Surface modification of polystyrene by plasma-induced UV graft-polymerization

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Abstract: As a very popular polymer in the numerous applications for fabrication of everyday life objects, the utilization polystyrene (PS) in tissue culture dishes requires the development of easy processes to achieve hydrophilicity and biocompatibility. In this study, bioactive molecule polyacrylamide (PAM) was immobilized onto PS surface by plasma-induced UV graft-polymerization to improve hydrophilicity and biocompatibility of PS surface.

Surface analyses following modification process included water contact angles (CA), attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The results revealed the effectiveness of this method on immobilizing PAM to PS surface, and the hydrophilicity of modified surface improved remarkably. In addition, cellular proliferation tests were implemented to validate the enhanced biocompatibility of modified PS surface.

Keywords: polystyrene, plasma-induced UV graft-polymerization, hydrophilicity, biocompatibility

1. Introduction

Polymers have become attractive materials in various technological applica--tions because they have many unique advantages such as their high flexibility for the fabrication and patterning with different shapes and thicknesses, low density, and low manufacturing cost etc [1]. However, modification of the chemical composition and structure of the polymer surface to improve the surface properties of bonda--bility, reactivity and hydrophilicity are also required for further applications in industry, engineering and medical research [2,3].

Polystyrene (PS) is one of the important polymers and has been used in biomedical material as tissue culture dishes, which also requires the developing of easy processes to achieve hydrophilicity and biocompatibility [4,5]. Surface modifica--tion is a powerful tool in tissue engi--neering, which can be used to enhance the performance of the surface [6]. There are several surface modification techniques available such as wet (acid, alkali), dry (plasma) and radiation treatments (ultraviolet radiation and laser) without affecting the bulk properties [7,8].

Plasma surface treatment, as a versatile and environmental benign technique, had the propensity for highly efficient surface chemistry modification for both organic and inorganic materials. However, plasma treatment alone was shown to be an insufficient surface

modification tool, and it has since been noted that polymeric plasma-treated surfaces do not retain their modified chemical properties over time and with air exposure [9]. In this study, bioactive molecule polyacrylamide (PAM) was immobilized onto PS surface by high frequency plasma-induced UV graft-poly--merization to improve hydrophilicity and biocompatibility of PS surface.

2. Experimental procedure

2.1 Materials and instrument

Biomedical grade polystyrene sample was cut into small pieces and ultrasonically cleaned in doubly ethanol and deionized water prior to surface modification treatments. Acrylamide (AM) was analytical reagent from Yili Chemical Co., Beijing, China. L929 cells were obtained from the central laboratory of tissue engineering, the Fourth Military Medical University, Xi'an, China.

PECVD300 high-frequency glow discharge plasma device (Beijing Taikenuo Technology Co., Ltd. PECVD500-HF glow discharge plasma power, 40-60kHz, Plasma Research Center, Beijing Jiaotong University); UV generator (Medium pressure mercury lamp: 1000 W, Wavelengths: 280~385 nm, PHILIPS Co., Dutch); DZF-6020 vacuum oven (Shanghai Yiheng Scientific Instrument Co., Ltd.)

2.2 High frequency plasma-induced UV graft-polymerization process

The cleaned PS films were put into the reaction chamber, pumped the base pressure to under 1 Pa. In order to get the activation the samples were pretre--ated by Ar plasma at room temperature (25 °C) in certain conditions such as pla--sma pretreatment time, Ar pressure and high frequency (HF) power. The pretre--ated PS films were denoted as Ar-PS.

The pretreated PS films were immersed in a certain concentration of AM solution, irradiated by UV for 50 min and the AAm monomer graft polymerization reactions occur on the surface. The grafted PS samples were ultrasonic cleaning with ethanol for 2 min, removing the surface polymerization of monomers and homopolymers. After vacuum drying at room temperature, the obtained samples were denoted as: PAM-Ar-PS.

2.3 Surface characterization

The surface chemical compositions were characterized using the attenuated total reflection fourer transform infrared spectroscopy (ATR-FTIR) (EQUI NOX55 Bruker Co., Germany) and X-ray photoelectron spectroscopy (XPS) (AXIS ULTRA, Kratos Analytical Co., Britain). The surface wettability was evaluated by contact angle (CA) using video-based contact angle measuring device (OCA20 Dataphysisc Co., Germany).

2.4 Cells proliferation

The material biocompatibility of the

different samples is evaluated by culturing of L929 fibroblasts. The growth was measured by counting of the cells at 4 days, using MTT assary as described by Faghihi et al. [10]. The number of cells was also evaluated by absorbance, using enzyme linked immune detection at the wavelength of 490 nm.

3. Results and discussion

3.1 The ATR-FTIR analysis

Fig. 1 is the ATR-FTIR spectra of pristine PS (a); PAM-PS (b); PAM-Ar--PS (c). the spectra are similar between Fig. 1a and Fig. 1b, which indicate that AM can not graft-polymerize on the PS surface using UV without initiator and plasma pretreatment. Compared with Fig. 1a, the new peaks appear at 3000-3680 cm^{-1} in Fig. 1c due to the oxygenic groups for the plasma pretreatment and the red-shifted amino stretching in AM.

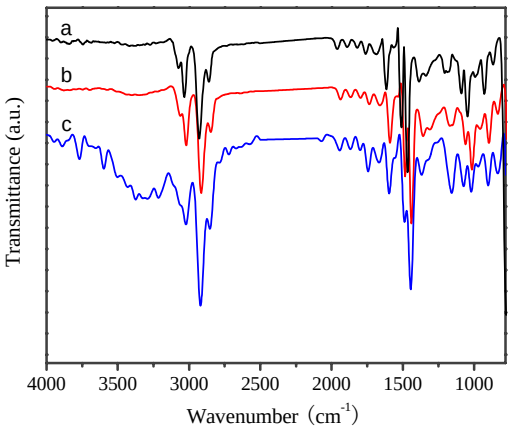

Figure 1. ATR-FTIR spectra of pristine PS (a); PAM-PS (b); PAM-Ar-PS (c).

The peaks increase at 2917 cm^{-1} and 2850 cm^{-1} after the UV graft-polymer--ization for the methylene in AM molecules. The new peak at around 1700 cm^{-1} and 1270 cm^{-1} corresponds to the amide group (-CON-) in AM molecules. The changes in the spectra show that PAM has been immobilized onto the surface.

3.2 The XPS analysis

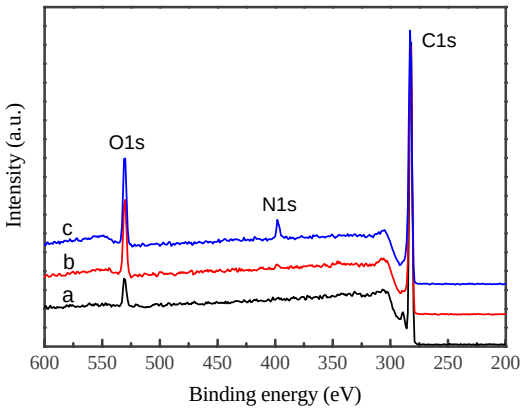

Figure 2. XPS spectra of pristine PS (a); PAM-PS (b); PAM-Ar-PS (c).

Table 1. Element contents of pristine PS (a); PAM-PS (b); PAM-Ar-PS (c).

Samples	C1s (at%)	O1s (at%)	N1s (at%)
a	96.98	3.02	/
b	91.21	8.79	/
d	86.00	9.92	4.78

Fig. 2 shows the XPS spectra of the different PS samples. Compare Fig. 2b with Fig. 2a, the increased oxygen content due to the plasma treatment and the nitrogen content was observed in Fig. 2c, which is attributed to nitrogen of PAM on the PS surface.

3.3 Wettability analysis

The water contact angles of pristine PS, Ar-PS and PAM-Ar-PS are 88.9 °, 4.1 °, and 30.8 °, respectively. This first decreasing and then increasing is consistent with our modification process on the PS surface. The significant

reduction of the contact angle, from 88.9° to 4.1 °, shows the presence of hydrophilic oxygen-containing polar groups on the Ar-PS surface and the increase in contact angle of PAM-Ar-PS explains that PAM has been integrated onto the PS surface as well. The contact angle of modified PS surface is much smaller than pristine PS as the PAM contains the polar amino groups, which in turn proves PAM has been successfully grafted onto PS surface.

3.4 Cellular compatibility test

Tab. 2 shows the results of cytoto--xicity assay of different PS surfaces, on which the fibroblasts cultured for 4 days at 37 °C.

Table 2. Results of cytotoxicity assay of different PS

Samples	OD $X\pm s$	R/%	CTS	p
pristine PS	0.643±0.037	68.3	2	<0.05
PAM-Ar-PS	0.763±0.036	81.0	1	<0.05
Negative control	0.942±0.009	100		

In Tab. 2, it is obvious that the optical density (OD) of the sample PAM-Ar-PS is larger than pristine PS, and the relative growth rate (R) 81% reflects the better growth status of L929. The cytotoxicity scale (CTS) of the surface is 1, which suggests that the modified sample is almost non toxic to L929 cells, up to snuff of the materials cytotoxicity in GB /T 16886.5-2003. Results of MTT assay reveal a significant difference between experimental group and negative control group (p<0.05), which showed the modified surface enhances the cell attachment and proliferation.

4. Conclusion

By high frequency plasma-induced UV graft-polymerization, PAM was graft-polymerized on the PS surface without initiator. CA result reveals that the hydrophilicity of modified surface improved remarkably and cellular proliferation tests validate the enhanced biocompatibility of modified PS surface.

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