

透明耐磨疏水有机硅改性丙烯酸树脂 的制备及性能

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摘要: **目的** 研究不同丙烯酸类单体以及硅烷偶联剂配比对所制得的树脂涂层自清洁性能与机械性能的影响。**方法** 以甲基丙烯酸甲酯 (MMA)、甲基丙烯酸羟乙酯 (HEMA)、丙烯酸丁酯 (BA) 3 种丙烯酸类单体与硅烷偶联剂 (KH570) 为原材料, 采用自由基聚合法制备了具有透明耐磨性质的疏水有机硅改性丙烯酸树脂, 加入羟基硅油使其交联固化, 增强机械性能。重点研究了树脂涂层的接触角、附着力、硬度、透光率及耐摩擦等性能。**结果** 有机硅单体成功与丙烯酸类单体发生共聚, 单因素优化后的树脂涂层的接触角为 106.7° , 与基体结合力为 0 级, 硬度为 H, 在可见光波段内, 涂覆在玻璃基底上的树脂最高透光率为 92.08%, 同时涂层具有良好的致密性。**结论** 将硅烷偶联剂 (KH570) 与丙烯酸类单体进行共聚, 硅烷偶联剂的长链明显提升了共聚物的疏水性与稳定性, 经交联固化后涂层表现出良好的机械性能与稳定性, 并且由于所加单体的折射率都 < 1.5 , 因而涂层表现出一定的增透效果。

关键词: 透明; 耐磨; 疏水; 有机硅; 丙烯酸树脂

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Preparation and Properties of Transparent and Wear-resistant Hydrophobic Silicone Modified Acrylic Resin

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ABSTRACT: With the rapid development of the photovoltaic industry, maintaining the optimal performance of such energy devices has become an important issue. In order to improve the self-cleaning and scratch resistance of photovoltaic solar panels

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in outdoor environments, this paper prepared silicone modified acrylic resins with transparent hydrophobic and wear-resistant properties by free radical polymerization using three acrylic monomers, including methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), butyl acrylate (BA), and silane coupling agent (KH570) as raw materials. After that, hydroxyl silicone oil is added to cross-link and cure it to enhance the mechanical properties. Single-factor experiments were conducted to optimize the ratio of monomer and curing agent. We focused on the contact angle, adhesion, hardness, light transmittance and friction resistance of the copolymer coating after the optimization of process parameters. TENSOR27 was used to conduct Fourier infrared (FT-IR) test on the resulting copolymer to characterize the occurrence of copolymerization reaction by the change of functional groups, and the contact angle was measured by JC2000DF contact angle measuring instrument to characterize the hydrophobicity of the copolymer coating. The hardness and adhesion of the copolymer coating were measured qualitatively by QHQ-A pencil hardness tester test and Cross-Cut Tester respectively. The transmittance of the coating in the visible wavelength band was tested with a Lambda 750S UV-Vis NIR spectrophotometer. The friction resistance of the coating was characterized by measuring the change of contact angle after different friction times. Finally, the impedance of the coating film was measured with a CHI660D electrochemical workstation to obtain its dense properties. The results showed that the silicone monomer was successfully copolymerized with acrylic monomer, and the best process parameters obtained after single-factor experiments were: methyl methacrylate (MMA) 7.6 g, butyl acrylate (BA) 2.4 g, hydroxyethyl methacrylate (HEMA) 1.0 g, silane coupling agent (KH570) 1.0 g and 0.1 g of hydroxy silicone oil. The copolymer coating obtained after single-factor optimization has a contact angle of 106.7° and possesses good hydrophobicity. The bonding force between the coating and the substrate is 0 and the hardness is H, showing excellent mechanical properties. The highest light transmission rate of the resin coated on the glass substrate is 92.08% in the visible wavelength band, with certain transmission enhancement performance. Meanwhile, the coating has good abrasion resistance and denseness. Therefore, we can see that the copolymerization of silane coupling agent (KH570) and acrylic monomer makes the long chain in the silane coupling agent (KH570) obviously enhance the hydrophobicity and stability of the copolymer, and enhance the mechanical properties and stability of the coating after cross-linking and curing. Because the refractive index of each added monomer is <1.5, the coating exhibits certain permeability enhancement properties.

KEY WORDS: transparency; wear-resisting; hydrophobic; organic silicon; acrylic resin

随着太阳能开发技术的不断进步,太阳能逐渐成为日常生活中一种重要的能源供给方式,保持此类能源设备的最佳性能已成为一个重要问题。太阳能的主要应用是以光伏组件的形式产生电能和集中太阳能热发电。灰尘、水渍等对光伏电池板的使用寿命和发电量有极大的影响,并且根据区域及其环境条件而变化^[1-3]。据报道^[4-5],在沙特阿拉伯干旱和降雨量较少的地区,这种损失可能高达 26%~40%,特别是夏季的灰尘,能使光伏板玻璃盖的透射率降低到 70%。

一般来说,小分子有机硅烷^[6-8]和氟化硅烷^[9-14]常被用作疏水剂来制备超疏水涂层。这类小分子虽然有着极好的疏水性,但在户外应用时往往极易被水解,从而失去其疏水性。Smith 等^[15]发现硅烷的水解稳定性与其分子长度有关:分子长度越短,硅烷越容易水解。这是因为水分子可接近短分子硅烷的硅氧键,而长链中的硅烷由于空间位阻使得水分子难以与它们的硅氧键接触,使其难以被水解,这为制备耐久型疏水膜提供了一种新的思路。

目前制备的低表面能材料主要依靠疏水基团在材料表面富集来降低其表面能从而达到疏水的效果,当表面被破坏后材料会丧失疏水性能。因此耐磨性、附着力、硬度与抗腐蚀性对于疏水

膜及其重要。长期以来,丙烯酸酯聚合物因其高透明度^[16]、优异的黏合性能^[17]、各种单体种类^[18]和高机械强度而备受关注。然而,其应用受到热稳定性、耐候性和耐污性不足的限制^[19]。有机硅与有机氟聚合物因其高键能和旋转角而被广泛用于改善各种材料的性能,它可以降低其他材料的表面张力和玻璃化转变温度,增强材料的热稳定性与化学稳定性^[20]。Lei 等^[21]以 2-[3-(2H-苯并三唑-2-基)-4-羟基苯基]乙基 2-甲基丙烯酸酯 (BHEM)、乙烯基三甲氧基硅烷 (VTMS) 和甲基丙烯酸六氟丁酯 (HFMA) 为改性单体,通过溶液聚合法成功制备了一系列氟硅丙烯酸树脂聚合物,其接触角最高能达到 93°。Feng 等^[22]以四乙氧基硅烷 (TEOS)、氯三甲基硅烷 (TMCS) 和苯基三乙氧基硅烷 (PhTES) 为原料,通过水解缩合反应合成了含苯基的有机硅树脂,其接触角最高达到 113°。

受此启发,本试验通过自由基聚合法将甲基丙烯酸甲酯 (MMA)、甲基丙烯酸羟乙酯 (HEMA)、丙烯酸丁酯 (BA) 3 种丙烯酸类单体与硅烷偶联剂 (KH570) 聚合成一种有机硅改性的丙烯酸树脂,并通过羟基硅油交联固化,获得具有性能稳定的透明耐磨疏水有机硅改性丙烯酸树脂,并对其结构

和性能进行详细研究。

1 试验

1.1 原料

甲基丙烯酸甲酯 (MMA)、甲基丙烯酸羟乙酯 (HEMA), 分析纯, 麦克林生化科技有限公司; 丙烯酸丁酯 (BA), 分析纯, 天津市永大化学试剂有限公司; 硅烷偶联剂 (KH570), 分析纯, 鼎海塑胶化工有限公司; 羟基硅油, 92%, 济南兴飞隆化工有限公司; 月桂酸二丁基锡, 纯度 95%, 麦克林生化科技有限公司; 偶氮二异丁腈 (AIBN), 经无

水乙醇重结晶后使用, 天津光复精细化工研究所。

1.2 有机硅改性丙烯酸树脂的制备

取 40 g 二甲苯加到四口瓶中, 搅拌加热至温度稳定在 85 ℃。随后在恒压滴液漏斗中加入一定质量配比的甲基丙烯酸甲酯 (MMA)、丙烯酸丁酯 (BA)、甲基丙烯酸羟乙酯 (HEMA)、硅烷偶联剂 (KH570) 和引发剂 (AIBN) 混合物, 将混合物缓慢滴入四口瓶中, 经过 3 h 后滴加结束, 并继续保温 3 h, 得到有机硅改性丙烯酸树脂。最后取有机硅改性丙烯酸树脂、羟基硅油和二月桂酸二丁基锡进行固化处理 (原理如图 1 所示), 混合均匀后涂板。

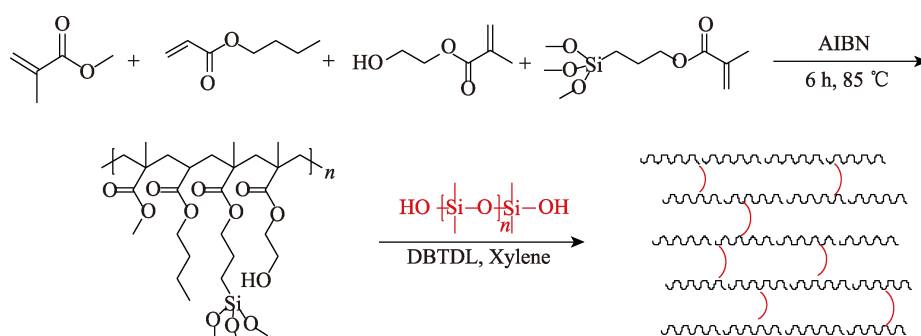


图 1 单体聚合与聚合物固化反应示意图

Fig.1 Schematic diagram of monomer polymerization and polymer curing reaction

1.3 结构表征与性能测试

采用 TENSOR27 对所得树脂进行傅里叶红外 (FT-IR) 测试, 测试范围为 400~4 000 cm^{-1} 。用 JC2000DF 型接触角测量仪检测涂膜静态水接触角, 水滴约为 5 μL , 样品测试结果为 5 个不同点接触角的平均值。依据 GB/T 6379—1986 标准, 用 QHQ-A 型铅笔硬度计检测漆膜硬度。依据 GB/T 9286—1988 标准用百格刀测量涂膜附着力。采用 Lambda750S 型紫外可见近红外分光光度计测量涂膜的透光率。采用 CHI660D 型电化学工作站测量涂膜的阻抗, 以涂层为工作电极 (低碳钢为基底, 工作面积为 1.54 cm^2), 铂片为辅助电极, 饱和甘汞电极为参比电极, 测试频率为 10^{-2} ~ 10^5 Hz, AC 幅值为 20 mV。

2 结果与讨论

2.1 结构分析

在引发剂 AIBN 的作用下, 各丙烯酸单体与有机硅单体中的 $\text{C}=\text{C}$ 打开, 链增长, 从而发生聚合反应, 将各单体聚合形成高分子化合物。将固化前与固化后的树脂进行 FT-IR 分析 (见图 2), 在 1 750 cm^{-1} 处未观察到明显的特征峰, 证明无 $\text{C}=\text{C}$ 双键, 表明聚合物中无自由单体; 1 595 cm^{-1} 处的峰为 $\text{C}=\text{O}$ 的特征吸收峰, 在 3 428 cm^{-1} 处出现 $-\text{OH}$ 特征吸收峰, 说

明 HEMA 单体参与了聚合反应; 在 775 cm^{-1} 处出现 $\text{Si}-\text{C}$ 的特征吸收峰, 在 1 115 cm^{-1} 处出现 $\text{Si}-\text{O}-\text{C}$ 的特征峰, 表明有机硅功能单体参与了聚合反应, 所合成的树脂为有机硅改性丙烯酸树脂。对比固化前后红外谱图可以发现, 固化之后的红外谱在 460 cm^{-1} 处的 $\text{Si}-\text{O}$ 弯曲振动特征峰明显增强, 说明羟基硅油成功进行了固化反应。

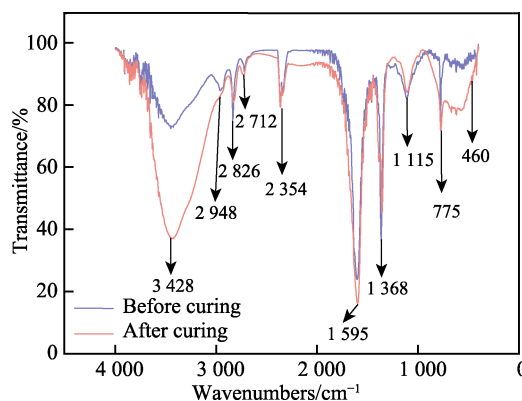


图 2 固化前后树脂 FT-IR 谱图

Fig.2 FT-IR spectrum of resin before and after curing

2.2 软硬单体比的影响

丙烯酸树脂中软硬单体比值主要影响树脂的玻璃化转变温度、硬度及附着力, 试验考察了不同软硬单体比对涂层性能的影响, 所得结果如表 1 所示。当

表 1 软硬单体比对树脂性能的影响
Tab.1 Effect of soft and hard monomer ratio on resin properties

Experiment number	MMA/g	BA/g	Conversion rate/%	WCA/(°)	Adhesion	Hardness	Vitrification temperature/°C
1	10.0	0	99.7	79.0	5	2H	—
2	9.0	1.0	96.5	75.6	2	2H	—
3	8.0	2.0	97.2	79.1	1	HB	71.7
4	7.6	2.4	96.8	81.6	1	HB	67.2
5	7.2	2.8	97.7	87.4	1	B	62.7
6	6.8	3.2	96.4	86.1	1	B	57.9
7	6.4	3.6	95.5	88.3	1	2B	47.1
8	6.0	4.0	96.2	89.1	1	3B	46.4
9	5.6	4.4	99.4	90.2	1	4B	44.7

树脂中软硬单体比过低(1:9)时,所得涂层附着力较差,无实用价值,因此未测定其玻璃化温度。随着软单体 BA 比例的增加,涂层的水接触角与附着力有升高的趋势,但同时硬度明显降低。综合考虑涂层各方面性能,第 4 号试验所得涂层具有足够高的硬度和附着力,同时玻璃化温度略低于第 3 号试验所得涂层,其树脂脆性也较低,因此选择第 4 号试验的配比(MMA 7.6 g, BA 2.4 g)为较优配比,并进行之后的单因素试验。

2.3 KH570 硅单体含量的影响

KH570 作为有机硅单体,引入丙烯酸树脂中主要是为了提高涂层表面接触角,降低涂层表面自由能,赋予涂层自清洁功能。试验考察了不同 KH570 含量对树脂性能的影响,所得结果如表 2 所示。从表 2 可以看出,加入 KH570 硅单体后,涂层水接触角有明显升高,但随混合硅单体含量继续增加,水接触角的变化趋势不明显,稳定在 80°左右。涂层硬度随 KH570 硅单体增加整体有所降低,但降低幅度较小,玻璃化温度随 KH570 硅单体变化不大。综合考虑涂层各项性能,KH570 硅单体为 2.0 g 时,涂层具有较好的硬度及疏水性。

表 2 KH570 硅单体含量对树脂性能的影响
Tab.2 Effect of KH570 silicone monomer content on resin properties

Experiment number	KH570/g	Conversion rate/%	WCA/(°)	Adhesion	Hardness	Vitrification temperature/°C
10	0	80.66	76.7	1	HB	67.1
11	0.5	86.33	79.9	1	B	71.6
12	1.0	96.82	81.6	1	HB	68.2
13	1.5	96.16	80.3	1	B	69.0
14	2.0	98.17	81.8	1	HB	68.0
15	2.5	93.34	80.0	1	B	67.0
16	3.0	90.05	79.4	1	B	69.2
17	4.0	90.86	80.3	1	2B	69.4

2.4 极性单体含量的影响

丙烯酸树脂中引入含羟基的极性单体,可以极大地增加树脂对基底的附着力,同时,亲水性羟基可降低涂层表面接触角。因此,对树脂中极性单体含量对树脂性能的影响进行考察,结果如表 3 所示。树脂玻璃化温度随极性单体含量的上升而上升,这是因为树脂中 KH570 很活泼, Si-OCH₃ 极易水解,与 HEMA 中活性羟基发生部分醇解形成部分交联结构^[23],限制聚合物中分子链的转动。从表 3 中可以看出,添加有极性单体 HEMA 的树脂均具有很好的附着力和较好的硬度,能满足实际使用需求。极性单体对涂层疏水性的影响较为特殊,HEMA 含量增加并改变涂层表面组成的同时,分子间部分交联使涂层的结构存在差异,表面组成和结构的改变使涂层接触角随 HEMA 含量的变化呈不规律性变化,当 HEMA 含量为 1.0 g 时,涂层具有最大的接触角。

表 3 极性单体含量对树脂性能的影响
Tab.3 Effect of polar monomer content on resin properties

Experiment number	HEMA/g	Conversion rate/%	WCA/(°)	Adhesion	Hardness	Vitrification temperature/°C
18	0.2	91.70	79.1	1	HB	58.9
19	0.4	88.59	81.1	1	HB	60.2
20	0.6	98.00	77.1	1	HB	63.9
21	0.8	99.01	79.5	1	HB	65
22	1.0	98.17	81.8	1	HB	68

2.5 固化剂用量的影响

以羟基硅油为固化剂,不仅可以增加聚合物分子间的交联度,提高树脂的物理性能,还能提高树脂中有机硅含量,提高树脂表面接触角。试验分析了不同羟基硅油含量对树脂性能的影响,结果如表 4 所示,发现树脂玻璃化温度、涂层附着力随固化剂用量的增加变化不大。有机硅油作为软性链加入树脂中后,树

脂的硬度略有降低。而树脂的水接触角随羟基硅油用量的增加而升高, 之后稳定在 92°左右, 这主要是因为有机硅在表面富集达到了饱和。综合树脂的各项性能, 在固化剂用量为 0.48 g 时, 有较好的硬度和水接触角。

表 4 固化剂用量对树脂性能的影响 Tab.4 Effect of curing agent dosage on resin performance					
Experiment number	Curing agent/g	WCA/(°)	Adhesion	Hardness	Vitrification temperature/℃
23	0.16	87.6	1	HB	66.6
24	0.33	89.9	1	HB	65.1
25	0.48	91.4	1	HB	64.8
26	0.68	92.3	1	B	66.4
27	1.05	91.9	1	B	65.6
28	1.72	92.3	1	B	63.8

2.6 正交试验结果分析

为进一步确定树脂的最优配比, 根据单因素试验结果设计了四因素三水平正交试验如表 5 所示, 所得正交试验结果如表 6 所示。从表 6 中可以看出, 在正交试验选取的水平范围内, 固化剂含量对水接触角的影响最大, 极性单体含量和软硬单体比的影响其次, 硅单体含量对水接触角的影响最小。综合正交试验所得的结果, 发现 4 个因素水平为 (2,2,3,1) (即与第 33 号试验相同) 时, 所得树脂水接触角最大, 各项综合性能最优。因此, 后续试验以 (2,2,3,1) 组作为硅丙烯酸树脂合成的最佳原料配比, 并研究该聚合物涂层的透光率、耐摩擦和致密性等性能。

表 5 正交试验中各因素水平对应的实际值 Tab.5 Actual values corresponding to the levels of each factor in the orthogonal experiment				
Horizontal number	mBA/mMMA	KH570/g	HEMA/g	Curing agent/g
1	3.2/6.8	0.5	0.2	0.1
2	2.4/7.6	1	0.6	0.25
3	2/8	2	1	0.6

表 6 正交试验数据 Tab.6 Orthogonal experimental data							
Experiment number	mBA/mMMA	KH570	HEMA	Curing agent	WCA/(°)	Adhesion	Hardness
29	1	1	1	1	102.3	1	2H
30	1	2	2	2	100.4	1	HB
31	1	3	3	3	96.7	1	B
32	2	1	2	3	95.7	1	HB
33	2	2	3	1	106.7	0	H
34	2	3	1	2	103.5	1	H
35	3	1	3	2	102.4	1	HB
36	3	2	1	3	98.1	1	B
37	3	3	2	1	102.9	1	HB

2.7 透光率

在 400~800 nm 可见光波长范围内对涂层的透光率进行测试, 结果如图 3a 所示, 涂膜不但足够透明, 还有增透的效果, 在可见光波段内涂膜玻璃基板的透射率都高于空白玻璃基板。空白玻璃基底在 508 nm 波长处达到最高透射率 91.31%, 涂膜玻璃在 488 nm 波长处达到最高透射率 92.04%, 树脂涂层大约提升了玻璃基底 1%的透光能力, 这是因为所加单体的折射率都 < 1.5 (MMA 为 1.41, BA 为 1.42, HEMA 为 1.45, KH570 为 1.43), 满足增透的条件^[24] (1.0 < 折射率 < 1.5), 因而表现出一定的增透性能。图 3b 为实际透光效果图, 涂膜玻璃基板与空白玻璃基板的透光程度相近, 字母清晰可见。

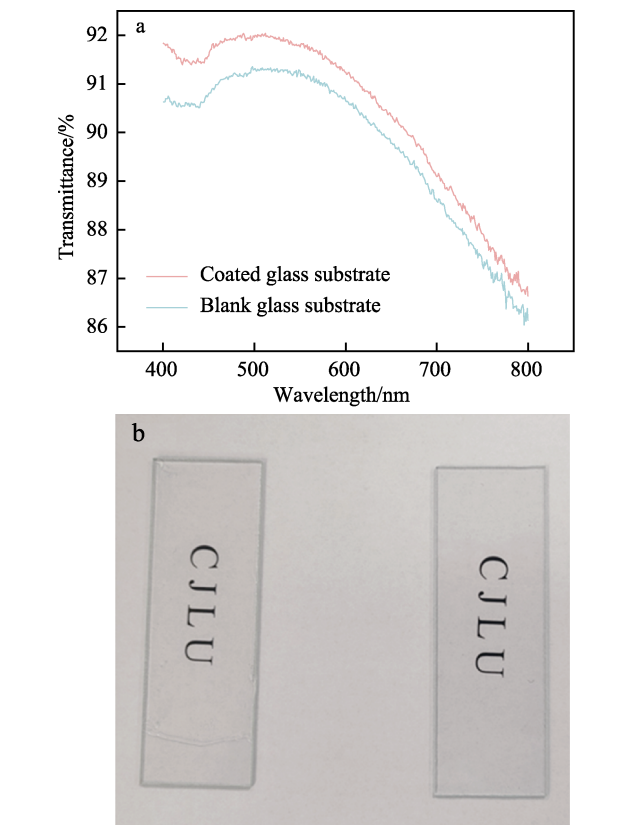


图 3 涂膜玻璃基板与空白玻璃基板在空气中的透射光谱 (a); 涂膜玻璃基板 (左) 与空白玻璃基板 (右) 实际透光效果图 (b)

Fig.3 Transmission spectra of coated glass substrate and blank glass substrate in air (a); actual light transmission effect of coated glass substrate (left) and blank glass substrate (right) (b)

2.8 耐摩擦性能

树脂涂膜的耐摩擦性能测试按照文献测试方法^[25]进行, 将树脂涂膜样品面朝下置于 1200 目的金相砂纸上, 在样品的另一面施加 100 g 砝码, 随后将样品以 2 cm/s 的速度向前和向后各移动 10 cm (如图 4 所示), 记为一个耐摩擦循环, 摩擦不同的循环次数后

用 JC2000DF 型接触角测量仪检测其表面润湿性的变化,通过接触角的数值变化反映出树脂涂膜的耐摩擦性能。

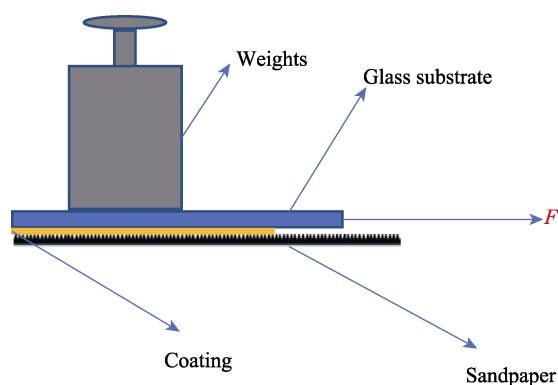


图4 摩擦测试示意图
Fig.4 Schematic diagram of friction test

如图5所示,经砂纸摩擦后,样品的接触角呈现出一定的规律性变化,由于经过砂纸摩擦,涂膜表面不同位置的粗糙度不同,且间隔一定循环次数后测量接触角时的点位不尽相同,因此,膜层的接触角随摩擦次数的增加波动增大。从整体结果来看,膜层接触角随着摩擦次数的增多而减小,经过60次的循环,膜层的接触角依然 $>98^\circ$,符合低表面能防污涂料的要求,涂层的耐磨性良好。树脂涂层拥有良好的耐磨性有两方面原因:(1)各分子链经过交联固化反应形成网状结构,可以有效地增加树脂涂层的耐磨性和稳定性;(2)各分子链支链上的 $-OH$ 之间易形成氢键,在氢键的作用下各分子链之间相互吸引,也能在一定程度上起到增加树脂涂层耐磨性的作用。

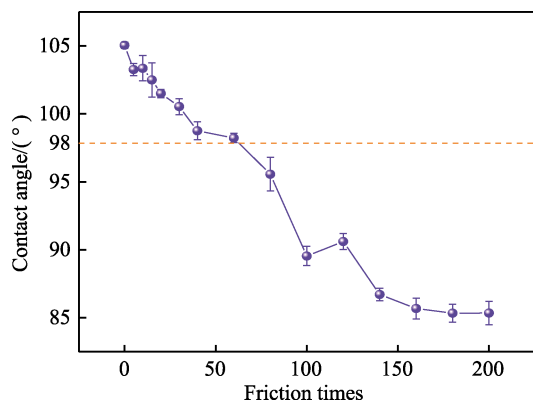


图5 摩擦不同次数后涂膜的接触角
Fig.5 Contact angle of coating film after different times of friction

2.9 电化学阻抗

理想的耐磨树脂材料除了具有很好的耐摩擦性能外,还必须同时具备优良的致密性。为了研究有机硅改性丙烯酸树脂的致密性,采用电化学阻抗谱(EIS)测试了树脂涂膜在3.5%NaCl溶液中的致密性

表现。

图6为树脂涂膜在3.5%NaCl溶液中浸泡的EIS谱图。从图6a中可以看出,Nyquist图为单容抗图,反映了涂层的信息,在此阶段主要是侵蚀介质在涂层中的传输过程。在测试过程中,未出现明显的扩散阻抗,表明涂层未出现溶胀,侵蚀介质未进入涂层中,进而表明涂层具有较好的致密性。

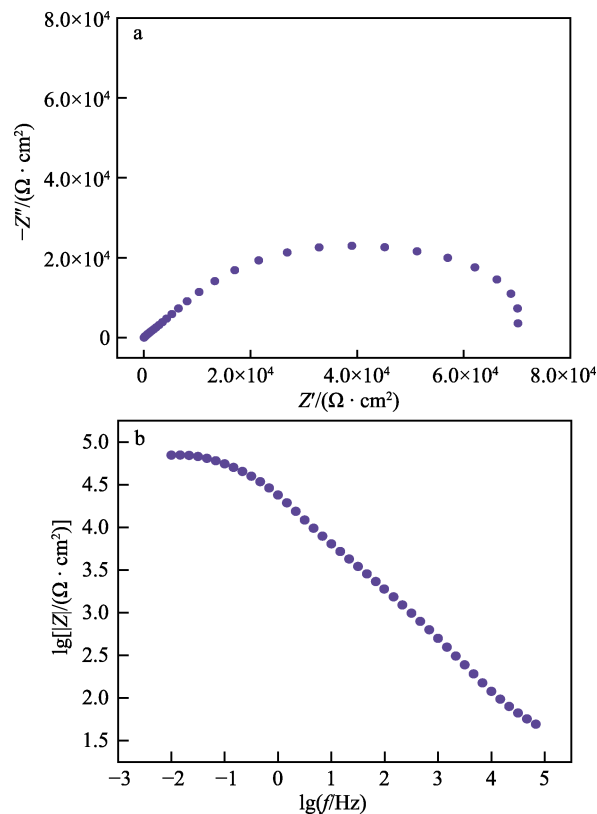


图6 涂层在3.5%NaCl溶液中浸泡的EIS谱图
Fig.6 EIS spectrum of coating immersed in 3.5wt.% NaCl solution: a) Nyquist diagram; b) Bode amplitude frequency diagram

3 结论

1) 采用自由基聚合法成功制备出了有机硅改性的丙烯酸树脂,接触角为 106.7° ,附着力为0级,硬度为H。

2) 经紫外可见近红外分光光度计测试,树脂具有一定的增透能力,可见光波段内,涂膜玻璃的最高透射率能达到92.04%。

3) 经电化学测试分析,树脂涂膜具有良好的致密性。

参考文献:

- [1] ZHONG Hong, HU Yan, WANG Yuan-hao, et al. TiO_2 /Silane Coupling Agent Composed of Two Layers Stru-

- cture: A Super-Hydrophilic Self-Cleaning Coating Applied in PV Panels[J]. *Applied Energy*, 2017, 204: 932-938.
- [2] MAGHAMI M R, HIZAM H, GOMES C, et al. Power Loss Due to Soiling on Solar Panel: A Review[J]. *Renewable and Sustainable Energy Reviews*, 2016, 59: 1307-1316.
- [3] ELMINIR H K, GHITAS A E, HAMID R H, et al. Effect of Dust on the Transparent Cover of Solar Collectors[J]. *Energy Conversion and Management*, 2006, 47(18-19): 3192-3203.
- [4] HU Yan, WANG Yuan-hao, YANG Hong-xing. TEOS/Silane Coupling Agent Composed Double Layers Structure: A Novel Super-Hydrophilic Coating with Controllable Water Contact Angle Value[J]. *Applied Energy*, 2017, 185: 2209-2216.
- [5] PARKIN I P, PALGRAVE R G. Self-Cleaning Coatings[J]. *Journal of Materials Chemistry*, 2005, 15(17): 1689-1695.
- [6] FENG Ke-ying, HUNG G Y, LIU Jia-shang, et al. Fabrication of High Performance Superhydrophobic Coatings by Spray-Coating of Polysiloxane Modified Halloysite Nanotubes[J]. *Chemical Engineering Journal*, 2018, 331: 744-754.
- [7] MATIN A, MERAH N, IBRAHIM A. Superhydrophobic and Self-Cleaning Surfaces Prepared from a Commercial Silane Using a Single-Step Drop-Coating Method[J]. *Progress in Organic Coatings*, 2016, 99: 322-329.
- [8] LI Ling-xiao, LI Bu-cheng, DONG Jie, et al. Roles of Silanes and Silicones in Forming Superhydrophobic and Superoleophobic Materials[J]. *Journal of Materials Chemistry A*, 2016, 4(36): 13677-13725.
- [9] GAO Li-kun, LU Yun, LI Jian, et al. Superhydrophobic Conductive Wood with Oil Repellency Obtained by Coating with Silver Nanoparticles Modified by Fluoroalkyl Silane[J]. *Holzforschung*, 2016, 70(1): 63-68.
- [10] LIU Shan-hu, LIU Xiao-jing, LATTHE S S, et al. Self-Cleaning Transparent Superhydrophobic Coatings through Simple Sol-Gel Processing of Fluoroalkylsilane[J]. *Applied Surface Science*, 2015, 351: 897-903.
- [11] GAO Li-kun, LU Yun, ZHAN Xian-xu, et al. A Robust, Anti-Acid, and High-Temperature-Humidity-Resistant Superhydrophobic Surface of Wood Based on a Modified TiO_2 Film by Fluoroalkyl Silane[J]. *Surface and Coatings Technology*, 2015, 262: 33-39.
- [12] ZHANG Hao, MA Yong, TAN Jiao-jun, et al. Robust, Self-Healing, Superhydrophobic Coatings Highlighted by a Novel Branched Thiol-Ene Fluorinated Siloxane Nanocomposites[J]. *Composites Science and Technology*, 2016, 137: 78-86.
- [13] CAI Ying, LI Jing, YI Ling-min, et al. Fabricating Superhydrophobic and Oleophobic Surface with Silica Nanoparticles Modified by Silanes and Environment-Friendly Fluorinated Chemicals[J]. *Applied Surface Science*, 2018, 450: 102-111.
- [14] WEST J O F, CRITCHLOW G W, LAKE D R, et al. Development of a Superhydrophobic Polyurethane-Based Coating from a Two-Step Plasma-Fluoroalkyl Silane Treatment[J]. *International Journal of Adhesion and Adhesives*, 2016, 68: 195-204.
- [15] SMITH E A, CHEN Wei. How to Prevent the Loss of Surface Functionality Derived from Aminosilanes[J]. *Langmuir: The ACS Journal of Surfaces and Colloids*, 2008, 24(21): 12405-12409.
- [16] KOTLÍK P, DOUBRAVOVÁ K, HORÁLEK J, et al. Acrylic Copolymer Coatings for Protection Against UV Rays[J]. *Journal of Cultural Heritage*, 2014, 15(1): 44-48.
- [17] MOTAMEDI M, RAMEZANZADEH M, RAMEZANZADEH B, et al. One-Pot Synthesis and Construction of a High Performance Metal-Organic Structured Nano Pigment Based on Nanoceria Decorated Cerium (III)-Imidazole Network (NC/CIN) for Effective Epoxy Composite Coating Anti-Corrosion and Thermo-Mechanical Properties Improvement[J]. *Chemical Engineering Journal*, 2020, 382: 122820.
- [18] YU Shu-na, ZHOU Yu-ming, ZHANG Tao, et al. Preparation and Characterization of Acrylate Copolymers Modified by Fluorine and Silicon for Application in Release Films[J]. *Polymer-Plastics Technology and Engineering*, 2014, 53(6): 531-538.
- [19] HUANG Kai, LIU Yu-long, WU Dong-fang. Synthesis and Characterization of Polyacrylate Modified by Polysiloxane Latexes and Films[J]. *Progress in Organic Coatings*, 2014, 77(11): 1774-1779.
- [20] MUTHURAJ R, GROHENS Y, SEANTIER B. Mechanical and Thermal Insulation Properties of Elixum Acrylic Resin/Cellulose Nanofiber Based Composite Aerogels[J]. *Nano-Structures & Nano-Objects*, 2017, 12: 68-76.
- [21] LEI Hui-bin, HE De-liang, GUO Yan-ni, et al. Synthesis and Characterization of UV-Absorbing Fluorine-Silicone Acrylic Resin Polymer[J]. *Applied Surface Science*, 2018, 442: 71-77.
- [22] KUO C F J, CHEN Jiong-bo. Study on the Synthesis and Application of Silicone Resin Containing Phenyl Group[J]. *Journal of Sol-Gel Science and Technology*, 2015, 76(1): 66-73.
- [23] ZHU Ben-feng, LIU Ze-han, LIU Jiao, et al. Preparation of Fluorinated/Silanized Polyacrylates Amphiphilic Polymers and Their Anticorrosion and Antifouling Performance[J]. *Progress in Organic Coatings*, 2020, 140: 105510.
- [24] CHI Fang-ting, ZENG Yi-yang, LIU Cheng, et al. Highly Stable Self-Cleaning Antireflection Coatings from Fluoropolymer Brush Grafted Silica Nanoparticles[J]. *Applied Surface Science*, 2020, 507: 144836.
- [25] LIU Yan-ze. Research on a Superhydrophobic Coating of Highly Transparent Wear-Resistant Inorganic/Organic Silicon Composite Resin[J]. *Coatings*, 2021, 11(3): 338.