

## Steam and Heat Setting of Nylon 6 Fiber.

### VI. Water Adsorption on Nylon 6 Fiber\*

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#### Synopsis

Water adsorption of nylon 6 fibers subjected to various heat-setting treatments was measured over the range of 0-80% R.H. with a quartz balance, and the water adsorbed on the first layer ( $v_m$ ) was calculated. The value of  $v_m$  was largest for unset fiber, intermediate for steam-set fiber, and the smallest for dry-heat-set fiber. The inner surface areas in nylon calculated from  $v_m$  are  $4-5 \times 10^6$  cm.<sup>2</sup>/g. The value obtained by dividing  $v_m$  by the amorphous fraction ( $1 - \alpha$ ) of heat-set fibers appears to be related to the number of intermolecular bonds per unit volume of the amorphous region. The smaller values of  $v_m$  thus obtained for the dry-heat-set fibers indicate that polymer molecules in the amorphous region form many intermolecular bonds and are more closely packed than those in the unset and steam-set fibers.

#### 1. INTRODUCTION

Water adsorption has been used to investigate the structure of synthetic high polymers since Bull,<sup>1</sup> Pauling,<sup>2</sup> and Mellon et al.<sup>3</sup> applied it to the structural investigation of proteins. For example Abott and Gooding<sup>4</sup> and Hutton and Gartside<sup>5</sup> described isotherm and hysteresis of water adsorption on nylon 66. Hoshino and Yumoto<sup>6</sup> calculated the free energy, entropy, and heat of adsorption of water on undrawn and drawn nylon 6 fibers and the results were applied to the B.E.T. and Sherman-Smith isotherms.

Long<sup>7</sup> and Furuya<sup>8</sup> measured the diffusion velocity of water in nylon 6 and 610, and reported that the values were smaller in these than in other fibers. The relation between the effects of heat setting and moisture adsorption on nylon 6 was described by Hoshino and Yumoto.<sup>6</sup> Furuya<sup>8</sup> measured the amount of water adsorbed and the degree of swelling along the fiber axis at various relative humidities on steam-set and dry-heat-set nylon 6 fiber. The change of moisture regain of nylon 6 fiber subjected to heat setting or treatment with phenol solution was observed by Petukhov and Paskhver.<sup>9</sup>

Polyamide and protein fibers adsorb from 4 to 10% (on the weight of fiber) water in an ordinary atmosphere. The adsorbed water may be present in two different states, that is, bound water and condensed water.

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The former is held by the hydrogen bonds with amino or acid amide group. Pauling<sup>2</sup> has indicated from the data obtained by Bull<sup>1</sup> for nylon 66 that the number of localized sites with which water molecules are able to form hydrogen bond is about 6% of the total carbonyl and amide groups. If such hydrogen bonds formed between water molecules and unbonded acid amide groups in the polymer, the amount of bound water may be proportional to the number of free amide groups forming no intermolecular hydrogen bond in the amorphous regions, that is, the amount of bound water per unit volume of amorphous region will be related to the number of junction points among molecules in the amorphous region. On the basis of the above hypothesis, the water vapor adsorption of steam-set and dry-heat-set nylon 6 was measured and the amount of water adsorbed on the first layer was calculated by using the B.E.T. equation. The effects of heat-setting on structural changes in the amorphous region are discussed on the basis of these results in relation to those of previous reports.

## 2. EXPERIMENTAL

### Materials

Drawn nylon 6 filament (100 den./24 fil.) with a draw ratio of 3.71, supplied in 1 g. hanks, was used as original material. The hanks were extracted in a Soxhlet apparatus with a 1:1 mixture of alcohol and benzene for 6 hr. and then with diethyl ether for 2 hr.

### Heat Setting

Steam-set materials were prepared as follows. The purified hank was preparatively heated in a setting chamber for 10 min. at 80°C. then set in vacuum for 10 min. Steam-setting was carried out at 110, 120, 130, or 135°C. for 10 min., and the hank was dried in vacuum.

In dry heat setting, the hank was preheated for 1 hr. at 60–90°C. in nitrogen, and then heated in a Wood's metal bath for 20 min. at temperatures of 140, 160, or 180°C.

### Apparatus

The weighing bottle method does not give high accuracy in the low and high humidity region. Therefore, in this experiment the quartz balance method, as used by Chipalkatti and co-workers<sup>11</sup> for measuring the adsorption of organic vapors on wool, was used. A sketch of the apparatus is shown in Figure 1.

The material is hung on the quartz balance in a glass tube *A*. Exchange of the sample can be done easily by opening plate *b*. Humidity in the tube *A* is regulated by changing the concentration of aqueous sulfuric acid solution in a flask *B*. The bore of cock *a* and the internal diameter of the connecting guide tube are made wide so that the rapid diffusion of water vapor is possible. An oil diffusion pump is attached at point *d* for the

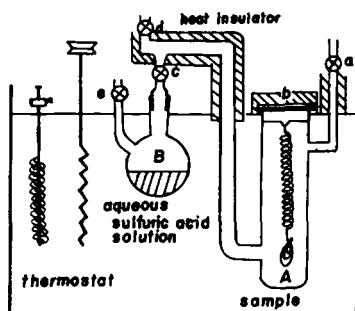


Fig. 1. Apparatus for measurement of water adsorption.

reduction of the pressure in *A*. A manometer (0–760 mm. Hg) attached at point *a* may be used to determine the water vapor pressure and detect any air leaks to the sample holder *A*.

### Procedure

Before the measurements of water vapor adsorption, it was ascertained that load–elongation curves of the quartz balance at various temperatures are accurately linear. The elongation of the balance was measured with accuracy of 1/100 mm. by use of a traveling microscope.

A sample which had been predried for more than a week in a desiccator over  $P_2O_5$  was hung on the quartz balance, and was then further dried under reduced pressure ( $10^{-3}$ – $10^{-4}$  mm. Hg) at  $40^\circ\text{C}$ . over  $P_2O_5$  (in flask *B*) for 6 hr. The equilibrium value of the quartz balance was defined as the absolute weight of the sample. The relative humidity in *A* was successively changed from 1.0 to 80%. Especially in low humidity (below 15% R.H.) the measurements were repeated many times. After a measurement, the concentration of sulfuric acid in the flask *B* was determined by titration and the humidity was determined accurately.

### 3. RESULTS AND DISCUSSION

The measurements were carried out at  $27$  and  $40 \pm 0.2^\circ\text{C}$ . Some adsorption curves at various humidities at these temperatures are shown in Figure 2. The adsorption reached equilibrium in about 1 hr. at low humidity for 30 min. at high humidity.

Moisture regains at various relative humidities are given in Table I and are shown in Figures 3 and 4. At the same humidity, the moisture regain is the highest for the unset fiber, intermediate for the steam-set fiber, and lowest for the dry-heat-set fiber. Moreover, the moisture regain decreases with increasing heat-setting temperature. Furuya<sup>9</sup> and Petukhov and Paskuher<sup>10</sup> reported that the moisture region of the steam-set fiber increases in high humidity region, but in the present experiments no such tendency is clear.

TABLE I

Conditions of heat setting		At 27°C.		At 40°C.	
Type	Temperature, °C.	R.H., %	Moisture regain, %	R.H., %	Moisture regain, %
No treatment	—	1.1	0.18	1.7	0.09
		2.3	0.23	2.7	0.23
		3.0	0.35	2.8	0.20
		4.4	0.41	5.0	0.40
		6.1	0.65	6.2	0.45
		9.4	0.72	10.0	0.74
		15.7	1.21	12.7	0.81
		26.4	1.82	26.8	1.51
		34.9	2.30	35.7	2.00
		46.5	3.09	47.0	2.75
		60.6	4.22	64.0	4.01
		79.7	6.10	79.6	5.31
		Steam-set	110	1.1	0.14
3.0	0.27			2.8	0.17
6.0	0.53			6.0	0.38
12.5	0.85			13.0	0.73
22.8	1.40			26.8	1.35
33.5	1.97			35.7	1.85
46.3	2.80				
62.5	3.94				
79.5	5.51				
Steam-set	120	1.1	0.15	1.7	0.14
		3.0	0.27	2.8	0.18
		4.2	0.32	4.8	0.39
		6.0	0.50	7.1	0.47
		9.8	0.64	10.0	0.64
		12.5	0.84	10.7	0.65
		17.7	1.09	12.7	0.74
		22.8	1.36	26.9	1.36
		34.3	1.94	35.7	1.78
		46.0	2.61	47.5	2.50
		62.5	3.88	63.7	3.69
		79.7	5.52	79.0	4.96
		Steam-set	130	1.2	0.12
3.0	0.26			2.9	0.19
4.5	0.39			4.5	0.39
6.1	0.57			7.3	0.45
9.5	0.61			9.5	0.61
15.7	0.94			13.0	0.69
18.0	1.02			18.0	1.02
27.4	1.49			27.0	1.30
34.9	1.96			35.7	1.76
46.3	2.72			47.5	2.49
62.5	3.96			63.7	3.72
79.7	5.62			68.0	4.06

## Adsorption Isotherms for Water Vapor

Conditions of heat setting		At 27°C.		At 40°C.	
Type	Temperature, °C.	R.H., %	Moisture regain, %	R.H., %	Moisture regain, %
Steam-set	135	1.1	0.08	1.5	0.10
		2.2	0.19	2.6	0.18
		3.0	0.22	2.7	0.20
		4.5	0.33	5.0	0.33
		6.1	0.44	6.1	0.35
		9.5	0.62	10.0	0.61
		11.9	0.75	13.0	0.68
		22.8	1.15	26.8	1.30
		34.1	1.85	35.7	1.75
		46.3	2.63	47.5	2.51
		62.0	3.90	64.1	3.97
		79.5	5.36	79.8	5.57
		Dry-heat-set	140	1.15	0.16
3.1	0.24			2.7	0.19
3.2	0.28			3.3	0.24
4.5	0.31			4.9	0.34
5.5	0.43			7.3	0.46
9.6	0.63			9.8	0.57
12.0	0.75			13.0	0.73
25.4	1.42			27.0	1.31
34.6	1.85			35.7	1.75
46.3	2.59			47.0	2.39
63.5	3.65			62.6	3.35
79.5	4.79			78.6	4.47
Dry-heat-set	160			1.1	0.11
		1.9	0.17	2.7	0.16
		3.3	0.23	4.2	0.25
		4.3	0.31	5.0	0.31
		5.4	0.39	6.0	0.38
		9.4	0.57	9.8	0.53
		11.9	0.70	12.7	0.67
		25.4	1.28	26.9	1.25
		34.3	1.69	35.7	1.63
		46.5	2.31	47.8	2.24
		63.0	3.29	64.1	3.14
		79.5	4.42	79.6	4.50
		Dry-heat-set	180	1.4	0.18
2.0	0.17			2.2	0.19
2.9	0.27			2.9	0.18
4.4	0.30			4.9	0.33
6.2	0.47			7.3	0.40
9.5	0.59			10.0	0.58
17.4	0.93			13.4	0.66
26.6	1.35			27.5	1.16
35.1	1.72			35.7	1.52
46.8	2.33			47.5	2.08
61.2	3.09			64.1	3.01
80.2	4.38			79.5	3.97

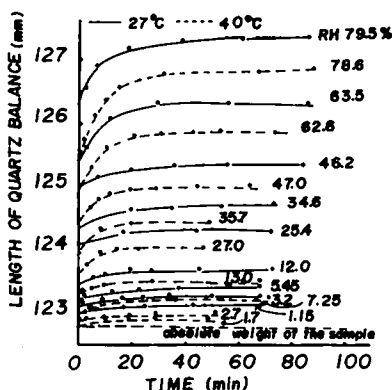


Fig. 2. Water vapor adsorption curves for sample dry-heat-set at 140°C.

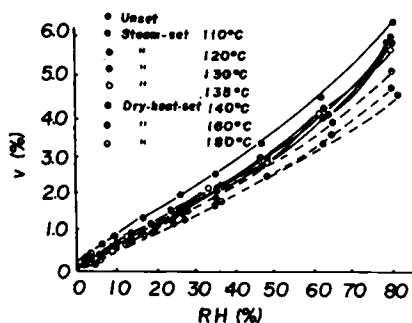


Fig. 3. Adsorption isotherms for water vapor at 27°C.

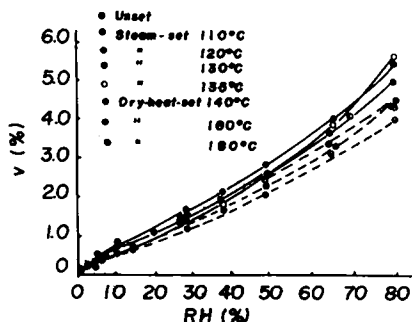


Fig. 4. Adsorption isotherms for water vapor at 40°C.

The density of the samples used in this experiment were measured by a density gradient column of  $\text{CCl}_4$  and ligroin. The degree of crystallinity was calculated from the obtained density according to the equations of Price<sup>12</sup> and Hunter and Oakes.<sup>13</sup> The values are given in Table II.

TABLE II  
Characteristic Values for Nylon 6 Fiber Subjected to Various Heat-Setting Treatments

Treatment	Conditions of treatment		Water adsorbed	Internal surface	Density $\rho$ , g./cc.	Degree of crystallinity $\alpha$ , %	$\frac{100v_m}{100 - \alpha}$
	Temperature, °C.	$v_m$ , %	on first layer $v_m$ , %	area $\Sigma$ , cm. <sup>2</sup> /g. $\times 10^5$			
Unheat-set	—	1.85	5.22	1.1485	34.1	2.82	
Steam-set	110	1.78	5.03	1.1498	35.7	2.78	
	120	1.72	4.85	1.1510	36.8	2.72	
	130	1.69	4.77	1.1530	38.7	2.76	
	135	1.68	4.74	1.1552	40.7	2.84	
Dry-heat-set	140	1.65	4.65	1.1490	34.6	2.52	
	160	1.59	4.49	1.1496	35.5	2.46	
	180	1.49	4.20	1.1521	37.8	2.40	

The B.E.T. curves were plotted according to eq. (1) from each point on the experimental isotherms at 27°C. (shown in Fig. 3):

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m C} + \left( \frac{C - 1}{v_m C} \right) \frac{p}{p_0} \quad (1)$$

where  $p$  is the water vapor pressure,  $p_0$  is the saturated vapor pressure at the measurement temperature,  $v$  is the moisture regain at  $p$ ,  $v_m$  is the amount of water adsorbed on the first layer, and  $C$  is a constant.

The results are shown in Figures 5 and 6. In these figures the plotted points in the region of 10–60% R.H. lie on straight lines, at humidities higher and lower than this range the points deviate from these lines.  $v_m$  was calculated from these data and is given in Table II.  $v_m$  decreases on heat setting, and this relationship is similar to that between moisture regain and setting temperature shown in Table I.

On the basis of the assumption that the water molecules adsorbed on the first layer form a monolayer on the inner surface of the fiber, the inner surface area could be calculated from eq. (2):<sup>14</sup>

$$\Sigma = S(v_m/22.400) \times 6.02 \times 10^{23} \quad (2)$$

where  $\Sigma$  is the inner surface area and  $S$  is the area per water molecule. The value of  $S$  used as 10.6 Å.<sup>2</sup>, which was calculated by Livingston.<sup>15</sup> The calculated values of  $\Sigma$  are also given in Table II. It is found from these values that the inner area of heat-set nylon 6 is 4–5  $\times 10^5$  cm.<sup>2</sup>/g., which agrees well with the value obtained by Rowen et al.<sup>16</sup> for nylon 66 (4.50  $\times 10^5$  cm.<sup>2</sup>/g.). The water adsorption isotherms of heat-set nylon 6 show that steam setting and especially dry heat setting decrease the amount of adsorbed water, and these tendencies are most distinct in the low humidity region. Therefore the differences among the adsorption isotherms might be related to the variations in fine structure of the polymers. In the region of 10–60% R.H. the B.E.T. curves show good linear relationships and

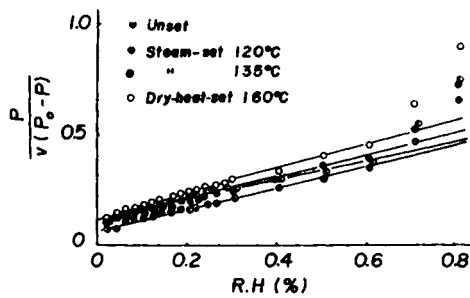


Fig. 5. B.E.T. curves from Table I.

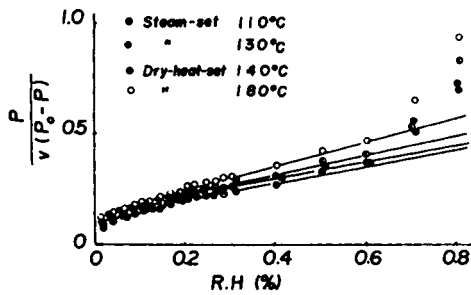
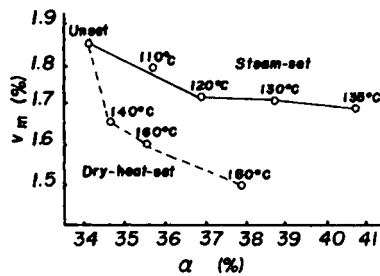
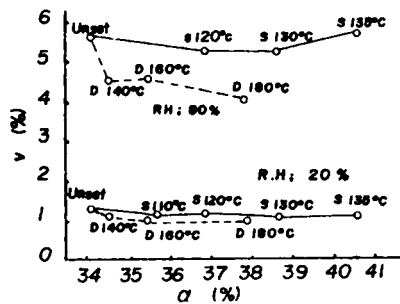


Fig. 6. B.E.T. curves from Table I.

Fig. 7. Relation between  $\alpha$  and  $V_m$ .Fig. 8. Relation between  $\alpha$  and  $V$  at  $40^\circ\text{C}$ .: (S) steam-set samples; (D) dry-heat-set samples.



the moisture regains are less than 2%, so that water will be adsorbed as monolayers. Bull,<sup>1</sup> Hoshino,<sup>6</sup> and Furuya<sup>17</sup> calculated  $v_m$  from the experimental data in this humidity range and obtained values close to our experimental result. As shown in Table II,  $v_m$  decreases from 1.85% to 1.49% on heat setting. If  $v_m$  is proportional to the number of free acid amide groups, the decrease of  $v_m$  means there is a decrease in the number of acid amide groups which do not form hydrogen bonds. The decrease might be caused by a decrease in water adsorption sites by formation of crosslinks among molecular chains, owing to generation or growth of crystals in the amorphous region. Therefore, to estimate the amount of water adsorbed per unit volume in the amorphous regions, the values of  $v_m/(1 - \alpha)$ , where  $\alpha$  is the crystalline fraction, were calculated. These are shown in Table II. If the amorphous fraction  $(1 - \alpha)$  calculated from density is used, these values indicate that the adsorbed water per unit volume of the amorphous region tends to increase or to remain unchanged for steam setting, but decreases markedly for dry heat setting. The relation between crystallinity and  $v_m$  is shown in Figure 7.

This figure shows a clear difference between steam setting and dry heat setting, i.e., for the same crystallinities the amount of water adsorbed on steam-set fibers is larger than that on dry-heat-set fibers.

The relation between crystallinity and moisture regain at 20 and 80% R. H. at 40°C. is shown in Figure 8. The moisture regain  $v$  of each material at 20% R.H. is lower than  $v_m$ ; therefore it seems that all the inner surface is not yet covered with water. As moisture regain depends on the number of adsorption sites, differences in the moisture regain of fibers having the same crystallinity reflect differences in the number of bonds among molecules. Therefore, in Figure 8 it is natural that the moisture regains of dry-heat-set materials which have fewer free acid amide groups in the amorphous region are lower than those of steam-set ones.

The moisture regain at 80% R.H. is the sum of  $v_m$  and condensed water in the fiber. The amount of condensed water may depend on closeness of packing of the molecules in the amorphous region. This is shown in Figure 8, i.e., the amount of condensed water in steam-set fiber is more than that in dry-heat-set fiber. The same trend was observed at 27°C. These results may support the speculation that the molecular packing is looser in steam-set than in dry-heat-set materials.

In materials, such as nylon 6, having polar groups, the inner surface area calculated from the water on the first layer relates to the number of polar groups, so that the resulting area is not the real one. This is clear from the difference between our result and that of Rowen and Blaine<sup>16</sup> obtained from adsorption of nitrogen. However, these results give information on the structural changes in polymers. Heats of adsorption for water were calculated from the isotherms at 27 and 40°C. but no significant results were obtained.

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## Résumé

L'absorption d'eau par différentes fibres de nylon 6 recuit à chaud est mesurée de 0-80% R.H. avec une balance à quartz, et on calcule l'eau adsorbée sur une première couche ( $V_m$ ). La valeur de  $V_m$  est la plus grande pour la fibre non recuite à la chaleur, moyenne pour la fibre recuite à la vapeur et la plus petite pour celle recuite à chaud et à sec. Les aires de la surface intérieure du nylon calculées à partir de  $V_m$  sont de 4 à  $5 \times 10^6$  cm<sup>2</sup>/g. On suppose que la valeur obtenue en divisant  $V_m$  par la fraction amorphe ( $1 - \alpha$ ) des fibres recuites à chaud est reliée au nombre de liaisons intermoléculaires par unité de volume de la partie amorphe. Les valeurs plus petites ainsi obtenues pour les fibres recuites à chaud et à sec signifient que les molécules de polymères dans la région amorphe forment de nombreuses liaisons intermoléculaires et sont serrées étroitement si on les compare aux fibres non recuites et celles recuites à la vapeur.

## Zusammenfassung

Wasseradsorption verschiedener hitzebehandelter Nylon-6-Fäden wird in einem Bereich von 0-80% rel. F. mit einer Quarzwaage gemessen, und die von der ersten Schicht ( $V_m$ ) adsorbierte Wassermenge wird berechnet. Der Wert von  $V_m$  ist für die nicht hitzebehandelte Faser am grössten, mittel für dampfbehandelte und am geringsten für trockenhitzebehandelte Fasern. Die aus  $V_m$  berechnete Grösse der inneren Oberfläche in Nylon beträgt  $4-5 \times 10^6$  cm<sup>2</sup>/g. Es wird angenommen, dass der durch Division von  $V_m$  durch die amorphe Fraktion ( $1 - \alpha$ ) von hitzebehandelten Fasern erhaltenen Werte in Beziehung zur Zahl der intermolekularen Bindungen pro Volumseinheit des amorphen Anteils steht. Die auf diese Weise für die trockenhitzebehandelten Fasern erhaltenen kleineren Werte bedeuten, dass Polymermoleküle im amorphen Bereich viele intermolekulare Bindungen und eine dichte Packung im Vergleich zu den nicht hitze- und den dampfbehandelten Fasern bilden.