J Mater Sci (2011) 46:7917–7922
DOI 10.1007/s10853-011-5920-y

LETTER

Au nanoparticles grafted on plasma treated polymers

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Received: 4 July 2011 / Accepted: 30 August 2011 / Published online: 15 September 2011

Introduction

Surface modification of commonly used polymers has been of increasing interest during last decades [1]. The formation of hydrophilic structures on polymer surface improves wettability, dyeing capacity, and biocompatibility of polymers without altering their favourable bulk mechanical and physical properties. Proper surface modification offers an easy way to increase the reactive potential of rather non-reactive surfaces of pristine polymers through introduction of new functional groups. Functionalized surfaces with high concentration of reactive and easily accessible groups seem to be of interest for the development of biocompatible materials, which could accept and immobilize amino acids and proteins [2]. Also, immobilization of a hydrophilic polymer onto hydrophobic surface of another polymer is not feasible without a special pre-treatment to enhance the surface polarity and reactivity of the polymer substrate [3].

Nanoparticles are at the centre of research interests because of their unique physico-chemical and optoelectric properties which are of interest for fundamental and applicational reasons [4, 5]. Ordered arrays of nanoparticles have been applied in optical, electronic and biosensing devices [6–8], but their utilization is strongly dependent on the availability of the techniques employed to immobilize the nanoparticles onto solid substrates. Usually, the immobilization can be performed via covalent or an electrostatic interaction between the nanoparticles and solid substrates [9–11].

Gold nanoparticles, due to their unique electrical, optical and photophysical properties, are expected to play a role in variety of potential applications as electronic and sensor materials [12–15]. Because of its well known stability, non-reactivity and bioinertness the gold is used with advantage in medical diagnostics [16], Raman spectroscopy [17], biological imaging [18] and biosensors [19]. The structures, combining gold nanoparticles with polymers, are promising materials for biomedical applications [20, 21]. Since gold is the most inert metal, the adhesion between gold nanoparticles and polymers is expected to be very poor. However, gold can easily react with thiol (-SH) groups, which can be fixed on the polymer surface modified beforehand in a proper manner e.g. by plasma discharge, irradiation with ultraviolet light from an excimer lamp or by ion irradiation [22–25].

In this study surfaces of four thermoplastic polymers (polyethylene, polyethyleneterephthalate, polytetrafluoroethylene and polystyrene) were modified by plasma discharge and subsequently grafted with dithiol to introduce thiol (–SH) groups. Dithiol is expected to be fixed via one of its –SH groups to radicals created by the preceding plasma treatment. The other free –SH group is allowed to interact with gold nanoparticles (see schema in Fig. 1). The main goal of this study is to examine the effect of the plasma treatment and the dithiol grafting on the binding of gold nanoparticles on the polymer surface. Surface chemistry and radical concentration of four thermoplasts (pristine and modified by the plasma discharge) are studied by

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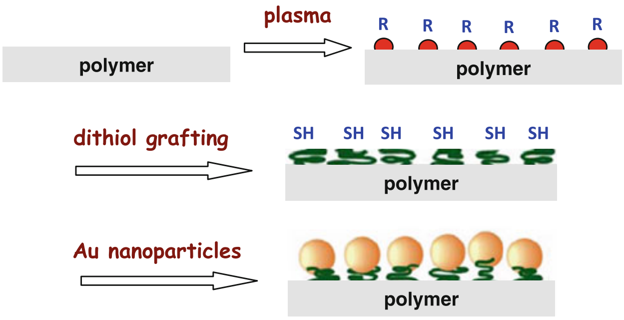

Fig. 1 Scheme of polymer modification by plasma activation (R-radical), grafting with dithiol (-SH) and with gold nanoparticles

X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR). Characterization of the surface morphology and the roughness of the plasma treated polymers and vizualization of gold nanoparticles is accomplished by atomic force microscopy (AFM).

Experimental

Materials, plasma modification and grafting

Biaxially oriented high density polyethylene (PE, density 0.952 g cm^{-3}) in the form of 40 μm thick foils (supplied by Granitol Ltd., Czech Republic), biaxially oriented polyethyleneterephthalate (PET, density 1.3 g cm^{-3}, 23 μm foil, Goodfellow Ltd., UK), polytetrafluoroethylene (PTFE, density 2.2 g cm^{-3}, 50 μm, Goodfellow Ltd.) and biaxially oriented polystyrene (PS, density 1.05 g cm^{-3}, 30 μm, Goodfellow Ltd.) were used in this study.

The samples were modified in direct (glow, diode) Ar^{+} plasma on Balzers SCD 050 device under following conditions: gas purity 99.997%, flow rate 0.3 L s^{-1}, pressure 10 Pa, electrode distance 50 mm and its area 48 cm^{2}, chamber volume approximately 1000 cm^{3} and plasma volume 240 cm^{3}. Exposure time was 120 s, discharge power 8.3 W and the treatment was accomplished at room temperature.

Immediately after the plasma treatment the samples were inserted into methanol solution of biphenyl-4,4′-dithiol (Figs. 2a, 5.10^{-3} mol L^{-1}) for 2 h. This dithiol form, with its rigid structure, was chosen to eliminate binding by both available –SH groups to activated polymer surface. In a control experiment the etching of the modified polymer surface by methanol was also examined in 2 h leaching [26, 27]. To coat the polymers with the gold nanoparticles the plasma treated samples were immersed for 2 h into freshly prepared colloidal solution of Au nanoparticles (see Fig. 2b), about 25 nm in diameter (citrate reduction [25, 28]). Finally the samples were immersed into distilled water and then dried under N_2 flow.

Diagnostic techniques

Properties of the samples modified by the plasma treatment, by etching and grafting with dithiol and coated with gold nanoparticles were studied using various methods mentioned above.

Concentrations of O, C, F, Au and S in the modified surface layer were measured by X-ray photoelectron spectroscopy (XPS) 24 h after the grafting with Au nanoparticles. Omicron Nanotechnology ESCAProbeP spectrometer was used to measure photoelectron spectra (error of 10%). Exposed and analyzed area had dimension 2 × 3 mm^{2}. X-ray source was monochromated at 1486.7 eV with step size 0.05 eV, the take off angle was 0° according to surface normal. The O1s, C1s, F1s, S2p and Au4f peaks were studied. The spectra evaluation was carried out by CasaXPS programme [25].

Surface morphology and roughness of pristine and modified samples were examined by AFM using VEECO CP II setup (both of tapping and phase modes). Si probe RTESPA-CP with the spring constant 0.9 N m^{-1} was used. By repeated measurements of the same region (1 × 1 μm^{2}

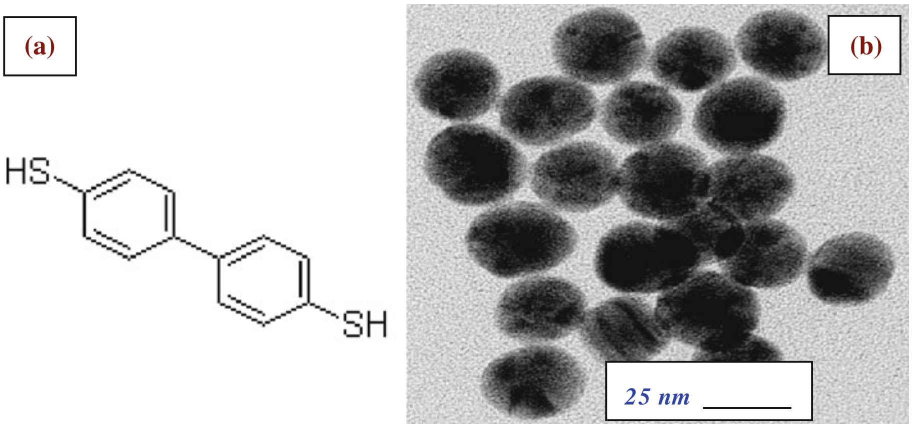

Fig. 2 Molecular structure of biphenyl-4,4′-dithiol (**a**) and TEM images of gold nanoparticles from transmission electron microscope (**b**). For structural characterization we use TEM (JEOL JEM-1010, USA) operated at 80 kV

in area) we certified that the surface morphology did not change after five consecutive scans. The mean roughness value (R_a) represents the arithmetic average of the deviations from the centre plane of the sample.

The concentration of free radicals, with an error of 5%, was determined by electron paramagnetic resonance spectroscopy (EPR) with an x-band spectrometer Elexsys E-540, Bruker-Biospin. The samples were placed in a quartz tube and measured 5 h after the treatment (methanol resp. dithiol) at RT. The experimental conditions were as follows: the magnetic field range 600 mT, sweep time 180 s, magnetic modulation 0.4 mT and field modulation 100 kHz. The standards Mn/ZnS and Cr/MgO were used for the g-factor calibration and for quantitative evaluation of the spectra. Identification and evaluation of EPR signals were performed by comparison with the standards [29].

Results and discussion

Chemical structure of modified surface layer

Plasma treatment leads to a cleavage of chemical bonds (C–H, C–C and other), to an ablation of the polymer surface layer, creation of free radicals and conjugated double bonds [28]. Activated polymer surface can be grafted with molecules, e.g. with thiol groups. The binding of the molecules is mediated by free radicals, present on the activated surface. The binding on double bonds has not been proved in previous experiments [25]. The bond breaking leads to fragmentation of the polymer chain and to the ablation of polymer surface. Cleavage of the molecular chains and creation of low mass molecular fragments facilitates solubility of the initially insoluble polymer in common solvents, e.g. water, methanol [26, 27].

Radical concentration (spin amount), determined by EPR method on the plasma treated, methanol etched and dithiol grafted polymers is shown in Fig. 3. It is seen that, after the plasma treatment, free radicals are created on the polymer surface but the radical concentration is strongly different in different polymers. The highest concentration of the free radicals is found on the plasma treated PS and a slightly lower concentration on PTFE. This can be due to the higher ablation rate of PTFE with its well known low radiation resistance [29, 30]. The free radical created on PTFE may partially be removed from the PTFE surface during the plasma treatment thanks to higher PTFE ablation rate. The radical concentrations on the plasma treated PET and PE are significantly lower. Exceptionally high radical concentration on the plasma treated PS is probably due to the stabilization of the radicals by a mesomeric effect of the benzene rings, the process which is known in organic chemistry [29].

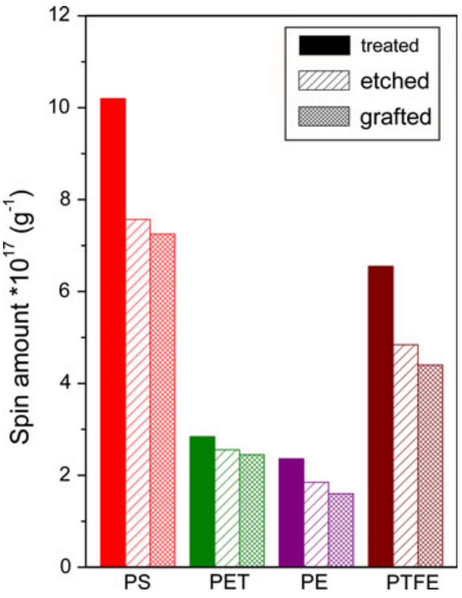

Fig. 3 Spin amount (i.e. free radical concentration) determined for PET, PS, PE and PTFE, plasma treated for 120 s, methanol etched (etched) and then grafted with gold nanoparticles (grafted). The measurement was accomplished 2 h after the plasma treatment, 15 min after the etching and 15 min after the gold nanoparticles grafting

By the EPR method the effect of the etching of the modified polymers in methanol was examined too. This is important since the methanol is used for grafting with gold nanoparticles and the effects of etching and grafting should be resolved in this way. From Fig. 3 one can see that the etching leads to a dramatic decrease of the radical concentrations especially on PS and PTFE. It was found earlier that the oxygen in the plasma treated PS (and in the PTFE too) is bound to low-molecular degradation products (LMWOS-low-molecular weight oxidized structures [30]) and that its content decreases after the sample rinsing. The rinsing of the free radicals, observed in the EPR spectra, may initiate a cross-linking in the polymer surface layer. This process has actually been observed in a couple of previous articles [31, 32]. It is further seen from Fig. 3 that the treatment of the plasma activated surface of all polymers with dithiol (–SH) results in another significant decrease of free radical concentration, the decrease indicating that the dithiol is mostly bound to degraded molecular chains via free radicals.

The composition of 8–10 first surface atomic layers of pristine and plasma treated polymers, dithiol grafted and coated with gold nanoparticles polymers was investigated using XPS method. Typical XPS spectrum for modified PTFE is shown in Fig. 4. Concentrations of C, O, S, Au and F, determined by XPS in pristine and plasma treated and with dithiol and Au nanoparticles grafted polymers, are shown in Table 1. In polymers with no initial oxygen

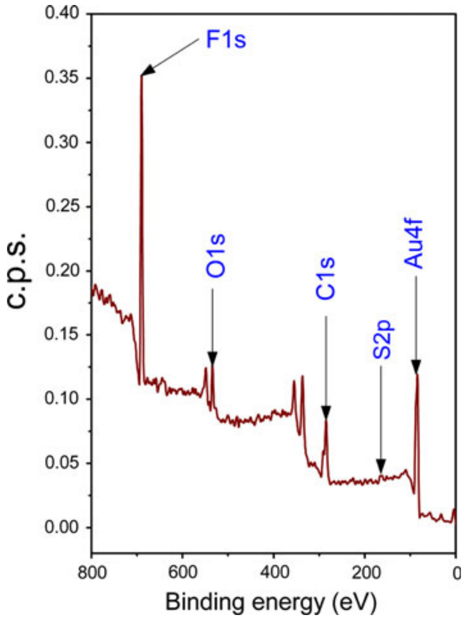

Fig. 4 XPS spectrum of the plasma treated and with dithiol and Au nanoparticles grafted PTFE. The F(1s), O(1s), C(1s), S(2p) and Au(4f) peaks are clearly seen

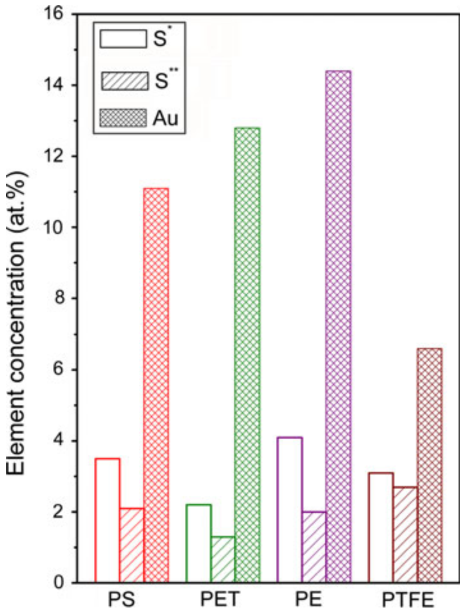

Fig. 5 Concentration of sulphur and gold in the polymer surface layer, after the dithiol grafting (S^*) and after the dithiol and gold nanoparticles grafting (S^{**})

content, the oxygen appearance is a result of unintentional oxidation during the plasma treatment. After the treatment the highest oxygen concentration was found in PE, lower in PS and lowest in PTFE. In PET a decrease of the oxygen concentration is observed after the plasma treatment. The decrease indicates that the degradation of the oxygen containing groups outweighs their production. Low oxygen content in the PTFE maybe due to the high ablation rate of PTFE [29]. It was shown previously that the carbonyl, carboxyl and ester groups are created in the polymer surface layer by the oxidation [33, 34]. The thickness of the polymer surface layer affected by the plasma discharge is estimated to be about 60 nm, according to RBS measurement [35, 36].

Concentrations of sulphur and gold in the surface layer of polymers after the dithiol grafting (S^*) and the dithiol and gold nanoparticles grafting (S^{**}) are shown in Fig. 5. It is seen from Fig. 5 that the grafting with the gold nanoparticles leads to a decrease in the sulphur concentration in all polymers examined. The effect is observable due to the fact that the XPS method is sensitive only to 8–10 surface atomic layers [37]. Fraction of the sulphur atoms on the samples grafted with gold nanoparticles is in gold "shadow" and can not be seen in XPS spectra. With only exception of PTFE, the sulphur concentration declines about twice after the coating with the gold nanoparticles but the gold concentration remains relatively high. This is understandable since the gold is not bound as single atoms but in the form of nanoparticles, 25 nm in diameter. From the comparison with Fig. 3 it is seen that the sulphur concentration is not correlated with the free radicals concentration in the polymer surface layer (compare e.g. PTFE and PE). The observed differences in the sulphur and free radical concentrations maybe due to different surface

Table 1 Elements [C(1s), O(1s), S(2p), Au(4f) and F(1s)] concentrations (in at.%) determined from XPS measurements in pristine PS, PET, PE and PTFE, those plasma treated for 120 s (treated) and grafted with dithiol and Au nanoparticles (grafted) (polymer/plasma/SH/Au)

Sample	Element concentration (at.%)				
	C(1s)	O(1s)	S(2p)	Au(4f)	F(1s)
Pristine PS	100	–	–	–	–
PS/plasma/SH/Au	73.9	12.9	2.1	11.1	–
Pristine PET	72.4	28.6	–	–	–
PET/plasma/SH/Au	68.3	17.9	1.4	12.4	–
Pristine PE	100	–	–	–	–
PE/plasma/SH/Au	70.3	13.1	2.0	14.6	–
Pristine PTFE	33.4	–	–	–	66.6
PTFE/plasma/SH/Au	56.6	8.3	2.7	6.6	25.8

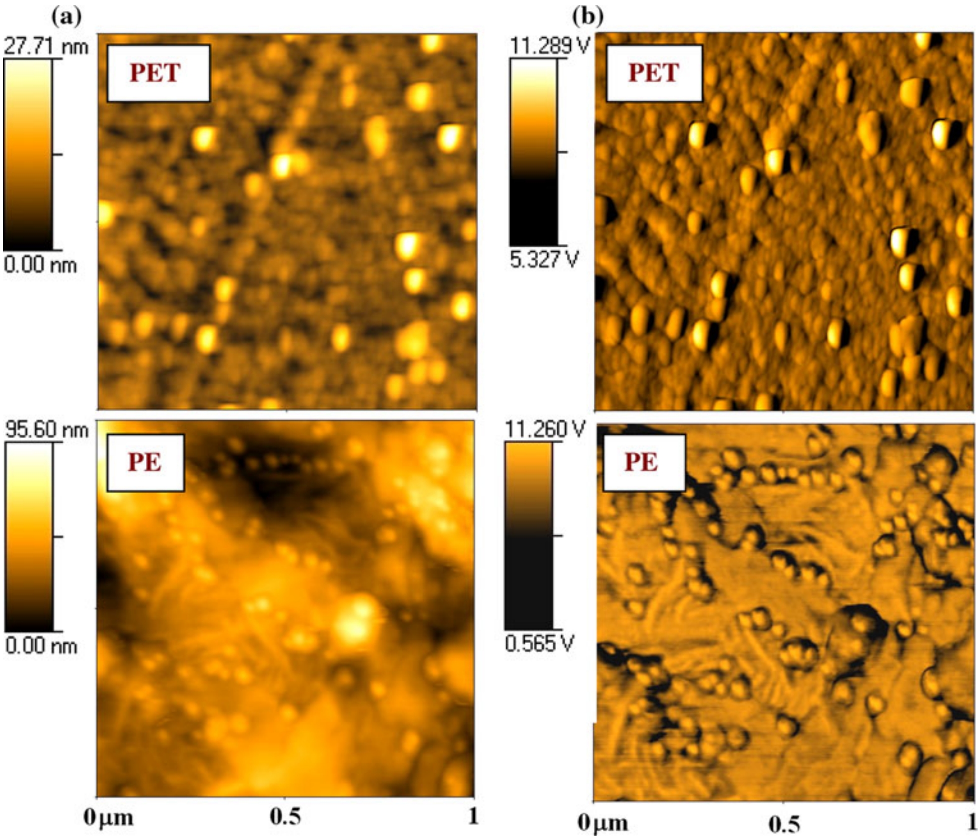

Fig. 6 AFM images of PE (**a**) and PET (**b**) treated by plasma, grafted by dithiol and then grafted with Au nanoparticles taken in tapping (*left*) and phase mode (*right*)

roughness of the polymers after the plasma treatment [29]. There are also differences in the accessible depths between different diagnostic methods. Whilst the EPR determines the free radical content in whole modified surface layer, the XPS is sensitive only to first few atomic layers.

Surface homogeneity of Au nanoparticles on polymers

Surface morphology of polymers, plasma treated and then grafted with dithiol and gold nanoparticles, was studied by AFM method. The results are illustrated in Fig. 6 where the images from the initially unpolar PE and polar PET are compared. For the sake of completeness the AFM images, taken in both tapping and phase modes are shown. The distribution of the gold nanoparticles over the polymer surface is probably affected by the polymer surface morphology which is changed by the plasma treatment. After the plasma treatment the surface roughness of PE ($R_{a\ PE} = 8.4$ nm) is significantly higher than that of PET ($R_{a\ PET} = 1.9$ nm) [29]. The gold particles are spread homogenously on the polymer surface but on the PET a particle aggregation is observed.

Grafted gold nanoparticles do not create continuous coverage of the polymer surface and it is therefore not surprising that the electrical resistance of the gold coated samples is the same as for pristine polymers [25]. From Fig. 6 (AFM) and Table 1 (XPS) it is evident that more gold nanoparticles is grafted onto the surface of plasma treated PE in comparison to PET.

The gold nanoparticles homogenously distributed over the polymer surface may have a positive effect on interaction with living cells (tissue engineering) [26] or they may facilitate adhesion of additional gold structures to polymeric substrates (electronics) [25].

Conclusion

It was shown that the plasma treatment results in degradation of polymer chain and creation of free radicals and excessive oxygen groups. After the treatment of the plasma modified polymers with dithiol the concentration of free radicals declines since the free radicals mediate the dithiol binding on polymer molecular chains. The presence of gold and sulphur (from dithiol) on the polymer surface after the grafting with gold nanoparticles was proved by XPS measurement. After the plasma treatment the highest oxygen concentration was found on PE, lower on PS and lowest one on PTFE. In PET, with its oxygen containing molecule, the oxygen content decreases as a result of the plasma treatment. In this case the polymer degradation overweighs the production of new, oxygen containing structures. Grafting from methanol solution is accompanied with a polymer etching. The presence of gold particles on the grafted polymers was proved by AFM methods too. The gold nanoparticles are distributed relatively homogenously over the polymer surface, the finding which maybe of importance for future application of gold-polymer structures in tissue engineering and electronics.

Acknowledgements This study was supported by the GA CR under the projects 106/09/0125, 108/10/1106 and 106/09/P046, Ministry of Education of the CR under the program LC 06041, and AS CR under the project KAN200100801. The authors thank Dr. P. Stopka from IIC of ASCR for performing the EPR measurements.

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