Plasma polymer / metal composites: role of the structure and the nature of the polymer matrix on the distribution of metal nanoparticles

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Abstract: The amount and distribution of metal nanoparticles (AgNPs) in a plasma polymer matrix are studied according to the chemical structure and the nature of the polymer. The structure of the polymer (polyallylalcohol, pp-AAl) is modified by varying the plasma parameters such as polymerization time, input power and (post)-discharge times. Moreover, two other matrices are studied: plasma polyaniline (pp-ANI) and plasma polyheptadecafluoro-1-decene (pp-HDFD).

Keywords: plasma polymer/metal nanocomposites, silver nanoparticles, metal distribution.

1. Introduction

Among the several approaches to elaborate polymer/metal nanocomposites, the generation of metal nanoparticles from a metal precursor in the polymer, considered as a simple route, can be carried out by mixing the polymer with the metal salt then reduced by different physical (photoirradiation, thermal treatment) or chemical treatments [1,2]. In a lot of studies, the polymer matrix is synthesized by conventional ways (chemical or electrochemical ones) [3-6].

In our work, the matrix is synthesized by plasma polymerization which is an ecofriendly process (e.g., solvent free) compared to conventional methods. Different plasma polymers with different functional groups are chosen, containing nitrogen (polyaniline), alcohol)), fluorine oxygen (poly(allyl or (poly(heptadecafluoro-1-decene)) functions. The polymers are then impregnated in AgNO₃ metallic solution followed by a chemical reduction in NaBH₄ in order to generate silver nanoparticles (AgNPs). In the literature, these composites have been mainly studied for their antibacterial properties whereas their chemical and morphological structures have been little examined [7,8].

The objective of this work is thus to study the distribution of AgNPs and their interactions with the different matrices according to the nature of the functional groups of the polymers and their chemical structure (cross-linking, concentration of functional groups...).

2. Experimental

Plasma polymerized (pp) aniline (ANI), allyl alcohol (AAl) and heptadecafluoro-1-decene (HDFD) have been synthesized and deposited in a cylindrical aluminium reactor capacitively coupled with two parallel electrodes with a r.f. generator (13.56 MHz). The adhesion of the plasma polymer layers to the different types of substrates was enhanced by argon plasma pre-treatment (P = 100 W, F = 10 sccm, t = 1 min). pp-ANI, pp-AAl and pp-HDFD films have been elaborated in pulsed mode at a power equal to 30 W, a duty cycle (D.C.) of 50% (defined as D.C. = discharge time (t_{on}) / (discharge (t_{on})+post-discharge (t_{off}) times), and a frequency of 30 kHz. In order to avoid thickness dependence, different deposition times

(8, 20, and 5 min, respectively for the polymerization of ANI, AAI and HDFD) were selected to obtain the same thickness of about ~285 \pm 5 nm. The plasma polymers were then successively dipped in 0.1 M AgNO₃ for 3 h and 0.1 M NaBH₄ aqueous solutions for 1 h at room temperature and under continuous stirring. Between each step, the composites were rinsed with distilled water and dried with air.

3. Results and discussion

3.1. Influence of the polymer structure on AgNPs distribution

The plasma polymer structure depends on the plasma parameters such as the polymerization time, the input power (*P*), the discharge (t_{on}) and post-discharge (t_{off}) times. This study has been done with pp-AAl as matrix.

The increase of the polymerization time in the range 5-30 min leads to an increase in the silver nanoparticle concentration in the plasma polymer. Such a rise of AgNPs concentration can be explained by the roughness increase observed when varying the polymerization time improving the mechanical anchoring of metallic particles.

The study of the input power and discharge time has been conducted thanks to XPS analysis. The C1s high resolution XPS spectra of pp-AAl elaborated in different conditions can be decomposed in four components at (i) 285 eV attributed to C-C, C-H, C=C; (ii) 286.4 eV assigned to C-OH/R; (iii) 287.8 eV due to C=O and (iv) 289.2 eV assigned to COOR. It appears that all the oxygenated groups decrease when P or ton raises, especially the C-OH/R groups as shown in Figure 1. This figure shows also the decrease of the Ag percentage in high energy plasma. It appears than that the OH functional groups enable pp-AAl to interact with metal ions from aqueous solution and fix them in the matrix by dipole-ion attraction. A lower hydroxyl content is then associated to a lower amount of metal particles, as proved by XPS quantification giving 0.9% of silver for P = 30 W and $t_{on} = 17 \ \mu s$, and 0.2% for the other two conditions.



Fig. 1. XPS quantification of C-OH/R groups and Ag NPs in pp-AAl matrix elaborated under different plasma conditions.

Concerning the effect of t_{off} , a higher quantity of hydroxyl groups is observed in the polymer when elaborated at higher t_{off} (Figure 2). Therefore, an important amount of AgNPs should be introduced in the matrix. However, we observe a delamination of the polymer from the substrates if synthesized at high t_{off} as shown in Figure 2. No AgNPs can then form in the polymer. Therefore, a compromise has to be found between a high amount of hydroxyl groups and the mechanical properties of the matrix.



Fig. 2. FTIR spectra of pp-AAl and the composites before and after reduction, with pp-AAl elaborated at

(a) $t_{off} = 17 \text{ } \mu \text{s or (b)} t_{off} = 150 \text{ } \mu \text{s } (P = 30 \text{ } \text{W}, t_{on} = 17 \text{ } \mu \text{s})$

3.2. Influence of the polymer nature on AgNPs distribution

Different matrices have been studied containing various functional groups such as amine (pp-ANI), hydroxyl (pp-AAl) and fluorinated (pp-HDFD) ones. The objective is to study the interactions between AgNPs and the different matrices that are going to influence the amount and the distribution of the metal in the polymer.

The silver atomic percentage depends on the nature of polymer, since pp-ANI shows the most significant amount of silver (4.9%), then pp-AAI (0.9%) and pp-HDFD matrix (0.1%). One of the main reasons for this difference is the type of interaction that exists between the polymer functional groups and the metal ions. In order to study these interactions, the Ag 3d high resolution XPS spectra have been decomposed (Figure 3).



Fig. 3. Ag 3d_{5/2} high resolution XPS spectra of (a) pp-ANI, (c) pp-AAl, (e) pp-HDFD after impregnation, and (b) pp-ANI, (d) pp-AAl, (f) pp-HDFD after impregnation+reduction.

For pp-ANI (Figures 3-a,b) and pp-AAI (Figures 3c,d) matrices containing silver, the Ag $3d_{5/2}$ peak envelop is decomposed into two components at 366.9 eV and 368.9 eV, which correspond to silver oxide (Ag^{+I}) and metallic silver (Ag°) , respectively. It is known that a metal ion having a higher standard potential $(E^0(Ag^+/Ag) = 0.8$ V) than a polymer, once in contact, can be spontaneously reduced by this last to form zero-valent metal. This is the case of pp-ANI used as a polymeric matrix and as silver reducing agent. The incomplete reduction even after adding NaBH₄, may be explained by the strong interaction between Ag⁺ and nitrogen functions, and the possible formation of complex as shown by XPS (Figures 3-a,b).

Based on the standard potential of pp-AAl (E^0 (C=O/C-O) = -0.16 V), Ag⁺ is reduced to the metallic form (97.2 % of Ag[°]) by this last (Figures 3-c,d). Contrary to pp-ANI, no silver ions are observed after reduction, and all the remaining Ag⁺ ions are converted to Ag[°] by NaBH₄ which is a stronger reducing agent (E^0 (H₂BO₃⁻/BH₄⁻ = -1.24 V) than the polymer matrix. Therefore, the only type of interaction between Ag⁺ and OH functions is the electrostatic one.

For pp-HDFD (Figures 3-e,f), the $Ag3d_{5/2}$ decomposition shows that silver is present in its metallic state. Due to the weak interaction between silver ions and the fluorine components (0.1% Ag), it can be predicted that the oxygen functions present in a very small quantity (0.4%) could interact with the silver ions and reduce them.

Therefore, the plasma polymers play the role of reducing agents, contributing to the formation of metallic particles.

The samples were investigated by transmission electron microscopy (TEM) to visualize the size and

shape of silver particles. Spherical nanoparticles of 7.4 \pm 0.4 nm and 12 \pm 1.2 nm mean diameter are obtained for pp-AAl and pp-ANI as matrices, respectively (Figure 4). The smallest metal inclusions with the narrowest size distribution are produced by using pp-AAl (Figures 4-b,e). For pp-HDFD, the weak chemical affinity between silver and the fluorocarbon film contributes to aggregate silver nanoparticles, inducing a broader size distribution in the range of 6 to 40 nm (Figures 4-c,f). Accordingly, we can say that silver nanoparticles likely prefer to interact with each other rather than with the pp-HDFD matrix.



Fig. 4. TEM images and Ag particle size distribution of (a,d) pp-ANI, (b,e) pp-AAl, and (c,f) pp-HDFD after impregnation+reduction.

4. Conclusion

To summarize, the highest amount of metallic NPs in the plasma polymer matrix is obtained when the latter is elaborated under low energy plasma conditions. However, the mechanical properties of the polymer must be taken into account. Moreover, all the polymers are able to reduce AgNPs allowing then to avoid the reduction step. In terms of silver amount, pp-ANI with amine functions shows a very pronounced affinity towards AgNPs, in comparison to the other polymer matrices explained by the structure of pp-ANI rich in π electrons.

5. References

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