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Preparation of castor oil-based fatliquoring agent via a Pickering emulsion method for use in leather coating

Azam Sardari, Ali Asghar Sabbagh Alvani, Seyed Reza Ghaffarian

Abstract A castor oil-based fatliquoring agent for use in leather coating was prepared via Pickering emulsions stabilized by metal–organic frameworks (MOFs). The partially oxidized ZIF-8 (POZIF-8) nanoparticles were used as MOF in the presence of a castor oil-based dispersant. The results of the stability test showed that the presence of POZIF-8 nanoparticles leads to a stable oil/water emulsion with higher oil content than other nanoparticles, such as TiO_2 and ZnO. The stabilized structure of the prepared fatliquoring agent was characterized by transmission electron microscopy (TEM). TEM image indicated that the castor oil either was surrounded or was encapsulated by MOF. The prepared fatliquoring agent was applied to the leather. Then, in order to prove the existence of POZIF-8 nanoparticles in collagen fibers, the cross section of the fatliquored leather was examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). These analyses revealed the good dispersion of POZIF-8 nanoparticles from grain to flesh side. The physical and mechanical properties of the fatliquored leather were compared with those of the control leather sample, which was fatliquored by a conventional agent. The results show that the prepared fatliquoring agent significantly improved mechanical properties, lightfastness, softness, and fullness of leather.

Keywords Fatliquoring agent, Leather, Castor oil, Pickering emulsion

Introduction

Leather processing involves many chemical reactions and mechanical processes.[1] In order to get excellent leather, one of the most important processes is the fatliquoring process. In this process, a proper crude oil is introduced into leather tissue to lubricate the collagen fibers.[2,3] In addition to lubricating the collagen fibers, fatliquoring agent is generally beneficial for the quality of leather, especially for softness and flexibility.[4] The bonding strength between collagen fibers and fatliquoring agent plays an important role in preventing the collagen fibers from migrating outside and also in aging properties of leather.[2] Natural animal fats and vegetable oils are the most frequently used raw materials for fatliquoring agents, which are emulsified in water after chemical modifications. These traditional fatliquoring agents, due to reactive sites (double bonds), are susceptible to hydrolysis and oxidation under UV irradiation and, thereby, lead to a degradation of leather.[5] Nano-emulsions[6] and amphiphilic acrylate copolymers[7] are among the alternatives to traditional fatliquoring agents, but they contain a lot of harmful chemicals that have a negative effect on the environment. In fact, the need to protect the environment has imposed restrictions on the use of additional quantities of chemicals.[8] Therefore, scientists are interested in designing and developing alternative, sustainable, environmentally friendly materials.[9] They attempted to utilize fatliquoring agents with the fewest chemical compositions to reduce negative impacts on the final product properties and the environment.

A. Sardari, A. A. Sabbagh Alvani (✉),
S. R. Ghaffarian,
Color and Polymer Research Center (CPRC), Amirkabir University of Technology, Tehran 158754413, Iran
e-mail: sabbagh_alvani@aut.ac.ir

A. Sardari, A. A. Sabbagh Alvani, S. R. Ghaffarian,
Department of Polymer Engineering and Color Technology, Amirkabir University of Technology,
Tehran 158754413, Iran

A. A. Sabbagh Alvani,
Advanced Materials Group, Iranian Color Society (ICS),
Tehran 1591637144, Iran

One of the proposed alternatives is Pickering emulsion that replaced conventional emulsion. In conventional emulsion process, stabilization is done by surfactants and co-surfactants at the oil/water interface, while in Pickering emulsion process, stabilization is done by inorganic nanoparticles, such as nano-TiO_2,[10,11] ZnO,[12] and colloidal silica.[13,14] These nanoparticles are located at, or very near, the oil/water interface.[15,16] The first time Pickering emulsion was investigated was by Dr. Ramsden in 1903, followed by Pickering in 1907.[17,18]

In comparison with conventional emulsion, Pickering emulsions have two unique properties: a greater ability to disperse high volume fractions of discontinuous phase and higher stability against coalescence.[19] As the unsaturated bond of leather chemicals and collagen strands can be damaged under light and heat circumstances, introducing nanoparticles during the fatliquoring process can enhance the UV resistance of the leather.

According to Pickering emulsion concepts, metal–organic frameworks (MOFs) can also be used as alternatives for stabilizing nanoparticles. MOFs compounds are composed of hydrophilic metal ions or hydrophilic clusters as connectors and hydrophobic organic ligands as linkers. These surface-active materials can emulsify liquid droplets to form Pickering emulsions. They are the newest type of solid porous composite compounds, discovered in 1989 by Robson.[20,21] They have successfully found use in many fields ranging from applications such as gas storage, separation, the adsorptive removal of hazardous materials, catalysis, or drug delivery.[22,23]

Zeolitic imidazolate frameworks (ZIFs) based on transition metals and imidazolate linkers are a subclass of MOFs that are topologically isomorphic with zeolites (3D crystalline, hydrated alkaline, or alkaline-earth aluminosilicates).[24,25] ZIFs exhibit interesting properties relevant to low density, high porosity, high surface area, shell permeability, chemical and physical stability, and so on. Recently, ZIF-8 has received great attention due to its potential long-term stability in methanol and water as well as ultraviolet absorption and reflection properties. The hydrophobic pore of ZIFs repels water molecules, hence eliminating the chance of hydrolysis by water. This hydrophobic character is very beneficial in terms of applications to have good adsorption affinities with lipophilic materials.[26]

Vegetable oils have been widely used in various industries, because of their advantages such as being inexpensive, readily available, and a renewable resource. Among the vegetable oils for the production of fatliquoring agents, castor oil is one of the most important candidates, because of its unique structure. Castor oil is a viscose, pale yellow, nonvolatile, and nondrying oil, and it has 90% ricinoleic acid. This acid has 18 carbon atoms, a hydroxyl group on the 12th carbon, and a double bond between the 9th and 10th carbons. The presence of hydroxyl groups and the carbon–carbon double bonds make it valuable for many chemical reactions and modifications. In addition, its chain is long enough to act as a fatliquoring agent. In the present work, a fatliquoring agent was prepared by a mechanical combination of the partially oxidized ZIF-8 (POZIF-8) and castor oil-in-water media in the presence of anionic carboxylated-castor oil. POZIF-8 nanoparticles are capable of forming an oil-in-water emulsion system. It was applied to the leather and its properties, such as mechanical properties, lightfastness, and softness, were compared with those of the leather coated by a conventional fatliquoring agent. The prepared fatliquoring agent has a lot of castor oil. However, it has high stability and makes less extracted fat and higher mechanical properties in the leather than the control sample.

Experimental

Materials

Castor oil (industrial grade: density @ 20°C=0.951 gr/cm^3, viscosity @ 20°C=970–1100 cP, iodine value= 86.3 g iodine/100 g oil) was purchased from Shanghai Aladdin Industrial Co., Ltd. (Shanghai, China). Zinc nitrate hexahydrate, 2-methyl imidazolium, silver nitrate, and methanol were all provided from Sigma-Aldrich. Stannic chloride ($SnCl_4$), γ-alumina, and hydrogen peroxide were provided from Shin-Etsu Chemical Co. (Tokyo, Japan).

Preparation of metal–organic framework ZIF-8

ZIF-8 was synthesized using the same procedure described in detail elsewhere.[27] In brief, zinc nitrate hexahydrate 5.87 g (0.0197 mol), and 2-methylimidazole 12.98 g (0.158 mol) were separately dissolved in 40 ml of methanol. After that, the ligand solution was added into the metal solution and the mixture was stirred vigorously at room temperature for 120 min, resulting in a milky solution. The reaction product was then centrifuged and was washed several times with ethanol to remove excess reactants. Then, ZIF-8 nanoparticles were dispersed into 60 ml ethanol solution containing 35 mM silver nitrate to be partially oxidized into zinc oxide. Finally, the product was dried in an oven at 60°C for 12 h to obtain the white crystalline product of POZIF-8.

Preparation of castor oil-based dispersant

Castor oil-based dispersant was prepared as previously described.[28] In brief, castor oil was first epoxidized using γ-alumina as catalyst and hydrogen peroxide as the oxidant. The ring-opening polymerization of epoxidized castor oil was carried out using stannic chloride ($SnCl_4$) as catalyst at room temperature. Hydrolysis of the product was performed using NaOH solution at 100°C for 12 h under condensing conditions. The average molecular weight of carboxylated-castor oil was obtained at about 2500 g/mol. The carboxylated-castor oil molecules can share the carboxylate anion groups as an anchor in ZIF-8 nanoparticles, thereby establishing and protecting them against hydrolysis.

Preparation of fatliquoring agent

For comparing the efficiency of POZIF-8 with conventional nanoparticles, such as ZnO and TiO_2 to form a stable castor oil-in-water emulsion, several Pickering emulsions were prepared under the same experimental conditions. Different amounts of castor oil (10, 30, 50, and 60 g), 5 g carboxylated-castor oil, and 1.5 g nanoparticle (separately, POZIF-8 or nano-TiO_2 or nano-ZnO) were mechanically dispersed into distilled water at room temperature and 600 rpm for 2 h. The emulsions were further homogenized by the application of the ultrasonic frequency for 40 min. The Pickering emulsion consisting of 1.5 g POZIF-8 and 50 g castor oil was named POZIF-8-Fat50, and after fatliquoring process of leather was characterized.

Process of leather fatliquoring

To explore the applicability of POZIF-8-Fat50 (consisting of 50 g castor oil) upon leather, fatliquoring was accomplished. Chrome-tanned cow leather was taken for the experiment and cut into 12 cm × 15 cm samples. Sulfated castor oil is considered as conventional fatliquoring for the comparison of the leather properties. The thickness of leather specimens was about 1.2 mm. The leather was fatliquored by either conventional or POZIF-8-Fat50 fatliquoring agent in multisteps. At first, the leather was wetted back in 100 wt% H_2O and 1 wt% rewetting agent for 1 h at 25°C, and then washed with 100 wt% H_2O. After, the leather was fatliquored with 15 wt% fatliquoring agent and 100 wt% H_2O for 1.5 h at 50°C. It should be noted that all weights are based on the weight of the chrome-tanned cow leather. Finally, the leather was air-dried and softened by dry drumming. The finished leather was characterized by the various physical, chemical, and mechanical analyses.

Characterization

The surface morphology and microstructure of POZIF-8 nanoparticles were characterized by (SEM, ZEISS Gemini), and the fatliquored leather was examined by SEM–EDS. The crystallinity of POZIF-8 was evaluated using Philips, model X-pert X-ray diffractometer operating at 40 kV, using Cu as the radiation source. The scans were obtained using a scan step size of 0.03 with a scan step time of 0.25 s. The adsorption isotherm of POZIF-8 nanoparticles was measured at the boiling temperature and saturation pressure of nitrogen; then, the specific surface area was obtained using the Brunauer–Emmett–Teller (BET method, Quantachrome ChemBET 3000). The zeta potential of POZIF-8-Fat50 was measured using Nano ZS ZEN 3600, Malvern particle analyzer. The internal structure of POZIF-8-Fat50 was investigated using (TEM, JEOL 1200EX).

Fat content in fatliquored leather was extracted in a Soxhlet apparatus for approximately 3 h using ethanol as solvent, according to the SLTC Official Method (SLC4, SLTC 1996). The fat extracted percentage from leather is expressed by the following equation:

$$\text{Fat extracted} = \left(1 - \frac{M_\mathrm{f}}{M_\mathrm{i}}\right) \times 100 \tag{1}$$

where M_i and M_f are weights of the leather samples before and after extraction, respectively.

The specimen in dumbbell shape (1 cm × 15 cm) according to ISO 3376 type was strained at a crosshead speed of (100 ± 10) mm/min using Shimadzu Universal Tensile Testing Machine for measuring tensile strength (N/mm^2) and elongation at break (%). Tensile strength is maximum load to rupture of the leather cross-sectional area. Elongation is the percentage increase in length of leather under tension. Tear strength (N/mm) measurement, the load required to tear the cross-sectional thickness of the leather, was also carried out according to ISO 3377. The reported results of mechanical properties were an average value of three measurements. The lightfastness of fatliquored leathers was tested according to the standard procedure of ISO 105-B02 and was ranked from 1–5 points with higher points given for better performance. Measurement of leather softness was carried out according to ISO 17235 using the ST300 leather softness tester. The higher value of softness indicates better performance of leather. The fullness parameter, the ratio of the thickness difference of the leather before and after fatliquoring ($T_\mathrm{a} - T_\mathrm{b}$) to the thickness of the leather before fatliquoring (T_b), was calculated using the following equation:

$$\text{Fullness} = \left(\frac{T_\mathrm{a} - T_\mathrm{b}}{T_\mathrm{b}}\right) \times 100 \tag{2}$$

The thickness of leather samples was measured using a vernier caliper.

Results and discussion

SEM observation of POZIF-8 nanoparticles

Figure 1 shows the scanning electron microscopy (SEM) image of POZIF-8 nanoparticles. The morphology of crystals is mainly tetragonal, and particle size is about 300 nm. When ZIF-8 is partially oxidized to ZnO, the morphology of crystals changed in comparison with the reported pure ZIF-8 in open literature.[29,30] In fact, the shape of cube of ZIF-8 was extended in POZIF-8 nanoparticles, changed from cubic to tetragonal morphology.

XRD Pattern of POZIF-8 nanoparticles

The XRD pattern of POZIF-8 is shown in Fig. 2. It is observed that POZIF-8 is composed of ZIF-8 with characteristic peaks (101), (002), (112), (200), (013), and (222) at the Bragg angles of around 7.38, 10.42, 12.77, 14.75, 16.50, and 18.08, respectively,[30,31] and ZnO with characteristic peaks (100), (002) and (101) at about 31.77, 34.42, and 36.25, respectively.[32]

Sorption isotherms of POZIF-8 nanoparticles

The adsorption isotherms are the relationship between porous structure and sorption type. According to IUPAC classification, there are six representative adsorption isotherms that determine pore type.[33] The BET method is a common method for determining surface areas from adsorption isotherms. Figure 3a shows the nitrogen sorption isotherm of POZIF-8, which belongs to type-I adsorption isotherm and represents microporous structure. The BET surface area and microporous volume of POZIF-8 were obtained at about 1250 m^2/g and 0.7 cm^3/g, respectively. Additionally, as shown in Fig. 3b, distribution of pores width is between 7 Å and 14 Å. Pores are classified according to their size, and pores with size (5–20) Å are termed as micropore.[33]

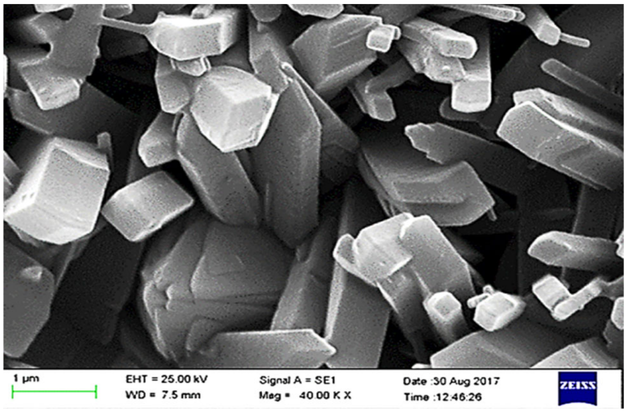


Fig. 1: SEM image of POZIF-8

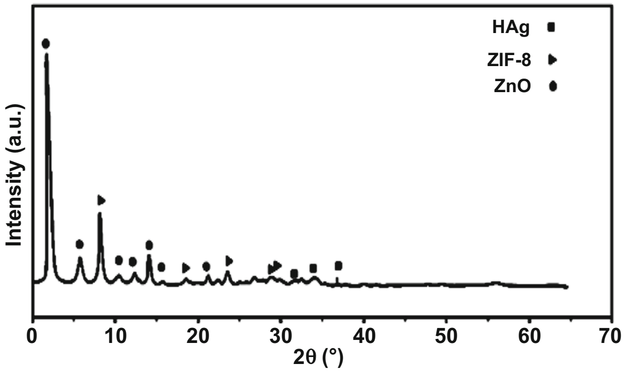


Fig. 2: XRD pattern of POZIF-8

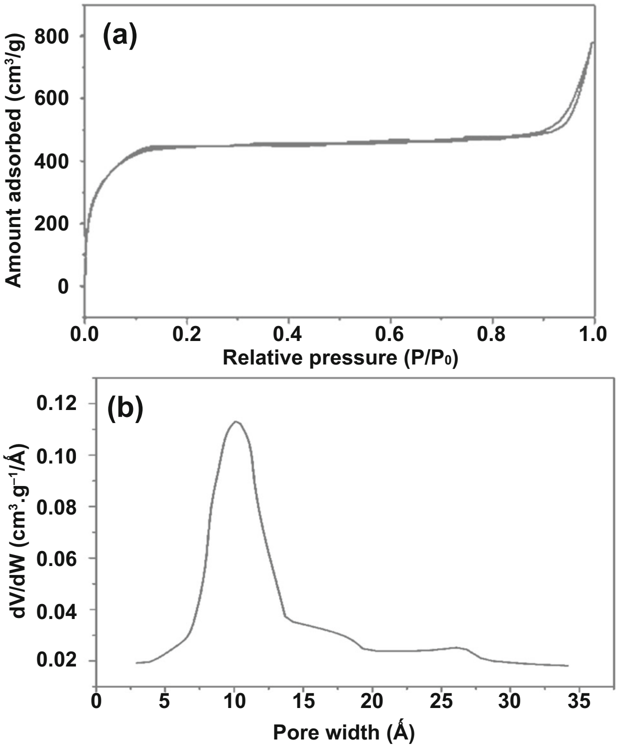


Fig. 3: (a) N_2 sorption isotherm of POZIF-8, (b) pores width distribution

Visual stability of POZIF-8-Fat50

The prepared emulsions stability of POZIF-8, ZnO, and TiO_2 was assessed by visual observing samples as a function of time, and the samples checked for any phase separation. The stability images are presented in Figs. 4 and 5.

As shown in Figs. 4 and 5, the prepared Pickering emulsion with POZIF-8 was more stable than nano-ZnO and nano-TiO_2 at all concentrations of oil. Whereas the prepared Pickering emulsions by both nano-TiO_2 and nano-ZnO are unstable at a high content of castor oils (60 g), POZIF-8-based Pickering emulsion is stable without any phase separation for more than 2 months. More stability of POZIF-8-Fat, which is the result of electrostatic repulsion of the

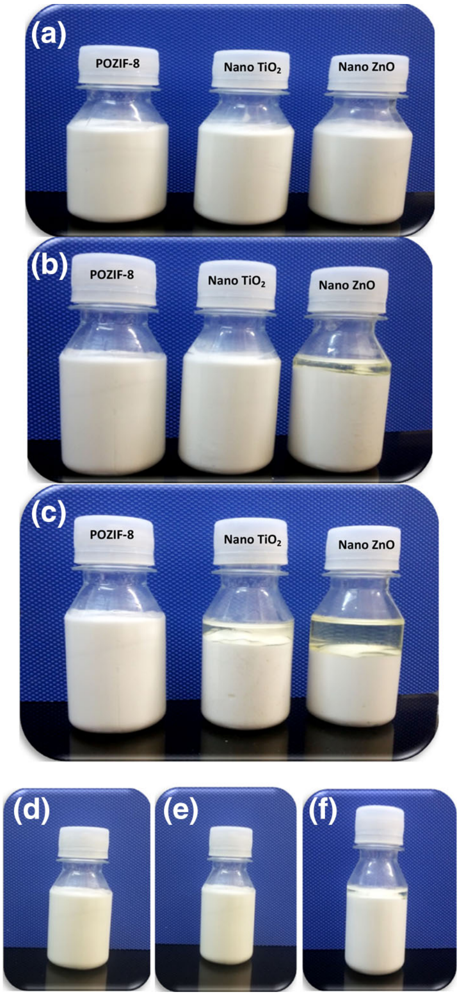


Fig. 4: Stability photos of (POZIF-8, nano-TiO_2, nano-ZnO)-Fat consisting of 10 g castor oil after (a) 10 days, (b) 90 days, (c) 120 days and POZIF-8-Fat50 after (d) 10 days, (e) 90 days, (f) 120 days

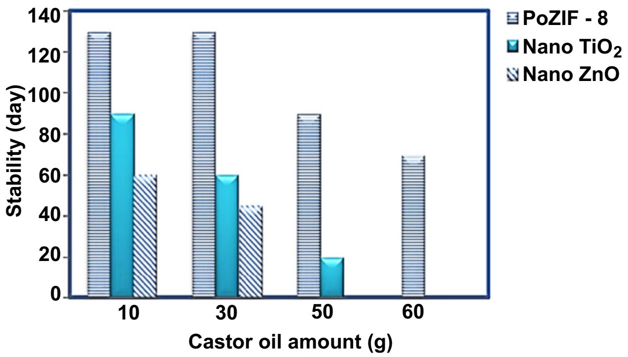


Fig. 5: Emulsion stability of (POZIF-8, nano-TiO_2, nano-ZnO)-Fat

positive charge of Zn ions, clearly indicates the important role of the POZIF-8 nanoparticles in stabilizing oil-in-water emulsions. Among prepared samples by TiO_2 and ZnO, the maximum stability is 90 days, which is equal to the stability of the POZIF-8-Fat50. For this reason, the POZIF-8-Fat50 was selected for further characterization.

Zeta potential of POZIF-8-Fat50

Figure 6 shows the zeta potential of POZIF-8-Fat50. Nanoparticles with a zeta potential range from −10 mV to +10 mV are considered approximately neutral, while nanoparticles with zeta potentials of greater than +30 mV or less than −30 mV (cationic and anionic, respectively) are considered strongly electrostatically stable.[34] The zeta potential value of POZIF-8-Fat50 was obtained at about +48.1 mV which means the high degree of stability. Furthermore, the positive value of zeta potential indicates that the cationic charge dominated more in the system, probably originating from zinc ions.

TEM observation of POZIF-8-Fat50

The Pickering emulsion was analyzed by transmission electron microscopy (TEM) to explore internal structure of POZIF-8-Fat50. Figure 7 shows that the system is divided into three regions: MOF-rich phase is shown by dark spots, the oil-rich phase is shown by light spots, and the MOF-oil phase is shown by light gray spots; the latter forms the major part of the emulsion.

In the MOF-oil phase, the porosity of MOF is filled with castor oil gust molecules. This has two advantages for the leather. Firstly, oil cannot easily migrate out of the leather. Secondly, in the leather these oils are gradually released into leather fibers as a long-term lubrication, thereby increasing the product's service life.

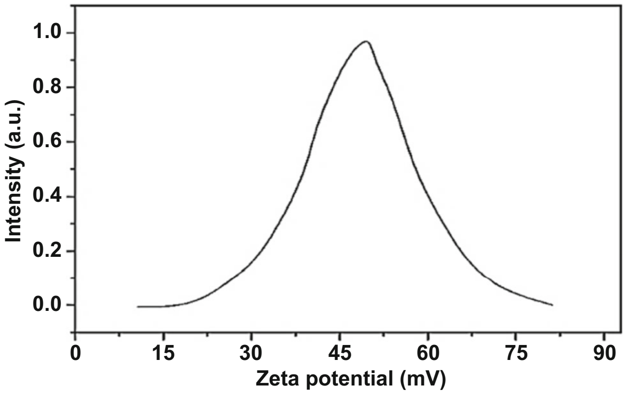


Fig. 6: Zeta potential of POZIF-8-Fat50

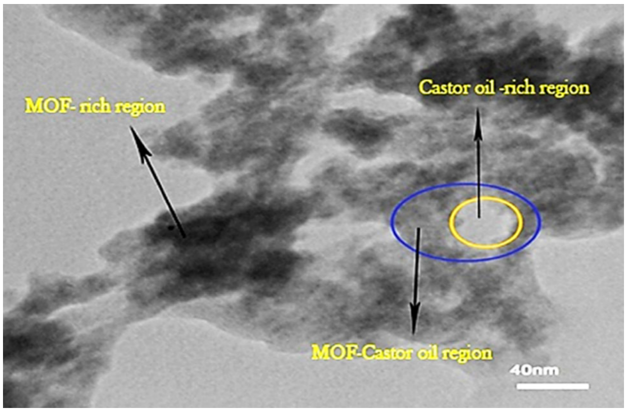


Fig. 7: TEM image of POZIF-8-Fat50

EDS spectra of fatliquored leather

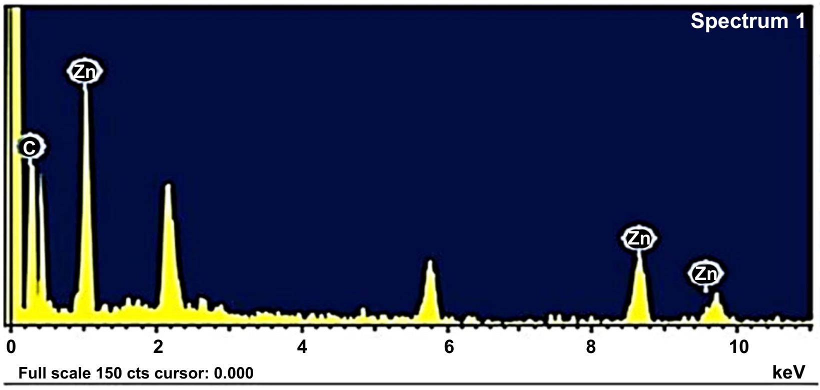
In order to prove the existence of POZIF-8 in collagen fibers, the surface and cross section of the fatliquored leather were examined by SEM equipped with the energy-dispersive X-ray spectroscopy (EDS). Figure 8 shows the EDS surface element analysis of the leather area, giving the composition and content of trace elements in the leather sample. The elements of C, N, O, S, and Cr are related before fatliquoring process. The element of Zn detected among the collagen fibers originated from POZIF-8 nanoparticles. The average content of Zn is 0.74 wt%, which confirms the permeation of POZIF-8 nanoparticles into the leather collagen fibers and binding affinity with them.

Figure 9 shows the SEM image of a cross section of the leather sample to investigate the distribution of POZIF-8 from grain to flesh side. Figure 9 illustrates Zn atom is evenly distributed from the grain layer to the flesh layer. POZIF-8 nanoparticles containing castor oil, due to a good affinity with collagen fibers, can easily penetrate deeply into the leather layers and interact with them.

Fatliquored leather properties

The measured properties of the coated leather samples by either POZIF-8-Fat50 or conventional fatliquor are compiled in Table 1. Also, the lightfastness of the leather samples is shown in Fig. 10.

As Table 1 shows, the fat extracted from coated leather by POZIF-8-Fat50 is lower than that of the



Element	Weight%	Atomic%
CK	50.28	54.51
NK	6.33	5.91
OK	25.77	23.50
ZnK	0.74	0.61
SK	4.58	5.36
CrK	12.30	10.11
	100.00	

Fig. 8: EDS analysis of fatliquored leather

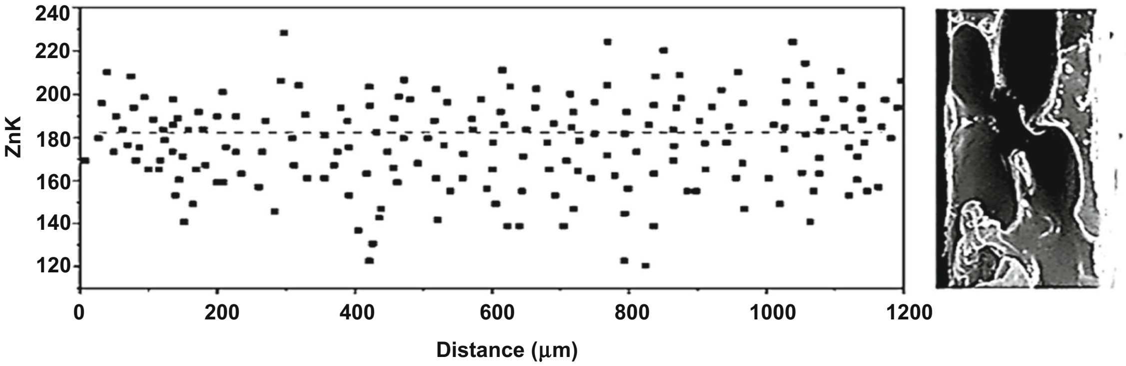


Fig. 9: SEM-EDS of the longitudinal section of fatliquored leather

Table 1: Properties of coated leathers by either POZIF-8-Fat50 or conventional fatliquor

Sample	POZIF-8-Fat50	Conventional
Fat extracted (%)	7.2	9.4
Tensile strength (N/mm^2)	19.8	15.1
Elongation at break (%)	124	66.2
Tear strength (N/mm)	56.2	41.3
Lightfastness	≥4.5	3
Softness (mm)	9	7.5
Fullness (%)	8.5	8

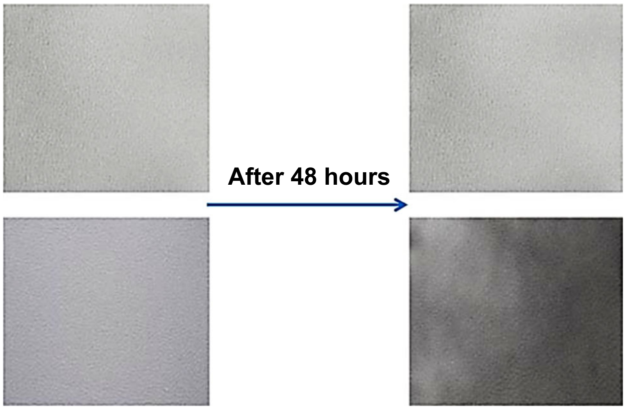


Fig. 10: Lightfastness of coated leather samples by (upper picture: POZIF-8-Fat50, lower picture: conventional fatliquor)

control leather. Therefore, it can be concluded that a large amount of applied POZIF-8-Fat50 was absorbed by collagen fibers and shows better performance of POZIF-8-Fat50 as fatliquoring agent. The mechanical properties of fatliquored leather samples were compared with each other. All mechanical properties (i.e., tensile, elongation, and tear) of the coated leather by POZIF-8-Fat50 were higher than that of the control leather. Therefore, introduction of surrounded castor oil by MOF as fatliquoring agent into the leather leads to improvement of mechanical properties. A significant increase in elongation at break as compared to the control leather is obtained due to high penetration of castor oil in collagen fibers. More tensile strength and tear strength can be explained by good interaction between POZIF-8 nanoparticles containing castor oil and collagen fibers. In fact, POZIF-8-Fat50 was well separated in the leather. As shown in Table 1 and Fig. 10, the lightfastness property of coated leather by POZIF-8-Fat50 is better than that of conventional fatliquor. The UV optical absorption characteristics of the ZnO clusters existing in POZIF-8 have a significant effect on light performance of fatliquored leather fibers. The ZnO has high optical absorption in both UVA and UVB light and as a result, can reduce the effects of ultraviolet radiation on collagen fibers.[35] Zinc ion in POZIF-8 can chemically link with functional groups on the collagen fibers and shield them against UV exposure. The softness of coated leather by POZIF-8-Fat50 was better than that of the control leather. Therefore, the flexibility of the molecule chain of collagen fibers was unexpectedly increased in the presence of MOFs. This is probably due to the high castor oil content included in POZIF-8 nanoparticles, plasticizing collage chains. The fullness of the coated leather sample by POZIF-8-Fat50 was higher than that of the control sample, which shows the penetration and compatibility of the prepared fatliquoring agent with leather fibers.

Conclusions

In this study, a new fatliquoring agent was successfully prepared by emulsifying castor oil in water with help of POZIF-8 and a castor oil-based dispersant. The stability tests show that the prepared Pickering emulsion by POZIF-8 has a higher degree of stability than the prepared Pickering emulsions by nano-TiO_2 and nano-ZnO. The results indicate that the introduction of POZIF-8 in fatliquoring agent could improve mechanical properties, lightfastness, softness, and fullness of the fatliquored leather. Therefore, it can also be used as an alternative to conventional fatliquoring agent for leather coatings.

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