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Improvement in surface characterisitcs of polymers for subsequent electroless plating using liquid assisted laser processing

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Abstract

Metallization of polymers is a widely used process in the electronic industry that involves their surface modification as a pre-treatment step. Laser-based surface modification is one of the commonly used techniques for polymers due to its speed and precision. The process involves laser heating of the polymer surface to generate a rough or porous surface. Laser processing in liquid generates superior surface characteristics that result in better metal deposition. In this study, a comparison of the surface characteristics obtained by laser processing in water vis-à-vis air along with the deposition characteristics are presented. In addition, a numerical model based on the finite volume method is developed to predict the temperature profile during the process. Based on the model results, it is hypothesized that physical phenomena such as vapor bubble generation and plasma formation may occur in the presence of water, and it is because of these effects that causes an increase in surface porosity.

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Keywords: Laser processing; surface modification; metallization; electroless platin; finite volume method

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1. Introduction

Metallization of polymers and polymer-based materials is a widely used industrial technique for a variety of applications that include electric, electronic and mechatronic devices, and decorative purposes [Charbonnier and Romand (2003)]. Electroless plating is one of the most commonly used metallization techniques for polymers. The process involves surface modification of the polymers to improve adhesive properties and subsequent activation of the surface with an electroless catalyst (typically by submerging it in a Sn/Pd solution), and the activated surface is plated using electroless auto-catalytic process by immersing it in an electroless bath (Ni or Cu solution) [Yang et al.

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(2011)]. The other techniques of polymer metallization include chemical plating [Stremsdoerfer et al. (2003)], physical vapor deposition [Mittal (1991)], plasma and ion beam etching [Kupfer and Wolf (2000)] and chemical vapor deposition [Duguet et al. (2013)]. In comparison to other processes, electroless plating is economically cheap as it uses very simple equipment. In addition, electroless process offers a large flexibility of the thickness and volume of metal deposition with a uniform surface finish.

Nomenclature

T	Temperature (K)
T_b	Normal boiling temperature (K)
T_c	Critical temperature (K)
k	Thermal conductivity (K)
c_p	Specific heat (J/kg-K)
ρ	Density (kg/m^3)
I	Laser Intensity inside the substrate (W/m^2)
α	Absorption coefficient (m^{-1})
t_p	Pulse duration (μs)

The deposition quality and the interfacial bond strength between the polymer and the metallic layer is mainly governed by the surface characteristics of the polymer. Therefore, surface modification plays an important role in the metallization of the polymers. Surface modification based on plasma, wet-chemical or mechanical methods can be used to generate a rough surface to facilitate metallization of the polymer [Oher (2003); Penn and Wang (1994); Dayss et al., (1999)]. However, these processes are not area-selective and rely on the usage of a mask. One of the most superior techniques of polymer surface modification is the photo-chemical treatment by using a laser radiation. The laser radiation causes photo-thermal or photo-chemical decomposition of the polymer surface, generating a highly rough surface. The process is not only fast, but is also area-selective.

Frerichs et al. (1995) carried out surface modification of polymers for subsequent metallization with three different processes viz. laser radiation, wet-chemical and plasma etching processes. The authors observed an evident improvement in surface roughness with laser radiation that resulted in superior adhesive properties between the polymer and the metallic layer. The surface characteristics of the laser modified surface are largely influenced by the laser parameters such as wavelength, intensity, number of pulses and pulse duration. Zhang et al. (2013) carried out laser polymer surface modification process using several industrial lasers and did a comparative study. The authors measured the surface characteristics in terms of surface porosity function. Higher surface porosity was observed to result in a superior metal deposition. Based on the porosity function, the authors experimentally identified the suitable lasers and the range of operating conditions that can result in optimal surface characteristics for better electroless deposition. Horn et al. (1999) performed electroless copper deposition on an excimer laser pretreated poly-butylene terephthalate and observed very strong adhesive properties between the polymer and the deposited metallic layer.

In this work, experiments are carried out to compare the surface characteristics obtained in the presence of air vis-à-vis water and the subsequent deposition characteristics for both the cases. The experiments were carried out using Nd:YAG laser on a polycarbonate surface and the resulting surface characteristics were measured. In addition, a numerical model was developed to estimate the temperature variation during the laser heating process. The study is aimed at understanding the possible reasons that results in improved surface characterisitics for laser processing with ambient water.

Section 2 presents the experimental work. The modeling approach is described in Sec. 3 and the results are discussed in Sec. 4. The important conclusions of the work are summarized in Sec. 5.

2. Experiments

The surface modification experiments were carried out using a Q-switched Nd:YAG laser. The laser properties and the experimental conditions are listed in Table 1. Polycarbonate sheet was used as the substrate material. In order to increase the laser absorptivity of the substrate material, it was doped with light-absorbing pigment particles (micrometers in size) with a weight fraction of 11%. Experiments were carried out both in air and water. In the case of water, the height of the water level was about 2 cm above the polymer surface. The modified surfaces were observed using scanning electron microscopy (SEM).

The laser machined surfaces were activated using a Sn solution and were plated by electroless autocatalytic copper bath (Rohm Haas Circuposit® 3350) at 45 deg. C for 90 min. The thickness of the metallic (copper) layer was measured using FISCHERSCOPE® X-RAY XDVM®-W, which uses X-rays to measure the volume of the metallic layer. The uncertainty of the measuring system is within of 10%. The measured volume is used to estimate the average thickness of the deposited metallic layer.

Table 1. Experimental conditions.

Wavelength	1064 nm
Power	5 W
Pulse duration (t_p)	50
Repetition rate	10-55 KHz
Scanning speed	0.5-1.5 m/s

3. Modeling Approach

To understand the fundamental mechanisms occurring in laser ablation in water that result in a highly porous structure, a 2D numerical model based on the finite volume method was used. The validation of the model was presented by the authors in their earlier work [Marla et al. (2016)]. The polymer sample is represented as a rectangular block (see Fig. 1) with ambient fluid (air/water) on top of it. The laser-matter interaction is assumed to be purely photo-thermal in nature, completely ignoring the photo-chemical aspects. This is a reasonable assumption for an near-IR radiation irradiating a polymer such as polycarbonate. Therefore, the 2D heat conduction equation with a volumetric heat source that represents the absorbed laser radiation was solved to estimate the temperature of the polymer sample. The equation is given by:

$$\rho c_p \frac{\partial T}{\partial t} = k\nabla^2 T + \alpha(x,y)I(x,y). \qquad (1)$$

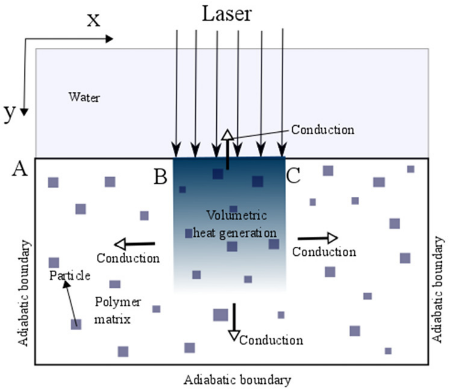


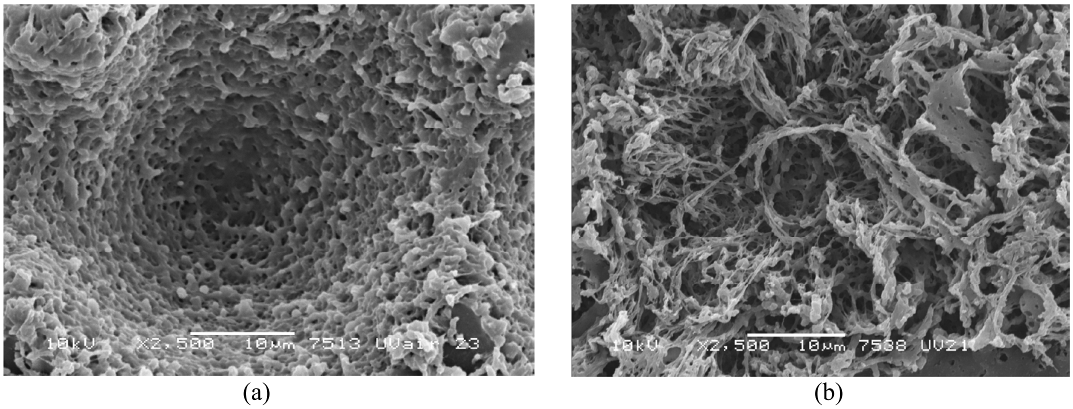
Fig. 1. Schematic of the model.

The last term in Eqn. 1 is the heat source term that represents the laser radiation absorption. The heat source accounts for the heterogeneous nature of heating in the polymer with variable absorption coefficient due to the presence of light absorbing micro-particles (pigments). The particles are assumed to be uniformly distributed. The spatial absorption coefficient $\alpha(x,y)$ depends on the distribution of the particles in the polymer matrix. The spatial variation inside the substrate, $I(x,y)$ is obtained using the Beer-Lambert Law [Marla et al. (2011)]. While the top surface is assumed to be a convective boundary, all the other surfaces are assumed to be adiabatic. The temperature of the ambient (water) was estimated by solving the energy conservation equation. The heat transfer in the ambient fluid is assumed to be due to both convection and conduction.

4. Results and discussion

4.1. Experimental observations

A comparison of surfaces obtained from laser processing of polycarbonate in air and water using SEM images is shown in Fig. 2(a) and 2(b), respectively. Under similar laser processing conditions, the surface characteristics obtained by laser processing in air and in water are quite different. In the presence of air, some of the material is ablated (or vaporized) that leads to formation of a trench on the surface. In comparison, the volume of the ablated material is insignificant with water as ambient fluid. In addition, water is seen to produce a highly porous structure.



(a) (b)

Fig. 2. SEM images of surfaces obtained from laser processing in (a) air and (b) water.

Figures 3(a) and 3(b) show a comparison of the deposited metallic layer thickness for laser processing in air and water at different repetition rates and laser scan speed, respectively. The data are single data points measured with an uncertainity within 10%. The data in Fig. 3(a) were obtained at a contstant scan speed of 1 m/s and in Fig. 3(b) were obtained at a constant repetition rate of 30 KHz. It is evident that deposited metallic layer thickness on a surface laser processed in water is at least 4 times higher in magnitude as compared to those on laser processed in air. It is quite clear that the surface generated using a porous or spongy surface with low ablation as in the case of water is better suited for subsequent electroless deposition. The porous surface could play a major role during the activation process, providing sites for Sn atoms to adhere to the polymer surface. The absence of the porous layer in the case of air may not hold the Sn atoms that help in the subsequent plating process.

The deposition thickness in the case of air (see Fig. 3(a)) decreases with an increase in repition rate and increases with an increase in scan speed. An increase in repetition rate and a decrease in scan speed are related to an increase in laser energy deposition for a given area. This suggests that a lower laser energy irradiation leads to a better deposition characteristics in air, perhaps due to less vaporization of the surface. In comparison, the trend obtained in the case of water is very different. In both cases, the deposition thickness is seen to first increase and then decrease with an increase in repetition rate or scan speed, suggesting that an optimal laser characteristics are required to facilitiate better deposition characteritics. The deposition thickness is much higher in the case of water across the range of parameters considered in the study. Thus, laser processing in water appears to be an efficient surface modification process with low material removal and high surface roughness and porosity.

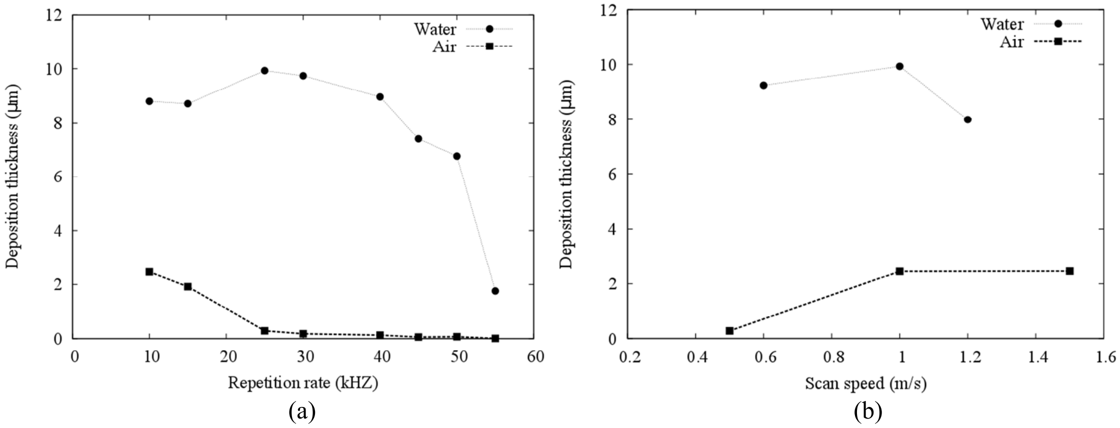


Fig. 3. Thickness of deposited metallic layer at various values: (a) Repitition rate and (b) Scan speed.

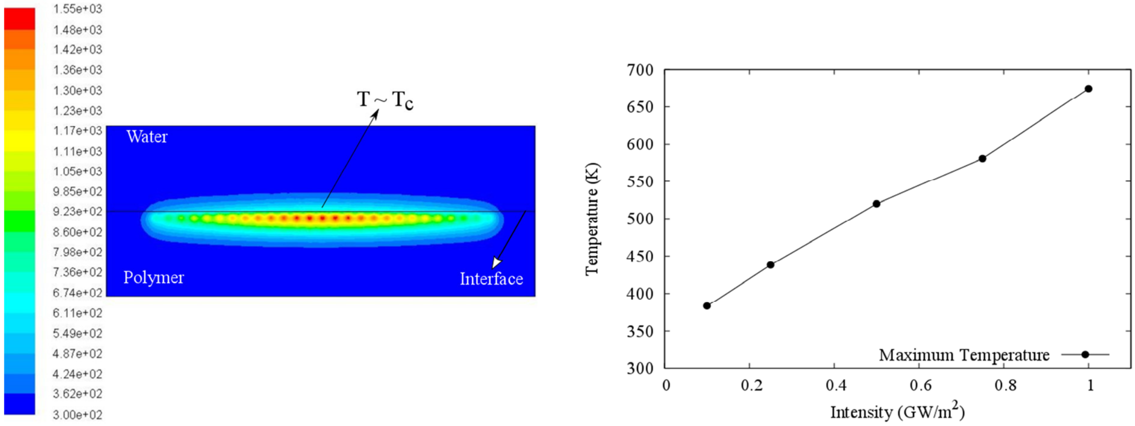
4.2. Simulations of laser processing in water

In order to understand the effect of water on the laser ablation process, numerical simulations were carried out to predict the temperature profile of both polymer and water during the laser heating process. The material properties used in the model are listed in Table 2. Vaporization of water and thermal decomposition of polymer and doped-particles are ignored in the simulations. Water is considered to be transparent to laser radiation; whereas, the absorption coefficient of polymer and particles are taken as 10^3 m^{-1} and 10^6 m^{-1}, respectively. The thermophysical properties of the particles and the polymer are assumed to be the same. The typical range of laser intensity irradiating the polymer surface are in the range of 10^8-10^9 W/m^2. Figure 4 (a) shows the temperature profiles of polymer and water at the end of the pulse (t_p=50 μs) obtained for a single laser pulse of intensity of I_0=10^9 W/m^2. The polymer-water interface is represented by a line. The temperature profile in the polymer is heterogeneous as the model accounts for the presence of light-absorbing micro-particles. These can be clearly seen with a much higher temperature than that of the polymer matrix. Simulations carried out at two different laser intensities with a Gaussian laser pulse suggests that a very narrow region in the water phase (~ 5 μm) at the interface gets heated to high temperatures. Figure 4(b) shows the variation of maximum temperature in the water phase at different intensities of incident laser radiation. The maximum temperature is seen to increase continuously with an increase in laser intensity. In the typical range of laser intensities corresponding to the experimental conditions, the maximum temperature in the water phase is always above the normal boiling temperature (T_b) and is as high as the critical temperature (T_c) for I=10^9 W/m^2.

Table 2. Material properties used in the model.

Property	Polycarbonate	Water
Specific heat (J/kg-K)	1200	4187
Thermal conductivity (W/m-K)	0.2	0.6
Density (kg/m^3)	1215	1000

The high temperature in the water phase at the interface could lead to several mechanisms that could possibly influence the nature of the heating process. Firstly, the high temperature in the water phase near the interface could result in vaporization of water and vapor-bubble generation. The presence of laser-induced vapor bubbles have also been experimentally observed by Isselin et al. (1998). The fact that the temperature can be as high as the critical temperature, there is a possibility of homogeneous nucleation with a very high pressure in the vapor bubbles. The pressure can be as high as 22 MPa (critical point pressure of water), thus exerting a high pressure on the polymer surface resulting in 'water hammer' effect [Zhu et al. (2001)]. It can be argued that the generation of vapor bubbles and the high pressure exterted by them could be the reason for the resulting highly porous surface structure during laser processing of polymers in water. Secondly, the high temperature vapor would absorb the incoming laser radiation due to an increase in its absorptivity and can lead to the formation of vapor plasma above the target surface. Due to its high laser absorptivity, the laser plasma can shield the incoming laser. Thus, reducing the laser intensity falling on the substrate. Plasma shielding is a very well known phenomenon that has been observed to occur in most of the laser-material interactions that involves vapor formation [Marla et al. (2014)]. This plasma shielding effect is perhaps the reason why the polymer does not vaporize as much as it does in the case of laser processing in air.



(a) (b)

Fig. 4. (a) Simulated temperature profile of polymer and water, (b) variation of maximum temperature in the water phase at different laser intensities.

Therefore, the resulting highly porous structure with less vaporization in the case of laser processing in water can be mainly due to vapor bubble generation and plasma shielding effect. In the current paper, the focus is on understanding the possible mechanisms that could result in the formation of a porous structure. However, it is only through a detailed modeling of the bubble generation, plasma formation and other effects that can help us understand the process in a great depth.

5. Conclusions

Laser-based surface modification is seen as a potential pretreatment process in the metallization of polymers using electroless plating. For better deposition characteristics, it is required that the polymer surface is rough and porous. While laser processing in air results in a trench (or hole) caused due to vaporization, laser processing in water generates a highly porous structure with low material removal. The presence of a porous structure helps in enhancing the surface seeding by catalyst (Sn/Pd ions) along the depth and improves the adhesion of metal atoms with the substrate. This subsequently improves the deposition characteristics during the electroless plating process.

The numerical simulations of laser processing in the presence of water suggests that water gets super-heated, which can lead to the generation of vapor bubbles. For higher laser fluences, the water gets heated to the critical temperature that can possibly result in homogenous nucleation. Subsequently, this could lead to exertion of high pressure on the polymer surface. In addition, the presence of vapor can lead to the formation of a dense plasma that could shield the target from the incoming laser radiation. These phenomena occurring in laser processing in water could be the potential reasons for the generation of a highly porous structure on the polymer surface.

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References

Charbonnier, M., Romand., M., 2003. Polymer pretreatments for enhanced adhesion of metals deposited by the electroless process. International Journal of Adhesion and Adhesives. 23(4), 277–285.

Dayss, E., Leps, G., Meinhardt, J., 1999. Surface modification for improved adhesion of a polymer–metal compound. Surface and Coatings Technology. 116–119, 986–990.

Duguet, T., Senocq, F., Laffont, L., Vahlas, C., 2013. Metallization of polymer composites by metalorganic chemical vapor deposition of cu: Surface functionalization driven films characteristics. Surface and Coatings Technology. 19th European Conference on Chemical Vapor Deposition (EuroCVD19). Varna, Bulgaria, 230, 254–259.

Frerichs, H., Stricker, J., Wesner, D. A., Kreutz, E.W., 1995. Laser-induced surface modification and metallization of polymers. Applied Surface Science. 86(1–4), 405–410.

Horn, H., Beil, S., Wesner, D. A., Weichenhain, R., Kreutz, E. W., 1999. Excimer laser pretreatment and metallization of polymers. Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms. 151, 279–284.

Isselin, J., Alloncle, A., Autric, M., 1998. On laser induced single bubble near a solid boundary: Contribution to the understanding of erosion phenomena. Journal of Applied Physics. 84(10), 5766–5771.

Kupfer, H., Wolf, G. K., 2000. Plasma and ion beam assisted metallization of polymers and their application. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 166–167, 722–731.

Marla, D., Bhandarkar, U. V., Joshi, S. S., 2011. Critical assessment of the issues in the modeling of ablation and plasma expansion processes in the pulsed laser deposition of metals. Journal of Applied Physics.109, 021101.

Marla, D., Bhandarkar, U. V., Joshi, S. S., 2014. A model of laser ablation with temperature-dependent material properties, vaporization, phase explosion and plasma shielding. Applied Physics A. 116(1), 273–285.

Marla, D., Zhang, Y., Jabbari, M., Sonne, M. R., Spangenberg, J., Hattel, J. H., 2016. A computational model for heterogeneous heating during laser irradiation of polymers doped with light absorbing micro-particles. Applied Physics A. Under Review.

Mittal, K. L., 1991. Metallized Plastics 2: Fundamental and Applied Aspects. In: Springer US, Boston, MA., pp. 81–95.

Oehr, C., 2003. Plasma surface modification of polymers for biomedical use. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 208, 40–47.

Penn, L. S., Wang, H., 1994. Chemical modification of polymer surfaces: a review. Polymers for Advanced Technologies. 5(12), 809–817.

Stremsdoerfer, G., Ghanem, F., Saikali, Y., Fares-Karam, A., 2003. Copper deposition by dynamic chemical plating. Journal of Materials Science. 38(15), 3285–3291.

Zhang, Y., Hansen, H. N., De Grave, A., Tang, P. T., Nielsen, J. S., 2011. Selective metallization of polymers using laser induced surface activation (LISA)—characterization and optimization of porous surface topography. The International Journal of Advanced Manufacturing Technology. 55(5-8), 573–580.

Zhang, Y., Hansen, H. N., De Grave, A., Tang, P. T., Nielsen, J. S., 2013. Verification of a characterization method of the laser-induced selective activation based on industrial lasers. The International Journal of Advanced Manufacturing Technology. 68(5-8), 1775–1783.

Zhu, S., Lu, Y. F., Hong, M. H., Chen, X. Y., 2001. Laser ablation of solid substrates in water and ambient air. Journal of Applied Physics. 89(4), 2400–2403.