

Characterization of KEVLAR* Fibers Using Selected Probes

S. REBOUILLAT,^{1†} M. ESCOUBES,² R. GAUTHIER,² and A. VIGIER²

¹Du Pont (UK) Limited, Maydown Research Center, P.O. Box 15, Londonderry BT 47 1TU, Northern Ireland;

²Laboratoire d'Etudes des Matériaux Plastiques et des Biomatériaux, URA CNRS 507-Université Lyon 1, 43, Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

SYNOPSIS

The characterization of KEVLAR-29 fibers has been performed by studying their interactions with three model compounds in gaseous form. Water, aniline, and epoxystyrene were used for this purpose. The effects on the nature of these interactions of two types of surface engineering, namely the coating with an epoxy resin and a reactive plasma treatment, were also studied. The results obtained from the three analytical techniques used in this work provide a more fundamental understanding of the fiber bulk properties vs. their surface characteristics. The diffusion, condensation, plasticization, and adsorption mechanisms involved during the interactions between the probes and the KEVLAR fibers are evidenced and discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Fibers made from aromatic polyamides exhibit very high tensile strength, excellent resistance to impact and vibrations, and good thermal and chemical resistance.¹⁻⁴ These properties situate aramid fibers at a competitive level with mineral fibers (carbon and glass) in the production of fiber reinforced composite materials.⁵ Several attempts have been made to combine aramid fibers with thermoset⁶⁻⁸ and thermoplastic⁹⁻¹² matrices, but experience has shown that in most cases only moderate interfacial adhesion occurs. To exploit the excellent properties of aramid fibers in polymer composite materials, it appears necessary to further improve the adhesion by modifying the surface of the fibers with appropriate treatments. Several ways have been explored:

- Increase of the surface roughness and porosity by bromine treatment.¹³
- Deposition of commercially available coupling agents⁶ or coatings.¹⁴

- Reaction between specific reagents and free functional groups or groups grafted on the fiber surface:
- After exposure to acid or basic hydrolysis of the aramid chains, it is possible to induce a reaction between a diepoxide and chains terminated by an amino group.¹⁵
- The mobile hydrogen of the (—CO—NH—) group can be reacted with methacryloyl chloride,^{16,17} or substituted, after metallation, by an acid (—CH₂—COOH) or an epoxy (—CH₂—CH—[O]—CH₂) group.¹⁸
- The irradiation by microwaves¹⁹ or radio frequency²⁰⁻²⁴ type plasma in an atmosphere of ammonia or amine. Using this technique, Allred et al.²¹ have shown that amino groups can be attached to aromatic rings of the fiber surface at a concentration of one group per repeating unit.

Despite intensive efforts, all these treatments remain detrimental to the mechanical properties of the fibers. Hence a compromise has to be found between the tailoring of the surface and the minimization of the detrimental effects. It is equally important to establish a fundamental understanding of the fiber surface properties and of the interaction mechanisms involved at the fiber-matrix interface.

* Du Pont's registered trademark for its high-strength para-aramid fibers.

† To whom correspondence should be addressed.

Table I ESCA Results for the Three Fibers Studied

Fibers	Sample F	Sample E	Sample P	Theoretical
O/C	0.72	1.26	0.63	0.14
N/C	0.12	0.15	0.25	0.14

The present work relates to the characterization of the aramid fibers using model compounds. In particular, we have chosen model compounds representative of the functional groups involved in the preparation of epoxy composites. The study also attempts to characterize fiber after surface treatments.

MATERIALS

The selected KEVLAR-29 yarns have the following characteristics: the number of filaments per yarn bundle is 1000 and the diameter of a monofilament is 12 μm . Three types of fibers have been studied:

1. KEVLAR-29 finish free yarn supplied by E. I. DuPont de Nemours. These fibers have received no special treatment and shall subsequently be referred to as sample F, which is here considered as the reference material.
2. KEVLAR-29 fibers yarn with a commercial type of epoxy resin (referred to as sample E, considered in this study as an experimental product). Using a standard dipping procedure, sample E is coated with 1% of epoxy resin from Nagase Chemical Ltd. (trade name, NER010A; chemical name, glycerol polyglycidyl ether).
3. KEVLAR-29 yarn treated with microwave plasma in an atmosphere of ammonia, with a 1 min exposure time at a frequency of 0.433 GHz, according to the ITF-LYON method²⁵ (referred to as sample P).

As a means to characterize the material tested, their surface was analyzed by ESCA using a Vacuum Generator Clam-100 spectrometer:

1. The atomic ratios O/C and N/C of the three types of fibers F, E, and P (just after plasma treatment) are shown in Table I. Concerning the O/C ratio, the three fibers exhibit a fairly high surface oxidation level compared to the theoretical value. This is not unusual for polymeric surfaces. The slightly bigger amount of surface oxygen for sample E is attributed to the epoxy deposition. Concerning the N/C ratio, the P fiber exhibits an increase due to the plasma treatment.
2. The change in the N/C ratio is recorded as a function of lag time for the P fiber (Table II). This N/C ratio slightly decreases with time from 0.25 to 0.20, which is still 1.7-fold the N/C ratio observed for the control fiber F.

EXPERIMENTAL TECHNIQUES

Calorimetry-Gravimetry Coupling

The interaction studies include simultaneous determinations of the vapor pressure isotherms and the interaction molar heats as described by Escoubes et al.²⁶ The equipment contains two chambers: one is equipped with a microbalance (sensitivity = 0.01 mg) to follow the weight variations of the sample—a microcalorimeter is fitted in the other chamber to measure the heat flow (sensitivity = 0.01 J). Both chambers are kept at 20°C. Two samples from each specimen are used, one in each chamber. The atmosphere in the two chambers is reduced to 10⁻⁵ Torr. The specimens are dried to constant weight. Then they are exposed to an atmosphere containing the vapor reagent kept at a constant partial pressure. The generator is an evaporator containing the reagent maintained at a constant preset temperature. All data are continuously recorded using a computer. The molar heats are obtained in kJ mol⁻¹ from the ratio of the heat flow and the weight uptakes (absolute precision 10%, reproducibility better than 5% except near saturated pressure).

Table II ESCA Results for the P Fiber as a Function of Lag Time

	Sample F (Reference Fiber)	Sample P: Lag Time Influence (Hours after Plasma Exposure)						
		8	36	89	176	225	277	368
N/C	0.12	0.25	0.21	0.19	0.20	0.18	0.21	0.20

During the exposure at a constant partial pressure, the weight uptakes are recorded until the equilibrium is reached. The data can be plotted versus the time square root. A straight line is obtained if the weight uptakes are governed by the diffusion process. The kinetic curves can then be fitted to the diffusion mathematics models derived from Fick's laws.

KEVLAR filaments are long cylinders of radius a where the diffusion occurs everywhere radially. Fick's second law (1) gives the concentration C at each point as a function of the distance r to the center of the cylinder ($0 \leq r \leq a$) and the time t . D is the diffusion coefficient.

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

By introducing the following boundary conditions: $C = 0$ for $t = 0$ at each point except at the surface where the equilibrium is reached instantaneously, and $C = C_0$ for $t \geq 0$ at the surface, a simplified solution is obtained. If M_t is the quantity of diffusing substance which has entered the cylinder in time t , and M_∞ the corresponding value after infinite time, then we have

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-Dt\alpha_n^2} \quad (2)$$

α_n are the positive roots of the Bessel function. When t is small, we have

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{1/2} - \left(\frac{Dt}{a^2} \right) - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{3/2} + \dots \quad (3)$$

D can be computed from (3) using the first term of the equation and the slope of the linear part of the relation $M_t/M_\infty = f(\sqrt{t})$. This value can be optimized by iterative calculations so that the theoretical equation best fits the experimental data (2).

Inverse Gas Chromatography

In this case, the KEVLAR fibers are used as the stationary phase in a chromatographic column. The retention times of various reagents (probe molecules), injected at as low a concentration as possible,^{27,28} are measured. The retention time, which is related to the magnitude of the interactions between

the probes and the fiber, characterizes the adsorption phenomena of the pure probes on the given fiber. The column (4.7 mm in diameter and 1 m length) is tightly packed with bundles of fibers, minimizing the dead volume. The packing factor is around 0.55–0.60. The volume of the carrier gas necessary for the elution of the probe, divided by the mass unit of stationary phase, represents the specific volume of retention V_g given by

$$V_g = \frac{jQt_r}{m} \quad (4)$$

where Q is the flow rate of the carrier gas, t_r is the reduced retention time, m is the mass of fiber, and j is the corrective term of James and Martin, which takes into account the pressure drop along the column, given by

$$j = \frac{3(P_1/P_0)^2 - 1}{2(P_1/P_0)^3 - 1}$$

where P_1 and P_0 are the inlet and outlet pressures of the column.

V_g is extrapolated to the retention volume V_{g0} corresponding to the theoretical infinite concentration. This type of extrapolation provides information which is statistically relevant to the description of the adsorption of single probe molecules on the most active sites of the fiber surface. Three different types of adsorption parameters can be calculated from the experimental data treatment:

1. ΔH_0 , the enthalpy of adsorption, is obtained from the slope of $\ln(V_{g0})$ versus $1/T$. This value is then compared to the energy of condensation of the probe. These two values are equal only when no specific interactions occur between the adsorbed probe and the fiber; this is the case for nonpolar probes such as alkanes.
2. γ_s^D , the dispersive component of surface free energy of the fiber, can be obtained using the work of adhesion, W_{adh} , of a probe, which can exchange dispersive interactions with the solid phase. W_{adh} is given by

$$W_{adh} = 2\sqrt{\gamma_s^D} \sqrt{\gamma_{CH_2}}$$

Two methods can then be used to calculate γ_s^D :

- The theory of Gray²⁹ considers the contribution of one methylene group γ_{CH_2} :

$$W_{\text{adh}} = 2\sqrt{\gamma_s^D}\sqrt{\gamma_{\text{CH}_2}} = -\frac{\Delta G_A}{NA_{\text{CH}_2}}$$

$$\text{with } -\Delta G_A = RT \ln \frac{V_{g0}(C_{n+1})}{V_{g0}(C_n)}$$

$$\sqrt{\gamma_s^D} = \frac{RT}{2NA_{\text{CH}_2}\sqrt{\gamma_{\text{CH}_2}}} \ln \frac{V_{g0}(C_{n+1})}{V_{g0}(C_n)} \quad (5)$$

where N = Avogadro's number, A_{CH_2} = surface of a methylene group (6 \AA^2), and $\gamma_{\text{CH}_2} = 35.6 \text{ mJ m}^{-2}$.

- Dumas–Martin's method³⁰ considers the adsorbed probe (on surface A) as a liquid (γ_L^D), leading to the relation:

$$-RT \ln V_{g0} + Cte = 2NA\sqrt{\gamma_s^D}\sqrt{\gamma_L^D} \quad (6)$$

In this case the slope of $RT \ln V_{g0}$ versus $A\sqrt{\gamma_L^D}$ gives $2N\sqrt{\gamma_s^D}$.

3. ΔG_{sp} , the specific free energy of interaction in the case of polar probes, is obtainable from the difference in ordinate between $RT \ln V_{g0}$ and the reference straight line obtained for n -alkanes.

EXPERIMENTAL RESULTS

To characterize the KEVLAR fibers, three model compounds were chosen: water, aniline, and epoxy-styrene. Water was selected due to the hydrophilic nature of the aramid fibers. Aniline and epoxy-styrene are representative of the functional groups present in the monomers used for the synthesis of the epoxy matrices. The results are presented separately for each technique:

Results Obtained by Calorimetry–Gravimetry Coupling

Figure 1(a,b,c) gives the isotherms $M_\infty = f(P/P_0)$ of the different fiber samples (F, E, P) with the three model reagents: water (a), aniline (b), epoxy-styrene (c).

Figure 2(a,b) gives the molar interaction enthalpies $\Delta H = f(P/P_0)$ of the different fibers with water (a) and aniline (b) (the y coordinate of each point represents the average enthalpy at the selected partial pressure given by the x coordinate). The heat flows obtained with epoxy-styrene are too weak to be exploited.

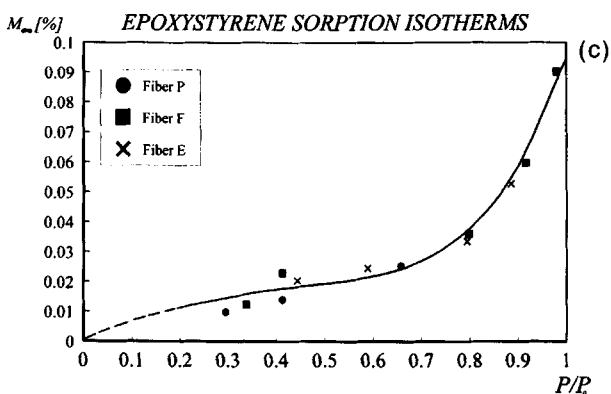
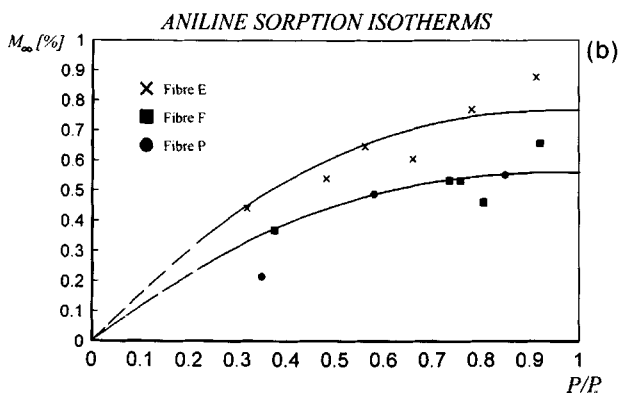
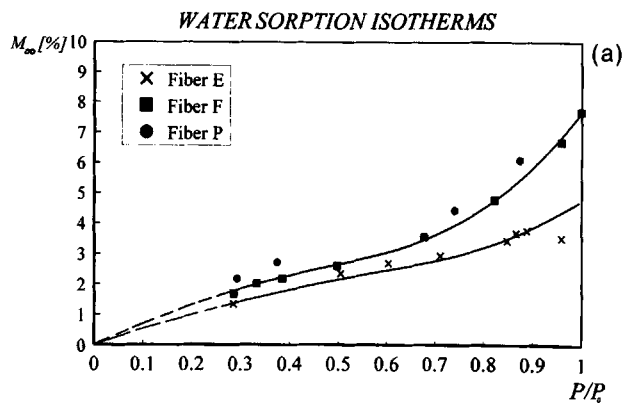


Figure 1 Sorption isotherms of the F, E, and P fiber samples with water (a), aniline (b), and epoxy-styrene (c).

Figure 3(a,b,c) represents the sorption kinetic data $M_t/M_\infty = f(\sqrt{t})$ of the untreated F fiber with the three reagents at various partial pressures.

Results Obtained by IGC Technique

Table III gives the molar enthalpies of adsorption ΔH_0 of aniline and epoxy-styrene used as probe mol-

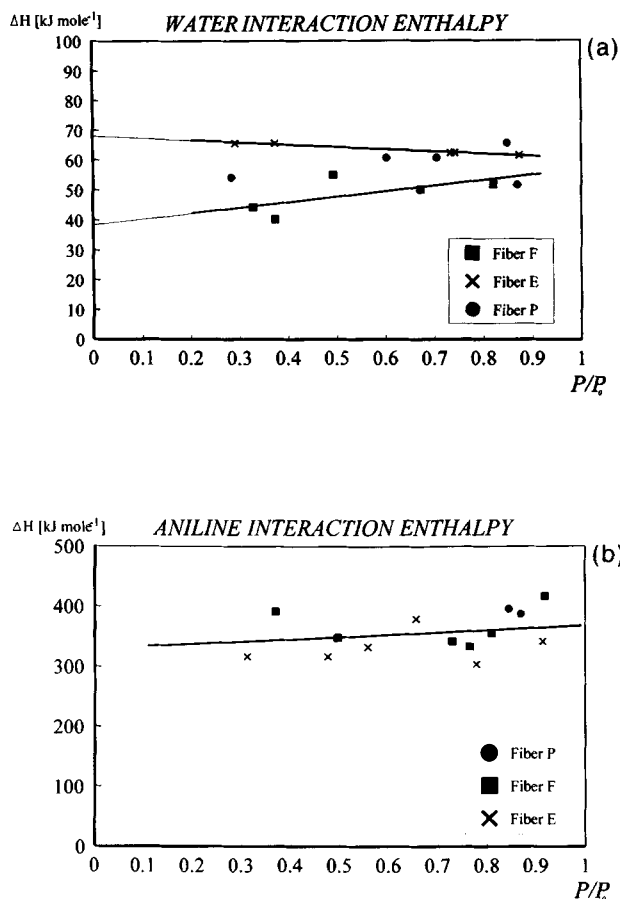


Figure 2 Molar interaction enthalpies of the F, E, and P fiber samples with water (a) and aniline (b) at various partial pressures.

ecules with the three types of fibers. For water, the diffusion happens so quickly that it is not possible to separate the surface phenomena; the peak is poorly defined and no retention time can be given.

For the determination of the dispersive component of the surface energy γ_s^D , four *n*-alkanes (C_8 , C_9 , C_{10} , and C_{12}) have been injected. Figure 4 shows the usual linear relation and Table IV gives the γ_s^D values of the three fibers obtained by the two different methods previously described.

For polar molecules such as aniline and epoxy-styrene, we observe a higher interaction energy than for the alkane of the same $A\sqrt{\gamma_L^D}$ value. Table V summarizes the specific free energies of interaction.

DISCUSSION

The BET specific surface of the tested fibers is 0.23 m^2/g .²⁴ Assuming a complete coverage of each filament by a monolayer of probe molecules, one can

calculate the weight ratio of adsorbable reagent to fiber : water, 0.006% (molecular area = 10.5 \AA^2)³¹; aniline, 0.08% (molecular area = 39 \AA^2)³¹; and epoxy-styrene, 0.010% (molecular area = 46 \AA^2).

It is also worth outlining that if during the interactions between the selected model compounds and the KEVLAR fiber a diffusion process is involved, then the contribution of any kind of adsorp-

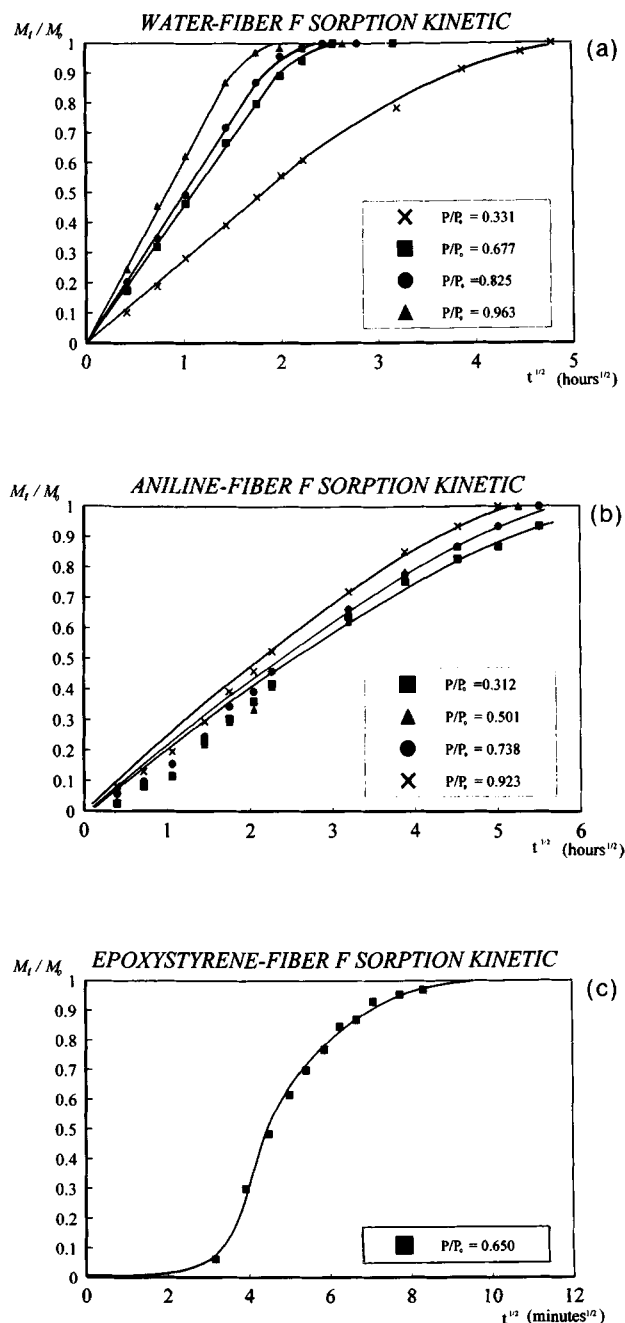


Figure 3 Sorption kinetic curves of the reference fibers with water (a), aniline (b), and epoxy-styrene (c).

Table III Interaction Heats from Chromatographic Data

Fibers	ΔH_0 (kJ mol ⁻¹)	
	Aniline	Epoxyystyrene
F	59 ± 3	45 ± 3
E	48 ± 3	54 ± 3
P	56 ± 3	66 ± 3

tion phenomena will be difficult to determine. This is more likely to happen when measurement are done at the equilibrium stage, i.e., for the coupling technique. On the other side the IGC will be more favorable to the analysis of the fiber surface characteristics since the diffusion potential is largely reduced by the operating conditions.

The Diffusion of Model Compounds

Figure 3(a,b) shows a clear case of diffusion since the uptakes of water and aniline are linearly related to the time square root.

Water Diffusion and Plasticization

The isotherm curves [Fig. 1(a)] present a rather flat sigmoidal shape. The weight uptakes at the be-

ginning of the plateau region near $P/P_0 = 0.4$ are around 2 to 3%, which is much more than what a complete monolayer of water on the fibers would represent (0.006%). It is clear that water diffuses into the fiber to be sorbed in the amorphous phase, at its interface with crystallites and inside crystallites slits.

The weight uptake kinetics represented on Figure 3(a) can be computerized using Eq. (3) to calculate the water apparent diffusion coefficients versus P/P_0 . Figure 5 confirms that the experimental data fit well with the theoretical Fickian curve given by Eq. (2). State of the art diffusion theory would interpret the exponential increase of the coefficient of diffusion with the equilibrium water content, M_∞ , shown in Table VI and on Figure 6, as a plasticization effect by water in the amorphous phase. An explanation could be related to the increase of the mobility of the chain occurring during plasticization resulting in an enhanced diffusion rate. The plasticization coefficient, γ , as well as the diffusion coefficient corresponding to the theoretical nil concentration, D_1 , can be calculated using the following relation:

$$D = D_1 \exp \gamma M_\infty$$

The D values are very close to those obtained by Sekita and Anzai³⁹ and slightly smaller than those obtained for regular KEVLAR by Fukuda et al.⁴⁰

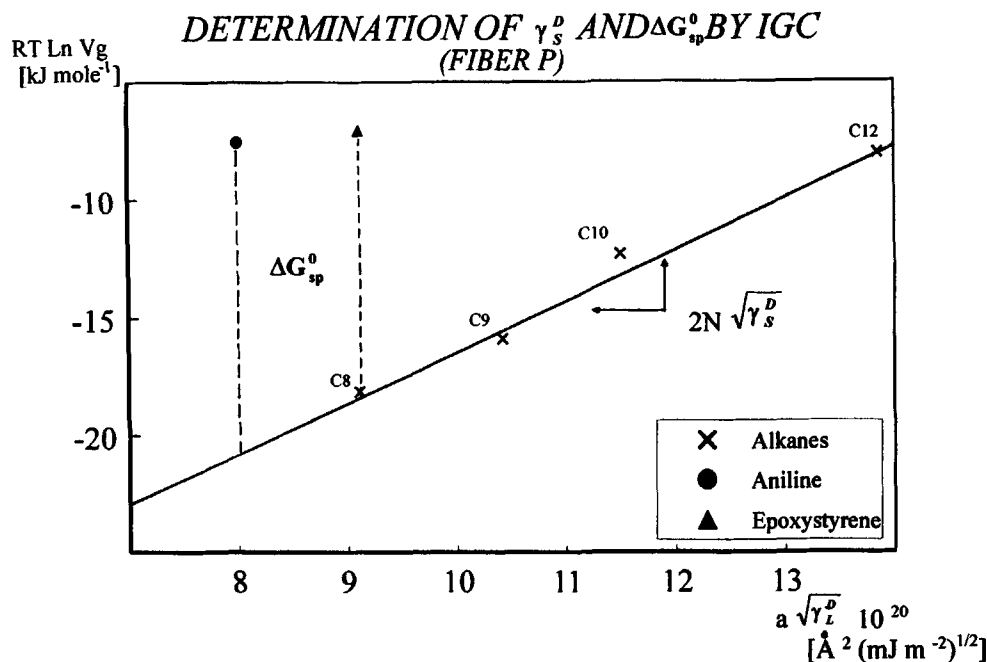


Figure 4 Determination of γ_s^D and ΔG_{sp}^0 by the IGC technique (P fiber).

Table IV Dispersive Component of Surface Free Energy, γ_s^D , of the Fibers

Fibers	γ_s^D (mJ m ⁻²)	
	Gray Method	Dumas-Martin Method
F	40 ± 2	40 ± 4
E	34 ± 2	33 ± 3
P	35 ± 2	31 ± 3

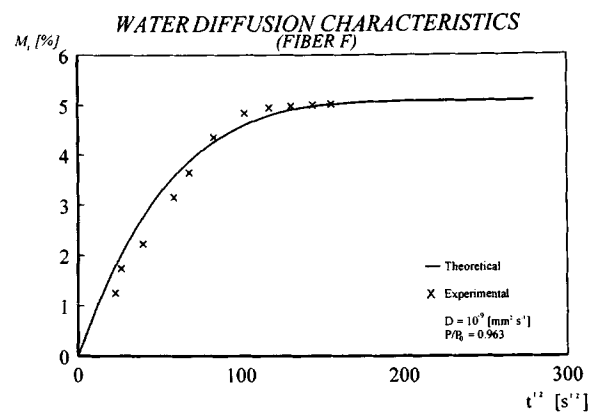
The plasticization characteristics computed from the data given in Table VI are $\gamma = 0.37$ for the coefficient of plasticization and $D_1 = 0.95 \times 10^{-12}$ cm² s⁻¹ for the diffusion coefficient extrapolated at a theoretical zero concentration.

In the case of the reference fiber, F, the interaction enthalpy versus P/P_0 [Fig. 2(a)] increases linearly from -45 to -60 ± 5 kJ mol⁻¹. According to the literature,^{41,42} one H bonding with CO represents -29 kJ mol⁻¹ and one H bonding with NH represents -33 kJ mol⁻¹. Consequently, a double hydrogen bridge between two CO implies -58 kJ mol⁻¹, and, a double hydrogen bridge between CO and NH implies -62 kJ mol⁻¹. The initial value of -45 kJ mol⁻¹ found in the present study for low partial pressure tends to suggest that the first sorbed water molecules have to break some interchain or inter crystallite preexisting CO...HN bonds. This result would be confirmed by Wang et al.⁴³ At higher water content, the accuracy of the measurements does not allow a clear separation of the two types of interactions (between two CO or between CO and NH). We can only conclude that the amide oxygen may assume an important role as suggested by Chatzi et al.,³⁴ but not an exclusive one (see Scheme 1).

These findings also suggest that the increase of the diffusion coefficient with the water content and the apparent plasticization may be due to the fact that at high vapor pressures the water can penetrate more easily into the inter crystallite or interchain spaces. Notice that the hydration enthalpy of -60 kJ mol⁻¹ found here is in agreement with the values

Table V Specific Free Energy of Interaction of the Three Fibers for Aniline and Epoxystyrene

Fibers	ΔG_{ep} (kJ mol ⁻¹)	
	Aniline	Epoxystyrene
F	11	8.6
E	13.1	10.6
P	13.2	11.7

**Figure 5** Fick's diffusion model according to Eq. (2).

obtained at low water content by Fukuda et al.³⁸ (one must take into account that in this later case liquid water was taken as the reference state). It is also interesting to mention that Fukuda et al. found a decreasing relationship between the enthalpy and the relative humidity. This result is not in agreement with our observations.

To discuss quantitatively the sorption data, we may have to first take into account the crystallinity degree of the studied fibers, which is taken as 72.2% in volume according to Fukuda et al.³⁸ This value gives 75.2% in weight using 1.5 g/cm³³⁸ and 1.44 g/cm³⁴⁶ as the respective densities of crystallites and fibers. The noncrystalline rate is then 24.8 wt %.

In the amorphous phase, there are 2 CO—NH groups per repeating unit of 238 g. If each carbonyl group CO and each amino group NH provide one hydrogen bond with a water molecule (which is also bonded to another CO—NH group), there will be two water molecules sorbed in 238 g of amorphous phase, i.e., in 960 g of KEVLAR. This specific sorption is then of 3.75%. Yet the isotherm of Figure 1(a) gives a water regain between 5 and 6% near 90% RH where no "liquid type" water is evidenced from the enthalpic data. The difference could be due to water sorbed on the specific amide sites of the crystallite surfaces according to the same double bridging mechanism, i.e., either between two crystalline blocks in slits of very small width or between the crystallites and the amorphous medium.

Table VI Water Diffusion Coefficients at Various Partial Pressures for F Fibers

P/P_0	0.33	0.55	0.68	0.90	0.96
M_∞ (%)	2.1	2.6	3.9	5.4	6.5
$D \times 10^{12}$ (cm ² s ⁻¹)	1.4	3.0	4.3	5.3	9

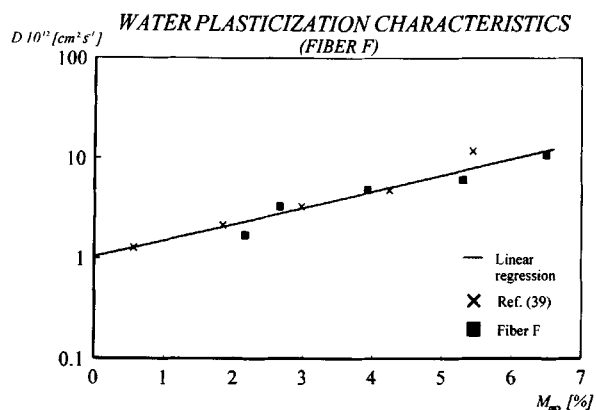


Figure 6 Water plasticization effect in F fiber.

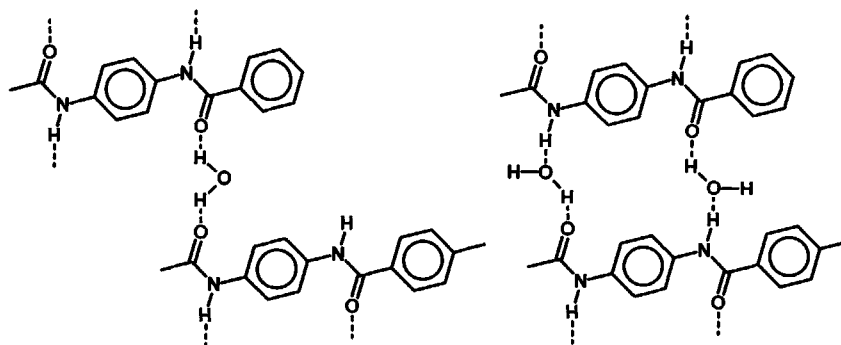
We can now try to evaluate this potential water regain using the surface area of the crystallites. A well known model³³ described the crystalline structure as developed in stacks of ordered lamellar perpendicular to the fiber axis separated by defect layers with a periodicity of 30 to 40 nm obtained from transmission electron micrographs. X-ray diffraction analysis developed by several authors³²⁻³⁷ and recently by Jackson et al.⁴⁷ confirms the fiber axis dimension of the crystallites near 40–50 nm and gives a quasicircular cross section around 5 nm. This value, used to calculate the surface area, gives 533 m^2/g of crystal, hence 400 m^2/g of KEVLAR. On this surface we have 2 CO—NH sites for about 80 Å^2 (per repeating unit), hence 2 potential double bridged water molecules per 80 Å^2 . But Jackson et al.⁴⁷ emphasize that only one-half of these crystallite surface sites can hydrogen bond. Then a simple calculation gives an additional 1.5% of sorbed water due to the intercrystallite slits (but less if one takes into account the double bridges between crystallite surfaces and amorphous medium). In any case, the global sorption (3.75 + 1.5%) is in good agreement with the experimental isotherm.

A further result of interest is the influence of surface treatments on the water sorption. According to the very low BET (N_2) surface adsorption (a monolayer would represent 0.006% of water), it is expected that no difference will be observed after surface treatments. However, as shown in Figure 1 (a), a decrease of the water sorption of the E fiber is observed vs. the reference sample F. Furthermore, the kinetic data indicate a slower diffusion process. These findings suggest that the epoxy resin deposition blocks the accessibility of some sorption sites in the superficial zones, most likely in the intercrystallite slits. Another effect of surface treatments appears in Figure 2(a) for the P fibers. The molar interaction enthalpy remains constant around a value of -60 kJ mol^{-1} on the whole range of P/P_0 . A possible explanation is that the plasma treatment significantly may provoke a cleavage of the preexisting interchain or intercrystallite bonds in the superficial zones. This is supported by the fact that the KEVLAR superficial zones are more highly ordered than the core (skin-core structure^{35,44}), and so exhibit a high density of these bonds.

Aniline Diffusion with Condensation

The isotherms [Fig. 1 (b)] exhibit a plateau section from $P/P_0 = 0.4$. The weight uptakes are greater than the calculated value (0.008%) based on a BET adsorption phenomena. There is a diffusion process as indicated by the kinetic study [Fig. 3 (b)], but, at saturation, the aniline content corresponds only to 1 mol per 30 repeating units of amorphous phase. It is then difficult to propose a homogeneous sorption mechanism. A possible explanation is that the isotherms are characteristic of structural microporous solid (type IV of the BET classification). Aniline is condensed during diffusion in the interchain spaces.

The high interaction heats exhibited on Figure 2 (b) (around $-350 \pm 50 \text{ kJ mol}^{-1}$) confirm this ex-



Scheme 1 Models of H bonded water molecules between aramid chains.

planation. In fact, the filling of a pore at the condensation pressure implies two phenomena: the disappearance of the superficial tension of the sorbed film and the compression of the sorbate to the normal hydrostatic pressure of the liquid linked to the pore by a plane meniscus. These phenomena are well known to involve heat flows leading to fairly high interaction enthalpies since the weight uptakes are very weak during these phenomena.⁴⁵

Since Fick's law is well in agreement with the experimental data as shown in Figure 3(b), the diffusion coefficients can be computed. These are given in Table VII. Opposite to the case of water there is only a small increase of the coefficient D with aniline content.

In terms of the surface treatment effect on the aniline sorption, the experimental results denote small differences between the different fiber candidates [Fig. 1(b)]. Nonetheless, one can notice that fiber E tends to sorb more aniline than the others, which is opposite of what we observed with water. The blocking effect of the epoxy resin in the inter crystallite slits, as previously suggested for water, has no effect in this case as aniline diffuses in the amorphous zones of the fibers. On the other hand, a chemical affinity between aniline and the epoxy resin may favor the diffusion-condensation process.

Adsorption of Model Compounds and KEVLAR Surface Properties

Adsorption Isotherms

As previously mentioned, the adsorption on the BET (N_2) surface may be observed provided that the reagent cannot diffuse. It is the case for epoxystyrene in spite of its rather subtle differences in physical characteristics with aniline. Fick's diffusion law is not respected, and the equilibrium is reached within "minutes" rather than "hours" as shown in other cases [Fig. 3(c) vs. Fig. 3(a,b)].

Figure 1(c) shows that, using the epoxystyrene probe, a single adsorption isotherm is obtained for the three fibers. The weight gains are of a different magnitude than for water and aniline (<0.1% near saturation pressure). The curve shape is sigmoidal with an exponential growth toward higher pressures (type II in the usual classification of adsorption isotherms). The weight uptake at the inflexion point, located around $P/P_0 = 0.25$, almost corresponds to the calculated monolayer (0.01%). The heat flows, measured in the calorimetric chamber, are small compared to the blank. Consequently, no values of the adsorption enthalpy can be given.

Table VII Aniline Diffusion Coefficients at Various Partial Pressures

	P/P_0			
	0.372	0.501	0.732	0.923
M_∞ (%)	0.37	0.54	0.53	0.64
$D \times 10^{12}$ ($cm^2 s^{-1}$)	0.8	0.77	0.86	1.1

Surface Interactions and the IGC Results

The values of ΔH_0 obtained from the IGC analysis for aniline and epoxystyrene with the three fibers are summarized in Table III. By comparing these values with the respective liquefaction energies, E_L , of aniline and epoxystyrene, respectively -48 and -52 $kJ mol^{-1}$, one has access to the interaction energies involved. High interaction energies are observed in the case of the aniline molecule with the reference F fiber and the plasma treated P fibers [$\Delta(\Delta H_0) = 8$ $kJ mol^{-1}$ vs. E_L]. For the epoxystyrene, the interactions are weaker with F fibers but they increase with the epoxy-coated E fiber, which may be due to a dissolution mechanism, and further increase [$\Delta(\Delta H_0) = 14$ $kJ mol^{-1}$ vs. E_L] after plasma treatment, which this may be due to the interactions between epoxystyrene and the NH_2 groups created by the plasma treatment at the surface.

These aspects are confirmed by the values of the specific free energy ΔG_{sp} given in Table IV. As illustrated in Figure 4, both probes exhibit an additional interaction energy compared to the alkanes. The values obtained for the aniline are around 2 $kJ mol^{-1}$ above those obtained with the epoxystyrene for the three fibers. The surface treatments lead in both cases to a 2 to 3 $kJ mol^{-1}$ increase of ΔG_{sp} .

It is also interesting to note in Table IV that the two treatments decrease the dispersive component of the KEVLAR surface energy ($\Delta = 8 \pm 2$ $mJ m^{-2}$) with a remarkable agreement between the Gray method and the Dumas-Martin approach.

CONCLUSION

The characterization of aramid fibers (KEVLAR-29) has been performed by studying the interactions between three selected probes in gaseous form (water, aniline, and epoxystyrene) and the fibers. It has been possible to estimate the influence, on the nature of these interactions, of two surface treatments to which the fibers were submitted, i.e., a commercial

epoxy coating and a microwave plasma treatment in ammonia atmosphere. Gravimetry coupled with calorimetry and inverse gas chromatography are the analytical techniques used in this study. Here are the key conclusions:

- Water molecules are sorbed in the intercrystalline slits and in the amorphous zones. Sorption proceeds by a mechanism involving a double hydrogen bridging between two carbonyl groups CO, but also between CO and NH groups. The use of an epoxy sizing limits access to the intercrystalline slits, leading to lower water gains and smaller apparent diffusion coefficients.
- Aniline molecules diffuse into the superficial amorphous zones with capillary interchain condensation. Consequently, heat flows involved are high. In this case the epoxy coating seems to favor the diffusion phenomenon.
- Epoxystyrene molecules are adsorbed only on the BET (N₂) surface.

The affinity of aniline and epoxystyrene for the KEVLAR surface has been evidenced by IGC, where diffusion is avoided. Aniline shows a high affinity for the bare fiber F, which is not increased by the surface treatments. However, in the case of the epoxystyrene the surface treatments appear to favor the interactions with the fibers, especially microwave plasma treatment with ammonia, where chemical affinity between the amino groups and the epoxy groups is existing.

REFERENCES

1. L. Penn and F. Larsen, *J. Appl. Polym. Sci.*, **23**, 59 (1979).
2. G. Chrétien, *Technique et Documentation (Lavoisier)*, **2**, 28 (1986).
3. S. Rojstaczer, D. Cohn, and G. Marom, *J. Mater. Sci. Lett.*, **3**, 1028 (1984).
4. J. R. Brown and B. C. Ennis, *Text. Res. J.*, **47**, 62 (1977).
5. K. M. Von Hillermeier, *Kunststoffe*, **66**, 802 (1976).
6. D. J. Vaughan, *Polym. Eng. Sci.*, **18**, 167 (1978).
7. D. C. Timm, A. J. Ayorinde, C. H. Lee, L. F. Steele, and N. C. Plass, *Polym. Eng. Sci.*, **24**, 930 (1984).
8. L. J. Matienzo, T. K. Shah, and J. D. Venables, *J. Mat. Sci. Lett.*, **4**, 1519 (1985).
9. Z. Yu, A. Ait-Kadi, and J. Brisson, *Polym. Eng. Sci.*, **31**, 1222 and 1228 (1991).
10. J. L. G. Ribelles, J. M. Sebastia, R. M. Soler, M. M. Pradas, A. R. Greus, and J. J. S. Anton, *J. Appl. Polym. Sci.*, **42**, 1647 (1991).
11. S. K. N. Kutty and G. B. Nando, *J. Appl. Polym. Sci.*, **42**, 1835 (1991).
12. M. Avella, G. Della Volpe, E. Martuscelli, and M. Raimo, *Polym. Eng. Sci.*, **32**, 376 and 383 (1992).
13. M. Berznick, J. Banbaji, H. Gutmann, and G. Marom, *Polym. Commun.*, **28**, 55 (1987).
14. Y. W. Mai and F. Castino, *J. Mater. Sci. Lett.*, **4**, 505 (1985).
15. A. S. Hoffmann, T. S. Keller, A. Miyake, B. D. Ratner, and B. J. McElroy, *Polym. React. Eng., Proc. Pac. Chem. Eng. Congr., 3rd*, **2**, 54 (1983).
16. H. J. Petsalas and A. G. Andreopoulos, *J. Appl. Polym. Sci.*, **38**, 593 (1989).
17. A. G. Andreopoulos, *J. Appl. Polym. Sci.*, **38**, 1053 (1989).
18. M. Takayanagi, S. Ueta, W. Y. Lei, and K. Koga, *Polym. J.*, **19**, 467 (1987).
19. M. R. Weitheimer and H. P. Schreiber, *J. Appl. Polym. Sci.*, **26**, 2087 (1981).
20. R. E. Allred, E. W. Merrill, and D. K. Roylance, *Polym. Sci. Technol. (Mol. Charact. Compos. Interfaces)*, **27**, 333 (1985).
21. R. E. Allred, E. W. Merrill, and D. K. Roylance, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **24**, 223 (1983).
22. J. R. Hollahan, B. B. Stafford, R. D. Falb, and S. T. Payne, *J. Appl. Polym. Sci.*, **13**, 807 (1969).
23. E. M. Petrie and J. C. Chottiner, *Proc. 40th Annu. SPE Tech. Conf. Exhib.: ANTEC'82, Soc. Plast. Eng., St Louis, MO* (1982).
24. R. d'Agostino, F. Crammarossa, S. de Benedictis, and G. Ferraro, *Plasma Chem. Plasma Process.*, **1**, 19 (1981).
25. O. Demuth, *Procédés électriques dans les traitements de surface, DOPEE, 4ème trimestre 93-7* (1989).
26. M. Escoubes, M. Pineri, and E. Robens, *Thermochim. Acta*, **82**(1), 149 (1984).
27. A. V. Kiselev, in *Advances in Chromatography*, J. C. Giddings and R. A. Keller, Eds., Marcel Dekker, New York, 1967.
28. D. R. Lloyd, T. C. Ward, and H. P. Schreiber, *Inverse Gas Chromatography*, ACS Symposium Series No. 391, ACS, Washington D.C., 1989.
29. S. Katz and D. G. Gray, *J. Colloid Interface Sci.*, **82**, 318 (1981).
30. C. Dumas-Martin, Thèse Mulhouse, Février, 1988.
31. F. M. Fowkes, *Hydrophobia Surfaces*. Academic Press, New York, 1969, pp. 40 and 47.
32. A. M. Hindeleh, N. A. Halin, and K. A. Zig, *J. Macromol. Sci. Phys. B*, **23**(3), 289 (1984).
33. M. Panar, P. Avakian, R. C. Blume, K. H. Gardner, T. D. Gierke, and H. H. Yang, *J. Polym. Sci.-Polym. Phys. Ed.*, **21**, 1955 (1983).

34. E. G. Chatzi, H. Ishida, and J. L. Koenig, *Appl. Spectrosc.*, **40**(6), 847 (1986).
35. E. G. Chatzi, M. W. Urban, H. Ishida, and J. L. Koenig, *Polymer*, **27**, 1850 (1986).
36. R. Barton, *Paracrystallinity-Modulus Relationship in Kevlar Aramid Fibers*, A.C.S. National Meeting, Philadelphia, PA, 1984.
37. M. G. Northolt, *Eur. Polym. J.*, **13**, 64 (1981); **10**, 799 (1974).
38. M. Fukuda, M. Ochi, M. Miyagawa, and H. Kawai, *Textile Res. J.*, **61**(11), 668 (1991).
39. Y. Sekita and H. Anzai, *Rep. Prog. Polym. Phys. Jpn.*, **24**, 203 (1981).
40. M. Fukuda and H. Kawai, *Textile Res. J.*, **63**(4), 185 (1993).
41. R. Puffr and J. Sebenda, *J. Polym. Sci., Part C*, **16**, 79 (1967).
42. J. P. Soulier, M. Escoubes, A. Douillard, and B. Chabert, *J. Chim. Phys.*, **73**, 423 (1976).
43. J. Z. Wang, D. A. Dillard, and T. C. Ward, *J. Polym. Sci., Polym. Phys.*, **30**, 1391 (1992).
44. M. Fukuda and H. Kawai, *Textile Res. J.*, **63**(4), 185 (1993).
45. A. V. Kiselev, *Solid-Gas Interface*, Vol. II, Butterworths, London, 1957, pp. 187-198.
46. H. H. Yang, *Aromatic High Strength Fibers*, Wiley Interscience, New York, 1989, pp. 228-230.
47. C. L. Jackson, R. J. Schadt, K. H. Gardner, D. B. Chase, S. R. Allen, V. Gabara, and A. D. English, *Polymer*, **35**, 1123 (1994).

Received February 20, 1995

Accepted May 10, 1995