

Esterification Process Induced by UV Irradiation of Shellac thin Films Deposited by Matrix Assisted Pulsed Laser Evaporation

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In this work we report on the deposition of UV resistant shellac thin films by matrix assisted pulsed laser evaporation (MAPLE). The films obtained starting from a solution of 1-2 wt% shellac in methanol were very smooth and their chemical structure was preserved after the laser transfer. Upon short exposure time (u to 60 min), UV irradiation did not induce significant modifications in the films composition and surface appearance, while upon increasing the irradiation time (240 min) an esterification process of shellac can be observed.

Keywords: shellac, thin films, matrix-assisted pulsed laser evaporation, UV irradiation

Matrix Assisted Pulsed Laser Evaporation (MAPLE) is a laser based deposition technique especially used for the deposition of biomaterials and soft materials. In MAPLE, a focused laser beam irradiates a solidified (frozen) target consisting in the interest material dissolved in a proper solvent (matrix) in a few mass percent (0.1-5 wt%). During irradiation, the target material is evaporated, the solvent is eliminated by the pumping system and the soft material is condensed onto a receiver as a thin film [1-5]. Through the advantages of this method is the ability to obtain films with controlled thickness and good adherence to the substrate, difficult to be achieved by other classical techniques [6-7].

Shellac is a natural material formed by several esters and polyesters, a resin secreted by *Kerria lacca* bug on trees in India. The main applications of shellac range from pharmaceuticals, as capsules for drugs designed for colon absorption [8], to food industry as water barrier against dehydration of aliments [9], and protective coatings [10]. In the last years, there are reports on using shellac as substrate and isolator in organic and flexible electronics [11-12].

Experimental part

Shellac wax-free purchased from Sigma-Aldrich was dissolved in methanol in 1-2 wt% and froze by liquid nitrogen in order to obtain the solid target which was irradiated by the forth harmonic of a Nd:YAG laser (wavelength 266 nm, repetition rate 10 Hz). The number of pulses was 72.000 for all the experiments and the fluence was varied in the range 0.4-0.8 J/cm². Infrared transparent silicon was used as a substrate and placed at 4 cm distance of the target. The as deposited films were irradiated by a UV lamp emitting at 254 nm (1.1 mW/cm²) [13]. The irradiation of the samples was made for 15, 60 and 240 minutes. Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray Photoelectron Spectroscopy (XPS) were employed to study the surface morphology and chemical stability of the irradiated films.

Results and discussions

In figure 1, a thin film of shellac deposited as a result of 72.000 pulses at 0.4 J/cm² fluence is presented. The film is about 1015 nm and has a roughness of 0.5 nm on a 40x40

μm². A deposition rate of 0.15 Å/ pulse was achieved. The film is very uniform and completely covers the silicon substrate.

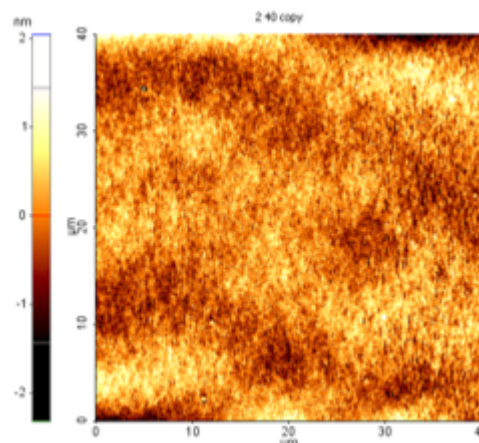


Fig. 1. AFM image on a thin film deposited by MAPLE starting from 2 wt % shellac in methanol target on silicon substrate

UV irradiation tests were made on samples of shellac grown on Au covered silicon with 72.000 pulses at 0.8 J/cm² fluence, starting from a frozen target of 1 wt % shellac in methanol. The thickness of the films is about 850 nm and the RMS roughness is 56 nm. Morphological macroscopic changes cannot be identified for the UV exposed samples. At micrometer range (fig. 2), the evolution of the surface morphology (computed over areas of 20x20 μm²) and contact angle show insignificant

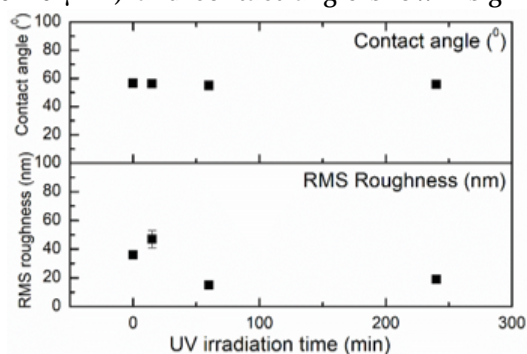


Fig. 2. Contact angle and RMS roughness for different time exposure at UV irradiation for a film of shellac deposited on Au/Si substrate

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modification. A slight decrease of the RMS roughness can be noticed.

FTIR spectra were performed for the deposited sample and for the UV treated samples (fig. 3.a). The large band centered at 3400 cm^{-1} corresponds to OH vibration; this band is also typical for the MAPLE deposited films. The two peaks at 2857 and 2930 cm^{-1} are attributed to the stretching vibrations of CH_2 . Bending vibrations of CH_2 can be seen at 1462 cm^{-1} . As stated also by M. Licchelli et al. in [14] and by Derrick et al. in [15], the 1715 and 1733 cm^{-1} peaks are ascribed to $\text{C}=\text{O}$ stretching vibration in acids and esters (fresh shellac), respectively. The $\text{C}-\text{O}$ stretching vibration for esters, acids and alcohols can be identified at 1247 , 1195 and 1051 cm^{-1} [16, 17]. $\text{C}=\text{C}$ stretch vibration corresponding to alkenes can be seen at 1633 cm^{-1} . As mentioned before, we used shellac wax free, as it can be seen from the absence of the wax typical absorption double bands at 720 and 730 cm^{-1} . Dewaxed shellac leads to clear films with good adherence [17].

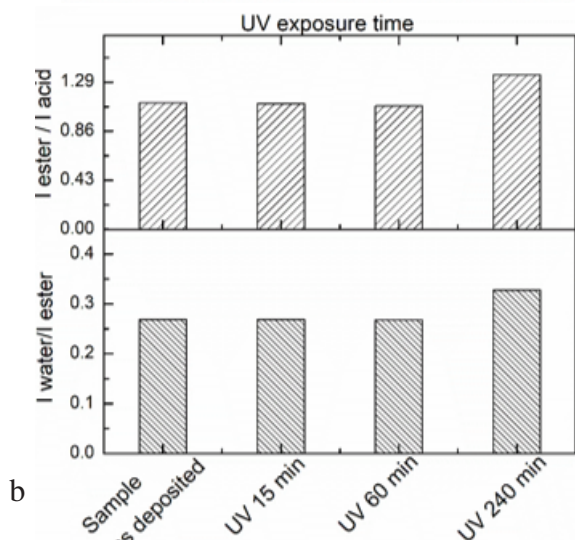
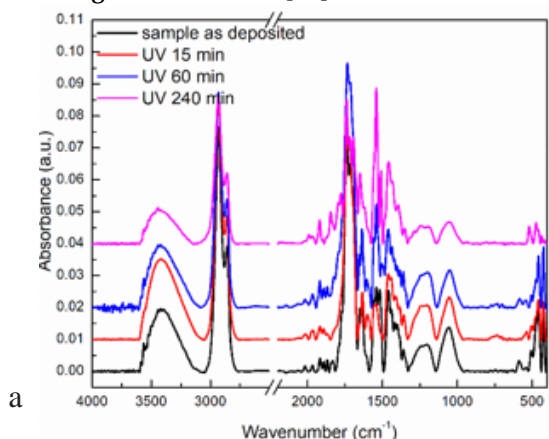


Fig. 3. FTIR spectra (a) of shellac films and normalized integral intensities (b) $I(1733\text{ cm}^{-1})/I(1715\text{ cm}^{-1})$ and $I(3423\text{ cm}^{-1})/I(1733\text{ cm}^{-1})$ for different time exposure at UV irradiation

In order to see the evolution of the chemical structure of the as deposited sample and UV exposed ones, we have compared the carbonyl bands for ester functional groups and for acid groups, by evaluating the behavior of the ratio $I(1733\text{ cm}^{-1})/I(1715\text{ cm}^{-1})$ upon UV irradiation. As we can see, the material composition does not change in the first 60 minutes of UV irradiation, while using longer UV exposure (240 minutes) leads to more polymerized sample (the ratio $I(1733\text{ cm}^{-1})/I(1715\text{ cm}^{-1})$ increases with 17%) as result of esterification. Another way to characterize the polymerization degree of shellac is to observe the amount

Table 1
ATOMIC CONCENTRATION OF THE SHELLAC FILMS, INITIAL AND UV IRRADIATED FOR 240 min

	Atomic concentration (at %)		
	C 1s	O 1s	N 1s
As deposited sample	85.79	12.32	1.89
240 minutes UV exposed film	78.13	21.87	-

of water present in the material. The ratio of peak intensities for the ester (1733 cm^{-1}) and for OH vibrations (3423 cm^{-1}) were evaluated, conducting to a similar behavior, namely for the first 60 min of UV irradiation there is no modification in the chemical structure of the films. For the sample exposed the longest time to UV light, the increase of the esterification degree is accompanied by an increase of the water molecules incorporated in the lac film (OH functional groups).

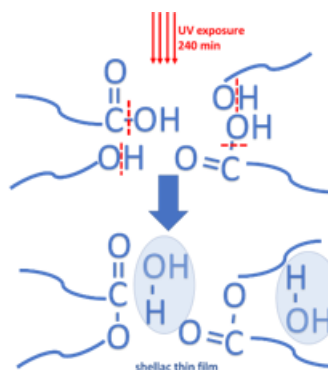


Fig. 4. Shellac crosslinking principle

The atomic compositions obtained by XPS investigation for the as deposited sample and for the 240 min UV irradiated sample are presented in table 1.

As it can be calculated from the results presented in table 1, the atomic ratio between oxygen and carbon increases from 0.14 to 0.28 after UV excitation. The processes encountered during UV irradiation are schematically illustrated in figure 4: the OH bonds in COOH groups are broken, esters are formed in the same time with the formation of OH free radicals. These processes are also confirmed by FTIR investigation and point out towards a combination of film esterification and crosslinking process, which may induce the film densification. The nitrogen presence in the initial films is due to the deposition procedure for MAPLE [18], which implies target freezing by liquid nitrogen as well as introduction of nitrogen in the deposition chamber during ventilation, in order to avoid air admission and condensation of water in the system. Despite the nitrogen presence in the films, their properties are not significantly modified, suggesting its inclusion mostly in gaseous form. After photo treatment, the nitrogen cannot be detected anymore, suggesting the gaseous desorption, which may appear due to the rearrangement of the structure during the esterification process. The elimination of nitrogen gaseous inclusions combined with the material crosslinking are most probably responsible for the observed roughness decrease.

Conclusions

Smooth, continuous thin films of shellac were deposited by MAPLE. The UV radiation impact onto films was tested and the films ability to be used as protective coatings under

solar radiation conditions has been demonstrated. The degradation of the films under continuous exposure at 254 nm irradiation for 1 h (1.1 mW/cm²) did not induce degradation. Longer irradiation time, leads to surface polymerization and oxidation. The roughness of the surface is lower, due to desorption and crosslinking phenomena, while no defects or cracks are formed on the film surface. These properties suggest that the described films can be used for organic electronics.

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