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Surface modification of PVDF by plasma treatment for electroless metallization

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Surface properties of polyvinylidene fluoride (PVDF) films have been modified in a controlled manner, by treatment in a radio frequency nitrogen plasma, and a microwave one, at different treatment powers. It was proved that both plasma treatments significantly improved the adherence and the quality of the deposited metal layer. The RF plasma treatment seems to be less efficient in respect with the microwave plasma one, for small powers, but the obtained results are similar at discharge powers higher than 50 W.

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1. Introduction

Polyvinylidene fluoride (PVDF) films are very useful in a wide range of applications, such as: different types of sensors, automotive, pipes and fittings, bearings, linings and vessels, wire insulation [1,2]. Unfortunately, the poor adhesion strength of the metal directly deposited onto PVDF film, which is a consequence of its low free surface energy, has to be overcome. Plasma technology, corona discharge, bombardment with charged particles have been used in order to improve the wettability, printability, biocompatibility and other related surface properties of the polymeric materials [3]. Low-pressure plasma treatment is a well-known method to modify the surface of polymers [4], presenting advantages in contrast to chemical treatments. It is a fast treatment, it is suitable for the treatment of complex geometric samples and it modifies the surface chemistry producing an increase in the adhesion properties [5].

In this work, there are presented some results on surface modifications of PVDF properties under nitrogen microwave and, respectively, radiofrequency (RF) plasmas. Subsequent copper deposition has been realized on the pre-treated samples, evidencing the properties and the morphology of the deposited metal layer, as well as the adherence between this one and the PVDF surface.

2. Experimental

Films of non-piezoelectric polyvinylidene fluoride (PVDF) (0.25 mm in thickness) have been purchased from Goodfellow, UK. This fluorinated polymer is a white, semi-crystalline, semi-opaque one. Its density is 1.76 g/cm^3 and its upper working temperature ranges between 135 and 150 ºC. The solvents and the other chemicals were of reagent grade. They were purchased from Aldrich and were used as received.

A previous study was followed on PVDF treated in a microwave nitrogen plasma [6], in the following conditions: gas flow=10 sccm (standard cubic centimeter per minute), distance between the bottom of the excitator and the sample=10 cm (afterglow region), treatment duration= 1 min, and treatment power comprised between 20 and 80 W.

PVDF films have been also treated in a radiofrequency nitrogen plasma (the gas flow: D=10 sccm, the exposure time: t=120 s), at different treatment powers (P) (25, 50, and 75 W). The choice of a higher treatment time in the case of RF plasma treatment when compared with the case of the microwave one was done due to the smaller frequency of the first one [7,8].

Properties and morphology of PVDF films before and after plasma treatment have been measured by contact angle measurements, scanning electron microscopy (SEM), ATR-FTIR spectroscopy, and atomic force microscopy (AFM).

Pre-treated PVDF samples have been covered with a copper layer, using an electroless plating procedure, previously described [9]. The mass and the thickness of the deposited copper layer, as well as the thermodynamic work of adhesion between the metal layer and the polymer samples have been determined.

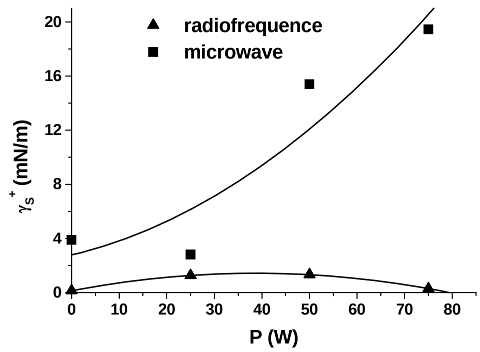
3. Results and discussion

3.1. Modification of PVDF properties under plasma treatment

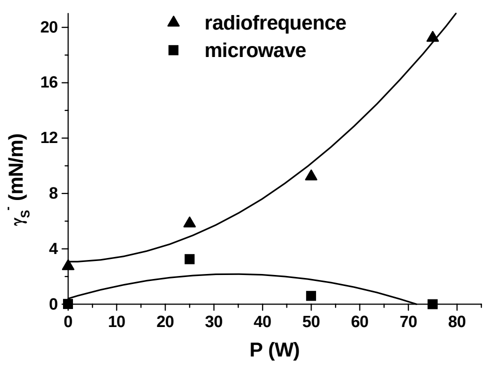
Components of the free surface energy and the total surface energy for PVDF treated in the two types of plasma are presented in Table 1 and Fig. 1. Lifshitz-van der Waals component (γ_s^{LW}) is much stable for the surfaces RF plasma treated, while for those exposed in a microwave plasma it takes higher values for a discharge power comprised between 20 and 50 W. The acid-base component of the free surface energy (γ_s^{ab}) continuously increases with the discharge power for the polymer treated in both plasmas. This behaviour could be explained by the fact that N_2 or NH_3 plasma treatments give rise to N–containing functionalities, such as: amine ($-NH_2$), imine (–CH=NH), nitrile (–C≡N) on polymer surfaces, as well as oxygen–containing groups, such as amide ($-CONH_2$), due to post-discharge atmospheric oxidation [10], as it was also evidenced by ATR-FTIR (see Table 2). The bigger values of the free surface energies and of its components in the case of the microwave plasma treatment than in RF plasma treatment could be explained by the higher energy of the former one, which induces a higher ion density. However, at high powers, the type of the used discharge seems to not have a significant effect on these properties.

Table 1. Components of the free surface energy and of the total surface energy for PVDF treated in RF and MW nitrogen plasma.

P (W)	γ_s^{LW} (mN/m)		γ_s^{ab} (mN/m)		γ_s (mN/m)	
	microwave	RF	microwave	RF	microwave	RF
0	33.93	33.93	2.88	2.88	34.32	34.32
25	36.33	34.00	5.8	7.08	42.39	41.09
50	37.66	34.56	15.8	10.55	53.66	45.11
75	33.72	33.35	19.5	19.52	53.17	52.87



a



b

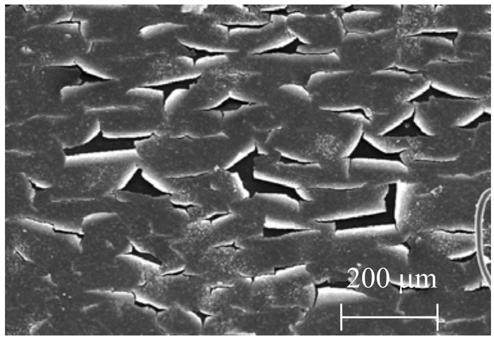
Fig. 1. Electron acceptor (a) and electron donor (b) components of the free surface energy for PVDF plasma treated.

Table 2. Bands evidenced in FTIR-ATR spectra of PVDF plasma treated.

ν (cm^{-1})	Assigned group
600 – 650	C–F
1000 – 1400	$-NH_2$
1300	C–N
1600	C=C
1600 – 1800	C–F, oxygen containing groups
1700	C=O
2800 – 3100	CH_2
2850, 2920	C=C
2880 – 2958	$-NH_2$
3300	N–H

3.2. Results on the metallization of the pre-treated PVDF films

PVDF-plasma pretreated films have been subsequently covered with a copper layer, by means of an electroless plating procedure.



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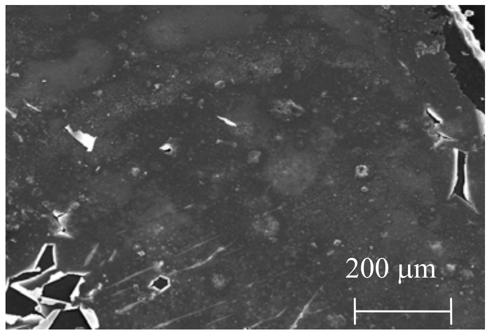

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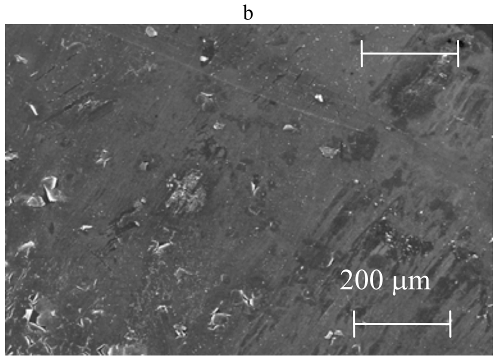

c

Fig. 2. SEM micrographs for metallized PVDF: untreated (a); RF plasma treated, at 25 W (b) and 50 W (c). Magnification: 97 X.

SEM results evidenced that all the pre-treated samples have a higher degree of coverage with copper than the untreated film, the layer of copper being more homogeneous. The smoothness of the copper layer deposited on PVDF surface significantly increased with the treatment power (Fig. 2).

The amount of the deposited copper and the thickness of the metal layer were significantly higher for the treated PVDF samples in respect to the untreated one (Fig. 3).

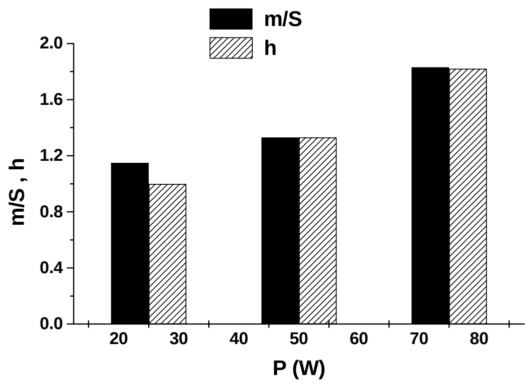

Fig. 3. The quantity of deposited copper reported to the area unit of the sample (m/S) and the thickness of the copper layer (h) vs the treatment power. The values are reported to those corresponding to the untreated sample.

Evaluation of the thermodynamic work of adhesion between the deposited copper layer and PVDF surfaces on the basis of free surface energy determination evidenced an increase of this one with increasing the treatment power (Fig. 4). This fact is a proof of the improvement of the copper adhesion at the treated PVDF surfaces, compared to the pristine sample. This behaviour could be explained by the introduction of polar groups at PVDF surface plasma treated, thus allowing favorable acid-base interactions at the polymer-metal interface. In the meantime, the improved adhesion could be due to the increase of the surface roughness with the treatment power (AFM technique evidenced an increase of PVDF roughness after plasma treatment comprised between 1.12 and 1.39, depending on the discharge power).

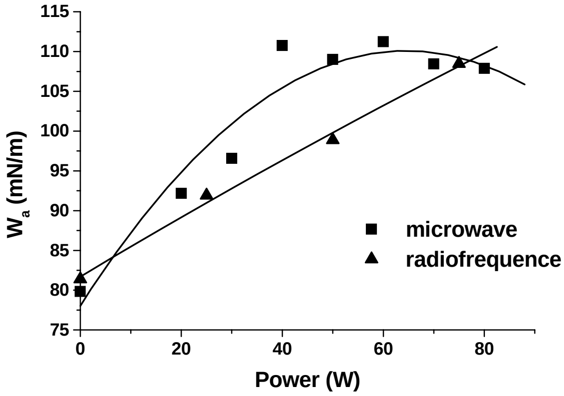

Fig. 4. Thermodynamic work of adhesion between the deposited copper layer and PVDF surfaces plasma treated vs the discharge power.

4. Conclusions

Well adhering coating on polymer films requires a convenient pre-treatment. Modification of the surface properties of PVDF films by microwave and RF nitrogen plasma exposure, using appropriate treatment conditions, induced a significantly improved homogeneity and adhesion of the copper layer to the polymer surface. The RF plasma treatment seems to be less efficient in respect with the microwave plasma one, for small powers, but the obtained results are similar at discharge powers higher than 50 W.

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