

Thermoanalytical Behavior of Moisture in Aromatic Polyamide and Polyimide Films

Sachio YASUFUKU[†] and Minoru TODOKI^{*}

Tokyo Denki University, Tokyo 101-8457, Japan

**Toray Research Center, Inc., Shiga 520-0842, Japan*

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We have reported on thermoanalytical studies of Aromatic Polyamide (Aramid) film of hydrophilic nature in comparison with polyimide (PI) film of hydrophilic nature.^{1,2} The weight loss of moisture-conditioned films in Thermogravimetry Analysis (TGA) was equal to the water absorption value for the Aramid film but it was lower than the water absorption value for the PI film.¹

In the present paper, we performed the Moisture Evolution Analysis (MEA),³ which enabled us to directly measure the moisture evolution from the films. The results are compared with the weight loss and the water absorption values to elucidate the origin of the rather abnormal behavior of the PI film.¹

EXPERIMENTAL

MictronTM Aramid films of one mil (0.025 mm) and KaptonTM polyimide films of one mil were used.^{1,2,4} Sample codes A, B, C, and D refer to the PI films of various moisture-conditionings. All the samples were vacuum dried for two days and then kept for two days at controlled temperature and humidity as described in Table I. Codes A', B', C', and D' refer to Aramid films of the corresponding conditioning. In the following, a "moisture-conditioned film" implies the sample just after it is removed from the controlled atmosphere mentioned above. Unless otherwise stated, experiments were conducted at 23 ± 2°C and 50 ± 5% RH. Each of the data shown is the result of one experimental run.

The water absorption was measured for a pad composed of several ten layers of films. The pad was weighed within two minutes after it was removed from the moisture-conditioning atmosphere of Table I. The increase of mass from the vacuum-dried state (*i.e.*, before conditioning) was taken as the water absorption. The data, as given in Tables I and II, are described in % of the mass of moisture-conditioned film to facilitate comparison with the TGA and MEA data.

For measurements of TGA, a piece of the film is transferred to a Pt vessel after removal from the conditioned atmosphere and weighed within two minutes, and then inserted into the thermobalance. The mass of the film was measured as a function of temperature. Details of measurements were reported.¹

The equipment and the measuring principle of MEA

were already reported.³ A piece of the moisture-conditioned film was placed in a nickel boat and inserted into the oven of the MEA equipment. It took about 10 seconds. The oven atmosphere was kept at 23 ± 2°C and 50 ± 5% RH for 60 min. Then the temperature was raised to 200°C in 20 min and then kept at 200°C for 40 min under dry nitrogen gas flow. The amount of evolved moisture per unit mass of the conditioned film was measured during this process with the precision ± 0.02%. The film was weighed after it was brought to the laboratory condition of 23 ± 2°C and 50 ± 5% RH.

RESULTS

The water absorption values, in% of the mass of moisture-conditioned film, are given in Table I. The data for all the conditions but D and D' are in good agreement with the corresponding data of previous report.¹ The values for PI of conditions B and C agree with the reported values of corresponding conditions.^{1,5,6} The values for D and D' may have larger uncertainty since the measurement involved manual wiping with gauze.

Figure 1a represents the results of TGA test of Aramid. The mass of film is shown in % of the mass of conditioned film. The results are in agreement with those of previous paper.¹ The weight loss, or the amount of vaporized moisture, increased with increasing temperature. It leveled off at temperatures higher than 100°C and approached the water absorption value as shown in Table II. The result is typical of a humid hydrophilic film.⁴

Figure 1b shows the results of TGA test for PI films. The qualitative features of the vaporization process were in good accord with the previous report but the quantitative agreement was not as good as for Aramid films.¹ The evaporation started at the very beginning of meas-

Table I. Water absorption for Aramid and polyimide films. Values are in % of the mass of moisture-conditioned sample

	Aramid Film	Polyimide Film
After vacuum dried	0 (A')	0 (A)
After kept at 23°C & 50% RH	1.05 (B')	1.45 (B)
After kept at 23°C & 100% RH	1.93 (C')	2.95 (C)
After soaked in water at 23°C	1.80 (D')	4.27 (D)

[†]To whom all correspondence should be addressed.

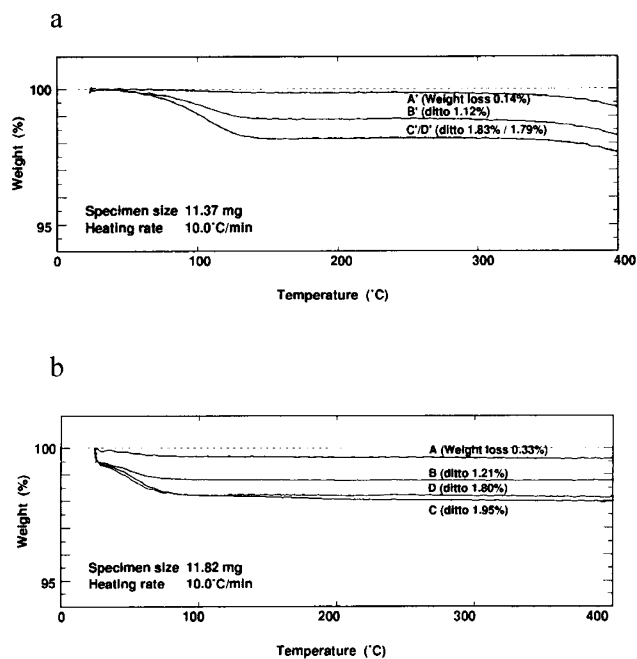


Figure 1. TGA curves (a) for Aramid films, A', B', C', and D' and (b) for PI films, A, B, C, and D.

Table II. Water contents determined by three methods. Values are in % of the mass of moisture-conditioned sample

Polyimide Film

	Water Absorption	Weight Loss	Amount of Evolved Moisture
A	0	0.33	0.22 (0.11)
B	1.45	1.21	1.48 (1.35)
C	2.95	1.95	2.31 (2.20)
D	4.27	1.80	2.58 (2.45)

Aramid Film

	Water Absorption	Weight Loss	Amount of Evolved Moisture
A'	0	0.14	0.14 (0.02)
B'	1.05	1.12	1.23 (0.21)
C'	1.93	1.83	1.99 (0.37)
D'	1.80	1.79	2.17 (0.49)

urement at low temperature and continued until it leveled off at about 70°C. There was no vaporization in the vicinity of 100°C. The TGA test for humid PI films, for samples C and D in particular, is relatively inaccurate due to the extraordinary moisture vaporization at low temperatures. This causes errors in manual operations at the early stage of measurement. For samples A and B, with only moderate vaporization at low temperatures, the final weight loss was in fair agreement with the water absorption as shown in Table II.

Figures 2a and 2b show the MEA curves of the Aramid films A' and C', respectively. In both cases, a small moisture evolution was detected in the MEA curves at the beginning, at 23 ± 2°C, and a large moisture evolution was observed at about 100°C. Marked evolution was not noticeable at higher temperatures. The evolution was naturally higher for the more humid sample C than for A. The integrated amounts of evolved moisture at 200°C are shown in Table II, in % of the mass of conditioned film. The amount of the evolved moisture is in good

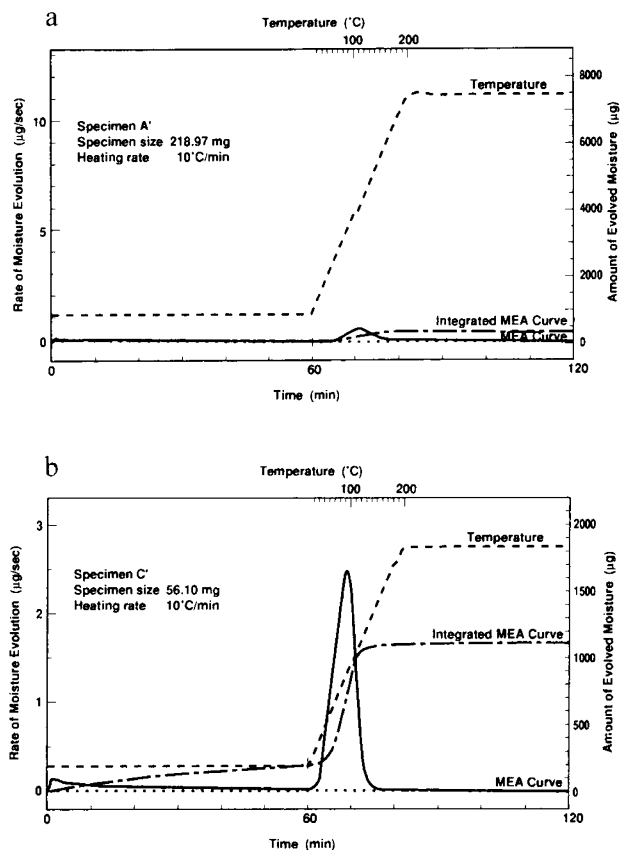


Figure 2. MEA curves for Aramid films (a) A' and (b) C'.

agreement with the weight loss in TGA test for the Aramid film, except for the case of sample D' with possibly lower accuracy of measurement. The values in the parenthesis represent the evolved moisture in the first burst, *i.e.*, before heating starts.

Figures 3a and 3b show the MEA curves of the PI films A and C, respectively. In the case of humid film, C, a bursting moisture evolution was observed at the beginning of measurement, in the atmosphere of 23 ± 2°C and 50 ± 5% RH. The rate of moisture evolution was small and decreased steadily in the succeeding process of heating from 23 ± 2°C up to 200°C, except for a small peak at about 80°C. The amounts of evolved moisture evaluated from the integrated curves at 200°C are shown in Table II. The total amount of evolved moisture was close to the water absorption value for samples A and B but was smaller for samples C and D. The results for D may not be worth discussing since the uncertainties in either of the measurements should be quite large as mentioned earlier. For the sample C, the evolution at the early stage of experiments, such as weighing in the atmosphere of 23 ± 2°C and 50 ± 5% RH, could be the origin of error. However, the amount of evolution at this stage was estimated as 0.1–0.2%, which is much smaller than the difference, 0.64%, between the values of the second and the fourth columns for C. One may conclude that the amount of evolved moisture was less than the water absorption value for humid PI films. The amount of the evolved moisture at 23 ± 2°C and 50 ± 5% RH, represented by the value in parenthesis, is a large fraction of the total amount of evolved moisture for humid PI films in remarkable contrast with Aramid films.

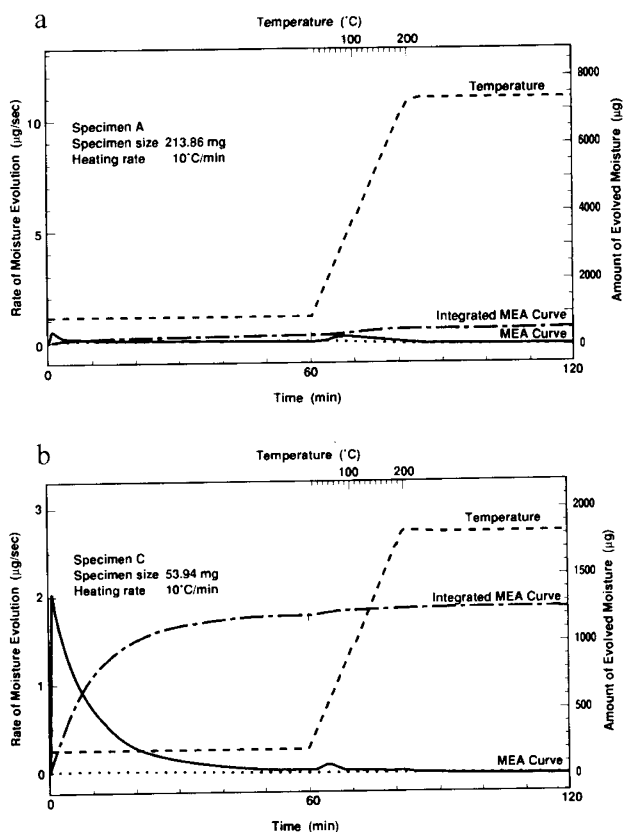


Figure 3. MEA curves for PI films (a) A and (b) C.

DISCUSSION

Three quantities, the water absorption, the weight loss, and the amount of evolved moisture, are in rough agreement with each other and represent the water content of the Aramid films. Figure 2b represents a typical moisture vaporization behavior of a humid hydrophilic polymer film.³ The evolved moisture at about 100°C is attributed to the internally bound moisture while that evolved at $23 \pm 2^\circ\text{C}$ is attributed to the surface attaching moisture. The latter amount is represented by the values in parenthesis of Table II. The concepts of "surface attaching moisture" and "internally bound moisture" were introduced by the present authors to represent the two types of absorbed moisture for hydrophilic polymer films.³ The concepts just differentiate the easiness to remove the moisture and their microscopic implications are still to be clarified. Obviously the surface attaching moisture is far less than the internally bound moisture for the humid Aramid films.

For PI films, the total amount of evolved moisture in MEA test is a little less than the water absorption value and the difference is not due to experimental uncertainty. The weight loss in TGA test underestimates the

water content due to the experimental error as mentioned. We assign the first major peak of moisture evolution for the humid film, C, in the atmosphere of $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$, to desorption of water adsorbed on the film surface, the surface-attaching moisture.³ The second minor peak at about 80°C, much smaller than the first peak, is assigned to the release of the water absorbed inside the film, the internally absorbed moisture. As shown in Table II, the surface attaching moisture (values in parenthesis) is the dominant portion of the evolved moisture for humid PI films, B, C, and D. There was essentially no moisture vaporization in the heating process of MEA test for these samples.

An NMR study revealed the existence of two states of water, surface attaching moisture and internally oriented moisture, in a Kapton film with water absorption at room temperature.⁵ This result may support our proposal that the moisture evolution at the room temperature corresponds to the surface attaching moisture. The internally bound moisture, which should vaporize in the heating up to 200°C in the MEA test, does not completely vaporize and remains as the internally oriented moisture. This portion of the moisture may have been consumed in some kind of chemical reaction. It is reported that polyimide reacts with water at elevated temperatures, accompanying an imide-ring opening reaction.⁷ The behavior of moisture has not been investigated, to our knowledge, for conditioned PI films at elevated temperatures and the above conjecture is still to be proven.

It was revealed that the amount of evolved moisture in the MEA test for humid polyimide films is a little less than the water content. The weight loss in the TGA test underestimates the water content due to the weight loss during the manual handling of the sample at the early stage of the test. The absorbed water is mostly in the state of surface attaching moisture which can be removed in dry air at room temperature. Some of the rest of moisture, internally bound moisture, may be evaporated in the heating to 200°C but some portion remains in the film probably as a result of chemical reaction with the polymer.

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