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# Surface modification of poly(ethylene terephthalate) by plasma polymerization of poly(ethylene glycol)

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**Abstract** Poly(ethylene glycol) (PEG) was 'polymerized' onto poly(ethylene terephthalate) (PET) surface by radio frequency (RF) plasma polymerization of PEG (average molecular weight 200 Da) at a monomer vapour partial pressure of 10 Pa. Thin films strongly adherent onto PET could be produced by this method. The modified surface was characterized by infra red (IR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), cross-cut test, contact angle measurements and static platelet adhesion studies. The modified surface, believed to be extensively cross-linked, however showed all the chemical characteristics of PEG. The surface was found to be highly hydrophilic as evidenced by an interfacial free energy of about 0.7 dynes/cm. AFM studies showed that the surface of the modified PET became smooth by the plasma polymerized deposition. Static platelet adhesion studies using platelet rich plasma (PRP) showed considerably reduced adhesion of platelets onto the modified surface by SEM. Plasma 'polymerization' of a polymer such as PEG onto substrates may be a novel and interesting strategy to prepare PEG-like surfaces on a variety of substrates since the technique allows the formation of thin, pin-hole free, strongly adherent films on a variety of substrates.

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## Introduction

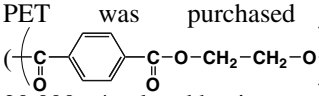
The surface properties of materials play a pivotal role in determining their biocompatibility, strongly influence the biological response and determine their long-term performance in vivo. Hence, it is important to design biomaterials with the right surface properties. Biomaterials also must possess bulk properties that meet other requirements, especially physical and mechanical properties in order to function properly in the biological environment. As it is difficult to design biomaterials fulfilling both needs, a common approach is to fabricate biomaterials with adequate bulk properties followed by modification of its surface to enhance the surface properties [1]. Different surface modification strategies such as physical, chemical, plasma and radiation-induced, have been employed to generate desirable surface properties on biomaterials. Modifications based on deposition of plasma polymers [2] and plasma treatments are highly substrate independent [3]. Plasma polymerization has unique practical advantages which include (i) confirmative ultra thin film deposition, (ii) good adhesion to the substrate material and (iii) formation of chemically and physically durable surfaces [1, 3].

Poly(ethylene terephthalate) (PET) is used in cardiovascular implants such as sewing rings of the mechanical heart valve prostheses, vascular grafts and angioplasty balloons

because of its excellent mechanical properties and moderate biocompatibility [4–6]. To improve the blood compatibility of PET, one of the widely employed methods is to modify its surface using poly(ethylene glycol) (PEG), well known for its blood-compatible, non-immunogenic, non-antigenic and protein-resistant properties [7]. PEG has been immobilized onto a variety of polymer surfaces using techniques such as physical adsorption, graft polymerization, covalent grafting, blending etc. [8–13]. Lopez et al. [14] reported the modification of substrates by plasma polymerization of tetraglyme ($CH_3$–O–($CH_2$–$CH_2$–O)$_4$–$CH_3$) to obtain a PEG-like surface. Argon plasma treatment followed by exposure to air has been used to graft poly(ethylene glycol methacrylate) by Qiu et al. [15]. Recently, an atmospheric pressure glow discharge technique has been employed by Zang et al. [16] to modify polymer surfaces with PEG by pre-adsorption of PEG onto the surface and subjecting the polymer to glow discharge. To the best of our knowledge, no attempt seems to have been made to prepare a polymer film directly from PEG by radio frequency (RF) plasma polymerization of PEG in its vapour phase to modify PET or any other surfaces possibly because of the low vapour pressure of even low molecular weight PEGs at moderate temperatures. This study was therefore undertaken to examine how a low molecular weight PEG would behave in its vapour phase when subjected to plasma 'polymerization' onto a substrate such as PET or glass.

## Materials and methods

### Materials

PET was purchased from Dupont, Japan (  , molecular weight 5,000–20,000 g/mol and having approximately 30% crystallinity). Samples of 3 cm × 1.5 cm × 1 mm size were washed with non-ionic soap solution followed by several rinses using singly distilled water. Specimens were then sonicated in doubly distilled water for 15 min and dried in an air oven at 50 °C. PEG of average molecular weight 200 (PEG-200) was purchased from Kanto Chemical Co. Inc., Japan and was used as such. We also used micro glass slides to coat plasma polymerized PEG (PP-PEG) for Infra red (IR) and adhesion strength studies, after successive washing of the glass slides ultrasonically in acetone and distilled water and then drying them in an air oven at 50 °C.

### Methods

Plasma polymerization of PEG was done with an improvised plasma polymerization unit consisting of a borosilicate glass tube approximately 0.5 m long having an outer diameter of 0.035 m fitted with a monomer inlet, air inlet, argon inlet, pressure gauge and rotary pump. Power from radio frequency (13.56 MHz) oscillator power supply was capacitively coupled to the deposition chamber by means of copper foils wrapped around the tube. Pictorial diagram of the apparatus can be obtained from one of our previous reports [17]. The film was produced in RF plasma under a vapour pressure of 10 Pa with argon flow rate 0.1 ccm and at 10, 30, 50, 75 and 100 W for 5 min. For obtaining PEG vapour, the monomer was heated up to 220 °C. Surface characterization of PP-PEG was conducted using IR (JIR-7000 Jeol, Japan), scanning electron microscopy (JSEM 7400F, Jeol, Japan), and atomic force microscopy (operated in DFM mode) (AFM-SPA 300, Seiko Instruments). For recording the IR spectra, PP-PEG coated onto the glass substrates was scrapped and pelletized with KBr. Contact angle measurements were done using a goniometer (Rame'Hart, USA). Captive air-in-water and octane-in-water techniques were employed and the values reported are average of six measurements on each sample. Surface energy parameters were calculated according to Andrade et al. [18]. Preliminary blood-compatibility assessment was done by in vitro platelet adhesion studies using platelet rich human plasma.

### Adhesion strength studies

The adhesive force of PP-PEG thin films onto glass substrates was estimated by the cross-cut test in which an adhesive tape is used to peel off a thin film cross-cut to 100 (10 × 10; 1 × 1 mm each) from the glass substrate. The adhesive strength is expressed by the index from '0' to '10', depending on the extent of retention of the squares on peeling off the tape, where index '0' means complete detachment of cross cut squares and index '10' denotes no detachment of the cross cut squares [19]. Since plasma polymers show very good adhesion onto a variety of substrates, the results obtained from the adhesive force studies were used as a guideline to select the RF power to be employed for the surface modification.

### Platelet adhesion experiments

For platelet adhesion studies, PP-PEG coated and uncoated PET substrates were exposed to platelet rich plasma (PRP) from human blood as reported previously [13]. Adhered platelets were fixed with 2.5% glutaraldehyde solution, freeze-dried in a laboratory freeze dryer, coated with gold (thickness of 50 Å) and examined in the SEM.

## Results and discussion

Plasma polymerization of PEG onto both glass and PET resulted in colourless, highly transparent polymer films.

**Table 1** The adhesive force of the plasma polymerized poly(ethylene glycol) (PP-PEG) films deposited onto glass substrates estimated by the cross cut test (0: complete detachment 10: no detachment)

| Radio frequency (RF) power | 10 W | 30 W | 50 W | 75 W | 100 W |
|---|---|---|---|---|---|
| Adhesive index | 6 | 7 | 10 | 10 | 10 |

The results of the cross cut test to determine the adhesive character of PP-PEG to the glass substrates are given in Table 1 for different plasma powers. These results showed that the PP-PEG films could be peeled off easily when low plasma powers were employed as compared to higher plasma powers. We found that PP-PEG films produced at 50 W adhered to the glass substrates very strongly. Since the adherence to the substrates plays a crucial role in the surface modification, we employed PP-PEG films obtained at 50 W for further studies. The adhesive studies employed on the polymers deposited on the PET samples also showed almost similar nature of adhesiveness. Plasma polymers produced at higher powers (75 or 100 W) showed almost same results as of 50 W regarding adhesion strengths, however the substrate PET was found to undergo some damage at these powers although there was no problem with glass. Also, it is reported that higher RF plasma powers often destroy the monomers [20] and therefore moderate RF power would be ideal (50 W in our case) for considering surface modifications.

Figure 1 depicts the IR spectra of PEG and PP-PEG prepared at 50 W. The peaks at 833, 887, 941 $cm^{-1}$ in PEG and at 779 and 910 $cm^{-1}$ in PP-PEG were assigned to C–H in-plane bending. Peaks at 1,072 and 1,118 $cm^{-1}$ and at 1,029 and 1,076 $cm^{-1}$ correspond to the C–O–C vibration in PEG. The peaks at 1,249, 1,295, 1,349 and 1,396 $cm^{-1}$ in PEG correspond to C–C stretching vibrations. The peaks

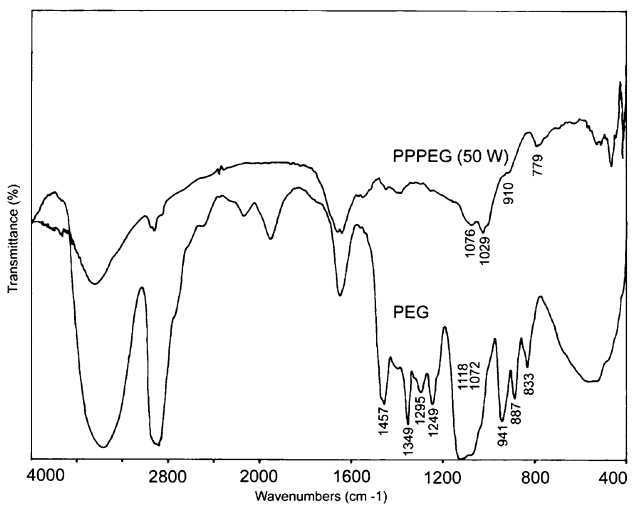



**Fig. 1** IR spectra of PEG and plasma polymerized poly(ethylene glycol) (PP-PEG) prepared at radio frequency (RF) power of 50 W

at 2,877 $cm^{-1}$ in PEG and 2,854 $cm^{-1}$ in PP-PEG represent C–H stretch vibrations. The strong band structure appearing at 3,355 $cm^{-1}$ in PEG and 3,444 $cm^{-1}$ in PP-PEG indicates the presence of O–H bonds. The slight variation in the position of peaks in PP-PEG in comparison with the corresponding peak positions in PEG may be due to the change of PEG from the liquid state to the plasma polymerized solid state [21, 22]. Thus, the IR spectral evidence clearly shows that we obtained the polymer film of PEG with out much destruction of its structure.

The fact that characteristic C–H and C–C bending modes are absent or reduced in intensity in the plasma polymerized specimen indicates the possibility of cross-linked polymers. This cross-linking nature is very common in the plasma polymers and thus it is practically impossible to arrive at any definite conclusions regarding their structure, considered as one of the drawbacks [20]. However, we are more interested in the surface properties of these films and its behaviour in the biological milieu.

The film gently scrapped from the surfaces was found to be insoluble in water thus suggesting that the film is a highly cross-linked network.

AFM was employed to examine the surface morphology of the PET and PP-PEG coated PET surfaces. Figure 2a shows the surface morphology of the PET substrate. Figure 2b shows the nature of the surface of the PP-PEG coated PET substrate at 50 W RF power and shows that the PP-PEG films are almost smooth and uniform in coverage of the substrate. The surface modification involving plasma polymerization of a polymer itself generates a smooth and uniform surface is particularly noteworthy and could be considered as a pointer to better hemocompatibility as PEG is known to be blood-compatible polymer [23]. It should be noted that the vapour pressure of PEG employed was very low (10 Pa) and the temperature used was very high (220 °C) for heating the PEG. Even under these conditions, it is noteworthy that such thin films could be formed on substrates in a uniform fashion.

Table 2 depicts the contact angle data obtained from the PP-PEG treated and untreated PET substrates. The untreated PET has a hydrophobic surface exhibiting an air-in-water contact angle of 82°. After the surface modification, the water contact angle decreased to 30° and the interfacial free energy between water and PET decreased from 20.64 to 0.71 dynes/cm. These results clearly indicate that surface modification of PET with PP-PEG results in a highly hydrophilic surface [4].

Static platelet adhesion studies showed significant difference in the platelet adhesion character of untreated PET and PP-PEG modified surfaces. Figure 3a and b show the SEM obtained from the above mentioned samples. Considerably reduced adhesion could be seen on the modified surface as opposed to virgin PET surface which promotes

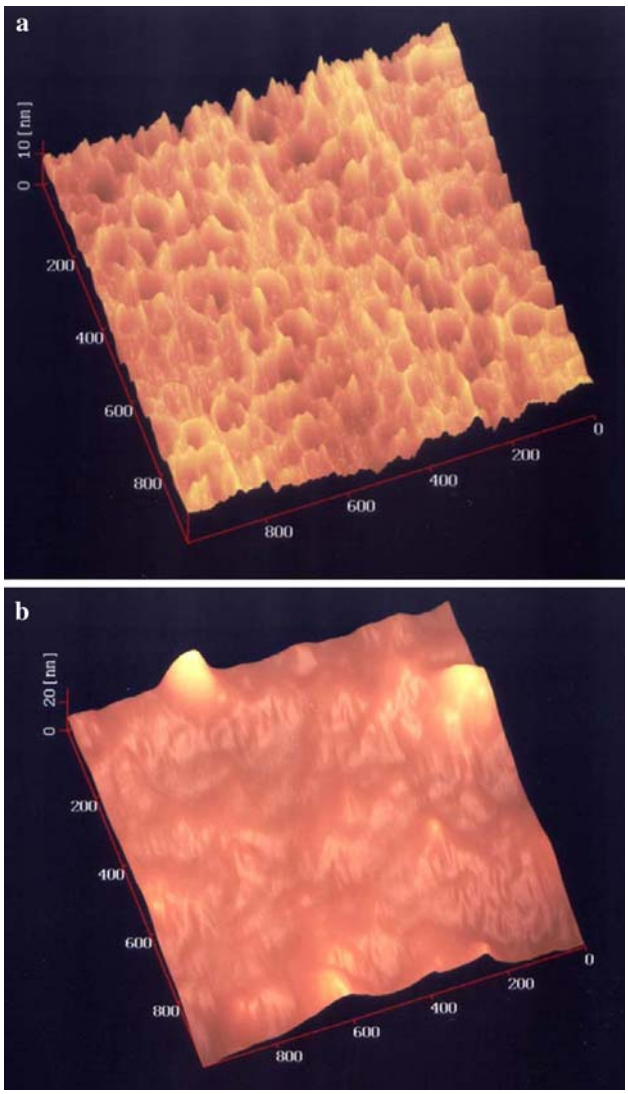



**Fig. 2** Atomic force microscopy (AFM) of unmodified poly(ethylene terephthalate) (PET) surface (**a**) and plasma polymerized poly(ethylene glycol) (PP-PEG) modified PET surface at (**b**) 50 W

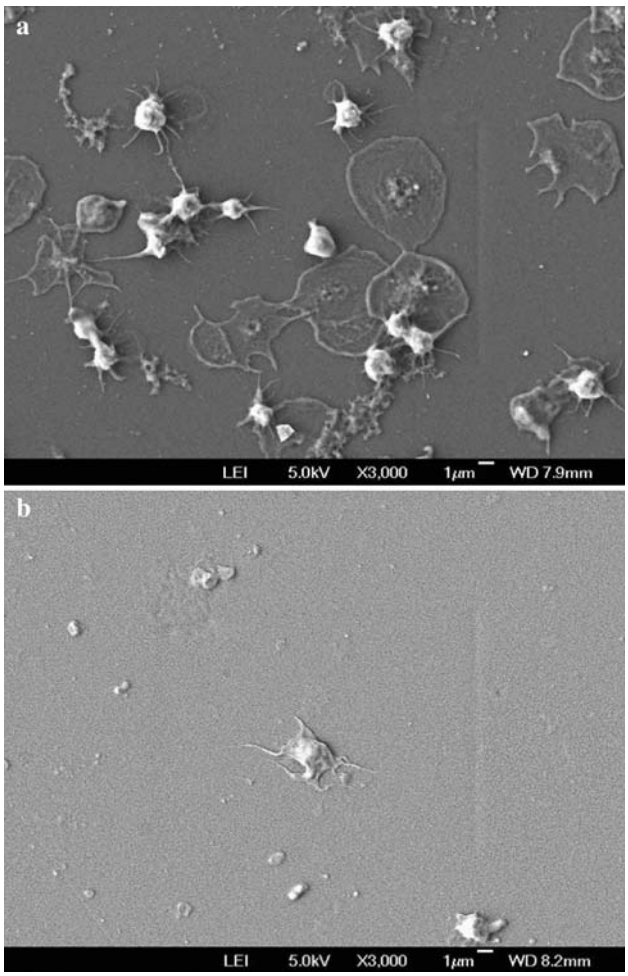



**Fig. 3** Scanning electron microscopy (SEM) showing platelet adhesion on to unmodified poly(ethylene terephthalate) (PET) surface (**a**) and plasma polymerized poly(ethylene glycol) (PP-PEG) deposited PET surface (**b**)

adhesion and aggregation of platelets pointing to its thrombogenic nature.

Plasma polymerization of PEG therefore generates a surface which is less thrombogenic. It is well known that grafting PEG onto a polymer surface can increase the hydrophilicity of the surface as well as make it less thrombogenic [7]. Plasma surface modification using tetraglyme [14] or ethylene oxide [24] has been resorted for generating a PEG-like surface. At very low vapour pressures, it is seen in this study that a thin, hydrophilic PEG-rich surface can be produced on PET as well as glass. In comparison with chemical or radiation-induced grafting of PEG, plasma polymerization has the unique advantage that a highly uniform surface coverage on the substrate could be obtained as a thin film which is strongly adhered onto the substrate irrespective of the nature of the substrate. Using PEG as such for such modifications has the advantage that it is very quick and the procedure is simple.

**Table 2** Contact angles and surface energy parameters of unmodified poly(ethylene terephthalate) (PET) and plasma polymerized poly(ethylene glycol) (PP-PEG) deposited PET

| Sample | $\theta$ air (deg) | $\Phi$ octane (deg) | $\gamma$ s/v$^{d}$ (dynes/cm) | $\gamma$ s/v$^{p}$ (dynes/cm) | $\gamma$ s/v (dynes/cm) | $\gamma$ s/w (dynes/cm) |
|---|---|---|---|---|---|---|
| PET | 82 ± 1 | 96 ± 1 | 16.40 | 14.49 | 30.89 | 20.64 |
| PP-PEG–PET (50 W) | 30 ± 1 | 34 ± 3 | 20.42 | 42.54 | 62.96 | 0.71 |

## Conclusion

In this study, we have shown that highly transparent, colourless, smooth and pin hole-free film from PEG can be prepared by plasma polymerization of PEG itself. Even though PEG had to be heated to a very high temperature of 220 °C to obtain vapours for plasma polymerization, it was significant that a polymer film which retained the hydrophilic and cell-repelling properties of PEG could be formed on substrates such as glass and PET at very low vapour pressures. Since plasma polymerized films could be deposited onto a variety of substrates irrespective of its nature and shape, the method reported here would be useful for generating PEG-like films on polymeric and non-polymeric biomaterials for improving their biocompatibility.

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