# Special Review Paper: Applications of Microwave in Leather Field: Further Research for Leather Chemists and Technologists

by
Jinwei Zhang,[1,2] Jiacheng Wu[1,2] and Wuyong Chen[1,2]*
[1]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education,*
Sichuan University, Chengdu 610065, China,
[2]*National Engineering Laboratory for Clean Technology of Leather Manufacture,*
Sichuan University, Chengdu 610065, China

## Abstract

Summarized in this article is the substantial research and technology on applications of microwave in leather industry for effectively utilizing microwave in leather making. It includes effluent disposal, pretreatment for analysis, chemicals synthesis, leather drying and wet end processing. Also, the future studies based on microwave-assisted leather manufacturing are put forward. Microwave could shorten sludge drying time, indicating the use of microwave in leather effluents disposal could give a potential method for minimizing pollution. As an efficient pretreatment method, microwave assisting digestion and extraction could be used for the leather routine and hazard materials detection without any negative effect. In leather chemicals synthesis, faster reaction rate with better products could be obtained under microwave, suggesting it could be used in the processes further. Leather drying with microwave had advantages of fast drying such as uniform water distribution and higher area yield without hardening and shrinking. Furthermore, microwave in leather dyeing and tanning could improve the color fastness and hydrothermal stability of the leather. These studies demonstrated microwave was not only an excellent heat resource but also has a special non-thermal effect in leather making, which had some positive influences on the processes and leather properties. It is necessary to study the function and mechanism of microwave in leather making and the influence of microwave on leather properties and structure, especially non-thermal effect in the processes. This will give a potential choice for innovating leather technology, improving leather performance and promoting efficient. In summary, microwave introduced in leather industry will be an important further research field for leather chemists and technologists.

## Introduction

Microwave is an electromagnetic wave with wavelength from 300MHz to 300GHz. In order to prevent interfering with radio communication, broadcast and radar system, the frequencies of microwave used in civil fields are 915MHz and 2450MHz.[1] Water and foods absorb microwave to produce heat, thus microwave oven is widely used in daily life. Microwave heats substance from inner through the energy generated by molecules friction with advantages of fast, uniform and energy saving. In addition, microwave has a significant influence on materials with high dielectric loss tangent, leading a selective heating property. Furthermore, heating will be immediately stopped when microwave switches off.[2] Therefore, microwave has been used for papers, woods, leathers, tobaccos and herbs drying as an excellent energy resource.[3-7]

Vander hoff[8] found the acrylate, acrylic acid and a-methylacrylic acid emulsion polymerization rate was accelerated by microwave in 1969. Gedye *et al.*[9] compared the differences of benzamide hydrolysis, toluene oxidation, benzoic acid methyl esterification and $SN_2$ nucleophilic substitution between microwave assisted and traditional condition in 1986, and the results indicated microwave could accelerate reaction rate obviously and the fastest rate was 1240 times higher than conventional. Now, microwave is widely used in chemistry synthesis to obtain a faster reaction rate with a higher reaction degree at a milder reaction condition.

The microwave was applied for drying in leather industry at first time in 1972.[5] Then, it was used for leather drying combined with vacuum and heat pump.[10-12] Also, it was used for drying leather coat.[13] Besides, as less reagents and samples consumption without elements volatilization, microwave was used to digest leather samples for determination of metal content, or to extract substances in leather to measure some hazard materials such as azo dyestuffs, hexavalent chromium and so on.[14-18] Furthermore, microwave was used in tanning,[19] dyeing[20] as well as leather chemicals modification and synthesis.[21, 22]

*Corresponding author, e-mail address: wuyong.chen@163.com
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The article will summarize the researches and technologies on applications of microwave in leather industry and put forward some further suggestions about microwave-assisted leather making for leather chemists and technologists.

## 1. Indirect Applications of Microwave in Leather Industry

### 1.1 Microwave-assisted Leather Effluents Treatments

There is large amount of sludge produced in leather making. It is time and energy consuming to dry the sludge which mainly contains protein and organic contaminants. It took 18 days to dry the sludge from water content 74.34% to 5.36% on natural conditions, and 7 hours to reduce the same sludge moisture to 3.31% in oven at 165°C, but only 14min was needed to decrease the sludge water content to 3.28% with 900W microwave, hence, microwave heating was a fast and energy saving method for leather sludge drying with sterilization.[23] Also, microwave could destroy the floc structure of sludge by changing water distribution and reducing the viscosity of sludge to improve the dewatering performance, for example, after 648W microwave irradiating 60s as a pretreatment and then adding cationic polyacrylamide(CPAM), the settling velocity, capillary suction time and specific resistance to filtration decreased by 25.0%, 48.9% and 34.7% respectively compared with only CPAM treatment.[24] In addition, microwave had some positive effects on effluents oxidation, reduction, photocatalytic oxidation and Fenton oxidation.[25] In short, microwave application in leather effluent treatments will give some potential methods for minimizing pollution.

### 1.2 Microwave-assisted Pretreatment for Leather Analysis and Determination

The proper pretreatments are necessary before leather analysis and determination, for instance, digestion and extraction. Microwave is more suitable for these pretreatments due to its rapid heating. A quick water content measurement for leather was assisted by microwave within 90min and the obtained data was more stable than traditional.[26] There are advantages of higher digestion rate, lower sample lost and better repeatability, therefore, microwave was used for leather digestion to determine tanning metal contents.[15] Under 20-200W microwave, chromium(III) reacted easily with chrome azurol S and the detection ranges of chromium(III) was from 0.03 to 60mg/L and 68 samples could be tested within 1h under the circumstance.[27] After microwave assisting extraction, the precision and repeatability was better for azo dyestuffs determination.[16] With microwave-assisted extraction as a pretreatment, the detection limit of azo colorants content in leather reached to 1mg/kg.[28] Besides, microwave assisted extraction was used in leather hexavalent chromium, [17] phthalates, [18] glycol ethers residual detections.[29] In brief, Microwave-assisted pretreatments will be more widely applied in leather routine and hazard materials detection due to its efficiency and accuracy.

### 1.3 Microwave-assisted Leather Chemical Synthesis

Many studies proved that microwave could promote a chemical reaction, quicken the reaction rate and decrease reaction active energy.[9, 30, 31] Wang *et al.*[21, 32, 33] used microwave as a heat resource in valonia tannin sulphonation and crosslinking processes, showing there were more obvious effects with 7min microwave than 150min traditional heating, in addition, the leather tanned by the modified product had smoother grain, better elasticity and 3°C higher shrinkage temperature. Also, the molecular weight distribution of the modified tannin was narrow down (Fig.1B) compared with conventional heating(Fig.1A). Sulphonation is an essential reaction in vegetable extract production to improve solubility and permeability, however, the process is subjected to high temperature.[34] If microwave was used in the process, the reaction efficiency as well as product properties might be improved.

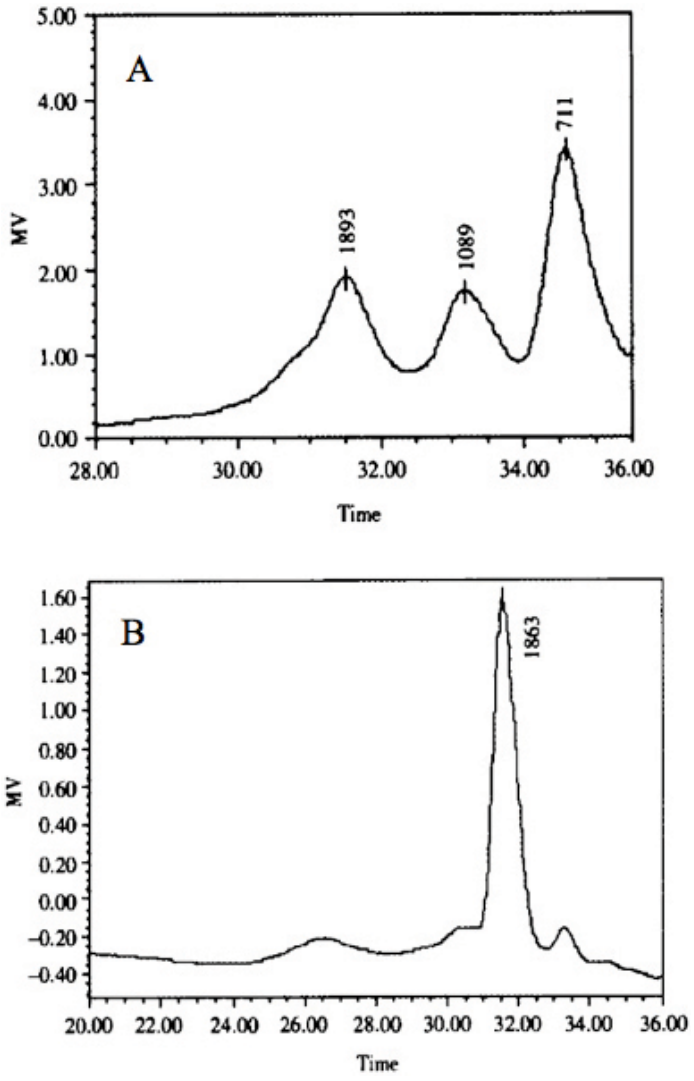


Figure 1. molecular weight distribution of modified volania extract by GPC (A: conventional heating; B: microwave heating)[21]

Under microwave, an organic silicon leather smoothing agent was synthesized by ring opening polymerization of octamethylcyclotetrasiloxane, the reaction time was shortened and the product was more stable.[22] There are many polymers used in leather making, like polyacrylic and polyurethane as retanning or finishing agents, however the studies on microwave-assisted in the polymer synthesizing for leather have not been reported. As microwave could promote polymerization reactions as well as product properties, [8,35,36] as an efficient method, microwave might be used in the synthesis of leather chemicals such as synthetic tannins and resins in the future.

**2. Applications of Microwave in Leather Drying**

Since microwave heating is a fast, even and energy saving process without temperature gradient in materials, it is widely used in leather drying. Water content in the microwave dried leather was more uniform, therefore the leather was much softer and flatter. what's more, the process was more rapid without damage of the leather structure.[5,10] When microwave coupled with vacuum of 724mm Hg, the drying rate was much fast, and the area yield, handle and mechanical properties of the leather could match with the control.[11] Also, microwave-assisted with vacuum was used for drying the delimed pelt to decrease water content to about 33%, this method could improve splitting precision and reduce chromium waste without any negative influence on grain leather.[37] Furthermore, microwave-assisted heat pump was compared with only heat pump for drying the chrome and vegetable tanned leather, the results indicated that the drying rate of the microwave-assisted was much rapider and the properties of the leathers were comparable.[12]

Microwave was also used to dry leather coating, resulting in smoother surface as well as better cold tolerance and leather mechanical properties.[13] In order to illustrate the reason that microwave had better performances in the coat drying, the films of polyacrylic, polyurethane and casein were dried under microwave, the results showed the microwave dried could result in a lower glass transition temperature of film with less bubbles.[38]

Because microwave in leather drying has some notable merits, it is necessary to study energy and substance transfer or dynamic in the process in order to provide a theoretical foundation. An exponential model was built to analyze a relationship between the microwave power and the drying time, rate as well as leather moisture, a simple way was made to predict dry process through a mathematic model rather than empiricism.[39] Based on the results of chrome leather dried with different microwave powers and air velocities, a dynamic model was established through measuring temperature, drying rate and heat flow to descript the drying mechanism. In the experiment, it only took 5min to dry leather while traditional convection needed more than 55min, moreover, the structure of leather was not damaged in such fast drying.[40] Heat flux in the leather microwave and convention drying was measured, the results illustrated the net heat flux in the convection drying was always zero, however, the leather under microwave had higher temperature than its surroundings at the beginning and middle of drying (Fig. 2), indicating the leather in the process absorbed electromagnetic energy and transferred to heat rather than absorbing heat from environment. The research had explained the reasons why microwave drying was fast and effective. [41]

There were three stages in microwave drying: the heating-up, the constant drying rate, and the falling drying rate. At the end of drying, the moisture of leather decreased and the drying rate slowed down obviously, so the hardening and shrinking of leather did not appear in the process.[42] A model based on water content and dielectric constant was used to analyze this process, the drying rate slowing down with moisture decreasing was considered to be responsible for uniform water distribution and soft handle.[43] In order to study heat transfer in microwave drying, a model for laminar materials drying was established to interpret the relationships among the dynamics, rate and temperature in the process. The results showed that the heat generated by microwave was strongly concerned with the moisture in the materials, the higher water content in leather was, the greater

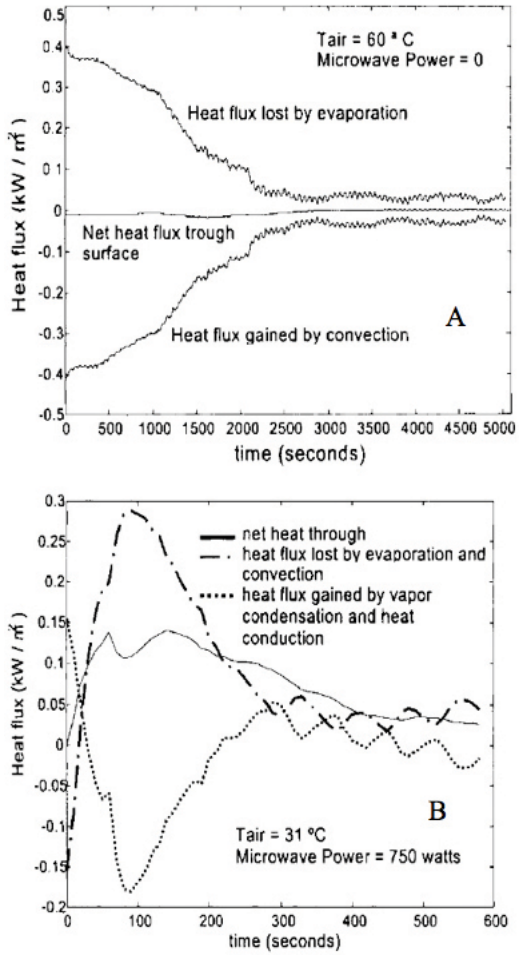


Figure 2. Heat fluxes through the surface during drying process. (A: convective drying, B: microwave drying) [41]

microwave energy was absorbed (Fig.3).[44] Besides, microwave had very high energy utilization ratio and its heat efficiency was higher than 85% according to enthalpy calculation.[45]

Many models had been established to explain leather microwave drying in static and dynamic, and the better understands were achieved for the process, however, there were some special effects in leather drying, which could not be illustrated just with a thermal effect of microwave, such as vegetable tannin, did not migrate to the surface of leather,[11] the leather with different fatliquoring content had different drying rate,[46] there was more uniform fat distribution in the leather.[47] These facts were the signs that microwave could not only increase system temperature but also have some extra effect on leather properties. This effect may be called a non-thermal effect.

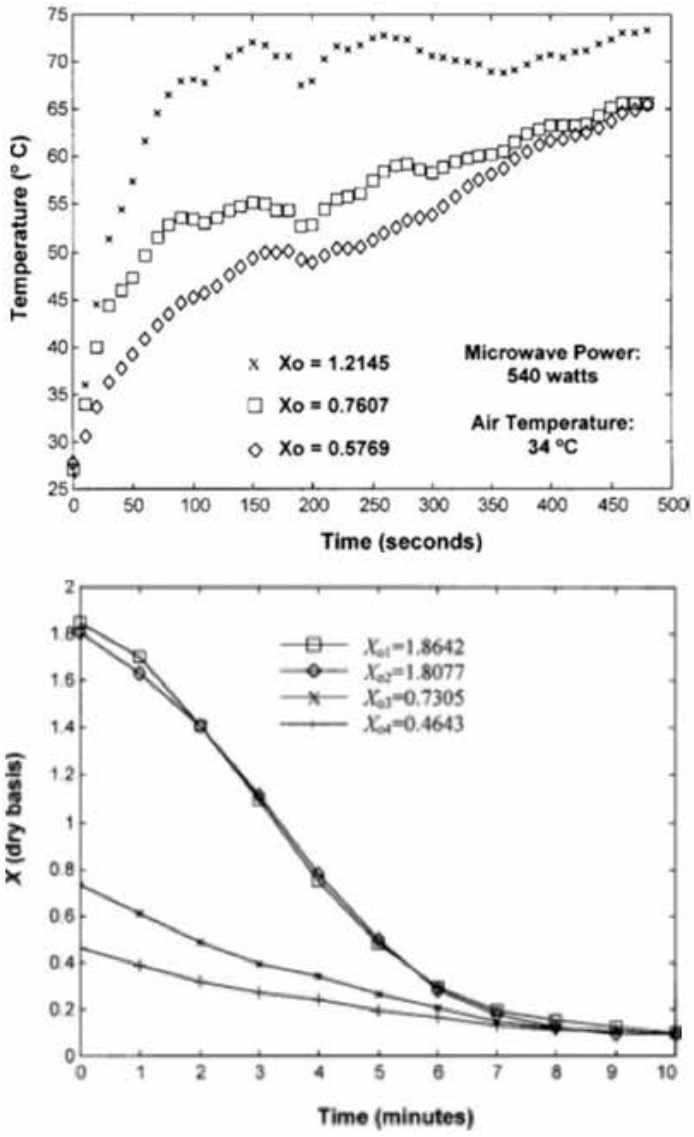


Figure 3. Temperature evolution at the center of leather samples (left) and drying curves (right) in the microwave applicator for different moisture contents. $X_0$(initial moisture content of dry basis) [44]

Present studies are mainly involving in the rate and dynamics in microwave drying, but more and more proofs have demonstrated microwave could affect leather components, structures and properties through the non-thermal effect. Thus, it is urgent to study the non-thermal effect in microwave drying and to elaborate the special effects on leather properties.

**3. Applications of Microwave in Wet End**

There are some arguments on whether microwave has non-thermal effect, but more and more evidences have testified the non-thermal in microwave-assisted reactions. Although microwave and traditional heating could accelerate a chemical reaction rate, the more promoting effects was only observed in the situation under microwave. Furthermore, the lower activation energy and different dynamic also took place in microwave-assisted chemistry. [48,49] Dipole moment in a system is usually zero, but induced dipole of polar molecules and instantaneous dipole of nonpolar molecule caused by microwave would result in a quite different phenomenon that dipole moment in a system is no longer zero. It is a unique phenomenon under microwave.

Usually, the energy of light quantum of microwave in civil filed is only $10^{-5}$eV. The ionic and covalent bond energy are about 5 to 7eV, even a hydrogen bond energy is 0.04-0.44eV, so, microwave could not break any chemical bond from views of energy aspect.[50] However, microwave could change a reaction process through other way. Shirzad *et al.*[51] found that microwave photons might excite some vibrational models whose frequencies were close to the microwave frequency of 2.45 GHz in $SN_2$ reaction. Generally, it could image that microwave would impact a reaction through extra interaction between molecules like increasing effective collision possibility, changing collision direction and generating additional oscillation for contributing to a chemical reaction.

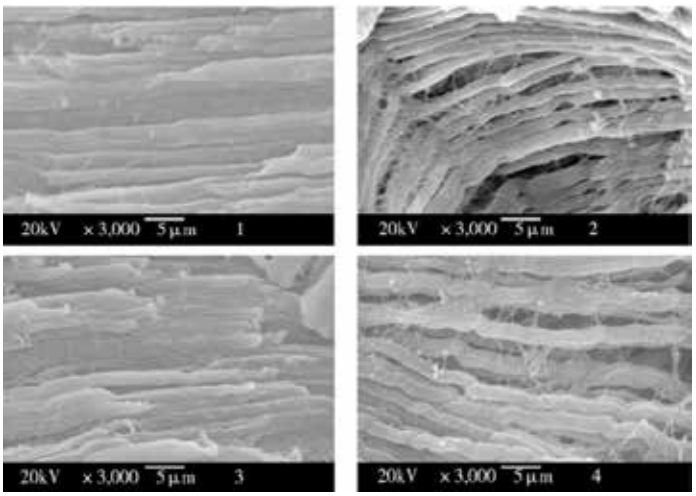


Figure 4. SEM images of wet blue tanned with microwave and without microwave (1 and 3 was without microwave at pH 3.0 and 3.6; 2 and 4 was with microwave at pH 3.0 and 3.6) [19]

Leather making is a series of complicated heterogeneous chemical processes, in which skins or hides and leathers absorb chemicals from floats and react with the substances inner themselves. Usually, these processes are carried out with temperature, so microwave could be used for heating in the processes, in which the non-thermal effect of microwave might take place and benefit the processes.

Tanning is the most important process in leather making, by which hides or skins are changed into leathers. Several researches focused on collagen crosslink with microwave. Ruijgrok *et al.*[52] found non-thermal effect did not exist in the experiment that collagen reacted with glutaraldehyde below 20°C under microwave. But the other studies found there had a better cross-linkage between collagen and glutaraldehyde at higher temperature under microwave, and the shrinkage temperature reached to 72.0-85.1°C after reacted at 50°C for 1-5min.[53] This might be due to the non-thermal effect has a relationship with microwave power. At lower temperature, microwave power is too weak to cause the effect. This might be a reason why there was controversy on the non-thermal effect in a similar reaction. Some studies also proved the non-thermal effect in collagen crosslink at higher temperature. When collagen reacted with 0.65% glutaraldehyde under microwave, it only took 1min at 60°C and 5min at 50°C to reach the highest shrinkage temperature respectively, indicating microwave could improve the reaction obviously.[54] Microwave could heat a tanning system rapidly, for example, ten layers collagen sheets were stacked up and reacted with glutaraldehyde solution under microwave, the system temperature could reach to 45°C within 3min, in addition, the shrinkage temperature on the surface sheet increased by 20°C and in the center increased by 10°C. [55]

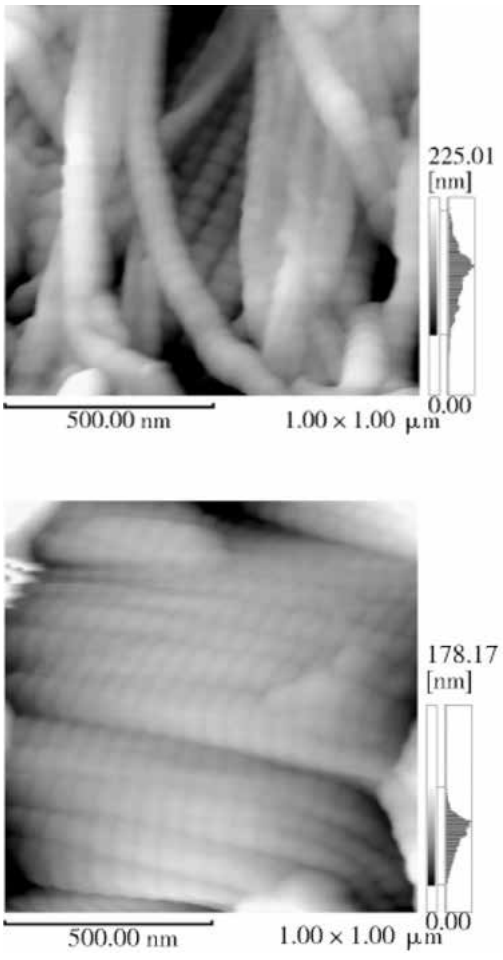


Figure 5. AFM images of wet blue tanned at pH 3.6. (a without microwave, b with microwave)[19]

In practical, as leather has some thickness with a weaving collagen matrix, sufficient time is essential for chemicals to penetrate into the leather. In the processes, collagen is sensitive to temperature, if the temperature is higher than its shrinkage temperature, the leather will be damaged. According to prior studies, microwave had an extra influence on collagen triple helix structure, which could decrease the denature temperature and enthalpy proved by ultra-sensitive differential scanning calorimetry and circular dichroism.[56] As consequence, if microwave is used in leather making, the system temperature should be 30°C lower than the shrinkage temperature of the leather and hide, or used for the tanned leather in post tanning to prevent them damaged by microwave.

In a chrome tanning with microwave-assisted, the shrinkage temperature and the tear strength of leather were 2.5°C higher and 7.5N/mm larger than the control, moreover, the collagen weaving and micro-structure was not damaged (Fig.4 and Fig.5). [19] When microwave was used to heat the dyed crust to 60°C with 65% moisture, it could strengthen combinations between dyestuff and leather to improve color rub fastness compared with the control,[20] showing microwave could make a stable combination between collagen and chemicals like tanning agents and dyestuffs.

So far, there is few report on microwave used in wet end. But it might also infer that microwave could promote the interactions between collagen and chemicals based on the present studies, therefore, it would be a great potential for applying microwave in wet end with positive effects.

**4. Expectation of Applying Microwave in Leather Making**

There are two effects in microwave acting on substance, thermal and non-thermal. Thermal effect comes from medium absorbing microwave to convert into heat. Non-thermal effect refers to phenomena of a system responding for substance absorbing microwave energy, which can not owe to the temperature changing. It is generally accepted that microwave could accelerate reaction rate, reduce active energy and change dynamics, hence, there is non-thermal effect in some reactions under microwave.[1, 48-50] Also, more and more studies had testified the effect existing in leather making. For example, microwave

could improve the mechanical properties and cold tolerance of coating, [13,38] increase the hydrothermal stability of leather, [19, 54, 55] uniform fat distribution in leather and strengthen combinations between collagen and chemicals.[46, 47]

Microwave could accelerate the coordination rate of chromium(III) with EDTA, only 3min was enough for finishing the reaction.[57] It could also speed up the hydrolysis rate of chromium sulphate and chromium nitrate, and impact on their olation.[58, 59] If microwave was used in metallic tanning such as chromium, aluminum and titanium, it could accelerate the hydrolysis and olation of the tanning liquor to improve the tanning process and the tanned leather performance. Hence, it will be a new research field to study metallic tanning agent hydrolysis and olation as well as the combination between collagen and tanning agent under microwave, which might contribute to improving leather properties and innovating tanning process.

As microwave could decrease particle size of fatliquor and increase dielectric constant (Fig. 6), [47] it could be used in fatliquoring not only as a heating resource but also for improving fat penetration, resulting in fat uniformity in leather. Also, microwave has some additional effects on colloid properties of tannin solution, [60] thus, if the effect of microwave on colloid is studied in detail, it might be benefit to the process where colloid materials like dyestuff and tannin are applied.

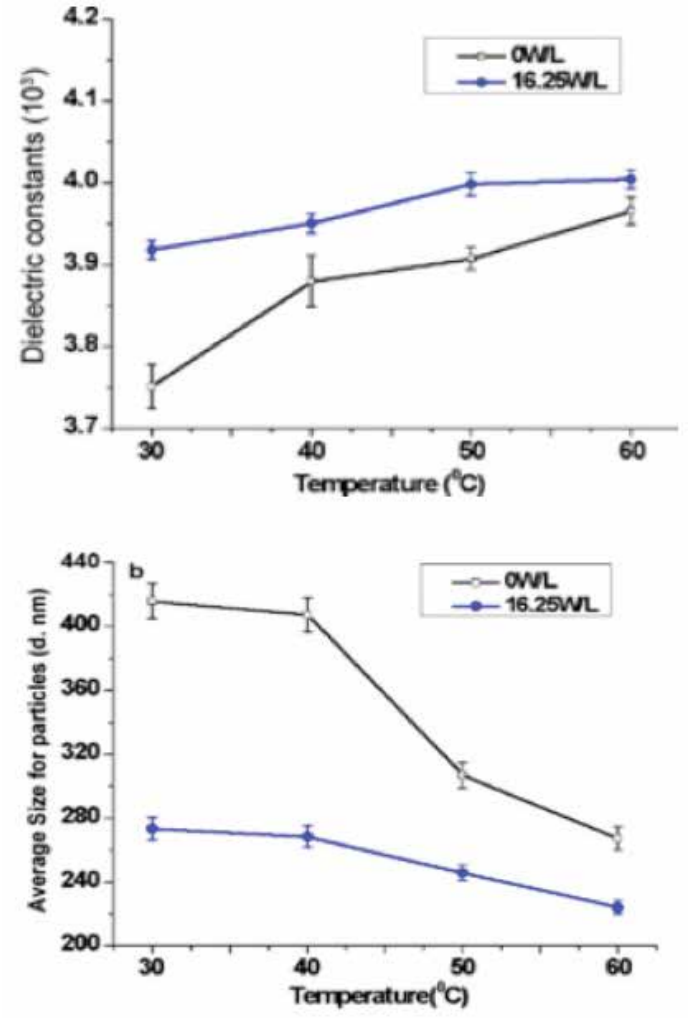


Figure 6. the influence of microwave on fatliquoring agent dielectric constant and particle size[47]

Usually, the polymer tanning and retanning agents, like polyacrylic and polyurethane, are prepared by monomer polymerization in a chemical factory. As microwave could reduce reaction active energy and accelerate rate, under microwave, these materials might be synthesized at a lower temperature, even lower than the shrinkage temperature of leather without obviously negative effect on polymers and collagen properties. In this way, in-situ polymerization might be used in the tanning process assisted by microwave to take the advantages of fast and uniform penetration of monomer. Also, during the process, monomer polymerization together with collagen crosslinking could be carried out for improving tanning effects and leather performances. This might be an innovation way for leather making.

**5. Summary**

Microwave is an excellent heating resource with advantages of rapidity, uniformity and energy savings. Therefore, it has been applied in leather drying, chemical syntheses and modification, effluent and sludge treatment as well as pre-treating for leather processing and hazard materials analysis, which are all subjected to certain temperatures. However, more and more studies prove microwave could accelerate reaction rate, promote reaction degree and change reaction kinetic, suggesting the existence of non-thermal effect in a chemical reaction. Also, the non-thermal effect of microwave could exist in the drying, tanning and fatliquoring in leather making, and have a positive effect on the processes and subsequent leather properties. As a consequence, it is necessary to study the function and mechanism of microwave in leather making and the influence of microwave on leather properties and structure, especially the non-thermal effect of microwave processes, to give a potential choice for innovating leather technology, improving leather performance, reducing pollution and promoting efficient. For these reasons, leather chemists and engineers should direct more research to microwave in present day leather making, while on the other hand, microwave-assisted leather making offers a new and promising research field of future research.

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Few people realize that Leather Making is the world's oldest manufacturing process, thus the world's oldest industry. Tanning—the process of converting hides and skins into leather—is also the world's first science. Also, because of the pure craftsmanship involved, tanning may well be the world's first art form.

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Anyone who doubts that a sheepskin has up to 30,000 fibers per square inch has only to count them.

NOTHING TAKES THE PLACE OF LEATHER

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