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磺化聚醚醚酮负载银纳米颗粒抑菌膜制备及性能

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摘要: 用浓硫酸将聚醚醚酮(PEEK)材料磺化后作为基膜材料,将银纳米颗粒(AgNPs)嵌合到膜材料中合成 SPEEK-AgNPs 抑菌膜。用傅里叶变换红外光谱仪、扫描电子显微镜、原子力显微镜及 X 射线等方法分析该膜的特征,通过 Ag^+ 释放实验测试其安全性,并采用抗菌膜实验和悬浮抗菌实验测定其抗菌性。结果表明,磺化改性后的 SPEEK 材料与 AgNPs 结合良好,负载率较高,AgNPs 在膜上平均尺寸为 10~105 nm。在不同的释放条件下, SPEEK-AgNPs 膜的 Ag^+ 释放量总体上维持在安全浓度范围内。SPEEK-AgNPs 膜可以有效抑制大肠杆菌、铜绿假单胞菌及金黄色葡萄球菌,其抑菌率高达 95% 以上。制取的 SPEEK-AgNPs 可以在安全的前提下较好的预防微生物污染,有良好的应用前景。

关键词: 聚醚醚酮;磺化;纳米银;干湿相转化法;抗菌膜;性能

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Preparation and Performance of Sulfonated Polyetherether Ketone Loaded Silver Nanoparticles Antibacterial Membrane

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Abstract : Polyetheretherketone (PEEK) material was sulfonated with concentrated sulfuric acid as the base membrane material, and silver nanoparticles (AgNPs) were embedded into the membrane material to synthesize SPEEK-AgNPs antibacterial membrane. The characterization of the film was analyzed by Fourier infrared spectroscopy, scanning electron microscopy, atomic force microscopy and X-ray. Its safety was tested by Ag^+ release experiment, and its antibacterial activity was determined by antibacterial film experiment and suspension antibacterial experiment. The results show that the sulfonated SPEEK material is well combined with AgNPs, the loading rate is high, and the average size of AgNPs on the film is 10 ~ 105 nm. Under different release conditions, the Ag^+ release of SPEEK-AgNPs membrane is generally maintained in the safe concentration range. SPEEK-AgNPs membrane can effectively inhibit escherichia coli, pseudomonas aeruginosa and staphylococcus aureus, and its antibacterial rate is up to 95% or more. In conclusion, SPEEK-AgNPs prepared can better prevent microbial pollution on the premise of safety, and has a good application prospect.

Keywords : polyetheretherketone ; sulfonate ; silver nanoparticle ; dry-wet phase inversion ; anti-biofilm ; property

随着对节能环保技术的需求日益增长,膜分离作为一种绿色、节能、高效的分离技术,在水处理、气体分离、溶质浓缩提取领域得到了广泛的应用^[1]。聚醚醚酮(PEEK)是一种高性能的工程塑料,因其优异的热稳定性、化学耐性和力学强度,近年在膜分离领域得到越来越广泛的应用^[2]。然而,传统的

PEEK 膜亲水性能较差,在使用过程中,其表面易受到各种污染物的附着,特别是会受到微生物侵染与富集^[3],这会极大影响 PEEK 膜的分离性能,降低膜的使用寿命^[1]。

微生物附着在膜表面后,会不断进行代谢和繁殖,其分泌的代谢产物会在薄膜表面形成以多糖、蛋

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白质和核酸为组成成分的致密的保护层^[4]。传统的抗生素难以透过保护膜对其中的微生物起作用^[4-5]。针对膜表面微生物污染问题,最有效的方法是对膜材料表面基质进行化学改性,一方面改善膜材料基质的表面特性,降低细菌在材料表面附着和繁殖的可能性^[6],另一方面将一些抗菌成分引入到膜基质中,持续抑制膜表面的微生物作用^[7]。

纳米银颗粒(AgNPs)是常用杀菌成分^[8],研究表明,它可能通过破坏细菌细胞壁^[9]或质膜上^[10]的肽聚糖,影响细菌细胞构造的正常功能,持续抑制细菌的生长^[11]。笔者针对AgNPs与聚合物相容性差的特点,通过磺化PEEK,增强PEEK表面相容性和亲水性,提升AgNPs与PEEK表面的联结,使制取的SPEEK-AgNPs材料具有高亲水性和抗菌性,可广泛适用于膜分离领域,以减少膜使用过程中表面的生物污染。

1 实验部分

1.1 主要原材料

PEEK: VICTREX 450 G, 英国Vitrex公司;

浓H₂SO₄(质量分数98%)、N,N-二甲基乙酰胺(DMF)、硝酸银: 分析纯, 广东化工厂;

琼脂培养基: 中国环凯微生物科技有限公司;

大肠杆菌、铜绿假单胞菌及金黄色葡萄球菌菌株: 广东省细菌采集中心。

1.2 主要设备及仪器

傅里叶变换红外光谱(FTIR)仪: Vector 33型, 德国Brucker公司;

原子力显微镜(AFM): Multimode8型, 德国Brucker公司;

X射线衍射(XRD)仪: D8advanceX型, 德国Brucker公司;

表面接触角测量(OCA)仪: OCA15型, 德国Dataphysics公司;

吸附测定仪: JW-BK222 N2型, 深圳市晶玮博科技有限公司;

扫描电子显微镜(SEM): Nova Nano 3700型, 美国FEI公司;

X射线能谱(EDS)仪: Quantax XFlash型, 德国Brucker公司;

原子吸收光谱(AAS)仪: Z-2000型, 日本日立公司。

1.3 试样制备

PEEK磺化: PEEK与98%浓硫酸混合比例为

10 g/200 mL, 反应时间为12, 18, 24 h的磺化聚醚醚酮(SPEEK), 分别编号为SPEEK1, SPEEK2, SPEEK3^[12]。

SPEEK-AgNPs膜的制备: 使用干湿相转化法制取SPEEK膜, 将薄膜浸在2.5 g/L的硝酸银水溶液2 h后使用0.25 mol/L的维生素C水溶液中浸泡15 min以接枝AgNPs, 即得到SPEEK-AgNPs薄膜。

1.4 性能测试

磺化度测定: 根据滴定法, 计算材料离子交换容量(IEC)和磺化度(DS)^[1]。

FTIR分析: 用FTIR仪对制取的材料在600~4000 cm⁻¹范围进行化学结构表征。

微观结构观测: 在20 kV范围下, 用SEM观察膜表面的显微结构, 用AFM观察膜的拓扑结构。

亲水性测试: 用OCA仪测量膜的接触角以表征材料亲水性。

吸水性(δ)测试: 根据干湿膜的比值计算吸水率 δ 。

AgNPs的接枝: 利用XRD测量膜上AgNPs的接枝情况。

AgNPs的分布: 对膜表面进行EDS衍射分析, 分析膜表面主要元素(C, S, O和Ag)的浓度。

Ag元素的释放: 通过测定在Ag⁺浸没溶液中的浓度来监测其释放程度^[14]。

抗菌性测试: 通过对大肠杆菌、铜绿假单胞菌和金黄色葡萄球菌的抑菌圈, 估计材料抗菌性。同时用细菌悬液计算其抗菌性^[7]。

1.5 数据分析

每次测量至少重复三次, 最终结果以均数 $\pm$ 标准差表示。

2 结果与讨论

2.1 SPEEK的磺化度及表征

PEEK的磺化过程可以看作—SO₃H取代—H的过程^[14]。起初, 有大量的—H位点供—SO₃H取代, 随着反应的进行, —H位点逐渐减少。因此H⁺释放量可以用来衡量SPEEK材料的离子交换能力。因此, 如图1所示, 在反应的初期, IES呈现快速增长的趋势。随着时间的延长, —SO₃H取代的位点越来越多, IEC上升趋势逐渐放缓, 并趋于平衡。由于DS与IEC呈正相关, 其在磺化过程中的增长趋势与IEC相似。一般来说, 较高的DS意味着磺化过程的难度更大。然而, 它也导致了PEEK材料更

高的表面活性,以及更高的亲水性,从而提高了生物污染的抗粘附能力^[15]。

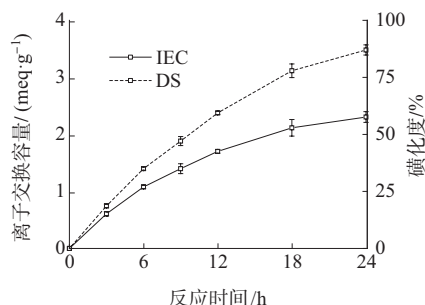


图1 SPEEK磺化过程中的IEC与DS变化趋势

图2为PEEK与SPEEK的FTIR谱图,可看到在 1100 cm^{-1} 处有明显的 $-\text{SO}_3\text{H}$ 特征吸收峰^[15],随着材料DS升高该特征峰会明显升高。另外,在 $4000\sim 3200\text{ cm}^{-1}$ 之间的 $-\text{OH}$ 特征峰是水合作用典型标志,表明该材料亲水性有显著改善^[15]。此外, $-\text{OH}$ 中的氧原子具有电负性,能吸引金属离子,这有利于聚合物与Ag之间建立更强的连接。

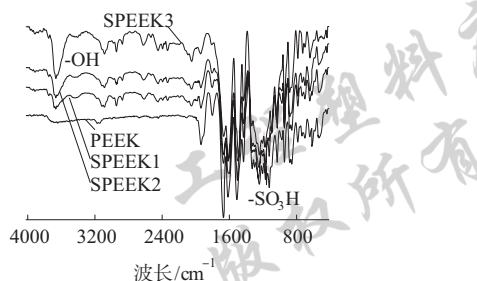
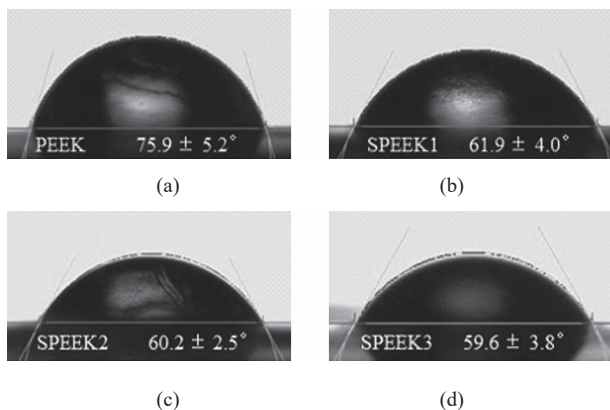


图2 PEEK与SPEEK的FTIR谱图

测量聚合物与表面水滴的接触角,可判定材料亲水性。图3为PEEK与SPEEK的接触角。如图3所示,与PEEK相比,由于 $-\text{SO}_3\text{H}$ 的存在,SPEEK膜的水分接触角增加了60%左右。这表明磺化后材料的亲水性提高,这使膜表面更容易润湿,可以抑



a—PEEK ; b—SPEEK1 ; c—SPEEK2 ; d—SPEEK3

图3 PEEK与SPEEK的接触角

制膜表面的浓度极化,这对于防止污染物,特别是微生物污染物的粘附意义重大^[16]。

通过氮吸附仪进行比表面积分析(BET)是反映材料多孔性的有效手段。图4为PEEK与SPEEK的 N_2 吸收测定。图4显示,所有薄膜都有相似的吸附、解吸等温线^[16]。DS较高的SPEEK薄膜孔隙分布范围较大^[17]。这可能是因为 $-\text{SO}_3\text{H}$ 的引入使聚合物主链以平行、扭曲和折叠的方式减少聚合物的二级结构,进而导致吸附 N_2 减少。图5显示通过BET和水吸收实验测量材料总孔隙体积和水吸收率。由图5可知,PEEK与SPEEK总孔隙体积和水吸收率随着DS的增加而减小。

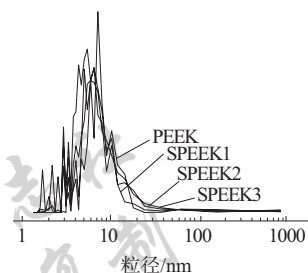


图4 PEEK与SPEEK的 N_2 吸收测定

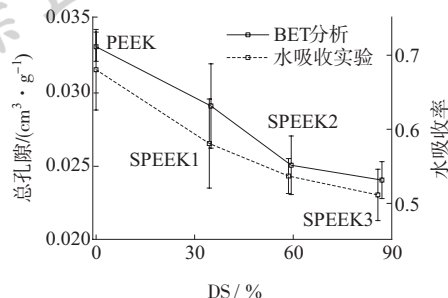
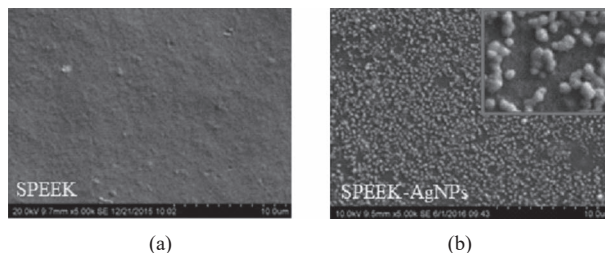


图5 BET与水吸附法测定PEEK与SPEEK总孔隙体积和水吸收率

2.2 SPEEK-AgNPs膜的微观结构

图6为SPEEK与SPEEK-AgNPs的SEM照片,由图6可以看出大量AgNPs成功嵌入膜表面,粗略测量它们的尺寸在 $10\sim 105\text{ nm}$ 。



a—SPEEK ; b—SPEEK-AgNPs

图6 SPEEK与SPEEK-AgNPs的SEM照片

图7为SPEEK和SPEEK-AgNPs的AFM照片。图7的AFM扫描结果显示,SPEEK表面平整,平均起伏高度在 7 nm 左右。但由于AgNPs的引入,

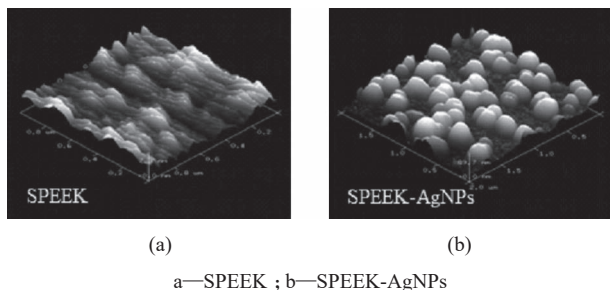


图7 SPEEK和SPEEK-AgNPs的AFM照片

SPEEK-AgNPs的起伏高度增加到了约90 nm。

表1为EDS对膜表面C, O, S和Ag的含量分析。结果表明,在未经磺化的PEEK膜表面引入AgNPs,只检测到1%的Ag元素引入成功,而在不同DS的SPEEK膜表面,检测到了12.5%~19.6%的Ag元素。这表明磺化处理可以极大增强膜表面对AgNPs的作用,增加AgNPs引入的数量。

表1 PEEK与SPEEK材料负载的元素含量 %

材料	Ag	C	O	S
PEEK-AgNPs	1.1 ± 0.1	81.3 ± 1.4	17.6 ± 1.4	0 ± 0
SPEEK1-AgNPs	12.5 ± 2.3	63.4 ± 4.2	20.5 ± 2	3.6 ± 0.2
SPEEK2-AgNPs	16.2 ± 3.4	57.8 ± 2.5	20.9 ± 3.5	5.1 ± 0.1
SPEEK3-AgNPs	19.6 ± 2.8	52.7 ± 3.3	21.2 ± 1.9	6.5 ± 1.4

2.3 SPEEK-AgNPs膜的抗菌性

AgNPs对人的毒作用低,但有很强抗菌性^[13]。与其他有机抑菌剂如呋喃酮或乳酰胺相比,AgNPs的抗菌效率更高,同时AgNPs还可以减少微生物耐药性的产生^[7,12,18,19]。在已有的研究中,使用AgNPs作为抗菌剂的应用较为广泛^[20-23]。

图8描述了XRD分析Ag元素在膜上的负载情况。由图8可看出,纯PEEK为典型非晶体结构,在 2θ 值为 20° 有一特征峰,而元素Ag在 2θ 值为 $38.2^\circ, 43.8^\circ, 64.7^\circ, 77.2^\circ$ 有4个典型的衍射峰^[24]。因此, SPEEK-AgNPs的XRD曲线包含了Ag元素和SPEEK的显著特征峰。

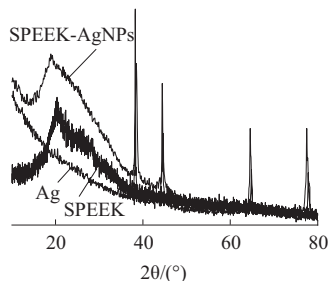
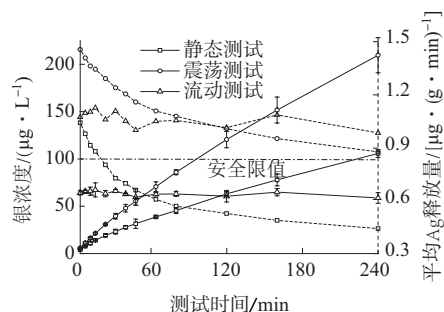


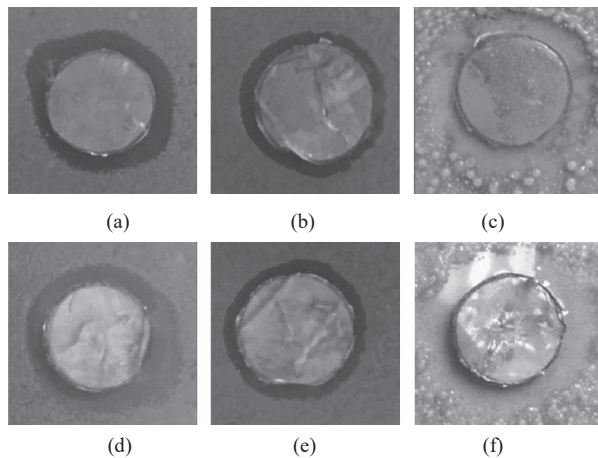
图8 XRD分析Ag在SPEEK上的负载情况

纳米Ag材料接触水后会在水中逐渐释放出 Ag^+ 。如图9所示,在静态和振荡条件下 Ag^+ 的释放量均随时间的延长而减小,240 min后分别达到

0.44, 0.87 $\mu\text{g}/(\text{g} \cdot \text{min})$ 。在流动水中, Ag^+ 的释放相对稳定,为1 $\mu\text{g}/(\text{g} \cdot \text{min})$ 。与100 g/L的饮用水银元素含量安全限值相比^[25], SPEEK-AgNPs膜的 Ag^+ 释放量维持在安全浓度以下。

图9 不同情况下 Ag^+ 的释放浓度

Ag^+ 的释放决定了SPEEK-AgNPs膜的抗菌性能。图10显示了不同膜的抑菌带,与SPEEK膜相比SPEEK-AgNPs膜的抑菌带较宽,对微生物抑制作用更明显^[26]。SPEEK的抗菌性可能因为 $-\text{SO}_3\text{H}$ 的强氧化性^[27],但其抑菌效果很微弱。表2进一步展示了不同膜材料在细菌悬浮液中抗菌性的定量分析, SPEEK膜只具有较弱的抗菌性,对不同菌株的抑菌率在20%左右。与此同时, SPEEK-AgNPs对不同菌株都展示了较强的抑制作用,其抑菌率达到95%以上。



SPEEK: a—大肠杆菌; b—铜绿假单胞菌; c—金黄色葡萄球菌
SPEEK-AgNPs: d—大肠杆菌; e—铜绿假单胞菌; f—金黄色葡萄球菌
图10 SPEEK与SPEEK-AgNPs在不同菌株培养皿上产生的抑菌带

表2 不同材料的抗菌性定量分析 %

样品	大肠杆菌	铜绿假单胞菌	金黄色葡萄球菌
PEEK	0 ± 0	1.1 ± 0.3	1.5 ± 0.1
SPEEK	19 ± 2.3	25.2 ± 1.6	21.9 ± 3.6
SPEEK-AgNPs	95.1 ± 3.1	97.5 ± 1.3	95.7 ± 2.8

3 结论

(1) 通过磺化提高PEEK膜表面活性,磺化后的

SPEEK 材料亲水性能增加,随着磺化度的提升,材料孔隙减少。将 AgNPs 嵌入 SPEEK 表面,制取具有高亲水性与高抗菌性的 SPEEK-AgNPs 膜。磺化改性后的 SPEEK 材料与 AgNPs 结合良好,负载率较高,纳米 Ag 在膜上平均尺寸为 10~105 nm。

(2) 在不同的释放条件下, SPEEK-AgNPs 膜的 Ag⁺ 释放量总体上维持在安全浓度范围内。SPEEK-AgNPs 膜可以有效抑制大肠杆菌、铜绿假单胞菌及金黄色葡萄球菌,其抑菌率高达 95% 以上。研究的 SPEEK-AgNPs 在许多情况下可以取代传统的 PEEK 材料,以避免微生物污染。

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