CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 2, No. 3, 2008 Chemistry

Fernando Urena-Nunez[1, 2], Enrique Vigueras-Santiago[1], Susana Hernandez-Lopez[1], Karla Linares-Hernandez[1] and Isabel Linares-Hernandez[1]

STRUCTURAL, THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF UV-GRAFT POLYMERIZATION OF ACRYLATED-EPOXIDIZED SOYBEAN OIL ONTO GOAT LEATHER

Laboratorio de Investigacion y Desarrollo de Materiales Avanzados (LIDMA), Facultad de Quimica-UAEM, Paseo Colon esquina con Paseo Tollocan, Toluca, Estado de Mexico. C.P. 50000, Mexico, shernan@uaemex.mx

[2] Instituto Nacional de Investigaciones Nucleares, Km 36.5 carretera Mexico-Toluca, Salazar Estado de Mexico, CP 52045

Received: April 04, 2008

Abstract. Graft of acrylated-epoxidized soybean oil onto goat leather was achieved using UV-radiation. Graft percentage, structural, morphological and thermal characterizations are discussed in terms of: morphology of the leather grafted face and the UV-radiation dosage. The obtained results are of importance since an environmental friendly monomer could be used to change or improve some properties of leather articles.

Keywords: leather, acrylated-epoxidized soybean oil, graft copolymer, UV-radiation.

1. Introduction

Leather manufacturing is a technology which has developed over many centuries using goat, sheep, and pig skin, among others. The properties of the leather end-product vary depending upon the kind of hide as well as the method used to tan, treat, and finish the hide used to make it. Finishing gives the leather essential properties for its ultimate use. Leather is used in a wide variety of applications as clothing, shoes, handbags, and accessories as well as in automotive industry. For many years, a lot of research on leather modification by gamma-radiation grafting processes using common volatile monomers as butyl acrylate [1,2] and methyl methacrylate [3-5] as well as their copolymer [6] in emulsion systems have been reported. However acrylated-epoxidized soybean oil (AESO) renders thermosetting compounds by thermal [7, 8], gamma, ultraviolet radiation [8] or copolymerization process [7, 10]. It has been used as surface coatings with all necessary flexible, lightly crosslinked amorphous polymers with little structural strength. Acrylated-epoxidized triglyceride resins are used as toughening agents, protective coatings, and ink vehicles [10]. Recently, it and its composites [8, 10, 11] have focused on infrastructure of automotive, construction, aircraft, military and electronic industries [10-12]. Typically, triglyceride-based polymers form gels, which can be hard or soft depending on the level of functionalization of the triglycerides, extent of polymerization, comonomer [7] type and content (in case of copolymerization) reaching a wide range of acceptable structural applications [13]. Once polymerized, polymer derived from AESO (polyAESO) is very stable under UV and gamma radiation exposition [9]. In addition, AESO is considered as a environmental friendly monomer due to being derived from natural oil. These kinds of chemically modified triglycerides are gaining importance in different areas due to the fact that their polymer and composites products have mechanical, electrical, and thermal properties similar or better than those of the oleo-polymers. Those are the grounds to state that AESO is a good candidate as a high-quality surface protector of leather. Due to ease handling of AESO (non volatile, soluble in organic common solvents, nonflammable, among others) some characteristics of the graft as homogeneity, stability, full covering, and acceptable appearance could be achieved by controlling the exposition time to the UV-radiation and to the monomer solution.

2. Experimental

2.1. Reactants

Acrylated-epoxidized soybean oil was supplied by Sigma-Aldrich, Co. It contains 4.2 acrylate groups. Before using it, the inhibitor was removed by using a removing column (supplied by Sigma-Aldrich, Co.). Acetone and ethyl acetate (Sigma-Aldrich Co.), used for washing the ungrafted and grafted leather and to solve the monomer, respectively, were all analytical grade. Benzophenone (Sigma-Aldrich Co.) was the sensitizer and was used as received.

Leather samples. The experiments were carried out with formol tanned skin from a young goat. Its natural appearance was fairly uniform beige without visual physical damages. The skin did not undergo any additional treatments being absolutely crude.

Graft reaction. Graft reaction was produced in a programmable UVP-shortwave crosslinker, CL-1000 series equipment with a maximum wavelength of 254 nm. The UV-irradiance was 0.05W/cm^2. The samples were exposed to the irradiance for 2, 4 and 15 h, receiving doses of 360 J/cm^2, 720 J/cm^2 and 2,700 J/cm^2, respectively.

2.2. Characterization

Scanning electronic microscopy. Surface morphology of natural and grafted leather was examined with a scanning electron microscope (SEM, JSM-5900LV) without conductive covering.

EPR. Paramagnetic spectra were recorded on a Varian E-15 spectrometer, operating in the X-band. Ungrafted and grafted leather were cut in thin strips (~1.0cm x 3 mm large x thick) and introduced into a quartz probe. The spectra were recorded at room temperature and atmosphere.

FTIR. Infrared spectra in transmittance mode were recorded on a Nicolet Avatar 360 FTIR spectrometer. A total of 64 scans at a spectral resolution of 4 cm^{-1} were used in all cases. The samples were prepared by sanding the samples with steel sand, obtaining dust that was mixed with KBr and pressed at 8 tons for 1 min in order to produce lucid plates. FTIR spectra in diffuse transmittance mode were taken with complete samples exposing only one face before and after being grafted.

Thermal analysis. TGA evaluations were performed in a modulus SDTQ 600 from TA Instruments at a scan rate of 293 K/min under nitrogen flux from 298 to 873 K and DSC analysis were performed in a Perkin Elmer DSC-7 at 293 K/min from 298 to 873 K. The samples were sanded as explained for FTIR characterization.

2.3. Grafting process

Ten circles 1cm in diameter were obtained randomly from the leather (LE) for each experiment. The circles were washed with acetone under mechanical agitation for 15 min in order to eliminate dust and some impurities from hanging and storage. Following that, they were dried under vacuum for 12 h. Two kinds of studies were conducted in order to evaluate their effect on the graft percentage and on the morphological properties. The first one was concerned with the penetration of AESO trough the leather. For this, the samples were immersed into a 38 % v/v solution of AESO containing 2 % v/v of benzophenone for 2, 30 and 60 min. After that, only one face (outer or inner) was UV-irradiated for 4 h. The second study consisted in exposing the samples previously weighed and immersed for 30 min into the same solution to different UV-doses. Then one face was irradiated at different doses expressed in grafting time: 2, 4 and 15 h. The same experiments for new samples were done for the other face. After graft reaction, the samples were soaked again in acetone for 30 min to extract the solvent, monomer, and/or homopolymer. The samples were finally dried under vacuum for 24 h and weighed to calculate the graft percentage according to the following formula:

$$Graft\% = \frac{W_{LE+AESO} - W_{LE}}{W_{LE}} \cdot 100$$

where W_{LE} is the weight of natural leather without grafting, $W_{LE+AESO}$ – the weight of leather sample after grafting.

3. Results and Discussion

Graft percentage were higher for the outer face (grain layer) than for the inner one (flesh side) as it can be seen in Figure 1. For outer face 9.8 % was obtained for graft when sample was immersed for 1 min; 12.5 % and 13 % for 30 and 60 min, respectively. No important absorption changes were observed after 1h; in fact the difference between 30 and 60 min was only 0.5 %. The same behavior was observed for the inner face but with much lower graft percentage: 2.8, 3.7 and 3.8 %, for 2, 30 and 60 min, respectively. Other dilutions different from 38 % v/v of AESO/ethyl acetate were used, however some irregularities were observed after samples were copolymerized. For the most diluted prepared solution (23 % v/v of AESO/ethyl acetate) the covering of the UV-exposed face was uneven with some zones without polymer. On the other hand, for the most concentrated one (45 % v/v of AESO/ethyl acetate) the leather surfaces were brilliant and homogeneous but after washing with acetone, some polymer was peeled from the leather. This indicated that a concentrated solution (more viscose) does not penetrate enough into the leather and minimum or not entire grafting is achieved. For 38 % solution, the grafting and covering of the polymer onto the leather was most favorable. Leather surface was homogeneously brilliant and no peeling of the polymer was macroscopically observed.

With those results, the effect of the UV-dose in samples previously immersed for 30 min in the 38 % AESO-solution was evaluated. They were irradiated for 2, 4 and 15 h. Minimum graft percentage was obtained at 2 h of polymerization in both inner and outer faces, being always higher for the outer face (8.8%) than for the inner face (2.2 %) (Fig. 2). Insignificant differences of graft percentage were obtained for 4 and 15 h of irradiation time in all cases, and 4 h seems to be the time that permits to achieve the maximum graft percentage under these conditions.

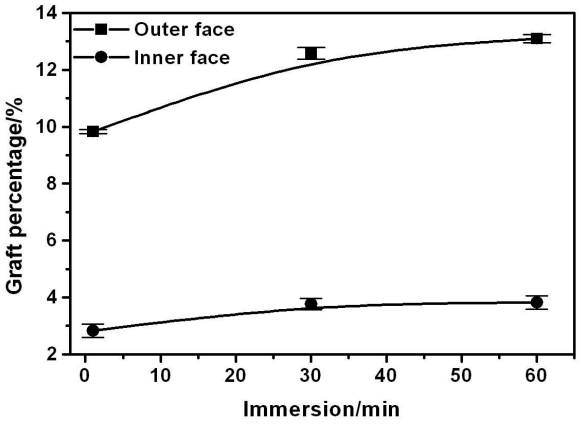


Fig. 1. Graft percentage respect to immersion time of goat leather into a 30 % AESO/ethyl acetate solution (v/v)

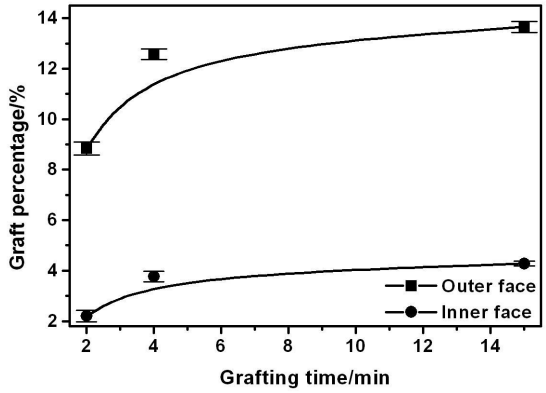
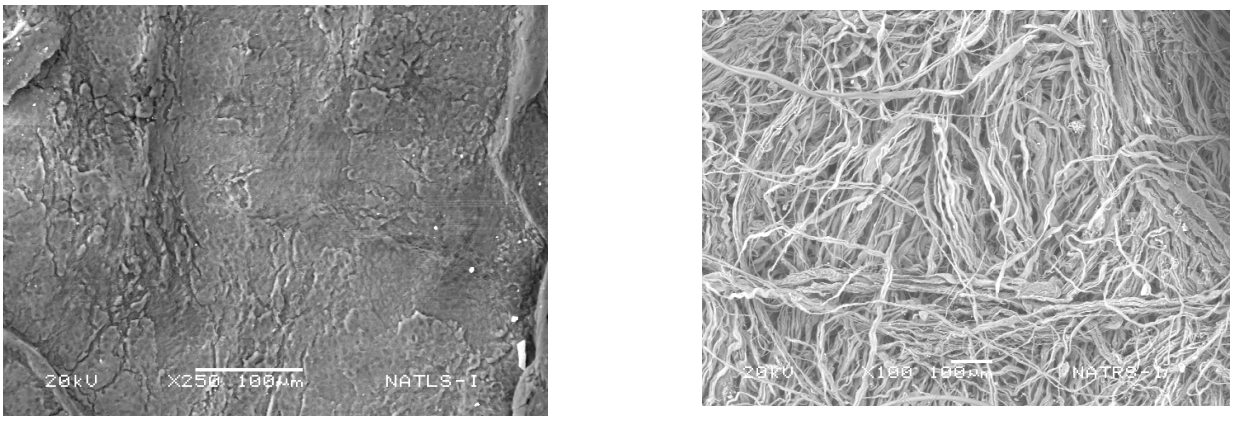


Fig. 2. Graft percentage respect to grafting time under UV radiation

The differences in graft percentage between inner and outer face under the same conditions are due to the morphology of the faces, which is dissimilar. Outer face (Fig. 3) is a compact and wrinkle surface. It surely lets AESO solution penetrate homogeneously producing higher graft than the inner face. On the other hand, inner face is constituted by long collagen fibrous protein that could be impregnated by the same monomer solution but not homogeneously and no so deep. The evidence is presented in Fig. 4 showing the micrographs of both faces after grafting. Outer face shows a homogeneous polyAESO film, covering some hair and some pores. However, a different effect was observed on the inner face. Fibers look randomly "glued" by polyAESO and it is possible to distinguish holes among them while under some of these holes there are more glued fibers and so on. Micrographs showing the transversal border of inner and outer samples grafted 4hs after immersion by 30 min is presented in Fig. 5. PolyAESO was identified as a brilliant zone and it could be measured as 10 µm and 30-36 µm for outer and inner grafted faces, respectively. The graft thickness for the inner face apparently was wider than for the outer one, however it does not mean that all 36 µm are filled with polyAESO; this polymer is only glueing some fibers without filling the holes among them, as it was described before. Moreover, the thickness for the inner face is not the same along the transversal border while outer face presented a compact and homogeneous graft along it. As graft percentage of inner face is low and almost constant for the immersion and grafting time, no penetration to midcorium was observed for this face. In order to make a relationship between graft percentage with the immersion and grafting time, the thickness was measured in the same way, obtaining the following tendency: for outer face the polymer thickness increases with the increase of grafting time: for 2 h, 5 µm; for 4 h, 10 µm and for 15 h, 20 µm. Penetration depth for inner face was almost the same (between 30 and 36 µm) regardless of grafting time. These results are in agreement with the described before in function of the morphology of the faces.

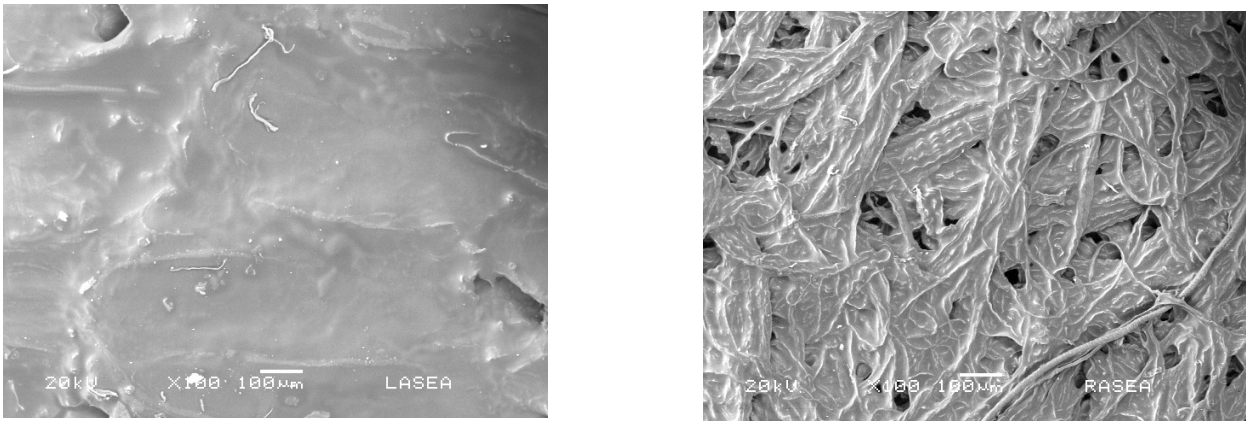
At this point is important to give an explanation for the relation between increasing of the graft percentage to the grafting time observed for the outer face. At higher exposition to UV-radiation, graft could increase due to the two following effects: (i) an enhanced reaction (bonding) between the free radicals from the leather with macroradicals from the polyAESO or ii) the extent of AESO polymerization (growing of the polyAESO) increases once it has been grafted on the leather. To discriminate them, the acetone after washing the 2h-grafted samples was analyzed. AESO monomer (soluble) was detected instead of homopolymer (insoluble), indicating that graft percentage increases as UV-exposition time increases due to the second supposition. That means that grafting reaction takes place between radicals from leather collagen and AESO and then or simultaneously the polymerization of AESO continues. If the first supposition were true, ungrafted homopolymer would be detected in the solvent. It is important to take into account that if irradiation time influences cross-linking density, this characteristic should be very important for mechanical properties [9] as toughness, strength, *etc*.

To verify the presence of polyAESO and the graft reaction, FTIR and EPR spectroscopes were used, respectively. Describing the FTIR spectra, we can distinguish the signals corresponding to leather and to polyAESO, independently of the grafted face. In a FTIR-reflectance experiment only the spectra of the polymer that covers the surface on the complete grafted face was observed. This spectrum was not of such good quality as the transmittance mode using KBr plates, but it was useful for detecting the presence of the polyAESO on the entire outer or inner surface leather. Using FTIR-transmittance mode characteristics bands of pure polyAESO UV-polymerized for 4 h were detected at 3447 cm^{-1} (O-H), 2928 cm^{-1}, 2856 cm^{-1} ($–CH_2–$, $–CH_3$), 1740 cm^{-1} (–C=O), 1456 cm^{-1} ($–CH_2–$, $–CH_3$), 1160 cm^{-1} and 1076 cm^{-1} (C–O). The main identified bands for natural leather (Fig. 6) are:



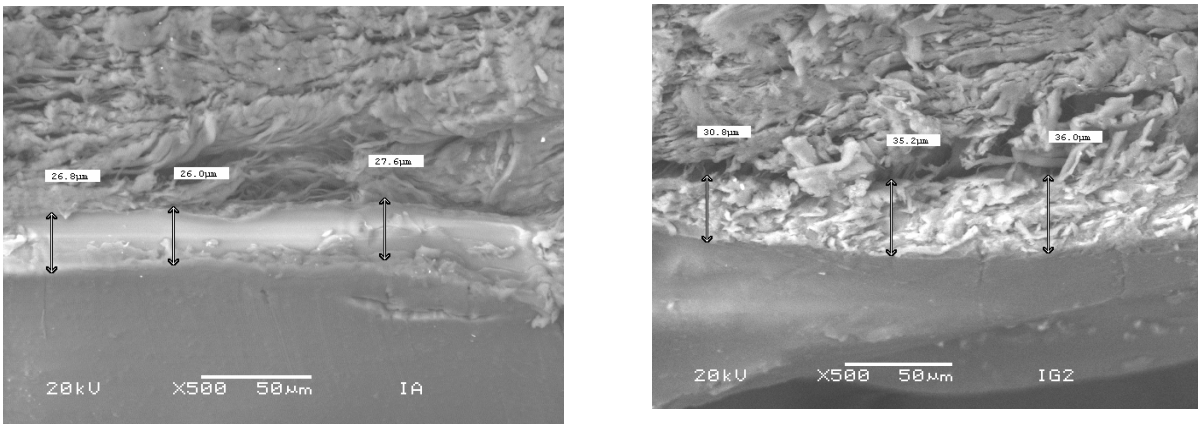
a) b)

Fig. 3. Natural goat leather: outer face (a) and inner face (b)



a) b)

Fig. 4. Grafted outer face Ou_{30_4} (a) and inner face In_{30_4} (b)



a) b)

Fig. 5. Micrograph of transversal area of grafted leather samples: outer face Ou_{30_4} (a) and inner face In_{30_4} (b)

3660–3530 cm^{-1} ($N–H_{amide}$), 2922 cm^{-1}, 2856 cm^{-1} ($–CH_3$, $–CH_2–$), 1643 cm^{-1} (–OC–N), 1540 cm^{-1} (N–H), 1450 cm^{-1} (C–H), 1239 cm^{-1} (NH–CO), 1076 cm^{-1}, 1028 cm^{-1} (C–O). For the outer sample 4 h grafted after being immersed for 30 min (OU_{30_4}), we observed a spectrum very similar to LE; however for grafted leather the carbonyl signals corresponding to polyAESO (1740 cm^{-1}) additionally to those of natural leather (Fig. 6) are different being the main evidence of the presence of the polymer.

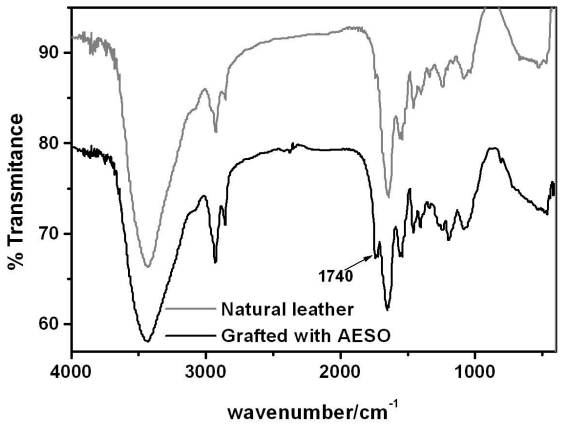


Fig. 6. FTIR spectrum for natural leather after being washed with acetone (LE) and after being grafted with AESO ($Ou_{30–4}$)

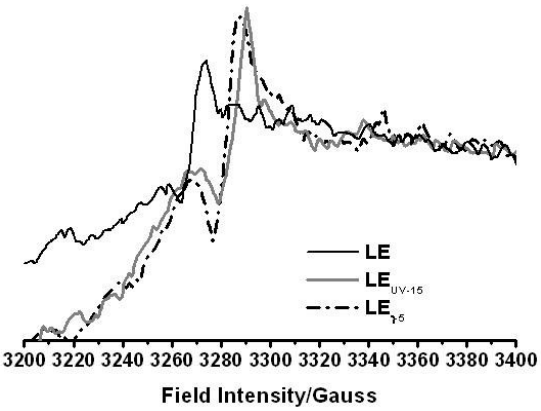


Fig. 7. EPR spectra for natural leather (LE_t), same natural leather irradiated 15 min with UV radiation (LE_{uv-15}) and natural leather irradiated 5 kGy with gamma radiation (LE_{g-5})

EPR spectroscopy was carried out in order to confirm the possibility of covalent bonding between AESO and leather *via* free radicals species. The presence of free radicals in natural leather could be due to growing centers for polyAESO and/or reactive species that recombine with macro AESO radicals. It is well known that peroxy free macroradicals exist on the skin (collagen) [5, 14, 15] and they were detected in samples of natural leather (LE), as we can see in Fig. 7**.** Its spectrum shows only a complex signal centered at 3268 Gauss corresponding to some peroxy radicals on ∝- carbon from aminoacids, mainly from the alanine, which is the major constituent of collagen (–CO–NH–CH(OO·)–CO–NH–). In order to probe it, a sample of natural leather was submitted to UV-radiation for 15 min under environmental conditions (LE_{uv-15}) showing an EPR spectra with a centered well defined signal at 3285 Gauss being practically the only one (Fig. 7). To compare the type of free radicals obtained from irradiating the leather with gamma radiation, the most used method for skins grafting, a natural leather sample was irradiated at 5 kGy ($LE_{\gamma-5}$). Its EPR spectra (Fig. 7) showed the same signal as LE_{uv-15} at 3283 Gauss and some other smaller defined signals in the range of 3340 and 3405 Gauss. The main free radical signal at 3285 Gauss is due to an oxy-macroradical (–CO–NH–CH(O·)–CO–NH–) generated by decomposition of peroxy radicals on skins [5] by exposition to UV and gamma radiation. It is highly probable that graft of AESO on goat leather was through the oxy-macroradicals. We could confirm grafting because no peeling was observed as it happened when the concentrated solution of AESO (45 % v/v) was used. In this last case, a relatively thick AESO film on the leather diminished or completely blocked the UV-radiation penetration and the generation of oxy-macroradicals necessary for bonding. These conditions only rendered homopolymer of AESO that was observed as an insoluble yellow solid which was filtered from the acetone in which the sample after UV-irradiation was washed.

Due to the complex structure of polyAESO and skin composition, it turns difficult to propose a polymerization mechanism and a definite structure for graft, that is why an approximation is given below in Fig. 8. We started from the sensitizer decomposition (I) and from the oxy-macroradicals on the leather proteins. This oxy-macroradical is sited on an alanine aminoacid (III), the part (II) of the protein could be any other aminoacid. The oxy-macroradical (III), considered as the growing polymer chain, is able to react with an acrylic group of the ASEA monomer (IV), and simultaneously or after that other acrylic group of the ASEA could polymerize by the effect of the initiator radical (V) with more ASEA monomers and/or copolymerize with more oxy-macroradicals from leather, and so on. As we can see, the final structure (VI) could be a very cross-linked one, depending on grafting time.

On the other hand, we evaluated the effect of the graft on the thermal properties of the leather. Figs. 9 and 10 show the DSC and TGA curves for pure polyAESO polymerized for 2 h which only presented a small exothermal at 606 K due to the cross-linking of residual acrylate groups. Its TGA curve showed one decomposition step at 623 K. For 4 and 15 h polyAESO did not show any transitions into the range of 298 and 623 K. Natural leather showed a wide exothermal from 323 to 473 K approximately. Usually, heating dries out, embrittles, and

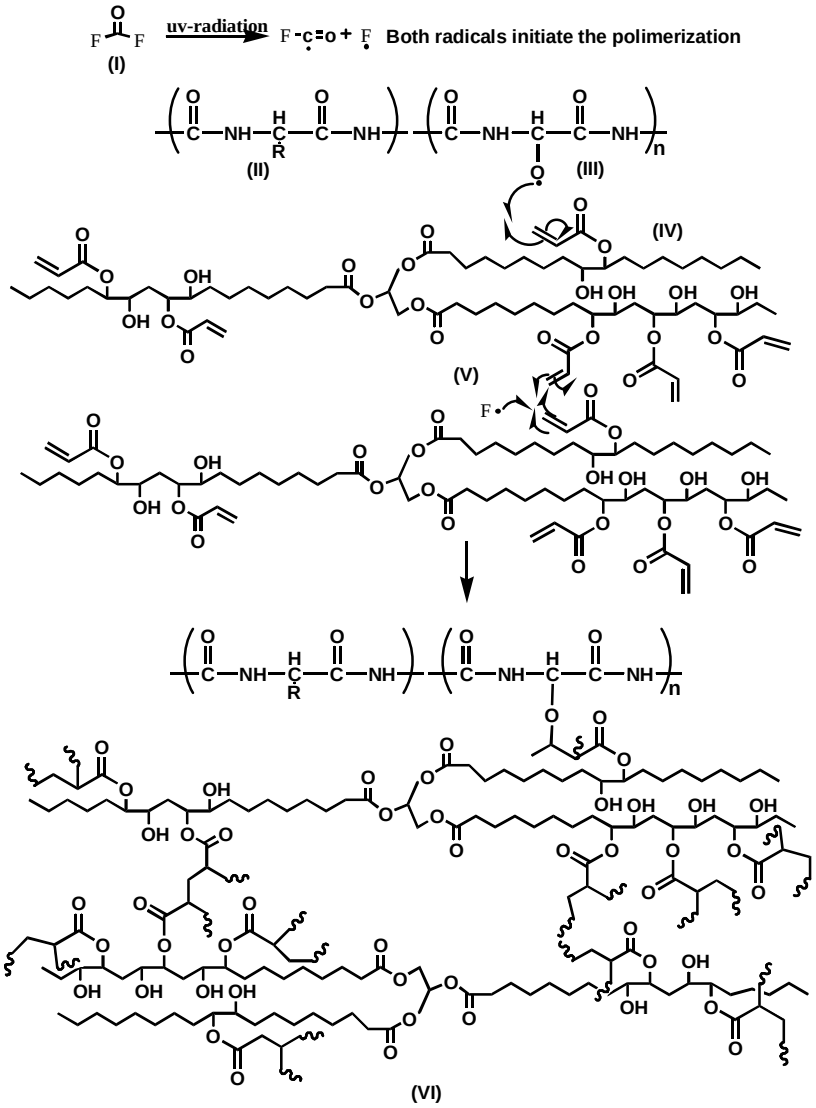


Fig. 8. Mechanistic propose of grafting and crosslinking between leather and AESO produced by UV-irradiation

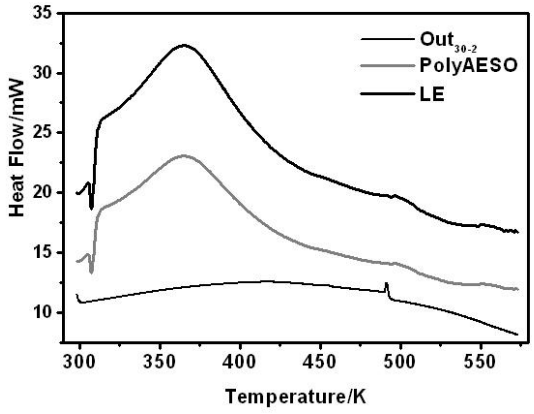


Fig. 9. DSC curves for natural leather (LE_t), polyAESO polymerized for 2 h using UV-radiation and a sample of leather grafted for outer face (Ou_{30-2})

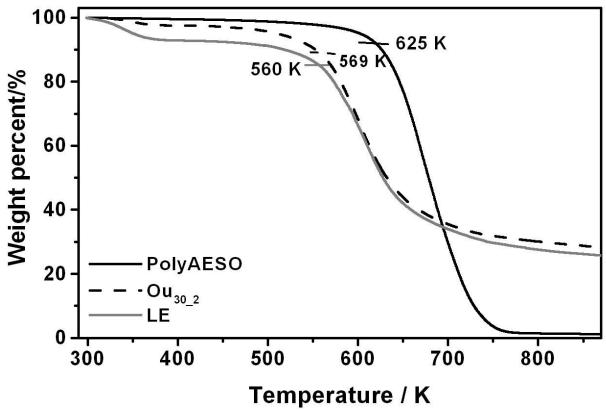


Fig. 10. TGA curves for natural leather, polyAESO UV-polymerized for 2 h and a sample of leather grafted for outer face (Ou_{30-2})

deforms skins by producing shrinkage and contraction of their fibrous proteins around 333–340 K. Such a wide exothermal includes lost of water (7.2 % as it was determined by TGA), the shrinkage deformation and immediate degradation process at 560 K. Graft of polyAESO seems to diminish the two first processes – the wide exothermal disappears, lost of water is only 5.5 %, and the decomposition temperature is improved by 10 K. The same effects were observed in samples with different immersion and grafting times. These facts evidence that polyAESO is covalently bonded to the skin fibrous proteins giving a stable network and avoiding or diminishing its deformation (shrinkage).

4. Conclusions

Graft of acrylated-functionalized soybean oil on goat leather initiated by UV radiation was confirmed by EPR experiments. Growing centers (oxy-macroradicals) were detected on natural leather after its exposition to UV and gamma irradiation. Also, grafting was proved by thermal properties in which graft diminished the deformation heating process of the leather and increased the decomposition temperature by 10 K. These thermal properties were affected in the same way regardless of the used conditions for grafting. Both of the variables – immersion and UV-exposition time – were associated to the thickness of graft (graft percentage) which also depended on the morphology of the faces. Outer face has the ability of absorbing and retaining monomer due to its compact structure; however the inner face constituted by long fibers blocked the passage of the monomer solution to the midcorium. In this case graft percentages were very low (2-4 %) in comparison to those of the outer face at the same grafting conditions (8-14 %). Optimal conditions of grafting were considered as 30 min of leather immersion in a 38% v/v AESO solution and 4h of polymerization. At 30 min the leather seems to have its maximal absorption capacity and after 4 h of polymerization graft percentage and thermal properties practically didn't change. PolyAESO was homogeneously grafted onto the entire surface of leather faces as was proved by SEM and reflectance FTIR for all the grafting conditions. Grafting time had a lighter effect on the graft percentage than immersion time and it is important to take into account that even 4 h was considered as the optimal grafting time; higher or lower irradiation dosage could affect other important properties like the mechanical ones. Thus, the study of the dependence of these properties on the graft conditions established in this work could render a range of materials with different mechanical behavior.

Acknowledgements

This research was supported by UAEM under project 1981/2004-II.

References

[1] Pietrucha K.: Radiat. Phys. Chem., 1982, **19**, 219.
[2] Pietrucha K. and Kroh J.: Radiat. Phys. Chem., 1986, **28**, 373.
[3] Pietrucha K, Pekala W. and Kroh J.: Radiat. Phys. Chem., 1981, **18**, 489.
[4] Pietrucha K.: Radiat. Phys. Chem., 1982, **19**, 227.
[5] Pietrucha K. and Kroh J.: Radiat. Phys. Chem., 1985, **25**, 451.
[6] Badran A., Nasr H., El-Halawany N. and Mohamed W.: Polym. Plastics Techn. Eng., 2007, **46**, 79.
[7] Lu J., Khot S. and Wool R.: Polymer, 2005, **46**, 71.
[8] Wool R., Kusefoglu S., Palmese G, Khot S. and Zhao R.: Pat. USA, 2000.
[9] Hernandez-Lopez S, Martin del Campo-Lopez E. *et al.*: Adv. in Tech. Mat. and Mat. Proc. J., 2006, **8**, 220.
[10] Wool R.: 3rd Annual Green Chemistry & Engineering Conference. Moving Toward Industrial Ecology. Bio-based synthesis and processing, 1999; 78.
[11] La Scala J., Sands J., Orlicki J. *et al.*: Polymer, 2004, **45,** 7729.
[12] Hernandez-Lopez S., Vigueras-Santiago E., Mercado-Posadas J. and Sanchez-Mendieta V.: Adv. in Tech. Mat. and Mat. Proc. J., 2006, **8**, 214.
[13] Khot S., Lascala J., Can E. *et al.*: J. Appl. Polym. Sci., 2001, **82**, 703.
[14] Pietrucha K., Pekala W. and Plonka A.: Radiat. Phys. Chem., 1980, **16**, 315.
[15] Meybeck A.: Int. J. Cosmetic Sci., 1979, **1**, 199.

СТРУКТУРНІ, ТЕРМІЧНІ ТА МОРФОЛОГІЧНІ ХАРАКТЕРИСТИКИ УФ-ПРИЩЕПЛЕНОЇ ПОЛІМЕРИЗАЦІЇ АКРИЛАТ-ЕПОКСИДОВАНОЇ СОЄВОЇ ОЛІЇ НА КОЗЯЧУ ШКІРУ

Анотація. *Проведено прищеплення акрилат-епоксидованої соєвої олії на козячу шкіру з використанням УФ-випромінювання. Встановлено відсоток прищеплення, морфологічні та термічні характеристики в залежності від морфології поверхні шкіри і дози випромінювання. Отримані результати вказують на безпечність використання такого мономеру для покращення властивостей шкіряних виробів.*

Ключові слова: *шкіра, акрилат-епоксидована соєва олія, прищеплений полімер, УФ-випромінювання.*