

SURFACE MODIFICATION OF POLYMERS

Allan S. Hoffman

(Center for Bioengineering, FL-20, University of Washington, Seattle, WA 98195, USA)

ABSTRACT

The principal objectives and methods of surface modification of polymers are reviewed in this paper. The methods covered include physical, chemical, mechanical and biological.

INTRODUCTION

Many diverse applications of polymers in "every-day" uses, in industrial uses, and in medical uses, depend upon physical, chemical and biological interactions of molecules or microorganisms at their surfaces. Table 1 gives some examples of these applications.

If a polymer surface does not have the desired properties for a particular application, then undesirable surface events can lead to failure of the material and the device or system containing it. Examples of such failures include: (a) delamination of an adhesive bond, (b) permanent staining of a fabric, (c) fouling of membranes with proteinaceous films, (d) a false positive or false negative immunoassay result, (e) bacterial growth on catheters, and (f) clotting of a dialyser or blood oxygenator during dialysis or open-heart surgery. Modification of polymer surfaces for improved blood compatibility has been an active area of research in the past twenty years. (Reference 1 reviews this field).

It is also important for the surface chemist to realize that the surfaces of normal, "as fabricated" polymers usually do not have the same compositions as the bulk phase. This can be due to adsorption of contaminants from the surrounding environment (e. g., oils, soils or bacteria), desorption of impurities and surface active compounds from the bulk phase (e. g., lubricants added as process aids), oxidation or hydrolysis of surface groups, and preferred molecular orientation of surface groups (e. g., to minimize surface free energy). Often these effects occur unevenly across a surface

area, in "spots", "islands" or "domains." Surfaces can also have local physical defects, such as scratches, which can be a problem in some applications.

Table 1 Some examples of applications where polymer surface properties are important

"Every day" applications	Industrial applications
• absorbent materials • adhesion • printing on films • dyeing of fabrics • static dissipation • oil repellancy in air • oil release in detergent solutions • food packaging	• ion exchange • chromatographic separations • membrane separations • catalysis • electrical conduction • light reflection • analytical sensors
Medical and biotechnological applications	
• cell culture dishes • cell supports in fermentation processes • biodegradable polymers • biosensors and diagnostic assays • sterile packaging • protein and cell separations	• blood and urinary catheters • bandages • healing responses at surfaces of implants • hemostatic sponges and fabrics • blood circulation devices • drug delivery devices

Therefore, it is not only desirable but also vital to modify polymer surfaces, whether merely to clean them or to modify them physically, chemically, mechanically or biologically, in order to control the subsequent surface interactions and responses which are required for any particular application. Sometimes it is desirable to carry out the surface modifications in specific patterns across a surface, using special techniques borrowed from lithography.

Table 2 Polymer surfaces are usually modified to increase or to reduce surface...

• hydrophilicity ("wettability") • ionic charge or pH • adsorption of molecules • adhesion of microorganisms • permeation of molecules	• chemical or biological reaction kinetics • roughness or friction • electrical, optical or acoustic properties • impurities • domains or patterns of the above.
--	--

This is a growing area of surface modification, especially on a micro- and nano-scale (see below). Table 2 summarizes the general objectives of surface modification of polymers.

Table 3 Methods for polymer surface modification**I. Physico-chemical methods****A) Treatment with active gases and vapors, or radiation**

- Deposition of polymers from active gases and vapors
(e. g. , gas discharge [RFGD], chemical vapor, flame spray)
- Active gas or accelerated ion treatments
(e. g. , etch, ablate or oxidize using RFGD, corona discharge or ion beam; ion implantation)
- Crosslinking of surface molecules(e. g. , RFGD, ionizing radiation, UV)

B) Solution treatments or bulk phase desorption

- Solution deposition of polymers and amphiphiles
(e. g. , polymer coatings, IPNs, surfactants, SAMs)
- Desorption of surface active compounds from bulk
(e. g. , desorption of surfactants from bulk to surface)
- Chemical treatments to modify surface groups
(e. g. , oxidize, sulfonate, chlorinate, acetylate, quaternize)
- Chemical conjugation of molecules to surface groups(e. g. , silanating agents, PEG)

C) Combinations of A) and B)

- Graft or IPN polymerization
(e. g. , initiation by ionizing radiation, UV, O₃, or RFGD, followed by polymerizations)
- Patterns or domains of the above(e. g. , microlithographic techniques)

II. Mechanical methods

- Roughening(e. g. , from micro-rough to porous surfaces)
- Micromanipulation(e. g. , using STM, AFM probes)

III. Biological methods

- Physical adsorption of biomolecules
(e. g. , proteins, peptides, ligands, receptors, drugs, lipids)
- Physical adsorption and self-crosslinking of biomolecules
(e. g. , same biomolecules as above, where feasible)
- Chemical conjugation of biomolecules to surface groups
(e. g. , same biomolecules as above)
- Cell seeding and growth to confluence

Many different methods for polymer surface modification have evolved over the past fifty years. They can be divided here into three categories: physicochemical, mechanical and biological methods (Table 3). The physico-chemical methods can be further subdivided into: (A) gas phase methods, including gases containing active species such as free radicals, electrons, ions and excited molecules, or electromagnetic radiation, such as visible light, U. V. and gamma rays; (B) liquid and bulk phase methods, involving physical desorption from the bulk phase, or chemical reactions at the surface; and (C) combination methods, utilizing (A) and (B) in sequence.

Because of their great versatility, radio frequency gas discharge treatments (RFGD) have been increasingly used to modify surfaces [2-5]. The plasma gas of RFGD contains vacuum U. V. radiation plus many reactive species, such as free radicals and energetic electrons and ions. The vacuum U. V. radiation plus free radicals can cause many different reactions on the polymer surface, depending on the gas or vapor used in the plasma, the reactor geometry and operating conditions^[6,7]. The major effects of RFGD include surface etching or ablation, surface crosslinking, and deposition of a new polymer coating on the substrate polymer. Table 4 lists some of the many different types of gases and vapors which have been used in gas discharge processes, and their surface effects.

Table 4 Surface modification by gas discharge treatments

A. Etching gases (e. g. , air, argon, H₂, N₂, F₂) • crosslink • oxidize • form reactive species	B. Non-depositing, reactive gases (e. g. , H₂O, NH₃) • form reactive groups (-OOH, -OH, -COOH, -NH₂, -CHO)
C. Depositing gases and vapors (e. g. , monomers as TFE, AAc and organics as CH₃OH, acetone) • hydrophobic polymer coatings (HC, FC, silicones) • ionic polymer coatings (acidic, basic) • polar polymer coatings (-OH, -O-, -C=O, -CO₂, -CONH₂)	

METHODS FOR CONVERTING HYDROPHOBIC TO HYDROPHILIC SURFACES

One of the most active areas of surface modification has been to convert nonpolar, hydrophobic surfaces to polar, hydrophilic and water wettable surfaces^[1-3,5]. There are many diverse uses for such modified surfaces, as noted above. Table 5 summarizes some of the specific methods used to converting nonpolar surfaces to hydrophilic surfaces. It should be noted that for a polar surface in air, polar groups will tend to orient away from the air surface and into the bulk phase in order to minimize surface free energy. However, when in contact with an aqueous solution, such groups will reorient to interact with the aqueous phase, once again in order to minimize interfacial free energy.

Table 5 Methods for hydrophilic surface modification of polymers

Active gas treatments

- Corona discharge (in air)
- Gas plasma discharge (oxidizing)
- Plasma deposition (hydrophilic gases or vapors)

Chemical reactions

- Gas phase oxidation (ozone)
- Liquid phase oxidation (H_2SO_4 , KMnO_4)
- Derivatization reactions (e. g. , anhydride reactions with surface OH groups; SOCl_2)

Surfactant or hydrophilic polymer immobilization

- Physical deposition (PEO surfactants, polymers)
- Chemical bonding (PEO-X)
- Inert RFGD surface crosslinking of surfactants (PEO surfactants, polymers)
- Desorption of block surfactant from bulk phase (PEO-silicone)

Graft polymerization

- Radiation initiation (gamma-ray, EB, UV or RFGD+HEMA, PEGMA, AAc)
- Chemical initiation (ozone+HEMA, PEGMA, AAc; ceric ion+OH surface groups+monomers)

Attachment of PEO to surfaces has been one of the most extensively studied treatments^[8-13]. If the molecular weight of the PEO is above ~ 500 — $1,000$ ^[10], the surface will resist protein adsorption and cell adhesion. Such a surface has been called “non-fouling”. Many methods have been used to incorporate PEO on polymer surfaces, and they are shown schematically in Fig. 1. A new method for immobilizing a PEO surfactant by crosslinking its hydrophobic “tail” to polymer surface groups in an argon RFGD has been applied to a number of different amphipathic compounds, in order to functionalize hydrophobic surfaces^[12,13]. Table 6 list some of the compositions which have been immobilized by this process.

Table 6 Surfactants and functional alkyls immobilized by argon or helium gas discharge treatments^[12,13]

PEO surfactants	
• Alkyl-PEO (“Brij”)	Alkyl tails with reactive polar end groups
• PEO-PPO-PEO (“Pluronics”)	• Alkyl amines
• Silicone-PEO (“Tegopren”)	Alkyl tails with ionic end groups
Other surfactants	• Alkyl sulfates
• Phospholipids	

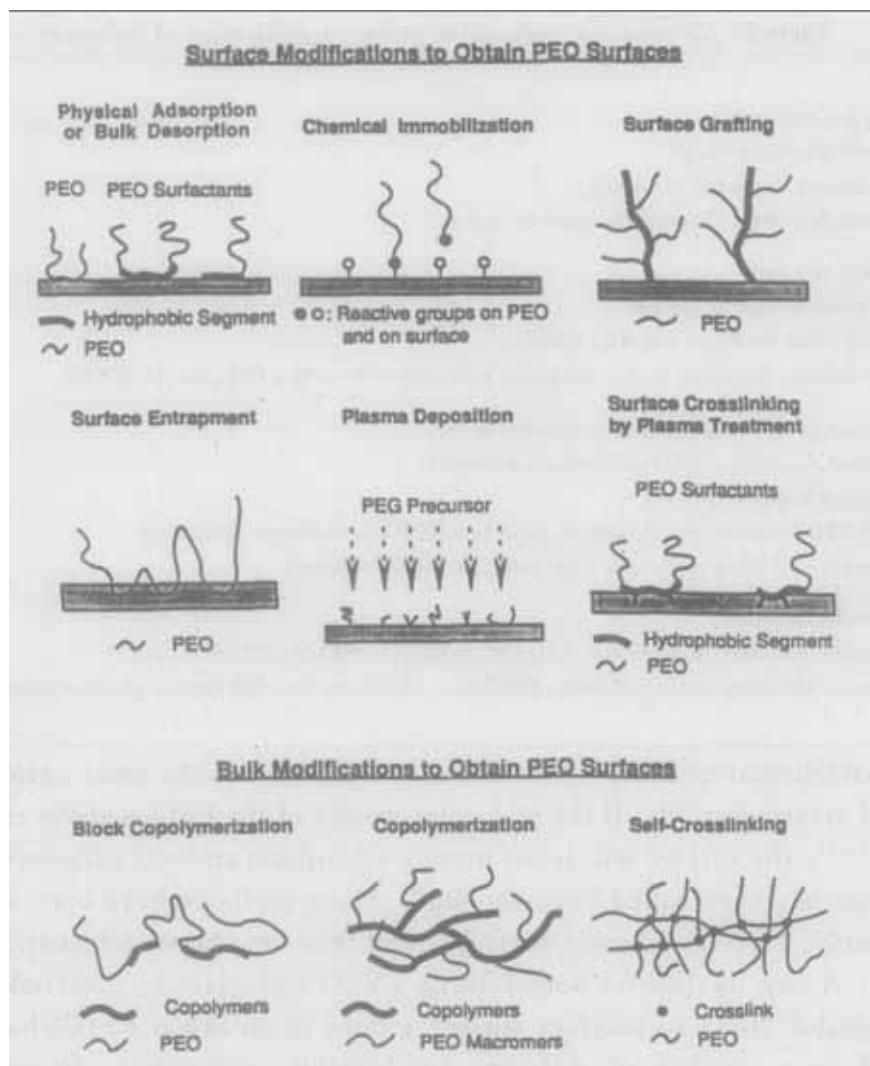


Fig. 1 Schematic methods for surface or bulk modifications of polymers to yield PEO surface compositions

The techniques of micro-lithography using visible or U. V. radiation have been used to deposit specific patterns of, for example, hydrophilic regions on a hydrophobic substrate, which may then be further derivitized with ligands such as cell receptor peptides^[14].

Biologic surface modification

Surfaces are modified biologically by immobilizing biomolecules and cells onto them (Table 3). Many diverse biomolecules may be immobilized using a wide variety of techniques^[15-17]. Examples are listed in Table 7.

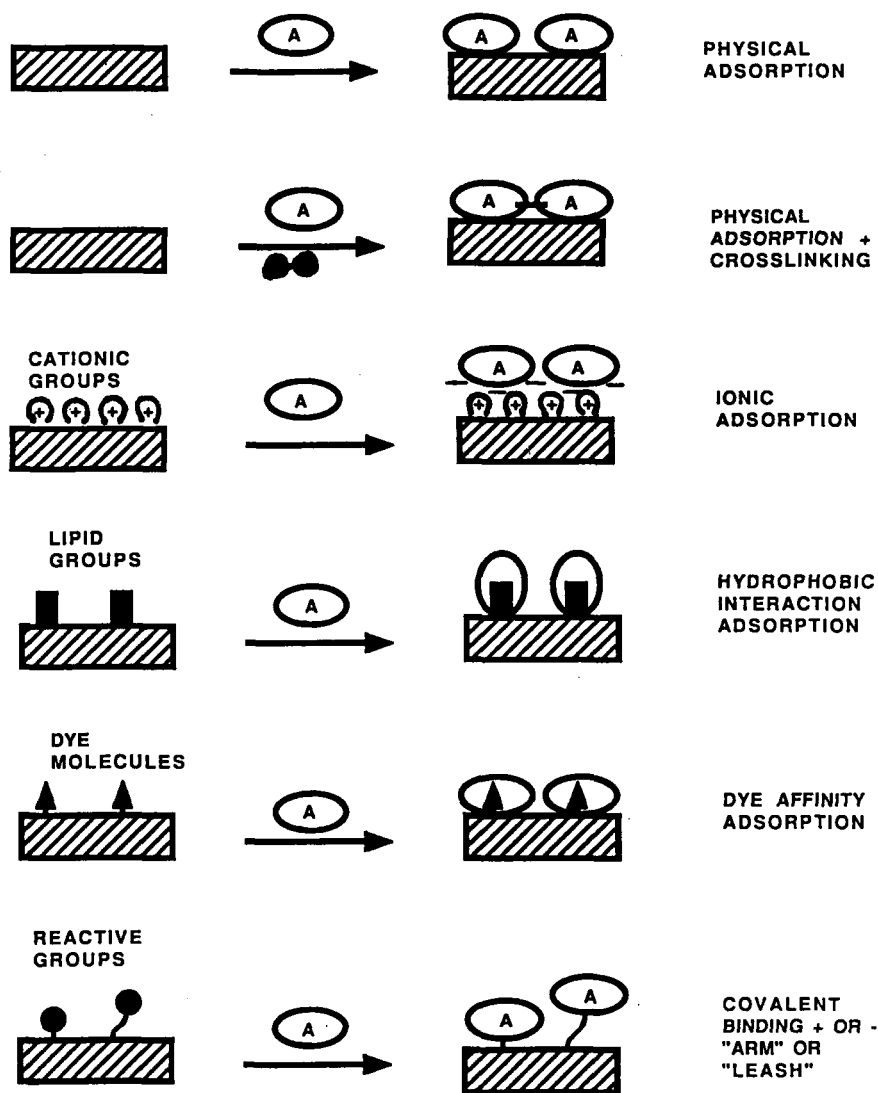


Fig. 2 Examples of methods for albumin immobilization on polymer surfaces

Table 7 Biomolecules which may be immobilized onto soluble or insoluble synthetic polymers

• Proteins or peptides • Saccharides • Lipids • Nucleotides	• Drugs • Ligands or receptors • Bioconjugates of the above
--	---

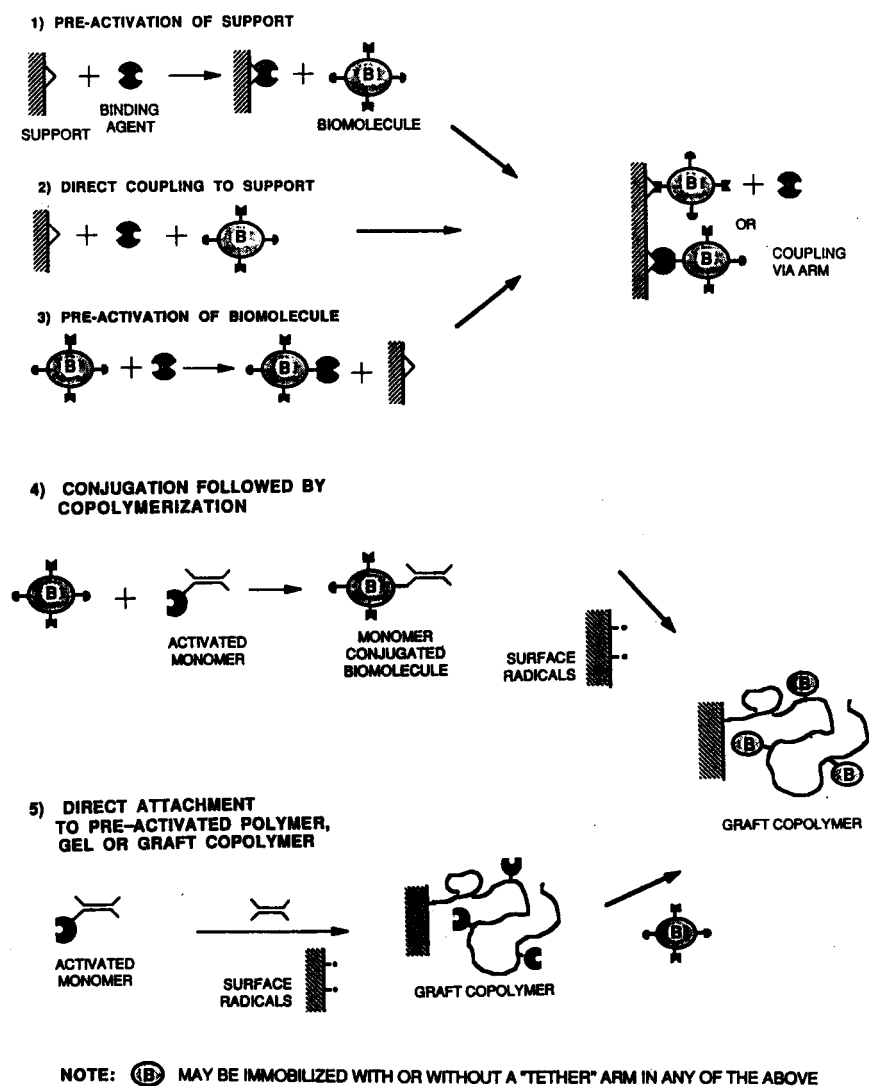


Fig. 3 Schematic methods for covalent immobilization of biomolecules

For example, albumin is often immobilized on surfaces in order to block non-specific adsorption of other biomolecules in an affinity separation or diagnostic assay, or to "passivate" biomaterial surfaces exposed to biological environments. A wide range of methods have been utilized to immobilize albumin, and they are shown schematically in Fig. 2, to illustrate the many different techniques available for immobilization of biomolecules such as proteins.

Biomolecules are covalently linked to surfaces when it is desired to

recover and recycle the immobilized biomolecule and/or when it is necessary to avoid desorption of the biomolecule^[15-17]. Fig. 3 shows schematic reactions for covalent immobilization of biomolecules.

CONCLUSIONS

This article has briefly reviewed the methods for modifying polymer surfaces. It can be seen that there is a diverse range of surface modification technologies which have been developed for use with the many different polymer compositions, properties, forms and applications.

Keywords:

Surface modification; Polymers; Biomolecules

Acknowledgement: I would like to acknowledge many stimulating conversations that I have had with Professor Feng over the past ten years. It has always been a pleasure to meet with him and to discuss polymer chemistry with him. He has a great deal of knowledge and wisdom in this field and I have always learned from him. I am also very much impressed by his ability to stay young and creative in his mind. I wish him many more productive and creative years in polymer chemistry.

REFERENCES

- [1] Hoffman, A. S., *Ann. NY Acad. Sci.*, **1987** 516, 96.
- [2] Gombotz, W. R. and Hoffman, A. S., "Gas Discharge Techniques for Modification of Biomaterials" in "Critical Reviews in Biocompatibility", Williams, D., ed., CRC Press, Boca Raton, FL, **1987**, 4.
- [3] Yasuda, H., "Plasma Polymerization", Academic Press, Orlando, FL, **1985**.
- [4] Iwata, H., et al., *J. Polym. Sci. Part A, Polym. Chem.*, **1988**, 26, 3309.
- [5] Terlingen, J. G. A., et al., *J. Appl. Polym. Sci.*, **1994**, 52, 35-53.
- [6] Danilich, M. J., et al., *J. Biomats. Sci., Polym. Ed.*, **1992**, 3, 195-216.
- [7] Uchida, E., Uyama Y. and Ikada, Y., *J. Appl. Polym. Sci.*, **1993**, 47, 417.
- [8] Harris, J. M., ed., "PEO Chemistry, Biotechnological and Biomedical Applications", Plenum Press, NY, **1992**.
- [9] Merrill, E. W. and Salzman, E. W., *ASAIO J.*, **1983**, 6, 60.
- [10] Nagaoka, S., et al., in "Polymers as Biomaterials", Shalaby, S. W.; Hoffman, A. S.; Ratner B. D. and Horbett, T. A., eds., Plenum Press, NY **1985**.
- [11] Desai, N. P. and Hubbell, J. A., *Biomats. Sci.*, **1991**, 12, 144.
- [12] Terlingen, J. G. A., et al., *J. Biomats. Sci., Polym. Ed.*, **1993**, 4, 165.
- [13] Sheu, M. S.; Hoffman, A. S. and Feijen, J., *J. Adhes. Sci. and Tech.*, **1992**, 6, 995.
- [14] Matsuda, T., et al., *ASAIO J.*, **1992**, 38, M243-M247.
- [15] Hoffman, A. S., *Clinical Mts.*, **1992**, 11, 61 and *Artif. Org.*, **1992**, 16, 43.
- [16] Kim, S. W. and Feijen, J., in "Critical Reviews in Biocompatibility", D. Williams, ed., CRC Press, Boca Raton, FL, **1985**, 4, 229-260.
- [17] Carr, P. W. and Bowers, L. D., "Immobilized Enzymes in Analytical and Clinical Chemistry", J. Wiley & Sons, NY, **1980**.