

## Sorption Kinetics of *p*-Nitrophenol by Oxidized Undrawn Nylon Filaments

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### Synopsis

The sorption kinetics of *p*-nitrophenol (PNP) onto undrawn nylon yarn from an organic, nonswelling solvent in a dye bath in which the concentration of PNP was being depleted were found to obey Hill's solution of the diffusion equation, suggesting the presence of a monolayer of absorbed PNP at the surface of the fiber. Diffusion coefficients were obtained using a nonlinear least-squares curve-fitting computer program. For undrawn nylon samples, oxidized for various lengths of time prior to dyeing, the diffusion coefficient increased as a function of oxidation time, rising particularly rapidly once the fibers developed microscopically visible surface cracks. The dependence of diffusion coefficient on oxidation time implies that oxidative degradation of the material is accompanied by formation of submicroscopic incipient cracks, permeable by PNP, of which at least some eventually develop into visible cracks after sufficient oxidation.

### INTRODUCTION

Vachon et al.<sup>1</sup> reported the development of visible cracks on the surfaces of individual nylon filaments after immersion of the filaments in an aqueous medium saturated with molecular oxygen at elevated temperatures. These cracks appear only after prolonged exposure to these conditions, i.e., 80°C for 10-12 hr for undrawn yarn and upward of 20 hr for the same material drawn 4×. Microscopic examination has not revealed the existence of cracks in yarn samples exposed to these oxidative conditions for shorter periods of time, despite continued changes in density, endgroup concentrations, and intrinsic viscosity as functions of treatment time.<sup>2</sup> Mechanical properties of the yarn also show continuous changes with treatment time.<sup>3</sup> A study of the sorption behavior of nylon yarns treated in such a manner was therefore undertaken with the aim of detecting changes in fiber structure as a function of treatment time, and establishing the relationship between crack formation on the one hand and chemical, physical, and mechanical properties of the material on the other.

### EXPERIMENTAL PROCEDURES AND RESULTS

#### Oxidation of Yarn

Undrawn nylon 66 yarn prepared without antioxidants was supplied by E. I. du Pont de Nemours and Co., Inc. The yarn was oxidized in a glass

resin-reaction flask by immersing samples wound around C-shaped glass rods in an aqueous medium buffered at pH 8.2 with  $\text{NaHPO}_4$  and  $\text{KH}_2\text{PO}_4$ . The temperature of the system was maintained at  $80^\circ\text{C}$ , and a regulated flow of oxygen of approximately 1000 cc/min at S.T.P. was continuously fed to the solution.

### Sorption

In the sorption experiments, 40 ml of a 0.047 mmole/l. solution of *p*-nitrophenol (PNP) in cyclohexane was used to treat 0.3 g of yarn. Depletion of the bath was monitored by periodically withdrawing samples of liquid and analyzing spectrophotometrically for PNP concentration. Sorption curves were obtained at  $19^\circ$ ,  $25^\circ$ , and  $35^\circ\text{C}$  for specimens of untreated yarn and yarns oxidized 4, 8, and 14 hr; sorption curves for untreated yarn were also obtained using a solution of 0.047 mmole/l. PNP in water.

The particular solvent/solute/substrate system has been chosen to provide a comparison with the sorption work of Giles and co-workers,<sup>4-6</sup> in which the aim was to measure surface areas of various solids. For fibers, PNP was found to be a good solute for this purpose when dissolved in a nonpenetrating, nonaqueous solvent. Attempts to utilize the Giles technique for detecting differences in nylon surface areas resulting from oxidative degradation and subsequent stress cracking were unsuccessful due to poor precision of surface area values. Instead, the effects of oxidation on nylon were investigated through the kinetic sorption of PNP, in a manner similar to studies of fiber structure by dyeing kinetics.

The amounts of PNP uptake in the untreated, 4-hr oxidized, and 8-hr oxidized yarns, at all three temperatures in the cyclohexane system, seemed to attain a temporary plateau in the early stages of the run (2-6 min). This short-time plateau may represent the monolayer absorption described by Giles,<sup>4-6</sup> with subsequent increase in uptake due to diffusion of PNP into the interior of the fiber. For samples oxidized for 14 hr in the PNP/cyclohexane system and for untreated samples in the PNP/water system, no plateau of this type was observed; the uptake curve rose monotonically from the beginning of the run. In these cases, the fiber surface is presumed to have been "opened up," by cracking in the highly oxidized samples and by swelling in the PNP/water system. In either case, PNP easily penetrates into the interior of the fiber, so that the monolayer, even if formed, is undetectable experimentally.

### ANALYSIS OF RESULTS

The kinetic sorption data were analyzed on the presumption that the pickup of PNP is analogous to that of a dye. The parameters of the theoretical equations investigated were determined by means of the Daniel and Wood<sup>7</sup> nonlinear least-squares curve fitting program (SHARE number 360D-13.6.007).

### Theoretical Diffusion Equation

Fick's second law for purely radial diffusion in a long cylinder is

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( rD \frac{\partial C}{\partial r} \right). \quad (1)$$

For the case of diffusion into an infinite cylinder from a perfectly stirred solution of limited volume, Crank<sup>8</sup> gives the following solution of the diffusion equation:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2 g_n^2} e^{-Dg_n^2 t/r^2} \quad (2)$$

where  $t$  = time,  $M_t$  = total mass of solute absorbed in the cylinder after time  $t$ ,  $M_\infty$  = equilibrium mass of solute in the cylinder,  $r$  = radius of the cylinder,  $D$  = diffusion coefficient, assumed to be a constant at any temperature,  $\alpha$  = volume ratio of solution to cylinder, divided by the partition coefficient, and  $g_n$  = positive, nonzero roots of  $\alpha g_n J_0(g_n) + 2J_1(g_n) = 0$ , where  $J_0(g_n)$  and  $J_1(g_n)$  represent standard Bessel functions.

For small  $Dt/r^2$ , eq. (2) can be appreciably simplified. If  $\alpha$  is very small ( $\ll 1$ ), corresponding to a small liquid/solid ratio and/or to partition favoring the solid, the appropriate equation is

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{1+1/4\alpha} \left[ 1 - \frac{\alpha(Dt/r^2)^{-1/2}}{2\pi^{1/2}(1+1/4\alpha)} + \frac{\alpha^3(Dt/r^2)^{-3/2}}{16\pi^{1/2}(1+1/4\alpha)^3} - \frac{3\alpha^5(Dt/r^2)^{-5/2}}{128\pi^{1/2}(1+1/4\alpha)^5} + \dots \right]. \quad (3)$$

If  $\alpha$  is very large ( $\gg 1$ ), corresponding to a large liquid/solid ratio and/or to partition favoring the liquid, the solution is

$$\frac{M_t}{M_\infty} = \frac{2}{\alpha} (1+\alpha) \left[ \frac{2}{\pi^{1/2}} \left( \frac{Dt}{r^2} \right)^{1/2} - \left( \frac{1}{2} + \frac{2}{\alpha} \right) \left( \frac{Dt}{r^2} \right) - \frac{4}{3\pi^{1/2}} \left( \frac{1}{8} - \frac{2}{\alpha} - \frac{4}{\alpha^2} \right) \left( \frac{Dt}{r^2} \right)^{3/2} + \dots \right]. \quad (4)$$

In applying these equations to the PNP/nylon system, it is assumed that the rate-controlling step is diffusion of PNP into the fiber. If the assumption is correct, then the sorption system should correspond closely to the theoretical model. However, use of the theoretical model normally assumes knowledge of the equilibrium state, which was not available, since in systems studied over long times, the solute was completely exhausted from the liquid phase. This failure to attain measurable equilibrium conditions in the liquid created uncertainty about the meaning of the parameter  $M_\infty$  and also prevented determination of the partition coefficient (thereby leaving  $\alpha$  unknown). Attempts to determine the partition coefficient, by changing volume ratios and initial PNP concen-

trations, all failed to yield measurable equilibrium conditions. Consequently, in fitting eqs. (3) and (4) to the data, both  $M_\infty$  and  $\alpha$  as well as  $D$  were treated as unknown parameters.

### Small- $\alpha$ and Large- $\alpha$ Models

Although the partition coefficient could not be measured with any accuracy, it was believed to be large because of the high affinity of PMP for the polar substrate and the low solubility in cyclohexane. The value of  $\alpha$  depends on both the solution-to-fiber volume ratio and the partition coefficient, but a very large value of the latter can ensure that  $\alpha$  will be small even for a relatively large volume ratio. As a result, although the sorption behavior of the PNP/cyclohexane/nylon system was expected to follow the small- $\alpha$  model, this model did not in fact provide a good fit of the data. The form of the residual pattern suggested the necessity of a quadratic term to improve the fit.

The large- $\alpha$  model, which includes a quadratic term, proved to fit the data well. However, the precision of the estimated values of the parameters, as evidenced by the 95% confidence limits calculated in the computer program, was poor; reliability of the large- $\alpha$  model was consequently poor in spite of high  $R^2$  values. The problem of obtaining high precision for parameter estimators in nonlinear equations is well known, especially where the number of parameters estimated is large.

### Hill's Equation

In the extreme case of the large- $\alpha$  model, where  $\alpha = \infty$ , only two parameters ( $D$  and  $M_\infty$ ) need to be estimated; greater precision can therefore be expected. This limiting case corresponds to the commonly used Hills' solution of the diffusion equation:

$$\frac{M_t}{M_\infty} = 1 - 0.692 (e^{-5.785 Dt/r^2} + 0.190 e^{-30.5 Dt/r^2} + 0.0775 e^{-74.9 Dt/r^2} + \dots) \quad (5)$$

which is applicable to the problem of diffusion into a cylinder from a bath of constant concentration.<sup>9</sup>

The data fit this equation very well. Results for all experimental runs are summarized in Table I. The estimated values of  $M_\infty$  were reasonable when compared with the measured terminal concentrations; the 95% confidence limits of the parameters were vastly improved over those in the general large- $\alpha$  model. Estimated values of  $D$ , which were of the order of  $10^{-9}$  cm<sup>2</sup>/min, seem reasonable. For example, for diffusion of an acid dye, Orange II, into undrawn nylon at 80°C, Davis and Taylor<sup>10</sup> report diffusion coefficients of about  $6 \times 10^{-8}$  cm<sup>2</sup>/min, while Vickerstaff<sup>9</sup> reports a range of values of  $6 \times 10^{-10}$  to  $1.4 \times 10^{-8}$  cm<sup>2</sup>/min for diffusion of various dispersed dyes into nylon at 80°C.

TABLE I  
Hill's Equation Parameters for PNP/Nylon Sorption System

Oxidation time, hr	<i>T</i> , °C	<i>M</i> <sub>∞</sub> , mmole/kg	<i>D</i> , (cm <sup>2</sup> /min) × 10 <sup>9</sup>	<i>R</i> <sup>2</sup>
0	19	4.62	0.202	0.914
		4.69	0.298	0.988
		3.14	0.707	0.984
	25	4.73	0.255	0.992
		3.80	0.408	0.980
		3.30	1.10	0.968
4	19	2.31	1.82	0.979
		2.78	1.05	0.900
		4.33	0.41	0.940
	25	2.03	1.81	0.937
		5.32	0.40	0.995
		2.77	1.76	0.988
8	19	4.93	1.01	0.995
		2.36	1.60	0.991
		3.66	2.07	0.977
	25	2.41	3.47	0.988
		3.77	0.97	0.968
		3.23	3.13	0.992
14	19	2.87	1.10	0.947
		3.75	1.59	0.978
		3.96	1.05	0.857
	25	5.26	7.90	0.972
		4.75	7.64	0.993
		4.93	6.23	0.996
0*	35	3.80	4.79	
	25	4.14	3.40	
	19	3.93	3.00	

\* Sorption from water.

## DISCUSSION

The apparent anomaly of the PNP/cyclohexane/nylon system behaving as though  $\alpha$  were large, although  $\alpha$  might *a priori* be expected to be small, might be resolved by postulating the formation of a constant concentration layer of PNP at the surface of the fiber. As a result, the parameter  $\alpha$ , as defined in relation to the fiber/liquid system, has no meaning because the fiber "sees" a constant concentration of PNP as its outer boundary, rather than a continuously depleting bath. It might be possible to redefine  $\alpha$  in terms of a partition coefficient between the fiber and the surface layer. But if the concentration of the latter is maintained at a constant level throughout the sorption run, the system will be equivalent to one in which the liquid-to-solid ratio is infinite (i.e.,  $\alpha = \infty$ ). Under these conditions, Hill's equation will describe the sorption kinetics.

Evidence for such a layer in untreated, 4-hr oxidized, and 8-hr oxidized samples is provided by the Giles-type plateau at the beginning of the ki-

netic sorption curves. In the highly cracked, 14-hr oxidized samples, no plateau was observed; but the applicability of Hill's equation to these samples also suggests that a constant concentration surface layer is formed. It appears that more rapid diffusion of PNP into the fiber in the 14-hr oxidized samples renders the transient plateau undetectable, at least by the experimental technique utilized here.

### Effect of Yarn Oxidation on Diffusion Coefficient

Averages of the individually estimated diffusion coefficients were calculated for each combination of yarn treatment and temperature (Table II). There was a noticeable effect of oxidation on the diffusion coefficient, but the effect of temperature over the small range studied was uncertain; and for the oxidized yarn samples,  $D$  appeared to be independent of temperature. Since the effect of temperature was slight, it was found convenient to lump together, for each treatment time, the values of  $D$  at the three temperatures. The diffusion coefficients so obtained increased gradually between 0 and 8 hr of oxidation, and more sharply between 8 and 14 hr of oxidation. Analysis of variance confirmed the effect of oxidation time on the diffusion coefficient.

The two parameters which determine the kinetic sorption behavior are the equilibrium uptake ( $M_{\infty}$ ) and the diffusion coefficient ( $D$ ). As indicated, measurable equilibrium between the liquid and the solid was not attained in the PNP/nylon system. There was a large excess of sorption sites, and chemical changes in the nylon as a result of oxidation would not be expected to alter this excess significantly. Therefore, study of the sorption behavior under these conditions should be indicative solely of physical changes in the fiber as a result of oxidation, changes which would be reflected in the diffusion coefficient.

Molecular orientation in the undrawn yarn was apparently unaffected by oxidation, while the density increased with increasing oxidation.<sup>2,3</sup> It might be expected, then, that the diffusion coefficient would decrease for the more compact, and presumably more highly crystalline, oxidized nylon. In actuality, the opposite effect was observed. It appears that the forma-

TABLE II  
Diffusion Coefficients for Sorption of PNP by Untreated and Oxidized Undrawn Nylon Yarns, as Calculated by Hill's Equation

Oxidn. time, hr	$D, (\text{cm}^2/\text{min}) \times 10^8$			Avg. over all temps.
	19°C <sup>a</sup>	25°C	35°C	
0	0.40	0.33	1.46	0.73
4	1.09	1.08	1.01	1.06
8	2.38	1.73	1.32	1.81
14	7.90	7.64	6.23	7.26

<sup>a</sup> Sorption temperature.

tion of cracks on the fiber surface results in more rapid penetration of the PNP, increasing the diffusion coefficient, which was substantially higher for the yarn samples with cracks than for those without. However, even for those samples without cracks, it appeared that the diffusion coefficient increased with oxidation time. This increase in  $D$  suggests that the fiber structure becomes looser as a result of oxidation (although the density increases and the orientation remains unchanged) and can possibly be explained in terms of incipient, submicroscopic cracks which arise during the early stages of oxidation and grow into visible cracks after oxidation for more than 8 hr.

### Effect of Water as Solvent

Hill's equation was also applied to the sorption data from water solution for untreated samples at 20°, 25°, and 35°C. Long-time points were not available for these runs, and without such points the results obtained from Hill's equation were erratic. However, the similarity of these sorption curves to those samples oxidized 14 hr in cyclohexane solution suggested that a reasonable estimate of the latter portion of the curves could be made.

Consequently, for each run, one long-time point was calculated, with uptake corresponding to complete exhaustion of the bath and at times corresponding to those of the cyclohexane runs. These calculated points were added to the original data and the new sets of data fitted by Hill's equation. (This procedure was essentially equivalent to specifying  $M_{\infty}$ .) A good fit of the data was obtained, and estimated values of  $D$  were intermediate between those of 8-hr and 14-hr oxidized samples in the cyclohexane system (Table II). These results, although they must be approached with some caution, seem to indicate that both the effect of oxidation and the effect of water on the PNP sorption behavior of the fiber was similar, each acting to open up the fiber structure.

However, the water accomplishes this purpose by swelling the fiber, whereas oxidation increases the interstitial areas of the fiber by means of stress cracking. The diffusion coefficient can be viewed as a measure of extent of opening of the structure, so that the higher  $D$  attributable to stress cracking after oxidation for 14 hr may be taken to indicate that this process is more effective in opening the fiber to PNP diffusion than is swelling by water.

### CONCLUSIONS

The sorption of PNP by undrawn nylon yarn involves the formation of an adsorbed solute layer at the surface of the fibers. The presence of such a surface layer makes it possible to describe the sorption kinetics by means of Hill's solution of the diffusion equation. The diffusion coefficient obtained by using the equation increases with an increase in the oxidation time to which the yarn substrate had previously been exposed. This dependence of diffusion coefficient on yarn oxidation time correlates quali-

tatively with the changes in various chemical and physical properties of the yarn, also as functions of oxidation time. The trends in these properties are indicative of alterations in yarn structure caused by the oxidative process even at times below those required to produce visible cracking. The sorption data in particular suggest the existence of submicroscopic, incipient cracks in fibers at an early stage of oxidation.

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