

The Effects of Morphology and Hygrothermal Aging on Water Sorption and Transport in Kapton® Polyimide

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Synopsis

A comparison of water sorption and diffusion behavior in 2 mil, as-received, Kapton® film, and in otherwise identical but hygrothermally aged samples, suggests chemical differences between the samples. These differences can be related to known polyimide chemistry and the specific history encountered by the samples. Although the sorption isotherms are similar for an as-received 0.3 mil sample studied earlier and for the as-received 2 mil samples studied here, the diffusion coefficient of water in the as-received 2 mil sample is approximately 300% larger than in the as-received 0.3 mil sample. This large effect is believed to be related to the presence of small, paracrystalline aggregates with large aspect ratios. Differences in orientation measured by birefringence for the two samples suggest that the barrier properties of Kapton® are strongly affected by the detailed morphological organization of the ordered aggregates. Comparison of the sorption isotherms for the as-received and hygrothermally aged 2-mil films suggests a significant increase in the hydrophilic nature of the aged film. This change is consistent with an apparent chemical reaction between water and uncyclized amic acid residues in the film. The tendency for water to cluster in as-received Kapton® is essentially eliminated by the chemical modification associated with hygrothermal aging. The hygrothermal aging produces a dramatic reduction in the water vapor diffusion coefficient at low vapor activities but a rather modest change at high activities.

INTRODUCTION

In a previous paper, we reported the sorption and transport properties of water vapor in 0.3 mil Kapton® polyimide over a range of temperatures and vapor activities.¹ In the present paper we report water vapor diffusion coefficients in a 2.0 mil Kapton® sample which are as much as 300% larger than those determined in the 0.3 mil film. Surprisingly, however, the sorption isotherms for the two samples differ by less than 10–15% for the entire range of activities studied. The permeabilities of the two films, comprised of diffusivity and solubility terms, therefore, would primarily reflect the large difference in water diffusivity between the samples. A detailed exploration of this effect was the primary objective of the present study.

During our investigation of differences between the 0.3 and 2 mil film

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samples, it became clear that a slow reaction between water and Kapton[®] was occurring even at 30°C. The effects of the reaction could be essentially eliminated by experimental design at 30°C, since the highly activated chemical reaction was essentially quenched in comparison with diffusion at these relatively low temperatures. For example, the aging effect was not apparent in experiments with the thin film since exposure times to water vapor were much shorter due to the more rapid sorption in the very thin film. The reaction became considerably more rapid at 60°C but eventually ceased after a sufficiently long exposure time. The film appears to have been "passivated" by its exposure to the water vapor, and subsequent sorption experiments indicated a simple diffusion process with no further reaction even at 60°C. Exploration of the fundamental cause and implications of this aging phenomenon on barrier and other physical properties was the second major objective of the present paper.

EXPERIMENTAL

Both the 0.3 mil and the 2.0 mil Kapton[®] films discussed in this study were provided by the E. I. DuPont de Nemours and Co. The films were standard samples with no surface treatments or special additives. The same sorption equipment and procedures used in our earlier paper were employed in the present study.¹

RESULTS AND DISCUSSION

Film Thickness Effects

Sorption

Complex sorption kinetic behavior, related to coupled diffusion and chemical reaction, tends to occur for the water-Kapton[®] system at high temperatures and vapor activities.² These complications related to chemical reaction are essentially negligible at 30°C for relatively short exposure times.² Under such conditions, which pertain to the present discussion, simple analyses may be applied with reasonable accuracy.¹

Water vapor sorption data at 30°C in 0.3 and 2 mil Kapton[®] are shown in Figure 1. The sorption levels of water in the two films are clearly similar. A detailed analysis of the concave curvature of the isotherms at low pressures in terms of the dual mode sorption model is reported elsewhere.² The convex upward curvature obvious in the two isotherms at high vapor activities can be analyzed in terms of the Zimm-Lundberg "clustering function" as described earlier.¹ Clustering phenomena are indicated not only by the convex high activity sorption isotherms, which would be observed even with Flory-Huggins swelling, but also by a tendency of the local diffusion coefficient of water decrease slightly with increasing concentration. As discussed later, such a tendency is, in fact, observed for both the thin and thick film samples. Clustering tends to occur when penetrant-penetrant interactions are favored over penetrant/polymer interactions. The results of the Zimm-Lundberg analysis suggest that clustering begins

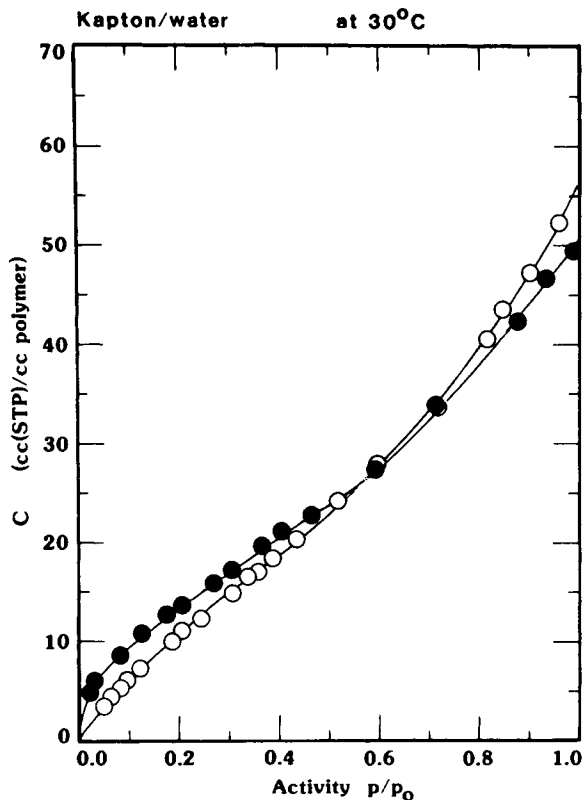


Fig. 1. Sorption isotherms for water vapor in 0.3 mil (●) and 2 mil (○) as-received Kapton® at 30°C.

above an activity of 0.60 for the 2 mil sample and above an activity of 0.70 for the 0.3 mil sample. This difference in the onset of clustering is only slightly greater than experimental uncertainty, and suggests that the two materials are inherently similar in terms of their hydrophilic nature.

Transport

Usually the diffusion of water is Fickian in relatively low-sorbing hydrophobic polymers, i.e., normalized sorption (or desorption) curves plotted against the square root of time tend to be initially linear.³ A typical water vapor sorption kinetic run in 2.0 mil virgin Kapton® shown in Figure 2 displays the characteristic linearity with the square root of time at short times. M_t and M_∞ refer to the mass sorbed (or desorbed) at time t and at infinite time, respectively. Diffusion coefficients (D_{av}) determined from the average of the sorption and desorption half-times for experiments at 30°C spanning the activity range from less than 0.1 to near unity are shown in Figure 3 as the half open points. The values of diffusion coefficients in Figure 3 were calculated in the conventional way as the average of the respective diffusion coefficients determined in each sorption and desorption run.⁴ The abscissa values represent actual sorbed concentrations in the polymer in equilibrium with the vapor phase pressure used in the respective

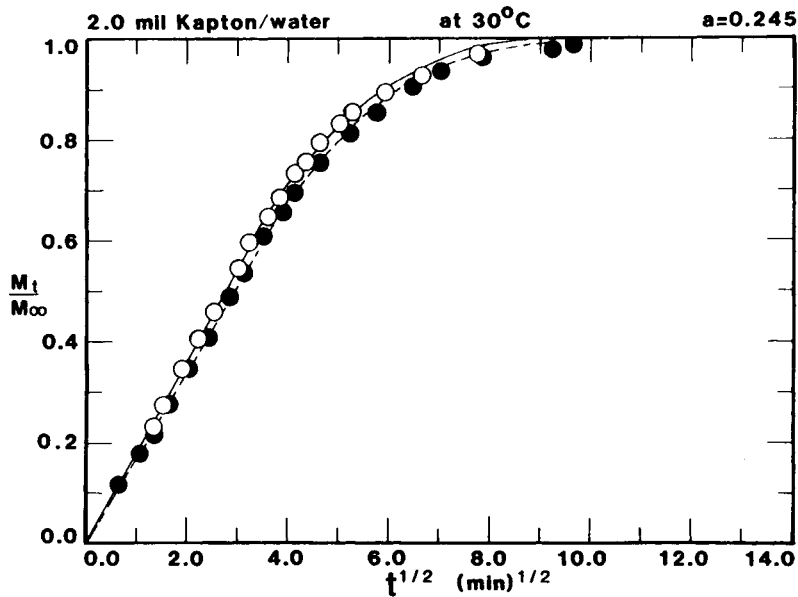


Fig. 2. Typical normalized sorption (○) and desorption (●) kinetics runs for 2 mil Kapton[®] at 30°C with a vapor activity of 0.245 in the sorption run and vacuum on the desorption run.

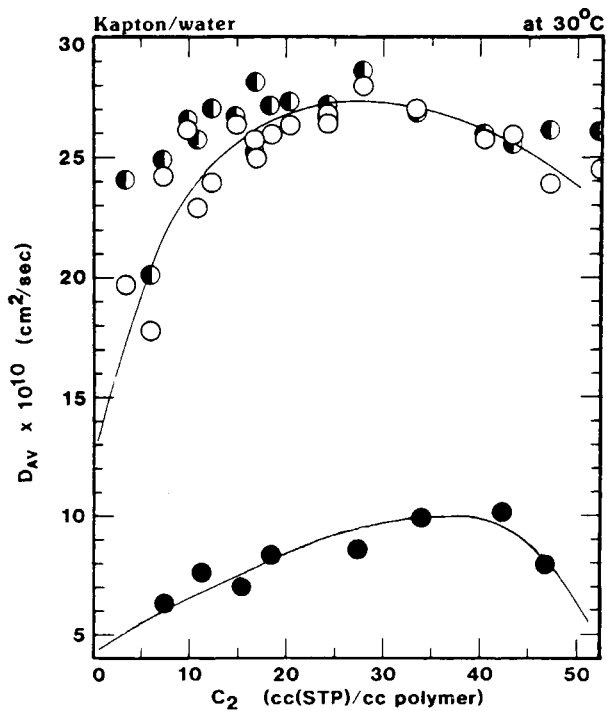


Fig. 3. Average concentration-dependent diffusion coefficients D_{av} estimated from sorption kinetics using: the "half time" method for 2 mil film (●), the "long time" method for 2 mil film (○), and the "long time" method for 0.3 mil film (●).

sorption run of the sorption/desorption cycle. The desorption was always carried out in a vacuum.

The corresponding values of average diffusion coefficients for both the 0.3 and 2 mil films determined by the so-called "long time" approximation⁵ are also shown in Figure 3. The diffusion coefficients in both films tend to decrease at higher sorbed concentrations consistent with the earlier discussion of clustering. This trend is more apparent for the 2 mil sample, consistent with the slightly stronger tendency for clustering in this film as indicated by the Zimm-Lundberg analysis discussed earlier.

The diffusion coefficients for the 2 mil film are in reasonable agreement as determined by the "half time" and "long time" estimation method. The diffusion coefficients in the 2 mil film are roughly three times larger than in the 0.3 mil film. This tendency is consistent with Sacher's permeability study of the Kapton® H₂O system⁶ and Patton and Iler's sorption kinetics studies of the Kapton® SO₂ system.^{4,7} Since such an effect is apparent for both Lewis acid and Lewis base penetrants, it probably arises from physical differences in the morphology of the two films rather than from substantially different chemical interactions of penetrants with specific groups in the polymer. Moreover, the water vapor sorption isotherms in Figure 1 further suggest that the inherent chemical properties of the two films are similar.

Isoda et al.⁸ have reported that as much as 88% of the repeat units in commercial Kapton® exist in paracrystalline aggregates with dimensions less than 150 Å along the chain axis direction and only 20–25 Å in thickness. This high degree of molecular aggregation should tend to suppress water sorption in Kapton®, since it is generally accepted that small molecules cannot invade ordered polymer aggregates. Assuming this is true for the water/Kapton® system, the similarity of the equilibrium sorption isotherms suggests that the volume fraction of segmental aggregates is essentially the same in the two films. The much larger birefringence value reported in Table I for the 0.3 mil film compared to the 2 mil film indicates that the thin film is considerably more oriented than the thicker film. Also, previous X-ray anisotropy studies of 0.3 and 2 mil films have indicated more substantial chain alignment in the plane of the 0.3 mil film compared to the 2 mil sample.⁹ Presumably the orientation of chains in the amorphous regions also controls the orientation of the aggregated regions and thereby their impedance to diffusion of water molecules due to tortuosity effects. More subtle effects, related to local penetrant mobility differences in the amorphous regions, caused by amorphous phase orientation, may also exist, but cannot currently be separated from the tortuosity effects noted above.

TABLE I
Birefringence Results on 0.3 mil and 2 mil Kapton®

Sample	Birefringence
0.3 mil	0.0972
2 mil	0.0177

Kapton® Water Reaction Phenomena

Sorption

Sorption isotherms for water in 2 mil Kapton® film measured at 30°C are shown in Figure 4 before and after long term exposure to water vapor at temperatures up to 60°C. The detailed exposure history and kinetic analysis of the process is described elsewhere.² This information is not relevant to the current discussion, since only the as-received and long-term aged film properties will be discussed here. It was found that the sorption isotherm eventually becomes stable after sufficiently long exposure to water vapor, and the film no longer displays signs of chemical reaction as it does at intermediate times leading up to the final "passivated" state. It is likely therefore, that the detailed exposure history simply determines the kinetics of approach to the final passivated state. The chemical reactions potentially involved in the passivation process are described later.

The data of Figure 3 reveal qualitative differences between the isotherm shapes for the as-received and aged or passivated samples. The final isotherm no longer shows the characteristic convex upwardly curving shape characteristic of clustering. Moreover, diffusion coefficient data discussed below show no tendency to decrease at high activities, further suggesting

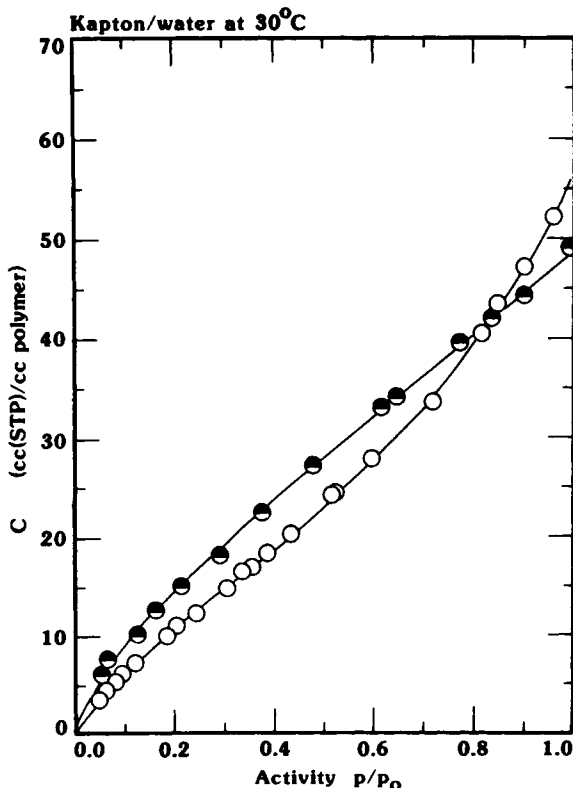
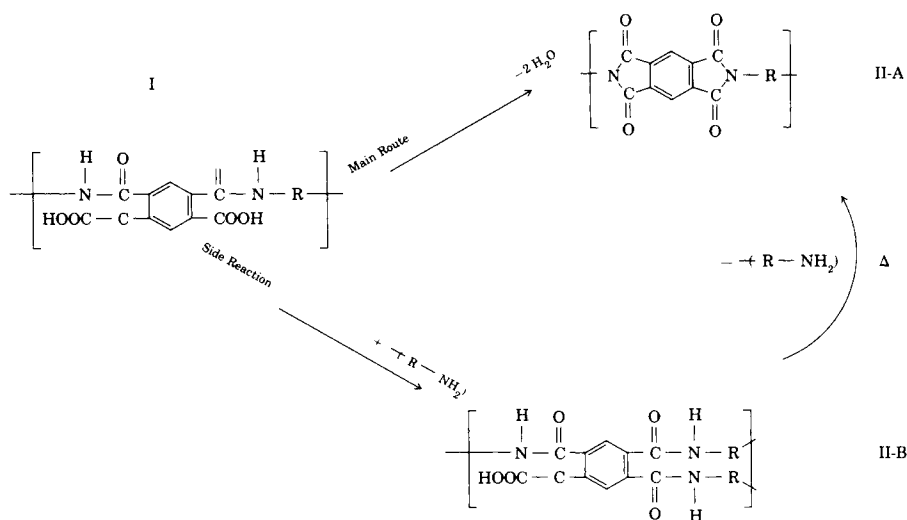
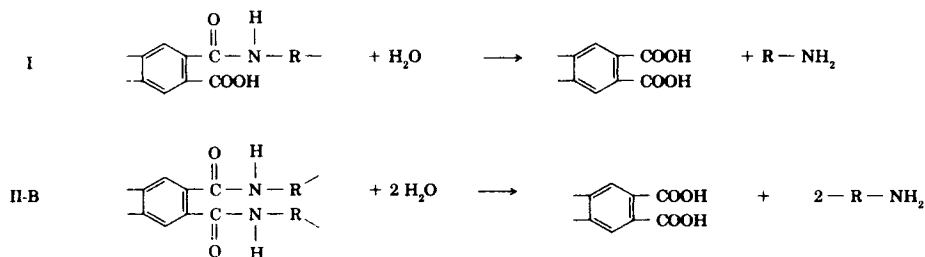


Fig. 4. Sorption isotherms for water vapor in 2 mil "as-received" Kapton® (○) and hydrothermally "passivated" Kapton® (●) at 30°C.

the absence of clustering in the aged film. The reduced clustering tendency is consistent with an increased hydrophilic nature in the passivated film. Only minor differences from the as-received films were detected in FTIR analysis of the aged films. During the aging process leading to the passivated film, the total accumulative amount of water incorporated irreversibly into the film amounts to 2.19 g/100 g of dry polymer. On the other hand, 9.42 g H₂O/100 g of dry polymer would be required to react with all the imide groups in Kapton.® This seems to suggest that up to 24% of the imide groups are involved in the passivation reaction. This reaction scheme involving hydrolysis of imide groups is somewhat implausible since imide groups tend to be relatively stable to hydrolysis. A more likely explanation can be advanced based on studies which suggest that commercial Kapton® contains up to 22% uncyclized polyamic residues.¹⁰⁻¹² Such studies indicate the possibility of the reaction scheme shown below leading to species 11-B, followed by insufficient final heat treatment to cause the side reaction product to become 11-A which is the Kapton® repeat unit¹⁰⁻¹²:



The close correspondence between the presence of 24% reactive groups from our study and the 22% uncyclized polyamic residues indicated by earlier studies is satisfying. Moreover, the well-known hydrolytic instability of such linkages is consistent with the observed low temperature reactivity. Reaction of species I with water would, of course give rise to chain scission, whereas reaction of 11-B with at least 2 water molecules is necessary to cause chain scission:



Water formed during the imidization reaction tends to cause small amounts of hydrolysis of unimidized species I with resultant formation of shorter chains terminated by amine or carboxyl groups. The amine-terminated chains, indicated by (H_2NR-) in the above reaction schemes can then give rise to small amounts of species 11-B above.

The preceding discussion strongly suggests that the reaction between water and Kapton® may lead to actual chain scission from 12 to 24% of the chain backbones, depending upon the relative amounts of species I and 11-B undergoing attack. The reactive incorporation of water during the scission reaction would also explain the increased hydrophilic nature of the aged polymer and lead to a decreased tendency of water clustering noted earlier.

Transport

Because of the chemical reaction noted above, a coupled reaction and diffusion treatment of the data are required in general, and are reported elsewhere for a variety of temperatures and activities.² At 30°C, however, the reaction is so slow that it can be essentially neglected and the simple Fickian "half time analysis" of sorption/desorption experiments, discussed in the previous section comparing 0.3 and 2 mil films, can be used to determine diffusion coefficients. Since, even for an as-received sample, less than 2% of the total water uptake during a given sorption run at 30°C is reactively incorporated in the polymer, this approximation is reasonable.

The data in Figure 5 represent the concentration dependence of the average diffusion coefficients of water in as-received and aged Kapton® evaluated from the sorption/desorption experiments. As before, the abscissa values represent actual sorbed concentrations in the polymer in equilibrium with the vapor phase pressure used in the sorption part of the sorption/desorption cycle. The data for the as-received 0.3 mil sample, discussed in the context of Figure 3., are also shown in this figure.

Except for the roughly threefold difference in diffusion coefficients, the qualitative responses of the two as-received samples look very similar and are markedly different than the response of the passivated film. Essentially no indication of clustering is suggested by the monotonically increasing diffusion coefficients for the aged film. This observation is consistent with the absence of convex curvature in the sorption isotherm for this sample as noted earlier. The type of concentration dependence apparent for the aged sample is consistent with either dual mode sorption¹³ or a simple plasticizing response.¹⁴ Although plasticization is certainly a possibility that cannot be ruled out, the rather moderate increase in sorption at low activities and the decrease in sorption at high activities apparent in Figure 5 for the aged sample, compared to the as-received sample, suggests that dual mode effects related to saturation of gaps in the polymer may be primarily responsible for the form of the concentration dependence of the diffusion coefficients. These effects are treated in detail elsewhere.²

The hygrothermal aging process studied for the 2 mil Kapton® film had small but measurable effects on water sorption in the film. The effects of aging on the water diffusion coefficient (and hence, effective barrier prop-

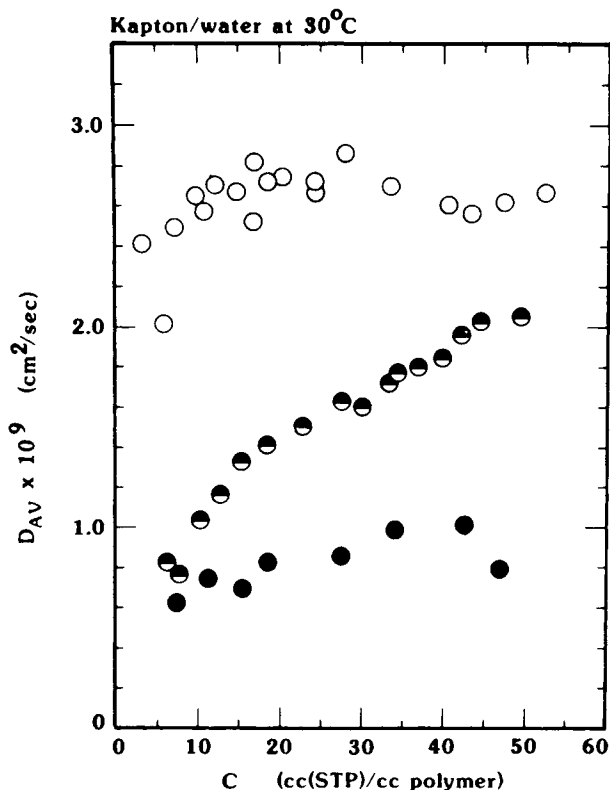


Fig. 5. Average diffusion coefficients D_{av} , estimated from sorption kinetics using the "half time" method for 2 mil "as-received" film (○) and 2 mil passivated film (◐). Solid points (●) are for the 0.3 mil film determined by the "long time" method.

erties) are more noticeable. Although the aging process produces an improved water vapor barrier at low activities, very little advantage exists at high activities. If the aging process involves a significant amount of hydrolytic chain scission, the mechanical properties of the aged film would be expected to be affected seriously. It has been reported that boiling in water for 10 days can cause some embrittlement with no detectable change in crystallinity from the treatment.¹⁵ A detailed mechanical property study was not undertaken to define subtle changes in the samples; however, no obvious embrittlement occurred in the aged samples in the present study. The retention of good film properties suggests that amide residues, shown in compound 11-B, may be principally involved in the passivation process studied here, since the alternate hypothetical reaction involving compound I causes considerably more chain scission damage per mole of water reacted.

CONCLUSIONS

Kapton® polyimide is a morphologically complex, clear, glassy material. Segmental aggregates, too small to scatter light, are believed to be important in determining the effective diffusion coefficient of water through the matrix. The similarity of sorption isotherms of different film thicknesses suggests that the volume fractions of such paracrystalline aggregates are

similar in the two films. The overall similarity of the shapes of both the sorption isotherms and local concentration dependence of the diffusion coefficients suggest that the inherent chemical nature of the nonaggregated regions in which sorption occurs is similar. The factor of 3 difference in the absolute value of the water diffusion coefficient in the 0.3 and 2 mil thick samples is believed to arise from differences in orientation in the two films measured by birefringence. The molecular aggregates presumably serve as tortuous impediments to water diffusion, and their quantitative effect should be strongly affected by the organization of these aggregates, since they tend to be thin and flat based on X-ray reports.⁸ The level and extent of perfection of biaxial orientation is likely to be an important factor in determining the organization of these aggregates and, in turn, the barrier properties of the film.

Kapton[®] has a tendency to undergo a small amount of hydrolytic attack. At room temperature, the reaction is measureable, but extremely slow, while at 60°C it can be easily detected. The locus of the attack is believed to be the roughly 20–25% of uncyclized amic residues reported to be present in typical film samples. A high temperature post-cure step, forcing species 11-B to become 11-A in the reaction scheme shown earlier should, therefore, significantly reduce this tendency to hydrolytic attack. The hydrolytic aging process appears to produce a material which exhibits considerably lower water vapor diffusion coefficients at low activities. Water appears to have no tendency to cluster in the aged sample as reflected by the simple concave water sorption isotherm and monotonically increasing diffusion coefficients.

In general, the aging process appears to produce a more hydrophilic material. It is reasonable to anticipate a correspondingly larger humidity dependence of electrical and other physical properties of the aged material compared to the virgin film.

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