by topcoat. TT2+2*Hydro does not show a significant change in burst strength.
As can be seen below, the flexural rigidity also increases for the coated 51 I/S after Removal + Hydro and no significant increase in burst strength is observed.
Flexural rigidity of 24 segmented pie fabrics was not measurable in machine direction for coated 24 segmented pie after two passes and remains not measurable in machine direction for 24 segmented pie after three passes after coating. The stiffness of the 24 segmented pie after one pass does not significantly rise after applying the topcoat. The reason for the different behavior of coated 24 segmented pie fabrics after one and after two passes hydro possibly is their surface structure. While there still not split bicomponent fibers among the split ones after one pass, the whole surface consists of a closed structure of split segments after two passes. The finer structure are more likely to stuck together by the applied adhesive after lamination without any room for movement at the top, resulting in greater stiffness.
Flexural Rigidity w/o and w/ Topcoat

Looking at the burst strength, there are slight fluctuations visible after coating the fabric. 24 segmented pie after one and two hydro passes increase after applying the topcoat, while the coated 24 segmented pie after three passes decreased a little.
Coated Mixed Media I also increased in flexural rigidity and was not measurable with the cantilever in machine direction.
No noticeable change in burst strength could be observed after coating Mixed Media I.
Initially super flexible modified tipped trilobal fabric highly increased in stiffness after coating. As the fabric is very thin and has a quite open structure after jet dyeing process, the adhesive deeply penetrated the majority of the fabric.

The relatively low burst strength is slightly increased after applying the grain finished topcoat.
The next focus is set on water vapor permeability, which plays an important fact in terms of comfort. Fabrics having the same fiber type are set into comparison before and after coating to see the change in breathability.

Starting with the monocomponent PET fabrics, it can be observed that water vapor transmission rate dramatically decreases after coating. PET VI without topcoat shows a little higher water vapor transmission rate than PET VI w/o Finish + Hydro. The same trend can be observed for the coated versions of PET VI and PET VI w/o Finish + Hydro + Topcoat respectively.
TT2 fabrics also strongly decrease after coating. The coated fabrics show all approximately the same water vapor transmission rate, even though TT2+2 and 3*Hydro and TT2+3*Hydro initially are more breathable without coating.
As shown below, 24 segmented pie fabrics also dramatically decrease after applying the topcoat and show quasi the same water vapor transmission rate.
Although 51 I/S fabric has a far smaller water vapor transmission rate than Mixed Media I or Modified Tipped Trilobal, there is no huge difference among the coated versions.
To survey the breathability of created artificial leathers and get an idea of competitiveness, a real leather piece as natural counterpart and various commercial polyurethane coated artificial leather samples are tested and directly set into comparison. As can be seen below, more than half of the created sample units have a higher water vapor transmission rate than real leather. They can also easily keep up with commercial available samples.

![Breathability Comparison](image)

Figure 213: Breathability Comparison

Just one outlier was detected, which has been marked by a green circle. The secret for extra high water vapor transmission rate can be detected in taking a close look at its coated surface.
As can be seen in Figure 214 the coated surface is apertured, having numerous tiny holes to facilitate water vapor passing through.
6 Summary and Conclusion

Summarizing, mechanical properties of all nonwovens, which have been chosen as artificial leather substrate, are compared before a look is taken at their performance after applying the topcoat.

The abrasion resistance is evaluated in comparing the weight loss and the surface changes after 20,000 rubs. As can be seen in the bar chart below, TT2+3*Hydro shows highest weight loss followed by Modified Tipped Trilobal. The PET fabrics did not lose any weight at all and 51 I/S fabrics and 24 segmented pie after the first hydro pass have very little weight loss.

Least surface changes after 20,000 rubs could be observed for TT2+2*Hydro, 51 I/S after removal + Hydro, 24 Seg. Pie after 1,2 and 3 hydro passes. Heavy wear was observed for PET fabrics, TT2 and Mixed Media I. In considering both, surface change and weight loss,
best abrasion resistance was achieved by 51 I/S after Removal + Hydro, followed by 24 Segmented Pie.

In order to compare burst strength of fabrics having various basis weights, measured values are normalized to a nominal weight of 200 g/m². As can be seen above, highest burst strength is achieved by PET VI and PET VI w/o Finish + Hydro, followed by 51 I/S after Removal + Hydro and 24 Segmented Pie 1st Pass Hydro, whereas least burst strength is obtained by Modified Tipped Trilobal and TT2.

Although burst strength of PETVI, PET VI w/o Finish + Hydro, TT2 + 2*Hydro, TT2+3*Hydro, 51 I/S after Removal + Hydro, 24 Segment Pie after third Pass and Mixed Media I slightly decreased after topcoat was applied and relatively low initial burst strength of TT2 and Modified Tipped Trilobal increased a little after coating, the small rates of
alteration lead to the conclusion that there was no significant change in burst strength after coating the fabric.

In terms of flexural rigidity, the created fabrics should on the one hand not be too flexible like the light weight modified tipped trilobal or on the other hand too stiff like for example the 24 segmented pie 3\textsuperscript{rd} Pass Hydro fabric to allow good workability and provide enough stiffness for possibly manufactured shoes. As has previously been shown, the flexural rigidity always increased after coating. This increase was however irregular: PET VI for example has a flexural rigidity of 0.56 \(\mu\text{Nm}\) in machine direction and 24 segmented pie fabric after the first hydro pass shows a significantly higher stiffness of 1.14 \(\mu\text{Nm}\) in machine direction. After coating the initially far more flexible PET VI is too stiff to be measured with the cantilever method, while the coated 24 segmented pie first pass hydro fabric lightly increased in flexural rigidity to a still measurable amount of 1.18 \(\mu\text{Nm}\) in machine direction.

From this, it can be deduced that the flexural rigidity after coating is governed by the fiber type and the structure of the nonwoven substrate, controlling the penetration depth and interaction with the adhesive during lamination. As it was not possible to predict the increase of flexural rigidity after coating, measured bending behavior of the substrate itself mainly helps to determine whether the stiffness already reached its upper limit prior coating and any increase would not be tolerable or whether fabric damaged occurred during manufacturing processes.
Next to looking at the flexibility, the appearance while bending the artificial leather, so that its grained surface is inside, is evaluated in terms of orange peel effect. Best results with least buckling wrinkles are obtained for 51I/S+Hydro, all 24 segmented pie fabrics after hydroentangling, Mixed Media I and Modified Tipped Trilobal. Worst results are achieved by monocomponent PET fabrics and the needled TT2 without subsequent hydroentangling.

Breathability of nonwoven substrates and final artificial leathers is compared in the following graph. Water vapor transmission rate of nonwovens is correlated to solid volume fraction and measured water vapor transmission rate for coated specimens are set in the same level to respective uncoated substrate to get an idea of the impact of the topcoat. In focusing on the pure substrates first it can be seen that water vapor transmission rate of most fabrics linearly rises with increasing solidity (see green circle). It is striking that the only fabrics which are not following this trend all consist of ultrafine fibers (see purple circle). Extremely fine fibers result in a very close structure, hindering water vapor to pass through as easily as through more open structures.
Although water vapor transmission rate of coated fabrics dramatically decreased, there is no constant behavior visible. Initially greatest breathability was shown by Mixed Media I, which does however not show highest permeability after coating. TT2 has one of the lowest water vapor transmission rates before coating, but is one of the five highest breathable coated fabrics. The only detected trend is that the bicomponent nonwovens comprising ultrafine fibers (51 I/S and 24 Segmented Pie) collectively have a smaller water vapor transmission rate than remaining more open structures.

In conclusion, after concentrating on understanding artificial leather manufacturing process, various nonwoven substrates have been created and evaluated throughout the formation process. Needling conditions were first successfully optimized for monocomponent staple fiber nonwoven fabrics before obtained knowledge is transferred on processing bicomponent staple fibers. Needled and or hydroentangled substrates were evaluated in terms of structural
and mechanical properties. Moreover spunbond and hydroentangled nonwovens comprising continuous fibers were produced and evaluated.

Investigations in terms of improving the abrasion resistance of relatively open structures which were susceptible to pilling and unwanted surface changes were done by impregnation and direct coating. A thin film of a water-based aliphatic polyether urethane and acrylic latex solution helped to protect the fabric from roughening and pilling.

To end up with artificial leather a technique for creating a three-coat transfer coating grain finish topcoat, based on water-soluble polyurethane, has successfully been established and optimized. Most promising monocomponent PET nonwoven fabrics, trilobal sheath core samples after each stage, removed and hydroentangled 51 island in the sea, hydroentangled 24 segmented pie after each pass, Mixed Media I and Modified Tipped Trilobal fabrics were chosen as base substrates for coating to create artificial leather. Appearance and mechanical properties of coated samples were analyzed and compared with one another before a direct comparison of obtained mechanical properties is done with uncoated substrates to study the impact of various nonwoven substrates during different formation stages on artificial leather. The importance of a smooth and even surface is illustrated by the comparison of the coated smooth and even hydroentangled top surface of 51 island in the sea fabric with its coated bottom surface which was not directly penetrated by the water jets. More orange peel effect was also observed for fabrics which have not passed through a heated laminator prior to coating process.
Last but not least, the best performance in appearance, sensual and mechanical properties is achieved by 51 Island in the sea, of which the sea has been removed before hydroentangling and 24 segmented pie after passing one time through the hydro. Although its fibers are relatively coarse in contrast to split 24 segmented pie and fibrillated 51 island in the sea, Mixed Media I also showed very good performance in terms of appearance haptic and mechanical properties with the exception of little abrasion resistance.
7 Future Work

7.1 Winged Fibers

Winged fibers are spun as bicomponent fibers (see Figure 218), of which sheath is essential for spinnability. After nonwoven formation the sheath is removed to end up with the winged lamella structure (see Figure 219) which provides numerous advantages [28].

In regard of apparel, the geometry of winged fibers provides quick and effective moisture transport for subsequent evaporation in surrounding air. This helps to increase wearer’s comfort [131]. Moreover, lamella structure increases fabric softness and leads to a nice and supple touch. Therefore it would be interesting to use winged fiber for creating artificial leather base fabric.

7.2 Coagulation

While the study at hand focused on creating and characterizing numerous nonwoven structures and their coatability for grain finished artificial leather, it would moreover be very valuable to concentrate on suede. Coagulation followed by buffing increases structural density and results in suede like surface with pleasant hand. In contrast to using the
traditional coagulation process, which incorporates hazardous solvents such as dimethyl formamide, it would be interesting to investigate more in coagulation of waterborne polyurethane systems.

7.3 Melt Blown Layer as Topcoat

Breathable fabric can also be achieved by melt blown technology in topping a nonwoven with melt-blown microfibers and subsequently thermally bond both layers at intermittent points [70]. Therefore, it would be interesting to investigate in substituting the coating process with meltblowing before finally applying further steps, such as embossing to imitate leather-like grain surface. Thereby hazardous chemicals and several coating layers plus curing processes could be eluded.
8 References


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Conshohocken, 2013.


