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生物质蜡制备疏水/超疏水材料的研究及应用进展

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摘要：生物质蜡凭借其可持续性、环境友好性以及独特的物理化学性质，成为制备疏水/超疏水材料的研究热点。文中综述了生物质蜡制备疏水/超疏水材料的机理及方法，着重介绍了生物质蜡相变重结晶特性和低表面能改性对制备疏水复合材料的研究进展。同时，文中还系统总结了生物质蜡在食品包装、油水分离和木材防护等应用领域的进展。最后，针对当前生物质蜡制备疏水/超疏水涂层所存在的问题进行了深入分析，并结合市场需求，对其未来发展方向和趋势进行了展望。

关键词：生物质蜡；棕榈蜡；蜂蜡；疏水；超疏水；重结晶；可持续
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源于自然界“荷叶效应”和“玫瑰花效应”的超疏水现象为人类开发可持续疏水材料提供了绝佳的解决方案[1]。为实现理想的疏水功能，需要用低表面能材料来构建微/纳米结构以实现[2, 3]。研究者们普遍采用超低表面能的含氟材料来制备疏水材料，但氟在环境中和人体内具有长久危害的沉积性[4]和致癌毒性[5]，目前欧美国家已经禁止使用[6]。根据元素周期特性，科研人员还开发出了硅烷改性材料来实现超疏水[7]，但与绿色可持续发展疏水材料理念仍然还有较大距离。

近年来，使用具有天然疏水特性的生物质蜡材料来设计具有疏水/超疏水特性的功能材料激发了研究者们的研究兴趣。生物质蜡分为植物蜡和动物蜡，应用于工业原料的植物蜡主要有棕榈蜡、小烛树蜡等，主要由长链脂肪酸(FA)、长链脂肪醇(FAL)和蜡酯(WE)等化学成分构成[8, 9]；动物蜡有蜂蜡、虫白蜡、鲸蜡等，是由烷醇和烷酸形成的酯类、游离脂肪酸和饱和烃类为主的成分构成[10]。生物质蜡因其独特的低表面能和结晶特性，成为制备可持续疏水材料的理想原料。本文简要介绍了生物质蜡制备疏水材料的机理和方法，着重综述了生物质蜡制备疏水/超疏水材料的最新研究进展，并总结了生物质蜡制备疏水材料的相关应用，最后对生物质蜡制备疏水/超疏水材料所存在的性能缺陷和发展趋势进行了总结与展望，为进一步开发生物质蜡环保疏水材料提供了参考。

1 生物质蜡疏水/超疏水材料的制备

1.1 生物质蜡制备疏水/超疏水材料的机理

生物质蜡的疏水机理涉及到其分子结构和性质。生物质蜡是由生物细胞生化聚合而成的能大量获取的天然蜡，由于生物蜡分子中的长碳链在水中无法形成氢键，通常具有较低的表面能，导致蜡对水等极性物质的亲和力较低[9]，从而表现出疏水性。生物质蜡独特的相变特性，使其在重结晶过程中能形成特定的微尺度界面晶体结构，这种结构可以增加

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表面与水之间的接触角，减少水分子与表面的接触面积，进一步增强疏水效果[11]。生物质蜡的疏水机理是其分子结构和结晶特性使得生物质蜡材料表面对水产生排斥作用，从而表现出良好的疏水性。

1.2 生物质蜡制备疏水/超疏水材料的方法

利用生物质蜡独特的疏水机理制备疏水/超疏水材料。一方面是作为构建微结构的主体，在生物质蜡蜡有机溶剂体系中，通过调节有机溶剂蒸发速率和过饱和水平[12]，在干燥过程中形成不同表面形貌的微纳米结构；也能通过冷却退火超声处理形成独立蜡微粒[12, 13]，再进一步应用于表面涂层疏水材料，这两者都是在生物质蜡相变结晶固化过程中形成疏水结构[14, 15]。另一方面可作为低表面能改性材料，将生物质蜡用乳化剂和其他功能组分制成蜡乳液[13]用于材料表面的疏水改性，对生物质蜡涂料主要通过物理涂覆法、喷涂法、铸膜法等应用于成膜。

2 生物质蜡复合材料

2.1 生物质蜡或蜡/蜡体系

不经过特殊处理的蜡涂层本身就具有疏水特性[12]，单组份蜡通过一定的工艺就可以实现疏水/超疏水结构。Alina等[16]在水熔融环境中制备12~15 μm的棕榈蜡颗粒应用于木质表面，经过蜡颗粒处理表面疏水（接触角CA=120°）高于用连续蜡膜形成的表面（CA=100°），主要是由于蜡颗粒增加了木材表面的粗糙度，从而导致气室的形成，拥有更好的疏水效果。Zhao等[17]在乙醇中加热溶解食品级蜡后，在40 ℃退火超声处理减小蜡微片尺寸，涂层CA达到158.2°，滑动角(SA)为7.3°，且具有强烈的耐水喷射和耐腐蚀性。Francis等[12]系统研究了溶剂和温度对蜡结晶过程中产生的微/纳米结构形貌及其对应的表面润湿性。通过调节结晶动力学，发现结晶过程中的饱和水平会影响静态和动态润湿状态下的表面形貌和水接触角。蒸发较快的丙酮相对于蒸发较慢的甲苯会产生更大的水接触角及增强的表面附着力。温度影响方面(Fig.1(a))，在≥60 ℃快速蒸发条件下，室温冷却诱导结晶会导致表面相对光滑，而在较低温度下的结晶主要是由溶剂蒸发控制的，从而产生了较高的水接触角。

不同生物质蜡的熔点不同[14]，其有不同结晶相变温度，根据这一特性，科研人员展开了大量混合蜡体系的应用研究。Zhang等[13]将混合蜡（蜂蜡和棕榈蜡熔点分别为61 ℃和80 ℃）用乳化剂乙酰三甲基溴化铵乳化。制成乳液应用于纸基表面后，CA迅速增加到145°左右，而在60~70 ℃退火后CA再增加10°以上，SA到10°以下。这是由于在介于2种蜡的相变结晶温度下固化，熔点较高的蜡保持固态，熔点较低的蜡熔化流出，使蜡涂层形成稳固连续“莲花”状态。Wang等[18]首次研究了生物质蜡在弹性基质上的润湿状态(Fig.1(b))，在55 ℃退火3 min可以使熔点较低的蜂蜡变形作为黏附剂，而熔点较高的棕榈蜡球形微粒结构不受影响，2种蜡之间形成的氢键也提高了涂层的完整一体性和拉伸超疏水性。Liu等[19]对比了烛台蜡/米糠蜡混合蜡热溶液与蜡乳液结晶形成不同表面密度(ρ_A)的微结构对润湿性的影响(Fig.1(c))，发现CA随着ρ_A的增加而增加，乳液型微细结构显著，表面密度低，其超疏水性也更强；相比之下热溶液的结构性稍弱，表面密度低，但其涂层强度明显提高。

2.2 生物质蜡与生物材料复合体系

生物质蜡疏水改性多糖、天然纤维、木质素等生物材料是近几年的研究热点。Jared等[20]应用纤维素或石松纤维提高表面粗糙度，用天然蜡分散体溶液降低体系低表面能，加热到(70~100 ℃)仍表现出最好的疏水性（CA ＞ 160°和SA < 7°）。Wang等[21]首次报道了丝瓜海绵(LS)为多孔骨架，使用米糠蜡和棕榈蜡作为改性剂溶于乙酸乙酯制成乳液。浸渍蜡层形成了复合颗粒/薄膜微观结构，使超疏水涂层(CA=151.7°，SA=7.8°)具有良好的稳定性(Fig.2(a))。同样的，Maryam等[22]将LS经过碱化和醛化处理去除杂质，浸涂乙酸乙酯溶解的棕榈蜡和蜂蜡，并用纳米石墨烯进一步强化，改性海绵的CA达158°，具有更高的耐温性和优异的油水分离能力。天然材料具有多孔一体结构的还有柚皮，Wang等[15]将棕榈蜡溶解在二甲苯中，加入乙醇使均相溶液逐渐转变为富溶剂相(Fig.2(b))，喷涂在冻干柚皮上后将立体结构压平。当乙醇体积分数提高到80%时CA达154°，并具有较好的吸油能力、分离效率和可重用性。

壳聚糖是一种天然的阳离子多糖，具有优良的生物相容性和生物降解性，适用于食品包装膜底

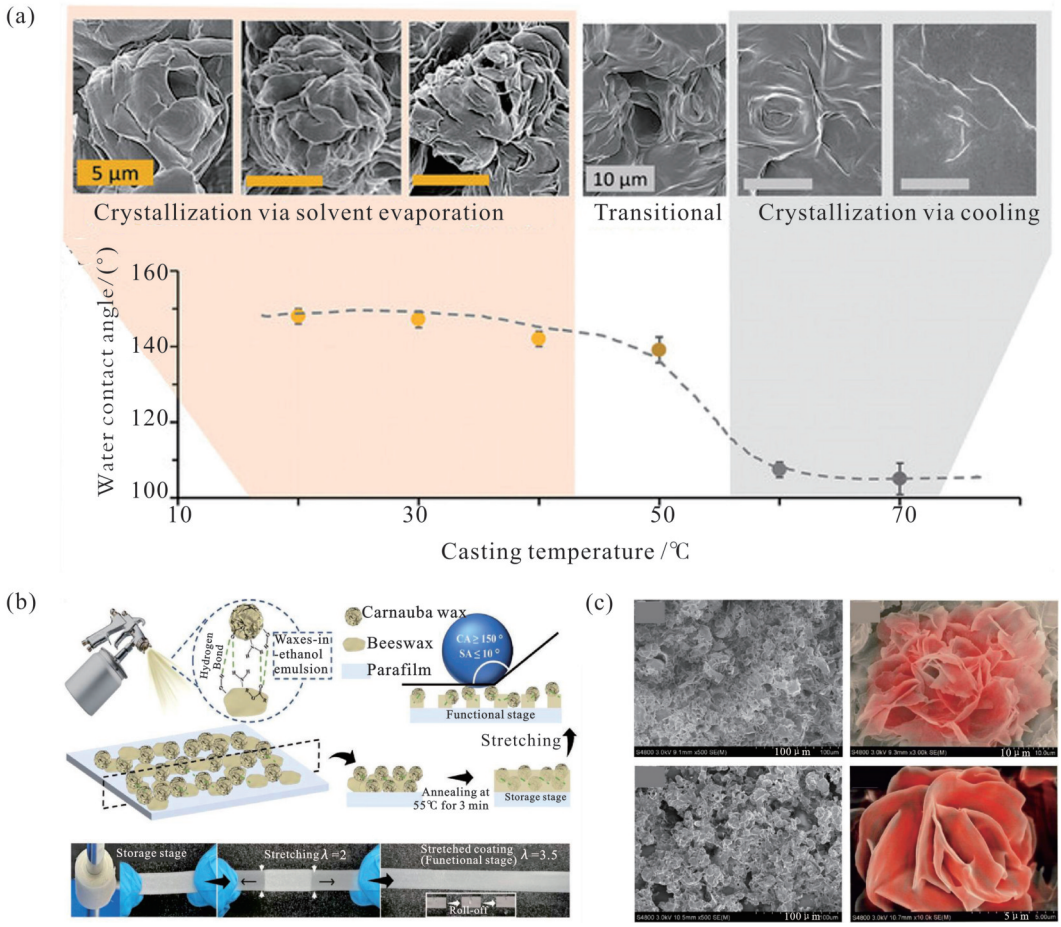


Fig. 1 (a) Temperature on solvent evaporation affects the surface morphology and wettability of waxes [12]; (b) schematic and tensile diagrams of the fabrication of hybrid wax coatings with tensile superhydrophobic properties[18]; (c) SEM and color high magnification images of ethanol emulsion coatings versus ethanol hot solution coatings[19]

物。Zhang等[23]在复印纸上涂上蜂蜡-壳聚糖混合物干燥,表面蜂蜡颗粒在高干燥温度下熔化成微尺度褶皱,从而使CA=138.3°。在酸性条件下,带正电荷的壳聚糖与带负电荷的蜂蜡之间的静电相互作用使涂层具有稳定结构作用力[24]。Zhang等[25]发现从咖啡豆中提取的可食用木质素可以有效提高涂层高温耐受性。该研究用蜂蜡在80 ℃能使咖啡木质素完全被包裹(Fig.2(c))(咖啡木质素与蜂蜡质量比为1:1),然后以丙酮和正己烷为溶剂喷涂到基材表面,在120 ℃加热60 min后CA可保持在150°以上,具有良好的热稳定性。Zhang等[26]使用蜂蜡改性木质素制备超疏水性和超亲油性棉花(Fig.2(d))也进行了类似验证。

2.3　生物蜡与无机微粒复合体系

自然界中广泛存在具有极强稳定性的二氧化硅被广泛应用于各种工业原料之中。Liu等[27](Fig.3(a))将多孔气相二氧化硅注入硅油作为基础,加入碳纳米管与硅橡胶混合,用蜂蜡疏水改性剂喷到基底上。CA可达162°,滚动角可低至4.8°,蜂蜡作为相变材料有助于材料的自修复,通过简单的热处理,可迅速恢复其优良的超疏水性和表面形貌。除了天然矿物二氧化硅,从人工培养的硅藻中提取的具有精细分层孔和大比表面积的硅藻颗粒也具有广阔的利用潜力。Sun等[28]以蜂蜡为相变材料在80 ℃乙醇溶液环境中填充硅藻颗粒(DF)微孔,制备了全生物质基超疏水蓄能涂层(Fig.3(b))。所有DF/蜂蜡复合涂层的水CA均在150°以上。在水射流破坏后在80 ℃的烘箱中加热20 min,又恢复到CA=156.4°,SA=7.1°。Zhang等[29]用棕榈蜡和二氧化钛作为稳定剂制成皮克林乳液,冷却分级得到48~70 μm和23~48 μm棕榈蜡微粒(Fig.3(c)),然后以PDMS固化剂将微粒吸附在壳聚糖甘油铸成的底膜上。涂层膜CA高

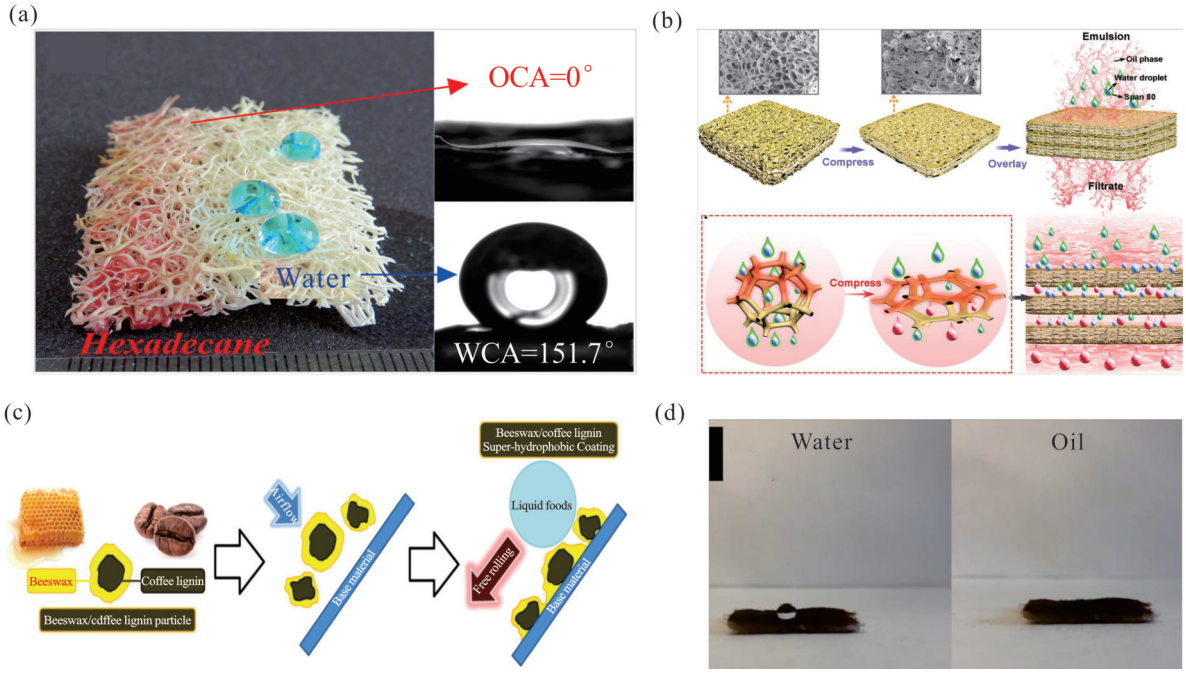


Fig. 2 (a) OCA and WCA measurements corresponding to hydrophobically modified LS[21]; (b) schematic diagram of the preparation and emulsion separation process of a superhydrophobic sponge from grapefruit peel[15]; (c) schematic diagram of heat-resistant edible superhydrophobic coatings prepared with coffee lignin and beeswax[25]; (d) images of water droplets and oil droplets on the surface of beeswax-modified lignin cotton[26]

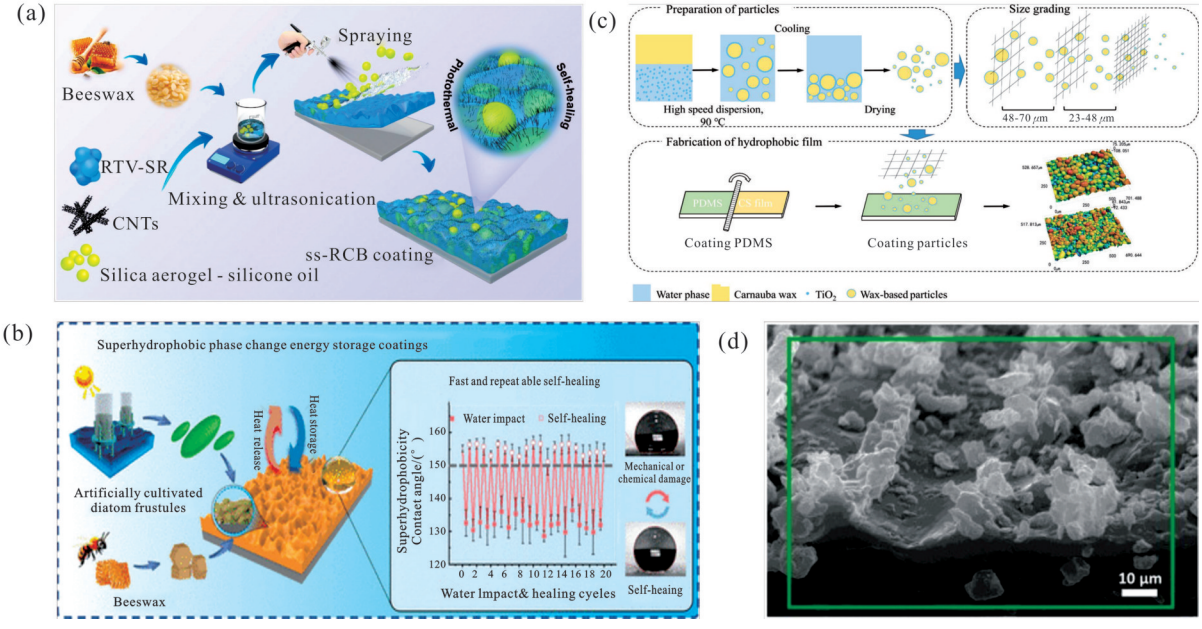


Fig. 3 (a) Schematic of the manufacturing process of ss-RCB coating[27]; (b) schematic of the preparation process of the coating and the contact angle of the water- cycling impact[28]; (c) manufacturing process of carnauba wax- based particles and chitosan-encapsulated membranes[29]; (d) SEM images of the hydrophobic Ag@Wax@PDMS-paper surface[31]

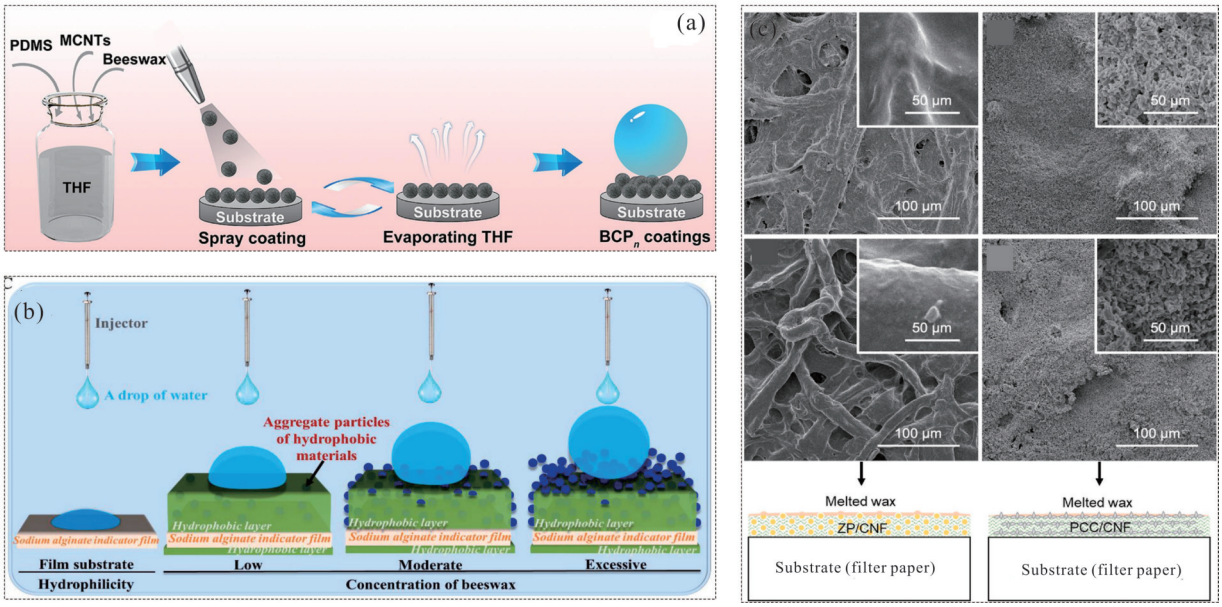


Fig. 4　(a) Preparation process and contact angle of BCPn coatings[32]; (b) effect of beeswax concentration on hydrophilicity/ hydrophobicity of the films and schematic diagram of the mechanism[34]; (c) SEM images and schematic diagrams of paper cross-section for ZP/ CNF and PCC/CNF papers treated with beeswax and candelilla wax, respectively[36]

于135°，但磨损后CA反而增大，且小粒径(23~48 μm)比大粒径(48~70 μm)具有更好的疏水性。Shreya等[30]向氯仿中加入棕榈蜡和氧化铝连续加热搅拌，然后在300 kPa压力下喷洒到玻璃基板上。分层结构的涂层形态由微尺度的突起、亚微孔和突起组成，表现出超疏水性(CA > 150°，SA < 5°)。相比之下，其他矿物和动物蜡会表现出温和的疏水行为。单质银纳米颗粒也是构建纳米级粗糙度的有利材料，Furkan等[31]将棕榈蜡乙醇分散体喷涂在模板法制成的微结构PDMS膜表面，最后气相沉积法在基板上涂覆Ag二级微结构(Fig.3(d))。多功能的Ag@Wax@PDMS-纸张表面对水和其他液体非常排斥，水CA=169°，SA=3°，甚至对粘性食品表现出防污作用，减少残留食物>97%。

2.4　生物蜡与其他材料复合体系

在制备光热转化材料中，Weng等[32]通过喷涂蜂蜡、多壁碳纳米管(MCNTs)和PDMS的四氢呋喃分散体混合物构建超疏水表面(Fig.4(a))。MCNTs的刚性使其在溶剂蒸发时保持球形结构，从而形成具有纳米结构的微粒，喷涂一次即可达到CA=158.3°和SA=1.4°，其太阳能热转换效率可达到82.2%。聚二甲基硅氧烷(PDMS)与生物质蜡配合使用的涂层十分普遍[33]，Shi等[34]研究了用蜂蜡/PDMS溶液提高海藻酸钠/纤维素纳米晶体/黑大豆种皮花青素pH指示膜的疏水性(Fig.4(b))。当蜂蜡浓度为5%时，水的CA=111.5°，即使薄膜在100%的湿度下保存10 d，水CA依然为108.3°。复合材料中加入硅烷疏水效果明显，黄婵娟等[35]将正硅酸四乙酯处理后的棉织物在棕榈蜡乳液和聚乙烯蜡乳液复配液中浸渍处理后，棉织物表面可形成一层包覆层,疏水角可达到155°，棉织物具有超疏水效果，经500次摩擦之后CA才下降1.9%左右。Wang等[36]以玉米醇溶蛋白/果胶浓缩液(ZP)为基质，然后加入CNF或沉淀碳酸钙(PCC)提供耐热微/亚微米形态铸造成膜，最后喷涂无表面活性剂的蜂蜡或茶花蜡乳液，为涂层提供高表面粗糙度和低表面能(Fig.4(c))。蜂蜡和烛台蜡表面均出现了15~30 μm大小的颗粒，除“全脂牛奶”外对流食具有超疏性。

3　生物质蜡功能化应用

3.1　食品包装

食品包装一方面是防止食品黏附在基材表面，使得拥有更好的消费体验；另一方面，超疏水结构本身固有的抗菌功能及其他功能组分的加入赋予包装

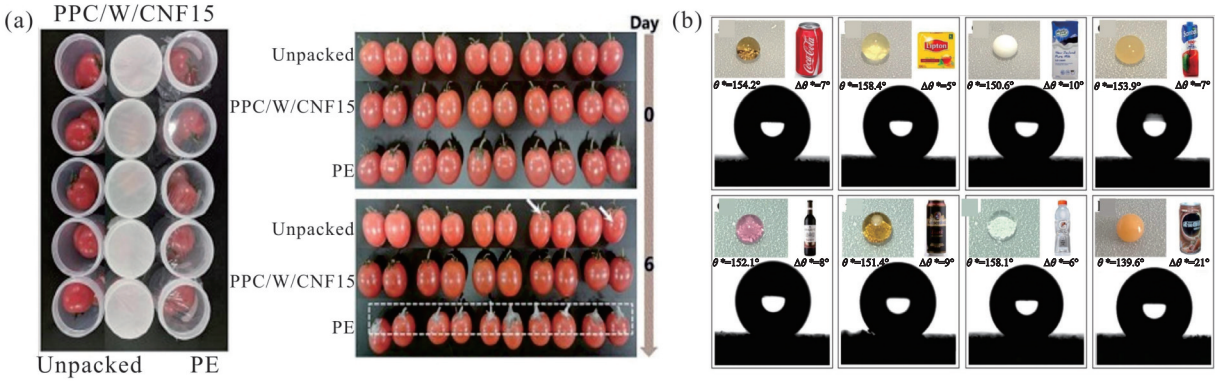


Fig. 5 (a) Changes in the appearance of virgin fruit preserved for 6 d with different treatments[37]; (b) water contact angle θ^* of edible superhydrophobic interfaces with liquid foodstuffs[38]

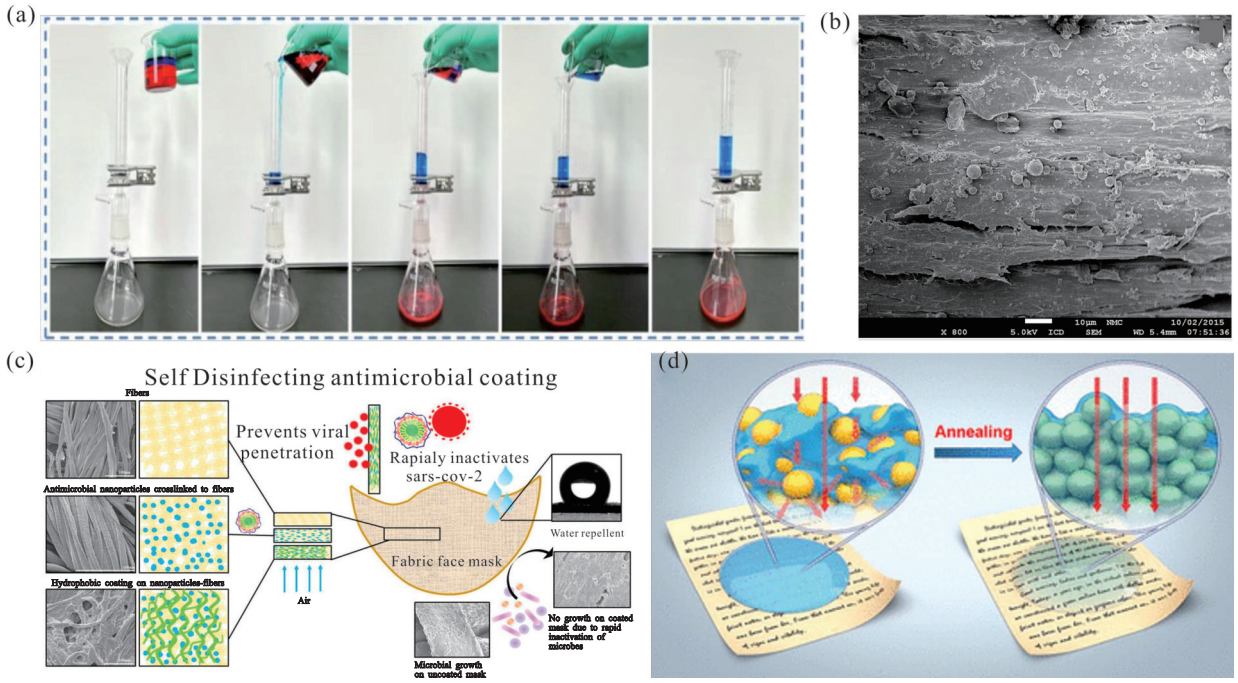


Fig. 6 (a) Palm wax/PDA-Fe_3O_4@PPAF oil/water gravity separation process[40]; (b) SEM image of wax particles wood protective coating[16]; (c) schematic diagram of a self-sterilising antimicrobial hydrophobic mask[44]; (d) high transmittance hydrophobic paper protection[45]

材料优良的抗菌性能。Arihant等[16]将不同比例混合昆虫蜡(蜂蜡和虫胶蜡)溶解在加热乙醇中,喷涂在纸、杯子和碗上,发现混合昆虫蜡在60 ℃退火处理后表现出最优的排斥性,对3%醋酸和10%乙醇,CA在139°~145°之间,对果汁、碳酸饮料和蜂蜜等食物也具有很好的阻隔性。Zhu等[37]以菠萝皮纤维素为基质,菠萝皮CNF为增强相,棕榈蜡为疏水剂,制备出多功能CNF复合薄膜(CA>100°)。该薄膜表现出抗紫外线性和抗氧化性能,有效延缓了圣女果的采后变质进程(Fig.5(a))。传统的超疏水表面制备方法不适用于食品的柔性表面应用,Li等[38]将蜂蜡溶于丙酮和正己烷制得乳液,喷涂到用阿拉伯胶、明胶和甘油铸成的弹性膜表面,除含有乳化剂的食品外,对大多数液体食品都有较大的CA,蜂蜡的ρ≈0.55 mg/cm^{2}时,水CA达158.1°(Fig.5(b))。即使经过长时间的反复折叠和冲洗,该界面能够保持良好的超疏水性。这种仿生食用超疏水界面在减少高附加值液体食品的残留方面具有潜在应用价值。

3.2 油水分离

生物质蜡特殊官能团对油具有一定极性相亲

性,用生物蜡制成的含有吸油通道的复合多孔材料具有良好的油水分离能力。Nusret等[39]采用棕榈蜡和蜡烛烟体系制成的超疏水性(CA=172°,SA=3°)涂层膜,对正己烷和甲苯的水混合物通过量高达1061 L/(m^2·h),分离效率超过90%。Qi等[40]采用简易熔吹路线制备PP纤维毡,紫外线诱导的多巴胺在纤维上的快速聚合和浸渍小烛树蜡疏水改性。疏水层与粗糙微观结构的协同作用显著改善了油水选择性。通过Fig.6(a)所示方法,纤维毡的吸附能力达(10~20.48 g/g),分离效率高达99.02%,分离通量高达28662 L/(m^2·h),且至少可重复使用15次。

3.3　木材老化防护

防潮润湿是木材精加工过程中的一个重要难题,通常使用石化合成油漆涂层保护,但其不环保和对人体健康危害等问题限制了其使用,因而天然生物质蜡在此领域扮演了极其重要角色。Alina等[16]制备棕榈蜡颗粒用于木材表面(Fig.6(b))干燥棉布抛光,利用木材表面结构和蜡颗粒共同作用,水的CA达120°。在提高竹的疏水性和抗霉性能方面,Guan等[41]用石蜡和棕榈蜡混合纳米二氧化硅粉末在退火过程中制备角质化竹。纳米二氧化硅粉末的加入使得退火温度越高,角化竹子表面的疏水性越强。Akbar等[42]用棕榈蜡混合环氧树脂/PDMS双基质增强,可有效提高涂层的长期木材防水性能。使木材表面的CA达172°,SA<3°。与环氧树脂相比,混合PDMS涂层具有更优异的耐久性,能够经受120次循环的室外风化/老化和恶劣环境(如化学物质、超声波和海水)的考验。

3.4　其他应用

生物质蜡除了以上常规应用外,在自修复、医疗、书籍古籍保护等方面也有重要应用。生物质蜡的相变性,使得其具有在温度调控下的自愈合功能。Zhang等[43]研究了棕榈蜡和改性荧光橡胶与分散在氟硅树脂中纳米纤维相结合,得到了超疏水涂层(CA=157°±1.2°,SA=4.5°±0.4°),涂层被损伤的微/纳米结构在加热120 s后能够迅速重建,有助于提高涂层在苛刻条件下的疏水稳定性和使用寿命。根据对抗菌、抗病毒环保材料的需要,Kapil等[44]以柠檬酸为交联剂,通过简单的浸渍法将由壳聚糖、丁香酚纳米乳液交联到织物上,然后用蜂蜡二次疏水改性,10次洗涤后CA仍大于120°,可应用于一次性口罩(Fig.6(c))。Wan等[45]受水稻叶片功能表皮的生物启发,通过将生物蜡/二氧化硅杂交体喷涂在蛋白质沉积的生物纤维结构上,进行热退火相变固化透明涂层(Fig.6(d)),在历史书籍/艺术品的保存等方面都有应用前景。

4　结语与展望

尽管使用天然疏水材料生物质蜡制备疏水/超疏水材料已经取得巨大进展,但必须清楚认识到,在未来的开发和潜在应用中仍需应对一些挑战。以生物蜡构建的微结构难以满足耐用需求,需要进一步探索增强生物质蜡疏水材料的耐用性;为满足环保发展需求,开发绿色溶剂体系,特别是水性体系是未来可持续生产中的绝对趋势;在功能化开发与应用方面,首先实现食品包装等基础领域的应用需求,这也是当前最大市场需求。其次在疏水生物质蜡材料基础上在自修复、医疗、书籍古籍保护及取代矿物蜡等领域开发更多的应用案例。生物质蜡是可大量获取的具有天然疏水特性的可再生材料,其独特的理化性质,使其能够广泛应用于各个领域。在倡导低碳环保、绿色发展趋势中,生物质蜡疏水/超疏水材料在可持续高质量发展道路中拥有广阔的应用前景。

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Progress on Research and Application of Biomass Waxes in the Preparation of Hydrophobic/Superhydrophobic Materials

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ABSTRACT: Biomass wax, with its sustainability, environmental friendliness, and unique physicochemical properties, has become a research hotspot for the preparation of hydrophobic/superhydrophobic materials. This paper reviewed the mechanism and methods for the preparation of hydrophobic/superhydrophobic materials from biomass waxes, and highlighted the current research progress on the phase change recrystallization properties and low surface energy modification of biomass waxes for the preparation of hydrophobic composites. Meanwhile, this paper also systematically summarized the progress of biomass waxes in applications such as food packaging, oil-water separation and wood protection. Finally, the current problems in the preparation of hydrophobic/superhydrophobic coatings from biomass waxes were analyzed in depth, and a prospective outlook on the future development direction and trend of biomass waxes was given in the light of market demand.

Keywords: biomass wax; carnauba wax; beeswax; hydrophobic; superhydrophobic; recrystallization; sustainability