The Effect of Cloisite®Na+ Nanoclay Filler on the Morphology and Mechanical Properties of Loose Leather

by

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Abstract

Looseness describes a structural fault in leather, which leads to the development of wrinkles on the surface when the leather is bent inwards. It causes up to 7% of hides processed to finished leather to be downgraded or rejected at final inspection, requiring replacement and causing delay in meeting orders. Fillers can fill the interstitial spaces in loose leathers and make the looseness less pronounced. Here, the effect of Cloisite®Na+, a nanoclay filler, on loose cattle hides is investigated by electron microscopy and mechanical characterization. Whilst SEM studies show an apparent filling effect in the grain-corium boundary at increasing concentrations of filler, TEM images show that at an optimum concentration of 3% uniform dispersion of the filler along with good handle can be obtained. A gradual increase in tensile and tear strength is observed with increasing concentration of Cloisite® Na+, however softness measurements correlated with microscopic observations in that only at optimum concentrations can both good handle and mechanical strength be achieved. We discuss a possible mechanism for the change in mechanical properties and handle of the loose leather after treating with Cloisite®Na+. The mechanistic study of such treatments on low quality hides will result in the production of leathers with more uniform cutting area and added functionality.

Introduction

Looseness is a well-known quality problem in the leather industry, reputed to cause up to 7% of bovine leather produced in New Zealand to be downgraded, at a significant expense to the tanner.[1] From New Zealand hides alone, financial losses due to looseness in the finished leather are estimated to cost as much as $35 Million New Zealand per annum (23.1 Million USD). Leather is made of collagen fibers interwoven together into a network structure.[2,3] Collagen molecules consist of three intertwined protein chains that polymerize to form fibrils of varying length and thickness. In turn, collagen fibers are made of bundles of these fibrils, where tearing, stretching or squeezing leather can disrupt or break the collagen fiber network.[4-6] Looseness is a defect where the grain surface shows a wrinkly texture when it is subjected to compressive forces in the plane of the surface (Figure 1).[7,8] This is an undesirable defect that can significantly downgrade the quality and value of leather.

The main components of animal hides are fibrillar and non-fibrillar proteins (mainly collagen), natural fatty materials (triglycerides, fatty acids), glycoproteins and water. When a hide is processed into leather, the glycoproteins, non-collagenous proteins and other materials are mostly removed and the remaining fibrous proteins are subsequently chemically modified by tanning agents to make the network structure permanent. During the early process stage of liming the fiber bundles are opened up (loosened) allowing most of the non-collagenous materials to be removed.[9] The removal of these non-collagenous components creates open spaces, or voids, in the structure between fibrous layers. These open spaces, or voids, may be exacerbated or enlarged by a number of leather processing factors, such as the bacterial degradation of the raw stock,[10] excessive opening up in the beamhouse, inadequate neutralization-post tanning, poor fatliquor distribution or inappropriate fatliquor selection, excessive mechanical stressing, especially at incorrect moisture levels, and excessive drying. The water content in the hide is significantly reduced as it is converted into leather. Removal of natural fats from the fiber network can also cause the collagen fibers to stick together as the leather dries, increasing its stiffness.

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Very few studies on looseness have been conducted to date. Liu et al[11] used microscopy and mechanical characterization to investigate looseness and observed that the grain layer in loose leathers had a propensity to form sheet-like structures and had gaps between the interstitial and corium layers of the leathers. Mukhopadhyay *et al.*[12] described a non-invasive technique using planar interdigital sensor to detect looseness in pickled pelts. Various fillers and retans have been developed with the specific aim of rectifying looseness,[13-15] but to the best of our knowledge studies on their filling mechanism are yet to be reported. Layered silicate materials such as montmorillonite clays are used as inorganic fillers in polymer systems because of their ability to modify the mechanical properties of polymers at low cost.[16,17]

Cloisite®Na+ is a naturally occurring montmorillonite nanoclay with the molecular formula $[Na_{0.75}(Al_{3.25}Mg_{0.75})(Si_8O_{20})(OH)_4]$. It has gained much attention owing to its low weight ratio of filler to reinforcement properties, delivering lightweight yet resilient materials. Montmorillonite clay particles consist of stacks of 1 nm thick aluminosilicate layers (or platelets) with gaps in between them (interlayer).[18] When dispersed in water they expand (swell) and exfoliate into stacks of platelets (called tactoids).[18] Incorporation of the tactoids into a polymer matrix produces a composite structure with enhanced mechanical strength.[19] When a load is applied to the material, the stress can be transferred from the polymer matrix to the clay particles.[19] In leather making, montmorillonite clays and their composites have been used to impart characteristics such as flame retardancy,[20] fat-liquoring[21], finish,[22] and mechanical properties.[23]

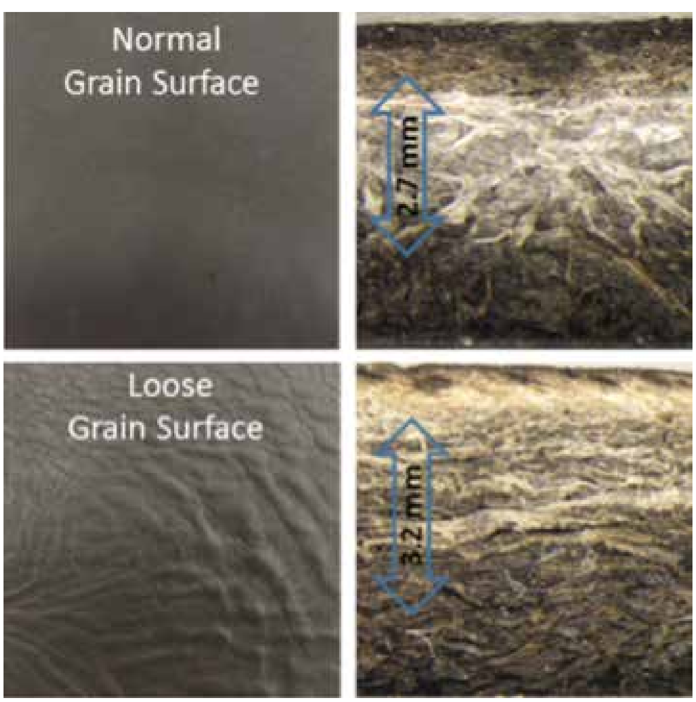

Figure 1. Photographic images of a normal and loose grain surface and their corresponding cross-sections.

Here we investigate the effect of adding a natural nanoclay filler Cloisite®Na+ to a "fatliquor" emulsion to treat loose leathers. Fatliquoring is a leather process by which natural or synthetic oils are introduced into the skins to coat individual fibers uniformly, preventing fibers from sticking to each other through lubrication and thereby imparting softness to the final leather. Additionally properties such as handle, flexibility and water resistance can also be introduced through fatliquoring. Fatliquors are mostly oil-in-water emulsions and in our study we use a commercial anionic fatliquor Densodrin CD (BASF), which is a ~50% paraffin/polysiloxane emulsion. Clays such as montmorillonite are known to aggregate with oil drops and aid their dispersion in water.[24-28] They may attach to the droplet surfaces, becoming partially immersed in the oil, and form a layer that encapsulates the drops to provide a barrier against drop coalescence.[29-31] Clay particles may also enhance drop stability to coalescence by forming three-dimensional networks in water that surround and entrap the drops.[29-31] We show that the mechanical properties of leathers treated with emulsions of oil-clay aggregates increase with clay concentration in the emulsions. This could be due to the clay particle/ oil drop aggregates penetrating into the leather and dispersing within the collagen fiber network.

Experimental Section

Materials

Cloisite®Na+ with a cationic exchange capacity (CEC) in the 80–95 mequiv/100 g range was obtained from Southern clay products (USA), stored at room temperature and used without further modification. Tanigan® PAK-N was obtained from Lanxess, Tanicor PW was obtained from Clariant, Mimosa was obtained from Tanac SA and Densodrin CD was obtained from BASF. Bovine wet blue hide was purchased from a local tannery. All other chemicals and reagents were analytical grade and used as received. The wet blue hides from the local tannery were evaluated for loose grain and those identified as having poor quality were selected for treatment with Cloisite®Na+.

Application of Cloisite®Na+ to Loose Leather

A uniform dispersion of Cloisite®Na+ in water (50g in 1L) was formed using a stirrer and then introduced after the fat liquoring stages at offers of 1% wt/wt, 3% wt/wt and 6% wt/wt to study the effect of varying concentrations on the morphology and mechanical properties of the leather. Six samples (~300g each) collected from the official sampling position (OSP) areas of two loose wet blue hides were cut out and divided into treatment and control samples and processed in Dose drums. The processed leather samples were not finished and were stored as crust in a conditioned environment, at 20°C and 65% relative humidity for 3 days prior to physical testing.

Characterization

Samples for transmission electron microscopy were fixed with osmium tetroxide and embedded in an araldite resin and then carbon coated prior to imaging. Cloisite®Na+ was imaged by preparing a dispersion in water and dropping the sample onto a carbon-coated copper grid. Low- and high-resolution TEM images were imaged and mapped using a JEOL 2100F Field Emission microscope operated at 200kV. EDX maps were recorded using a JEOL 2300 series SDD. For scanning electron microscopy studies, cross-sections from rectangular strips of leather crust were made by cutting from the grain surface to the flesh using a stainless steel blade and mounted on specimen stubs. The samples were then sputter-coated from a gold/palladium source and studied using a JEOL JSM 7000F field emission gun scanning electron microscope (Tokyo, Japan). The microscope was operated at 5.0 kV, and samples were viewed at a working distance of 15 mm.

Physical and Mechanical Characterization

Leather crust samples for physical tests were conditioned at 20±2°C and 65% relative humidity over a period of 3 days. The measurements were done parallel to the backbone and tests such as tensile strength, tear strength and elongation at break were examined as per standard ISO procedures using an Instron tensometer, model number 4467. Each test was conducted on five replicates from the six samples of the OSP region in each hide, and error bars were determined from the calculated mean and standard deviation. Leather softness was assessed using a BLC ST300 softness gauge.

Results and Discussion

Physical and Mechanical Studies of Cloisite®Na+ Treated Leather

The mechanical properties of the treated loose leathers at increasing concentrations of Cloisite®Na+ are listed in Table I. In general, an improvement in mechanical properties of the treated leathers was observed in comparison to the control loose leather. The tensile strength is the maximum load a material can withstand without breaking when being stretched to the original area of its cross-section and in leathers, is closely associated with the angle of weave, looseness and lubrication of the collagen fiber bundles.[2] Tear strength is the maximum load that a material can endure whilst being stretched.

Both tensile (25.7-32 N/mm2) and tear strength (119-129 N/mm) of the leathers increased linearly with clay particle concentration which indicates that the Cloisite®Na+ has impregnated through both grain and flesh regions of the loose leather acting as both a filler and reinforcing agent. The elongation at break further confirms this as a decrease from 60% for the control to 33% and 28% for the 3% and 6% treated Cloisite®Na+ samples was observed, respectively, suggesting that the clay particles are placed in the inter-fibrillar gaps in the leather. Softness, in leathers is a very important characteristic of its quality and can be defined as the deformation response of the material to external forces.[32] The ST300 Softness Tester produces a quantitative value which is in good agreement with the handle(feel) of the leathers and compares well with the subjective assessment of leather softness.[32,33] Softness measurements (ISO 17235) showed that the overall handle of the leathers is optimum at an offer of just 1% and then gradually decreases with increasing concentration of the nanoclay filler. While this is not marked in the 3% concentration (softness value of 22), in the case of the 6% there is a drastic decrease in softness (softness value of 15). This could be due to the nanoclay fillers flocculating in the fatliquor emulsions at high concentrations resulting in an uneven dispersion at the grain and corium surfaces, causing buildup of the filler on the surfaces of the leather as shown by microscopic characterization. Cross-sections of the Cloisite®Na+ treated loose leathers were imaged using scanning electron microscopy to study the effect of filler concentration on the overall morphology of the loose leathers.

Microscopic Observations of Cloisite®Na+ Treated Leather.

There are two structurally distinct layers in the cross-section of the loose leather control (Figure 2A). An upper layer of densely

Table I
Mechanical Properties of Cloisite®Na+ treated Loose Leather.

Loose Samples	Tensile Strength [N/mm2]	Tear Strength [N/mm]	Elongation at break [%]	Softness (ISO 17235)
Control	25.7 ±6	119.9 ±1	60 ±2	21
Cloisite® Na+ 1%	26.1 ±4	124.1 ±3	55 ±1	26
Cloisite® Na+ 3%	30.3 ±8	126.3 ±1	33 ±3	22
Cloisite® Na+ 6%	32.4 ±7	129.4 ±2	28 ±1	15

interwoven narrow (< 1 mm in diameter) collagen fibers (called the grain layer) and a lower layer of thicker bundles of fibers (corium). There is also a large zone (or junction) between the grain and the corium where the fiber structure is poorly defined. At a Cloisite®Na+ offer level of 1% wt/wt (Figure 2B) no significant change in the structure was observed. However at concentrations of 3% wt/wt and 6% wt/wt (Figures 2C and D), an obvious filling effect was observed. Although a vast improvement in the fiber structure along with an apparent filling effect was also observed, with the fiber bundles well divided in the corium compared to the control (Figure 2A) for all concentrations of nanoclay fillers, it is not sufficient to guarantee remediation of the effects of looseness. Factors such as handle, breathability and mechanical strength also need to be considered to ensure that the aesthetic properties of the leather are also maintained. To further investigate the effect of Cloisite®Na+ on the fibrous microstructure of the loose leathers transmission electron microscopy studies were undertaken.

Figure 3 is a low magnification TEM image of a loose section of a control leather displaying the grain layer, with the junction between the grain and corium showing large areas of voids and gaps ranging from a few hundred nanometres to micrometres in size. The lack of interconnect between the grain and corium layers causes the grain layer to move easily above the corium (flesh) layers, as it is no longer held firmly to the corium layer compared with normal or "tight" leathers, causing the grain surface to have a wrinkly appearance. At a concentration of 1% wt/wt the grain surface of the leather is observed to be coated with a thin layer (20-30 nm) of the nanoclay, as shown in Figure 4A.

Higher magnification images (Figure 4B) revealed that the clay particles exfoliate and orientate along the basal plane forming a continuous and smooth coating on the grain surface. However at this concentration the voids or spaces remained largely unfilled and vacant with very few areas showing penetration of the nanoclay filler. At a filler concentration of 3% the grain surface was found to be uniformly coated, with void spaces and gaps in the junction of the grain and corium layer also observed to be filled with the nanoclay fillers; most of the clay dispersed finely within the fiber network (Figure 5A). The clay particles also tended to exfoliate into smaller stacks (with high aspect ratios) that assemble around groups of fiber bundles (Figure 5B). Some of the clay particles that penetrate into the corium remain agglomerated as tactoids with sizes up to a few hundred nanometres and are able to fill void spaces in this layer (SI-3). STEM-EDS mapping images (not shown) of the 1% and 3% concentrations showed that the Cloisite®Na+ nanoclay filler was coated evenly on the grain surface for the former and filled for the latter and, composed evenly of Al and Si.

At the highest concentration of 6% of nanoclay filler, very poor penetration of the clay particles into the leather microstructure was observed. Instead the fillers appear to flocculate and stack at the grain surface of the leather (Figure 6). This could be attributed to an unstable fatliquor emulsion caused by the higher concentration of nanoclay filler,[34] which in turn leads to poor dispersion and coating of the nanoclay filler, a finding which is in agreement with the softness and handle measurements of the leather.

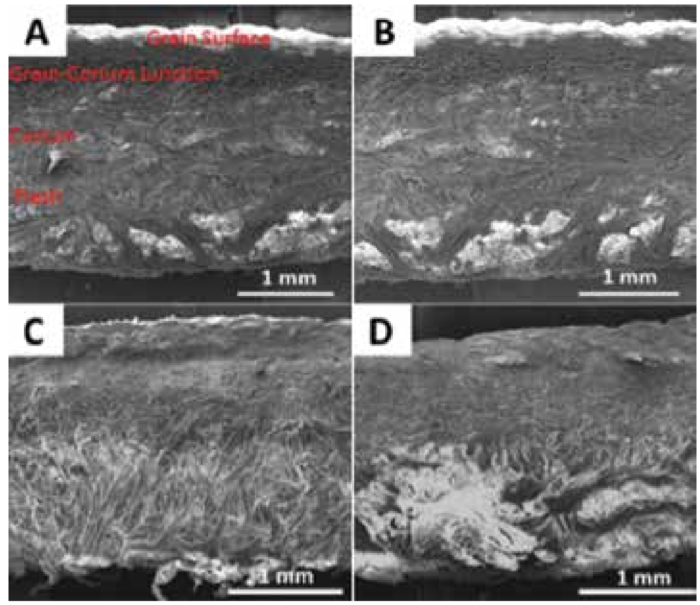

Figure 2. Cross-sectional SEM images of a loose leather control (a) and 1% (b), 3% (c) & 6% (d) Cloisite®Na+ treated loose leathers.

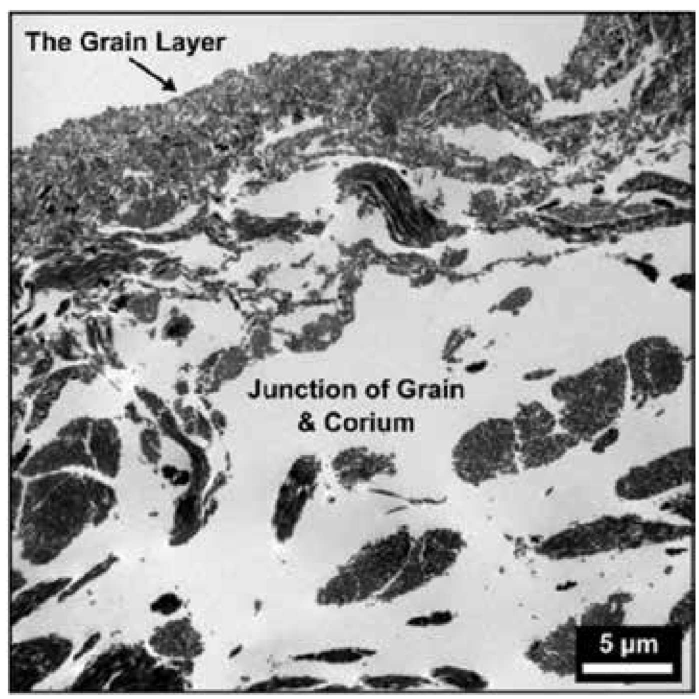

Figure 3. TEM image of a control "loose" leather showing the grain surface and void spaces at the junction of the grain and corium.

In summary, we have improved the mechanical strength of loose leather by altering the collagen fiber microstructure using oil-in-water emulsions containing clay nanoparticles. The clay nanoparticles aggregate with the oil drops in the emulsions and are transported into the collagen fiber network as the oil drops penetrate into the leather. The particles are dispersed within the collagen fiber matrix when the emulsions break and the oil drops wet and spread over the collagen fibers. The resulting fibrous network structures in the leather are characterized by the presence of clay tactoids, intercalated between bundles of collagen fibers.

Therefore, we speculate that the linear increase in the mechanical properties of the leathers with clay particle concentration indicates there are adhesive interactions between the clay tactoids and the collagen fibers. The clay particles deposited by

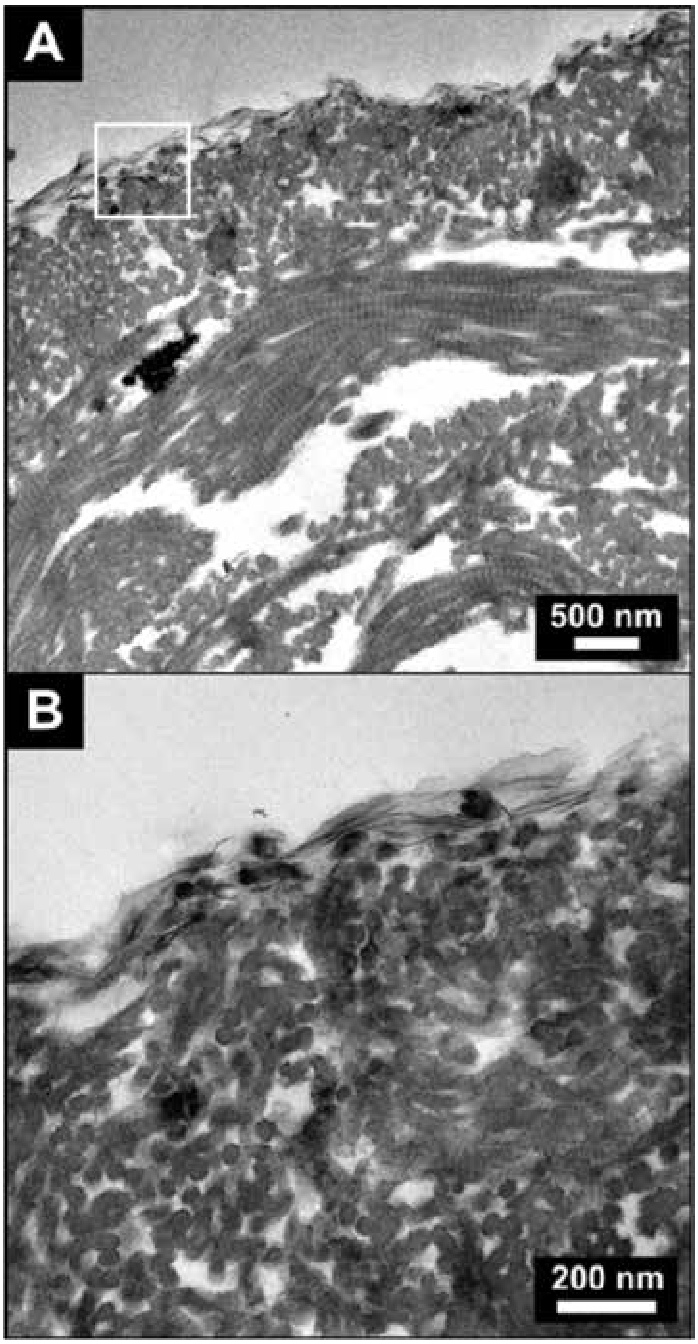

Figure 4. Low magnification TEM image of the grain surface of 1% Cloisite®Na+ treated loose leathers (B) higher magnification TEM image of rectangular section in A.

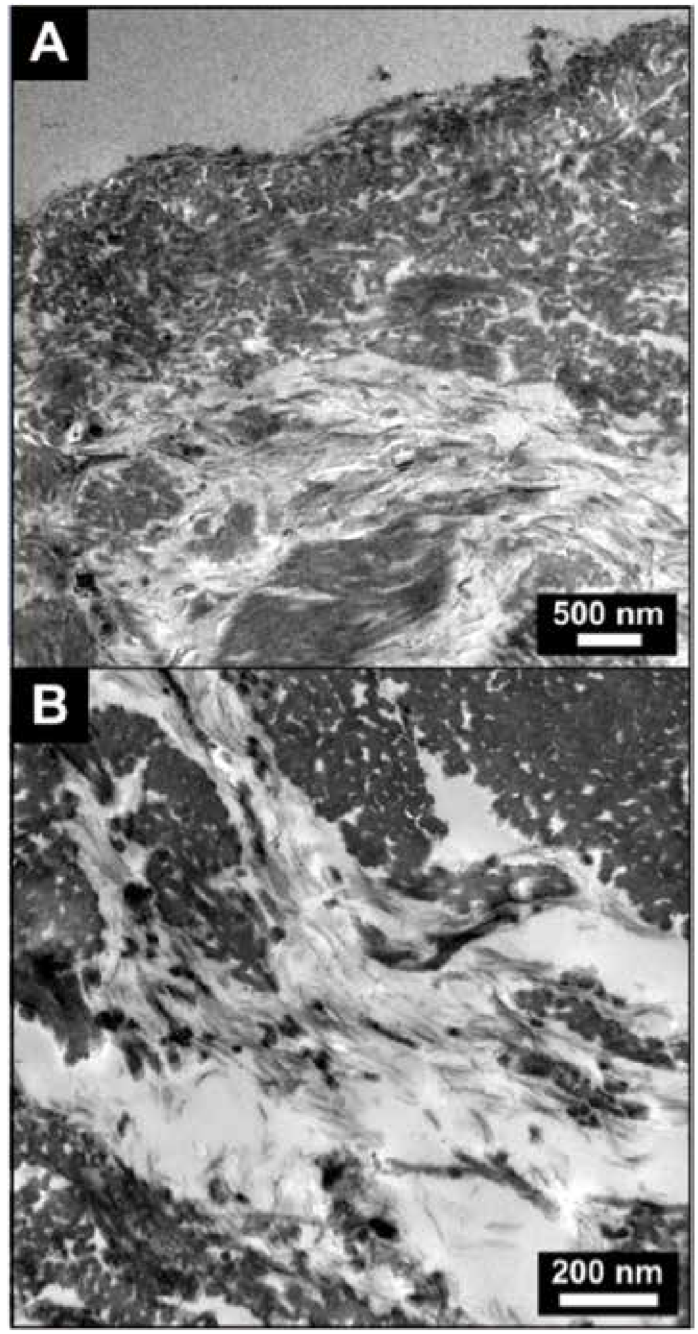

Figure 5. TEM image of the 3% Cloisite®Na+ nanoclay filler treated loose leathers showing (A) grain surface and grain-corium junction exhibiting filling, (B) areas of corium and flesh showing stacked nanoclay platelets filling void spaces.

the oil drops within the fiber network likely remain partially wetted by the oil. Adhesive interactions between the two solids would be mediated by the oil wetting both the clay particles and the fibers. Adhesion would improve the load transfer between the collagen matrix and the clay nanofillers when tensile stress is applied to the leather.

Although a vast improvement in the fiber structure along with an apparent filling effect, with the fiber bundles well divided in the corium compared to the control (Figure 5A) are observed for all concentrations of nanoclay fillers, it is not sufficient to guarantee remediation of looseness. This is due to the nanoclay fillers flocculating at high concentrations (6 wt%) at the grain and flesh surface resulting in uneven dispersion. It causes a buildup of the filler on the surfaces of the leather, as shown by microscopic characterization. This could be attributed to an unstable fatliquor emulsion caused by the high concentration of the nanoclay filler, which in turn leads to a poor dispersion and coating of the nanoclay filler and is in agreement with the softness and handle measurements of the leather.

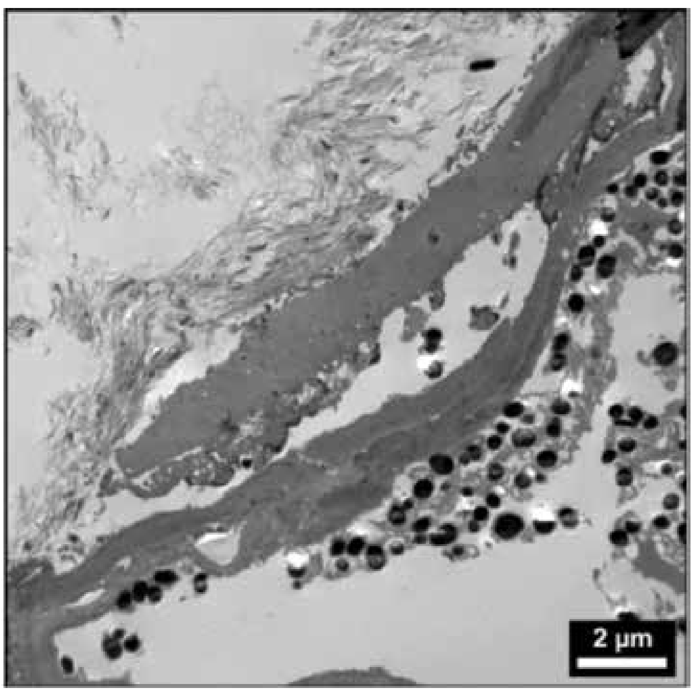

Figure 6. TEM image of grain surface at 6% Cloisite®Na+ nanoclay filler exhibiting aggregation and poor dispersion.

Conclusions

We have shown here that emulsions of oil drop-clay particle aggregates are beneficial for reinforcing the mechanical properties of loose leather. At an offer of 3% wt/wt of nanoclay filler both mechanical strength and filler properties were optimized, demonstrating that an apparent filling of the leathers alone is not sufficient to guarantee remediation of looseness with factors such as handle, breathability and mechanical strength also needed to be taken into consideration. Fillers have an important role to play in the processing of leathers and can have a beneficial effect on the overall properties of the leather, if their mechanism of filling has been properly investigated and optimized.

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