

基于长链烷基诱导效应的低介电低损耗有机材料综述

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摘 要: 5G/6G 高频通信技术的飞速发展, 对介电材料提出了前所未有的苛刻要求: 不仅需要极低的介电常数 ($D_k < 2.8$) 和介电损耗 ($D_l < 10^{-3}$), 而且需要具有良好的疏水性以使材料的介电性能得以长期保持。传统材料的本征介电性能已难以满足需求, 而造孔等后修饰策略则往往以牺牲力学性能为代价。本文系统论述了一种基于“长链烷基诱导效应”的介电材料设计新策略, 阐述了该策略通过自由体积效应、极性控制及陷阱机制降低介电常数与介电损耗的协同机理, 并重点介绍了该策略在苝基聚合物、烷基苯基聚合物及生物基腰果酚聚合物三大体系中的成功实践。基于该类材料良好的疏水性能, 本文亦探讨了其在保障介电性能长期稳定性方面的潜力。最后, 展望了该领域未来的发展趋势与面临的挑战。

关键词: 非氟芳基低介电材料; 长链烷基; 无氧介电材料; 高频通信; 苯并环丁烯

Review on low-dielectric and low-loss organic materials based on long-chain alkyl inductive effect

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Abstract: The rapid development of 5G/6G high-frequency communication technology has placed unprecedented demands on dielectric materials: they require an extremely low dielectric constant ($D_k < 2.8$) and dielectric loss ($D_l < 10^{-3}$). Moreover, new low-dielectric materials must possess excellent hydrophobicity to ensure the long-term stability of their dielectric properties. The intrinsic dielectric properties of traditional materials struggle to meet these requirements, while post-modification strategies like pore generation often sacrifice mechanical performance. This paper systematically discussed a novel design strategy for dielectric materials based on the “long alkyl chain-induced effect”, elaborated the synergistic mechanism of reducing the dielectric constant and loss through free volume effects, polarity control, and trap mechanisms, and emphatically introduced successful implementation in three major polymer systems: fluorene-based polymers, alkylphenyl polymers, and bio-based cardanol polymers. In view of the excellent hydrophobic performance of the as-designed materials, this paper also discussed their potential in ensuring the long-term stability of dielectric properties. Finally, the future development trends and existing challenges in this research field were prospected.

Key words: non-fluorinated alkyl low-dielectric materials; long alkyl chains; oxygen-free dielectric materials; high-frequency communications; benzocyclobutene

0 引言

5G 通信时代, 信号传输向高频化 (毫米波段)、高速化 (理论传输速率可达 10 Gbps) 和低时延 (目标为 1 ms) 发展^[1-2], 对介质材料的介电性能提出了极高的要求。在 4G 及之前的通信时代, 信号传输频率相对较低, 传统高分子材料尚能满足需求。然而, 当传输频率提升至 5G 使用的 6 GHz 乃至毫米

波 (如 28 GHz) 频段时, 信号的趋肤效应加剧, 传输路径更易受干扰, 且介电损耗 (D_l) 急剧升高, 导致信号完整性下降、传输距离缩短及设备发热严重^[1-3]。表 1 列出了常见商用介电材料的介电性能, 可见传统介电材料在性能上已越来越难以满足新一代电子元器件的战略定位。虽然聚丙烯 (PP) 和聚四氟乙烯 (PTFE) 这一类聚烯烃因拥有低极性的烷基骨架, 表现出较低的介电常数 (D_k) 和 D_l , 能够较好的满足介电性能的需求, 但耐热性能差、加工困难或

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机械强度不足等缺点,限制了它们在高端领域的应用^[4-11];而耐热性能优异的酚醛树脂^[12-15]、双马来酰亚胺树脂^[16-17]等则因 D_k 和 D_f 偏高,导致信号传输损耗严重。行业内对5G材料有着明确的性能指标要求^[18],例如手机天线材料要求 $D_k < 3.0$ ^[19],同时要求 $D_f < 0.005$,高端应用领域则要求 $D_f < 0.001$ ^[20-22]。已经商业化的氰酸酯^[23]、聚(2,6-二甲苯醚)(PPO)^[24]和苯并环丁烯与二乙烯基硅氧烷(双封头)的偶联产物(DVS-BCB)^[25]等虽然能够基本满足介电性能的需求,但氰酸酯需要解决长期储存稳定性和提高耐热性能的问题,PPO亦需要克服尺寸稳定性差的缺点。对于DVS-BCB而言,如何降低成本,减少二聚体副产物的生成量,也是亟待解决的问题。因此,研发同时满足优异介电性能和耐高温性能要求的聚合物具有非常重大的价值和意义。

表1 常见商用介电材料的 D_k 与 D_f (20℃,1 MHz)^[23-24,26-32]

Table 1 D_k and D_f (20℃, 1 MHz) of common commercial dielectric materials^[23-24,26-32]

材料名称	D_k	D_f
酚醛树脂	5.0	0.10
环氧树脂	4.1	0.025
双马来酰亚胺	3.8	0.010
氰酸酯树脂	2.8	0.008
聚苯醚	2.7	0.003 2
聚酰胺	3.7	0.016
聚酯	3.0	0.016
聚乙烯	2.2	0.0003
聚酰亚胺	3.4	0.010
聚丙烯	2.1	0.000 3
聚四氟乙烯	2.1	0.000 2
聚三氟氯乙烯	2.5	0.017
聚氨酯	7.1	0.060
聚氯乙烯	4.0	0.14
聚氟乙烯	7.4	0.009

为突破性能瓶颈,研究者们曾探索通过造孔的方式引入空气来降低整体介电常数^[33-37]。造孔的核心原理在于通过引入介电常数接近1.0的空气,利用简单的混合介质模型,显著降低材料的整体介电极化响应,从而有效提升材料的低介电性能。尽管造孔技术在一定范围内有效,但其也存在固有的局限性:无论是化学造孔剂的脱除还是生物基的梯度孔形成,造孔本质上是在材料中引入结构缺陷,会不可避免地导致材料的力学性能下降^[38-39]。此外造孔的工艺复杂且对参数调控极为敏感,造孔剂的形

状和含量直接影响孔隙的形状和分布,工艺不当极易导致孔径分布不均或孔结构塌陷,进而引起电场畸变,反而增加材料的介电损耗或降低击穿强度。特别需要指出的是,造孔可能导致材料的吸水率升高,会劣化材料在潮湿环境下的介电性能。

在此背景下,本课题组创新性地提出了“长链烷基的诱导效应改善材料介电性能”的理论。该理论的核心理念是将长链烷基作为理想的“低介电沼泽”,精准引入到刚性的苯并环丁烯树脂骨架中,从而完成分隔分子主链,降低整体极化效应的目的。这种策略并非简单的物理混合,而是在分子尺度上进行精确的设计:大自由体积的长链烷基能在不破坏聚合物连续相的前提下,有效扩大链间距,模拟并实现了造孔技术降低材料介电常数的效果;同时,长烷基侧链低极性的本质继承了聚烯烃低损耗的优点,烷基链区域本身还可作为电荷陷阱,进一步抑制电导损耗。更为重要的是,刚性的芳香主链完美地补偿了聚烯烃耐热性能的不足。通过这种多机制协同,成功绕过了传统方法的固有缺陷,为制备下一代高性能低介电材料开辟了一条全新的道路。本文将详细分析“基于长链烷基的诱导效应”的作用机理,并展示将这一理论应用于实际研究的突破性工作,最后展望基于长链烷基诱导效应的聚合物材料的未来发展趋势和可能面临的挑战。

1 长链烷基诱导效应调控介电性能的机制研究

1.1 自由体积效应与密度调控机制

自由体积效应指的是通过引入刚性或体积庞大的基团,增加高分子链之间未被占据的固有空间,这种设计减少了单位体积内可极化的原子数量和电子密度^[40-42]。当电场施加到材料上时,这些“空荡荡”的区域不会发生有效的响应,从而从整体上降低了材料的极化能力,使介电常数下降。同时,被撑开的分子链其运动也受到限制,链段摩擦产生的弛豫损耗随之降低^[42-44]。

根据经典的Clausius-Mossotti方程, D_k 与单位体积内的偶极子数量(N ,与材料密度正相关)和分子极化率(α)直接相关,如式(1)所示。

$$\frac{D_k - 1}{D_k + 2} = \frac{4\pi}{3} N\alpha \quad (1)$$

从式(1)可以看出, D_k 与 N 成正比。长链烷基作为“低介电沼泽”,能有效增大聚合物链间距,降

低堆叠密度(如图1所示),且烷基侧链的引入增大了材料的自由体积,减少了单位体积内可极化的芳香环等高频极化单元的数量(N),从而导致 D_k 降低。

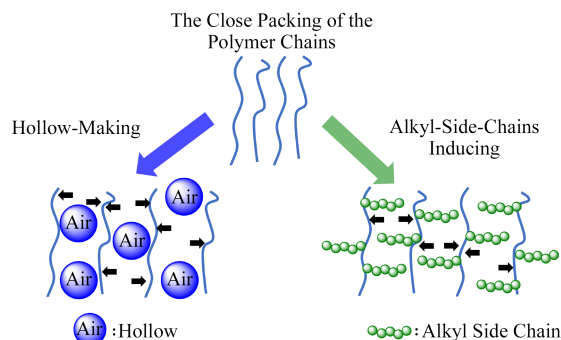


图1 材料造孔与烷基侧链诱导增大聚合物链间距示意图

Fig.1 Schematic diagram of the spacing between polymer chains increased by making hollows in the material and inducing alkyl side chains

许多研究者为了增加材料的机械强度会选择向聚合物中引入芳香族化合物的结构,但这也导致分子链之间表现出明显的 π - π 堆叠效应,增大分子链之间的堆叠密度,从而劣化材料的低介电性能。例如LOU X J等^[45]合成了一种新型的含芳香侧基介电聚合物(PNB2APS),并通过与金刚烷酰化芳族烯(NBAd)共聚,有效削弱了芳香族介电聚合物的强堆积作用,进一步降低了芳香族介电聚合物在高电场下的电导率损失,由此产生了一种新的共聚物P(NB2APS-co-NBAd),如图2(a)所示。作者还进行了分子动力学模拟,发现PNB2APS由于侧基较大的位阻,导致共聚物的密度仅为1.18 g/cm³,自由体积分数仅为40.2%。由于共聚了少量的NBAd, NB2APS-co-NBAd的密度下降至1.12 g/cm³,自由体积分数增加到41.6%。金刚烷基团让芳香侧链间距从6.8 Å扩大到7.4 Å,减弱了 π - π 堆叠效应,如图2(b)所示。当NBAd的摩尔分数为5%时, P(NB2APS-co-NBAd)表现出最低的 D_f (1 kHz)。

1.2 极性控制与极化行为调控机制

D_f 主要来源于交变电场中偶极子的滞后响应(极化损耗)和载流子的定向迁移(电导损耗)^[42,46]。烷基链由低极性的C-C与C-H键构成,其键矩远小于聚合物中常见的-C=O、-C-O-C-、-OH等强极性基团。烷基链作为低极性单元,不仅降低了材料的本征电子极化率,还抑制了偶极子在高频下的转向极化,是获得低 D_f 的关键。

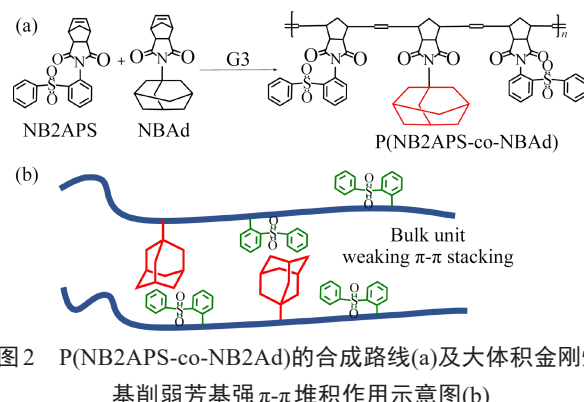


图2 P(NB2APS-co-NBAd)的合成路线(a)及大体积金刚烷基削弱芳基强 π - π 堆积作用示意图(b)

Fig. 2 Synthesis route of P(NB2APS-co-NBAd)(a) and schematic diagram of bulky adamantyl groups weakening the strong π - π stacking of aromatic groups(b)

通过大量的实验发现,聚合物中的氧原子尽管能够提高聚合物与基体的粘合力,但它对聚合物的 D_f 有负面影响^[47-48]。本课题组^[49]研究了两种基于含氧和含硅的氟化物固化后的介电性能(如图3所示),结果表明,不含氧原子的单体固化后表现出10⁻⁴量级的 D_f ,而含氧材料的 D_f 则仍保持在10⁻³量级,表明氧元素对聚合物的 D_f 具有重要影响。

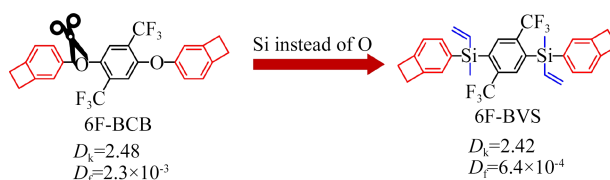


图3 含氧和含硅材料固化后的介电性能比较

Fig.3 Comparison on dielectric properties of oxygen-containing and silicon-containing materials after curing

1.3 载流子输运与陷阱机制

在高温或高频电场下,电导损耗成为介电损耗的主导因素,其机制主要包括普尔-弗伦克尔发射、跳跃电导和肖特基发射^[42,44,46,50-51]。烷基侧链的引入能够有效抑制这些过程。聚合物中松散堆积的长烷基链区域,其局部的电子云密度与有序区域不同,可形成有效的电荷陷阱。交联点本身可作为深陷阱捕获载流子,而烷基链形成的纳米微区同样具备此功能。载流子在烷基链形成的陷阱之间跳跃或发射时,需要克服更高的能垒,增加了载流子输运的路径曲折度和活化能,有效抑制了高温高电场下的电导损耗^[52-55]。

1.4 疏水性与界面稳定机制

环境湿度是导致材料介电性能劣化的重要因素。水分子($D_k \approx 80$)的强极性会显著增加材料的整

体极性和介电损耗,水分在材料内部的累积会大幅缩短介电材料的使用寿命。因此材料的本征强疏水性是保障其介电性能长期稳定性的关键^[51, 56]。长链烷基能在材料表面或界面形成致密排列的分子层,阻挡水分子接触和扩散至材料内部。低表面能的烷基链(如甲基-CH₃、亚甲基-CH₂-)富集于材料表面,能显著降低材料表面能,削弱其对水分子的吸引力^[57],从而维持材料在湿热环境下的介电性能长期稳定性。

2 基于长链烷基的诱导效应合成的低介电和超低介损有机材料

基于对长链烷基诱导效应作用机制的深入理解,本课题组以苯并环丁烯为固化基团^[58-61],合成了一系列“全烃”聚合物,并研究了这些聚合物的介电性能,用实际数据充分印证了提出的理论。下面根据聚合物主链的化学结构,系统梳理并对比不同体系的研究进展,揭示长链烷基诱导效应的普适性与特殊性。

2.1 苧基聚合物体系

苧基聚合物具有刚性的平面共轭结构和高热稳定性,是理想的高频低介电材料骨架。本课题组^[62]系统研究了烷基链长度在该体系中的调控作用,如图4所示,在苧-苯并环丁烯(FBCB)体系中,随着侧链从丁基(C₄)增至十八烷基(C₁₈), D_k 从2.62单调下降至2.45, D_f 也保持在 5.0×10^{-4} 以下的超低水平。这主要归因于长链烷基对苧环紧密 π - π 堆积的有效阻隔和自由体积的持续增大。

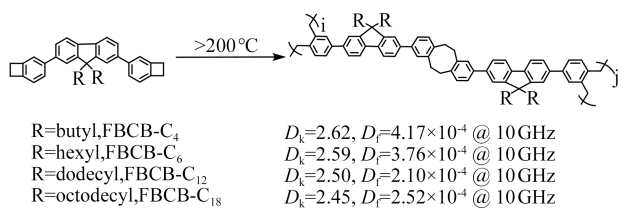


图4 苧基单体分子聚合示意及单体固化后的介电性能
Fig.4 Schematic of fluorene-based monomer polymerization and dielectrical properties after monomer curing

此外,我们还研究了芳基基团作为侧链的苧基聚合物^[62](固化FB和PDFB,如图5所示)。通过对比苧基聚合物的介电性能可以明显看出,尽管具有相似的苧基主链,固化的FB在0.15~30 MHz频率范围内表现出低 D_k 值(2.70)和高 D_f 值(0.028)。这些数据表明烷基侧链引入对聚合物的介电性能有显著的影响。

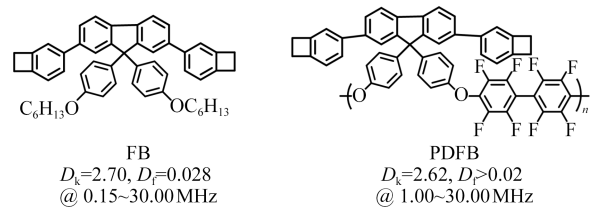


图5 其他苧基单体及固化后的树脂介电性能
Fig.5 Other fluorenyl-based monomers and dielectric properties of the cured resin

从应用前景来看,介电材料的低吸水性是目前备受关注的指标,因为它保证了介电性能的稳定性,尤其是在潮湿的应用条件下。通过监测固化后的树脂在沸水中浸泡一定时间后的质量变化来研究其吸水性,结果如表2所示。从表2可以看出,PFBCB-C₄在沸水中浸泡72 h后吸水率为0.34%,而含有较长烷基链的PFBCB-C₁₂和PFBCB-C₁₈的吸水率低至0.06%,这些数据表明较长的烷基链不仅为树脂带来更好的介电性能,也带来较低的吸水性。此外还测量了4种固化后的树脂在沸水中浸泡后的介电性能(10 GHz),如表2所示。

表2 固化后树脂的吸水率、水接触角和吸水后介电性能
Table 2 Water absorption, water contact angle and dielectric properties after water absorption of the cured resin

聚合物	吸水率/%	D_k	水接触角/(°)
PFBCB-C ₄	0.34	2.66	94
PFBCB-C ₆	0.28	2.64	95
PFBCB-C ₁₂	0.06	2.56	97
PFBCB-C ₁₈	0.06	2.48	98

为了理解PFBCB-C₁₂和PFBCB-C₁₈与PFBCB-C₄和PFBCB-C₆相比显示出非常低吸水率的原因,表2中还列出了4种固化后的树脂膜表面上的水接触角,4种固化树脂的水接触角分别为94°、95°、97°和98°。如此大的水接触角意味着4种固化后的树脂具有良好的疏水性,可以保障低介电材料介电性能的长期稳定性。

2.2 烷基苯基聚合物体系

为剥离复杂主链结构的影响,本课题组^[41]还设计了以简单苯环为核心的模型体系。该研究进一步验证了长链烷基诱导效应的普适性,并揭示了新的见解。环烷基侧链和单链烷基侧链均可对固化后的树脂介电性能产生影响,与之前报道的烷基取代的苧基聚合物系列的情况类似。相比于烷基取代的苧基聚合物系列的研究,烷基苯基聚合物系列

研究创新地引入了非链型烷基基团——环己基作为烷基侧链,系统对比了对称双己基苯(BBCB- C_6)与不对称的己基-环己基苯(BBCB-cyclo- C_6)之间的性能差异,如图6所示。研究表明,刚性的环己基侧链能显著提升材料的 T_g ($>350^\circ\text{C}$) 和热尺寸稳定性 (CTE 降至 $86\times 10^{-6}^\circ\text{C}^{-1}$),且其对介电常数的影响与线性己基链相当,为在保持低 D_k 的同时大幅改善材料的耐热性提供了新思路。

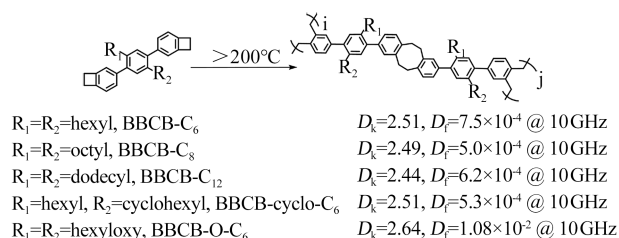


图6 苯基烷基单体分子聚合示意及单体固化后介电性能

Fig.6 Schematic of phenyl alkyl monomer polymerization and dielectrical properties after monomer curing

文献[41]同样考虑了含极性原子长链(烷氧基)对材料介电性能的影响。将烷基($-C_6H_{13}$)替换为烷氧基($-O-C_6H_{13}$)后,固化后树脂的 D_k 从 2.51 升至 2.64, D_f 急剧增大至 1.08×10^{-2} 。结果表明,追求“全烃”化学结构,避免引入任何高极性杂原子,是实现超低损耗的关键。PBBCB- C_6 ~PBBCB- C_{12} 、PBBCB-cyclo- C_6 、PBBCB-O- C_6 固化物的密度依次为 1.028、1.012、0.956、1.032、1.064 g/cm^3 。对于 PBBCB- C_6 ~PBBCB- C_{12} 固化物,其密度随着烷基侧链长度的增加而降低,这一结果表明,较长的烷基侧链确实可以增大聚合物链的自由体积,导致聚合物的密度降低。相对应地,这些固化物的 D_k 值随着烷基侧链的延长而降低。然而,含有氧原子的 PBBCB-O- C_6 因为更紧密的链间堆积(密度为 1.064 g/cm^3),使得 PBBCB-O- C_6 中单位体积内氧原子的数量增加,导致聚合物整体极性增加,表现为更高的 D_k 和 D_f 值。这一结果再次印证了“全烃”化学结构在自由体积控制和极性控制双机制作用下的优越性。

本课题组还通过测量固化后树脂的吸水率来表征其疏水性,结果如表3所示。所有固化后的树脂在沸水中浸泡 72 h 后,其吸水率均低于 0.20%。对于具有全烷基侧链的聚合物,其吸水率随着侧链长度的增加而降低。在这些聚合物中,PBBCB- C_{12} 表现出最低的吸水率(0.02%)。将固化后树脂在沸

水中保持 72 h 后,还研究了固化后的树脂 D_k 值变化。从表3可以看出,含氧 PBBCB-O- C_6 的吸水率与不含氧 PBBCB- C_6 的吸水率相同,但在一定的湿度条件下,聚合物的 D_k 值仅略有增加,再一次印证了良好的疏水性保证了固化后的树脂即使在潮湿条件下也能保持较低的介电性能。在许多情况下,含氧聚合物的吸水率通常比不含氧聚合物的吸水率高,这一现象表明烷基侧链对固化后的树脂吸水率起主导作用,而对于具有不对称烷基侧链的 PBBCB-cyclo- C_6 ,其较高的吸水率可能是由于刚性的六元环己基引起的侧链松散堆积导致。

表3 固化后树脂的吸水率和吸水后介电性能(10 GHz)

Table 3 Water absorption and dielectric properties (10 GHz) after water absorption of the cured resin

聚合物	吸水率/%	D_k	D_f
PBBCB- C_6	0.10	2.54	1.29×10^{-3}
PBBCB- C_8	0.05	2.51	7.9×10^{-4}
PBBCB- C_{12}	0.02	2.45	8.8×10^{-4}
PBBCB-cyclo- C_6	0.25	2.55	1.88×10^{-3}
PBBCB-O- C_6	0.10	2.66	9.72×10^{-2}

2.3 生物基腰果酚聚合物体系

利用可再生资源开发生物基低介电材料,可以兼具环境友好性与性能优势^[47,64-72]。鉴于生物基腰果酚(具体结构如图7所示)含有长的烯基侧链,将其氢化后,可以得到含有长烷基链的酚,而这种酚转化的热固性材料是否可以利用长链烷基诱导效应来合成高性能低介电材料仍有待研究。

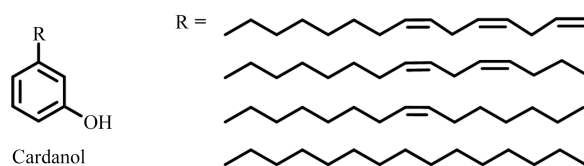


图7 腰果酚结构

Fig.7 Structure of cardanol

从腰果酚出发,本课题组^[71]研究并合成氢化腰果酚单体,如图8所示,并对其固化后的树脂介电性能进行研究。结果显示,含氢化腰果酚的单体 HCBCB 同样显现出长链诱导效应,其固化产物在 10 GHz 下的 D_f 依然在 10^{-4} 量级,而当侧链换成短的甲基时, D_f 升高为 10^{-3} 量级。得益于长烷基链构建的强疏水微环境,HCBCB 固化产物在沸水中浸泡 96 h 后吸水率仅为 0.16%,远低于对照样品 1-BCB 的 0.63%,凸显了其在苛刻环境下应用的潜力。研究

发现,在沸水中浸泡 96 h 后,HC-BCB 固化产物在 10 GHz 频率下的 D_k 为 2.6, D_f 为 1.38×10^{-3} ,而对照样品 1-BCB 的固化产物则表现出较高的 D_k (2.87) 和 D_f (6.45×10^{-3})。对比固化产物在沸水中浸泡前后的介电数据,可见 HC-BCB 固化产物的 D_f 相较浸泡前增加了约 3 倍,而 1-BCB 固化产物的 D_f 相较浸渍前增加了近 5 倍。这些数据进一步说明长烷基侧链的诱导效应对提高无氧芳基聚合物的介电性能是有益的,同时也说明烷基侧链良好疏水性可以保障聚合物介电性能的长期稳定,延长材料的使用寿命^[72-74]。因此材料自身的强疏水性是保障介电性能长期稳定性的关键。这是因为长链烷基能在材料表面或界面形成致密排列的分子层,阻挡水分子接触和扩散至材料内部。低表面能的烷基链(如甲基- CH_3 、亚甲基- CH_2 -)富集于材料表面,能显著降低材料表面能,削弱其对水分子的吸引力,从而维持了材料介电性能在湿热环境下的长期稳定性。

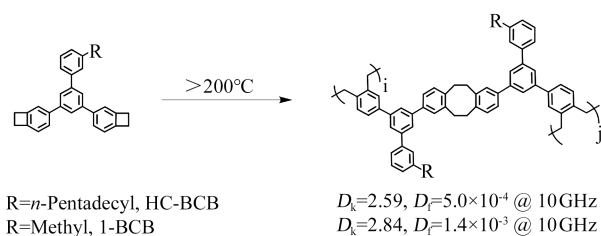


图8 氢化腰果酚基单体及固化产物的介电性能

Fig.8 Hydrogenated cardanol monomers and dielectrical properties of the cured products

3 总结与展望

本文系统描述了基于长链烷基诱导效应合成低介电常数与超低介电损耗有机材料的设计理念、作用机制及其在苄基、烷基苯基和生物基腰果酚三大聚合物体系中的成功实践。通过引入长链烷基作为“低介电沼泽”,实现了自由体积效应、极性控制、陷阱机制与疏水界面稳定性的多重协同,有效解决了传统材料无法满足新型高频通信器件介电性能要求的问题。本课题组基于长链烷基诱导效应所开发的材料在 10 GHz 频率下展现出 D_k 最低至 2.45、 D_f 最低至 2.10×10^{-4} 的优异性能,并具备卓越的疏水性与湿热稳定性,为下一代高频通信器件提供了理想的介电材料候选体系。

在 5G/6G 移动通信、毫米波雷达等领域,对基板材料的 D_k 和 D_f 将会越来越严苛的要求。本课题组开发的烷基侧链聚合物,正是满足下一代高频高

速通信需求的理想候选材料,但其走向大规模应用仍面临一些挑战。首先该策略虽然在介电性能上取得突破,但长烷基链的引入可能增加合成步骤及纯化的难度,影响材料的经济性与规模化制备。未来需在分子设计上进一步优化,在保持低介电性能的同时,提升合成效率与工艺兼容性。另外一个突出的问题是非极性的全碳氢树脂与基底和铜箔的附着力较低^[76-77],需要在改善材料介电性能的同时,兼顾其力学性能。已知氧原子可以有效提高聚合物与基体的粘附性,因此,如何保持材料粘附性和介电性能的平衡,即氧元素在材料中达到多少量时,材料既具有良好粘附性,又具有优异介电性能,是研究者今后的努力方向。

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