Gas permeation in plasma-polymerized vinyl bromide

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Vinyl bromide was polymerized and deposited onto rubber substrates in a glow discharge plasma. The plasma polymer was characterized using scanning electron microscopy and Rutherford backscattering. Permeation characteristics of the plasma polymer were investigated by measuring gas permeability coefficients in substrate films before and after deposition.

(Keywords: plasma polymerization; gas permeability; composite membrane)

Introduction

Commercially important uses for polymers which require strict control of gas transport include separation membranes and barrier packaging materials[1–3]. Plasma polymerization[4,5] is a technique well suited to the investigation of new polymers and polymer structures for these applications. By this method, polymeric films on the order of 0.1 μm in thickness can be formed on substrate surfaces. These films are often highly adherent and free from gross defects or pinholes. If such a film exhibited an extraordinarily low permeability, it could be applied to the surface of a bulk material to improve its barrier quality. Likewise, if the plasma polymer possessed an attractive selectivity towards a gas mixture, a thin layer could be deposited onto a highly permeable or porous substrate. This would form a type of asymmetric membrane, which combines selectivity with high flux because of the small thickness of its separating layer[6]. An air separation membrane of this type, utilizing plasma-polymerized vinyl pyrazine, has recently been described in the US patent literature[7].

Several authors have reported successful alteration of substrate permeabilities and selectivities by application of a plasma-polymerized coating[8–13]. While these results have been encouraging, the number of plasma polymers that have been fabricated, characterized and subsequently investigated as to their gas permeability characteristics remains quite small.

This study examines gas permeation in plasma-polymerized vinyl bromide. This gaseous monomer was chosen for its bromine substituent. A plasma polymer containing this halogen may be potentially attractive for a barrier or gas separation application. Several studies[14–17] have demonstrated that polymeric materials containing bulky substituents, and in particular bromine, can exhibit low gas permeabilities due to restricted intersegmental chain mobility, which can also lead to high selectivities towards penetrant gases of differing sizes[18].

Experimental

Plasma polymerization was conducted in the reaction apparatus depicted in *Figure 1*. The flow-through reactor consists of a modified glass bell-jar, 152.4 mm in diameter with a 50.8 mm diameter reactant inlet tube. Two gaseous reactants can be independently introduced to the reactor through MKS Baratron Type 1100 mass flow controllers. Power to generate a glow discharge in the reactor is supplied through a six-turn copper induction coil which surrounds a 65 mm length of the reactor. Coil power is provided by a 0–500 W radio frequency (r.f.) (13.56 MHz) generator through an impedance matching network (RF Plasma Products Inc.). Downstream from the reaction chamber is a mechanical vacuum system with liquid nitrogen trap. Reactor pressure can be set and maintained independently of reactant flowrate using a pressure transducer/butterfly valve control system from MKS Baratron Systems. Reactor pressures typically employed were in the range 65–250 Pa.

Plasma polymer was deposited onto flat, 65 mm diameter circular substrates, which were placed horizontally in the centre of the reactor cross-section. The substrate material used was 1 mm thick vulcanized poly(dimethylsiloxane) (PDMS) sheeting, supplied by Dow-Corning Inc. Before being placed inside the reactor, the substrate films were washed and ultrasonically cleaned in deionized water.

To begin the reaction procedure, the reactor containing a substrate disc was pumped down to the desired

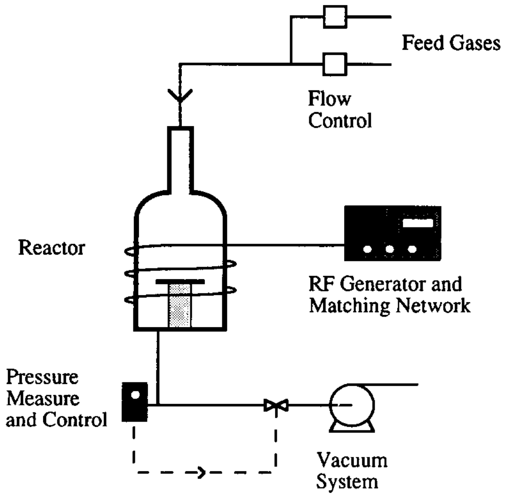

Figure 1 Plasma polymerization apparatus

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operating pressure, and held for 5 min. The mass flow control system was then activated, and the vinyl bromide reactant (as received from Matheson Gas Company), together with argon as a diluent, were fed to the reactor. Three minutes after initiation of reactant flow, r.f. power at the operating power was turned on, igniting the plasma. After the desired time of reaction, power to the coil was shut off. The reactor was held under vacuum for 5 min in the absence of glow before being opened to the atmosphere.

Preliminary tests demonstrated that vinyl bromide formed solid polymeric material on substrates when exposed to the glow discharge. A parametric study was conducted to identify reaction conditions which resulted in a high polymer deposition rate (determined by measuring substrate weights before and after deposition) and a uniform surface covering (as observed in an optical microscope).

The following set of conditions was chosen to produce plasma polymer films for further characterization and permeability testing: substrate position at bottom of induction coil; vinyl bromide and argon flowrates, each at 10 cm^3(STP) min^{-1}; r.f. power at 160 W; total reactor pressure of 133.3 Pa; and reaction time of 1 h. These conditions resulted in plasma polymer deposition of 0.14 mg cm^{-2} of substrate surface.

Results and discussion

Plasma polymer characterization. The physical nature of the deposited plasma polymer was investigated using scanning electron microscopy (SEM). Plasma-treated substrates were cut to expose cross-sections, and coated with a thin layer (50 Å) of evaporated gold in order to make surfaces conductive.

The SEM analysis showed the plasma polymer deposit to be in the form of a continuous film with good thickness uniformity. Surface layer thicknesses were measured to be 0.45 ± 0.05 μm. *Figure 2* is a micrograph of an exposed sample cross-section showing the plasma polymer layer (light coloured) on a PDMS substrate (dark; bottom section of figure). In this view, the treated surface is tilted slightly towards the camera. The plasma polymer cross-section appears as the thin band of approximately 0.5 μm. Directly above this region in the figure is an oblique view of the plasma polymer exterior surface.

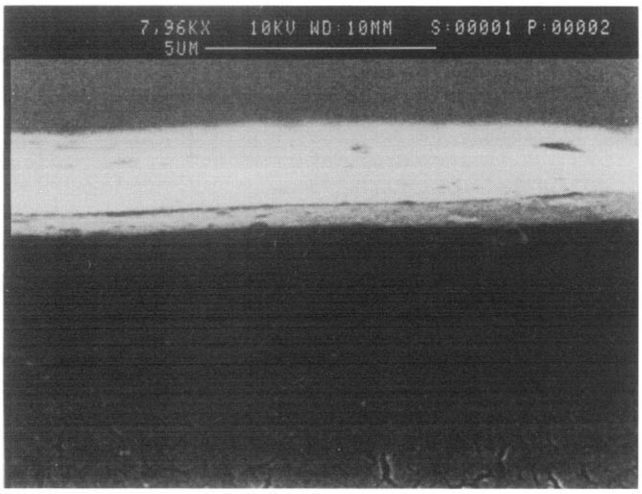

Figure 2 SEM view of sample cross-section showing plasma polymer layer on PDMS substrate (sample surface tilted towards camera, see text)

The bromine content of the surface coating was investigated with Rutherford backscattering[19] (3 MeV He^+ particles), performed at the Cambridge Accelerator for Materials Science in Cambridge, MA, USA. This technique is used to detect medium atomic weight species in solids, and to map their concentration as a function of depth.

The backscattering spectrum for a PDMS substrate coated with the plasma polymer (again, with an evaporated gold top layer) exhibited a clear signal identified as particle scattering from bromine nuclei (see *Figure 3*), confirming that bromine had been successfully incorporated into the surface layer. The finite width of this peak is a measure of the plasma polymer thickness, as particles scattered from sites within the coating are progressively less energetic than those from the surface. The uniform signal height over this energy range indicates that the bromine content of the deposited coating is constant throughout its thickness.

Lower energy signals on the left of the spectrum are due to scattering from lighter elements (including carbon, oxygen and silicon) in the surface coating and the PDMS substrate. These smaller species generate less frequent scattering per atom[19], so their peak heights are inherently small compared to that for larger elements. This, combined with the fact that there is overlap of signals from substrate and plasma polymer elements, makes it difficult to use this portion of the spectrum for accurate compositional analysis of the coating.

Instead, relative bromine concentration in the plasma polymer was estimated by comparing the backscattering spectrum to a computer-simulated spectrum for PDMS covered with a 0.45 μm layer of material whose relative atomic composition is set to be that of the vinyl bromide monomer, C_2H_3Br. Note that this would also be the relative composition of conventional poly(vinyl bromide).

The bromine signal in the experimental spectrum is lower than in the simulation (*Figure 3*), indicating a bromine deficiency in the plasma polymer. Comparison of bromine peak heights between the spectra indicates that the bromine concentration (molar) in the plasma polymer is approximately 80% of that in the simulated material.

This result is not unexpected. Halogen deficiency in the plasma polymers of other vinyl halides has been

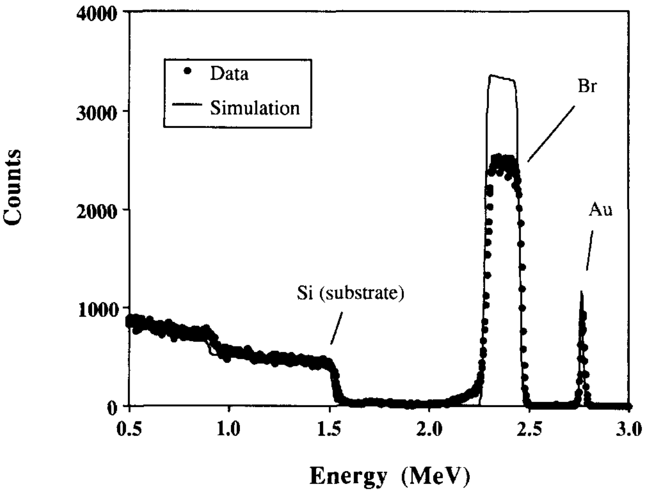

Figure 3 Experimental *versus* simulated Rutherford backscattering spectra for substrate with deposited plasma polymer

reported previously. Halogen contents measured by Westwood[20] of plasma-polymerized vinyl fluoride and vinyl chloride were approximately 30 and 55%, respectively, of 'expected' concentrations based solely on monomer composition. This information, together with the current observation for vinyl bromide, suggests that the halogen deficiency in these plasma-polymerized compounds is less pronounced as the halogen atomic weight increases.

Gas permeability. Steady-state gas permeability coefficients (P) were measured using a variable volume permeability apparatus of the type described in ASTM D-1434[21].

The first row of *Table 1* contains measured P values for several gases in PDMS substrates before plasma polymer deposition. These are referred to as P_1. The relatively high P_1 for CO_2 is a result of the high solubility of this easily condensable gas in the substrate material[22].

Coefficients were also measured for a PDMS substrate after 1 h exposure to an argon (no vinyl bromide) plasma at 100 W. This was done to check whether the glow discharge itself caused a change in the substrate, such as extensive crosslinking, which might alter its permeability. After exposure to this non-polymerizing plasma for 1 h, no significant change in permeability coefficients was detected (values within 2% of P_1). The observation that PDMS permeability coefficients are virtually unaffected by exposure to the argon plasma confirms earlier findings of Kawakami *et al.*[12].

Sample permeability was markedly depressed after deposition of the 0.45 μm layer of polymerized vinyl bromide. Permeability coefficients for this composite film (PDMS plus plasma polymer) are referred to as P_c in *Table 1*. The detectable change in P caused by the ultrathin coating indicates that the plasma polymer is considerably less permeable than the PDMS.

Based on the earlier SEM analysis, it is expected that the composite film permeability can be described by a simple model for permeation through two layers arranged in series[23]. The model states that for each gas, P_c will be related to the respective permeability coefficients of the substrate and plasma polymer, P_1 and P_2, by:

$$l_c/P_c = l_1/P_1 + l_2/P_2 \tag{1}$$

where l_c, l_1 and l_2 are thicknesses of the composite, PDMS substrate and plasma polymer, respectively.

Using the experimentally determined parameters P_1, P_c and all ls, plasma polymer permeability coefficients were determined using this equation. These calculated P_2 values appear in the last row of *Table 1*.

As expected, this analysis shows that the plasma polymer is several orders of magnitude less permeable than the rubbery PDMS substrate. The barrier quality of the deposited material is good, but not extraordinary. P_2 values are similar, for example, to those observed in polycarbonate[22] – a glassy, non-crystalline material. Permeability in the polymerized vinyl bromide is not as low as that reported for heavily brominated polybutadiene[16,17]. Increasing the bromine content of the plasma polymer, by using a different monomer or conducting the polymerization in the presence of elemental bromine, may produce a more exceptional barrier.

Table 1 Permeability coefficients[a].

	He	Ar	N_2	CO_2
P_1	390	650	290	2490
P_c	340	420	230	1900
P_2 (calculated)	1.19	0.53	0.50	3.60

[a] P in barrer (10^{-10} cm^3(STP) cm/cm^2 s cmHg)

Compared to PDMS, the plasma polymer appears to be more discriminating to transport on the basis of penetrant size. For example, the ratio of P for helium, the smallest gas tested, to P for any of the larger species, is higher in the plasma polymer than in the substrate. This is consistent with the expectation that the polymerized vinyl bromide would be a material which impeded gas transport because of restricted intersegmental mobility, which can selectively inhibit diffusion of larger compounds. Compared to PDMS, the selectivity of the plasma polymer is more strongly influenced by 'mobility' selectivity[24], which is based on differences in gas diffusion rates as opposed to gas solubilities.

In summary, the bromine-containing thin film produced by plasma polymerization provides some barrier capability, and selectivity changes compared to the substrate material. Further investigations of these polymerization reactions, together with physical/chemical characterization and gas permeability studies, will continue to improve our general understanding of relationships between gas permeation and polymer structure, and may potentially lead to the development of new materials with superior properties.

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