Effects of Argon Plasma Treatment on Surface Characteristic of Photopolymerization PEGDA–HEMA Hydrogels

Guoxin Tan,[1] Rong Chen,[1] Chengyun Ning,[2] Lin Zhang,[1] Xiongjie Ruan,[1] Jingwen Liao[1,2]

[1]Department of Applied Chemistry, Institute of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China
[2] Department of Inorganic Materials, College of Material Science and Engineering, South China University of Technology, Guangzhou 510641, China

ABSTRACT: The aim of this research was to determine the influence of argon plasma treatment condition on the surface properties of poly(ethylene glycol) diacrylate (PEGDA)–hydroxyethly methacrylate hydrogel films, a kind of scaffold materials for tissue engineering. The changes of surface properties have been evaluated by contact angles, X-ray photoelectron spectra (XPS), and scanning electron microscopy (SEM). From the contact angle measurements of different liquids, the surface free energy of the hydrogel was calculated according to approaches by Owens–Wendt–Kaelble. Results showed that the contact angle of the hydrogel to water decreased remarkably after argon plasma treatment, which was caused by the changes in morphology (SEM images) and chemical composition (XPS results) of the argon plasma-treated surface. The surface free energy increased with the increase of the argon plasma treated time and power, and these increasing was mainly due to the increase of polar component. The XPS results confirmed that plasma oxidation reaction produced oxygen-containing functional groups onto the surface. This functional group played an important role in increasing the hydrophilic properties of the hydrogel. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 459–465, 2012

Key words: plasma treatment; surface free energy; hydrophilicity; microscopy; PEGDA–HEMA hydrogel

INTRODUCTION

Surface characteristics of material such as hydrophilicty/hydrophobilcity, surface energy, charge property, and surface roughness greatly influence cell attachment and growth on the material.[1] Many approaches, including surface modification and bulk modification, have been developed to improve cell affinity of the polymeric biomaterials.[2,3] Various methods have been used for obtaining a hydrophilic polymeric surface, including plasma treatment, UV/ozone, silanization, radiation-induce graft polymerization, and photoinduced graft polymerization. Among these methods, plasma treatment is a unique method for modifying the surfaces without altering bulk properties. This approach is increasingly becoming an established technique to modify surfaces for biomaterials. Plasma treatment has been used to increase surface wettability (by introduction of hydroxyl functionality) to enhance the performance

of the catheters.[2] Many researches are focused on the increase of surface oxygen concentration and interfacial adhesion of the cells on the surface of biomaterials. To improve the hemocompatibility of the films, Park et al.[4] modified the surface of PU films by microwave-induced argon plasma treatment and found that the treated PU films could enhance the behaviors of endothelial cells. A number of plasma gas treatments have been used to introduce oxygen into the surface of polymer materials, of which oxygen is itself the most common.[5] Another out of many plasma gases, inert argon is used to modify and reorganize the chemical groups on the surface. However, it has also been observed that argon plasmas can be used to introduce oxygen functionality into the surface.[6,7]

Photoinitiated polymerization is an attractive technique for the *in situ* formation of hydrogels as it provides unparalleled spatial and temporal control over the formation of the material. Ansetha[8] evaluated water-soluble lithium acylphosphinate salt for its ability to polymerize diacrylated poly(ethylene glycol) (PEGDA) monomers rapidly into hydrogels, while maintaining high viability during direct encapsulation of cells. Poly(ethylene glycol) (PEG)-based materials are widely investigated for biomedical applications as the result of several advantageous properties such as biocompatibility, low immunogenicity, and the ease of use. It is one of the most used

materials for tissue engineering, which are already authorized by the Food and Drug Administration (FDA) for clinical use. Langer et al.[9] encapsulated mammalian cells within PEGDA-based hydrogels, which has great utility for a variety of applications ranging from tissue engineering to cell-based assays. PEG functionalized with diacrylate (PEGDA) or dimethacrylate groups, which are crosslinked to form nondegradable hydrogels in the presence of UV photoinitiators,[10] are used in various biomedical applications such as the microencapsulation of islets, controlled release vehicles, adhesion prevention barriers,[11] and bone restorations.[12] It is reported that cartilage-like tissue are prepared by PEG-based photopolymerizing hydrogels after encapsulation of bovine chondrcytes both *in vitro* and *in vivo*.[13] Poly(2-hydroxyethyl methacrylate) (pHEMA) is another of important hydrophilic macromolecules, which are not enzymatically degraded directly with acidic or alkaline solutions, due to their superior biocompatibility, high permeability to small molecules (i.e., tissue metabolites), and hydrophilic properties.[14] It is reported that the PEGDA-based hydrogels were prepared by UV radiation under nitrogen and 2-hydroxy-1-[4-(hydroxyethoxy) phenyl]-2-methyl-1-propanone was used as a photoinitiator.[15,16]

In this study, we characterized the surface properties of photopolymerized PEGDA-HEMA hydrogel films before and after argon plasma treatment at different treated power and time. The surfaces were evaluated by contact angles, X-ray photoelectron spectra (XPS), and scanning electron microscopy (SEM). Furthermore, the surface free energy of the hydrogel was calculated according to the approaches by Owens–Wendt–Kaelble.

EXPERIMENTAL

Material

PEGDA ($M_n = 600$) was obtained from Sartomer company. HEMA was purchased from Acros Organic Company. 2-Hydroxy-1-[4-(hydroxyethoxy) phenyl]-2-methyl-1-propanone (a water-soluble UV initiator commercially available as Irgacure-2959) was bought from Ciba Specialty Chemicals, Switzerland. PEGDA, HEMA, and Irgacure-2959 were used without further purification.

Preparation of photo-crosslinking PEGDA–HEMA hydrogels

PEGDA and 2-hydroxyethly methacrylate (HEMA) monomers were dissolved in distilled water with gentle stirring to make a 20%(w/v) solution, with 2-hydroxy-1-[4-(hydroxyethoxy) phenyl]-2-methyl-1-propanone (0.5 wt %) as a photoinitiator. The solu-

tions were placed into Teflon module and polymerized by UV light ($\lambda_{max} = 365$ nm, intensity 800 µV/cm^2) under nitrogen for 10 min at room temperature. The hydrogels were soaked into distilled water, replaced periodically, and finally dried under a vacuum for 48 h for modification.

Modification of PEGDA–HEMA membranes

Plasma treatment was performed in a plasma generator (Model DL-01, Suzhou Omega Machinery Electronic Technology Co., China) under 0.8 L/min argon gas. The plasma chamber was evacuated to 7 Pa after the dry hydrogel film was placed in the chamber. When the pressure of the chamber was stabilized, glow discharge plasma with a frequency of 40 MHz was created at a predetermined power and time. After it was taken out from the chamber, the plasma treated samples were further exposed to the oxygen atmosphere for 10 min.

Characterization

Surface elemental composition of PEGD–HEMA films was analyzed by XPS. XPS analyses were performed using an Axis UltreDLD (Kratos Analytical, UK) with a monocharomatic Al-K radiation source (1486.6 eV) at a power of 150 W. Survey and high-resolution region scans of the C1s peak region (275–295 eV) and O1s peak region (532–535 eV) were recorded using pass energy of 160 eV and 40 eV, respectively. Concentrations of various C1s and O1s peaks were calculated from the relative peak areas.

Widely used methods for the calculation of the solid surface free energy included the Owens–Wendt–Kaelble, Wu, van Oss–Chaudhury–Good, and Li–Neumann–Kwok approaches. Owens–Wendt–Kaelble approach, the most important two-liquid method for the γ_S determination, was used to calculate the solid surface free energy of PEGDA–HEMA hydrogels in this work. According to the Fowkes theory that interactions between nonpolar solid and liquid can only be attributed to London dispersion forces (omitting the spreading pressure, π_e), and it was suggested by Owens–Wendt–Kaelbel that dispersive (*d*) and hydrogen (*h*) forces may be important across the interface for polar solids (*S*) and liquids (*L*). Considering a geometric mean (GM) relationship, the following equation is recommended for γ_S calculation[17]:

$$\gamma_s = \gamma_s^D + \gamma_s^P \tag{1}$$

$$W_A = \gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^D \gamma_L^D} + 2\sqrt{\gamma_s^P \gamma_L^P} \tag{2}$$

TABLE I
Faction of Carbon Functional Groups from High-Resolution C1s and O1s XPS Peak
of Hydrogels Before and After Argon Plasma Treatment

|	C1s (%)			O1s (%)	
	—C—H, —C—C—	—C—O—	—COO—	O1s1	O1s2
Chemical shift (eV)	284.60	286.10	288.52	532.29	533.51
Untreated	56.070	35.068	8.862	100	0
Treated (70 W, 120 s)	26.933	64.704	8.363	90.332	9.668

$$\begin{cases} \gamma_{L_1}(1 + \cos\theta_1) = 2\sqrt{\gamma_s^D \gamma_{L_1}^D} + 2\sqrt{\gamma_s^P \gamma_{L_1}^P} \\ \gamma_{L_2}(1 + \cos\theta_2) = 2\sqrt{\gamma_s^D \gamma_{L_2}^D} + 2\sqrt{\gamma_s^P \gamma_{L_2}^P} \end{cases} \quad (3)$$

where W_A is a work of adhesion in eq. (2), γ_L is the liquid surface tension, and γ_S^D and γ_S^P are the nonpolar and polar components of surface free energy in eq. (1). To obtain the surface energy γ_S value, the contact angles of two liquids on the solid surface were measured. The contact angle θ_1 and θ_2 of PEGDA–HEMA films to distilled water and diiodomethane were measured on air surface of the films, respectively, using an OCA15 (Germany) contact angles meter. A drop of distilled water or diiodomethane (1 μL) was introduced on the prepared film, and the contact angle was measured immediately from the image of the water drop. Five independent determinations at different sites of a film surface were averaged, and γ_S^D and γ_S^P can be calculated according to eq. (3).

The surface morphologies of the samples were observed by SEM. The samples were dried and sputter-coated with gold and observed under a Philips (Holland) XL 30 scanning electron microscope.

RESULTS AND DISCUSSION

The PEGDA–HEMA hydrogel film before and after argon plasma treatment was characterized by XPS. As shown in Table I, the C1s region peaks of PEGDA–HEMA film included three peaks. The first peak at 284.6 eV was attributed to the C1s of the aliphatic carbon bonds (—C—C—) or carbon-hydrogen bonds (—C—H—). The second peak at 286.05 eV was due to the C1s of —C—O— bonds. The third peak at 288.53 eV was ascribed to the C1s of —COO— bonds.[18] It was noticeable that the relative composition of the three peaks of C1s changed after argon plasma modification, as presented in Figure 1. Analysis of the C1s spectrum by constrained curve fitting demonstrated an obvious decrease in the intensity of the —C— peak, a moderate decrease of the —COO— peak, and an distinct increase of the —C—O— peak intensity. This indicated that the —C— bonds have been changed into —C—O bonds after argon plasma treatment. After that, the films were exposure to air, which can create relative sites such as peroxide group on the surface of hydrogel film. On the other hand, O1s2 was evidently incorporated into the surface of PEGDA–HMEA film after plasma treatment (Fig. 2 and Table I). The possible reason was the
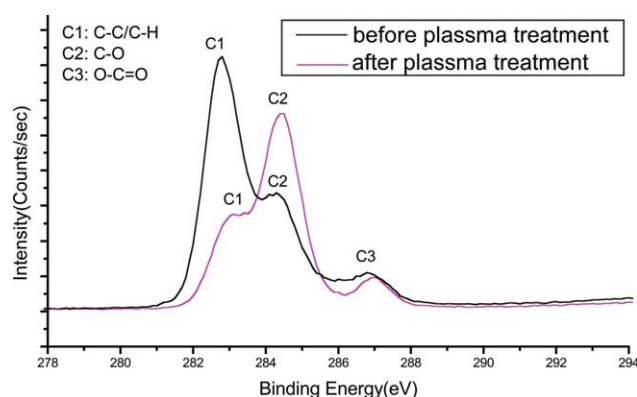
Figure 1 C1s spectra of PEGDA/HEMA hydrogel before and after plasma treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
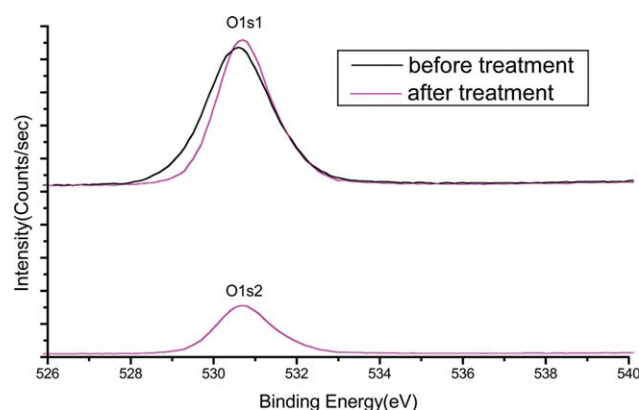
Figure 2 O1s spectra of PEGDA/HEMA hydrogel before and after plasma treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
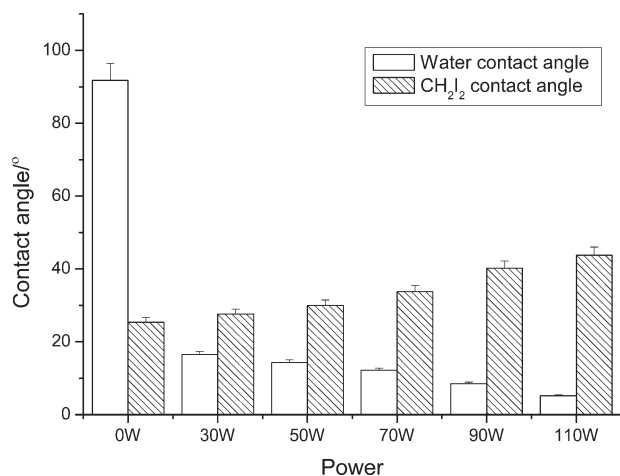
TABLE II
Quantitative Elemental Analysis of Untreated and Ar Plasma-Treated PEGDA/HEMA Surface

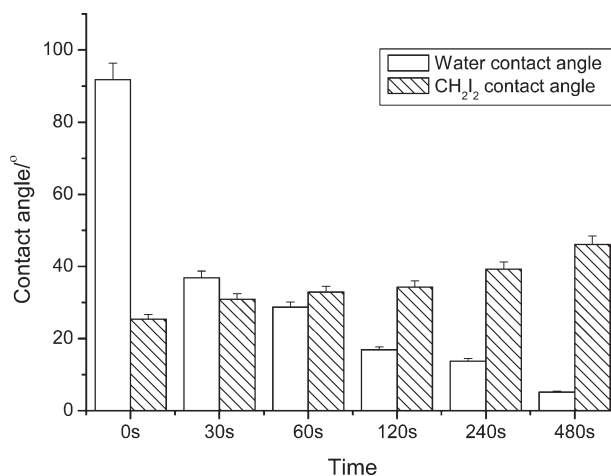|	C (At %)	O (At %)	N (At %)	O/C
Untreated	77.088	22.912	–	0.297
Treated	74.610	25.974	0.416	0.348

cleavage of ester bonds and formation of —O—O— bond on the surface of PEGDA–HEMA film after plasma treatment.

As plasma treatment was exposed to oxygen in air, a great increase of O1s and a slight increase of N1s could be observed on the surface of PEGDA–HEMA hydrogel films. As shown in Table II, compared to untreated sample, oxygen atomic percentage increased sharply from 22.912 to 25.974% at a power lever of 70 W for 120 s on the hydrogel surface. The increase of O/C ratio confirmed that the oxygen-containing groups were incorporated onto the PEGDA–HEMA film surface, which led to the improvement of surface hydrophilicy of the films.

The contact angles to water and diiodomethane of the PEGDA–HEMA films were calculated at different plasma treatment conditions by sessile-dropping techniques. As demonstrated in Figures 3 and 4, a great decrease of the contact angle to water and an increase of the contact angle to diiodomethane were observed with the increasing plasma treatment power and time. The general decrease in contact angle to water indicated that the surface hydrophilicity of the argon plasma-treated films had been improved, which was consistent with the increase of surface oxygen concentration (Table II). As shown in Figure 3, the contact angle of water decreased from 92° to 10° with the increasing plasma treatment power from 0 to 120 W, and there was also a contin-

Figure 4 Effect of Argon plasma treated time on contact angle of PEGDA–HEMA film to water and diiodomethane.

uous decrease of the contact angle to water with increasing plasma treatment time (Fig. 4). The results indicated that the increase of both the plasma treatment power and time further improved the hydrophilic property of the surface of PEGDA–HEMA films.

Surface free energy of the PEGDA–HEMA films was calculated by eqs. (1–3), and the results were displayed in Figures 5 and 6. The polar component of the untreated sample was 0.59 mJ m^{-2} and increased to 50 mJ m^{-2} with increasing treated power, and the dispersive component was change from 45.3 to 22.5 mJ m^{-2} (Fig. 5). However, when the film was treated more than 30 W, the surface free energy did not change anymore. It could also be seen from Figure 6 that the surface free energy was stabilized at 70 mJ m^{-2} when the plasma treatment time was more than 60 s. The results displayed that there was a saturation of the plasma effect on the films. We confirmed that surface free energy of the

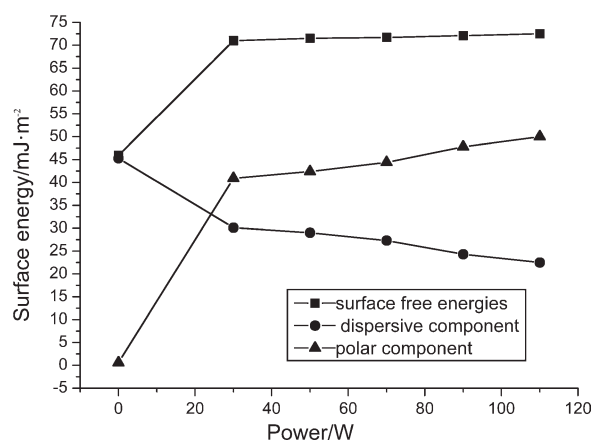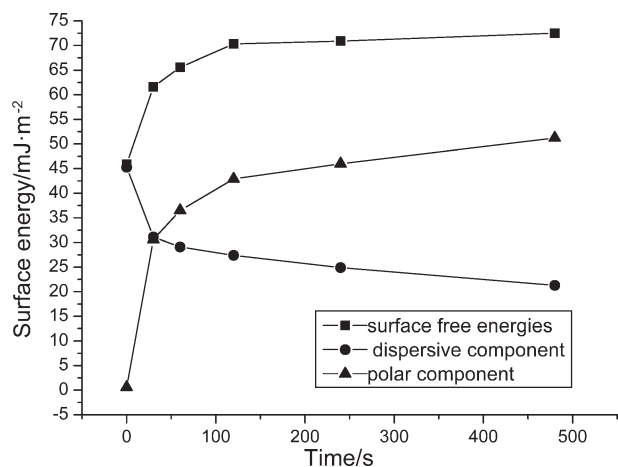
Figure 3 Effect of argon plasma processing power on contact angle of PEGDA–HEMA film to water and diiodomethane.

Figure 5 Influence of plasma processing power at 120 s on surface energy.

**Figure 6** Influence of plasma treated time at 70 W on surface energy.

hydrogel films increased with increasing the plasma treatment power and time, mainly due to the increase of polar component.

Figures 7 and 8 showed the SEM images of the surface of PEGDA–HEMA films before and after argon plasma treatment at different treated power and time, correspondingly. Rough surface was clearly observed on the plasma treatment films. It was obviously found that there were several concave regions on the surfaces after plasma treatment. It can be seen that with increase in the plasma treatment power and time, polymeric films surface roughness increased in the certain time level (120 s) and a certain power level (70 W). It was interesting in Figure 8(d) that many microspores with the diameter of 0.5–1μm were observed on the surface at plasma treatment of 70 W and 240 s. Compared to the untreated films [Figs. 7(a) and 8(a)], both higher plasma power and longer treatment time increased the surface roughness of the film. The principle of low-temperature plasma treatment was to alter the physical structure and chemical composition of the PEGDA–HEMA hydrogel surface making the surface become more "open." In the case of low-temperature plasma treatment with argon, the experimental results showed that the surface hydrophilic property could alter the surface energy property of the PEGDA–HEMA hydrogel. In general, surface hydrophilic property is directly related to surface energy, that is, more energetically stable surface results in less wettable surface. The SEM images shown in Figures 7 and 8 also demonstrate that low-temperature plasma treatment causes the increase of surface roughness. The increase of surface roughness also induces the increment in the specific surface area. It means that the oxidation creates oxidized functionalities leading to an increase in surface energy after plasma treatment. The low-temperature plasma treatment not only causes the increase in surface
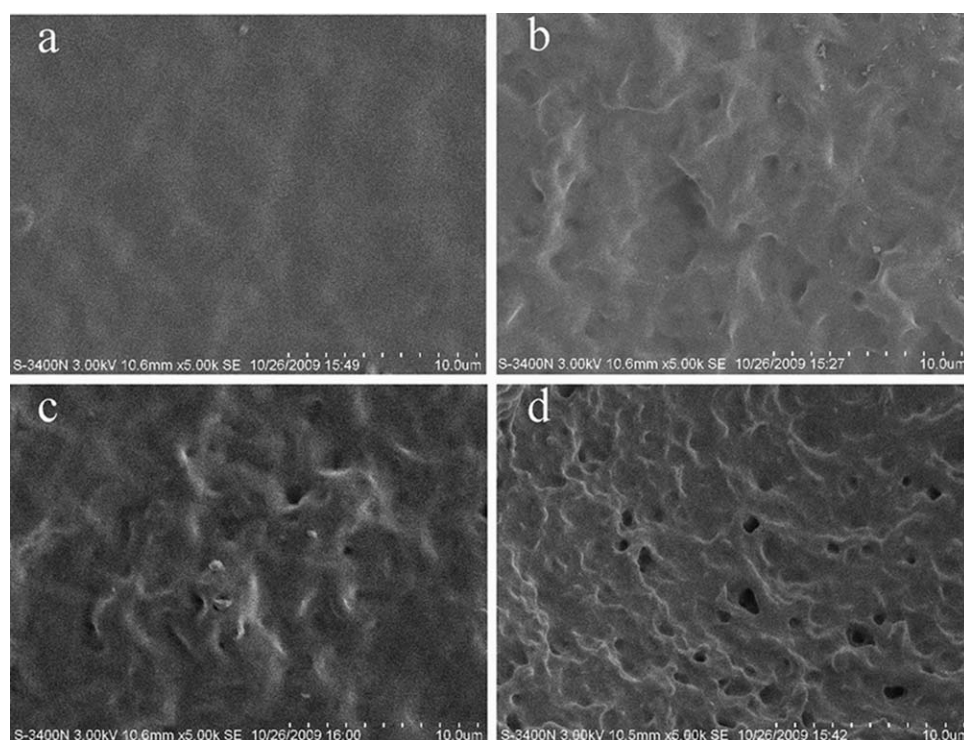
Figure 7 SEM micrograph of PEGDA/HEMA films at different plasma treatment power for 120 s (a) untreated, (b) 30 W, (c) 70 W, and (d) 110 W.
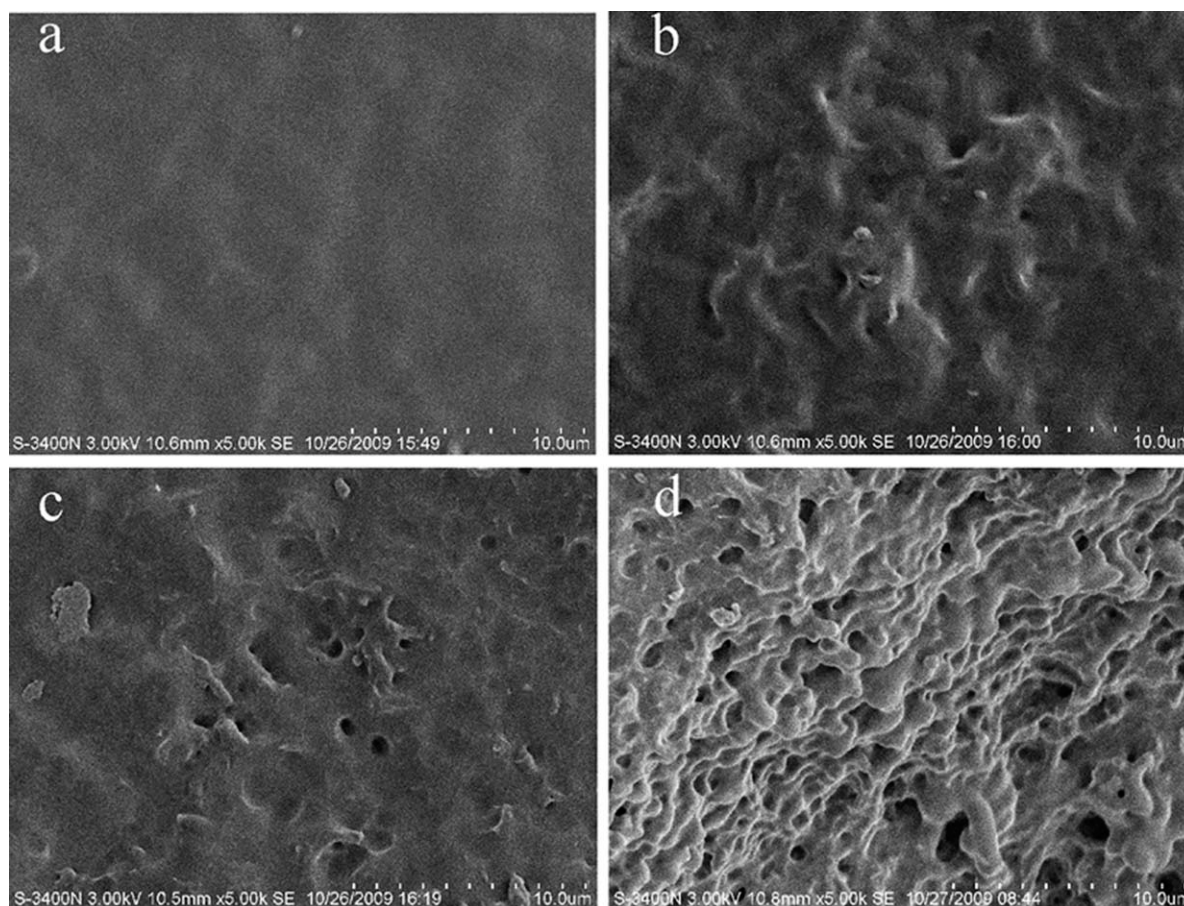
Figure 8   SEM micrograph of PEGDA/HEMA films at 70 W for different plasma treatment time (a) untreated, (b) 60 s, (c) 120 s, (d) 240 s.

roughness but also introduced the hydrophilic groups onto the gel surface.

CONCLUSIONS

Surface characteristics greatly influence attachment and growth of cells on biomaterials. Surface performance of argon plasma-treated PEGDA–HEMA hydrogel films have been studied morphologically and chemically in this work. The contact angle to water decreased considerably after argon plasma treatment compared to the untreated samples was caused by the changes in morphology (SEM images) and chemical composition (XPS results) of the argon plasma-treated surface. The increase of O/C ratio confirmed that the oxygen-containing groups were incorporated onto the PEGDA–HEMA film surface, which led to the improvement of surface hydrophilicy of the films. As morphology changes could cause hydrophilicity of the films changes, the surface free energy was increased for the argon plasma-treated films compared to that of the untreated. The prepared samples were kept in air after plasma treatment; plasma oxidation reaction produced oxygen-containing functional groups, which were attached to the polymer surface. These functional groups formed and played an important role in increasing the hydrophilic properties of the hydrogel. The results indicated that surface free energy of the hydrogel films increased with increasing the plasma treatment power and time, mainly due to the increase of polar component. Considering the known excellent biocompatibility of PEGDA and HEMA of the photo-crosslinking process, we envision that this hydrogel material could be potentially used in tissue engineering and for the purpose of directing the growth and migration of cells.

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