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Synthetic Polymeric Membranes

Characterization by Atomic Force Microscopy

Springer

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Preface

This book concentrates on atomic force microscopy (AFM), a method recently developed to study the surfaces of synthetic polymeric membranes. AFM is becoming a very important tool for the characterization of synthetic polymeric membranes. The development of membranes of improved performance depends on the exact knowledge of the morphology of a thin selective layer that exists at the surface of the membrane. The control of the morphology of the selective layer is crucial for the design of synthetic polymeric membranes. With a relatively short history of only twenty-five years, AFM has firmly established its position as a method to characterize the membrane surface.

Each chapter of this book includes information on basic principles, commercial applications, current research, and guidelines for future research. Each chapter is summarized at the end and contains a comprehensive list of references.

The introductory chapter gives a brief overview of synthetic polymeric membranes and their applications both in industrial processes and in biomedical fields. It also gives an overview of studies on membrane surface morphology by various methods.

Chapter 2 deals with the synthesis of membranes, the properties of membranes, and the application of membranes. The beginning also identifies the three types of membranes (i.e., biological, synthetic, and theoretical) and their applications.

The details of AFM are discussed in Chap. 3. It is divided into two parts. In the introduction, a brief history of the development of AFM is given, followed by a list of manufacturers and their products. The second part contains the details of the AFM components and the experimental protocols for different AFM modes, i.e., contact, non-contact, and tapping. As the synthetic polymers are soft, generally tapping mode is preferred to study the polymeric membranes. Details of the AFM image analysis, in conjunction with synthetic polymeric membranes, are also given.

The fourth chapter examines the nodular structure of the membrane surface observed under AFM. It has been known for a long time that macromolecules form nodules at the membrane surface, and the size and the shape of the nodules strongly govern the membrane performance. In conjunction with an advanced technique such as plasma etching, AFM can reveal the nodular structure at the membrane surface more clearly than any other technique. In this chapter, the relationship between the nodular structures and the membrane preparation conditions is discussed for flat sheet membranes in the first part and hollow fibers in the second part. This chapter also deals with the roughness at the membrane surface.

Chapter 5 explores the pore structure of the membrane. Pores are clearly observed under AFM when their sizes are more than 1 nm. The method to characterize the membrane surface by the mean pore size and the pore size distribution is described, and the results are compared with those obtained from other more conventional methods.

Unlike Chaps. 4 and 5, Chap. 6 deals with the cross-sectional view of the membrane when observed under AFM. Since the technique of capturing cross-sectional views was developed only recently, relatively few images are currently available. However, this technique may have a strong influence on future research, particularly in studying cell growth under the membrane surface and fouling by blocking membrane pores.

Chapter 7 discusses the use of AFM to investigate the adhesion of particles to polymer surfaces. Adhesion of particles on membrane surfaces is the main cause of fouling. In the beginning of the chapter, a short note on DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory (a theory of the stability of colloidal dispersions) has been given. However, few studies of adhesion in the membrane field by AFM have been reported. The pioneer work of Bowen's school has been described.

Finally, in Chap. 8, attempts are made to correlate the AFM parameters, such as nodule and pore sizes, to the membrane performance data. Membranes used for a variety of membrane processes, including reverse osmosis, nanofiltration, ultrafiltration, microfiltration, gas and vapor separation, pervaporation, and other membrane separation processes, are covered in this chapter. AFM parameters are also correlated to membrane biofouling. This chapter also includes applications of AFM to characterize biomedical materials, including artificial organs and drug release.

Thus, the book covers all aspects of AFM studies on the characterization of synthetic polymeric membranes. The authors believe that this book is the first attempt to find cause and effect relationships using AFM between membrane preparation, membrane characterization, and membrane performance for synthetic polymeric membranes applied in various separation processes. The authors also believe that the knowledge provided in this book will contribute to the design and preparation of improved synthetic polymeric membranes.

Importance of This Book

Although several books have already been published on AFM, they were written for different applications. The novel feature of this book is that it is focused on the study of synthetic membranes and their surfaces by AFM. For this reason, this book is monumental in the fields of both AFM and synthetic membranes. Another feature of this book is that it will provide a very useful guide to readers who wish to enter this field of study. By going through the chapters that deal with various AFM images, the reader will be exposed to the latest research results of the field. However, the strength of the book lies in its friendliness to the reader in describing details of AFM experimental methods and interpretation of experimental data, particularly when AFM is used to study membrane surfaces. Hence, the potential readers of the book are academic researchers who are investigating synthetic membranes and also R&D specialists who wish to improve and control the quality of synthetic membranes for various purposes.

This book may also attract a wider range of readers, since synthetic membranes are now considered to be one of the most important tools in the areas of seawater desalination, wastewater treatment, water production, food processing, treatment of pharmaceutical products, air and water cleaning, separation of chemical and petrochemical products, drug release, and other biomedical applications.

Ottawa, September 2007

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Abbreviations and Symbols

Δt	Temperature difference
λ	Heat of vaporization of the solvent (kJ kg – mol^{-1})
λ'	Ratio of solute radius and pore radius
μ	Viscosity
μ_p	Mean pore size
μm	Micron, micrometer
ρ	Density
σ_p	Standard deviation
Å	Angstrom
AFM	Atomic force microscopy
AFS	Atomic force spectroscopy
BSA	Bovine serum albumin
°C	Degree centigrade
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
C-AFM	Contact mode atomic force microscopy
cAMP	Adenosine 3′,5′-cyclic monophosphate
CE	Cellulose
cm	Centimeter
CTA	Cellulose triacetate
C_p	Heat capacity
Da	Dalton
DEHPA	Di-2-ethylhexylphosphoric acid
DLVO	DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory
DMAc	*N*, *N*-Dimethylacetamide
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
DSPM	Donnan-steric-pore model
DTPA	Di-2-ethylhexylthiophosphoric acid
ED	Electrodialysis
F	Force
f_{NaCl}	Apparent rejection of NaCl (%)
FE-SEM	Field emission scanning electron microscopy
FFT	Fast Fourier transform
G	Gravity constant

GBL	γ-Butyrolactone
gm	Gram
gm L^{-1}	Gram per liter
h	Hour
h	Thickness of the cast film
HEMA	Hydroxyethyl methacrylate
HFP	Hexafluoropropylene
HMDSO	Hexamethyldisiloxane
HPC	Hydroxypropylcellulose
J_v	Permeate flux (kg m^{-2} h^{-1})
J_w	Water permeate flux (kg m^{-2} h^{-1})
k	Spring constant
Kc	Thermal conductivity
kDa	Kilodalton
LEPw	Liquid entry pressure of water
LFM	Lateral force microscopy
Ma	Marangoni number
Mac	Critical Marangoni number
MD	Membrane distillation
MF	Microfiltration
min	Minute
mL	Milliliter
MPa	Megapascal
MPD	*m*-Phenylene diamine
M_w	Molecular weight
MWCO	Molecular weight cutoff
nN	Nanonewton
NC-AFM	Non-contact mode atomic force microscopy
NF	Nanofiltration
nm	Nanometer
NMMO	*N*-Methylmorpholine-*N*-oxide
NMP	*N*-Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
PA	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate
PE	Polyethylene
PEEK	Poly(ether ether ketone)
PEG	Polyethylene glycol
PEI	Poly(etherimide)
PES	Poly(ether sulfone)
PET	Poly(ethylene terephthalate)
PI	Polyimide
pMDA	Pyromellitic dianhydride

PMMA	Polymethyl methacrylate
ppm	Part per million
PP	Polypropylene
PAA	Polyacrylic acid
PPO	Poly(phenylene oxide) or poly(2,6-dimethyl-1,4-phenylene oxide)
PPO-C_6H_6	PPO membrane cast by PPO solution in benzene
PPO-C_6H_5Br	PPO membrane cast by PPO solution in bromobenzene
PPO-$C_6H_5CH_3$	PPO membrane cast by PPO solution in toluene
PPO-C_6H_5Cl	PPO membrane cast by PPO solution in chlorobenzene
PPO-CS_2	membrane cast by PPO solution in carbon disulfide
PPO-TCE	PPO membrane cast by PPO solution in trichloroethylene
PSf	Polysulfone
psi	Pound per square inch
PTFE	Polytetrafluoroethylene
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidene fluoride)
PVP	Poly(vinylpyrrolidone)
PWP	Pure water permeation
r_p	Pore radii
r_s	Solute radii
R	Gas constant
R'	Radius of sphere
R_a	Mean roughness
Ra	Rayleigh number
Rac	Critical Rayleigh number
rms	Root mean square
RO	Reverse osmosis
s	Second
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
SMMs	Surface modifying macromolecules
SPEEK	Sulfonated poly(ether ether ketone)
SPM	Scanning probe microscopy
SPPO	Sulfonated poly(phenylene oxide)
SPPOH	Sulfonated poly(phenylene oxide) in hydrogen form
SPS	Sulfonated polysulfone
STM	Scanning tunneling microscopy
T	Temperature
T_g	Transition temperature
TBP	Tributyl phosphate
TCE	Trichloroethylene
TEM	Transmission electron microscopy
TFC	Thin film composite

TFE	Tetrafluoroethylene
TIPS	Thermally induced phase separation
TM-AFM	Tapping mode atomic force microscopy
TMC	Trimesoyl chloride
TRIM	Trimethyl propane trimethacrylate
TTD	2,2,4-Trifluoro-5-trifluoromethoxy-1,3-dioxole
UF	Ultrafiltration
UV	Ultraviolet
V	Volt
VOCs	Volatile organic compounds
WAXS	Wide angle X-ray spectroscopy
wt.%	Weight percentage
XPS	X-ray photoelectron spectroscopy
Z	Difference between the highest and the lowest point within the given area (nm)

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