

Study on Porous Polymeric Membrane: Formation, Characterization and Performance

メタデータ	言語: eng 出版者: 公開日: 2017-10-05 キーワード (Ja): キーワード (En): 作成者: メールアドレス: 所属:
URL	http://hdl.handle.net/2297/33170

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学位の種類 学術博士
学位記番号 学博乙第8号
学位授与の日付 平成2年3月25日
学位授与の要件 論文博士 (学位規則第5条第2項)
学位授与の題目 STUDY ON POROUS POLYMERIC MEMBRANE
(高分子多孔膜に関する研究)
—Formation, Characterization and Performance—
(—膜形成, キャラクタリゼーション機能—)

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学位論文要旨

Recently, polymer membrane are attracting a keen attention as precise media of separating materials. The separation of materials by means of polymer membranes can be readily carried out without any phase change at room temperature using a compact apparatus, which can be operated with a relatively small amount of energy consumption as compared with other conventional methods. Among numerous methods proposed hithertofor for preparation of polymeric membrane the solvent cast method is a method of vast technological importance, because this method is overwhelmingly the most popularized one, which enables us to produce membrane with a wide range of mean pore size.

Figure I shows relationships between casting conditions and performance of membranes prepared by the solvent casting method. It is highly expected that the performance of a membrane is predominantly governed by pore characteristics and supermolecular structures, which are formed through phase separation phenomena of casting solutions, and the phase separation is unquestionably controlled by the casting conditions. Then, there will be strong and linear relations: casting conditions \rightleftharpoons pore or structure formation \rightleftharpoons pore and supermolecular characteristics \rightleftharpoons performance of membrane. If we could established

these relations very quantitatively, we could design and produce effectively membrane with desired performances.

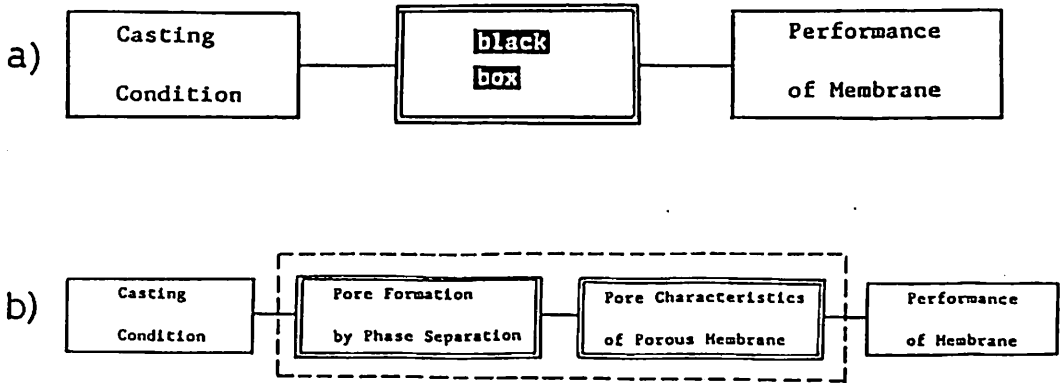


Fig. 1 Correlations between casting condition and performance.

The another started his research on synthetic membrane in mid 1960's, paying systematic efforts (1) to get a better and quantitative understanding of the theoretical background of pore formation, (2) to develop techniques for pore characterization of the polymer membranes, especially having the mean pore size of $10\sim 10^2$ nm, which are widely used as commercially available separation media of ultrafiltration and microfiltration process, and (3) to study the separation of gas mixture and liquid mixtures by porous polymeric membrane on molecular basis, including its application to medical field as artificial kidney.

The membrane formation in the casting process was shown to be explained as the phase separation phenomena of polymer solutions and the morphology, in

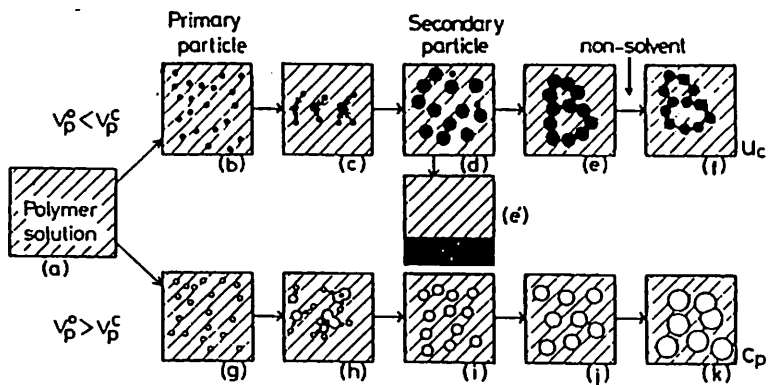


Fig. 2 Schematic representation of the formation of pores of in the casting process.

particular, shape of pore, is governed by the relative difference between the polymer concentration at membrane forming step v_p^o and the critical solution concentration v_p^c (Fig.2) : If $v_p^o < v_p^c$, the pore is noncircular and if $v_p^o > v_p^c$, the pore is circular. In the former case, the particle (i.e., a polymer-rich phase) growth concept was proposed : Nucleation and growth of nuclei to the primary particles and their amalgamation to yield the secondary particles with almost the same radius. Formation of pores by contact of the secondary particles. The theory was confirmed with the experiments. The pore characteristics was demonstrated to be controlled by the radius of the secondary particles S_2 and the two phase volume ratio R .

$$\log N(r) = \log 2N/[S_2^2(1 + \bar{x})] + \log[r - \{1 - (V\rho_s/\rho_p)^{1/3}\}S_2] + [r/S_2 - 1 + (V\rho_s/\rho_p)^{1/3}]^2 \log[\bar{x}/(1 + \bar{x})] \quad (1)$$

The pore size distribution $N(r)$ (r , the radius of pore) is given by eq(1). Here N is the pore density, $\bar{x} = N_o/N(N_o$, total number of particle per unit surface), V , polymer volume fraction of the polymer-rich phase, ρ_s and ρ_p , the density of the polymer-rich phase and the polymer.

In this way, now we can design the casting conditions giving membrane with desired pore characteristics (Chapter 2).

In ceachter 3, it was demonstrated for regenerated cellulose membrane from cellulose cuprammonium-acetone solution and cellulose acetate mambrane the existence of multi-layer structures in the membranes made by the solvent-casting method. For this purpose, a technique for evaluating the pore radius (r) distribution $N(r)$ of the hypothetical inner layers of the membranes parallel to and apart from the surface was developed. The morphological change with the thickness direction, as observed by electron microscopy was reasonably explained for these membranes by change in the polymer concentration with the thickness direction.

A rigorous theory of estimating the pore size distribution $N(r)$ of straight-through cylindrically and truncated-conically porous membrane from mercury intrusion (MI), bubble pressure-fluid permeability (BP), ultrafiltration-permselectivity (UP) and gas permeability (GP) methods were proposed. The physical meanings of the various mean pore size, determined by MI, flow rate, GP, UP and surface area methods, were clarified for the above membranes. Experimental apparatus for MI, BP, UP, and GP were designed and constructed. Electron micrographic (EM) method was also proposed with the help of stereology for estimating the pore characteristics of porous polymeric membrane having the pore diameter larger than 10 nm and this method was modified for

hollow fiber membrane (i.e., aslant sliced thin sectional (ASTS) method). $N(r)$ evaluated by various methods were compared for a polycarbonate membranes with straight-through pores and cellulose acetate membranes.

The mean pore radii evaluated by various methods were successfully compared. A theory based on the particle growth concept was presented to estimate the probabilities of finding isolated (P_i), semi-open (P_s) and through (P_t) pores in the porous polymeric membranes, which are composed of small particles (Fig. 3). The theoretical relations between P_i , P_s , P_t and the structural parameters were derived and it became possible to estimate P_i , P_s , P_t from the porosity (Pr) data

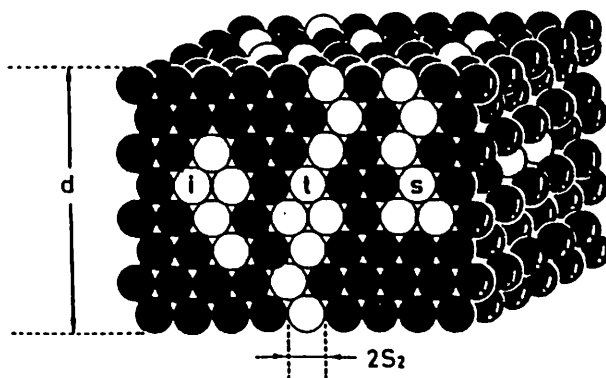


Fig. 3 Schema of a membrane structure composed of secondary (●) and vacant (○) particles: i, s and t stand for isolated-, semi-open-and through-pores, respectively.

Chapter 4 deals with the porous polymeric membranes as effective separation media for gas mixtures and liquid mixtures. A theory of gas permeation through porous polymeric membranes with the mean pore larger than 10 nm was presented. In the theory, in addition to dissolution/diffusion (D) flow, viscous (H) flow, slip (Sp) flow, free molecular (F) flow and surface diffusion (S) flow, proposed so far independently for three dimensional porous media, a concept of a new flow (VF flow) was introduced: It was shown experimentally that in a single pore H flow and F flow do not appear in the parallel combination, but in a given pore V flow is combined with F flow in series combination and in this case the overall flow for the given hole is defined as VF flow (Fig.4). The theory could explain the appearance of a minimum in the permeability coeffi-

cient $P(P_1, P_2)$ vs. average pressure \bar{P} ($\equiv (P_1 + P_2)/2$) plots obtained in 1930s by Azumi on gas flow in a glass capillary. The theory for a single hole was generalized to membrane with the pore size distribution and gas flow through membrane was classified into six categories, depending on the relative magnitude of the maximum and minimum pore sizes and the mean free path λ at inlet and outlet of the pore.

The experimental data on gas permeation through various membranes with straight-through pores were analyzed based on the theory.

The author observed the significant difference between measured and calculated gas permeability coefficients $P(P_1, P_2)$ for polymeric membrane dominated by free molecular flow (Fig.5). In order to explain this difference, the surface diffusion flow was taken into account and equation for $P(P_1, P_2)$ in the case F and S flow occur concurrently was derived for a porous membrane having a wide pore size distribution, assuming that the total gas flux is the sum of the fluxes through the individual pores. The calculated values of $P(P_1, P_2)$ for a polycarbonate membrane having straight-through pores agreed with the experimental values.

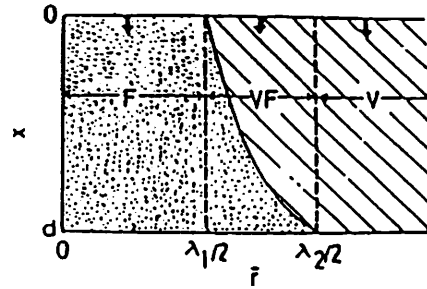


Fig. 4 Gas permeation mechanisms: Arrows indicate the flow direction.

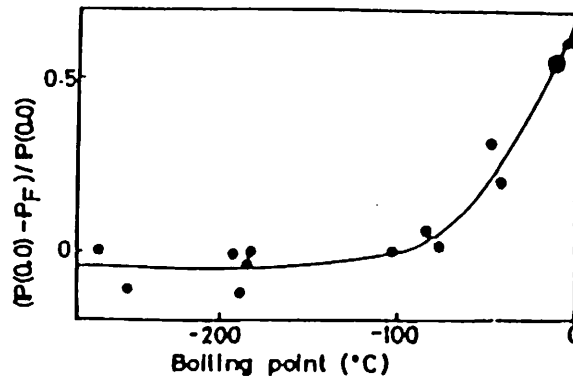


Fig. 5 Boiling point dependence of $(P(0,0) - P_F)/P(0,0)$ of polycarbonate membrane Nu0.03 for various gases:

$$P(0, 0) = \lim_{P_1, P_2 \rightarrow 0} P(P_1, P_2); P_F, \text{ permeability}$$

coefficient of free molecular flow; ●, organic gas; ○, inorganic gas.

A general theory for explaining the separation of particles in solution by ultrafiltration with a polymeric membrane (in the case of parallel filtration) was proposed as an extension of Ferry's and Renkins's theories. In new theory, four factors were considered: (1) the sieving effect due to collision between particles in the filtrand with the pore wall or the pore edge of the membrane (the steric factor), (2) viscous interaction between the particle and the pore wall (the viscous factor), (3) the hydrodynamic effect on the particle (the fractionation factor), and (4) intermolecular forces between the particle and the membrane (the intermolecular factor). Note that (1) only was considered in Ferry's theory, and (1) and (2) were taken into account in Renkins' theory. The ratio $\Psi(a)$ of the particle concentration in the filtrate to that of the filtrand (a , radius of particle) is expressed as a function of particle size, filtration conditions including the flow rate (shear rate) of the filtrand, and the molecular characteristics ($N(r)$ and porosity). The validity of the proposed theory was confirmed by the experiment.

As an example of high-grade application of liquid separation by membrane to medical field, a filtration-type artificial kidney (AK) using porous polymeric membrane was studied in a very systematic way in order to disclose its fundamental functions as kidney (Chapter 5). Ultrafiltration-type artificial kidney (UAK) was studied using porous cellulose acetate membrane. In our filtration-type Ak, it was confirmed that (1) no trace in the membrane dissolves in the blood, (2) optimum pore size lies between $0.06 \sim 0.1 \mu\text{m}$ ($60 \sim 100 \text{nm}$), (3) any pyrogenic materials are not contaminated with the membrane and (4) the blood does not coagulate when it contacts with the membrane. Three types (Mark I ~ III) Ak were designed and constructed and used for in-vitro examination. The three unsolved problems remained were also discussed. A theory was proposed for evaluating the ultrafiltration volume (UFV) during time t ($v'(t)$) in vivo of AK from the data of the hematocrit in vitro H_0 and UFV in vitro ($v(t)$) and the hematocrit in vivo $H\%$, under the conditions: the pressure difference in vitro $\Delta P \approx$ that in vivo $\Delta P'$ and the filtration area in vitro $S =$ that in vivo S' . The experiments verified the usefulness of the method proposed.

The marginal ability was estimated on a ultrafiltration type AK (Mark II). Mark II having effective filtration area of 100 cm^2 showed 40 % in ultrafiltration rate of water and only 4.3 % in uric acid excretion as compared with a human kidney. Mark II had to some extent permselectivity with respect to molecular size and this kind of permselectivity can be explained by the flow fractionation hypothesis. As physiology suggests, the only remedy to this unavoidable imbalance of exclusion of water and the waste materials, observed in Mark II, is addition of other functionality to simple ultrafiltration-type AK (i.e., multi-

functional AK).

論文審査の結果の要旨

当該学位論文について、平成元年12月5日に第1回審査委員会を、また12月18日に口頭発表会および第2回審査委員会を開催して次の審査結果を得た。

近年高分子多孔膜は、エネルギー消費量が少ない物質分離の精密な媒体として注目を集めている。多くの高分子膜の製造法の中で、溶媒キャスト法は広範囲の孔径の膜を作成できる点で重要であるにも関わらず、研究が少なかった。本論文ではこの点に着目し、(1)孔形成の理論的基礎、(2)高分子膜の孔の特性化、(3)これらの膜の医療分野への高度利用化、特に人工腎臓膜の試作などの研究を広範囲に行った。

この結果、高分子多孔膜の膜形成から孔構造の評価法、気体や液体の膜分離及び人工腎臓に至るまで系統的に研究し、粒子成長膜の多層構造、VFながれ、分別因子、ろ過型人工腎臓など多くの新しい概念や理論を提案した。これらの多くは現在定説となりつつある。

以上の結果は理論的にも優れた論文であり、また実用の腎臓透析膜の高性能化に寄与したもので、工業的にも価値が高く、博士論文に値すると判定する。

以上を総合して、申請者上出健二氏は学術博士の学位を受ける資格を有すると判定する。