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Evaluation of Polytetrafluoroethylene Surfaces by Nitrogen Physisorption and the Effects of Alkali Etching

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Abstract. Polytetrafluoroethylene (PTFE, Teflon^{TM}) is well known as a highly stable material with a very low energy surface. Nitrogen physical adsorption on this material aids in an overall paradigm development for vapor sorption on solid surfaces. Extreme measures are needed to generate porous PTFE. Some examples are presented for the amount, population and energy of these surfaces and pores.

Keywords: Teflon, physical adsorption, monolayer, multilayer, shielding, micropores, ASP methodology

Introduction

Polymerized PTFE is an extremely unreactive material, characterized by its chemical, electrical, and thermal stability. It is highly resistant to all but the most aggressive methods of high temperature degradation such as alkali metal defluorination. Physical adsorption is low energy association of sorbate molecules to surfaces where the sorption potential is progressively shielded by accrued sorbed components. Statistically, adsorption on internal and external surfaces is controlled by the sorption potential (E), defined in terms of amount sorbed (Γ):

$$\begin{aligned} E &= -RT\ln[P/P(\text{sat})] = E(0)\exp(-\theta) \\ &= E(0)\exp[-\Gamma/\Gamma(\text{monolayer})] \end{aligned} \quad (1)$$

unlimited on open surfaces and geometrically limited for internal regions. In addition, capillary condensation occurs at higher relative pressures liquid phase forms in accord with Young/LaPlace/Kelvin relation for surface tension, γ:

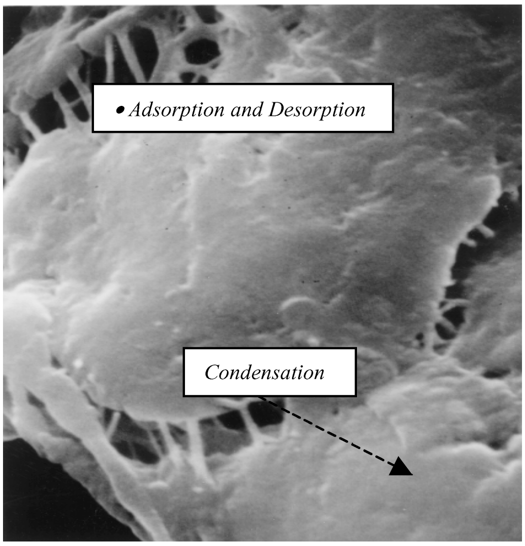
$$\text{Mean pore radius} = k\gamma V(\text{molar})(E/RT)^{-1} \quad (2)$$

for the liquid sorbate at the isothermal temperature. An open surface, free of micropores, will be described with a singular adherence to Eq. (1) followed by a higher pressure region defined by Eq. (2). The latter will define the fractal (roughness) nature of the surface in the mesoporous region. Such results provides a base parametric. Reference for comparative plots ($n, t, \alpha s, \theta$, etc.) and, thus, preclude interpolation to fixed values of pressure, and assumptions with respect to the chemical nature of the reference isotherm. ASP plots (Eq. (1)) elucidate surface interactions for materials containing micropores, supermicroporesc site association (Langmuir-BET), and chemisorption sites.

Experimental

Teflon Resin

Commercial grade Teflon^{TM} resin was obtained from the E.I. duPont Chemical Company. Pretreatment was limited to outgassing in situ at 100 C and 10–5 torr overnight. Negligible mass loss was noted due to this treatment (further evidence that no atmospheric species was sorbed). Electron microscopy of the resin, Fig. 1, shows that the resin surface is quite smooth with a minimal amount of convolution on the surface. Nitrogen adsorption/desorption data were obtained gravimetrically with a stainless steel system with no greases or oils that could contribute to contamination (Fuller et al.).



Micrograph 1. Electron micrograph of Teflon resin scale |-----| 1.3 μm.

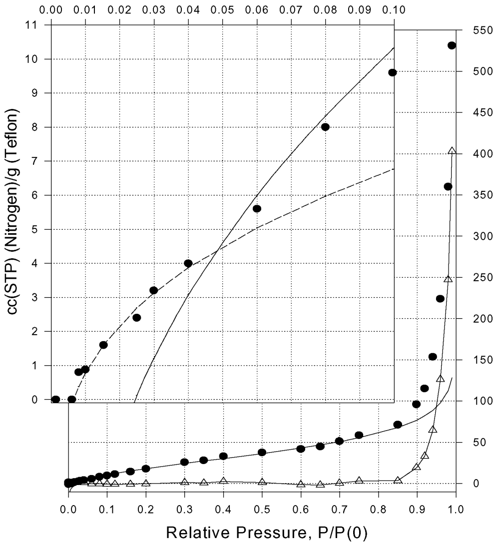


Figure 1. Nitrogen sorption isotherm (77 K) Teflon Resin-circle for: adsorption and triangles for condensation.

The nitrogen sorbate was 99.9995 percent pure. Computer aided data acquisition was employed to evaluate the reaction rates (kinetics) and equilibrium (steady state) mass changes at temperatures maintained with a stirred liquid nitrogen thermostat bath. This coolant was automatically replenished (±3 mm) on demand from a pressurized reservoir. Baffles were installed in the sample tube to minimize radiative heat transfer from the room temperature environment of the balance.

Etched Material

Samples of duPont Teflon (MP 1500J) were defluorinated with alkali metals in closed systems at elevated temperatures (Tanaike). Volumetric nitrogen sorption isotherms were used to calculate surface areas and porosity of the etched materials. Activated samples were coded: NaPTFE, KPTFE, and RbPTFE for the sodium, potassium, and rubidium defluorination. The lithium (LiPTFE) material spontaneously burst into flames.

Results

Teflon

Sequential application of the ASP method to the Teflon data (Figs. 2–4) denotes (a) threshold pressure {0.0054 $P(0)$}, below which no sorption occurs, (b) a small amount of microporsity filled at ca. 0.045 P(0), (c) open surface covered up to ca. 0.84 P(0), where (d) interparticulate condensation also occurs. At this writing no descriptive parameters (specific surface areas, micropore radii, micropore distribution, mesopore

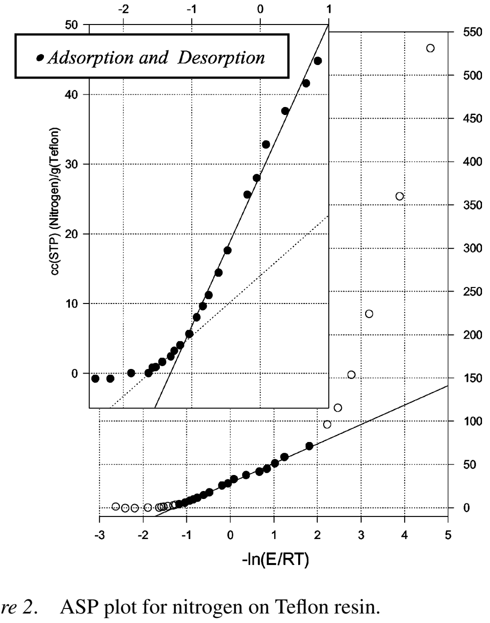


Figure 2. ASP plot for nitrogen on Teflon resin.

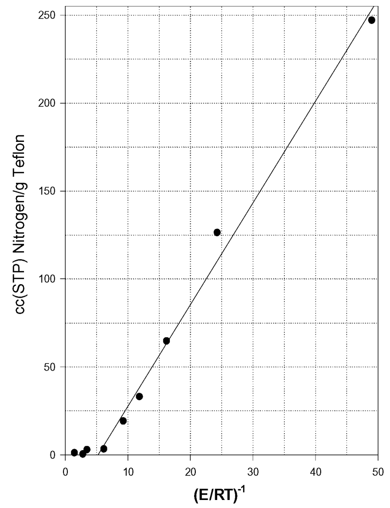


Figure 3. Mesopore condensation of nitrogen on Teflon resin.

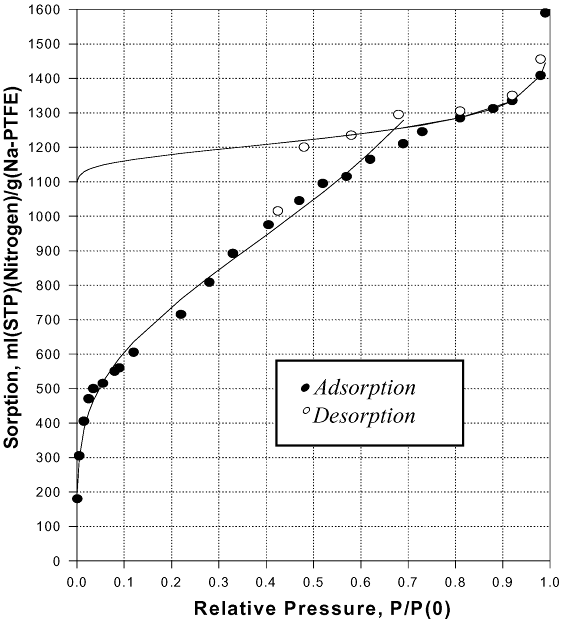


Figure 4. Nitrogen sorption isotherm: Sodium activated Teflon at 77 K.

size/distributions. In each case specific evaluations rely on ill-defined parameters (molecular size, sorbate structure, density of sorbed material, shape of pores, density of pore phase, surface tension variations, etc.). Note that this methodology provides excellent evaluation of the thermodynamics of the sorption processes with a minimum (essential) number of adjustable parameters. No sorption hysteresis is detectable for this material.

Activated Materials

Note the enhanced sorption, partially due to material loss (burnoff) in the activation process, as well as appreciable sorption hysteresis (desorption points above adsorption points). This is rather strong indication of mesopores with pore access through orifice sizes equal to or less than internal, subsurface, dimensions. The microporosity is noted in enhanced E^* (intercept) giving rise to much greater sorption at the very low pressure minimum (vacuum) achieved and maintained in to the volumetric instrumentation. At this writing any evaluation of sorption in these low pressures is speculative (Fuller et al.). Definitive evaluation of sorption mechanisms in this region requires independent evaluation of the topology and surface chemistry (such as Fig. 1) for mechanistic correlation.

NaPTFE

Figures 5 and 6 reveal considerable internal structure and some external surface with a very small amount of capillary hysteresis. One single data point, 0.99P(0), is indicative of the inevitable small amount of mesopore condensation.

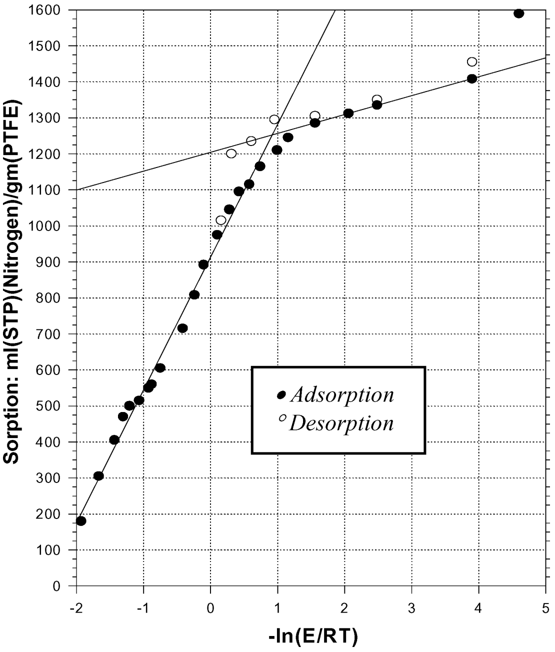


Figure 5. Nitrogen sorption ASP plot: Sodium activated Teflon.

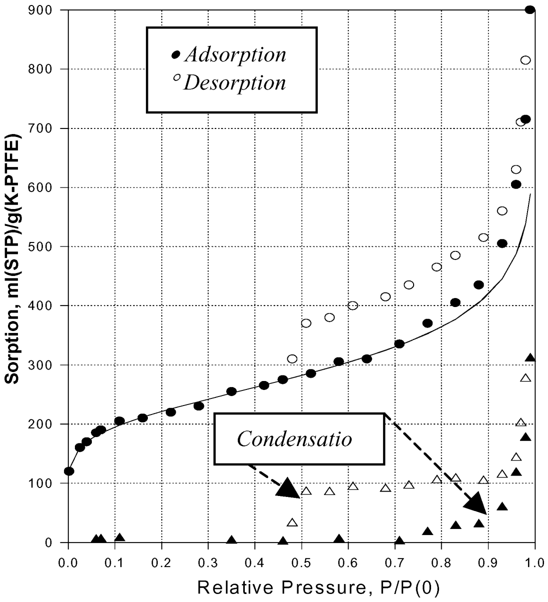


Figure 6. Nitrogen sorption isotherm (77 K) for potassium activated Teflon.

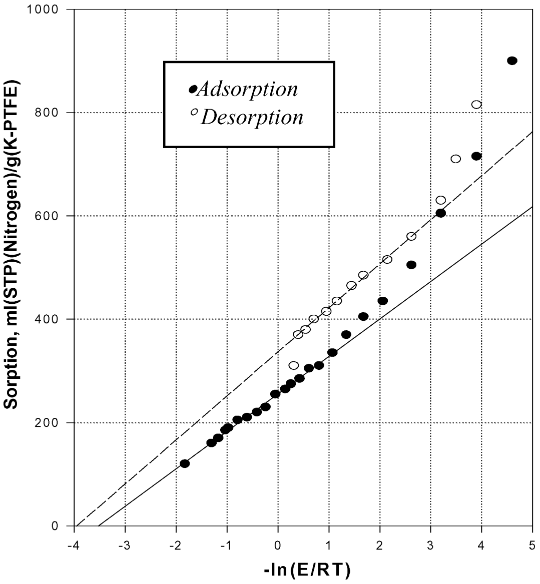


Figure 7. ASP Plot for nitrogen (77 K) sorption by potassium activated Teflon.

KPTFE

Figures 7 and 8 are the alternate presentations consistent with the presence of a much larger surface area (smaller particle size) and appreciable amount of interparticulate (mesopore) condensation where access is gained through restricted orifices. The mesopore condensation and the associated hysteresis are presented linearly in Fig. 9.

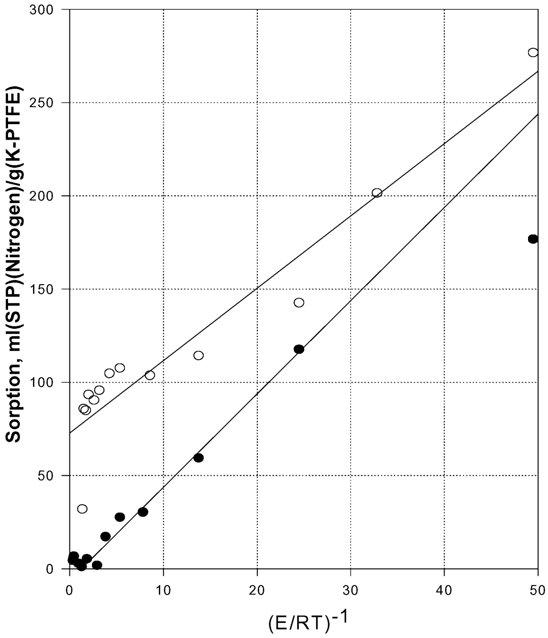


Figure 8. Mesopore condensation (77 K) on potassium activated Teflon.

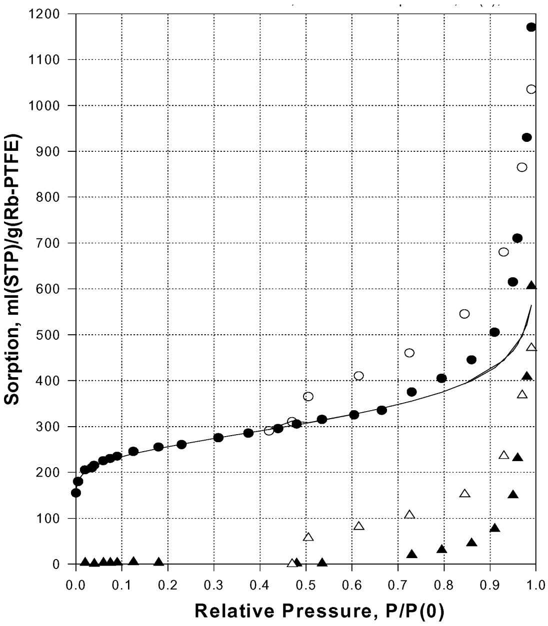


Figure 9. Sorption isotherm: Nitrogen (77 K) on rubidium activated Teflon.

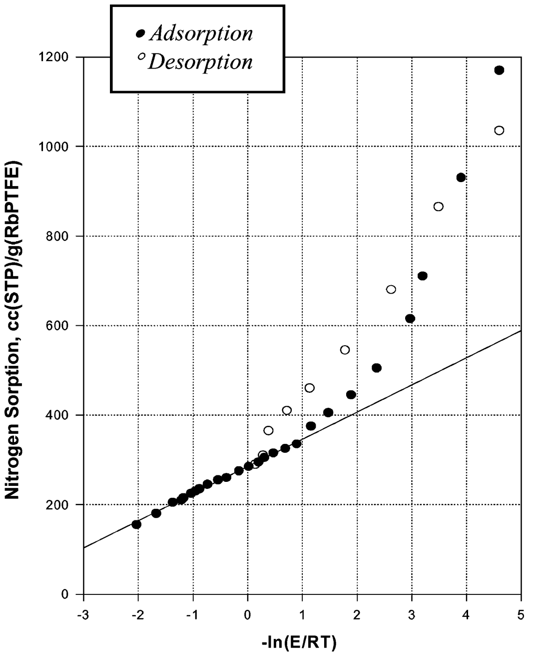


Figure 10. ASP plot: Nitrogen (77 K) on rubidium activated Teflon.

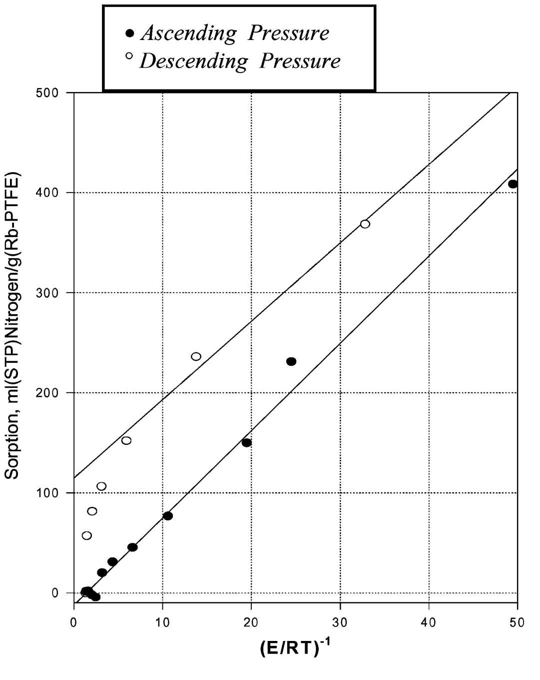


Figure 11. Mesopore condensation: Nitrogen on rubidium activated Teflon.

RbPTFE

Figures 10 and 11 are similar with appreciably more pronounced mesopore capillary condensation and hysteresis. Figure 12 is the linear plot of the mesopore condensation and hysteretic retention in terms of the dimensionless pore radii.

Conclusions

Physisorption isotherms show that the activation product is distinctly different for each of the defluorination processes, and the ASP technique successfully delineates the thermodynamics of each of the processes without the used of reference isotherms. Mechanistic interpretation is identical to comparison plots. In each case monolayer/multilayer formation occurs at intermediate pressures followed by capillary condensation, ultimately culminating in liquid phase formation. Micropores are filled at the much lower pressures (greater sorption potential) and are well described by the ASP analyses over the specific regions of applicability. The exponential variation of Polanyi potential with coverage appears to explain a large amount of sorption data in the ultramicropore, micropore, monolayer, and multilayer thermodynamic regimes. This methodology is simple, involves a minimum of postulates, utilizes very few adjustable parameters, employs simple calculations, but yet defines a great amount of sorption data. Note that each of the presentations here are linear with respect to the intensive parameter (sorption) in the sorption domains . Virtually all other transformations involve the extensive parameters, pressure, energy, pore size etc. Virtually all other analytical techniques (Langmuir, BET, FHH, Toth, DR, DK, Freundlich, etc.) involve complex transformations of the intensive quantity, Γ, or its dimensionless form, $\Gamma/\Gamma(\mathrm{m})$.

ASP Methodology

A brief review and recommendations are presented here to aid in detailed evaluation of surface morphology from physical sorption on solid surfaces, based on the concept of progressive shielding of sorption potential:

- *Acquire adequate data over wide pressure range.* The most informative data is in the very low pressure (vacuum) and high pressure (near liquid condensation) regions. Modern computer control of data acquisition allows unassisted operation to follow kinetics and assure equilibrium for definition of sorption processes.

- *Plot data in ASP format.* Exponential decrease in Polanyi potential with sorption is the norm for physical sorption whether in the finite capacity of micropores, or unlimited multilayers on open (flat) surfaces.
- *Examine for linear regions.* The fit is usually quite good (linear least squares correlation coefficients ($r^2 > 0.99$ in the examples shown here).
- *Calculate fit to the sorption isotherm.* The calculation is in terms of the ASP parameters and it is shown in this article for aesthetic and pedantic purposes.
- *Evaluate fractal roughness.* Pore filling {pore volume = pore radius$^{\text{(fractaldimension)}}$) with the dimension ranging from *one* for smooth surfaces to *three*. for the highly convoluted meso/macro-topology.
- *Utilize computer aided analyses.* Optimized analyses can be used to directly recursively calculate each of the above functions (imagine the tedium of this type of data analyses were we still relying on 10 place logarithm tables!!).

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