

水凝胶在腐蚀防护领域应用进展综述

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摘要: 水凝胶材料由于其独特的含水交联网络结构, 具有优越的亲水、润滑、耐磨、生物相容等特性, 是近年来发展极为迅速的高分子材料之一, 被广泛用于药物传输、软体机器人、可植入器官、传感器等生物医学等工程领域。在腐蚀防护领域, 水凝胶材料由于其独特性质逐渐受到学者的关注, 成为了新兴腐蚀防护材料之一。通过文献综述的方法, 对化学交联法与物理交联法两种水凝胶的主要制备方法进行对比, 对两种方法制备的水凝胶材料的结构和性质进行了对比, 进一步分析了水凝胶材料具有的独特性质, 及其在腐蚀防护领域的应用潜力。其中化学交联制备出的水凝胶, 其稳定性好, 力学强度高, 具有良好的耐磨防污性, 可制备出性能优异的海洋防污涂层。物理交联制备的水凝胶由于其内部具有三维网络空间结构可负载缓蚀剂, 且其内部存在大量的动态可逆键, 具有环境响应性, 能随着环境 pH、温度等变化而改变自身溶胀程度, 从而改变负载在水凝胶中的缓蚀剂的释放速率。因此, 对比传统固体缓蚀剂和液体缓蚀剂, 水凝胶智能缓蚀剂对金属有着更长效的腐蚀防护性能, 具有良好的应用前景。根据水凝胶材料的独特性质, 着重分析了水凝胶材料在腐蚀防护领域的应用现状, 并对研究前景进行了分析。目前制备水凝胶涂层多经过表面预处理、配制预凝胶溶液、交联固化等步骤, 并且水凝胶涂料可在不同材料、形状基底上进行涂覆, 为水凝胶防腐涂层的发展奠定了基础。

关键词: 水凝胶; 制备方法; 多孔结构; 刺激响应性; 腐蚀防护

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A Review: The Application of Hydrogels in the Field of Corrosion Protection

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ABSTRACT: Due to its unique water-containing cross-linked network structure, the hydrogel material has excellent hydrophilic, lubricating, wear-resistant, biocompatible and other characteristics. And the hydrogel material is one of the rapidly developing polymer materials in recent years. Functional hydrogel materials are widely used in biomedical engineering fields such as drug delivery, soft robotics, implantable organs and sensors. Then, in the field of corrosion protection, the unique properties of hydrogel material have gradually attracted the attention of scholars and the hydrogel becomes one of the emerging corrosion protection materials. In this paper, the main preparation methods of chemical cross-linking method and physical cross-linking method are compared. And the structure and properties of the hydrogel materials prepared by the two methods are compared in the paper. In this paper, the unique properties of hydrogel materials and their application potential in the field of corrosion protection are analyzed. The hydrogel prepared by chemical crosslinking has good stability, high mechanical strength, good wear resistance and antifouling properties. Then it can prepare marine antifouling coatings with excellent performance. The surface of medical equipment and marine ships is often prone to a layer of oil or organic matter, which allows microorganisms to multiply and accumulate here to form a microbial mucous membrane. The metabolites of microorganisms are often acidic and can cause corrosion of metal substrates. However, due to the good hydrophilic and oleophobic properties of hydrogels, it is difficult for oil stains to adhere to the surface of the hydrogel coating, which can reduce the corrosion of metals by microorganisms. Therefore, the good hydrophilic and oleophobic properties, low friction and self-healing properties of functional hydrogels are often used to prepare hydrogel coatings for marine anti-fouling-anti-corrosion coatings, mechanical skins and oil-water separation membranes. The hydrogel prepared by physical cross-linking has a three-dimensional network space structure inside that can be loaded with corrosion inhibitors. There are a large number of dynamic reversible bonds inside hydrogel, so the hydrogel has environmental responsiveness. The hydrogel can change its swelling with changes in environmental pH and temperature. Thereby it can change the release rate of the corrosion inhibitor loaded in the hydrogel. Compared with traditional solid corrosion inhibitors and liquid corrosion inhibitors, intelligent corrosion inhibitors have longer-lasting corrosion protection performance on metals and they have good application prospects. According to the unique properties of hydrogel materials, this paper focuses on analyzing the application status of hydrogel materials in the field of corrosion protection, and it analyzes the research prospects. At present, the preparation of hydrogel coatings usually goes through the steps of surface pretreatment, preparation of pre-gel solution, cross-linking and curing, etc. The hydrogel can be coated on substrates of different materials and shapes. Most of the hydrogel coatings have low friction, high wear resistance and oil resistance. Through different treatment methods, the hydrogel coating can have certain properties such as self-healing and environmental responsiveness. Functional hydrogels are responsive to environmental stimuli, and it can change the degree of self-swelling with changes in environmental pH, temperature, etc. Thereby the hydrogel can change the release rate of the corrosion inhibitor loaded in the hydrogel. At present, there are many researches on pH-sensitive intelligent corrosion inhibitors. Photosensitive and heat-sensitive intelligent corrosion inhibitors still need to be further developed. The use of hydrogel in combination with corrosion inhibitor has significant anti-corrosion performance on metals, which presents a new possibility for the development direction of anti-corrosion coatings.

KEY WORDS: hydrogels; preparation; porous structure; stimulus responsiveness; corrosion protection

水凝胶是以有机高分子为骨架结构、水为分散介质的一种凝胶材料^[1]。水凝胶材料由于其独特的含水

交联网络结构, 具有优越的亲水性^[2]、低摩擦性^[3-4]、透光性^[5]、防污性^[6-7]、渗透性^[8]、生物相容性^[9]等特

性而成为研究热点。材料表面涂覆水凝胶涂层能够使体系兼具基底的强度、硬度及水凝胶的亲水性、自润滑性、生物相容性和可控载药性等诸多功能。功能性的水凝胶更是在诸如药物传输^[10-11]、软体机器人^[12]、可植入器官^[13]、传感器^[14]、电子器件^[15]和农业^[16]等领域有广泛的应用前景。

金属材料在服役过程中由于环境中腐蚀介质侵害导致材料失效,进而造成安全隐患甚至危害人身财产安全^[17-19]。目前水凝胶在腐蚀防护领域已有初步的应用研究,如利用水凝胶良好的亲水疏油性,制备出优良的抗污涂层,能够作为医用防污涂层使用,有效解决医疗机械的失效问题^[20-22]。如利用水凝胶材料的低摩擦性和生物相容性制备的抗污涂层,可用于海洋防污领域降低海洋生物的附着,进而降低船舶行驶过程中的能耗^[23-24]。功能性水凝胶材料由于具备自修复性质,还可制备出本征自修复涂层^[25-27]。功能性水凝胶材料拥有三维网络空间结构可用于负载缓蚀剂,同时利用水凝胶材料的刺激响应性能制备成智能缓蚀剂应用于缓蚀剂的靶向释放^[28-29]。较之于将缓蚀剂负载在多孔 SiO_2 ^[30-32]和 MoF ^[33-34]材料等微纳容器中,水凝胶智能缓蚀剂具备制备简单、负载量高、智能响应以及可控释放等优势。

水凝胶所具有的独特性质逐渐被学者们关注并尝试应用在腐蚀防护领域^[35-37],但这种应用仍处在初期,还具有很广的研究前景。本文对水凝胶的制备方法、结构特征以及性能进行了综述,并对水凝胶材料在腐蚀防护领域研究、应用现状进行了总结与分析。

1 水凝胶的制备方法

水凝胶主要有化学交联和物理交联两种制备方法。其中化学交联主要包括:自由基聚合、辐射聚合和水溶性高分子交联。物理交联主要包括:离子间相互作用、结晶交联作用、氢键作用、疏水缔合作用^[38]。

1.1 化学交联法

1.1.1 自由基聚合

自由基聚合交联法是最常见制备水凝胶的化学方法,聚合物单体通过自由基聚合制备高分子水凝胶。Zhou 等^[39]通过自由基聚合法制备了 pH-温度敏感型聚丙烯酸-丙烯酰胺水凝胶,其溶胀度随 pH 值的变化而变化,具有负载缓蚀剂用于腐蚀环境的潜力。Yu 等^[40]通过自由基聚合制备了一系列聚 N-异丙基丙烯酰胺-丙烯酸水凝胶,能通过调整组分控制小分子缓蚀剂的释放行为。Wichterle 等^[41]通过共聚交联制得具有良好的亲水疏油性的聚甲基丙烯酸-2-羟乙酯水凝胶,在海洋防污领域有着良好的应用前景。

1.1.2 辐射聚合

辐射聚合是通过高能射线照射聚合单体溶液,使

其产生活性自由基,引发聚合反应形成共价交联网络。Leach 等^[42]利用甲基丙烯酸甘油酯和明胶,通过光聚合形成可降解的 GMHA 水凝胶,对海洋防污涂层环保材料有着重要意义。孙鹏等^[43]通过紫外光辐射聚合制备了高强度的聚乙烯亚胺/聚丙烯酰胺-聚丙烯酸钠杂化水凝胶,在海洋防污材料领域具有一定的应用价值。

1.1.3 水溶性高分子的交联

利用聚合物分子结构中的—OH、—COOH、—NH₂等极性基团,可以在保持良好亲水性的同时,通过结构互补使官能团之间发生加成或缩合等化学反应^[44]。Draye 等^[45]制备了无毒自交联体系水凝胶,该水凝胶具有良好的生物相容性,可作为环保的海洋防污涂层的材料。

化学交联制备水凝胶是通过共价键形成三维交联网络,通常具有结构稳定、力学性能较好等特征。

1.2 物理交联法

1.2.1 静电作用

通过离子间相互作用制备水凝胶可以分为两种:(1)聚电解质与带相反电荷的多价离子之间的静电作用形成物理水凝胶;(2)带相反电荷的两种聚电解质之间的静电作用形成聚电解质复合物水凝胶^[46]。静电作用制备离子交联水凝胶机理如图 1 所示。Zhao 等^[47]利用丙烯酸与 N,N'-二甲基氨基甲基丙烯酸乙酯之间的质子传递静电作用形成水凝胶,该凝胶对电场、电解质具有响应行为,可用于不同腐蚀介质中缓蚀剂的特异性响应释放。

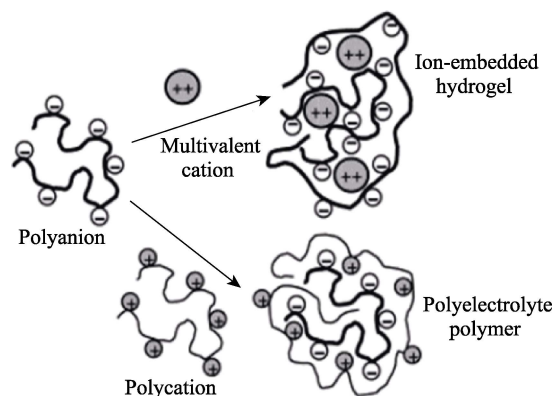


图1 离子交联水凝胶示意图^[46]

Fig.1 Schematic diagram of ionically crosslinked hydrogel^[46]

1.2.2 结晶交联作用

高分子在溶液中呈无规则线团分布,无规则线团结构随着温度的升高或降低而相互缠绕排列成有序结构形成微晶,这些微晶在网络中起到物理交联点从而形成凝胶。Ricciardi 等^[48]用聚乙烯醇水溶液制得了物理交联的水凝胶,首次采用冷冻解冻技术对聚乙烯醇水凝胶进行了系统、定量的研究。

1.2.3 氢键交联作用

高分子水溶液体系中可以起到物理交联点的作用不止有静电作用、结晶交联, 分子内、分子间的氢键作用同样可以作为物理交联点。Vihola 等^[49]利用水杨酸与酰胺形成的氢键作为交联点, 制得温敏性的物理交联水凝胶, 可以用于负载缓蚀剂, 并且能通过环境的温度、溶液 pH 值调控其中负载的缓蚀剂的释放速率。

1.2.4 疏水缔合作用

两亲性的接枝聚合物能够通过聚合物中的疏水部分在水中的缔合作用形成凝胶。Jiang 等^[50]通过疏水缔合作用制备了聚丙烯酰胺共聚体系水凝胶, 研究了聚丙烯酰胺体系凝胶的强度、自愈合性能及温敏性能, 对表面工程和防污涂层材料领域有重要意义。

物理交联是通过聚合物间非共价键形成的交联网络, 然而, 这种凝胶是非永久性的, 通过加热凝胶可转变为溶液, 也被称为假凝胶或热可逆凝胶。

1.3 化学交联与物理交联制备水凝胶的对比

水凝胶不同制备方法的优缺点如表 1 所示。化学交联形成的水凝胶结构强度常高于物理交联, 由于其稳定性好, 力学强度高, 具有良好的耐磨性, 可用于具有物理屏蔽作用的涂层。但如何去除未反应的交联剂是化学交联过程中的一个重要问题。物理交联制备水凝胶因不使用有毒交联剂而逐渐被重视。研究表明, 物理交联制备的水凝胶具有较好的热可逆性, 因而常被用于负载药剂、定向释放领域。因此可将腐蚀抑制药剂负载在此类水凝胶中, 用于腐蚀防护领域。近年来有研究人员将物理交联制备的水凝胶负载上缓蚀剂, 使传统的缓蚀剂具有可调节的释放速率, 能对金属防护起着良好的防护效果。水凝胶的化学稳定性主要取决于其中的有机高分子骨架, 一般稳定性较好, 能耐酸、碱、盐的侵蚀。但物理交联水凝胶, 在一定温度下会发生凝胶-溶胶的转化, 热稳定性较差。

表 1 水凝胶不同制备方法的优缺点
Tab.1 Advantages and disadvantages of different preparation methods of hydrogel

| | Method | Characteristic | Advantages and disadvantages |
|-----------------------|--|---|--|
| Chemical crosslinking | Free radical polymerization | Simple and commonly used | High strength and good stability, Initiators are toxic |
| | Radiation polymerization | Energy saving, pollution-free, easy to operate | |
| | Crosslinking of water-soluble polymers | There are many choices of monomer and synthesis technology, and subsequent characterization and statistical theory are convenient | |
| Physical crosslinking | Electrostatic interaction | The reaction conditions are mild and easy to implement | No initiator, thermally reversible |
| | Crystal crosslinking | Thermally reversible | |
| | Hydrogen bond crosslinking | pH and temperature affect the rate of drug release | |
| | Hydrophobic association | Concentration have a great influence on the gel state | |

2 水凝胶的结构与性质

2.1 水凝胶的结构

水凝胶具有三维网络状结构, 如图 2 所示, 聚丙烯酰胺/聚乙烯醇复合水凝胶^[51]、甲基纤维素水凝胶^[52]、聚丙烯酰胺和聚丙烯酸的双网络水凝胶^[53]、三甲基壳聚糖水凝胶^[54]的截面微观形貌均展示了水凝胶的多孔结构, 其内部为三维网状结构。水凝胶的三维网络空间结构也为负载缓蚀剂、药物和电解质提供了可能, 从而具有应用在腐蚀防护和表面工程领域的潜力。

2.2 水凝胶材料物理化学性质

水凝胶材料具有独特的含水交联网络结构使其具有许多独特的性能。水凝胶优越的亲水性是由于水凝胶材料骨架高分子含有大量的亲水基团, 这也使得

其与油污的接触角大, 使油污难以附着, 表现出一定的防油污性质。根据这一性质, 可研发出海洋防污涂料。同时水凝胶内部结构是不闭合的, 所以会表现出渗透性, 通过这一性质可制备出油水分离涂层。此外, 水凝胶还具备低摩擦性、透光性、生物相容性等优良性质。

虽然水凝胶拥有上述诸多优越性能, 但因其力学性能的不足而限制了在诸多领域的发展。在不损害水凝胶其他优越性能的前提下, 提高其力学性能, 是现在关于水凝胶的重要研究方向。通过界面黏接可制备高韧性复合材料, 同时纤维材料的抗疲劳性能也能得到显著提升^[55]。图 3 为水凝胶网络韧性与滞后性示意图。图 3a 表示在产生裂缝时, 聚合物链被高度拉伸, 它的拉伸分裂会耗散传导在链中的能量。图 3b 表示添加牺牲键的网络结构可将应力从裂纹处传递到网络的大部分, 降低裂缝对材料局部的破坏程度。图 3c 表示在裂纹处, 软基体大幅度剪切, 在每根纤维

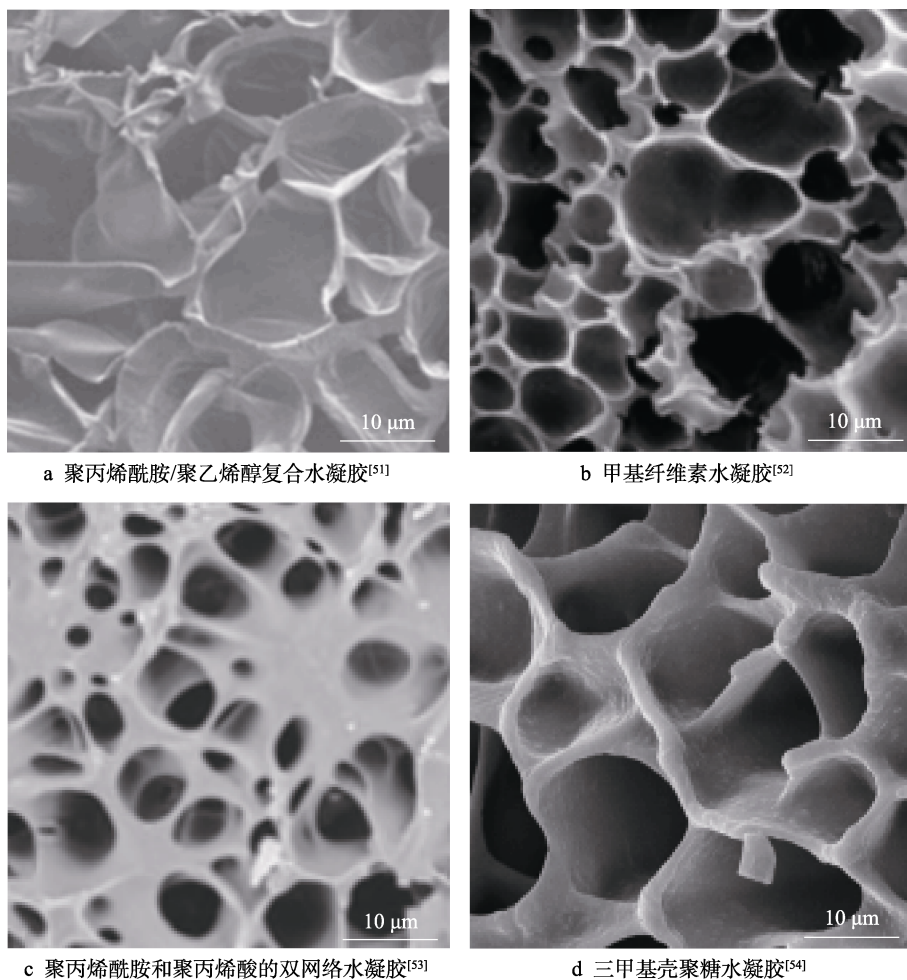


图 2 水凝胶扫描电镜照片

Fig.2 Scanning electron micrograph of hydrogel: a) polyacrylamide/polyvinyl alcohol composite hydrogel^[51]; b) methylcellulose hydrogel^[52]; c) double network hydrogel of polyacrylamide and polyacrylic acid^[53]; d) trimethyl chitosan hydrogel^[54]

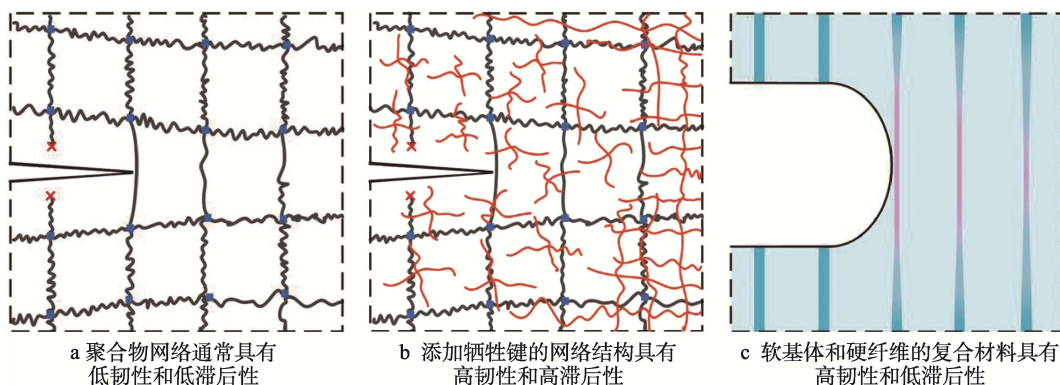
图 3 水凝胶网络韧性与滞后性示意图^[55]

Fig.3 Toughness and hysteresis of hydrogel^[55]: a) an unfilled polymer network typically has low toughness and low hysteresis; b) a primary network added with sacrificial bonds has high toughness and high hysteresis; c) a composite of a soft matrix and hard fibers has high toughness and low hysteresis

的长段上扩展很大的伸长率，而纤维的断裂则会耗散该段的能量。

通过改善水凝胶的内部结构，也可有效地提高其力学强度。有学者通过纳米纤维与聚合物分子链之间的氢键作用，制备出高强度水凝胶，其拉伸强度高

36 MPa^[56]。也有学者将可滑动的“O”形交联环作为交联点，减小交联网络中的内应力，增强水凝胶的力学性质^[57]。该种水凝胶材料的吸水能力极强，可以吸收自身质量的 620 倍，同时具有极强的拉伸、压缩性能和机械强度，拉伸、压缩、缠绕和打结都不会轻易

断裂。Chen 等^[58]利用一种新型的溶剂置换法, 将韧性水凝胶成功改造成低蒸发、抗结冰、含水量可控的韧性有机凝胶, 从而解决韧性凝胶在空气中易干和低温下易结冰问题。

近几十年以来, 国内外众多学者开发了大量高强度、高韧性水凝胶, 其中主要包括双网络水凝胶、滑环水凝胶、复合水凝胶、纳米颗粒增强水凝胶、胶束交联水凝胶等^[59]类型。本质上, 这些类型的水凝胶的合成关键在于利用断裂“牺牲键”来有效耗散能量, 进而增强水凝胶的机械性能, 使水凝胶在表面工程、腐蚀防护等领域应用更广泛。

2.3 水凝胶材料的独特性质

水凝胶由于结构特征还具有一些独特性能, 例如多数水凝胶在受到损伤后, 能进行比较快速的自修复, 因此被应用于机械皮肤的制备。而且水凝胶具有良好的防污性能和低摩擦性能, 使其也可用于海洋防污涂层领域。多数水凝胶由于其高分子骨架可负载一些功能基团, 常常具备对环境响应的能力, 如对光、热、磁、酸碱及一些化学物质敏感, 当受到特定的刺激后, 水凝胶会作出相应的响应, 因此可用于药物控

释领域、腐蚀防护领域。

2.3.1 自修复性质

功能性水凝胶由于具有良好的自修复性能, 可用于表面处理、机械皮肤和防污涂层等领域^[60]。在受到损伤时, 水凝胶中的聚合网状结构可利用剪切稀化、静电相互作用、氢键以及主客体相互作用等机理, 进行自修复, 见图 4。

有学者利用银-巯基配位作用构筑出具有三维网络结构的水凝胶, 使凝胶材料具备优异的自修复性能^[61], 可作为自修复涂层使用, 且该类水凝胶材料具有抗菌特性^[62], 可作为抗菌涂层使用。除银-巯基配位作用外, 国内外学者也常用氢键来制备具有自修复性的水凝胶材料。Rong 等^[63]利用氢键制备了一种具有自修复性能的抗冻导电水凝胶体系。

水凝胶的网络结构是通过交联点连接高分子链形成的。普通的交联结构往往是单一的共价键, 其被破坏后, 无法自行修复。而为了获得自修复能力, 交联结构应该是动态可逆的且比较容易打开的。因此如何获得强而高度动态可逆的交联结构是目前的研究热点^[64]。

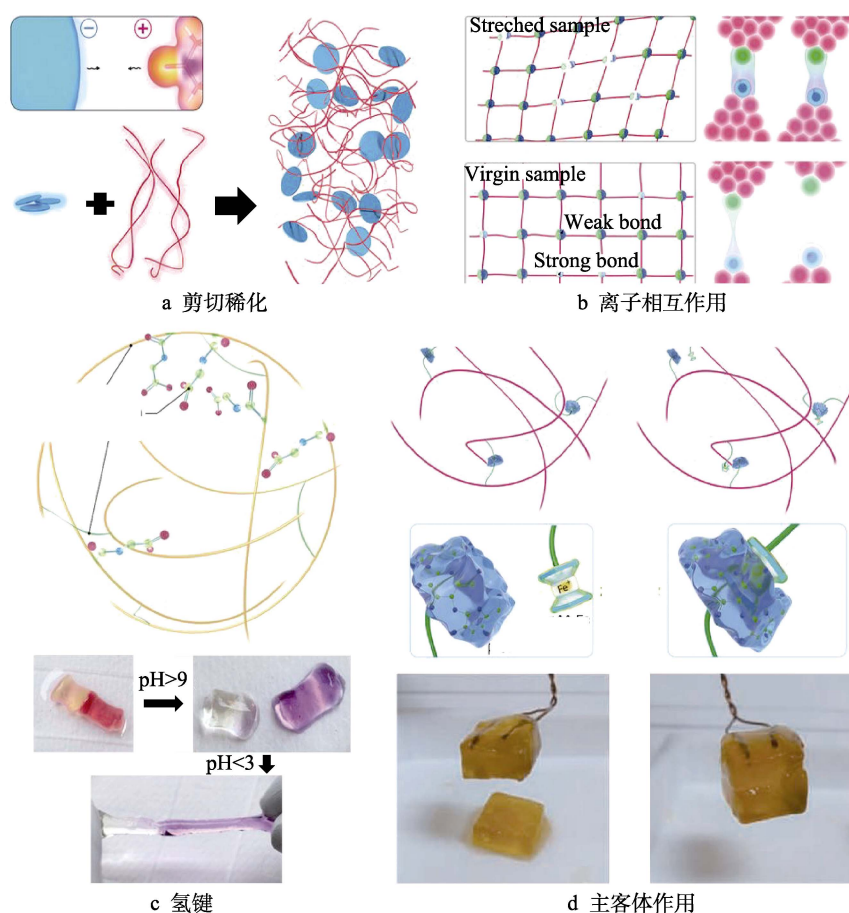


图 4 水凝胶自修复原理示意图^[60]

Fig.4 Shear-thinning and self-healing hydrogels^[60]: a) shear-thinning hydrogel through nanocompositing; b) ionic interactions; c) hydrogen bonds; d) host-guest coupling

2.3.2 刺激响应特性

智能刺激响应型水凝胶能够感应到外界环境微小变化后,其物理结构或化学性质会产生相应变化,包括温敏、光敏、磁敏和 pH 敏感型水凝胶等。由于温敏水凝胶有广阔的应用前景,近年来逐渐成为环境敏感型水凝胶的研究重点。随温度变化,一些高分子溶液呈现可逆的溶胶-凝胶转变,因此可利用这一性质,实现负载缓蚀剂和药物的可控释放^[65]。Cui 等^[66]利用模拟与试验,对热敏水凝胶体系的凝胶结构及机理进行了系统研究。Yang 等^[67]制备了一种

纤维素基水凝胶,该水凝胶展现出对 pH 和氧化还原的双重响应行为。图 5a 为 pH 刺激凝胶的溶胶-凝胶转变。染红的水凝胶加入盐酸溶液后,水凝胶会转变为溶液,加入三乙醇胺 (TEA) 又能转变为凝胶。图 5b 为氧化还原刺激凝胶的溶胶-凝胶转变。水凝胶经亚甲基蓝染色,加入二硫苏糖醇 (DTT) 后水凝胶转变为溶液,加入过氧化氢 (H_2O_2) 又能转变回凝胶。该纤维素基水凝胶可利用酰胺键和二硫键的可逆性实现溶胶-凝胶的转变,并且作者成功将负载在该水凝胶中的药物分子进行控制释放。该水凝胶也可负载缓蚀剂应用在腐蚀防护领域。

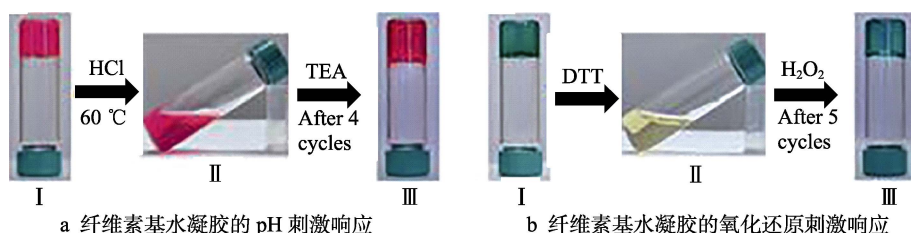


图 5 纤维素基水凝胶响应示意图^[67]

Fig.5 Schematic diagram of the response of cellulose-based hydrogels^[67]: a) pH stimuli-responsive sol-gel transition of cellulose-based hydrogels; b) redox stimuli-responsive sol-gel transition of cellulose-based hydrogels

刺激响应型水凝胶的特点是其溶胀行为在不同环境下有显著差异,利用这种特性可将其用作控释开关等,可将其负载缓蚀剂用于金属防腐,对金属的防护效果良好且保护时间长。

3 水凝胶材料在防腐领域的应用

经过前期的发展,功能性水凝胶材料已经广泛用于药物传输、软体机器人、可植入器官、传感器等生物学及工程领域,但水凝胶在腐蚀防护领域的应用才刚起步。功能性水凝胶由于具有良好的防污性、耐磨性和自修复性能等,可用于海洋防污涂层、机械皮肤等领域。而且功能性水凝胶具有刺激响应性,可负载缓蚀剂,制备出对环境响应的固体缓蚀剂用于腐蚀防护领域。

3.1 腐蚀防护涂层

水凝胶能够用于制备有特殊作用的腐蚀防护涂层。例如,医用器械和海洋船舶表面由于油污或有机物的附着会使得微生物聚集,形成微生物黏膜,进而产生微生物腐蚀。而水凝胶由于具有良好的亲水疏油性,能够有效减少油污的附着,可减少微生物对金属的腐蚀。因此能够利用功能性水凝胶的亲水疏油性、低摩擦性和自修复性,制备抑制微生物腐蚀的水凝胶涂层,用于医疗器械、海洋设备的防污-防腐蚀等。

Takahashi 等^[68]报道了一种简单而通用的方法,用于在包括各种材料和几何结构在内的各种固体表面上涂覆坚韧的双网络 (Double-Net, DN) 水凝胶。

双网络凝胶涂层工艺包括两个步骤,见图 6。首先,对基体表面进行处理,以形成含有自由基引发剂的聚醋酸乙烯酯 (PVAc) 底漆层,其中基体可为塑料、橡胶、陶瓷和金属等。然后将预制丙烯酸胺溶液涂覆在处理过的表面上,然后在紫外光照下进行聚合,得到凝胶涂层表面具有低摩擦性能和高耐磨性。对于具有复杂几何形状的表面,也能形成良好的抗污凝胶涂层。也有学者将具有氢键的水凝胶良好地黏附在不同基体上,基体可为玻璃、金属甚至皮肤等^[69]。

Yao 等^[70]首先将丙烯酸胺单体与偶联剂在水相中通过自由基共聚形成聚合物树脂主体,同时共聚物硅烷组分上的烷氧基水解形成反应性功能端——硅烷醇基;基底采用氧气等离子体处理后,涂覆水凝胶涂料,进入固化阶段——共聚物树脂链结构上的硅烷醇基缩水交联形成交联网络结构或与基底表面羟基脱水成键实现与基底交联黏附。经过配方优化,该水凝胶涂料基底黏附强度可达 $900 J/m^2$ 。此外,类似传统涂料,该水凝胶涂料也可呈粉末干态长时间储存,进一步提升其可运输性及应用简便性。水凝胶涂料制备与涂覆见图 7。

水凝胶材料也可应用在机械皮肤领域,如将水凝胶涂覆在金属、塑料和橡胶器械上,涂层具有柔软、光滑的表面,可以大幅减缓磨损程度。缓蚀剂也可被负载在水凝胶中,并控制其释放速度,降低器械的腐蚀程度^[71]。此外水凝胶涂层也可和多孔金属基底组成新型超亲水膜,其可以选择性地将油/水混合物中的水分离出来,其效率可达 99%,对油气田设备的腐蚀

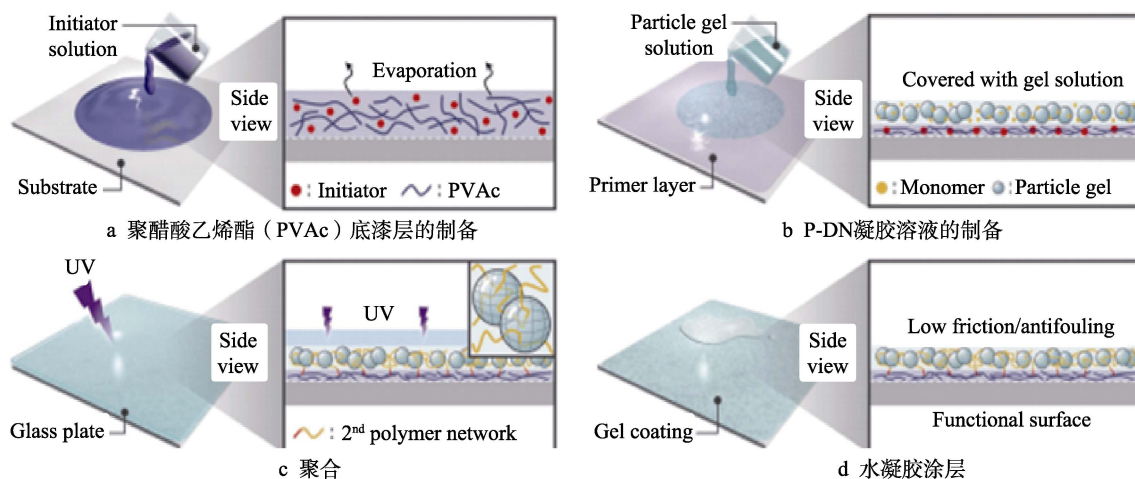


图 6 基于颗粒的双网络水凝胶 (P-DN 凝胶) 在固体表面上的涂覆过程示意图^[65]

Fig.6 Schematic illustration of the coating process of particle-based double network hydrogels (P-DN gels) onto a solid surface^[65]: a) preparation of polyvinyl acetate (PVAc) primer layer; b) preparation of P-DN gel solution; c) UV polymerization; d) hydrogel coating

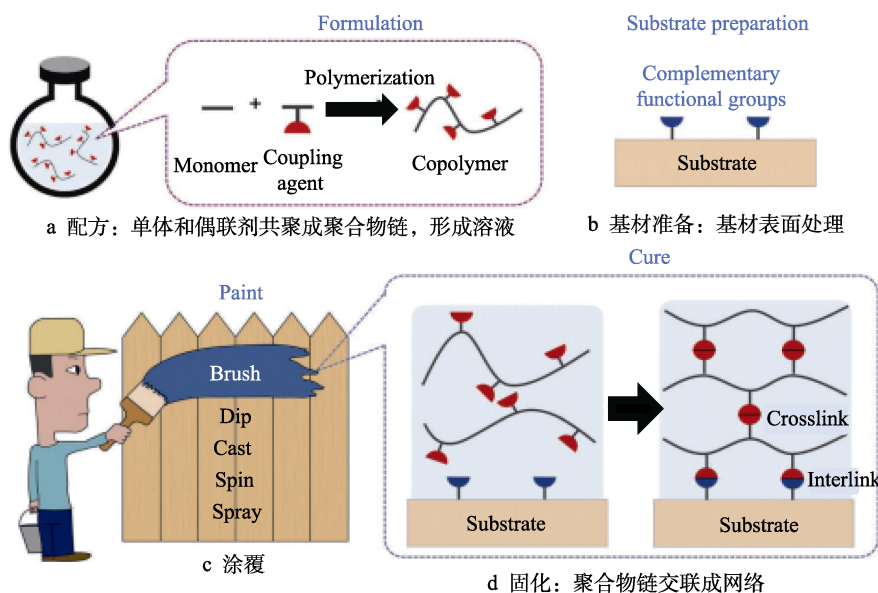


图 7 水凝胶涂料制备与涂覆^[67]

Fig.7 Preparation and coating of hydrogel coating^[67]: a) formulation: monomer units and coupling agents copolymerize into polymer chains, resulting in an aqueous solution; b) substrate preparation: substrate surface treatment; c) paint; d) cure: the polymer chains are cross-linked into a network

防护有着重要意义。在分离过程中, 油分不会污染膜, 更加有利于油分和膜材料的回收利用^[72]。

目前水凝胶防腐涂层已有初步发展, 王鑫等^[73]以过硫酸钾为氧化还原引发剂, 以四甲基乙二胺为促凝剂, 将 N,N-二甲基丙烯酰胺和纳米硅颗粒聚合, 制备出了一种具有自修复性能的二氧化硅基水凝胶。然后将噻唑类缓蚀剂负载在具有自修复性能的二氧化硅基水凝胶上, 负载缓蚀剂的水凝胶涂层具有良好的防腐蚀性能。文家新等^[74]将苯并三氮唑缓蚀剂负载在 pH 敏感型聚丙烯酰胺-聚丙烯酸杂化水凝胶中, 再将负载了缓蚀剂的凝胶粉末掺杂进醇酸树脂涂层中, 得到一种智能防腐涂层。盐雾试验和电化学阻抗谱结果表明, 该涂层在受到损伤时, 依然具有良好的

腐蚀防护性能。

水凝胶由于具备亲水疏油的特性, 已被应用于海洋防护涂层。Zhang 等^[75]制备了一种海洋防污涂层, 该涂层利用水凝胶的亲水疏油性, 使油污难以附着在涂层表面, 从而使海洋生物的附着量大幅减少。该涂层无毒无害, 相较传统海洋涂层防污效果良好、绿色环保。

目前制备水凝胶涂层多经过表面预处理、配制预凝胶溶液、交联固化等步骤, 可在不同材料、形状基底上进行涂覆。制备的水凝胶涂层大多具备低摩擦性、高耐磨性和防油污等。通过不同的处理方式, 可使水凝胶涂层具备一定的自修复、环境响应性等性能。众多学者的研究结果表明, 水凝胶用于涂层具有可行性与创新性, 也对涂层市场的发展具有重要意

义。同时,该类研究成果也将为凝胶材料在腐蚀防护领域的应用打开新的局面。缓蚀剂结合水凝胶涂层使用,实现新型防腐涂层是可行的,只是目前对于水凝胶涂层与基体的结合力和缓蚀剂从涂层的释放还需要进一步研究。

3.2 智能缓蚀剂

目前应用的缓蚀剂主要有液体缓蚀剂和智能缓蚀剂,尽管液体缓蚀剂具有成本低廉,易于使用的特点,但其用量大,消耗快。而智能缓蚀剂无需使用加药泵和其他设备,缓蚀剂的有效成分可在介质中缓慢释放,可以在软管壁上达到长期保护的目的^[76]。物理交联法制备的水凝胶由于其内部可逆键的存在,具有环境响应性能,可以调节负载水凝胶中缓蚀剂的释放速率,进行靶向释放,所以将水凝胶应用于智能缓蚀剂领域,有良好的发展前景。

Li等^[77]利用马铃薯淀粉和丙烯酸制备了一种 pH

响应型水凝胶,然后将缓蚀剂负载其中,由于该水凝胶在不同 pH 下会表现出不同的溶胀行为,进而起到智能缓释的作用。如图 8 所示,作者通过电化学测试和扫描电子显微镜分析,发现该负载缓蚀剂水凝胶通过控制释放行为,对铝合金的长期缓蚀性能比普通使用缓蚀剂方法好。有学者用 2-(二甲基氨基)乙基甲基丙烯酸酯制备了一种 pH 控释型智能缓蚀剂,该水凝胶在不同 pH 下具有不同的溶胀行为,从而可控制缓蚀剂的释放速率,对金属具有长期缓蚀性能^[78]。也有学者用壳聚糖和戊二醛交联制备出一种对 pH 响应型水凝胶,并将苯并三氮唑缓蚀剂负载在水凝胶中,得到一种固体缓蚀剂。该固体缓蚀剂对金属基体具有更长效的防护性能^[79]。智能缓蚀剂除直接投放使用外,也可在涂层中进行添加使用。Wen 等^[80]利用丙烯酰胺和丙烯酸制备了一种对 pH 响应的 BTA@PHVA/PEI 智能缓蚀剂,将其掺杂进醇酸涂层中,可使涂层在受到损伤时,对金属基体仍具备良好的腐蚀防护作用。

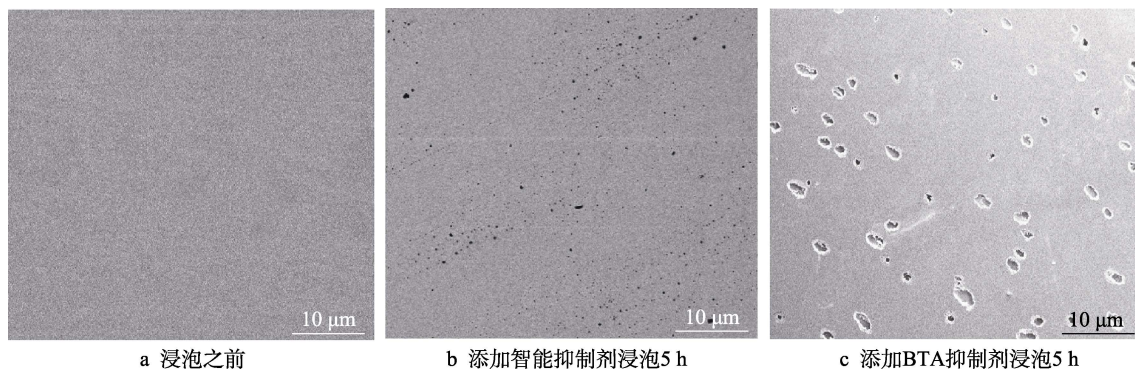


图 8 铝合金在 3.5% NaCl 溶液腐蚀前后的表面形貌^[77]

Fig.8 The surface morphology of aluminum alloy immersed in 3.5% NaCl solution^[77]: a) before immersion; b) with intelligent inhibitor for 5 h; c) with BTA inhibitor for 5 h

功能性水凝胶具有环境刺激响应性,能随着环境 pH、温度等变化而改变自身溶胀程度,从而可改变负载在水凝胶中的缓蚀剂的释放速率。目前 pH 敏感型智能缓蚀剂研究较多,光敏型和热敏型智能缓蚀剂还有待进一步开发。对比传统固体缓蚀剂和液体缓蚀剂,智能缓蚀剂对金属有着更长效的腐蚀防护性能,具有良好的应用前景。将水凝胶与缓蚀剂结合使用对金属的防腐性能比较显著,为防腐涂层的发展方向提供了一种新的可能。

4 结论与展望

1) 化学交联制备出的水凝胶,其稳定性好,力学强度高,具有良好的耐磨防污性,可将其制成涂层,用于海洋防污、机械皮肤、表面工程等领域,但还需克服水凝胶与基体界面结合力不足的缺点。

2) 物理交联制备的水凝胶由于其内部具有三维网络空间结构且存在大量的动态可逆键,具备环境响应性,可将其负载腐蚀抑制剂,制备成智能缓蚀剂,

用于腐蚀防护领域。由于其具有环境响应性,能随着环境 pH、温度等变化而改变自身溶胀程度,从而可改变负载在水凝胶中的缓蚀剂的释放速率。对比传统固体缓蚀剂和液体缓蚀剂,智能缓蚀剂对金属有着更长效的腐蚀防护性能,具有良好的应用前景。但缓蚀剂在水凝胶中的留存时间及其释放动力学等问题还需深入研究。

水凝胶虽然在各个领域都已得到了广泛的应用,但在腐蚀防护领域还有着巨大发展潜力。随着研究工作的不断深入,水凝胶及其复合材料将会在腐蚀防护领域发挥更大的作用。

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