Radiation-induced modification of polyurethane with hydroxyethyl methacrylate: blood compatibility

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Abstract. An attempt is made to develop the hydrophilic grafting of polyether urethane urea with hydroxyethyl methacrylate (HEMA) using ^{60}Co γ -irradiation for achieving optimum hydrophilic/hydrophobic property needed towards blood compatibility. Contact angle method and platelet adhesion from calf's blood are used to determine the suitability of these modified surfaces.

Keywords. Blood compatibility; platelet-adhesion; HEMA grafted polyether urethane; γ -irradiation.

1. Introduction

Surface energy and interfacial parameters of synthetic polymers have been of interest, since such parameters seem to have some inter-relationship (Lyman *et al* 1965) with blood compatibility. It has also been suggested (Sharma 1981a) that optimum distribution of polar-dispersion components on the surface may have sufficient bioadhesive potential to form a passivating layer, such that a more inert surface is presented to the blood. The good blood compatible surface can be achieved if surface energy parameters,

$$\alpha_s (= (\gamma_s^d)^{1/2}) \simeq 4.7 \text{ (dynes/cm)}^{1/2},$$

$$\beta_s (= (\gamma_s^p)^{1/2}) \simeq 3.0 \text{ (dynes/cm)}^{1/2}$$

and

$$\beta_s/\alpha_s \simeq 0.64 \text{ are adjusted (Sharma 1981b).}$$

We have therefore attempted to develop an optimum procedure to modify our polyurethane ureas, synthesised in our laboratory with polypropylene glycol (mol. wt. 1025) as described by Shibatani *et al* (1977) and characterised (Sharma and Ashalata 1982), with hydroxyethyl methacrylate (HEMA) using ^{60}Co γ -irradiation to achieve the desired surface properties. Our polymer PEUU had an initial tensile strength of $\sim 100 \text{ kg/cm}^2$ and % elongation of $\sim 157\%$ for a gauge length of 25.4 mm and cross head speed 20 mm/min, with pore size $\sim 50\text{--}100 \mu$ and number of pores on the surface $\sim 5000 \pm 1000/\text{cm}^2$ as viewed microscopically.

2. Method

Polyether urethane ureas (PEUU) are fabricated in the form of vascular grafts (5 mm diameter) from 30 g % solution in dimethyl formamide as described earlier (Sharma and Ashalata 1982).

These grafts are treated with acetone for $1-1\frac{1}{2}$ hr and kept in distilled water for 24 hr, changing the water several times. The samples are dried under vacuum at 343°K and weighed. Before swelling the samples, the HEMA (BDH, England) was evacuated and N_2 gas continuously bubbled through it. Samples are dipped in HEMA for ~ 5 min only since we want only the surface modification without much penetration of HEMA into the bulk of our samples. The samples are slightly pressed between two filter papers with constant pressure, and irradiation is performed on these samples at room temperature in a ^{60}Co gamma chamber with a constant dose rate of 0.25 M rad/hr and strength of 843 Rontgen/hr/m for different lengths of time up to 4 hr. After irradiation, the samples are treated with distilled ethanol for 48 hr to remove all ungrafted HEMA monomer from the samples (Jansen and Ellinghorst 1979).

3. Platelet adhesion

Washed calf platelets are prepared and suspended in tyrode solution (Sharma and Lissy 1982) for adhesion studies. The polymers under study are exposed to platelet suspension for 1 hr, rinsed with buffer under uniform flow for about 3 min, and the platelets are fixed with 2.5 % glutaraldehyde and stained with Coomassie blue G. The platelet density is detected using an optical microscope. Different fields are randomly read and averaged in a similar fashion for all samples.

4. Evaluation of surface energy parameters

The polymer surfaces are characterised using contact angle measurement (Zisman 1964) with a Goniometer at room temperature. The polymer films are cleaned by rinsing with ethanol. The organic liquids used for the measurements are more than 99 % pure. The dispersion $\alpha_s (= (\gamma_s^d)^{1/2})$ and polar $\beta_s (= (\gamma_s^p)^{1/2})$ components of surface energy γ_s are determined as described earlier (Sharma 1981b).

5. Results and discussion

The grafting yield and water uptake % is determined gravimetrically (Jansen and Ellinghorst 1979). There is no significant grafting yield up to 2 hr irradiation doses. Water uptake is also only $\sim 3\%$. However $\sim 20\%$ grafting yield is observed, when irradiation dose is 4 hr and water uptake % increase up to $\sim 7\%$. Inherent viscosity η_{inh} (dimethyl formamide as a solvent at $\sim 30^\circ\text{C}$) also increases gradually from $\sim 0.33 \text{ (dl/g)}$ non-irradiated, to $\sim 0.61 \text{ (dl/g)}$ after 4 hr of irradiation indicating the possibility of crosslinking *via* grafting with irradiation doses.

No significant variation is observed (*i.e.* within standard deviation range) in the number of platelets adhered ($\sim 3.5 \pm 0.7$ in all cases). Surface energy parameters seems to be affected with grafting. For 4 hr irradiation dose, $\alpha_s \simeq 4.6 \text{ (dynes/cm)}^{1/2}$ and $\beta_s \simeq 3.8 \text{ (dynes/cm)}^{1/2}$ compared to $\alpha_s \simeq 4.9$ and $\beta_s \simeq 2.85$ (2 hr, and $\alpha_s \simeq 5.1$ and $\beta_s \simeq 3.3$ (Bare *i.e.* non-irradiated).

Approximately 3 hr of irradiation time is required to achieve surface energy parameters $\alpha_s \simeq 4.7 \text{ (dynes/cm)}^{1/2}$ and $\beta_s \simeq 3 \text{ (dynes/cm)}^{1/2}$ as suggested earlier (Sharma 1981b) for blood compatibility. Since such surfaces may absorb albumin

preferentially (Lissy and Sharma 1981), adhesion of platelets will also be less in *in vivo* conditions instead of increasing due to hydrophilicity (Neumann *et al* 1979). Further increased dose may also lead to physical entanglement and crosslinking of homopolymerising HEMA in the PEUU metrics which may be difficult to extract afterwards (Jansen and Ellinghorst 1979).

Our future efforts will be to study in depth and extend the above studies and also develop biological interrelation with such concepts as described elsewhere (Nair and Sharma 1984) considering interaction with platelets and plasma proteins on such surfaces.

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