Surface Modification of Charcoal by Glow-Discharge: The Effect on Blood Cells

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Synopsis

Glow discharge polymerization of hexamethyldisiloxane was carried out on activated charcoal granules through the application of capacitively coupled RF plasma. The coats were examined with Auger and IR spectroscopies, and with SEM. The surface topography and the tenacity of samples coated with plasma were compared with that of the solution-coated ones. Mercury porosimetry was used to study the effect of the coat on pore size distribution. The effect of contact with blood on the number of blood cells were studied.

INTRODUCTION

A number of monomers have been plasma polymerized onto a wide range of substrates in the past. The resultant films offered excellent thermal, dielectric and optical properties which made them indispensable for diverse practical applications.[1] The plasma-polymerized films are in general crosslinked and possess superior adhesion qualities compared to the films obtained by non-plasma methods. Although the kinetics of the reactions are not known, there are many approaches trying to explain how it happens. In one approach, polymerization is assumed to take place on substrate as a result of monomer adsorption and subsequent bombardment of the monomer by active species and radiation produced in the plasma.[2] Another approach assumes that active species are produced in the gas phase and that these may interact among themselves or with the monomer to produce active species of larger molecular weight. The formation of a film occurs when both the original species and the oligomers diffuse to the substrate surface where they can react further.[3] In this work, a highly porous substrate—activated charcoal—was used and polymerization of hexamethyldisiloxane (HMDS) was achieved by using an RF generator. Activated charcoal is commonly used for removal of toxins in medicine. The first use of charcoal as a blood detoxifier was reported in the sixties.[4] Although hemoperfusion with charcoal is much more economical in comparison to dialysis, it may cause a drop in the number of blood cells especially in the platelets. In this study, the granules were coated to overcome this problem by creating a new blood compatible surface. The chemical structure of the coat and the effect on pore size distribution as well as on blood cells was examined.

EXPERIMENTAL

In the coating of the activated charcoal (Norit RBXS-1, a gift from Gambro, W. Germany), the reactor shown in Figure 1 was used. The reactor

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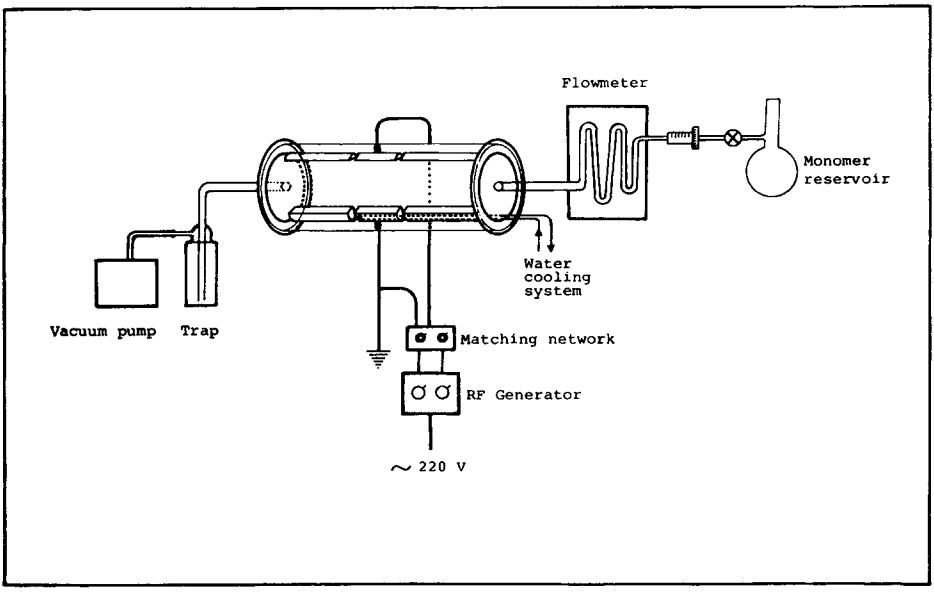


Fig. 1. Plasma setup.

mainly consisted of a glass tube (6 cm in diameter, 52 cm in length) into which two copper electrodes (14 × 4 cm^2) were placed 3.5 cm apart. On both sides of the electrodes, Teflon blocks were inserted in order to sustain a uniform flow of monomer gas. Power for this capacitively coupled reactor was supplied by a 13.56-MHz RF generator. The details of the reactor were reported earlier.[5] Activated charcoal which was previously washed, dried, and stored under vacuum was placed in a copper container and was brought to constant weight by application of vacuum. This sample (3.5 g) was taken with its copper container and placed into the reactor. The liquid monomer, which was degassed earlier, was charged into the system in gaseous form. A steady-state flow was maintained for 30 min before application of RF power. Polymerization conditions were kept constant at 20 W and 50 mL/min for applied power and monomer flow rate, respectively.

IR spectra of the polymers deposited on NaCl crystals were obtained directly. The polymer deposited on the aluminum foil, however, was scraped and the IR was obtained through a KBr pellet. Porosity tests to determine both the pore size and its distribution were performed by an Aminco-30000 psi digital readout porosimeter. The data, intrusion values vs. absolute pressure, are plotted on the AMINCO preprinted graph paper to obtain a cumulative pore volume distribution graph. The pore diameter is read directly from the top scale. Contact of charcoal granules with blood was achieved by the system shown in Figure 2. In these experiments, fresh sheep blood containing oxalate anticoagulant was used. Blood (100 mL) was put into the reservoir and after passing through the column (rate = 10 mL/min) was collected in a container. Hemolytic activity and cell count tests were carried out with this collected blood samples. In the hemolytic activity test, 5 mL of the collected blood was centrifuged at 2000 rpm for 10 min. The absorbance of released hemoglobin was measured spectrophotometrically at 541 nm. The same procedure was

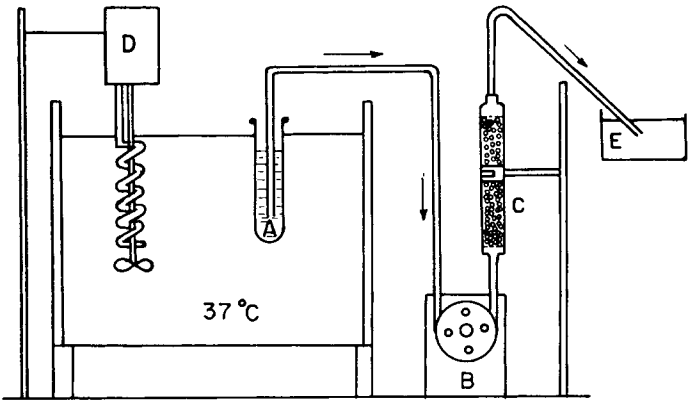


Fig. 2. Hemoperfusion system: (A) blood sample; (B) peristaltic pump; (C) charcoal column; (D) heater and stirrer; (E) collected blood sample.

applied to blood that has been passed through the empty column to serve as blank. For the determination of the total hemoglobin content of 5 mL blood, sample was diluted 10 times with distilled water to achieve complete hemolysis, and the absorbance was measured.

The blood cells were counted with hemocytometer after staining. For these processes, blood samples were diluted with staining solutions in special erythrocyte or leucocyte pipets.

Scanning electron micrographs of charcoal samples used in hemoperfusion experiments were taken after fixation of blood cells. In the sample preparation, the column containing charcoal was washed with isotonic phosphate buffer (100 mL) and charcoal was transferred to buffered glutaraldehyde solution (3%). After 15 min, glutaraldehyde solution was decanted, and distilled water sufficient to cover all the charcoal was added. After 30 min, water was decanted, charcoal was left to dry at room temperature, and SEM investigations were performed.

RESULTS AND DISCUSSION

Charcoal granules were coated with HMDS at 20 W and 50 mL/min for applied power and monomer flow rate, respectively. These were found to be the optimum parameters for charcoal as substrate.[6] Under these conditions, a weight increase of 28.5% was obtained in 1 h. (long enough to assume that all the adsorbed monomer is polymerized). In an earlier study, charcoal was coated with the same monomer under a different set of conditions and a weight increase of about 2% was reported.[7] The 28.5% weight increase can be explained by adsorption of the monomer molecules on the highly adsorptive substrate prior to their polymerization by the electrical discharge.

Auger spectra obtained from uncoated and coated samples are presented in Figure 3. The presence of Si_{LMN} absorption peak in the coated samples and its absence in the uncoated samples, and also the increase in intensity of O_{KLL} indicate enrichment of the surface with HMDS. IR spectra of polymer deposits on NaCl crystal or aluminum foil show the same absorption bands indicating that the chemical structure of both polymers are similar (Fig. 4).

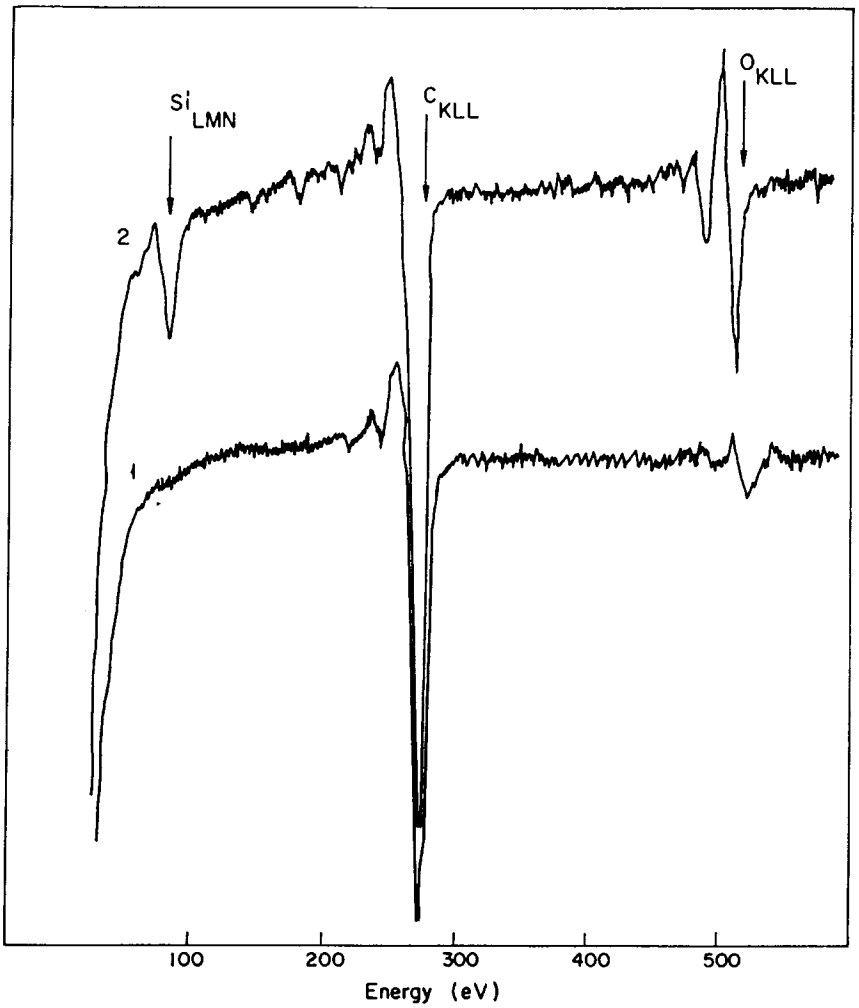


Fig. 3. Auger spectra of charcoal: (1) charcoal; (2) HMDS-coated charcoal.

The ratio of the intensities of absorption bands at 1250 to 1050 cm^{-1} are 0.60 for the deposits on NaCl crystal and 0.64 for aluminum. The band at 1250 cm^{-1} is for $—Si(CH_3)_3$ bending, and 1050 cm^{-1} is for Si—O—Si stretching; the almost identical values obtained for both substrates indicate that the coats are chemically very similar. A similar spectra for HMDS was reported earlier.[8] It was not possible to apply IR spectroscopy to the polymer coat which was deposited on charcoal. However, because of the high adsorptive capacity of charcoal, there may be some adsorption of impurities (e.g., water, oxygen, carbon dioxide, etc.) onto its structure, and these may also take part in plasma polymerization leading to a slightly different coat than that obtained with the other substrates.

It is observed in Figure 5 and Tables I and II that the percent porosity of charcoal decreased only marginally from 34.1 to 32.9% upon coating. A more

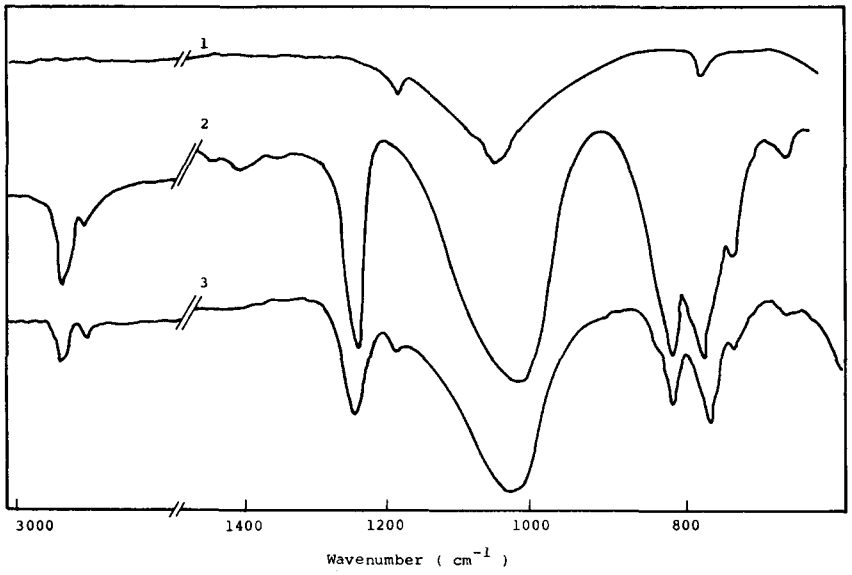


Fig. 4. IR spectra: (1) HMDS monomer; (2) HMDS polymer on aluminum; (3) HMDS polymer on NaCl crystal.

significant change, however, is observed in the pore size distribution. It seems that the uncoated charcoal reaches a penetration value of 0.40 mL/g at about 0.5 μm above which a substantial change is not observed with further increase of pressure. Same trend is observed in the coated sample, but the penetration value there is 0.32 mL/g. The densities of the uncoated and coated samples are calculated as 0.7539 and 0.9162 g/mL, respectively. The increase in

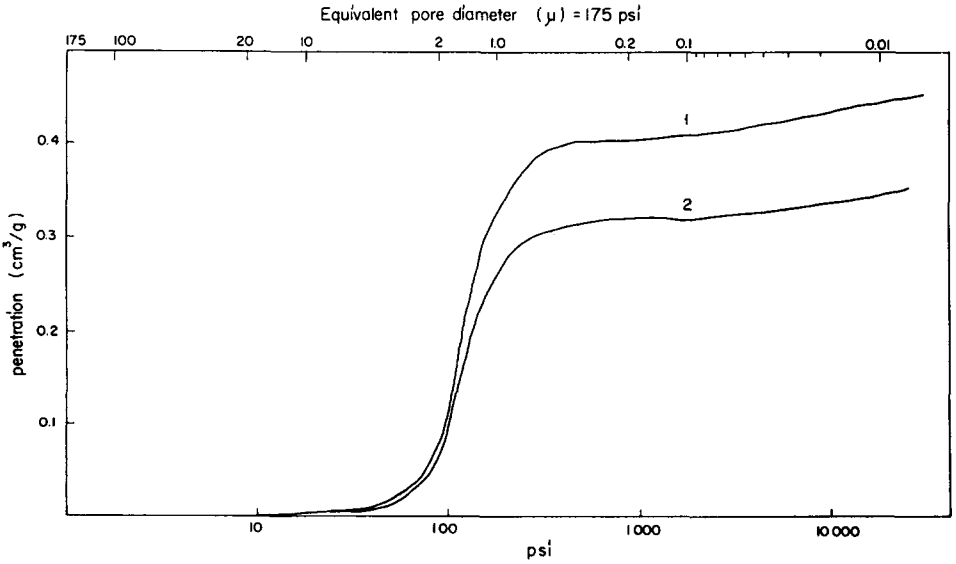


Fig. 5. Pore size distribution curves: (1) charcoal; (2) HMDS-coated charcoal.

TABLE I
Mercury Porosimeter Data for Uncoated Charcoal[a]

P gauge (psi)	Penetration (cm^3/g)	Cumulative penetration
0	0.0078	0
25	0.0163	0.0085
50	0.0249	0.0171
100	0.1720	0.1642
200	0.3637	0.3559
500	0.4078	0.4000
750	0.4111	0.4033
1000	0.4128	0.4050
1300	0.4144	0.4066
2000	0.4181	0.4103
5000	0.4315	0.4237
10000	0.4454	0.4376
15000	0.4524	0.4446
20000	0.4597	0.4519
25000	0.4577	0.4499
28000	0.4597	0.4519

[a] T (°C) = 28, d_{Hg} (at 28°C) = 13.5266 g/cm^3, P_{atm} = 13.22 psi; volume of container = 5.2731 cm^3, volume of Hg = 4.9494 cm^3; weight of container + sample = 48.5567 g; weight of container + sample + Hg = 115.5059 g; weight of sample = 0.2447 g, volume of sample = 5.2731 − 4.9494 = 0.3236 cm^3; density of sample = 0.2447/0.3236 = 0.7560 g/cm^3; % porosity = 0.7560 × 0.4519 × 100 = 34.2.

TABLE II
Mercury Porosimeter Data for Coated Charcoal[a]

P gauge (psi)	Penetration (cm^3/g)	Cumulative penetration
0	0.0062	0
25	0.0113	0.0051
50	0.0252	0.0190
100	0.1346	0.1284
200	0.2892	0.2830
400	0.3174	0.3112
750	0.3232	0.3170
1000	0.3239	0.3177
1300	0.3261	0.3199
2000	0.3294	0.3231
5000	0.3371	0.3309
10000	0.3444	0.3382
15000	0.3550	0.3488
20000	0.3590	0.3528
25000	0.3594	0.3532
28000	0.3653	0.3591

[a] T (°C) = 27, d_{Hg} (at 27°C) = 13.5291 g/cm^3, P_{atm} = 13.22 psi; volume of container = 5.2731 cm^3, volume of Hg = 4.9746 cm^3; weight of sample + container = 48.5607 g; weight of sample + container + Hg = 115.8621 g; weight of sample = 0.2735, volume of sample = 5.2731 − 4.9745 = 0.2986 cm^3; density of sample = 0.2735/0.2985 = 0.9162 g/cm^3; % porosity = 0.9162 × 0.3591 × 100 = 32.9.

Fig. 6. SEM of charcoal (×1700).

density shows that the weight of charcoal per cubic centimeter is increased because of polymer deposition. On the other hand, almost identical porosity values indicate that this deposition is just a surface phenomena that does not close the pores. This is only possible with an ultrathin coating.

The effect of the coat on the adsorptive capacity of charcoal was given before, and it was observed that there was no substantial decrease in adsorptive capacity.[9]

SEMs presented in Figures 6 and 7 are of uncoated and coated charcoal samples and show a completely different surface and a definite coat which is not very smooth. It also appears that the coat is mechanically strong and has a strong adherence to the surface. SEMs of charcoal coated from solution with acrylic hydrogel (prepared by Smith and Nephew, U.K. for commercial use) reveal ruptures and cracks in the coat surface (Fig. 8). These ruptures might be due to the weakness of adhesion between the coat and the charcoal surface, thickness and/or low crosslink density of the coat. It was also reported that this kind of a coat substantially decreases the adsorptive capacity.[10]

In hemolytic activity tests, percent hemolysis was found as 0.035 for uncoated and 0.025 for the coated charcoal indicating no significant difference.

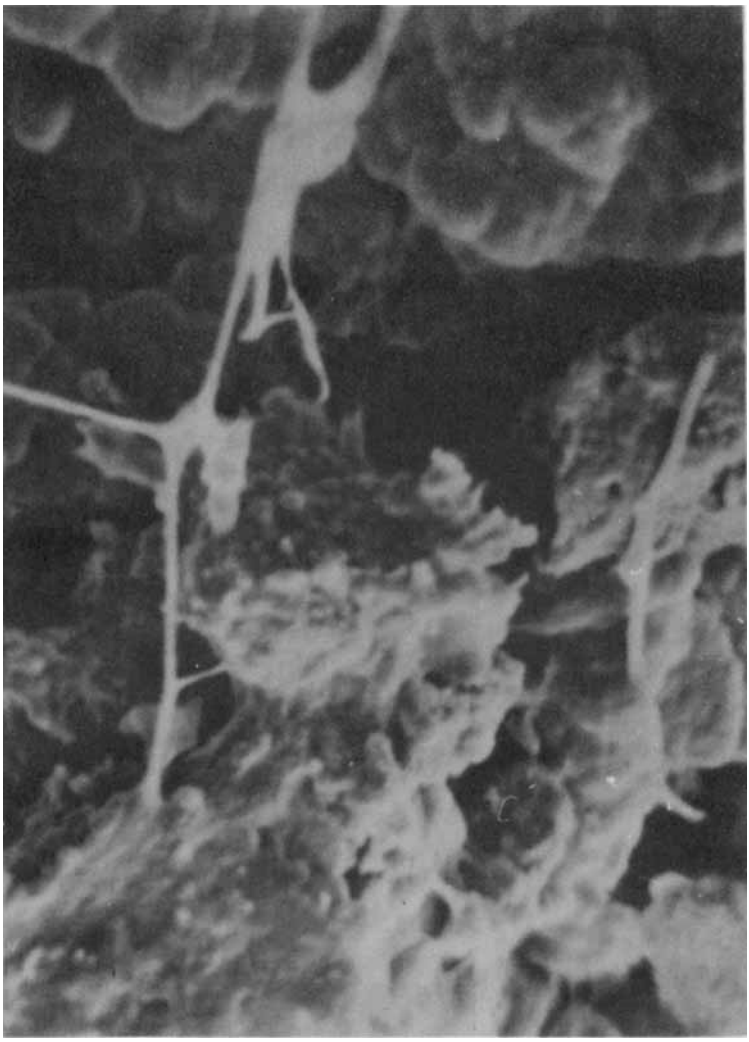


Fig. 7. SEM of HMDS-coated charcoal (×700).

In the cell counts, it was found that coated granules lead to 1.6% change in the number of platelets while uncoated granules cause a 29% reduction. A similar trend was observed for erythrocytes and leucocytes. While uncoated charcoal caused 9.9 and 7.0% reduction in the number of erythrocytes and leucocytes, respectively, coated granules did not lead to any reduction. Thus, it can be concluded that coating of the charcoals will drastically reduce the damage to platelets, erthrocytes, and leucocytes. As expected from the above results, the scanning electron micrographs of charcoal granules (obtained after hemoperfusion tests) show that, in the case of uncoated charcoal samples, large number of blood cells are present on the surface but almost none on the coated charcoal (Figs. 9 and 10).

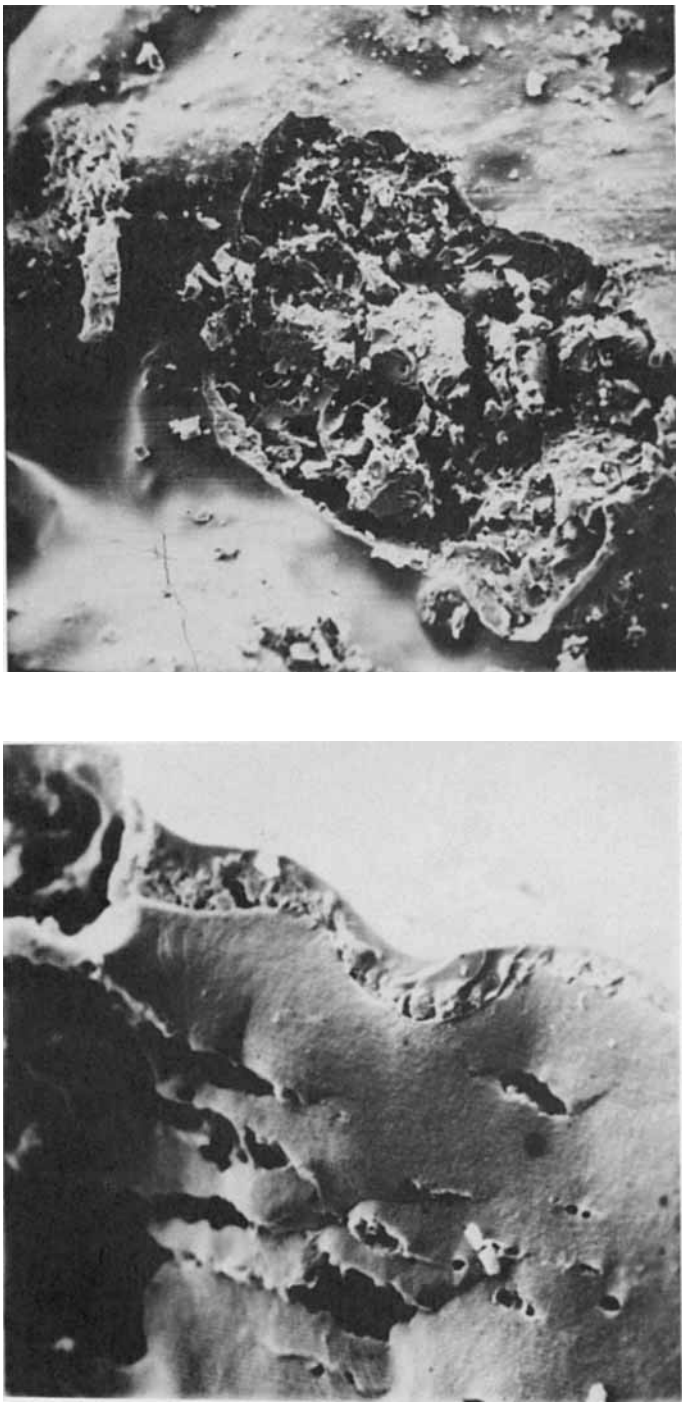
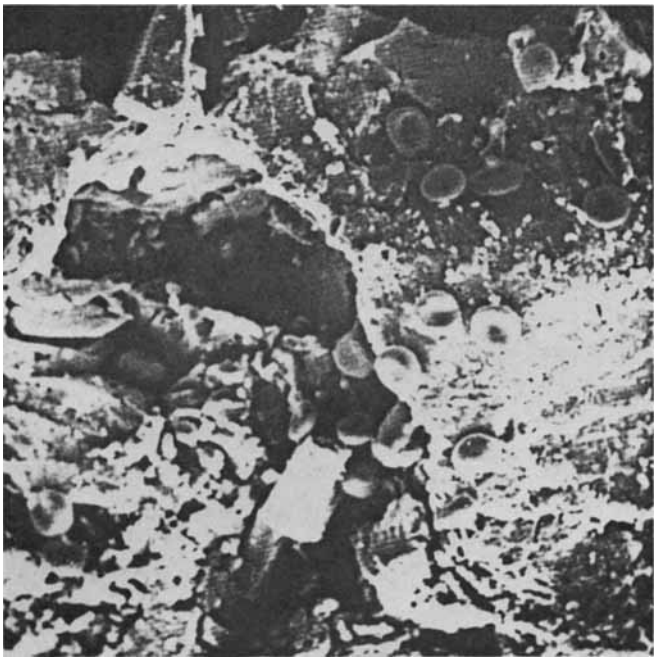


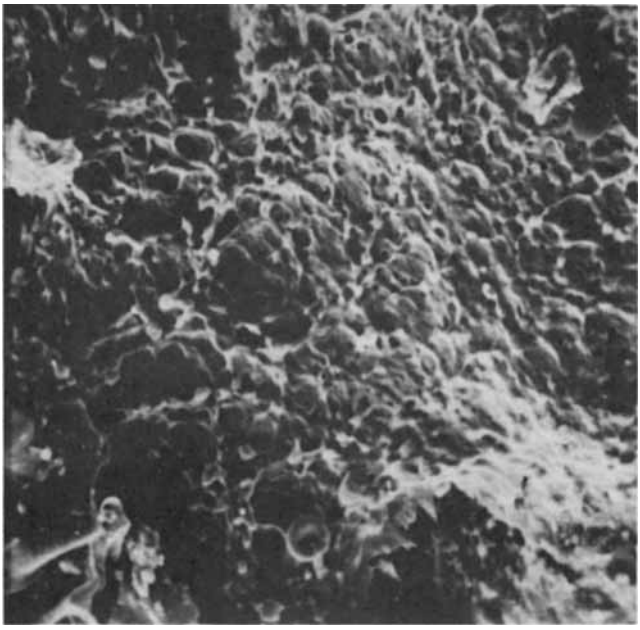
Fig. 8. SEM of solution-coated charcoal (×800).



(a)

(b)

Fig. 9. SEM of uncoated charcoal after Hemoperfusion (A) ×1700; (B) ×4000.



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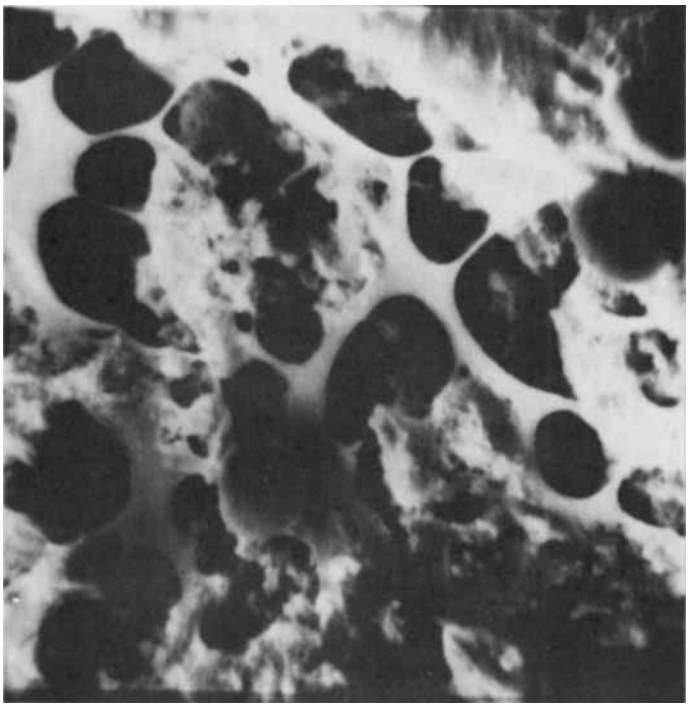

(b)

Fig. 10. SEM of coated charcoal after hemoperfusion (A) ×1700; (B) ×4000.

CONCLUSION

It is possible to polymerize an organic substance by using low temperature plasma polymerization technique on a very porous substance like activated charcoal in order to modify the surface properties without affecting the adsorptive capacity. Through this coating process, almost complete protection against the damages caused by uncoated charcoal on blood cells seems possible. In this case, it is believed that the first step in this coating process is the adsorption of monomer followed by polymerization by electrical discharge.

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