6. Optical and Dielectric Properties at High-Frequency (20GHz) of Sulfur-Containing Polyimides

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Abstract: High-frequency insulating materials with a low dissipation factor (D_f) have attracted increasing attention. Polymer-based dielectrics combining a high dielectric constant (D_k) and a low Df are demanded for film capacitors and microstrip antennas. Polyimides (PIs) are promising candidates for such applications owing to their excellent thermal resistance, mechanical strength, and chemical stability. In particular, sulfur-containing PIs (S-PIs), incorporating sulfur atoms in their backbones, are expected to exhibit a high D_k due to the high atomic polarizability of sulfur atoms [1, 2]. However, their D_k and D_f at higher frequencies remain unclear. In this study, we synthesized a series of S-PIs (Fig.1) and investigated their dielectric properties at 20 GHz, including polarization analysis, humidity dependence, and water-sorption behaviors.

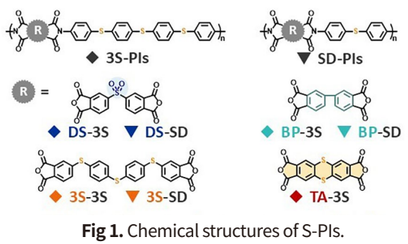

Fig 1. Chemical structures of S-PIs.

As the weight fraction of sulfur (S%) increases, the D_k and D_f of S-PIs generally increase and decrease, respectively. In particular, S-PIs containing 3S moiety (3S-PIs) exhibited higher D_k and lower D_f. The increased D_k is attributed to the enhanced electronic polarization resulting from higher S%, while the lower D_f may result from the reduced weight fraction of imide groups (Imide%) due to the heavy sulfur atoms, which also suppresses the dipole polarization [3]. Furthermore, the D_k and D_f of all S-PIs increase linearly with an increase in RH from 10% to 55 %. The slopes (hD_k and hD_f) of their linear approximation, representing RH sensitivity, are comparatively low for 3S-PIs, which is attributable to the lower electronegativity of sulfur atoms and the reduced Imide%. In addition, 3S-PIs containing thianthrene or sulfonyl moieties in the main chain (TA-3S and DS-3S) exhibit higher hD_k and hD_f compared to the other 3S-PIs. This originates from the expanded free volume due to their bent structures that promotes the sorption of water molecules. In conclusion, S-PIs, especially 3S-PIs, exhibit a favorable combination of high D_k, low D_f, and low humidity sensitivity, making them promising candidates for high-frequency dielectric applications.

Keywords: **Polyimide, Sulfur, Dielectric constant, Dissipation factor, High refractive index, Humidity dependence, Water sorption**

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18. 含酯基热塑性聚酰亚胺的热固改性及其挠性覆铜板的制备和性能

Preparation and property of thermosetting modification of ester-containing thermoplastic polyimide and the Flexible Copper Clad Laminates

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摘要：通过共缩聚的方法将含酯基结构的双 (4- 氨基苯基）对苯二甲酸酯（BAPT）引入到可溶性聚酰亚胺（PI）分子中，制备主链含酯基结构（Ph-O-C(=O)-）的热塑性聚酰亚胺（TPI）。由于活性酯在相关促进剂的作用下可与环氧树脂发生酯交换反应，因此使用双环戊二烯 / 苯酚缩水甘油醚（DCPD 环氧）对 TPI 进行热固改性，并将其制备成挠性覆铜板（FCCL）。首先，通过非等温 DSC 确定了由 DCPD 环氧改性 TPI 制备相应 FCCL 的固化工艺。然后通过对比测试发现：TPI 热固改性材料的热性能、尺寸稳定性和耐水性虽然略有变差但仍在可接受的范围之内，最重要的是其在 10 GHz 下介电常数从 3.00 下降到 2.81，且对应 FCCL 的的剥离强度为 2.06 N/mm，显著高于未改性 TPI 的 1.00N/mm。这种具有低介电常数、高粘接性能的基于 TPI 的热固化改性方法，为高性能柔性印制电路板（FPC）的发展提供了一种有效的途径。

关键词：热塑性聚酰亚胺，热固改性，环氧树脂，活性酯，挠性覆铜板

Abstract: A thermoplastic polyimide (TPI) containing reactive ester groups (Ph-O-C(=O)-) in the backbone was synthesized by incorporating bis(4-aminophenyl) terephthalate (BAPT) into a soluble polyimide molecular via copolycondensation. Since the active ester can undergo transesterification with epoxy resin under appropriate promoters, the obtained TPI was thermoset-modified by dicyclopentadiene/benzenephenol glycidyl ether (DCPD epoxy), and subsequently fabricated for flexible copper-clad laminate (FCCL). Non-isothermal differential scanning calorimetry (DSC) was first employed to optimize the curing process for preparing FCCL from the DCPD epoxy-modified TPI. Comparative analyses revealed that while the thermoset-modified TPI exhibited slightly reduced thermal properties, dimensional stability, and water resistance, these parameters remained within acceptable operational ranges. Notably, its dielectric constant at 10 GHz decreased from 3.00 to 2.81, while the peel strength of the corresponding FCCL reached 2.06 N/mm, which was significantly higher than that of the unmodified TPI of 1.00 N/mm. This TPI-based thermosetting modification strategy demonstrates a viable pathway for developing high-performance flexible printed circuit boards (FPC) with low dielectric property and enhanced interfacial adhesion.

Keywords: **Thermoplastic polyimide, thermosetting modification, epoxy resin, active ester, flexible copper clad laminate (FCCL)**

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