Surface modification of natural rubber latex films via grafting of poly(ethylene glycol) for reduction in protein adsorption and platelet adhesion

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Natural rubber (NR) latex films with surface grafted poly(ethylene glycol) (PEG) chains were prepared by UV-induced graft copolymerization of methoxy poly(ethylene glycol) monomethacrylate (PEGMA) onto the plasma-pretreated NR latex films. PEGMA macromononers of different molecular weights were used. The UV-induced graft copolymerization of PEGMA onto the plasma-pretreated NR latex films was also explored with PEGMA of different macromonomer concentrations and with different UV graft copolymerization time. The surface microstructures and compositions of the PEG-modified NR latex films were characterized by contact angle, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM) measurements. In general, higher macromonomer concentration and longer UV graft copolymerization time led to a higher graft yield. Water contact angle measurements revealed that the hydrophilicity of the NR latex film surface was greatly enhanced by the grafting of the PEG chains. The NR surface with a high density of grafted PEG was very effective in reducing protein adsorption and platelet adhesion. A lower graft concentration of the high-molecular-weight PEG was more effective than a high graft concentration of the low-molecular-weight PEG in reducing protein adsorption and platelet adhesion.

Introduction

Surface modification of polymers via molecular design is one of the most versatile means for incorporating new properties or functionalities into the existing polymers [1]. These properties or functionalities include improved surface hydrophilicity, hydrophobicity, biocompatibility, antistatic property and adhesion property [2–5]. Among them, biologically non-fouling surface properties have been of great experimental interest to many researchers. To create non-fouling surfaces, various water-soluble polymers have been used for surface grafting, including non-ionic, hydrophilic polymers, such as poly(acrylamide), poly(N,N-dimethylacrylamide), poly(vinyl alcohol), ethylene–vinyl alcohol copolymer, and poly(hydroxyethyl methacrylate), poly(ethylene glycol) (PEG), and poly(ethylene oxide) (PEO, MW $>$ 10 000) [6]. Grafting of these polymers can be achieved by surface graft copolymerization of the respective monomers, by coupling reaction, and by surface physical adsorption.

PEO is completely miscible with water in all proportions at all degrees of polymerization for temperatures up to slightly below 100 °C [7]. This property, among others, makes it one of the most protein-resistant or blood-compatible polymers. Many experiments on the modification of polymer substrates with PEO have been carried out. For example, Uchida *et al.* [8] successfully grafted methoxy poly(ethylene glycol) monomethacrylate (PEGMA) with different molecular weights (400, 1000 and 4000 g/mol) onto poly(ethylene terephalate) (PET) surfaces. Fujimoto *et al.* [9] graft-copolymerized PEGMA onto polyurethane (PU)

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surfaces. Allmer *et al*. [2] on the other hand, graft-copolymerized glycidyl methacrylate (GMA) on polyethylene films by UV irradiation in the presence of benzophenone before attaching PEG onto the graft-modified surface. In all cases, the amount of protein adsorbed on the PEO surface was reduced when compared to the untreated substrate. Also, the chain length and surface density of PEO have been found to significantly affect the effectiveness of PEO in reducing protein adsorption onto the graft-modified surfaces [10]. For example, Lee *et al*. [11] prepared ''PEO gradient surfaces'' in which the surface density of the grafted PEO chains was changed gradually along the sample length. Plasma protein adsorption and platelet adhesion on the PEO gradient surfaces were found to decrease gradually with increasing PEO chain length and the surface density. By attaching PEO molecules of different molecular weights on PET films, Gombotz *et al*. [12] found that a lower surface density of the high-molecular-weight PEO was more effective in reducing protein adsorption than a higher surface density of low-molecular-weight PEO.

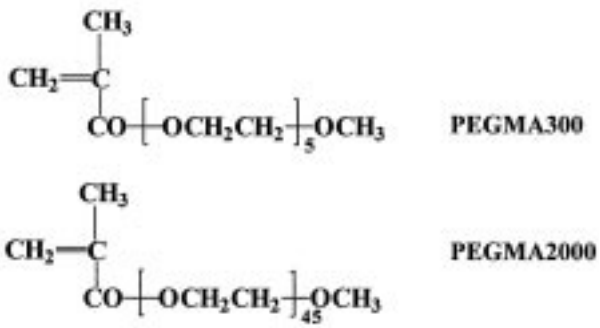
Natural rubber (NR) possesses excellent elasticity, flexibility and resistance against splitting. These attractive properties have resulted in a wide range of medical products manufactured from NR latex, including surgical gloves, tubings, catheters and balloons. However, the poor blood compatibility of NR compared to silicones and PUs prevents any direct biomedical applications of this material. As such, many attempts have been made to improve the blood compatibility of NR [13–16]. Razzak *et al*. [14, 15] succeeded in improving the blood compatibility of NR by radiation-induced grafting of N,N-dimethylacrylamide or N,N-dimethylaminoethyl acrylate. It was found that the blood compatibility of the graft-modified NR tubes was better than that of the medical grade silicone rubber tubes. Kislinovskaja *et al*. [16], on the other hand, modified the NR surface by two methods to enhance the blood-compatibility: (1) coating of a thin PU film with improved thromboresistant properties, and (2) surface immobilization of heparin.

On account of the promising experimental results reported thus far, the present study is carried out to determine the suitability of the plasma-activated NR latex film as a substrate for UV-induced surface graft copolymerization with methoxy PEGMA. If the protein-resistant properties of PEG or PEO can be incorporated onto NR surface, many other important applications in the biomedical field could be found for NR.

Experimental section

Materials

Natural rubber (NR) latex films having a thickness of about 0.35 mm was used in this study. It was prepared from the latex concentrate of Malaysian rubber trees and was lightly crosslinked by prevulcanization (sulfur 1.0 phr, zinc oxide 1.0 phr, zinc diethylditiocarbamate 0.5 phr) at room temperature for 6 days. X-ray photoelectron spectroscopic (XPS) analysis results suggested that the NR latex film contained about 0.4 atomic% sulfur in the surface region of the film. The surface of the film was cleaned, sequentially, with methyl alcohol and water for about 15 min each in an ultra-sonic bath and then dried in air. The methoxy PEGMA macromonomer samples, with molecular weights of about 300 (PEGMA300) and 2000 (PEGMA2000), used for surface graft copolymerization were obtained from Aldrich Chemical Co. of Milwaukee, WI. The PEGMA300 was supplied in its pure liquid form, while the PEGMA2000 was supplied in the form of 50 wt % ($\sim$ 0.2 mol/L) aqueous solution. The chemical structures of PEGMA300 and PEGMA2000 macromonomers are shown below:



UV-induced graft polymerization

The NR latex films were cut into strips of about 1 cm $\times$ 5 cm in size. They were pretreated with Ar plasma before graft copolymerization. A cylindrical type glow discharge cell, Model SP 100, manufactured by Anatech Ltd. of USA was used for plasma treatment. The plasma power applied was kept at 30 W at a radio frequency of 40 kHz. The film was placed between the two electrodes and subjected to the glow discharge for a predetermined period of 20 s at an Ar pressure of 0.5 Torr. The Ar plasma-pretreated NR latex films were then exposed to the atmosphere for about 10 min to affect the surface peroxide and hydroperoxide formation [17] before the UV-induced graft copolymerization process. For the UV-induced graft copolymerization with PEGMA300, each NR latex film was immersed in 20 mL of the water : ethanol (40 : 60) monomer solution, containing 1 mL of 0.05 mM riboflavin, in a Pyrex® tube. The dissolved oxygen, which could inhibit the radical-initiated polymerization, was consumed by photochemical reaction with riboflavin [18] during the graft copolymerization process. The concentrations of the PEGMA300 solution were varied from 0.2 to 0.8 M. The reaction mixture was subjected to UV irradiation for a predetermined period of time ranging from 0.25 to 2 h in a Riko Rotory, Model RH 400-10 W, photochemical reactor manufactured by Riko Denki Kogyo of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerization experiments were carried out at a constant temperature of 28 °C. After each graft copolymerization experiment with PEGMA300, the NR latex film was removed from the homopolymer solution and washed with a jet of ethanol. It was then immersed in a 40 °C ethanol bath with continuous stirring for 24 h, followed by rinsing in copious amounts of ethanol to remove the residual homopolymer. In the case of surface graft-polymeriza-

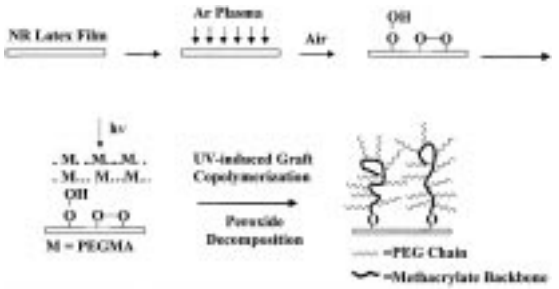


Figure 1 Schematic representation of the UV-induced graft-copolymerization process on an Ar plasma-pretreated natural rubber latex film.

tion with PEGMA2000, the process of graft copolymerization was similar to that described above, except that the PEGMA2000 macromomomer was dissolved in doubly distilled water. The concentration of the PEGMA2000 solution was varied from 0.025 to 0.2 M. After each graft copolymerization experiment with PEGMA2000, the NR film was removed from the homopolymer solution and washed with a jet of doubly distilled water. It was then immersed in a 40 °C water bath with continuous stirring for 24 h, followed by rinsing in copious amounts of doubly distilled water to remove the residual homopolymer. The process of the UV-induced surface graft copolymerization is shown schematically in Fig. 1.

XPS measurement

XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron take-off angle of 75° (with respect to the sample surface). The X-ray source was run at a reduced power of 120 W. The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum, or FWHM) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm$ 10%. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Water contact angle measurement

The static water contact angles were measured at 25 °C and 60% relative humidity using a telescopic goniometer (Rame-Hart Model 100-00(230)). The telescope with a magnification power of 23 × was equipped with a protractor of 1° graduation. For each angle reported, at least five sample readings were averaged. The angles reported were reliable to $\pm$ 3°.

AFM measurement

The surface topography of pristine and PEGMA graft-copolymerized NR substrates was examined in a Nanoscope III atomic force microscope (AFM) using the tapping mode (scan size 10 μm, set point 1.51 V, scan rate 1.0 Hz). The root-mean-square (RMS) roughness of the substrate surface was evaluated directly from the AFM image.

Protein adsorption

The proteins, bovine serum albumin (BSA, MW ≈ 70 000 g/mol) and γ-globulins (MW ≈ 156 000 g/mol), were obtained from Sigma Chemical Co. of St. Louis, MO. Each of the proteins was dissolved in the phosphate-buffered saline (PBS, pH = 7.4) to a concentration of 2 mg/mL. The PEG-grafted NR latex films were rinsed with PBS to rehydrate the surface prior to immersing in the protein solution. The adsorption was allowed to proceed at 25 °C for 24 h. The NR latex films were then removed from the solution, gently washed three times with PBS from a Pasteur pipet, and rinsed once with doubly distilled water to remove the PBS salt. After drying under reduced pressure, the protein-adsorbed surfaces were analyzed by X-ray photoelectron spectroscopy (XPS). The N1s peaks from the wide scan spectra were used as a marker for the analysis the of protein adsorbed on the surfaces.

Platelet adhesion

Heparinized blood from healthy dogs (supplied by the Animal Holding Unit, National University of Singapore) was used in this study. The blood was centrifuged at 200 g for 15 min to obtain the platelet-rich plasma (PRP). The PRP was diluted with PBS to give a concentration of about 1×10^5 platelets/μL. About 0.1 mL of the diluted platelet suspension was placed onto the NR sample surface and incubated at 25 °C for 30 min under a static condition. After incubation, the film surface was rinsed with PBS in order to remove the loosely adhered platelets on the film surface. After thorough rinsing with PBS, the platelets adhered on the surfaces were dehydrated in an ethanol-graded solution series (50%, 60%, 70%, 80%, 90% and 100%) for 10 min each. The ethanol on the surface dehydrated films was allowed to evaporate at room temperature. The platelet densities on the surfaces were estimated from the optical microscopic images.

Results and discussion

Argon plasma treatment

Fig. 2(a) and (b) show the respective XPS wide scan spectra for a pristine NR latex film surface and a 20-s Ar plasma treated NR surface after exposure to air for 3 h. A significant increase in the relative intensity of the O1s core-level signal as a result of the plasma treatment and air exposure can be observed. The corresponding C1s core-level spectra are shown in Fig. 2(c) and (d). In the case of pristine NR latex film, the C1s core-level spectrum is curve-fitted with two peak components. The main peak component at the BE of 284.6 eV is attributable to the C-H species while the minor

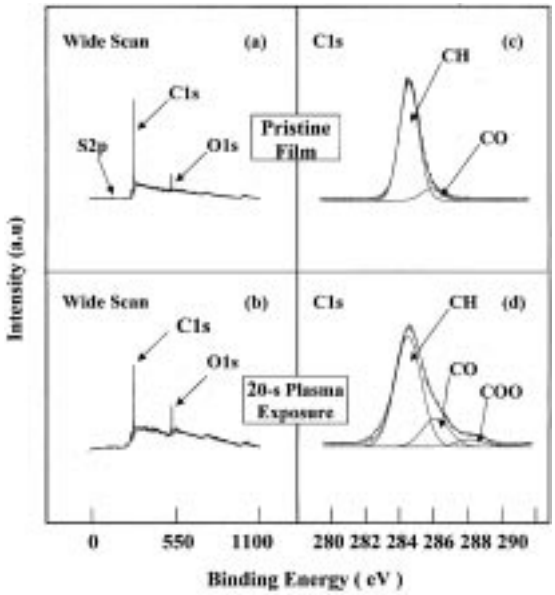


Figure 2 Wide scan and C1s core-level spectra of the pristine and the 20 s Ar plasma-treated NR latex films.

component at the BE of 286.3 eV is associated with the C-O species. In the case of the 20-s plasma treated NR, the C1s core-level spectrum is curve-fitted with three peak components, with BEs at 284.6 eV for the C-H species, at 286.3 eV for the C-O species, and the new peak component at 288.6 eV for the -O-C=O species [19].

The changes in the O/C atomic ratio and the static water contact angle of the NR latex film as a function of the Ar plasma treatment time are shown in Fig. 3. The O/C ratios were determined from the sensitivity factor-corrected O1s and C1s core-level peak area ratios. An increase in the O/C ratio and a decrease in the contact angle are observed upon increasing the Ar plasma treatment time of the NR surface. These results are similar to those reported previously for the synthetic polymer films, in which the O/C ratios of the polymer surfaces increase with Ar plasma treatment time [20, 21]. The O/C ratio and the water contact angle approach their respective constant values after 15 s of Ar plasma treatment under the present glow discharge conditions. The decrease in water contact angle may be due to the formation of oxygen-based polar groups on the surface, as a result of the glow discharge treatment. The glow discharge treatment of a polymer surface causes the breakage of some C-H bonds and the activation of the unsaturated bonds, leading to the formation of carbon radicals. The latter species can react with oxygen in air to form peroxides and hydroperoxides [17]. In addition to the initiation of surface vinyl polymerization, the decomposition of the peroxides and hydroperoxides can also result in the production of the various oxygen-based functionalities (hydroxyl group, ether, ketone, aldehyde, carboxylic acid, etc.) through reaction with additional oxygen [22, 23].

Surface graft copolymerization with PEGMA

The Ar plasma-pretreated NR latex films served as a good substrate for UV-induced graft copolymerization with PEGMA. Fig. 4(a) and (b) show the respective C1s core-level spectra for the 20-s Ar plasma-pretreated NR latex surfaces after 0.5 and 2 h of the UV-induced graft copolymerization with PEGMA300 at the macromonomer concentration of 0.8 M. Fig. 4(c) shows the corresponding C1s core-level spectrum for the PEGMA300 homopolymer surface. The presence of surface grafted PEGMA300 polymer can be deduced from the dominance of the C1s component centered at about 286.2 eV and attributable to the CO species, as well as the substantial reduction in intensity of the C1s core-level signal at 284.6 eV for the CH species. The C1s peaks component at the BE of 284.6 eV can be attributed to the CH_2 species of both the NR substrate and the backbone of the grafted PEGMA polymer. The minor peak component at the BE of 288.6 eV, on the other hand, is attributable to the O=C-O species [19]. The surface graft concentration of PEG can be represented simply by the XPS-derived [CO]/[CH] ratio. The C1s core-level spectra for the 20-s Ar plasma-pretreated NR latex surfaces after the UV-induced graft copolymerization with 0.2 M PEGMA2000 solution for 2 and 3 h, respectively, are shown in Fig. 4(d) and (e). For comparison purpose, the C1s core-level spectrum for the PEGMA2000 homopolymer surface is also shown in Fig. 4(f).

Fig. 5 shows the dependence of the surface graft concentrations and surface water contact angles of the NR latex films on the PEGMA300 and PEGMA2000 macromonomer concentrations used for the UV-induced graft copolymerization. For PEGMA2000, the maximum macromonomer concentration used was limited by that available from the supplier, i.e. $\sim$ 0.2 mol/L. The UV-induced graft copolymerization time was fixed at 2 h and the Ar plasma pretreatment time of the NR latex film at 20 s. The graft concentration increases and the water contact angle decreases correspondingly upon increasing the PEGMA monomer concentration used for graft copolymerization. The contact angles of the PEGMA300 and PEGMA2000 graft-copolymerized NR surfaces decreased to about 26° and 15°, respectively, at the optimum graft concentrations, from 78° for the pristine NR surface. The data in Fig. 5 also clearly show

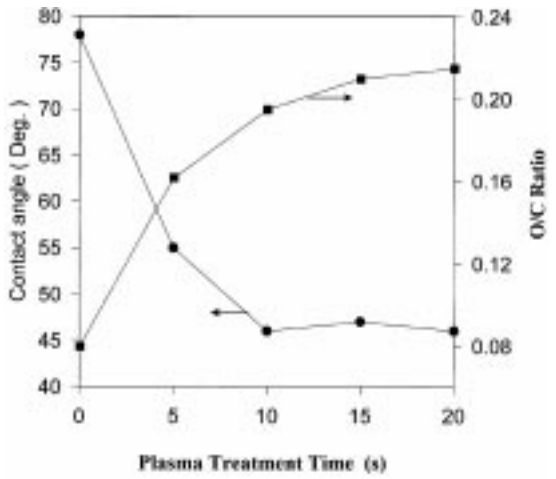


Figure 3 Changes in O/C atomic ratio and water contact angle of the NR surface as a function of the Ar plasma treatment time.

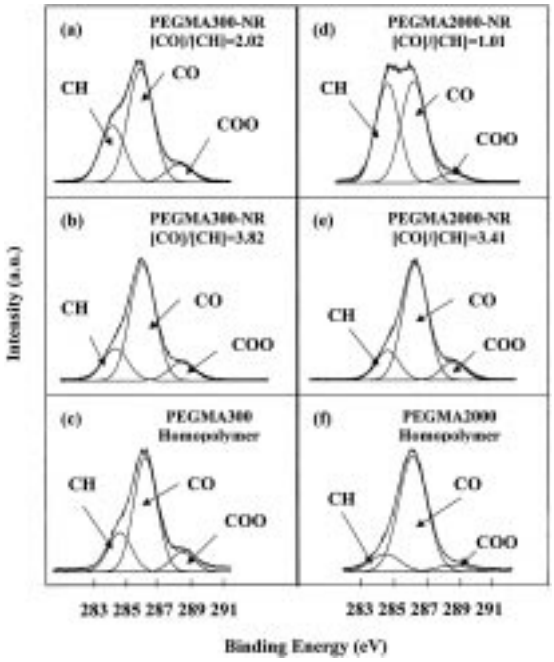


Figure 4 XPS C1s core-level spectra of (a) a PEGMA300 graft-copolymerized NR latex film (Graft Conc. = 2.02), (b) a PEGMA300 graft-copolymerized NR latex film (Graft Conc. = 3.82, (c) a PEGMA homopolymer, (d) a PEGMA2000 graft-copolymerized NR latex film (Graft Conc. = 1.01), (e) a PEGMA2000 graft-copolymerized NR latex film (Graft Conc. = 3.41), and (f) a PEGMA2000 homopolymer.

that the lower molecular weight macromonomer (PEGMA300) graft-copolymerizes more effectively than the higher molecular weight macromonomer (PEGMA2000). This phenomenon is probably attributable to the steric interference arising from the longer PEG side chains in PEGMA2000 macromonomers, as it has been suggested that the side chain lengths of the macromonomers do not have a pronounced effect on their reactivity [11]. Furthermore, the film graft-copolymerized with PEGMA-2000 has a lower contact angle than that graft-copolymerized with PEGMA300 although the graft concentration of the former is much lower. This result indicates that PEGMA2000 is more hydrophilic than PEGMA300.

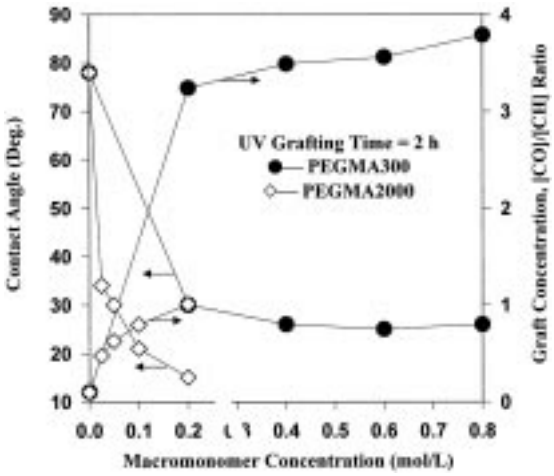


Figure 5 Effect of PEGMA macromonomer concentration on the water contact angle and the surface graft-copolymer concentration of the NR latex films.

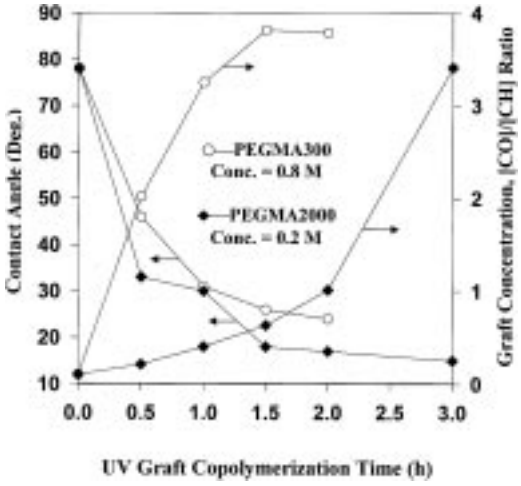


Figure 6 Effect of UV graft-copolymerization time on the water contact angle and the surface graft-copolymer concentration of the NR latex films.

PEGMA has also been graft-copolymerized onto the 20-s Ar plasma-pretreated NR latex films using different UV graft copolymerization times (0.5, 1, 1.5 and 2 h). The monomer concentration was fixed at 0.8 M for PEGMA300 and 0.2 M for PEGMA2000. As shown in Fig. 6, the graft concentration increases and the water contact angle decreases correspondingly upon increasing the UV graft copolymerization time. The data in Fig. 6 also show that the lower molecular weight macromonomer (PEGMA300) graft-copolymerizes to a higher extent than its higher molecular weight counterpart (PEGMA2000). In fact, the graft concentration of PEGMA300 reaches its maximum value (full surface coverage to beyond the probing depth of the XPS technique [24] after 1.5 h of UV graft copolymerization).

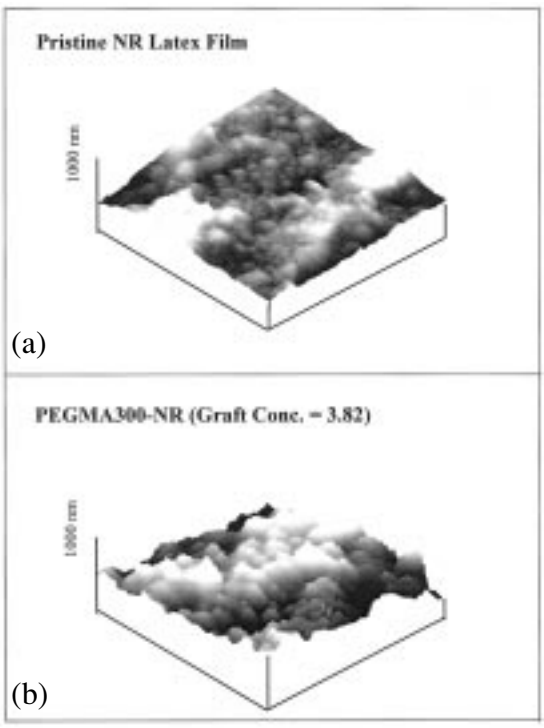


Figure 7 The three-dimensional AFM images of (a) a pristine NR latex film, and (b) the PEGMA300 graft-copolymerized NR latex film (Graft Conc. = 3.82).

On the other hand, the graft concentration of PEGMA2000 reaches a comparable value only after a long UV graft copolymerization time of 3 h.

Atomic force microscopy

Fig. 7(a) and (b) show, respectively, the three-dimensional AFM images of the pristine and the PEGMA300 polymer-modified NR latex film (graft concentration, [CO]/[CH] = 3.82). The RMS roughness in a 10 μm × 10 μm surface region for the pristine NR latex film is about 40 nm. After the surface graft copolymerization process with PEGMA300, the surface morphology has changed substantially. The RMS value of the PEGMA graft-copolymerized surface has increased to about 68 nm.

Protein adsorption

BSA and γ-globulin were adsorbed onto the pristine and the PEG-modified NR latex films. The relative amount of protein adsorbed on each surface was derived from XPS measurements. The intensity of the nitrogen signal from the peptide bonds provides a convenient indicator for the relative amount of protein adsorbed on the surface. Fig. 8 shows the XPS wide scan spectra of the control (pristine) NR latex film and the PEGMA graft-copolymerized NR surfaces after the protein adsorption in 2 mg/mL BSA solution or 2 mg/mL γ-globulin buffer solution. The intensity of the nitrogen peak (at the BE of about 400 eV) from the pristine NR surface in either Fig. 8(a) or (b) was much higher than those of the PEGMA graft-copolymerized surfaces, indicating a significantly larger amount of protein adsorption on the pristine (control) surface. The

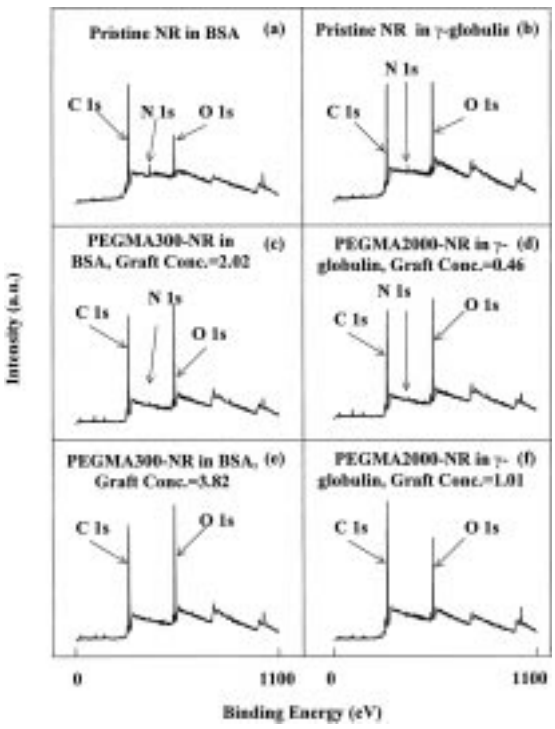


Figure 8 XPS wide scan spectra of the pristine NR latex film and the PEGMA graft-copolymerized NR latex films after exposure to 2 mg/mL of the protein buffer solutions.

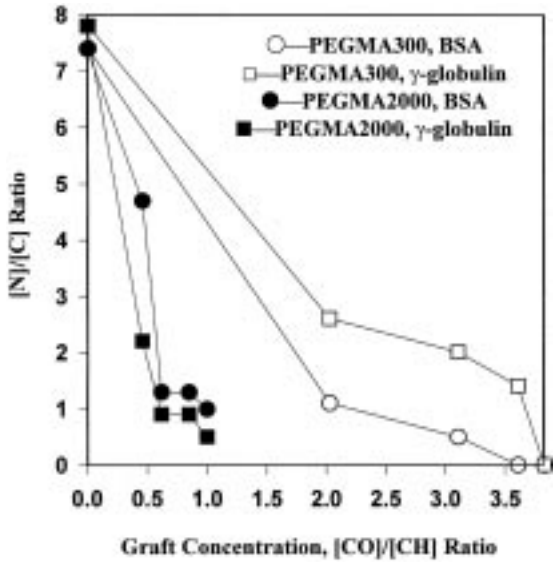


Figure 9 Effect of PEGMA graft concentration on the amount of protein adsorption on the PEGMA graft-copolymerized NR latex film.

strong affinity probably arises from the hydrophobic interaction of the protein molecules with the hydrophobic NR surface [11]. The relative amount of protein adsorbed onto the surface can be expressed simply as the [N]/[C] ratio. The relationships between the [N]/[C] ratio and the graft concentrations of the PEGMA300 and PEGMA2000 polymers are shown in Fig. 9. Thus, even with the incomplete surface coverage by the PEG chains, significant reductions in both BSA and γ-globulin adsorption can be observed. Generally, protein adsorption decreases with the increasing concentration of the surface-grafted PEG polymer. Possible explanations for the passivity of the surface with immobilized PEG towards proteins include its minimum interfacial free energy in water, its hydrophilicity, its high surface mobility, its steric stabilization effects, and most importantly, its unique solution properties and molecular conformation in water. The PEG molecule has a large excluded volume in water [7]. Due to the possession of flexible ether linkages in its backbone and the absence of bulky side groups, PEG is sterically less hindered than most hydrophilic polymers in the aqueous medium. Thus, it is one of the most flexible polymers in an aqueous medium among the common water-soluble polymers. As a result of the PEGs flexibility and large excluded volume in the aqueous environments, PEG grafted surfaces tend to repel protein molecules that approach the surfaces [11, 25]. In addition, the PEG chains grafted onto the surface assume a brush-like microstructure. This microstructure gives rise to dense chains which are highly effective in repelling the protein molecules [12]. These surface characteristics help to account for the fact that the PEGMA graft-copolymerized NR surface is very effective in reducing protein adsorption.

It can also be seen in Fig. 9 that the PEGMA300 graft-copolymerized NR surface has a lower [N]/[C] ratio resulting from exposure to BSA than that of the corresponding surface exposed to γ-globulin. The reverse is true for the PEGMA2000 graft-copolymerized NR surfaces. Direct comparison of the [N]/[C] ratios is

permissible for each type of PEG-modified surfaces after the adsorption of BSA and γ-globulin, as pure BSA and γ-globulin have a very similar [N]/[C] ratio of about 0.25. As it is known, BSA (MW ≈ 70 000 g/mol) is a much smaller molecule than γ-globulin (MW ≈ 156 000 g/mol). Thus, PEGMA300, having a much smaller molecular weight and a much smaller excluded volume than PEGMA2000, is less effective in repelling the γ-globulin molecule despite the fact that the PEGMA300 graft-copolymerized surface has a much high graft density. Thus, it can be hypothesized that the denser surface structure of grafted PEGMA300 is more effective in repelling smaller protein molecules, such as BSA, than larger protein molecules, such as γ-globulin, from adhering to the NR surface. The NR latex film surfaces with grafted PEGMA2000 chains show the opposite result. As the graft concentrations of the PEGMA2000 polymer for samples used in the experiment are lower, BSA, with a small molecular weight, can penetrate the grafted PEG layer more readily and interact with the uncovered NR surface. The γ-globulin, on the other hand, faces more difficulty in reaching the exposed NR surface due to its larger size. The protein adsorption data in Fig. 9 further suggest that PEG of higher molecular weight is much more effective in reducing protein adsorption, in general, than its lower MW counterpart, especially at low graft concentrations.

Platelet adhesion

For the platelet adhesion, platelet-rich plasma (PRP) separated from the blood of healthy dogs was incubated on the pristine and PEGMA graft-copolymerized NR surfaces, and the extents of platelet adhesion on the surfaces were observed by optical microscope. Fig. 10(a)–(e) show, respectively, the optical microscopic images of the platelets adhered to the pristine NR surface and the PEGMA graft-copolymerized NR surfaces. For the pristine NR surface (Fig. 10(a)), the particles with small size are platelets while the particles with much larger size are blood cells. In comparison with the various PEG-modified NR surfaces, (Fig. 10(b)–(e)), the surface of the pristine NR exhibits a much higher affinity for platelets. It can also be seen that for the surface graft-copolymerized with PEGMA of the same molecular weight, the platelet adhesion on the surface decreases with increasing PEG graft concentration. Furthermore, comparison of Fig. 10(b) and (c), or (d) and (e), suggests that, at comparable graft concentration, the PEGMA300 graft-copolymerized NR surface is less effective in reducing platelet adhesion than that of the PEGMA2000 graft-copolymerized NR surface. Therefore, it can be concluded that the PEG with shorter chain length (repeat unit number = 5) is not as effective in reducing platelet adhesion as the PEG with longer chain length (repeat unit number = 45). The PEGMA2000 graft copolymerized NR surface (graft concentration = 3.41) appears to be very effective in repelling platelet adhesion (Fig. 10(e)).

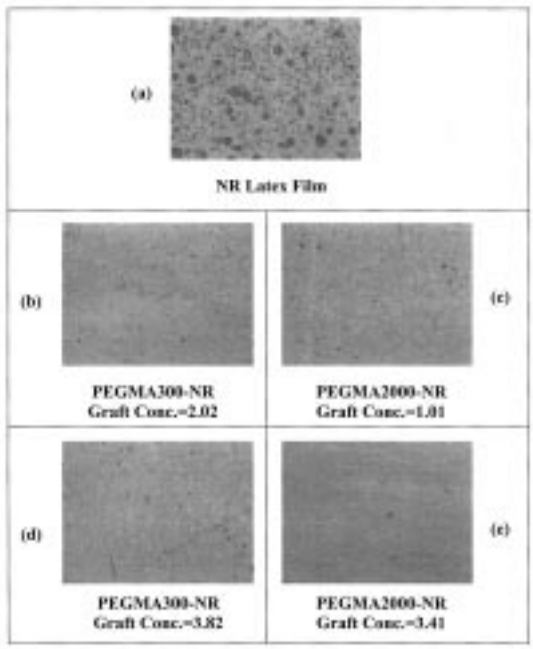


Figure 10 Microscopic images of the platelets adhered onto (a) a pristine NR latex film, (b) a PEGMA300 graft-copolymerized NR latex film (Graft Conc. = 2.02), (c) a PEGMA2000 graft-copolymerized NR latex film (Graft Conc. = 1.01), (d) a PEGMA300 graft-copolymerized NR latex film (Graft Conc. = 3.82), and (e) a PEGMA2000 graft-copolymerized NR latex film (Graft Conc. = 3.41).

Conclusion

NR latex film surfaces, when pretreated with Ar plasma, were readily susceptible to UV-induced graft copolymerization with methoxy PEGMA. The efficiency of graft copolymerization was affected by the molecular weight and concentration of the macromonomer, as well as the UV graft copolymerization time. In general, lower molecular weight, higher concentration of macromonomer and longer UV irradiation time led to a higher graft concentration. Contact angle measurements revealed that the hydrophilicity of the NR surface could be considerably enhanced by graft copolymerization with PEGMA. The PEGMA graft-copolymerized NR surfaces were very effective in reducing protein adsorption and platelet adhesion. It was also found that PEGMA300 (PEG with 5 repeat units) graft-copolymerized surface was more in reducing adsorption of the lower molecular weight protein (BSA) than the higher molecular weight protein (γ-globulin). The reverse was true for surface graft copolymerization with PEGMA2000 (PEG with 45 repeat units). On the other hand, NR surface grafted with PEG of higher molecular weight was much more effective in reducing protein adsorption and platelet adhesion than its counterpart grafted with lower molecular weight PEG, especially at low graft concentrations.

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