Development of a Simple Cup Method for Water Vapor Transmission Rate Measurements under High-temperature Conditions

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***Abstract*— A novel method has been studied to measure high-temperature water vapor transmission rates (WVTRs) for sealing materials such as epoxy encapsulants. Sealing materials are widely used as electronic components and must be moisture resistant under the damp heat test conditions for electronic components, e.g., 60 ˚C and 85 ˚C. To prevent samples from damage during high-temperature measurements using the conventional cup method, we built a new cup unit with a pressure-adjusting mechanism. This new cup is used to measure WVTRs without damaging the thin epoxy encapsulant membranes (thicknesses of 120–220 µm). Arrhenius plots of the WVTRs for epoxy encapsulants measured by using the new cup exhibit linear relationships between temperatures of 25–85 ˚C.**

Keywords—water vapor transmission rate; cup method; 60 ˚C 90% RH; 85 ˚C 85% RH; epoxy encapsulant

I. Introduction

Proper packaging of electronic components prolongs their lives and improves their reliability. To realize high-performance hermetic packages, high-barrier films [1–2] and encapsulants [3–4] have been widely developed, and their moisture barrier properties must be studied. For this purpose, a reliable method of measuring water vapor transmission rates (WVTRs) under high-temperature conditions of 60 ˚C and 85 ˚C, such as those utilized for damp heat testing, [5–6] is required [7].

The cup method [8] and conventional experimental measurement methods [9] (humidity sensor, infrared sensor, colorimetric sensor, and gas chromatography methods) are not defined by the ISO as high-temperature WVTR measurement techniques. Some new experimental measurement methods [10] (pressure sensor, atmospheric pressure ionization mass spectrometer, and calcium corrosion methods) adopted by the ISO in 2015 have defined the 60 ˚C 90% relative humidity (RH) and 85 ˚C 85% RH conditions. However, these new methods are intended for evaluating transmission rates of materials in the range of 10^{-6}–10^{-1} g m^{-2}d^{-1} [11]. Examples of such measurements include detecting moisture traces that diffuse through the sealed portions of laminated devices [12] or measuring WVTRs of glass alternative films such as silica-deposited films, organic-inorganic composites, and clay films.

The cup method specified in the ASTM E96 [13] is a basic and simple standard testing method for measuring WVTRs, which is suitable for studying sealing materials in the measurement range of 10^{0}–10^{3} g m^{-2}d^{-1} [11]. However, this method is not valid for taking WVTR measurements at high temperatures because of the deformation and damage of tested specimens caused by the increasing internal pressure in the cup under high-temperature conditions.

The purpose of this paper is to obtain data on the moisture barrier properties of encapsulants at high temperatures by using an easy and inexpensive measuring instrument. These data can be used to design encapsulants for electronic components. We examined the validity of the measured WVTR results using a new cup unit with a pressure adjustment mechanism.

II. Materials and Methods

A. Materials

Polyethylene terephthalate (PET, 25 µm thick, Lumirror S10, Toray Industries, Inc.), polypropylene (PP, 30 µm thick, OPP bag, WorkUp Co., Ltd.), polyethylene naphthalate (PEN, 25 µm thick, Teonex Q51, Teijin DuPont Films Japan Ltd.), and polyimide (PI, 100 µm thick, Mordohar PIF, Future Technology Co., Ltd.) films are used as purchased. Anhydrous Calcium chloride (for U-tubes, Wako Pure Chemical Industries, Ltd.) is used as a desiccant. An epoxy encapsulant (BESTONE PM-4, Tohto Chemical Industry Co., Ltd.) is utilized to produce membranes as described below.

B. Preparation of Specimens from Sealing Materials

A Teflon sheet (NITOFLON No.900UL, Nitto Denko Corp.) was placed on an automatic coating apparatus (PI−1210, Tester Sangyo Co., Ltd.), after which a film of sealing material was uniformly applied to the Teflon sheet with an applicator (SA−204, Tester Sangyo Co., Ltd.) and heated to 90 ˚C for 24 h. A solidified thin membrane was obtained by peeling off the sealing material layer from the Teflon sheet. A thickness of the produced thin membrane specimen was estimated as a 10-point average value measured with a constant pressure thickness gauge (FFA−2, Ozaki MFG. Co., Ltd).

C. *Test Method*

WVTRs of specimens were measured using the ISO 2528 Standard Method (cup method), while the cup was modified to a screw-type one (Imoto Machinery Co., Ltd.), as defined in the JIS L 1099 method description [14].

WVTR values (g $m^{-2}d^{-1}$) were calculated using the following equation:

$$\mathrm{WVTR} = \Delta q \,/\, A\Delta t \qquad (1)$$

where $\Delta q/\Delta t$ is the mass change of the cup per time unit (g d^{-1}), and A is the transmission area (m^2). Each plastic film was tested three times, while each epoxy membrane represented one specimen because it is difficult to produce specimens from the same sealing material with exactly the same thickness.

D. *Pressure-adjusting Gasket*

In order to avoid specimen damage caused by internal pressure variations in the cup, a new cup with a pressure-adjusting mechanism was developed. Fig. 1 shows the schematic of this cup, namely a conventional screw cup with an attached pressure-adjusting gasket. The gasket consisted of a PP gasket with side air vents and a laminated aluminum bag for collecting leaking air from the vents. The details of the utilized testing method have been previously described elsewhere [15].

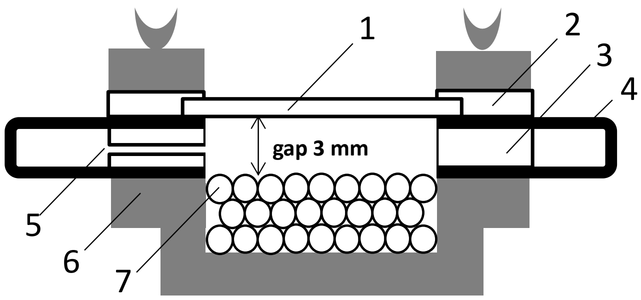

Fig. 1. A schematic of the new cup. 1: specimen, 2: elastomer, 3: PP gasket, 4: laminated aluminum foil bag, 5: side air vent, 6: cup, 7: desiccant.

III. RESULTS

A. *WVTRs of Plastic Films*

Fig. 2 shows the photographs of the conventional and new cups with PET specimens after measuring WVTRs at 85 ˚C 90% RH. The PET film attached to the conventional cup was inflated, assuming a dome shape outside the cup body. On the other hand, the PET film attached to the new cup retained its flat surface. The air in the conventional cup expanded to deform the PET film when heated at 85 ˚C. In the new cup method, the expanded air escaped to the soft and deformable bag space of the pressure-adjusting gasket, retaining the film shape.

Fig. 3 shows the WVTRs of various polymer films measured at 85 ˚C 90% RH with the conventional cup and new cup methods. The results obtained with the conventional cup method are systematically larger than those produced using the new cup. All specimens attached to the conventional cup exhibited deformation or damage detected by visual observation after the measurements. On the other hand, all specimens attached to the new cup retained their horizontal configuration after the measurements (as shown in Fig. 2 (b)). The difference of WVTRs described above are caused by an increase in the transmission area that is associated with film deformation. It is reasonable to suggest that the new cup with the pressure adjusting mechanism is capable of measuring WVTRs of various plastic films at high-temperature conditions without damaging the specimens.

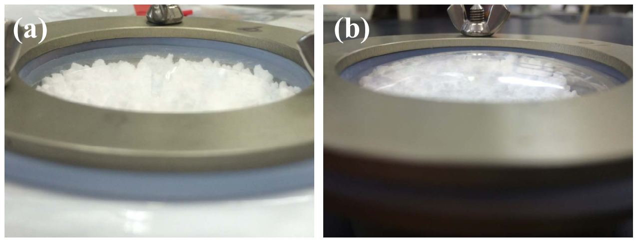

Fig. 2. Side views of the cups with attached PET specimens after measuring WVTRs using (a) the new cup and (b) the conventional cup.

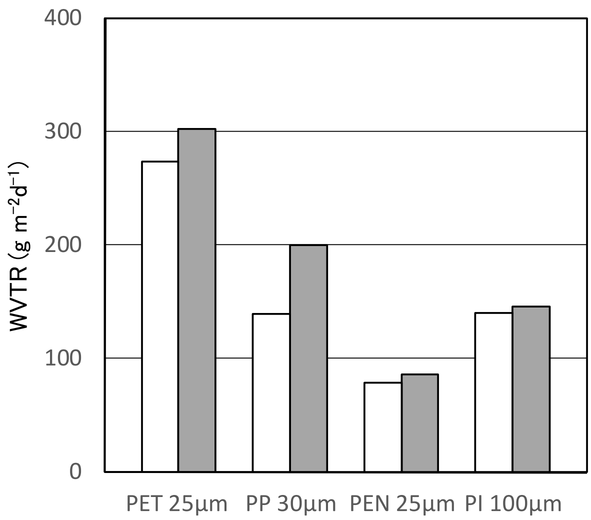

Fig. 3. WVTRs of PET, PP, PEN, and PI at 85 ˚C 90% RH. The white bars represent the values measured with the new cup method, and the gray bars denote the values obtained with the conventional cup method.

B. *WVTRs of epoxy encapsulants*

Fig. 4 shows the WVTRs of the epoxy encapsulant films measured using both the conventional and new cup methods. The thickness of each specimen ranged between 80 and 220 µm. The measurement times for these specimens were between 72 and 120 h, which were comparable to measurement times obtained when studying packaging films using the conventional cup method [8].

In the film thickness range of 120–220 µm depicted in Fig. 4, the WVTR values obtained with the new cup method were distributed along the corresponding rectangular hyperbola according to the relationship between the WVTR and the film thickness (l) which can be generally expressed by the following equation [16]:

$$\mathrm{WVTR} = P\Delta p / l \quad (2)$$

where P is the water vapor permeability coefficient, Δp is the difference between the partial water vapor pressures on different sides of the film specimen, and those coefficients are constant. The values obtained with the conventional cup method were located along the upper side of that curve. It can be assumed that the specimens attached to the conventional cup were damaged during measurements, resulting in errors that systematically increased the obtained WVTR values.

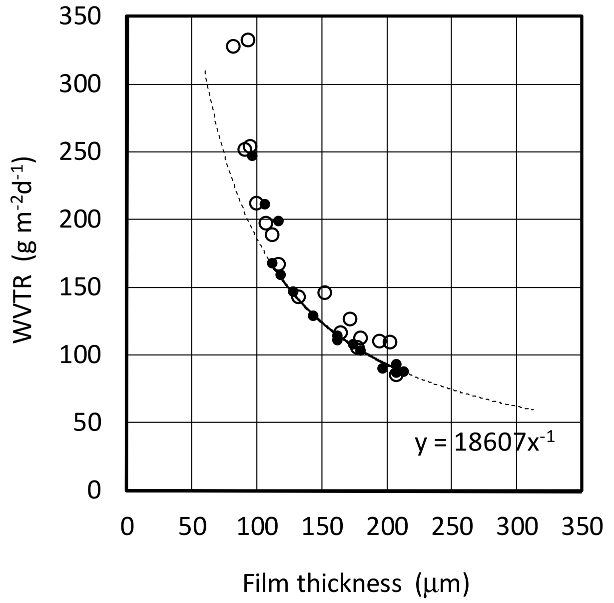

Fig. 4. WVTR values as functions of thickness of the epoxy encapsulant films measured with the new cup method (●) and the conventional cup method (○) at 85 ˚C 90% RH. The fitting curve was obtained for the values measured with the new cup method.

Fig. 5 shows the damaged epoxy encapsulant films after conducting measurements with the conventional cup method. The specimen depicted in Fig. 5 (a) was mostly characterized by a convex shape with the central portion exhibiting a concave shape. The convex shape was obtained due to the pressure rise in the cup during heating at 85 ˚C, while the concave shape was produced by the pressure relief originated from cooling during mass measurements. A possible reason for the concave shape of the specimen's central part can be described as follows. During the cooling stage of the mass measurement process, the conventional cup made of aluminum with high thermal conductivity was cooled faster than the convex specimen; subsequently, the outer peripheral region of the specimen near the aluminum cup was also cooled faster than its central region. As a result, the center of the specimen was distorted by pressure fluctuations because it was warmer and softer than the peripheral regions. Due to the repeating heating (water vapor transmission) and cooling (mass measurement) processes, the specimen was constantly deformed, which resulted in cracking of its central region as shown in Fig. 5 (b). On the other hand, no deformations or cracking were observed for the specimens measured with the new cup method.

In the thickness range of 80–120 μm (Fig. 4), the WVTR values measured with the new cup method were distributed above the rectangular hyperbola for the measured values obtained within the 120–220 μm region. It can be assumed that thin specimens with thicknesses below 120 μm were unable to avoid deformation during measurements using the new cup method. Thus, thicknesses of epoxy specimens should be adjusted to the 120–220 μm region to be suitable for the new cup method, which would prevent specimen damage and lead to shorter measurement times.

In the case of epoxy encapsulant specimens with thicknesses of 120–220 μm, the obtained WVTR data plotted as a function of film thickness were fit with equation (2). Using the obtained fitting parameters, the WVTR for a film with a thickness of 200 μm was found to be 93.0 g m^{-2}d^{-1} at 85 ˚C 90% RH. Similarly, WVTR values for multiple epoxy specimens with thicknesses of 100–300 μm were obtained at several temperatures in the region of 25–60 ˚C. The resulting data (including the data point at 85 ˚C) were fitted with a rectangular hyperbola, so that WVTRs could be estimated for the epoxy encapsulant specimen with a thickness of 200 μm.

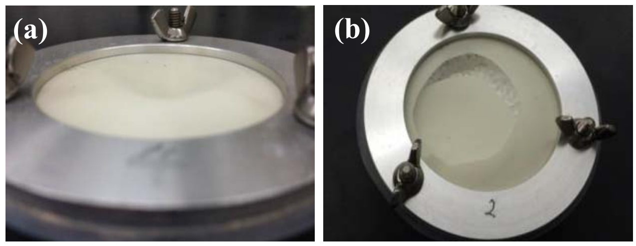

Fig. 5. Photographs of the epoxy encapsulant films after measurements with the conventional cup method at 85 ˚C. (a) A side view of the cup and the deformed specimen. (b) A top view of the cup and the cracked specimen.

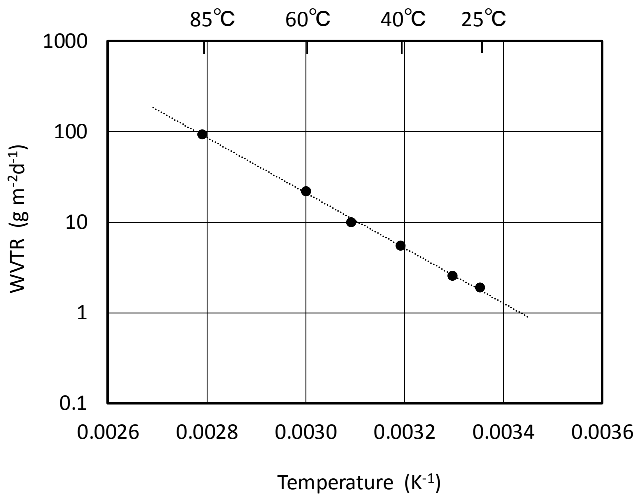

Fig. 6. Arrhenius plots of the WVTRs for the epoxy encapsulant membrane (PM–4, Tohto Chemical Industry Co., Ltd.) measured by the new cup method. The thickness of the specimen was 100–300 μm, and the plotted WVTR values corresponded to a specimen thickness of 200 μm.

Fig. 6 shows the inverse temperature dependence of the estimated WVTRs for the epoxy encapsulant specimen described above. A linear relationship was observed in the range of 25–85 ˚C. Thus, WVTRs of a typical polymer can be described by an Arrhenius-type equation. The linear relationship depicted in Fig. 6 is consistent with the results obtained for the epoxy encapsulant, which is stable in the given temperature range [17].

IV. CONCLUSION

The conventional cup method causes sample damage during measurements at high temperatures, resulting in erroneous increase in the measured WVTR values. The new method utilizing cups with pressure-adjusting mechanisms can avoid sample deformation. Furthermore, the new cup method prevents damage of thin specimens of epoxy encapsulants and reduces the WVTR measurement period. The Arrhenius plots of the WVTR values for epoxy encapsulant specimens obtained using the new cup method exhibited linear relationships between 25 and 85 ˚C due to the encapsulant stability in this temperature range. The new cup method was confirmed to be able to elucidate the water barrier properties of the epoxy encapsulants. The results of this study indicate that the new cup method can be used in moisture-proof design and evaluation of epoxy encapsulants.

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