# Quantitative Analysis of the Dielectric Properties of Various Polyimides at 10 GHz and Their Humidity Dependence Based on the Polarization Characterization

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## INTRODUCTION:

Polyimides (PIs) are expected to be used as high-frequency low-dielectric insulators, such as flexible substrates for wireless transmission and interlayers for antenna-in-packages [1]. However, conventional fully aromatic PIs generally show high dielectric constants ( $D_k \approx$ 3.2), high dissipation factors ( $D_f \approx 10^{-2}$ ), high refractive indices (n > 1.65), and high moisture absorption ( $\approx 3 \text{ wt\%}$ ) [2] due to the rigid molecular structures and polar imide groups. Moreover, the  $D_k$  and  $D_f$  of PIs are significantly affected by relative humidity (RH) in the operating (measurement) environment because water molecules show quite large  $D_k$  ( $\approx$ 60) and  $D_{\rm f}$  ( $\approx 0.5$ ) at around 10–20 GHz [3]. Although the RH dependence of  $D_k$  and  $D_f$  of PIs has been reported [4,5], its detailed mechanism has not been clarified. In this study, the  $D_k$  and  $D_f$  measured for 15 kinds of PIs (Fig. 1) at 10 GHz were quantitatively analyzed based on their chemical structures, refractive indices (n), and total  $(P_t)$ , dipolar  $(P_d)$ , and electronic ( $P_e$ ) polarizations per unit volume, in which  $P_t$  =  $P_d + P_e$ , and  $P_t$  and  $P_e$  are defined as  $P_t = (D_k - 1)/(D_k + 2)$  and  $P_{\rm e} = (n^2 - 1)/(n^2 + 2)$ , respectively. Moreover, the RH dependence of  $D_k$  and  $D_f$  was investigated by considering the interactions between PI chains and water molecules, i.e. hydrophobicity and hygroscopicity.

### **EXPERIMENTAL:**

PI films 50 x 50 mm in size and ca. 20 µm thick were prepared using the conventional two-step method followed by spin-coating and thermal imidization.  $D_k$  and  $D_f$  of the PI films were measured at 10 GHz in the transverse electric (TE<sub>011</sub>) mode using a cavity resonator (AET, Japan) connected to a vector network analyzer (Anritsu MS46122B, Japan). The RH dependence of  $D_k$  and  $D_f$  was measured in a home-built humidity-controlled chamber with an automated insertion device. RH level in the chamber (25–60%RH) was regulated by N<sub>2</sub> flow. The in-plane and out-of-plane refractive indices ( $n_{TE}$  and  $n_{TM}$ ) of PI films were measured using a prism coupler (Metricon PC-2010, USA) at a wavelength of 1310 nm.

## **RESULTS AND DISCUSSION:**

Based on the Clausius-Mossotti and Lorentz-Lorenz equations,  $P_d$  is related to the dipolar orientations in the polymer chains, while  $P_e$  is nearly proportional to the square of the refractive index  $(n^2)$  [6]. To examine the dielectric properties of polymers, each component of  $P_t (\propto D_k)$ ,  $P_e (\propto n^2)$ , and  $P_d$  ( $\propto$  dipole moment<sup>2</sup>,  $\mu^2$ ) should be separately evaluated because Maxwell's equation ( $D_k = n^2$ ) is applicable only for the optical domain ( $P_d = 0$ ).







**Fig. 2** Relationships between (a)  $P_t$  and  $P_e$ . and (b)  $D_f$  and  $P_d$ .

As shown in **Fig. 2(a)**,  $P_t$  shows a positive linear correlation with  $P_e$ , which indicates that  $P_t$  is mainly dominated by  $P_e$ . Moreover, the contribution of  $P_d$ , which corresponds to the difference between the linearly fitted line and that of  $P_t = P_e$ , is nearly constant and independent of  $P_e$ . This is supported by the fact that the contribution of  $P_d$  in  $P_t$  is only ~20%. This figure indicates that a reduction in *n* and  $P_e$  effectively decrease  $D_k$ , which is archivable by a decrease in packing coefficient ( $K_p$ ) and/or polarizability per unit volume (a/V) [7]. Thereby, the PIs having fluorinated or bulky alicyclic groups show smaller *n* and  $D_k$  values compared to the conventional PIs having rigid molecular structures with forming dense chain packing.

**Fig. 2(b)** demonstrates an obvious correlation between  $P_d$  and  $D_f$ , in which  $D_f$  is caused by dipolar relaxation. This fact indicates that  $D_f$  is closely related to  $P_d$ , and the PIs having intrinsically smaller  $\mu$  or restricted dipolar relaxation show smaller  $D_f$ . Accordingly, the fluorinated PIs containing  $-CF_3$  groups with smaller  $\mu$  or the fully aromatic rigid PIs forming dense molecular packing, which suppresses dipolar relaxation, exhibit smaller  $P_d$  and  $D_f$ . In contrast, the PIs containing alicyclic structures with large free volumes and/or polar ester groups with a large  $\mu$  show larger  $P_d$  and  $D_f$ . Note that the relationship between  $D_f$  and  $P_{d(TE)}$  derived from  $n_{TE}$  exhibits a higher correlation than that between  $D_f$  and  $P_{d(av)}$  derived from  $n_{av}$ . This indicates that the  $P_d$  and  $D_f$  of the PIs are anisotropic properties, and they are closely related to the in-plane components of  $\mu$  and its relaxation motion.

As shown in **Fig. 3**, the  $D_k$  and  $D_f$  at 10 GHz show linear increases with RH for all the PIs, which implies that both the  $D_k$ and  $D_f$  of PIs are significantly influenced by moisture in the operating (measurement) environment. The slopes of the linear fitted lines in **Fig. 3** differ depending on each PI. Notably, the  $D_f$ values extrapolated to the perfectly dried state converge to around 0.001, suggesting that the intrinsic  $D_f$  of each PI originated from their dipolar motion at 0 %RH is quite limited.

**Fig. 4** shows that the slopes in Fig. 3 ( $h_{Dk}$  and  $h_{Df}$ ) are in a higher linear relation, indicating the sensitivities to the humidity of  $D_k$  and  $D_f$  for each PI are closely correlated. These PIs can be classified into three groups based on their  $h_{Dk}$  and  $h_{Df}$  in terms of chemical structure and moisture sorption. The PIs with large fluorine contents and those derived from *s*BPDA dianhydride, which forms strong aggregation (group I), exhibit extremely low sensitivity to RH, and the partially fluorinated and alicyclic PIs (group II) show moderate sensitivities. In contrast, hygroscopic Kapton-H and nonfluorinated bio-based poly(ester imide)s with large fluore free volumes and flexibility (group III) show h



**Fig. 3** RH dependence of (a)  $D_k$  and (b)  $D_f$  measured at 10 GHz.



**Fig. 4** Relationship between  $h_{Dk}$  and  $h_{Df}$  derived from Fig. 3.

imide)s with large free volumes and flexibility (group III) show higher sensitivity to RH.

In summary, the  $D_k$  and  $D_f$  of 15 kinds of PIs at 10 GHz are explainable by the dipolar characterization, and they linearly increase with RH. Highly fluorinated PIs exhibit the lowest  $D_k$  and  $D_f$  with the lowest  $h_{Dk}$  and  $h_{Df}$ , originating from their small  $\alpha/V$  values and high hydrophobicity.

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