

KNbO₃ 纳米线/P(VDF-HFP)&PMMA 复合薄膜的储能性质

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摘 要: 高性能的铁电纳米材料经常被填充进聚合物, 来提高聚合物电容器的储能性质。通过水热法合成了结晶性好、长径比高的 KNbO₃ 纳米线, 并与偏氟乙烯-六氟丙烯和聚甲基丙烯酸甲酯聚合物复合制备了复合薄膜。KNbO₃ 纳米线大幅度提高了复合薄膜的极化强度, 略微降低了复合薄膜的击穿场强。当 KNbO₃ 纳米线的填充量为 7.5% (质量分数) 时, 储能性能达到最优值, 此时复合薄膜的储能密度为 14.3 J/cm³, 储能效率为 72%。本工作证实 KNbO₃ 纳米线填料可以有效增强复合薄膜的储能性质。

关键词: 聚合物储能电容器; 纳米线; 铌酸钾; 铁电材料

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近年来, 高能量存储密度聚合物电容器由于较快的充放电速率、高的工作电压、制备方法简单、柔性好等优点, 在脉冲电源、电动汽车电源等领域具有潜在的应用前景^[1-2]。聚合物电容器的储能密度(W_{rec})和储能效率(η)可以根据电滞回线计算得到^[3]:

$$W_{\text{total}} = \int_0^{P_{\text{max}}} E dP \quad (1)$$

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (2)$$

$$\eta = \frac{W_{\text{rec}}}{W_{\text{total}}} \times 100\% \quad (3)$$

式中: E 为电场强度; P 为极化强度; W_{total} 为充电能量密度。因此要想提高聚合物电容的储能密度, 必须提高它的极化强度和击穿场强。

但是纯聚合物电容器的极化强度非常低, 很难在储能密度上得到很大的提升。最近研究人员在聚合物中引入纳米填料以形成填料/聚合物基复合材料, 以改善其储能性能^[4]。其中一种重要的填料为铁电纳米材料, 因为填料具有铁电性, 因此可以大幅度提高复合材料的介电性能和极化性能, 同时纳米材料尺寸小、分散性好, 不会明显降低复合材料的介电损耗和击穿场强。对于复合材料, 填料的尺寸、形状、含量都对复合薄膜的储能性能产生很大的影响。其中, 一

维纳米线材料不仅具有纳米材料所具有的小尺寸效应、量子尺寸效应、表面效应及宏观量子隧道效应, 还由于其径向和轴向不同的尺度能连接宏观和微观范畴^[5]。将一维纳米铁电材料引入到复合材料中, 一方面高的长径比可以降低其比表面积, 进而增强其在聚合物基体中的分散性; 另一方面, 由于其具有较大的电偶极矩, 因此在较低的填料含量下能够获得较为优异的介电性能和储能性质。

相比钛酸钡等铁电材料, 铌酸钾(KNbO₃)的高的 Curie 温度(435 °C)和良好的铁电性能(单晶的机电耦合系数某个方向上达到了 0.69), 非常适合制备复合储能薄膜^[6]。Ge 等^[7]将 KNbO₃ 纳米颗粒与 PVDF 混合制备了复合薄膜, 1 kHz 下的介电常数达到了 37。但是 KNbO₃ 复合薄膜的储能性质研究非常少。

因此本工作通过水热法制备了结晶性好、长径比高的 KNbO₃ 纳米线, 并与偏氟乙烯-六氟丙烯&聚甲基丙烯酸甲酯[P(VDF-HFP)&PMMA]聚合物复合制备了复合薄膜。KNbO₃ 纳米线大幅度提高了复合薄膜的极化强度, 略微降低了复合薄膜的击穿场强, 当 KNbO₃ 纳米线的填充量为 7.5% (质量分数) 时, 储能性能达到最优值, 此时复合薄膜的储能密度为 14.3 J/cm³, 储能效率为 72%。

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1 实验

采用水热法制备 KNbO_3 纳米线, 所有原料均购于国药集团化学试剂有限公司。具体流程如图 1 所示, 将 36 g KOH 和 1 g Nb_2O_5 加入到盛有 60 mL 去离子水的塑料烧杯中充分搅拌 1 h, 并转移至水热反应釜中, 180 °C 反应 12 h 后, 用去离子水和无水乙醇对样品进行反复洗涤, 并烘干。将 0.1 g 聚甲基丙烯酸甲酯(PMMA)和 0.9 g 偏氟乙烯-六氟丙烯(P(VDF-HFP))加入 10 mL N,N-二甲基乙酰胺

(DMAC)中, 80 °C 溶解后得到 P(VDF-HFP)&PMMA 混合溶液; 将不同质量分数(0, 2.5%, 5.0%, 7.5%, 10.0%)的 KNbO_3 纳米线均匀分散至一定量 DMAC 中后, 将其加入 P(VDF-HFP)&PMMA 混合液中, 充分搅拌使得 KNbO_3 纳米线填料在基体中分散均匀。然后采用流延成型工艺制备 KNbO_3 /P(VDF-HFP)&PMMA 复合膜, 所有复合膜样品的厚度约为 20 μm 。在复合膜两面溅射直径为 2 mm 的金电极用于电学性能测试。

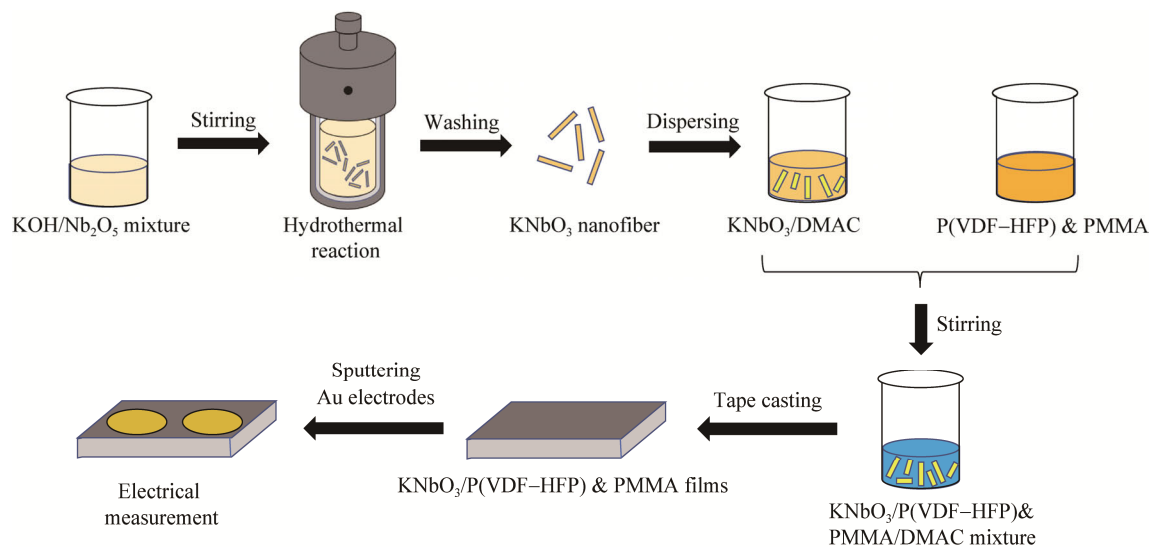


图 1 KNbO_3 /P(VDF-HFP)&PMMA 复合薄膜制备流程示意图

Fig. 1 Schematic diagram of the preparation of KNbO_3 /poly (vinylidene fluoride-co-hexafluoropropylene)&polymethyl methacrylate (P(VDF-HFP)&PMMA) composite films

X 射线衍射仪(XRD, D8 Advance, Bruker, 德国)用于 KNbO_3 纳米线的物相分析; 透射电子显微镜(TEM, JEOL2100F, JEOL, 日本)用于测试 KNbO_3 纳米线的微观形貌、选取电子衍射图谱(SAED)和能谱分析图(EDS); 阻抗分析仪(4294A, 安捷伦, 美国)用于测试陶瓷样品的介电常数 ϵ 和介电损耗 $\tan\delta$; 铁电分析仪(TF Analyzer 3000, aixACCT, 德国)用于测试复合薄膜的电滞回线(P - E), 测试频率为 1 Hz, 波形为三角波。

2 结果与讨论

图 2 为水热合成的 KNbO_3 纳米线的 XRD 谱。由图 2 可见, 样品为纯钙钛矿结构, 与正交 KNbO_3 结构标准卡片(JCPDS 32-0822)一致^[8-9]。从图 2 的内插图可见, 样品的(200)衍射峰明显不对称, 这说明 KNbO_3 纳米线为正交结构。衍射峰很尖锐, 强度很高, 说明样品的结晶度很高。衍射峰半高宽比较

大, 根据 Scherrer 公式, 可以看出样品的尺寸很小:

$$D = K\lambda / (B \cos\theta) \quad (4)$$

其中: K 为 Scherrer 常数; D 为晶粒尺寸; B 为样品衍射峰半峰高宽度; θ 为 Bragg 角。

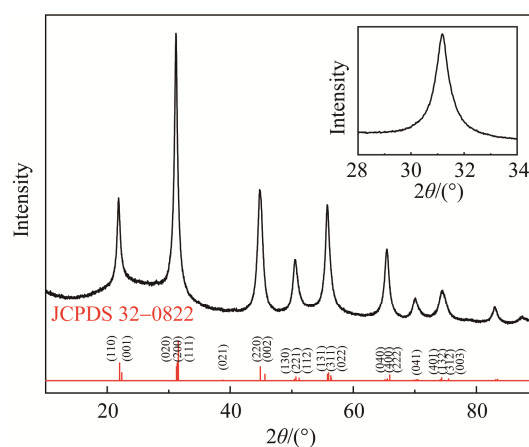
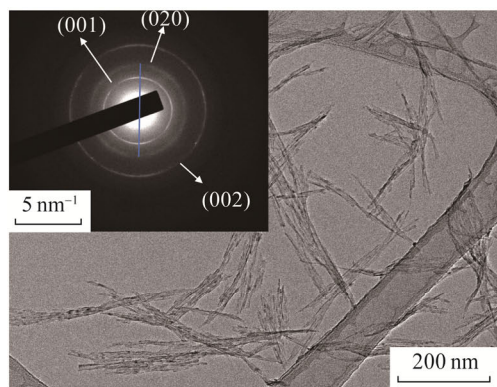


图 2 KNbO_3 纳米线的 XRD 谱

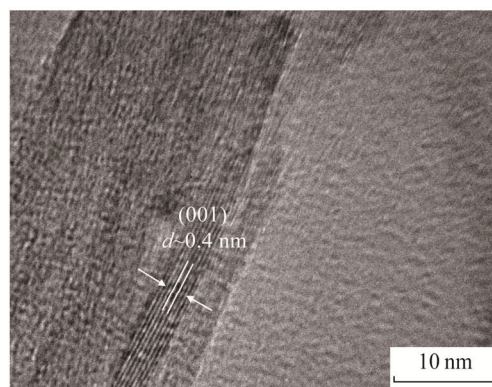
Fig. 2 XRD patterns of KNbO_3 nanofiber

然后利用 TEM 对 KNbO_3 纳米线的微观形貌进行了观察, 如图 3 所示。从 TEM 形貌照片(图 3a)可见, KNbO_3 呈一维纳米线结构, 大小均匀, 边缘清晰。纳米线长度约为 500 nm, 直径为 10~20 nm, 长径比约超过 25, 大的长径比能够有效地减小纳米填料的比表面积, 降低其比表面能, 因此降低纳米线在复合薄膜中的团聚^[10]。图 3a 内插图 of 纳米线的 SAED 图谱, 通过计算

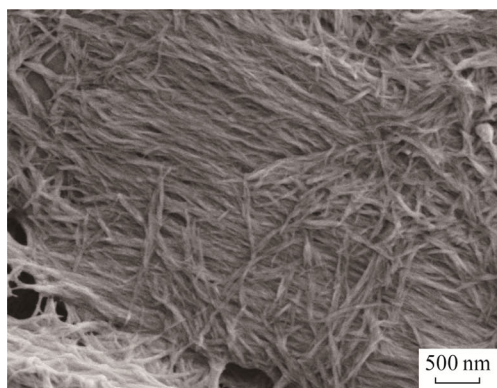
可知, 衍射环分别对应于正交相 KNbO_3 的(001)、(020)、(002)晶面, 结果与 XRD 测试结果一致。从图 3b 高分辨照片可见, 样品的晶格清晰, 晶面间距与(001)晶面相符。清晰的晶格条纹和衍射环说明制备的 KNbO_3 纳米线结晶性良好。从图 3c 的 SEM 照片, 可以看出合成的 KNbO_3 均为纳米线。从图 3d 的能谱面扫结果, 可以看出元素分布均匀。



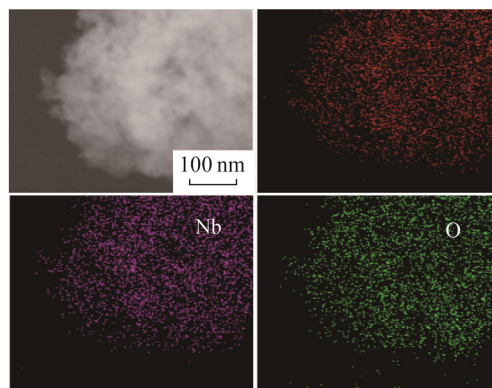
(a) TEM image of KNbO_3 nanofiber and selected area electron diffraction patterns of KNbO_3 nanofiber



(b) HRTEM image of KNbO_3 nanofiber



(c) SEM image of KNbO_3 nanofiber



(d) EDS mapping images of KNbO_3 nanofiber

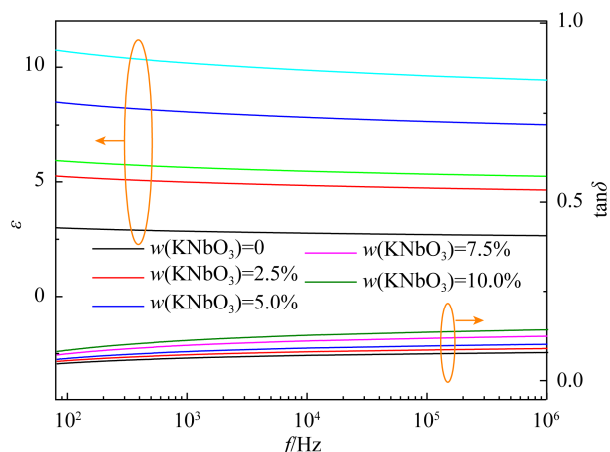
图 3 KNbO_3 纳米线的形貌和成分表征

Fig. 3 Micromorphology and element composition analysis of KNbO_3 nanofiber

图 4 为不同质量分数 KNbO_3 纳米线填充的 $\text{KNbO}_3/\text{P}(\text{VDF-HFP})/\text{PMMA}$ 复合膜的介电常数和损耗随频率增加的变化曲线。由图 4 可见, 所有样品的介电常数随频率的增加, 变化很小, 说明样品介电常数的频率稳定性很好。在高频处, 介电常数略有下降, 是由于高频时复合薄膜内部电偶极子翻转跟不上外界交流电场频率的变化, 无法与其进行响应。随着纳米线填料含量的增加, 复合薄膜的介电常数得到了有效的提高, 在 1 kHz 下, 0、2.5% (质量分数, 下同)、5.0%、7.5% 和 10.0% 的 KNbO_3

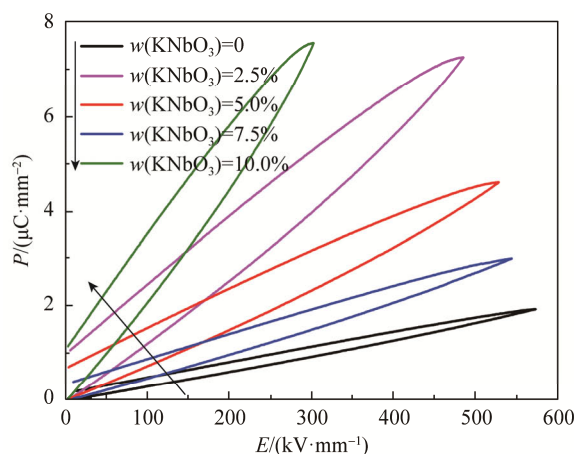
纳米线填充制备的复合薄膜介电常数分别为 2.8、5.2、6.1、8.2 和 11.5。添加 KNbO_3 纳米线的复合薄膜的介电常数高于未添加的复合薄膜, 是因为: 1) 合成的 KNbO_3 纳米线具有铁电性^[11], 对复合薄膜贡献了极化; 2) 纳米线与聚合物介电常数的差异在复合薄膜中引起了 Maxwell-Wagner-Sillars 界面效应^[12], 在界面处会形成电子陷阱, 大量电子被捕获而聚集在界面区域, 增强了纳米线与基体间的界面极化。由图 4 可见, 所有复合薄膜的全频率范围内, 介电损耗都低于 0.1, 说明样品中的缺陷浓

度较低^[13], 因此复合薄膜的介电强度很高, 进而增强了复合薄膜的储能密度。

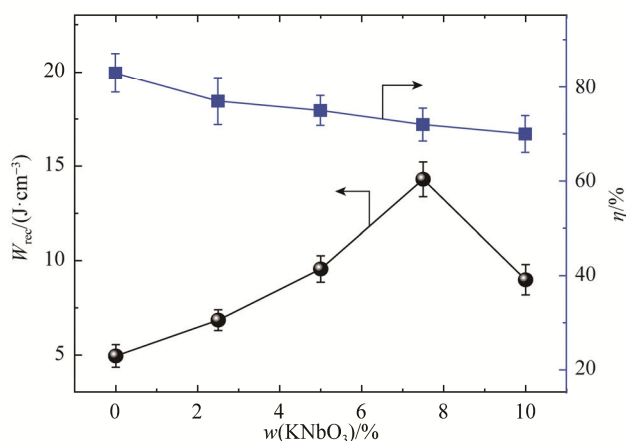


w is mass fraction.

图 4 $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA 复合薄膜的介电频谱
Fig. 4 Frequency dependence of dielectric constant (ϵ) and dielectric loss ($\tan\delta$) of $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA composite films



(a) Polarization (P)-electric field (E) hysteresis loops of the $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA composite films



(b) Recoverable energy storage density (W_{rec}) and energy storage efficiency (η) as a function of x

图 5 $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA 复合薄膜的储能性质

Fig. 5 Energy storage performances of the $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA composite films

根据电滞回线, 分别计算复合薄膜的储能密度和储能效率, 如图 5b 所示。复合薄膜的储能密度先增加后减小, 在填料含量为 7.5% 时达到最高, 刚开始储能密度的增加是由于薄膜的极化强度迅速增加导致的, 当填料含量为 10% 时, 复合薄膜的储能密度开始下降, 这是由于击穿场强迅速降低导致的。另外, 复合薄膜的储能效率随着填料含量的增加, 一直降低, 这是由于其内部损耗增加造成的。因此, 当 KNbO_3 纳米线填充量为 7.5% 时, 储能性能达到最优值, 储能密度为 14.3 J/cm^3 , 储能效率为 72%。

图 5a 为不同质量分数 KNbO_3 纳米线填充的 $\text{KNbO}_3/\text{P}(\text{VDF-HFP})$ & PMMA 复合膜的的电滞回线, 测试频率为 1 Hz。由图 5a 可见, 随着 KNbO_3 纳米线填料的增加, 复合薄膜的极化强度随之增加, 这与介电常数增加原因一致。另外, 随着 KNbO_3 纳米线填充量的增加, 复合薄膜的击穿电场逐渐降低, 这是由于填料加入到复合薄膜时, 界面区域局域电场的发生严重畸变, 导致某些区域的电场集中, 局域电场强度远高于样品的本征击穿场强, 导致这些区域发生击穿, 击穿产生大量的自由电子并放出热量, 这些自由电子会在电场的作用下加速并进入周围复合薄膜区域, 进而造成整个复合薄膜的击穿。当填充料含量非常高时, 填充料会发生团聚, 并对聚合物基体的均匀连续性造成破坏, 产生空隙、裂纹等微观结构缺陷, 这也会造成复合薄膜的击穿场强急剧下降^[14]。

3 结论

通过水热法合成了结晶性好、长径比高的 KNbO_3 纳米线, 并与 $\text{P}(\text{VDF-HFP})$ & PMMA 聚合物复合制备了复合薄膜。 KNbO_3 纳米线大幅度提高了复合薄膜的极化强度, 略微降低了复合薄膜的击穿场强。当 KNbO_3 纳米线的填充量为 7.5% (质量分数) 时, 储能性能达到最优值, 此时复合薄膜的储能密度为 14.3 J/cm^3 , 储能效率为 72%。研究结果表明, KNbO_3 纳米线填料可以有效增强复合薄膜的储能性质。

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Energy Storage Performance of $KNbO_3$ Nanofiber/P(VDF–HFP)&PMMA Composite Films

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Extended Abstract

Introduction Polymer-based dielectrics with ultrahigh power density, good flexibility and easy-processing have attracted much attention in powering electronics such as capacitor, power transmission, pulsed power systems and microelectronic systems. However, the low energy density affects the application in electronics industry. Recently, introducing the ferroelectric ceramic fillers with a high dielectric constant into the polymer matrix can improve the dielectric constant of polymer composite dielectric materials. In general, the microscopy of fillers has a great influence on the energy storage performance of polymer-based dielectric capacitors. One-dimensional nanomaterials are potential to fabricating the high-performance polymer-based dielectric capacitors due to their quantum size effect, surface effect and macroscopic quantum tunneling effect. When one-dimensional nano-ferroelectric materials are introduced into the composites, a high length–diameter ratio can reduce the specific surface area and enhance the dispersion in the polymer matrix. Also, the composites can obtain better energy storage properties with a lower filler content due to its large electric dipole. In this paper, $KNbO_3$ nanofibers with a good crystalline and a high length-diameter ratio were firstly synthesized *via* hydrothermal reaction. Polymer-based dielectric capacitors were then fabricated with $KNbO_3$ nanofibers and poly(vinylidene fluoride-co-hexafluoropropylene) & polymethyl methacrylate (P(VDF–HFP)&PMMA) polymers. The recoverable energy storage density and energy storage efficiency were analyzed.

Methods For the synthesis of $KNbO_3$ nanofibers, 36 g KOH and 1 g Nb_2O_5 were mixed in a 60 mL beaker and then were stirred for 1 h. Afterwards, the solution was transferred to a 100 mL reactor for hydrothermal reaction at 180 °C for 12 h. The particles were washed using deionized water and ethanol for several times and dried at 60 °C for 12 h. Finally, the composite films were prepared through a solution-casting method. 0.9 g P(VDF–HFP) and 0.1 g PMMA were dissolved in 10 mL N,N-Dimethylacetamide (DMAC) at 80 °C. $KNbO_3$ nanofibers with different mass fractions ($x=0, 2.5\%, 5.0\%, 7.5\%$, and 10.0%) were dispersed in the DMAC solution under magnetically stirring to obtain the mixture, and then the mixture was added into the P(VDF–HFP)&PMMA solutions. The composite films were prepared by a tape casting and subsequently dried at 90 °C. The thickness of the prepared films was 20 μm . Au electrodes (2 mm in diameter) were sputtered on the composite films for the coming electrical measurements.

Results and discussion Based on the crystal structure of the KNbO_3 nanofibers detected by XRD, the nanofibers exhibit a pure orthorhombic perovskite structure in coincidence with the standard JCPDS 32-0822. A high diffraction intensity reflects a good crystallinity of KNbO_3 nanofibers. In addition, the wide diffraction peaks show the small size of KNbO_3 nanofibers. From the TEM and SEM images, KNbO_3 nanofibers have a uniform morphology with a diameter of 10–20 nm and the length of ~500 nm. The distinct lattice fringes and selected area electron diffraction patterns confirm a good crystallinity of KNbO_3 nanofibers. Besides, all the elements uniformly distribute for KNbO_3 nanofibers.

The frequency-dependent dielectric constants of composite films with x of 0, 2.5%, 5.0%, 7.5%, and 10.0% are 2.8, 5.2, 6.1, 8.2, and 11.5, respectively. KNbO_3 nanofibers enhance the dielectric properties of composite films because of the intense ferroelectricity and the Maxwell-Wagner-Sillars interface effect. In addition, all the films exhibit a low dielectric loss, indicating the superior breakdown strength.

The polarization intensity at the same external electric field increases with the increase of KNbO_3 nanofiber fillers. Besides, the breakdown electric field reduces as the KNbO_3 nanofibers increase because a severe electric field deformation nearby KNbO_3 nanofiber fillers generates a high local electric field distribution. Therefore, the energy storage density firstly increases and then decreases, achieving an optimal value of 14.3 J/cm^3 when 7.5% (in mass fraction) KNbO_3 nanofibers are doped in the composite films. Also, the energy storage efficiency of the optimized composites is 72%.

Conclusions The ferroelectric nano-materials were filled into the polymers to enhance the energy storage performance of composite capacitors. KNbO_3 nanofibers prepared by a hydrothermal method exhibited a high aspect ratio and a good crystallinity. KNbO_3 nanofibers were mixed with P(VDF-HFP)&PMMA polymers to prepare $\text{KNbO}_3/\text{P(VDF-HFP)\&PMMA}$ composite films. The polarization strength of composite films was enhanced. Meanwhile, the breakdown strength of composite films slightly degraded. Therefore, the optimum energy storage density of 14.3 J/cm^3 and efficiency of 72% were achieved when 7.5% KNbO_3 nanofibers were doped in the composite films. The results indicated that KNbO_3 nanofibers could effectively enhance the energy storage performance of composite capacitors.

Keywords polymer energy storage capacitor; nanofiber; potassium niobate; ferroelectric materials