

基于多维协同的聚合物基复合薄膜的高温储能性能

谭艺鹏^{1,3}, 高 航^{1,3}, 冯梓文^{1,3}, 鲁霖飞^{1,2,3}, 邓家裕¹, 姚玲敏^{1,2,3}, 邓青林^{1,3}

(1. 广州大学物理与材料科学学院, 广州 510006; 2. 广东腐蚀科学与技术创新研究院, 广州 510275; 3. 广州大学黄埔研究院先进信息材料研究中心, 广州 510275)

摘 要: 不同维度的无机填料对聚合物基电介质的储能性能有着极大的影响。根据多维协同的理念, 将不同维度的氮化硼纳米片(BNNS)和一维二氧化钛纳米纤维(1DTiO₂)引入到聚酰亚胺(PI)中, 利用流延法制备了(BNNS-TiO₂-BNNS)/PI 复合膜(BTB/PI 复合膜)。结果表明: BTB/PI 复合膜在 10³~10⁶ Hz 和 25~200 °C 的范围内介电常数保持稳定, 介电损耗小于 0.025。最佳填料比的 BTB/PI 复合膜在 200 °C 下具备 3.04 J/cm³、88% 的高储能性能。本工作提出的聚合物基复合膜, 为高温聚合物的研究制备提供了一条行之有效的策略。

关键词: 复合材料; 多维材料; 介电性能; 高温储能性能

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聚合物电介质因为其柔韧性、成本低、高工作电压、耐腐蚀性、自愈性等优点, 被广泛应用于电能的转换与存储中^[1]。但是聚合物电介质的介电常数低(<10), 导致其储能密度低, 在实际应用必须中保持大体积^[2]。同时聚合物电介质通常耐高温能力差, 如商用的双向拉伸聚丙烯(BOPP)的使用温度必须在 105 °C 以下。然而在电动汽车、油气勘测、风力发电等工作温度达到 105 °C 以上, BOPP 在使用过程中必须使用冷却系统^[3]。由于聚合物本身的限制导致的大体积、额外的冷却系统不符合现代储能器件轻量化、节能化的设计理念^[4]。因此急需一款能够同时具备高储能性能和耐高温的聚合物基电介质。

聚酰亚胺(PI)、聚碳酸酯(PC)、聚醚酰亚胺(PEI)、聚萘二甲酸乙烯酯(PEN)、聚醚醚酮(PEEK)等聚合物内部有着芳香环、杂芳香环等刚性组分, 具备高玻璃化转化温度、优异的机械性能^[5]。但在高电场和高温下, 聚合物内部泄漏电流呈指数增长,

导致储能密度和效率的急剧降低^[6]。目前, 在提升有机无机电介质高温储能性能的研究中, 都是将单一维度(零维、一维、二维)无机填料引入聚合物。因为零维纳米颗粒的高比表面积和一维纳米线(棒)状的高长径比, 对复合材料极化能力的提高尤为明显^[7]。但对于零维纳米颗粒和一维纳米线(棒)结构的填料, 电场主要集中在它们的顶点周围, 这容易形成击穿路径, 从而降低耐击穿场强(E_b)和增加漏电流, 导致储能密度和效率的降低^[8]。在温度达到 150 °C 以上时降低得更为明显。例如 Fan 等^[9]通过静电纺丝法制备了 Ba(Zr_{0.79}Ti_{0.21})O₃ 纳米棒(BZTNFs), 并将其引入 PEI 中, 制备了 BZTNFs/PEI 复合膜, 在常温下获得了 6.05 J/cm³、94.4% 的高储能密度和高效率, 但在 150 °C 的高温下储能效率下降到 54.6%。二维材料是指具备高纵横比和横向尺寸的材料^[10]。将宽禁带的无机填料设计为二维结构作为绝缘屏障引入到聚合物中来提高耐击穿场强^[11]。如 Chen 等^[12]采用溶液浇铸法制备了含有

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第一作者: 谭艺鹏(1998—), 男, 硕士研究生。

通信作者: 姚玲敏(1987—), 女, 博士, 副教授;

邓青林(1990—), 男, 博士, 副教授。

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First author: TAN Yipeng (1998—), male, Master candidate.

E-mail: 1693433393@outlook.com

Correspondent author: YAO Lingmin (1987—), female, Ph.D., Associate Professor.

DENG Qinglin (1990—), male, Ph.D., Associate

Professor.

E-mail: Lingminyao@gzhu.edu.cn; qldeng@gzhu.edu.cn

二维氮化硼纳米片(BNNS)的 PEI 复合膜。在室温下 BNNS 含量为 4%(体积分数)的复合膜表现出极高的击穿强度($E_b \sim 700$ MV/m)及高储能效率($\eta \sim 93.6\%$)。同时在 150 °C 下, 击穿强度和储能效率保持在 500 MV/m 和 90.1%。但是复合膜的介电常数(ϵ_r)在 10³ Hz 下仅从纯 PEI 的 3.26 略微上升到含有 8% (体积分数) BNNS 含量的复合膜的 3.46。因此, 引入的单一维度填料倾向于增强复合材料的绝缘或极化的一种性质, 这限制了储能密度的进一步改善^[13]。

本文根据多维协同的理念, 利用流延法制备了(BNNS-TiO₂-BNNS)/PI 三明治结构复合膜(记为 BTB/PI 膜)。其中将高介电常数($\epsilon_r=110$)的二氧化钛(TiO₂)设计成一维纳米纤维结构, 并与 PI 复合作为 BTB/PI 膜的中间层。氮化硼纳米片(BNNS)是电绝缘和导热的, 其禁带宽度可达 6 eV, 耐击穿电场可达 800 MV/m^[14]。BNNS 的面内热导率可以达到 2 000 W/(m·k), 而体积较大的氮化硼(BN)粉体仅有大约 400 W/(m·k)^[15]。因此, 将 BNNS 与 PI 复合作为 BTB/PI 膜的绝缘、导热外层。结果显示, BNNS 体积分数为 7%、TiO₂ 体积分数为 1.5% 的 BTB/PI-7 复合膜获得最佳的储能性能。在 25 °C 下其储能密度高达 4.61 J/cm³(@465 MV/m), 是纯 PI 膜 2.21 J/cm³(@380 MV/m)的 208.6%。在 200 °C 下能够保持 3.04 J/cm³(@380 MV/m)的高储能密度、较纯 PI 膜 1.48 J/cm³(@335 MV/m)提升 206.1%, 同时储能效率保持在 88% 的高水平。在 200 °C, 其优异的储能性能超过了目前绝大多数有机无机电介质, 如 BNNS@BT-PBO 的 2.24 J/cm³^[16]、BTNFs/PI 的 1.74 J/cm³^[17]、S-P-S-2@200 °C 的 1.75 J/cm³^[18]。因此, 基于多维协同设计的 BTB/PI 复合膜为高温储能性能研究提供了一个行之有效的方法。

1 实验

1.1 材料

聚乙烯吡咯烷酮(PVP, 1300000, 阿拉丁)、钛酸四丁酯(AR, 阿拉丁)、乙酰丙酮(AR, 阿拉丁)、氮化硼(99.9%, 阿拉丁)、聚酰亚胺(PI, Matrimid 5218, 杜邦)、N, N-二甲基甲酰胺(DMF, AR, 阿拉丁)、乙醇(AR, 阿拉丁)。

1.2 氮化硼纳米片制备方法

通过液相剥离法制备的 BNNS, 剥离前后能够保持晶体结构的完整性^[19]。制备步骤: 取一定量的氮化硼粉末加入到 250 ml 的 DMF 中利用超声破碎

机震荡 24 h; 随后离心提取上清液烘干即可得到二维氮化硼纳米片材料。

1.3 二氧化钛纳米纤维制备方法

以钛酸四丁酯为钛源, 乙酰丙酮为防水解螯合剂, PVP 为助纺剂, 乙醇为溶剂, 配置二氧化钛纺丝胶体, 利用静电纺丝法制备二氧化钛纺丝毡, 将其 700 °C 烧结 3 h 后即可得到一维二氧化钛纳米纤维(1DTiO₂)。为改善 1DTiO₂ 在聚合物的相容性和分散性, 使用盐酸多巴胺进行表面改性。

1.4 BTB/PI 复合薄膜制备方法

分别配置不同体积比含量的 BNNS/PI 和 1DTiO₂/PI 的涂覆胶体, 按 BNNS/PI 作为上下层, 1DTiO₂/PI 作为中间层制备三明治结构复合薄膜。本团队之前的探索已证明体积分数为 1.5% 1DTiO₂ 为最佳比例。为探究最佳 BNNS 的填料比, 改变其与 PI 的体积分数为 3%、5%、7%、10%, 并将对应复合薄膜记为 BTB/PI-3、BTB/PI-5、BTB/PI-7、BTB/PI-10。

1.5 表征与测试

使用 PANalytical PW-3040-60 型 X 射线衍射仪, 对 BNNS 和 1DTiO₂ 进行结构、成分等的定性分析; 使用 JSM-7001F 型场扫描电子显微镜观测 BNNS、1DTiO₂ 的结构形貌。使用 Apreo 2S 型场发射扫描电子显微镜观测与测量复合膜截面情况与厚度; 使用同果科技的高低温介电温谱测试系统, 测试膜的频率、温度依赖性; 使用准静态 d33 测试仪、Trek HV 电压放大器、高低温测试平台组成的储能性能测试平台, 测试电介质薄膜在不同电压、温度下的电滞回线。

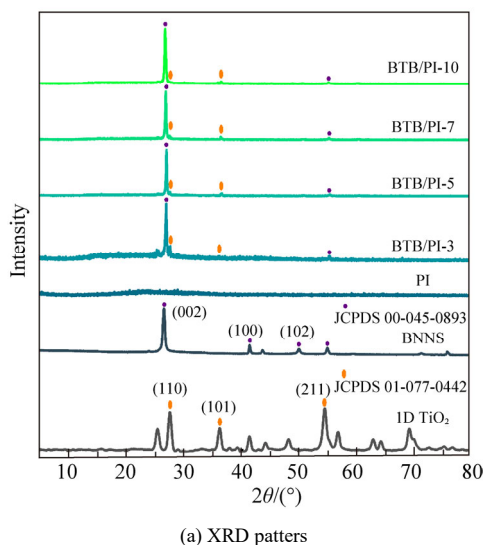
2 结果与分析

2.1 表征

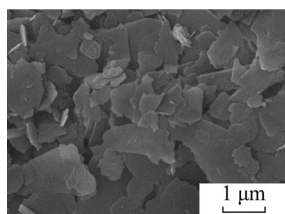
由图 1a 可见, BNNS 三强峰与标准卡片(JCPDS 00-045-0893)对应, 其晶体结构为六方型氮化硼。由图 1b 可见, BNNS 微观结构为片状结构; 由图 1a 和图 1c 可见, 1DTiO₂ 晶体结构为四方金红石型二氧化钛(JCPDS 01-077-0442), 微观结构为一维线状纤维(见图 2d), 且纤维连续性好, 无断裂。复合膜的 XRD 谱图较纯 PI 膜出现了 BNNS 和 1DTiO₂ 的衍射峰(见图 1a), 证明复合膜中 BNNS 和 1DTiO₂ 的存在。

图 2 为 BTB/PI-3、BTB/PI-5、BTB/PI-7、BTB/PI-10 复合膜经过液氮脆断后的 SEM 照片。由图 2 可见, SEM 测得复合膜的厚度分别为 22.40、25.36、24.34、25.36 μm ; 截面均匀致密、无明显孔

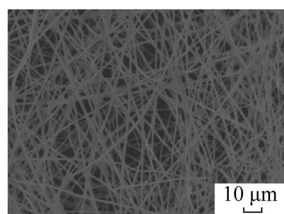
洞、分层明显。BNNS 分布在复合薄膜的外层、二氧化钛纤维分布在复合薄膜的中间范围，证明了复合薄膜的 3 层结构。



(a) XRD patterns



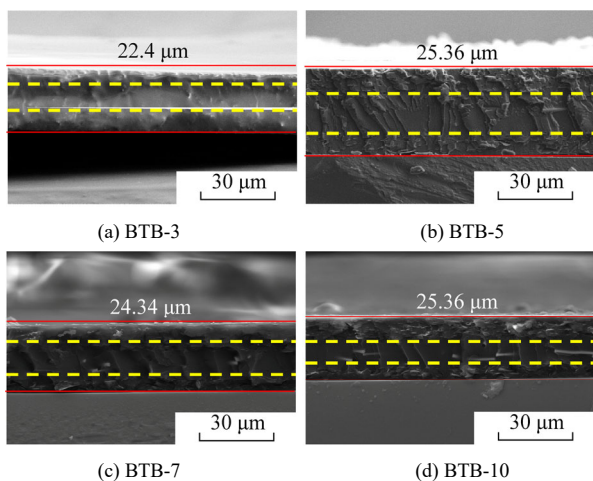
(b) SEM image of BNNS



(c) SEM image of 1DTiO2

图1 BNNS、1DTiO₂、纯PI膜和复合膜的XRD谱；BNNS和1DTiO₂的SEM照片

Fig. 1 XRD spectra of BNNS, 1DTiO₂, pure PI film and composites. SEM images of BNNS and 1DTiO₂



(c) BTB-7

(d) BTB-10

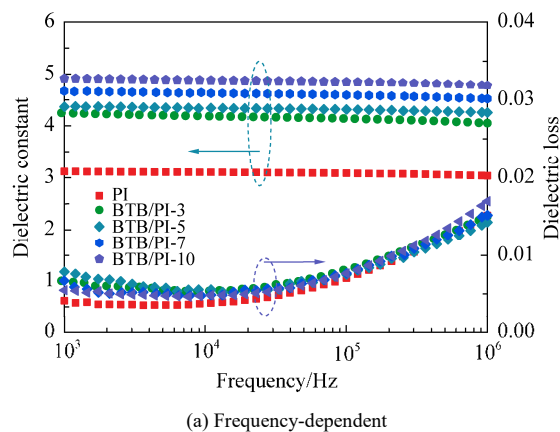
图2 BTB/PI-3、BTB/PI-5、BTB/PI-7和BTB/PI-10的SEM截面图

Fig. 2 SEM cross-sections of BTB/PI-3, BTB/PI-5, BTB/PI-7, and BTB/PI-10

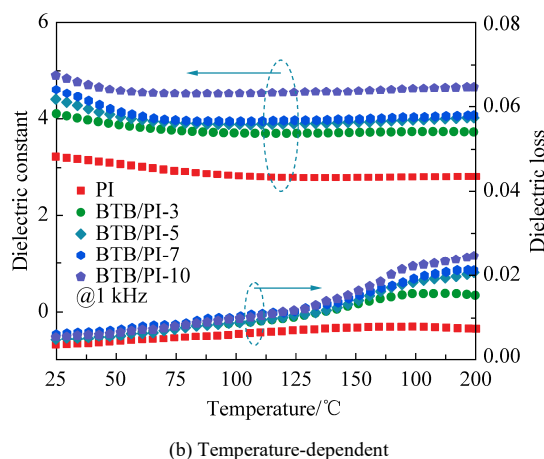
2.2 介电性能

图3为复合薄膜在 $10^3 \sim 10^6$ Hz 的频率依赖性

和在 $25 \sim 200$ °C 的温度依赖性。由图 3a 可见，BTB/PI 膜与纯 PI 的介电常数在 $10^3 \sim 10^6$ Hz 保持稳定，这得益于 PI 的刚性主链。BTB/PI 膜的介电常数随着 BNNS 含量的增加而增加。与纯 PI 膜的介电常数 3.12 相比，BTB/PI-3 提升到 4.20、BTB/PI-5 提升到 4.37、BTB/PI-7 提升到 4.67，BTB/PI-10 提升到 4.92。介电常数的增加主要由于高介电常数、高长径比的二氧化钛($\epsilon_r=110$)与大量 BNNS($\epsilon_r=4$)的加入、以及二氧化钛的一维结构和 BNNS 的二维结构与 PI 界面处产生的界面极化^[20]。由图 3b 可见，复合薄膜的温度依赖性，介电常数增加趋势与频率依赖性保持一致，并且在 $25 \sim 200$ °C 保持稳定。即使 BNNS 的体积分数增加到 10% 的高含量，复合膜的介电损耗在 $10^3 \sim 10^6$ Hz、 $25 \sim 200$ °C 的测试频率、温度下仍保持在 0.025 以下。



(a) Frequency-dependent



(b) Temperature-dependent

图3 纯PI膜、BTB/PI-3、BTB/PI-5、BTB/PI-7和BTB/PI-10复合膜的频率依赖性和温度依赖性

Fig. 3 Frequency-dependent and temperature-dependent of pure PI film, BTB/PI-3, BTB/PI-5, BTB/PI-7, and BTB/PI-10 composites

2.3 耐击穿能力

为了评估材料的耐击穿能力，利用 Weibull 分

布对材料进行了失效性分析。

$$P(E) = 1 - e^{-\left(\frac{E}{E_b}\right)^\beta}$$

其中: $P(E)$ 代表累积击穿概率; E 是实验测得的击穿强度; E_b 是累积击穿概率为 63.2% 时的击穿强度, 即 Weibull 击穿强度; β 是评估数据分散性的形状参数^[12]。图 4 为复合薄膜在 25、100、150 °C 和 200 °C 时的 E_b 和 β 因子。当温度从室温升至 200 °C 时, 纯 PI 的 E_b 从 380 MV/m 降至 337 MV/m, β 从 14.60 降至 8.04。这是由于复合薄膜内部载流子在高温下具有更高的能量和浓度, PI 主链更容易受到攻击而断裂^[21]。在测试温度下, BTB/PI-5 和 BTB/PI-7 的 E_b 和 β 因子较纯 PI 膜高。特别是 BTB/PI-7 在测试温度下都获得了最高的击穿强度和 β 因子。这得益于宽禁带高绝缘 BNNS 的加入, 其特殊的二维平面结构能够起到绝缘屏障的作用, 延长击穿路径或阻碍电子树的生长^[22], 防止电击穿的发生。并且 BNNS 具备高热导率能够快速的将复合薄膜内部的焦耳热快速散发到环境, 防止热击穿的发生^[23]。

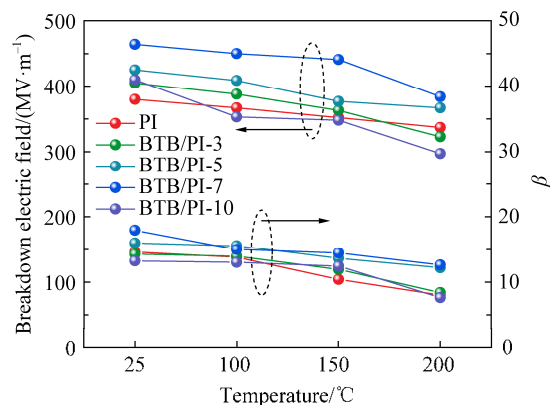


图 4 在 25、100、150 °C 和 200 °C 下, PI 膜和复合膜的威布尔击穿场强和 β 因子

Fig. 4 Weibull breakdown field strengths and β of PI and composites at 25, 100, 150 °C, and 200 °C

2.4 高温储能性能

为表征材料的储能性能, 测试复合薄膜在 25、100、150 °C 和 200 °C 的电滞回线。根据电滞回线计算得到的储能性能结果如图 5 可见。如 2.3 所述, 由于纯 PI 在高温下的 E_b 值较低和内部载流子浓

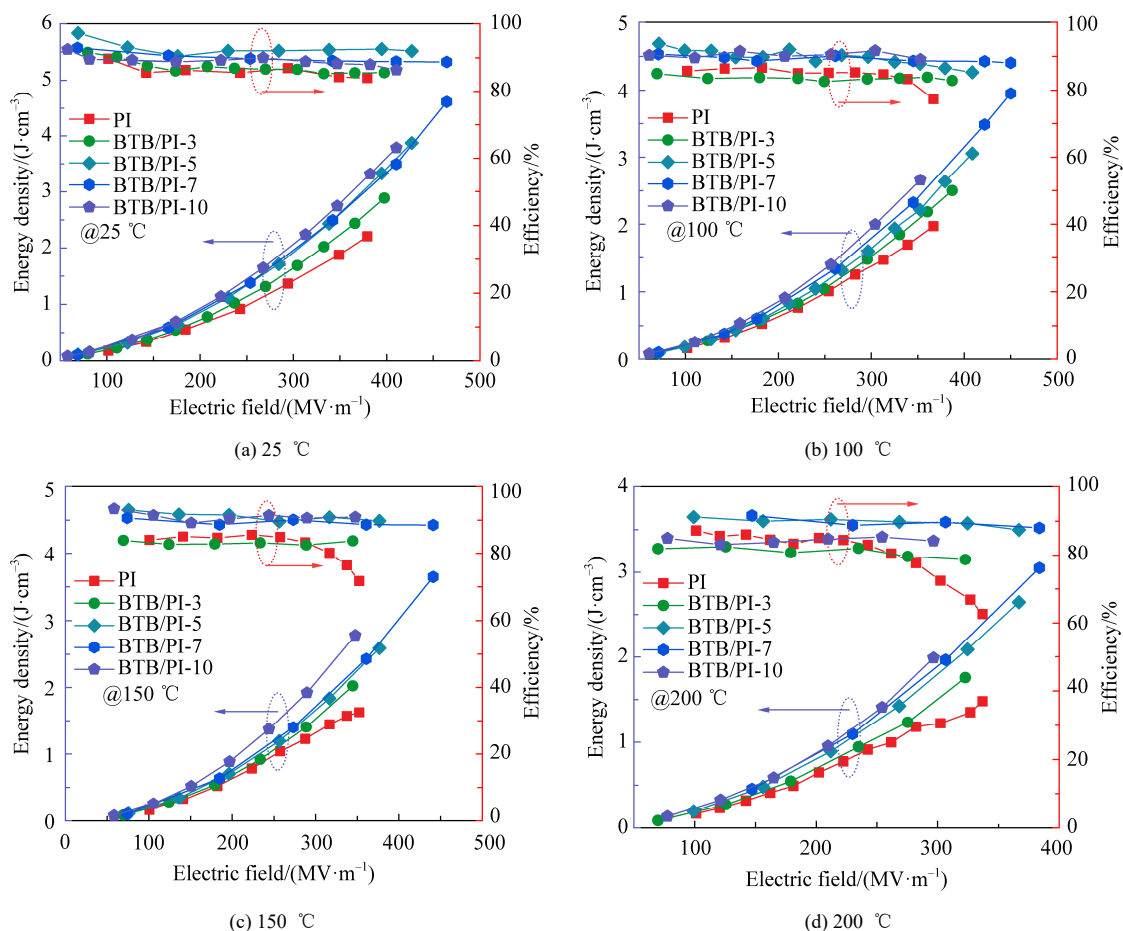


图 5 复合膜和纯 PI 膜在 25、100、150 °C 和 200 °C 的储能密度图

Fig. 5 Energy storage density plots of the composites and pure PI film at 25, 100, 150 °C and 200 °C

度高, 在 100、150 °C 和 200 °C 的储能密度、效率逐渐降低。但 BTB/PI 膜的储能性能都较纯 PI 高。在最佳的 BNNS 体积比下, BTB/PI-7 膜在测试温度范围内保持着最高的储能密度、稳定的高效率。25 °C 时(见图 5a), BTB/PI-7 储能密度和效率分别为 4.61 J/cm^3 、88.75%(@465 MV/m); 100 °C (见图 5b) 时为 3.95 J/cm^3 、88.08%(@450 MV/m); 150 °C (见图 5c) 时为 3.65 J/cm^3 、88.53%(@440 MV/m); 200 °C (见图 5d) 时为 3.04 J/cm^3 、88.00%(@380 MV/m)。其中在 200 °C 时, BTB/PI-7 膜储能密度是纯 PI (1.48 J/cm^3 @ 335 MV/m) 的 206.1%, 效率远超过纯 PI 膜的 62.6%。并且 BTB/PI-7 复合薄膜在 200 °C 的储能性能也是超过目前大多数高温电介质的研究(见图 6)。高温储能性能的提高源于多维协同夹层结构的设计能够结合 1DTiO₂ 和 BNNS 在极化、高绝缘、高导热的优势, 全面提升 PI 的高温储能性能。综上所述, 经过多维配位设计的 BTB/PI-7 复合薄膜的各项储能性能在 25~200 °C 范围内保持稳定, 在未来高温商业电介质中有很大的应用潜力。

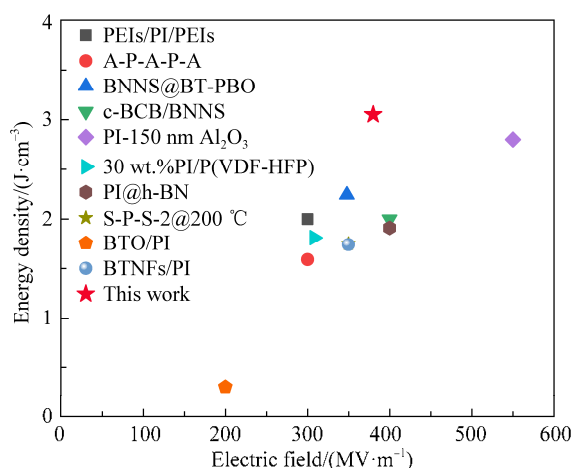


图 6 近年 200 °C 储能体系的性能比较^[16–18, 24–30]

Fig. 6 Comparison of the performance of the energy storage system at 200 °C in recent years^[16–18, 24–30]

3 结论

利用多维协同的思路, 在 PI 中引入不同维度的 1DTiO₂ 和 BNNS, 制备了 BTB/PI 复合薄膜。实验结果表明, BTB/PI 膜具有稳定的频率依赖性和温度依赖性。并且在测试频率和测试温度范围内, 介电损耗低于 0.025。在 200 °C 高温下, BTB/PI-7 获得 3.04 J/cm^3 的高储能密度。并且在 25、100、150、200 °C 的测试温度下, BTB/PI-7 储能效率高于 88%。证明通过在聚合物中引入不同维度填料, 加以合理

的结构设计, 可以充分结合不同材料在极化、耐击穿、耐高温的优势, 成功提高 PI 基复合薄膜的耐高温储能性能。这为高温环境下聚合物基介质薄膜的研究提供了一种可行的思路。

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High-Temperature Energy Storage Properties of Polymer-Based Composite Films Based on Multidimensional Synergy

TAN yipeng^{1,3}, GAO hang^{1,3}, FENG ziwen^{1,3}, LU linfei^{1,2,3}, DENG jiayu¹, YAO lingmin^{1,2,3}, DENG qinglin^{1,3}

(1. School of Physics and Materials Science, Guangzhou University, Guangzhou 510006, China; 2. Institute of Corrosion Science and Technology, Guangzhou 510275, China; 3. Research Center for Advanced Information Materials, Huangpu Research & Graduate School of Guangzhou University, Guangzhou 510275, China)

Extended Abstract

Introduction Polymer dielectrics play a crucial role in contemporary electronics because of their flexibility, low cost, high operating voltage, corrosion resistance, self-healing, etc., which are widely used in oil and gas exploration, and electric vehicles at operating temperatures (>105 °C). However, polymers necessitate the maintenance of a substantial volume during usage due to their low dielectric constant, thereby resulting in a diminished energy storage density. Furthermore, polymers demonstrate a relatively low thermal conductivity, and are susceptible to failure when exposed to high-temperature conditions. To function effectively in high-temperature conditions exceeding 105 °C, an extra refrigeration system must be incorporated into an electronic power system. This undoubtedly results in an increase in both energy consumption and overall weight of the system. Consequently, developing a new generation of polymer-based film capacitors with superior high-temperature energy storage capabilities becomes a necessity. In this paper, we utilized a multidimensional synergistic concept to comprehensively improve the high-temperature energy storage performance of PI-based polymer dielectrics *via* combining the electrical and thermal advantages of inorganic materials and polyimide (PI) in different dimensions.

Methods (BNNs-TiO₂-BNNs)/PI sandwich-structured composite films (denoted as BTB/PI film) were prepared by a casting method based on a concept of multidimensional synergy. Titanium dioxide (TiO₂) with a high dielectric constant was prepared into a

one-dimensional nanofiber structure by an electrostatic spinning method with PI as an interlayer of BTB/PI film. Electrically insulating and thermally conductive boron nitride was prepared into a two-dimensional nanosheet structure by a liquid phase exfoliation method with PI as an insulating and thermally conductive outer layer of the BTB/PI film. The frequency-/temperature-dependence of the films were examined by a model LRS-003 high and low temperature cooling and heating system and a model E4980 precision LCR meter. The PE loops for the films were determined by a linked test rig consisting of a model ZJ-6A quasi-static d33 tester, a model MODEL 610C Trek HV amplifier and a model BWT-001 variable temperature test rig at 25 °C and 200 °C, respectively.

Results and discussion The (BNNS-TiO₂-BNNS)/PI sandwich composite films with the thicknesses of 22–25 μm prepared are dense and uniform, without obvious holes and obvious delamination, having superior dielectric properties, breakdown strength and high-temperature energy storage properties. The results by frequency-/temperature-dependent tests indicate that the dielectric constant of BTB/PI films increases with the increase of BNNS content. Compared with the dielectric constant of pure PI film at 1kHz (*i.e.*, 3.12), BTB/PI-3, BTB/PI-5, 2BTB/PI-7 and BTB/PI-10 improve to 4.20, 4.37, 4.67 and 4.92, respectively. The dielectric loss of the composite film at 10³–10⁶ Hz and 25–200 °C is <0.025. From the breakdown strength of the material, the carriers inside the composite film have greater energy and concentration at high temperatures, making the PI chain more vulnerable to attack and breakage. The E_b of pure PI film thus decreases from 380 MV/m to 337 MV/m and the β reduces from 14.60 to 8.04 when the temperature increases from room temperature to 200 °C. However, the E_b and β of BTB/PI-5 and BTB/PI-7 are higher than those of the pure PI films at the tested temperature. At an optimal BNNS volume ratio, BTB/PI-7 achieves the maximum E_b and β at 25, 100, 150 °C, and 200 °C. This can be attributed to the incorporation of wide-band, high-thermal-conductivity BNNS, preventing the composite films from experiencing breakdown caused by electrical or thermal runaway. At 25, 100, 150 °C and 200 °C, the energy storage performance of BTB/PI film is higher than that of pure PI film. At an optimum BNNS volume ratio, BTB/PI-7 film achieves the maximum energy density and maintains a stable high efficiency in the tested temperature range. The energy density and efficiency of BTB/PI-7 film are 4.61 J/cm³ and 88.75% (at 465 MV/m) at 25 °C, 3.95 J/cm³ and 88.08% (at 450 MV/m) at 100 °C, 3.65 J/cm³ and 88.53% (at 440 MV/m) at 150 °C, 3.04 J/cm³ and 88.00% (at 380 MV/m) at 200 °C.

Conclusions The polymer-based composite films were obtained to enhance the high temperature resistant energy storage performance based on the multidimensional synergistic design. The BTB/PI film exhibited stable frequency/temperature-dependence with a dielectric loss of lower than 0.025 at 10³–10⁶ Hz and 25–200 °C. At 200 °C, BTB/PI-7 achieved a high energy density of 3.04 J/cm³. Moreover, the energy efficiency of BTB/PI-7 was higher than 88% at 25, 100, 150 °C and 200 °C. It was demonstrated that different materials with advantages (*i.e.*, high polarization, great breakdown strength, and high temperature resistance) were obtained via incorporating various dimensional fillers into the polymer and implementing rational structural design. Consequently, the high temperature-resistant energy storage performance of PI-based composite films could be significantly enhanced.

Keywords composites; multidimensional materials; dielectric properties; high temperature energy storage properties