Dielectric relaxation in polyimide nanofoamed films with low dielectric constant

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Polyimide nanofoamed films have been prepared from the polyimide precursors (PMDA-ODA) and poly(ethylene oxide) (PEO) in N,N-dimethylacetamide. The dielectric properties of the films were studied over the temperature range of $-150-150\ ^\circ$C and a frequency range of 1 Hz–10 MHz. The frequency dependence of the dielectric constant for nanofoamed films with different amounts of PEO was studied. An relaxation process at below the glass transition temperature of the polyimide nanofoamed films was found. The peak value of the dielectric loss increased with increasing amount of PEO. © *2008 American Institute of Physics.*
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In recent years, great attention has been paid to the low-k polymer and its composites as the next-generation interlayer dielectrics for multilayer interconnection in microelectronics.[1–6] In electronic packaging, low-k dielectric materials minimize cross talk and maximize signal propagation speed in devices. Aromatic polyimide (PI) has been widely used as an interlayer dielectric in microelectronic devices, thanks to its good mechanical properties, excellent chemical and thermal stabilities, high breakdown voltage, and low dielectric constant.[1–8] Simpson and St. Clair[3] have summarized the strategies used to lower dielectric constant in polyimides. In particular, fluorine is usually introduced into polyimide in order to further decrease the dielectric constant.[9] Furthermore, a high degree of free volume will offer as a low dielectric constant phase. In our recent study, silica tubes/PI composite films were investigated and the dielectric constant could be reduced to 2.9.[4] Moreover, a series of porous polyimide materials such as polyimide nanofoamed films prepared from PI and poly(ethylene oxide) (PEO) have been explored.[10]

One of the most suitable physical methods for the investigation of molecular mobility in low-k polymer samples under ac electrical field is the dielectric spectroscopy. This method makes it possible to obtain data on the molecular mobility of a macromolecule as a whole and of its main-chain segments, bulky side groups, etc. Dielectric losses in a polymer sample appear during thermal orientation of polar kinetic units. Although it has been reported that most of aromatic polyimide and copolyimide films exhibit relaxational processes (α, β, and γ relaxation) in their dynamic mechanical and dielectric behaviors,[11,12] there is limited relaxation studies on polyimides. In this letter, PI-PEO nanofoamed films were prepared via *in situ* polymerization and thermal treatment. A low dielectric constant was achieved. The dielectric properties of these nanofoamed films over broad temperature and frequency ranges were studied and the dielectric relaxation was discussed in details.

Pyromellitic dianhydride (PMDA) (Hangzhou Taida Ltd.) and oxydimethylaniline (ODA) (Beijing Chemical Reagent Ltd. China) were dehydrated prior to use. N,N-Dimethylacetamide (Beijing Yili Chemicals Reagent Co.) was used as received. PEO (Beijing Guoren Yikang Ltd., Beijing, China) was dried prior to use. Cross-sectional images of the polyimide hybrid films were studied by scanning electron microscope (SEM) (JEOL JSM-6335F FE) operating at an acceleration voltage of 15 kV. The dielectric constant was determined using a frequency-response (Novocontrol Alpha-analyzer) dielectric analyzer from -150 to $150\ ^\circ$C with scanning frequencies ranging from 1 to 10^7 Hz. To avoid the influence of water absorption, all tests were conducted under a dry nitrogen flow (20 ml/min) and the specimen thickness was controlled between 30 and 40 μm. The area of the stainless steel electrode used was $\sim$3.14 cm^2.

Figure 1 displays the cross-sectional SEM images of the polyimide nanofoamed films prepared with 5 and 7 wt % PEO content. A porous structure of the nanofoamed film can be clearly seen, where the white areas are voids left by the thermally decomposed PEO phase. Both spherical and nonspherical pores (diameters around 40–200 nm) with a small degree of interconnections can be observed. The reason for this deviation from the expected spherical morphology is due
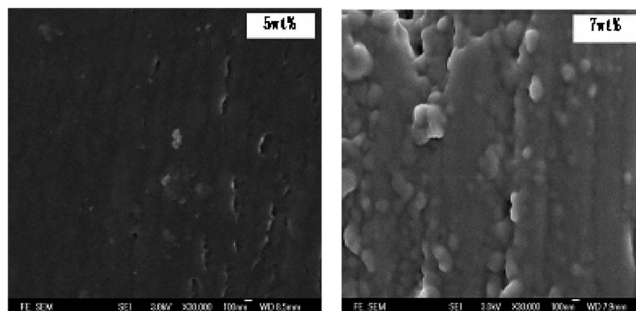

FIG. 1. The SEM images of polyimide nanofoamed films with 5 wt % PEO content (a) and 7 wt % PEO content (b).

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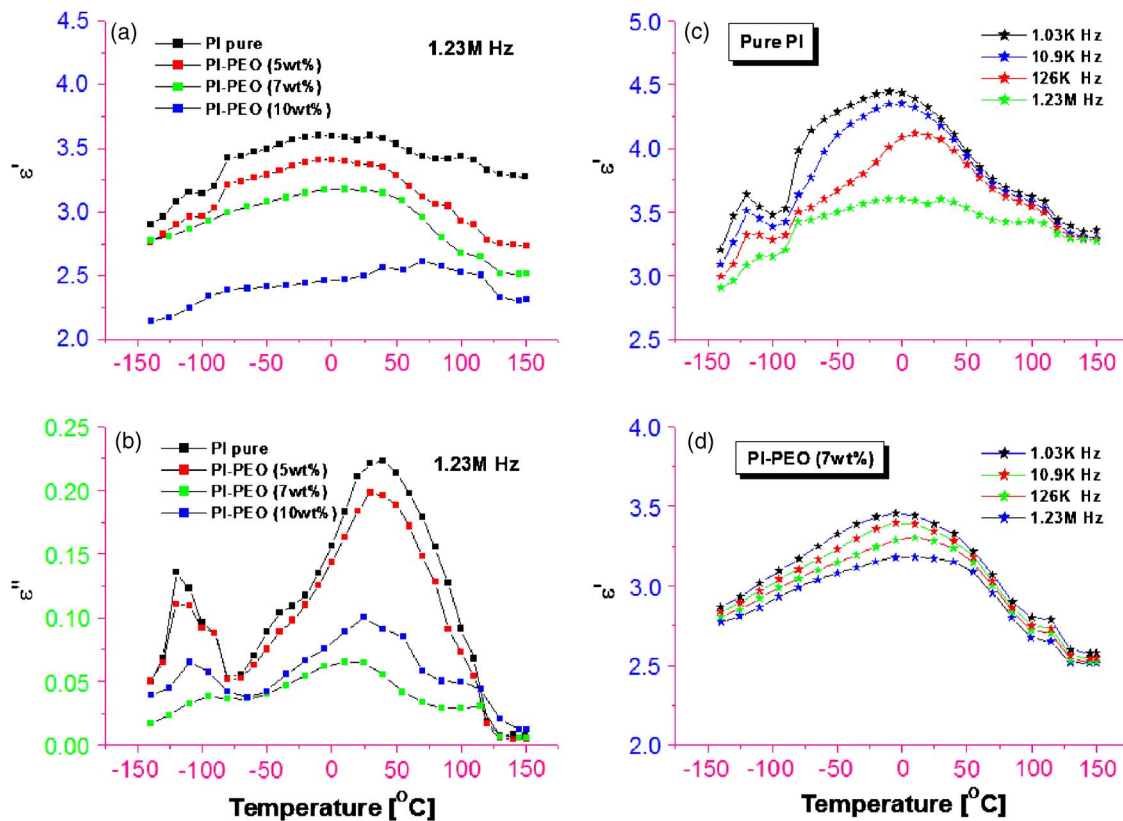c)Electronic mail: aphhuang@polyu.edu.hk.

FIG. 2. (Color online) The temperature dependence on the dielectric constant of PI-PEO foamed films.

to the foaming process. When the small molecules created from the thermally decomposed PEO escape from the PI matrix, they tend to change the shape and size of the original spherical pores and form interconnections between pores. Moreover, the pore size in the sample with 7 wt % PEO is larger than that in the sample with 5 wt % PEO.

The temperature dependence of real $[\varepsilon'(T)]$ and imaginary $[\varepsilon''(T)]$ parts of dielectric constant of PI-PEO nanofoamed films are shown in Fig. 2. It can be seen that the dielectric constant decreases with increasing amount of PEO used in the synthesis process. The dielectric constant of pure PI is 3.3 at 150 °C, which is comparable to the values previously reported (2.9–3.4).[13] The decrease of dielectric constant with increasing PEO content is simply due to the more free volume (pores, $\varepsilon' \sim 1$) generated with more PEO. It can also be found that the dielectric constant of the foamed film with 10 wt % PEO is below 2.6 in the temperature range from −150 to 150 °C, which is satisfied to the required dielectric constant ($\varepsilon \leqslant 2.7$) for next-generation interlayer low-k dielectric materials.

The $\varepsilon''(T)$ plots reveal the occurrence of two relaxation processes: the low and high temperature relaxations are defined, respectively, as γ and β transitions [Fig. 2(b)], like what has been reported that most of aromatic polyimide and copolyimide films exhibit relaxation processes (α, β, and γ relaxations) in their dynamic mechanical and dielectric behaviors.[11,12] A α relaxation process attributed to glass transition can be normally observed at temperatures above 300 °C.[14] The β transition occurs over a very wide temperature range, and the peak temperature T_β in $\varepsilon''(T)$ decreases with increasing PEO content [Fig. 2(b)]. Although the exact description is still uncertain, the β transition generally associated with local bond rotations along the polyimide back-

bone, showing a glasslike behavior.[15] The γ transition, which occurs over a relative narrow temperature range, has been observed previously in a limited number of studies. In the PI-PEO foamed films, the peak temperature T_γ in $\varepsilon''(T)$ increases very slightly with increasing PEO content [Fig. 2(b)]. The magnitude of both β and γ relaxation decreases in the nanofoamed films. The observed tendency of T_β and T_γ in PI-PEO films implies the coupling of β and γ transitions, which displays more clearly in Figs. 2(c) and 2(d). Figures 2(c) and 2(d) show the ε' versus temperature curves collected at four different frequencies on the PI and PI-7 wt % PEO samples, respectively. β and γ transitions are clearly shown in pure PI sample, but only a broad relaxation can be observed in $\varepsilon'(T)$ of PI-7 wt % PEO.

Further details on the effect of the PEO content were gathered by the frequency dependence analysis. Figure 3 shows $\varepsilon'(f)$ and $\varepsilon''(f)$ of PI-7 wt % PEO for a series of temperatures. Dielectric constants of polyimides, in general, are known to decrease gradually with increasing frequency, as shown in Fig. 3. The peak frequency in $\varepsilon''(f)$ increases with increasing temperatures. The peak value increases slightly first and then increases rapidly after a crossover temperature −50 °C (denoted by arrow). The above frequency dependence has been examined using the Arrhenius relationship $f \sim \exp(-U_0/k_B T)$, where U_0 is the activation energy and k_B is the Boltzmann constant. Observations of the PI-PEO films with different PEO content are summarized in Fig. 4, where $U_0 = 0.42$, 0.45, and 0.47 eV for γ transition in 5 wt % PEO, 7 wt % PEO, and 10 wt % PEO, respectively. The theories of Starkweather's theory[16] and Pellegnro *et al.*[17] predict an activation energy of 10.3 kcal/mol ($\sim$0.45 eV) of the γ relaxation process in polyimides, which is quite closed to our
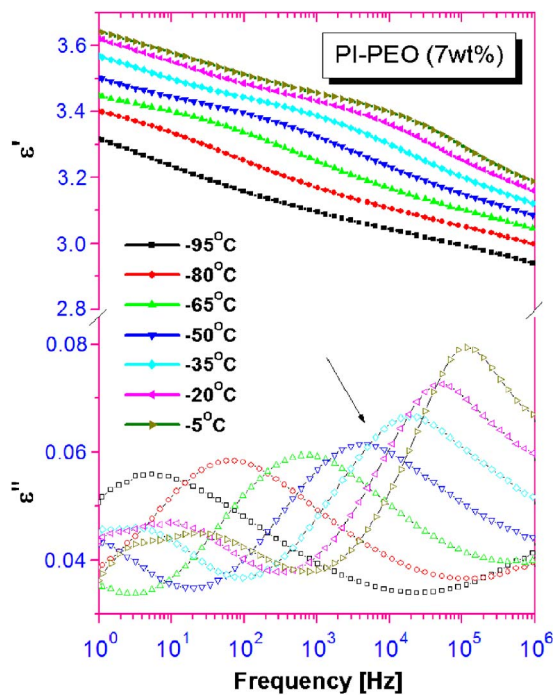
FIG. 3. (Color online) The frequency dependence on the dielectric constant of PI-PEO foamed films.

experiment results. As mentioned above, the magnitude of the γ relaxation decreases with increasing PEO content. Pissis *et al.* have reported that the γ relaxation of PI increases significantly in magnitude with increasing silica additives.[18] These results have been discussed in terms of an overall enhancement of small-scale molecular mobility by incorporation of silica nanodomains in PI, arising from loosened molecular packing of PI chains, as compared to pure PI. It should be noted in this connection that water uptake in PI was found to have the same effect as silica does on the γ transition of PI.[19] PEO used in our synthesis process only employ to enhance the free volume in PI. The decreasing magnitude of γ relaxation of PI-PEO films suggested that more free volume lead to small molecular mobility. The calculated activation energies of the β transition for 5 wt %
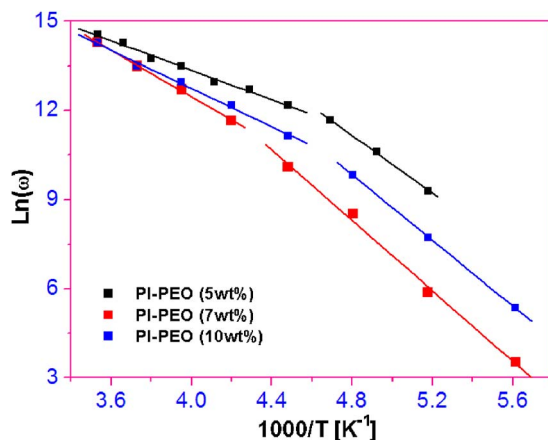
PEO, 7 wt % PEO, and 10 wt % PEO are 0.22, 0.34, and 0.28 eV, respectively. Pellegrino *et al.* suggested that the β transition in the PI is to be related to the noncooperative rotation of the phenylene unit, which occurs easily and at lower temperatures, and the rotation of the pyromellitic unit taking place in the higher temperature side of the transition.[17] The occurrence of these two different motions accounts for the broad and asymmetric profile of the β band. The Starkweather's theory predicts activation energies of 6.5 kcal/mol ($\sim$0.28 eV) and 10 kcal/mol ($\sim$0.43 eV) related to the phenylene unit and pyromellitic unit, respectively.[17] In our results, the activation energies of PI-PEO (0.22, 0.34, and 0.28 eV) are all close to the value of phenylene unit, suggesting that the rotation of phenylene unit plays more important roles. However, the intermolecular interactions may play a role in the actual relaxation process. In particular, it is well known that charge-transfer interactions are present in PI.

In summary, polyimide nanofoamed films have been prepared from the polyimide precursors (PMDA-ODA) and poly(ethylene oxide) (PEO) in N,N-dimethylacetamide. The dielectric constant decreases with increasing PEO content and a lower dielectric constant ($\varepsilon \leqslant 2.6$) has been achieved, suggests that PI-PEO nanofoamed films are very promising for next-generation interlayer low-k dielectric materials. The β and γ relaxation processes are observed in all the samples.

FIG. 4. (Color online) The experimental observation of the PI-PEO films with different PEO content.

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