

· 研究论文 ·

基于环氧树脂相转变的耐磨超双疏表面的制备与表征

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摘 要 既疏水又疏油的超双疏表面是疏液表面发展应用的重要趋势,然而,在受到外界摩擦时该类表面的微纳粗糙结构会因磨损而导致双疏性能迅速下降甚至丧失,向双疏粉体中加入高分子胶黏剂来构筑复合涂层是提高双疏表面耐磨性最为常用的方法,但往往由于双疏粉体会被胶黏剂包埋而效果不佳.本工作在自主合成出性能较佳的超双疏纳米粉体的基础上,利用溶解于良溶剂中的高分子胶黏剂加入到不良溶剂中会发生相转变而呈现出球状形貌的性质,将环氧树脂溶液滴入分散有超双疏纳米粉体的不良溶剂中,引发相转变后再通过超声处理促使双疏纳米粉体在环氧树脂相转变液滴表面紧密包裹形成细腻稳定的Pickering乳液滴,而后经喷涂固化得到由多层核壳微球组成的超双疏涂层.双疏粉体处于核壳微球表面保证了涂层的双疏性能不因胶黏剂存在而下降,多层自相似结构又赋予了涂层较好的耐磨性.经测试,厚度60 μm 左右的涂层可在负重200 g砝码情况下耐400#砂纸表面摩擦60个循环(总行程约1650 cm)后仍保持较佳的超疏水性和一定程度的疏油性.该方法原则上可以适用于任何能在不良溶剂中发生相转变的高分子胶黏剂,为耐磨超疏水/超双疏涂层的制备及应用提供了借鉴方向.

关键词 环氧树脂;超双疏表面;耐磨性;相转变;Pickering乳液;自相似结构

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超双疏表面是指水滴和油滴在其表面的接触角均大于 150° ,滚动角小于 10° 的一类表面^[1].相比单纯的超疏水或超疏油表面,超双疏表面的制备难度更大,一般均需在基材表面上构筑出以多孔结构^[2,3]、凹角结构^[4,5]和层次结构^[6,7]为代表的多重微观粗糙度,才能获得较好的双疏性.与制备难度成正比的是,超双疏表面在自清洁和抗污^[8~10]、流体减阻^[11,12]、防冰^[13,14]、耐腐蚀^[15,16]等方面比单一超疏水或超疏油表面更具优势,在

航空航天、海洋工程、能源、医疗、建材等领域具有更为广阔的应用前景,是疏液表面发展应用的重要趋势^[17,18].然而,基于微纳粗糙结构的超双疏表面较为脆弱,一旦表面的微结构或化学物质受到破坏,其超双疏性就会受到影响,甚至失效,如何提高超双疏表面的机械耐久性已经成为该领域的研究热点.

近年很多课题组开展了提高超疏水或超双疏表面耐磨性和耐久性的研究工作,也取得了较为

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丰硕的成果, 其中被采用最多的方法是用胶黏剂来提高涂层材料与基底之间的黏附力, 借以减少涂层在外力作用下因摩擦磨损而导致的脱落可能性, 常用的胶黏剂有环氧树脂^[19-21]、聚氨酯^[22,23]、聚二甲基硅氧烷(PDMS)^[24,25]、聚偏氟乙烯^[10,26]以及磷酸二氢铝^[27,28]等。此外, 设计涂层成分, 让被破坏的超疏水/超双疏涂层通过室温静置^[29]、形状记忆^[30]或者在紫外照射^[31,32]等外界条件刺激下能够进行自修复也是有效提升超疏水或超双疏涂层耐久性的一个方法。除此之外, 通过激光烧蚀^[33,34]、光刻蚀^[35,36]、3D打印^[37]等方法在基材表面制得规整的微结构, 将脆弱的超疏水或超双疏纳米颗粒嵌藏在微结构中也可以达到快速提升涂层机械稳定性的效果。例如, Wang等^[38]利用利用光刻、冷/热压等精细加工技术在硅片、陶瓷、金属、玻璃等基材表面构筑了以倒四棱锥微腔阵列为代表的微结构, 为超疏水纳米颗粒提供“铠甲”, 避免外力对纳米颗粒的直接磨损, 从而显著提高了表面的耐磨性能。虽然超疏水和超双疏表面耐久性提升方面的研究工作取得了较大的进展, 但从涂层性能和实际应用的角度看, 大多数方法仍存在一定的缺陷。以最为简单的胶黏剂增强法为例, 如果采用胶黏剂与双疏粉体共混的施工工艺, 胶用量少起不到强化作用, 胶用量大则往往会出现改性粉体被胶黏剂包埋从而导致涂层疏水或双疏性能下降甚至消失的问题; 而采取先在基材表面施胶再喷涂改性粉体的方式, 处于涂层外表面的改性粉体一旦被外力摩擦磨损后, 整个涂层就会全部失效。而自修复方法则存在制造成本较高、制备较困难且自修复次数有限等问题。微结构保护法虽然效果较好, 但微结构往往需要用到精密的激光或光刻蚀设备, 很难实现低成本规模化应用。可见, 耐久性差以及缺乏低成本且易于实现规模化生产的成熟技术路线仍然是超双疏表面制备及应用过程中亟须解决的2个重要问题。

为解决以上问题, 本工作基于溶解在良溶剂中的环氧树脂加入不良溶剂中会立即发生相转变而蜷缩为微球状结构这一特性, 重新设计了双疏粉体与胶黏剂的作用方式, 解决了胶黏剂对双疏粉体的包埋问题, 最终经喷涂得到的是由多层自相似的核壳微球构建的耐磨涂层, 有效解决了涂层的耐久性问题。

1 实验部分

1.1 主要原料

气相纳米SiO₂ (粒径7~40 nm), 连云港瑞创新材料科技有限公司; 正硅酸乙酯, 天津科密欧化学试剂有限公司; 1H,1H,2H,2H-全氟癸基三乙氧基硅烷, 上海易恩化学技术有限公司; 氨水(25%~28%), 山东科源生化有限公司; 双酚A型环氧树脂, 智仑新材料科技有限公司; 2-甲基咪唑, 上海阿拉丁生物科技有限公司; 四氢呋喃, 天津科密欧化学试剂有限公司; 石油醚和无水乙醇, 天津天力化学试剂有限公司。

1.2 实验过程

1.2.1 超双疏纳米粉体合成

1 g 气相纳米SiO₂加入50 mL无水乙醇中, 超声5~10 min使之分散均匀, 倒入三口烧瓶中在室温下磁力搅拌, 依次向烧瓶中加入250 μ L正硅酸乙酯(TEOS)、400 μ L全氟癸基三乙氧基硅烷(FAS-17), 5 mL氨水, 继续搅拌反应12 h。所得浊液5000 r/min离心15 min, 倒去上清液后凝胶用无水乙醇超声漂洗后再次离心, 凝胶55 $^{\circ}$ C真空干燥8 h, 研磨过400目筛后得到超双疏粉体。

1.2.2 相转变法制备耐磨超双疏涂层

称取1 g双酚A环氧树脂, 加入5 mL四氢呋喃, 搅拌溶解后得到A液; 称取0.5 g超双疏粉体, 加入4 mL石油醚, 超声3 min分散均匀得到B液。在室温快速磁力搅拌下将A液缓慢滴入B液中, 由于石油醚是双酚A环氧树脂的不良溶剂, 溶解在四氢呋喃的环氧树脂会发生相转变而得到白色乳浊液, 再超声5 min促使形成细腻稳定的Pickering乳液滴, 而后再向其中加入0.2 g的固化剂2-甲基咪唑, 搅拌10 min后将乳液喷涂在载玻片上, 室温晾2~5 min后将载玻片置于80 $^{\circ}$ C热风烘箱中固化2 h。

1.2.3 仪器表征

采用Nicolet is-10傅里叶变换红外光谱仪测试双疏粉体的表面官能团, 测试波数范围400~4000 cm⁻¹, KBr压片法; 采用日立公司H600型透射电子显微镜观察双疏粉体表面情况; 采用日本电子JSM-IT700HR型场发射扫描电子显微镜测试粉体以及涂层的表面形貌; 采用德国Kruss公司DSA25E型接触角测量仪测试涂层表

面水及各类油性溶剂的静态接触角.

1.2.4 涂层耐磨性表征

将400#砂纸(4.5 cm × 27.5 cm, 宽 × 长)固定在实验台面上, 裁剪喷镀有双硫涂层的载玻片用双面胶固定于200 g砝码下, 用细绳牵引砝码在砂纸表面上来回摩擦, 行程27.5 cm为1个循环, 每10个循环测一次水/油接触角.

2 结果与讨论

2.1 超双硫粉体的制备与表征

如图1(a)和1(b)所示, 所制备的双硫纳米粉

体粒径分散较为均匀, 由于合成过程中加入的正硅酸乙酯(TEOS)水解生成的更小的纳米SiO₂颗粒附着于气相SiO₂种子表面, 最终粉体表面呈现出较好的多层次粗糙度. 图1(c)红外光谱在波数1104和471 cm⁻¹处出现Si—O—Si的特征吸收峰, 1209和705 cm⁻¹处出现C—F键对应的吸收峰, 表明氟碳链已经接枝到粉体表面. EDS检测结果(图1(d))也证实粉体表面含有F元素, 且粉体表面F的原子比高达21%左右. 粉体表面疏水疏油的氟碳链以及多级微观粗糙度共同保证了其表面较佳的双疏性.

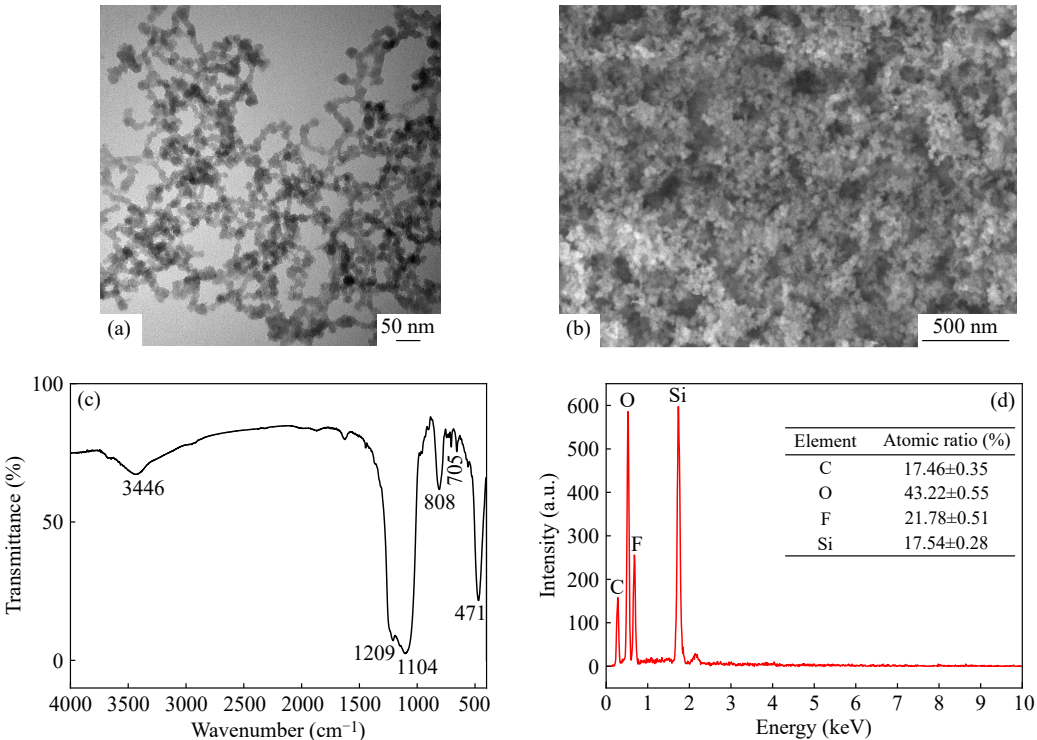


Fig. 1 TEM image (a), SEM image (b), FTIR spectrum (c) and EDS spectrum (d) of superamphiphobic nano-powders.

将所得超双硫粉体超声分散在无水乙醇中, 制得浓度为20 mg/mL的分散液, 喷涂于载玻片表面, 晾干后测试各类液体的静态接触角. 5 μL的水滴悬停在针头上无法滴落在涂层表面(图2(a), 电子支持信息视频S1), 水滴增加到10 μL后, 液滴在重力作用下滴落在载玻片表面会瞬间滚走(图2(b), 电子支持信息视频S2), 可见所得粉体的疏水性是很强的, 粉体涂层不仅水接触角大于150°, 滚动角也接近于0°. 用乙二醇(表面能约45 mJ/m²)、液体石蜡(表面能约35 mJ/m²)、橄榄油(表面能约34 mJ/m²)和甲苯(表面能约28.9 mJ/m²)作为油性液滴, 测得静态接触角分别为(159.7±

4)°、(155.9±2.5)°、(154.6±2.5)°以及(151.2±0.7)°, 均能达到超疏油的状态. 液滴的接触角数值与各类油性溶剂的表面能有一定的关联度, 表面能低的油性液体在双硫表面的接触角会稍低一些. 各类液体在涂层表面的滚动滑落情况视频见电子支持信息视频S3.

2.2 相转变法制备环氧树脂/双硫粉体复合涂层

图3对比了超声处理对相转变样品外观及乳液滴形貌的影响, 由于石油醚是环氧树脂的不良溶剂, 溶解于四氢呋喃中的环氧树脂遇到石油醚后迅速发生相转变而由舒展的线状结构蜷缩为球状形貌, 光线在乳液滴中发生散射和折射而导致

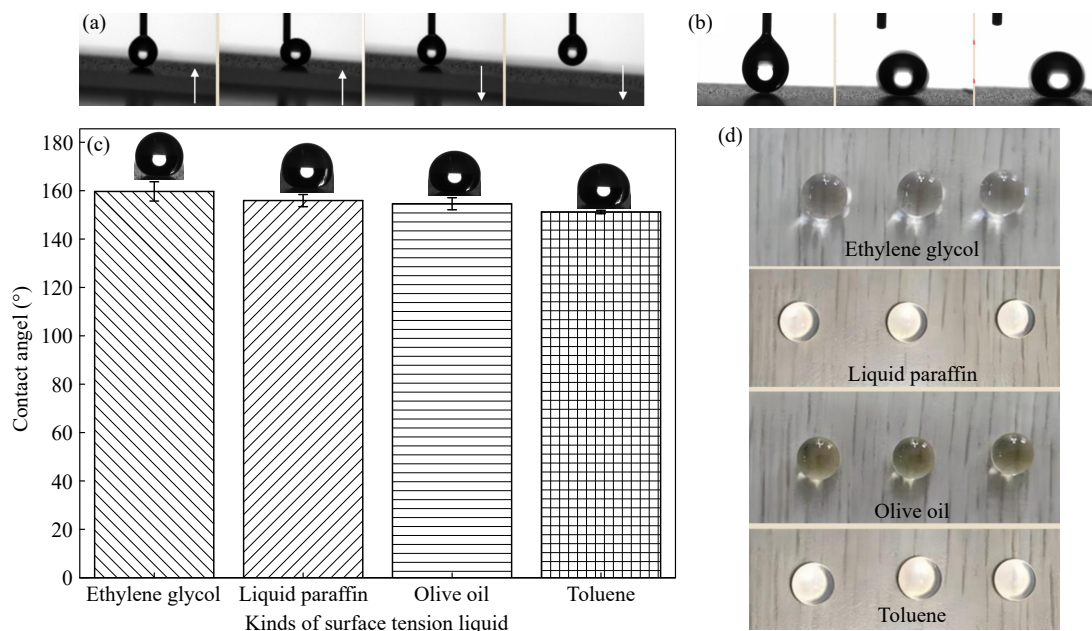


Fig. 2 Measurement results of the surface contact angle of superamphiphobic powder coatings: (a) the process of static contact angle testing for water, (b) scrolling screenshot of water droplet, (c) the static contact angles of four low surface energy liquids, (d) the existence states of four low surface energy liquids on the surface of superamphiphobic powder coatings.

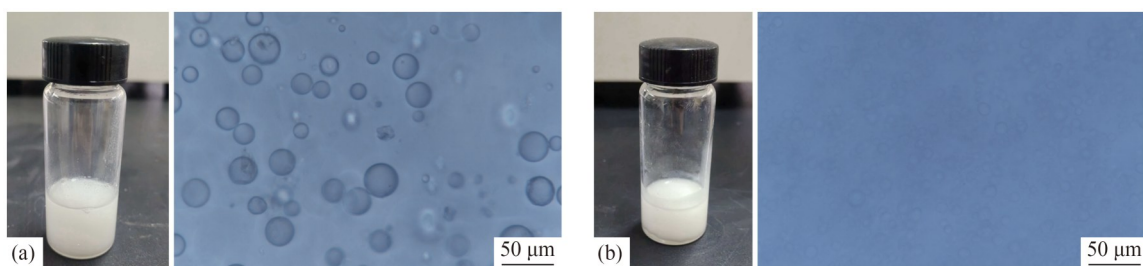


Fig. 3 Appearance and microscopic images of the phase transition system. (a) Before ultrasonic treatment; (b) After ultrasonic treatment.

液体呈现出乳白色, 未经超声处理的乳液滴在显微镜下呈现的是规则且饱满的球状形貌, 液滴尺寸较大, 此时可认为分散在乳液体系中的双疏纳米粉体尚未在相转变液滴表面进行有效包覆. 超声处理后, 乳液变得比较黏腻, 流动性变差, 颜色也明显加深, 显微镜下乳液滴尺寸变小, 球体透明度也大大减小, 应该是双疏纳米粉体在超声促进下与相转变的环氧树脂液滴发生了较为强烈的相互作用, 纳米颗粒在乳液滴表面进行了有效包覆, 使结构不是很稳定的相转变乳液滴转变为纳米颗粒作为表面稳定剂的 Pickering 乳液滴, 为后续得到结构较为稳定的环氧树脂/双疏粉体核壳微球奠定基础.

图 4(a) 和 4(b) 是喷涂于载玻片表面的多层环氧树脂/双疏粉体核壳微球涂层的微观形貌. 由于环氧树脂高分子与双疏纳米粉体相遇时迅速

发生了相转变, 因而树脂液滴大多以微米级的球状形式存在, 对纳米粉体的包埋作用大大减弱, 大量的纳米粉体在超声波的作用下对环氧树脂相转变聚集体表面进行了包裹, 形成了类似 Pickering 乳液的核/壳结构, 加入固化剂后这种结构得以保持. 该类环氧树脂/双疏粉体核/壳结构有利于最大程度发挥表面改性粉体的双疏效果, 固化后坚硬的环氧树脂核也能为粉体提供刚性支撑. 需要注意的是, 这类紧密堆积的多层核/壳微球涂层的每一层均具有自相似的结构, 在遇到外界摩擦而产生磨损后, 下一层的复合微球依然可以使涂层保持较好的双疏性和耐磨性. 图 4(c) 和 4(d) 则分别呈现了 C、O、F、Si 4 种元素在复合微球表面存在的状态, 可以看到 F、Si 等元素在微球的外表面分布比较均匀.

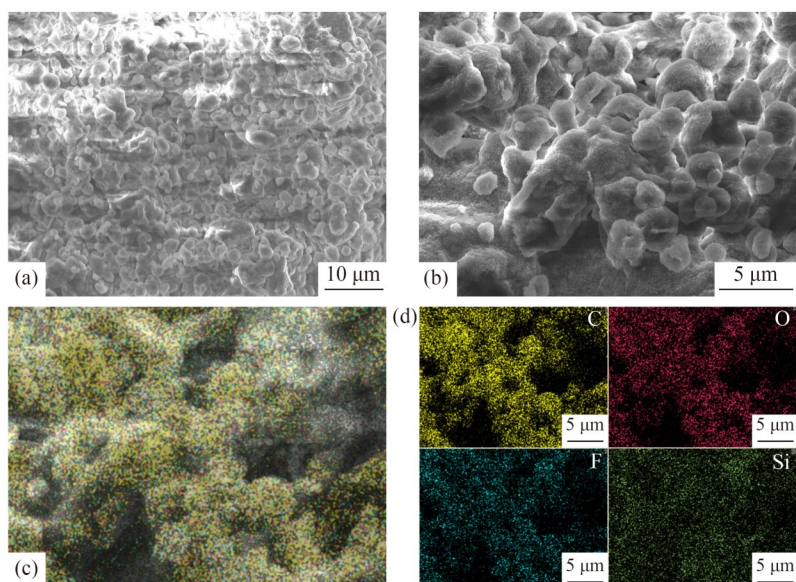


Fig. 4 SEM images of epoxy resin/superamphiphobic powder multi-layer core/shell microspheres coating. (a): $\times 2000$; (b): $\times 5000$; (c) Elemental mapping image of the coating; (d) Elemental mapping images of C, O, F, Si.

2.3 涂层耐磨性测试

涂层耐磨性主要采取砂纸打磨法测试(电子支持信息视频S4),即在200 g砝码下方黏附上电镀有环氧树脂/双疏粉体核壳微球涂层的载玻片,用细绳牵引砝码在长度约为27.5 cm的400#砂纸上来回摩擦,每拖动27.5 cm记为1个循环,记录涂层的接触角随摩擦次数的衰减情况.为对比起见,在对纯粉体涂层样板的初始接触角测量基础之上(图2),对纯环氧树脂涂层样板的初始接触角也进行测量(选取水和表面能居中的液体石蜡作为测试溶剂),并对两种板子也进行一定次数的打磨,对比其与复合涂层的双疏性与耐磨性区别.

由图5(a)可见,对于纯双疏粉体样板,经10个循环打磨,样板表面的粉体涂层就基本被打磨掉了,其对水及液体石蜡的接触角迅速下降为 $(46.1 \pm 1.5)^\circ$ 以及 $(31.2 \pm 1.0)^\circ$,丧失了双疏性;而对于纯环氧树脂样板(图5(b)),其水接触角初始值仅为 $(84.1 \pm 1.5)^\circ$,液体石蜡的接触角仅为 $(75.8 \pm 1.5)^\circ$,涂层不具备双疏性.经过20次打磨,水静态接触角稍有下降,但液体石蜡的静态接触角则迅速衰减至 20° 左右.相对应的,环氧树脂/双疏粉体复合涂层即使经过60次砂纸打磨,涂层的水接触角依然大于 150° ,保持在超疏水状态;而对其它低表面能液体,涂层的接触角衰减稍快,打磨50次时涂层的乙二醇、液体石蜡和橄榄油的静态接触角分别下降到 $(151.7 \pm$

$1.5)^\circ$ 、 $(150.8 \pm 1.5)^\circ$ 和 $(150.2 \pm 1)^\circ$,打磨60次时这3种液体的接触角全下降为 150° 以下,分别为 $(149.9 \pm 1)^\circ$ 、 $(147.6 \pm 1.5)^\circ$ 和 $(148.1 \pm 1.5)^\circ$.对于表面能更低、渗透性更强的甲苯,砂纸打磨30次时涂层表面接触角就已经下降为 $(147.6 \pm 0.6)^\circ$,打磨60次时接触角更是低到了 $(136.5 \pm 1)^\circ$.大部分油性溶剂接触角下降均发生在30次以后,为进一步判断膜层的状态对涂层双疏性的影响,分别观察打磨30、50及60次的载玻片的外观及扫描电镜放大照片(图5(d)~5(f)),可以发现随着打磨次数增多,涂层表面的摩擦痕迹越深,打磨30次,涂层表面体积较大的复合微球层应该已经被磨掉了,处于中间层的微球已经暴露出来了;打磨50次和60次时涂层表面已经出现了明显的划痕,部分划痕较深区域的膜层已经被砂纸打磨掉,与砂纸打磨方向一致的条纹清晰可见,扫描电镜放大后的膜层依然可见有微球涂层的存在,但表层及中间层已经被摩擦掉,仅剩较为平滑的底层,残留的微球不仅尺寸较小且致密性不足,最终导致涂层双疏性出现下降.

图6是复合涂层的侧面放大图,可以看到涂层厚度仅60 μm 左右(图6(a)),但其仍然可以耐受砂纸负重打磨约1650 cm后依旧可以保持较好的超疏水性及一定程度的疏油性,之所以能呈现出如此结果,分析认为有2个主要原因,其一,便是相转变设计策略使双疏粉体大多存在于环氧树脂表面而不是被其包埋,粉体表面的双疏性得

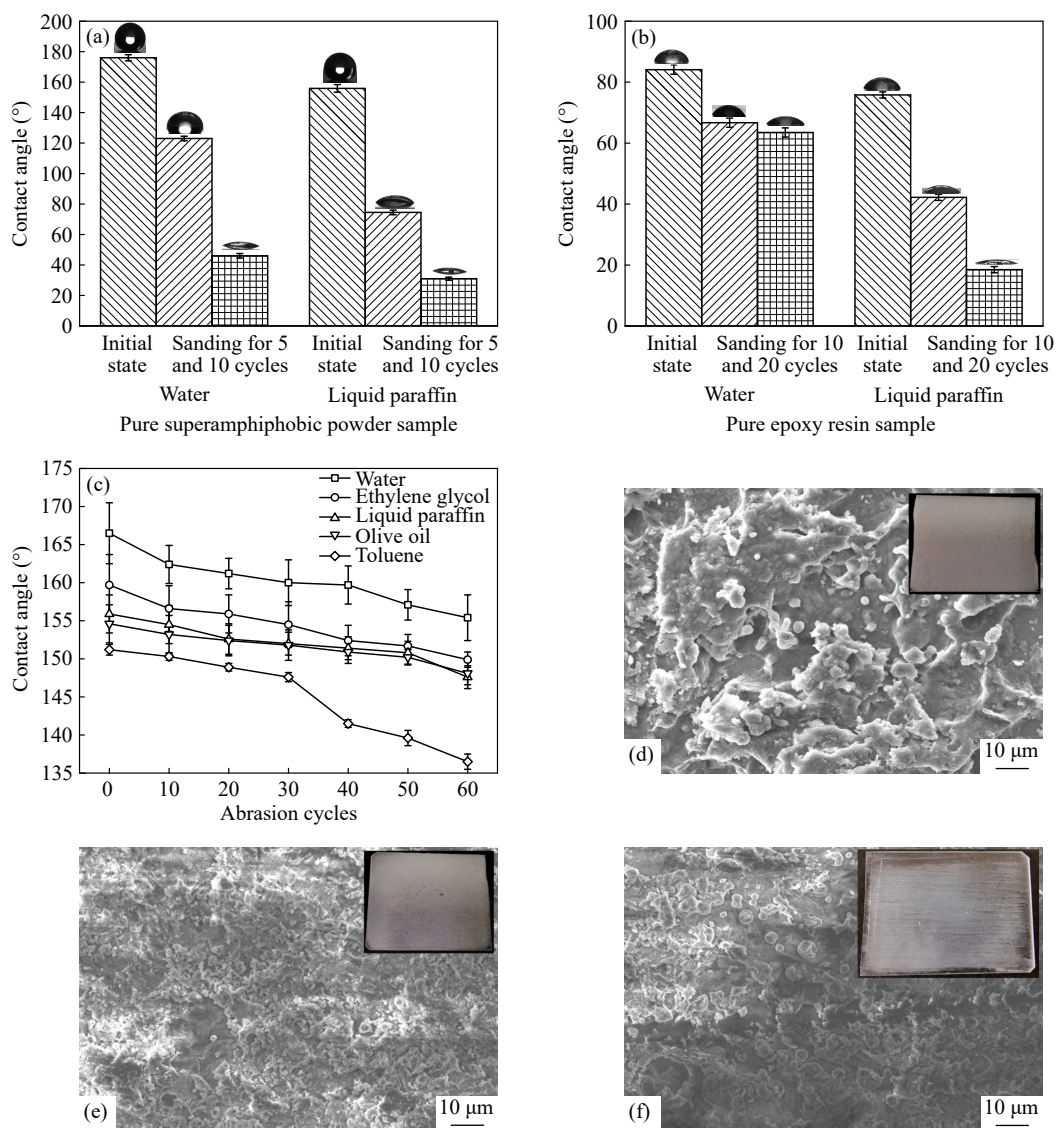


Fig. 5 Liquid-repelling and wearable performances of (a) the neat superamphiphobic powder coating, (b) pure epoxy resin coating and (c) epoxy resin/superamphiphobic powder composite coating; SEM images of composite coating after sanding (d) 30 cycles, (e) 50 cycles and (f) 60 cycles.

以最大程度保持, 喷涂后形成的多层结构中每层微球均具有自相似结构, 使得涂层性质不会因为表层被磨损而迅速衰减. 其二, 在喷涂以及后续的固化过程中首先发生的便是溶剂(包含不良溶剂)的快速挥发, 处于复合微球内部的尚未完全固化的环氧树脂亦会有一部分渗出而促使各层逐步连接为一个整体; 同时, 涂层在热风烘箱中加热固化时的受热规律应该是由表及里逐渐减弱, 使得涂层下方的环氧树脂在固化前具有稍长的渗出时间, 因而涂层的致密性和整体性也会呈现出从上到下逐渐增强的趋势. 从图6(b)可以看到, 与基底材料接触的最下方涂层自身不仅非常致密, 而且还与玻璃基底黏附的非常牢固. 因而可

以认为这种上层稍微疏松下层却较为致密的膜层结构有利于让复合涂层上半部分呈现出较好双疏性, 下半层却具有更佳的耐磨性. 在图5(c)中可看到, 液体石蜡、橄榄油及甲苯的接触角分别在50次后和30次后均有一个迅速下降的阶段, 估计此时双疏性更好的上半层已经出现了较明显的磨损.

为了明晰环氧树脂和双疏粉体在涂层耐磨性中所起的具体作用, 对纯环氧树脂涂层也进行了60个循环的砂纸打磨, 扫描电镜观察结果发现该涂层出现了大面积磨损脱落的现象(图7(a)), 残存的涂层连续性不佳. 对比环氧树脂/双疏粉体涂层, 发现纯的环氧树脂涂层并不比基于环氧树

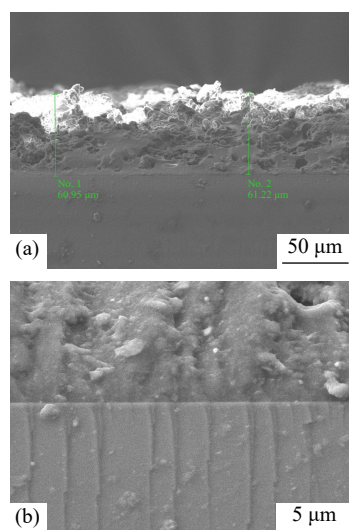


Fig. 6 SEM images of (a) coating thickness and (b) interfacial adhesion to the substrate.

脂相转变的复合表面更耐磨损。从图7(b)可以看出, 打磨后的涂层在微观上呈紧密的鱼鳞状排布, 分析认为这种刚性较强的结构反而容易被硬度更大的砂纸打磨掉, 而环氧树脂/双疏粉体多层自相似结构复合涂层可能由于微球体以及球体表面的纳米粉体的润滑效应, 反而表现出比纯环氧树脂涂层稍好的耐磨性。

2.4 相转变法制备耐磨超疏水/超双疏涂层的机理

基于以上表征及分析, 提出基于环氧树脂相

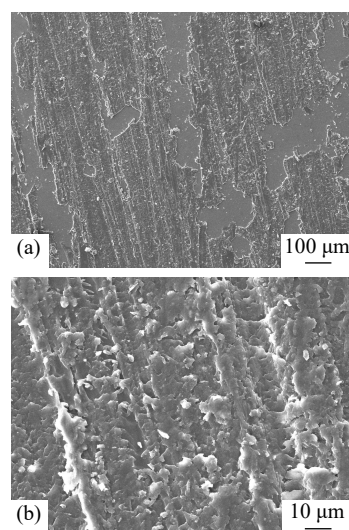


Fig. 7 SEM images of pure epoxy resin coating after sanding 60 cycles. (a) $\times 100$; (b) $\times 1000$.

转变制备耐磨超双疏涂层的机理(图8), 该方法主要为解决常用的胶黏剂增强法中纳米颗粒被高分子胶黏剂包埋而造成的双疏性能下降甚至消失的问题, 采用类似Pickering乳液滴的设计思维, 将高分子胶黏剂溶液滴加到分散有双疏纳米颗粒的不良溶剂中, 诱导胶黏剂相转变而成为分散在不良溶剂中的微小液滴, 快速搅拌或超声促进双疏粉体在小液滴表面紧密包裹而得到胶黏剂/双疏粉体核壳结构, 而后将此悬浊液喷涂或刷涂在基材表面, 固化过程中随着不良溶剂的挥发, 处

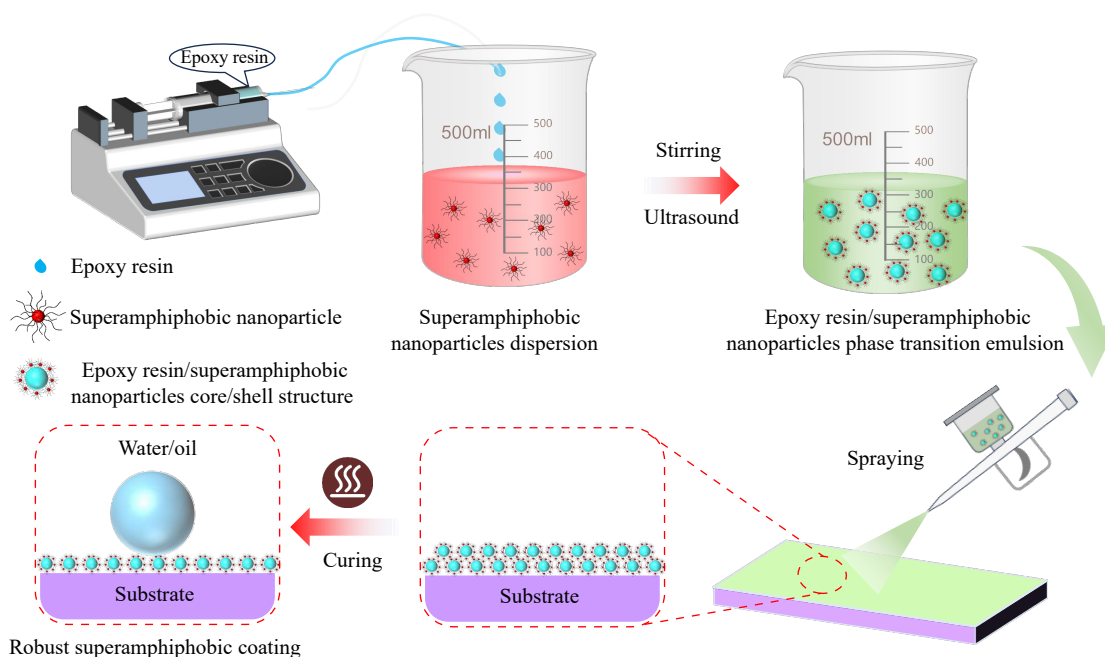


Fig. 8 Schematic diagram of the mechanism for preparing wear-resistant superamphiphobic coatings by phase transition method.

于微球内部的胶黏剂部分渗出并相互连接, 双疏纳米粉体在整个体系中也会起到微骨架的作用, 从而有利于得到既具有多层自相似结构和多重粗糙度, 又具有较强机械稳定性的超双疏涂层。

3 结论

利用高分子胶黏剂遇到不良溶剂会发生相转变的特性重新设计了胶黏剂与超双疏纳米粉体的

接触方式, 超声振荡进一步促进改性纳米粉体对胶黏剂微液滴的有效包裹, 得到了类 Pickering 乳液滴的核壳结构, 通过喷涂制备了具有多层自相似结构的耐磨超双疏涂层。此设计思想原则上可以适用于任何能在不良溶剂中发生相转变的高分子胶黏剂, 为耐磨超疏水/超双疏涂层制备技术提供了一个可行性较高的思路。

REFERENCES

- Li, H. J.; Wang, X. B.; Song, Y. L.; Liu, Y. Q.; Li, Q. S.; Jiang, L.; Zhu, D. B. Super-“amphiphobic” aligned carbon nanotube films. *Angew. Chem.*, **2001**, 113(9), 1793–1796.
- Li, F.; Du, M.; Zheng, Q. Dopamine/silica nanoparticle assembled, microscale porous structure for versatile superamphiphobic coating. *ACS Nano*, **2016**, 10(2), 2910–2921.
- Hegner, K. I.; Wong, W. S. Y.; Vollmer, D. Ultrafast bubble bursting by superamphiphobic coatings. *Adv. Mater.*, **2021**, 33(39), 2101855.
- Zhao, X.; Duan, Y. P. Improve the mechanical durability of superhydrophobic/superamphiphobic coating through multiple cross-linked mesh structure. *Colloids Surf. A Physicochem. Eng. Aspects*, **2022**, 642, 128560.
- Li, H. J.; Jin, Q. Q.; Li, H. B.; Tong, H.; Wang, K. K.; Chen, S. R.; Ouyang, G. F.; Wang, Z. K.; Li, Y. N. Transparent superamphiphobic material formed by hierarchical nano re-entrant structure. *Adv. Funct. Mater.*, **2024**, 34(3), 2309684.
- Zhou, N.; Hou, S. H.; Noh, I.; Liu, Q. Q.; Wang, Y. B.; Do Kim, H.; Zhou, Q.; Ohkita, H.; Wang, B. B. Constructing robust and multifunctional superamphiphobic surfaces by using two different nanostructures of silicon dioxide. *Langmuir*, **2025**, 41(9), 6376–6388.
- Zhang, D. J.; Wu, G. Q.; Li, H.; Cui, Y.; Zhang, Y. M. Superamphiphobic surfaces with robust self-cleaning, abrasion resistance and anti-corrosion. *Chem. Eng. J.*, **2021**, 406, 126753.
- Wang, C.; An, D.; Yang, T.; Gu, L. X.; Xie, M. X.; Lin, X. K.; Han, C. X.; Song, Y. Q.; Deng, Q. Y.; Wen, F. Self-cleaning and amphiphobic properties of octadecyltrichlorosilane self-assembled modified polytetrafluoroethylene films. *Colloids Surf. A Physicochem. Eng. Aspects*, **2024**, 684, 133132.
- Chen, D. D.; Gao, F.; Liu, T. Y.; Kang, J.; Xu, R. Z.; Cao, Y.; Xiang, M. Fabrication of anti-fouling thin-film composite reverse osmosis membrane via constructing heterogeneous wettability surface. *J. Appl. Polym. Sci.*, **2021**, 138(42), 51256.
- Peng, J. W.; Yuan, S. C.; Geng, H. L.; Zhang, X. G.; Zhang, M.; Xu, F.; Lin, D.; Gao, Y. Y.; Wang, H. Y. Robust and multifunctional superamphiphobic coating toward effective anti-adhesion. *Chem. Eng. J.*, **2022**, 428, 131162.
- Wang, Z. C.; Liu, X. J.; Ji, J. W.; Tao, T. T.; Zhang, T.; Xu, J. M.; Jiao, Y. L.; Liu, K. Underwater drag reduction and buoyancy enhancement on biomimetic antiabrasive superhydrophobic coatings. *ACS Appl. Mater. Interfaces*, **2021**, 13(40), 48270–48280.
- Fakhri, M.; Rezaee, B.; Pakzad, H.; Moosavi, A. Facile, scalable, and low-cost superhydrophobic coating for frictional drag reduction with anti-corrosion property. *Tribol. Int.*, **2023**, 178, 108091.
- Xiao, Z.; Chen, C. J.; Liu, S. Q.; Liu, C. Z.; Liu, W. L.; Cheng, Z.; Yu, X. Q.; Lu, Y.; Zhang, Y. F. Endowing durable icephobicity by combination of a rough powder coating and a superamphiphobic coating. *Chem. Eng. J.*, **2024**, 482, 149001.
- Wood, M. J.; Brock, G.; Debray, J.; Servio, P.; Kietzig, A. M. Robust anti-icing surfaces based on dual functionality-microstructurally-induced ice shedding with superimposed nanostructurally-enhanced water shedding. *ACS Appl. Mater. Interfaces*, **2022**, 14(41), 47310–47321.
- Ren, G. Y.; Qiao, Z. T.; Tuo, Y.; Zheng, W. J.; Chen, X. D.; Shang, J. F.; Xu, H. T.; Bai, L.; Cao, X.; Ma, H. X.; Gao, X. H.; Li, S. Y. Graded fillers method fabricating superamphiphobic coatings with high thermal conductivity, wear resistance and durable corrosion resistance. *Prog. Org. Coat.*, **2024**, 189, 108268.

- 16 Wei, J. F.; Li, B. C.; Jing, L. Y.; Tian, N.; Zhao, X.; Zhang, J. P. Efficient protection of Mg alloy enabled by combination of a conventional anti-corrosion coating and a superamphiphobic coating. *Chem. Eng. J.*, **2020**, 390, 124562.
- 17 Zhang, B. B.; Yang, G.; Xu, W. C.; Duan, J. Z.; Hou, B. R. Hybrid superamphiphobic anti-corrosion coating with integrated functionalities of liquid repellency, self-cleaning, and anti-icing. *J. Mater. Sci. Technol.*, **2024**, 184, 256–268.
- 18 Zhang, L. G.; Zhang, P. Y.; Guo, Z. G. Advances in the durability of biomimetic superamphiphobic surfaces. *Nano Today*, **2025**, 62, 102686.
- 19 Peng, J. Y.; Zhao, X. J.; Wang, W. F.; Gong, X. Durable self-cleaning surfaces with superhydrophobic and highly oleophobic properties. *Langmuir*, **2019**, 35(25), 8404–8412.
- 20 Elzaabalawy, A.; Meguid, S. A. Development of novel superhydrophobic coatings using siloxane-modified epoxy nanocomposites. *Chem. Eng. J.*, **2020**, 398, 125403.
- 21 Zhang, B. B.; Liu, X.; Zhan, T. R.; Hou, B. R. Bilayer coating fabricated on aluminum alloy substrates with superamphiphobicity, corrosion resistance, self-cleaning, and delayed icing properties. *J. Mater. Res. Technol.*, **2024**, 30, 8218–8227.
- 22 Zheng, Y. J.; Wang, K. L.; Sun, L.; Shi, H. L.; Zhang, X. Preparation of PFDTS-Kaolin/PU superamphiphobic coatings with antibacterial, antifouling and improved durability property. *Prog. Org. Coat.*, **2022**, 173, 107145.
- 23 Zhang, J. T.; Yang, J. Y.; Li, Q. Y.; Ding, J.; Liu, L. J.; Sun, T.; Li, H. H. Preparation of WPU-based super-amphiphobic coatings functionalized by *in situ* modified SiO_x particles and their anti-biofilm mechanism. *Biomater. Sci.*, **2021**, 9(22), 7504–7521.
- 24 Zhou, X. T.; Liu, J.; Liu, W. D.; Steffen, W.; Butt, H. J. Fabrication of stretchable superamphiphobic surfaces with deformation-induced rearrangeable structures. *Adv. Mater.*, **2022**, 34(10), 2107901.
- 25 Xiao, T.; Wei, K.; Wang, Y. D.; Jiang, L. H.; Xiang, P.; Li, X. Y.; Tan, X. Y. Transparent and durable PDMS(O)/HDTMS anti-icing surfaces derived from candle soot. *Surf. Coat. Technol.*, **2022**, 445, 128717.
- 26 li, J.; Xu, L. H.; Yuan, X. L.; Pan, H.; Wang, L. M.; Shen, Y.; Li, K. T. Preparation of robust and self-healing superamphiphobic cotton fabrics based on modified silica aerogel particles. *Colloids Surf. A Physicochem. Eng. Aspects*, **2022**, 651, 129634.
- 27 Jiao, X.; Li, M. T.; Yu, X. Q.; Yang, S.; Zhang, Y. F. Mechanically robust superamphiphobic ceramic coatings with releasable nanoparticle-capsules. *Chem. Eng. J.*, **2022**, 446, 137336.
- 28 Zhao, L. X.; Li, H. Y.; Zhou, K.; Liu, H. X.; Wang, J.; Zhang, B. B. Enhanced mechanical stability and corrosion resistance of superhydrophobic coating reinforced with inorganic binder. *J. Cent. South Univ.*, **2024**, 31(10), 3502–3516.
- 29 Nakayama, K.; Koyama, A.; Zhu, C. Y.; Aoki, Y.; Habazaki, H. Rapid and repeatable self-healing superoleophobic porous aluminum surface using infiltrated liquid healing agent. *Adv. Mater. Interfaces*, **2018**, 5(19), 1800566.
- 30 Zhang, J. J.; Wei, J. F.; Li, B. C.; Zhao, X.; Zhang, J. P. Long-term corrosion protection for magnesium alloy by two-layer self-healing superamphiphobic coatings based on shape memory polymers and attapulgite. *J. Colloid Interface Sci.*, **2021**, 594, 836–847.
- 31 Zhao, D. L.; Du, Z. K.; Liu, S. S.; Wu, Y. F.; Guan, T.; Sun, Q. L.; Sun, N.; Ren, B. Y. UV light curable self-healing superamphiphobic coatings by photopromoted disulfide exchange reaction. *ACS Appl. Polym. Mater.*, **2019**, 1(11), 2951–2960.
- 32 Li, W.; Ni, X. X.; Zhang, X. H.; Lei, Y.; Guo, J.; Jin, J.; You, B. UV-NIR dual-responsive nanocomposite coatings with healable, superhydrophobic, and contaminant-resistant properties. *ACS Appl. Mater. Interfaces*, **2020**, 12(42), 48101–48108.
- 33 Meena Narayana Menon, D.; Giardino, M.; Janner, D. Tunable pulsedwidth nanosecond laser texturing: from environment friendly superhydrophobic to superamphiphobic surfaces. *Appl. Surf. Sci.*, **2023**, 610, 155356.
- 34 Liu, Y.; Lu, J. Z.; Xue, W.; Zhang, Z. Y.; Zhu, H.; Xu, K.; Wu, Y. C.; Wang, B.; Lei, W. N. A strategy for fabricating multi-level micro-nano superamphiphobic surfaces by laser-electrochemistry subtractive-additive hybrid manufacturing method. *Colloids Surf. A Physicochem. Eng. Aspects*, **2023**, 663, 130946.
- 35 Kang, S. M.; Kim, H.; Choi, J. S.; An, J. H. Bioinspired omniphobic microchamber structure. *Adv. Mater. Interfaces*, **2021**, 8(12), 2100027.
- 36 Kim, H.; Kim, H. N.; Kang, S. M. Robust fabrication of double-ring mushroom structure for reliable omniphobic surfaces. *Surf. Interfaces*, **2022**, 29, 101778.
- 37 Yang, Y.; Ren, Z. Y.; Zhou, C. H.; Lin, Y. X.; Hou, L. X.; Shi, L. W.; Zhong, S. C. 3D-printed robust dual superlyophobic Ti-based porous structure for switchable oil/water emulsion separations. *Adv. Funct. Mater.*, **2023**, 33(15), 2212262.

- 38 Wang, D. H.; Sun, Q. Q.; Hokkanen, M. J.; Zhang, C. L.; Lin, F. Y.; Liu, Q.; Zhu, S. P.; Zhou, T. F.; Chang, Q.; He, B.; Zhou, Q.; Chen, L. Q.; Wang, Z. K.; Ras, R. H. A.; Deng, X. Design of robust superhydrophobic surfaces. *Nature*, **2020**, 582(7810), 55–59.

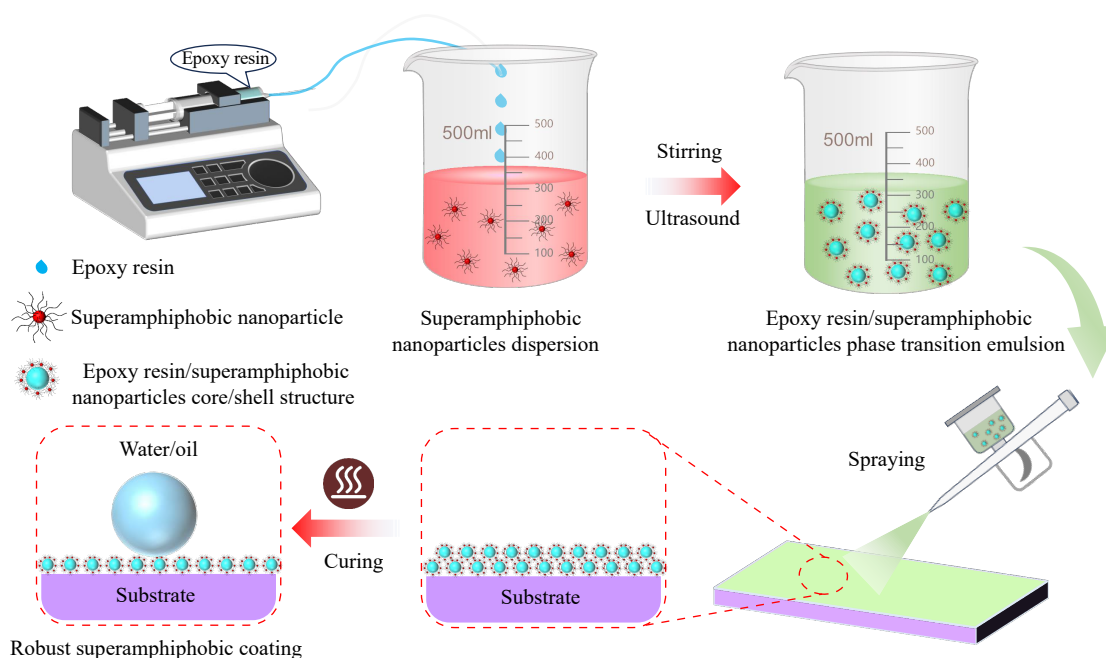
Research Article

Preparation and Characterization of Wear-resistant Superamphiphobic Surface Based on Epoxy Resin Phase Transition

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Abstract Superamphiphobic surfaces that are both hydrophobic and oleophobic represent an important trend in the development and application of liquid-repellent surfaces. However, when subjected to external friction, the micro-nano rough structure of such surfaces causes a rapid decline or even loss of their superamphiphobic properties owing to wear. The addition of high-molecular-weight adhesives to superamphiphobic powders to construct composite coatings is the most commonly used method for enhancing the wear resistance of superamphiphobic surfaces. However, the effect is often not good because the superamphiphobic powder can be embedded in the adhesive. To address this issue, in this study, superamphiphobic nanopowders with superior performance were synthesized. Then, taking advantage of the property that high-molecular-weight adhesives dissolved in good solvents undergo phase transition and form spherical morphologies when added to poor solvents, an epoxy resin solution was dropped into a poor solvent in which superamphiphobic nanopowders were dispersed to trigger the phase transition. Subsequent ultrasonic treatment promoted the tight coating of superamphiphobic nanopowders on the surface of epoxy resin phase-transition droplets, forming fine and stable Pickering emulsion droplets. A superamphiphobic coating composed of multiple core-shell microspheres was obtained after spraying and curing. The superamphiphobic powder was located on the surface of the core-shell microspheres, ensuring that the superamphiphobic properties of the coating did not decline in the presence of the



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adhesive. The multi-layer self-similar structure also endowed the coating with good wear resistance characteristics. Tests showed that a coating with a thickness of approximately 60 μm could withstand 60 cycles of friction on a 400# sandpaper surface under a 200 g weight without significant loss of superhydrophobicity and retained a certain degree of oleophobicity. This method can be applied to any polymer adhesive that undergoes phase transformation in poor solvents, providing a reference for the preparation and application of wear-resistant superhydrophobic/superamphiphobic coatings.

Keywords Epoxy resin; Superamphiphobic surface; Wear resistance; Phase transformation; Pickering emulsion; Self-similar structure