EFFECT OF SILANE COUPLING AGENT ON INTERFACIAL STRENGTH OF STAINLESS STEEL

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Abstract
This paper presents the improvement of interfacial strength of stainless steel-polymer hybrid materials by silane surface treatment. Two different deposition routes, a wet chemical dipping process and an atmospheric plasma deposition route were chosen to deposit the silane on the stainless steel surface. The conditions of both deposition routes were optimised. Pull-off testing (dolly testing, in accordance with ISO 4624:2002) was used to evaluate the interfacial strength of different samples. The dolly sample configuration was optimised for very thin plate with the help of numerical modelling. Strong improvements of the interfacial strength of the stainless steel-epoxy systems upto 60 MPa were observed after optimisation of the surface treatment conditions for both deposition routes.

1. Introduction

Stainless steel (SS) is a unique engineering material due to its excellent mechanical properties, corrosion resistance and recyclability [1]. Recently, stainless steel gained a lot of interest for composite applications. This steel-polymer hybrid materials offer: higher impact resistance, higher strength to weight ratio, better dimensional stability, and greater design freedom [2]. Apart from its superior mechanical properties, one of the drawbacks of stainless steel for polymer composite application is that it has comparatively poor interfacial strength towards polymeric materials [3]. Therefore it is very important to improve the interface for a better performance of steel-polymer hybrids. Several researchers propose different ways of treating metal surface to improve the interfacial strength towards polymeric material, like by grit-blasting or sand blasting, or by chemical etching, or by using coupling agents [4]. Silane based coupling agents as adhesion promoters are among the most used coupling agents to improve the interfacial strength of stainless steel. Generally, silanes are applied on to the metal surface in hydrolyzed state. During the hydrolysis, silanol groups are produced which can react with the available hydroxyl group on the metal surface and can form covalent linkage. The properties and quality of the silane layers are strongly dependent on the deposition conditions, like the preparation of the silane solution, deposition conditions and the condensation conditions [4]. In this work, γ-aminopropyltriethoxysilane (γ-APS) was chosen

to modify the stainless steel surface. Two different deposition routes, a wet chemical dipping process and an atmospheric plasma deposition route were chosen to deposit the silane on the stainless steel surface. The conditions of the wet chemical dipping process were studied to get the most optimised deposition condition. This includes the silane solution concentration, the dipping condition in silane solution, the rinsing condition of the surface treated samples and the condensation condition of the silane layer (time, temperature of the oven and effect of vacuum). The effect of different deposition conditions of the atmospheric plasma deposition route on the interfacial strength, which includes the type of precursor, the plasma powers, and the treatment time, were also studied. Pull-off testing (dolly testing, in accordance with ISO 4624:2002) was used to evaluate the interfacial strength of different samples. In accordance with the ISO 4624:2002, four different types of sample configurations are possible to measure the interfacial strength of metal plates. The different pull-off sample configurations are: a) dolly-dolly sample configuration, b) dolly-plate sample configuration, c) dolly-plate-dolly asymmetric sample configuration, d) dolly-plate-dolly symmetric sample configuration. The details are shown in figure 1. But, there is no clear information available in the literature regarding the most suitable sample configuration which can be used to characterise the very thin plates. Linear elastic numerical models were used to find out the most preferable pull-off specimen configuration for thin plates. Effect of different deposition conditions on the interface strength of steel-epoxy hybrid system were studied for both deposition routes.

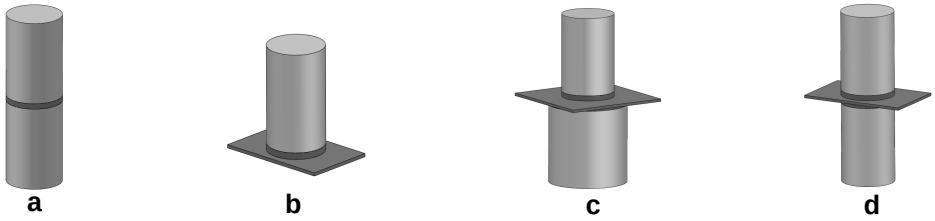

Figure 1: Comparison of possible sample configurations of pull-off testing. a: dolly-dolly sample (both dollies diameter is 20 mm); b: dolly-plate sample (diameter of dolly is 20 mm, plate thickness is 1 mm); c: dolly-plate-dolly-asymmetric sample (two different dollies of 20 mm and 30 mm in diameter, plate thickness is 1 mm); d: dolly-plate-dolly-symmetric sample (diameter of the both dolly is 20 mm, plate thickness is 1 mm).

2. Experimental Details

2.1 Materials

γ –APS was supplied by Sigma-Aldrich with 99% purity and the stainless steel plate was 0.8 mm thick 304 type (mirror polished) stainless steel. The epoxy resin was stoichiometric mixture of EPIKOTE 828 LVEL, supplied by MOMENTIVE, and 1,2 diamino cyclohexane, supplied by Sigma-Aldrich. Stainless steel dollies (diameter: 20 mm) were used to prepare the dolly samples for pull-off testing. Dollies were sandblasted and subsequently cleaned ultrasonically in an acetone bath before using it for the dolly sample preparation.

2.2 Wet chemical deposition technique

Silane solution was prepared by mixing γ-APS into a water/ethanol (90/10) mixture solvent. After that, the solution was kept for thirty minutes for the full hydrolysis of the silane. Steel plates were initially cleaned ultrasonically for fifteen minutes in an ethanol bath and were immersed immediately into the silane solution to avoid recontamination of the surface. Subsequently, it went through a rinsing process in an ethanol bath. Finally, the silane coated steel plates were placed in a vacuum enabled oven for the condensation of the silane film.

2.3 Atmospheric plasma depostion technique

Coating experiments were carried out in a typical parallel plate dielectric barrier discharge (DBD) atmospheric pressure reactor. One of the most distinctive feature of this apparatus is the mobility of the upper high voltage electrode which enables the deposition of homogeneous coating on the samples, placed on the botton grounded electrode. The gap between the electrode was fixed at 2 mm in order to assure stable plasma operation. The deposition process was performed by using nitrogen as main gas: nitrogen is injected in the palsma reactor as carrier gas to ignite and sustain the discharge but it is also used to generate the aerosol of the organic precursor by using a home made atomizer based on the Venturi's principle. After the plasma coating, the coated samples were gone throgh a thermal condensation process for the condensation of the silane film.

2.4 Dolly sample preparation

For adhesion strength measurement dolly samples were prepared by using dollies and the metal plate samples. For epoxy based dolly samples, the adhesive layer was first applied on to the surfaces of the dollies and to the metal plates, and then the joints were stuck together in a home made sample preparation set up. A dead weight (0.5 Kg for each sample) was used to maintain the uniform thickness. The coating thickness was maintained by the glass beads. The first step of the resin curing was performed by keeping the dolly samples at ambient temperature for overnight. The final curing was done in two stages in a heated oven: I. 80°C for 2 hour and II. 180°C for 1 hour. The thickness of the coating after cure was about 0.2 mm.

2.5 Adhesion strength measurement (Dolly testing)

The pull-off adhesion tests were performed with an Instron test bench (Instron 5885H, capacity 250 kN) in accordance with ISO 4624:2002. The dollies were pulled vertically away from its metal plate substrate with a jaw speed of 0.5 mm/min by means of a threaded screw with a fix lower jaw. During testing, the maximum load needed to break the dolly sample was recorded and at least six measurements were performed for each type of sample for an average value measurement. The stress at break was calculated by using equation 1. Where S is stress at break (in MPa), L is the load at break (in N) and D is the dolly diameter (in mm).

$$S = (L \times 4) / (\pi \times D^2) \quad (1)$$

3. Results and discussion

3.1 Optimisation of dolly sample configuration for thin plates

Numerical simulation based on linear elastic model was performed to study the stress distribution at the epoxy interface for different pull-off specimens. Influence of tensile loading and curing cycle on the stress distribution profile were checked numerically. Stress distribution along the normal direction due to a certain applied load at the epoxy-metal interface for different sample configuration is shown in figure 2. From the results, it is very clear that there is a significant effect of sample configuration on the stress distribution profile for different sample geometry. According the stress profile, the best sample configuration is dolly-dolly configuration ('a'). However, this sample configuration cannot be used for the plates. From the results, it can be seen that the stress distribution profile of sample configuration 'd' have good similarity with sample configuration 'a'. The conclusion can be made from the numerical calculation that the dolly-plate-dolly symmetric set up is the ideal set up for measuring the interfacial strength of very thin plates.

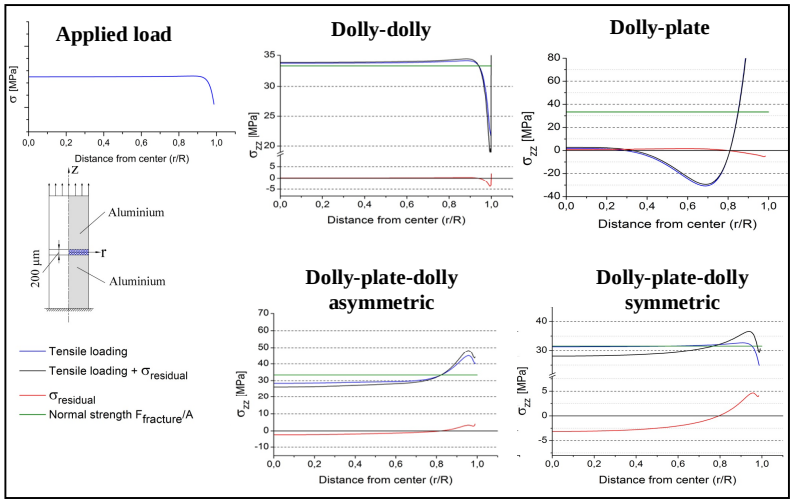

Figure 2: Linear elastic model: stress distribution at the metal plate/epoxy interface due to tensile loading for different pull-off configurations.

3.2 Optimisation of wet chemical deposition technique

The influence of different deposition conditions of wet deposition technique on the interfacial strength of steel-epoxy hybrid is shown in table 1. It can be observed that temperature of the condensation condition has a strong effect on the interfacial strength. For optimisation of rinsing condition, the samples were rinsed in an ethanol bath for different time interval. According the result, rinsing step is a very important step and it makes the silane coating more uniform by removing loosely adhered silane molecules. Different silane concentrations (1% v/v, 2% v/v and 5% v/v) were used to find out the optimum silane concentration. It can be observed that the interface strength strongly depend on silane concentration. It can be conclude that the optimum silane concentration is 2%, where 1% silane concentration might be giving incomplete covering of the surface and 5% silane concentration gives a thicker and non uniform coating. Effect of different dipping time intervals was studied. From the results, it can be seen that the shorter dipping time is not favourable. In conclusion, a strong improvement of interfacial strength can be obtained by optimising the deposition conditions.

Type of sample	**Treatment type**	**Wet coating deposition**			**Condensation condition**	**Stress at break (MPa)**
		Silane solution concentration (% v/v)	Dipping time (sec)	Rinsing time (sec)		
Blank	No treatment	-	-	-	-	29.87±3.8
Silane surface treated sample	Optimisation of condensation condition	2	30	3	50°C-1.5 hr (V)	46.2±2.57
					70°C-1.5 hr (V)	49.82±3.69
					90°C-1.5 hr (V)	44.19±3.65
	Optimisation of silane solution concentration and rinsing time	1	30	60	70°C-1.5 hr (V)	55.93±4.06
		2		No rinsing		44.9±6.39
		2		15		55.94±2.63
		5		60		47.96±4.4
	Optimisation of dipping time	2	10	60	70°C-1.5 hr (V)	41.42±9.44

***NT- no thermal condensation treatment; NV – no vacuum condition; V – vacuum condition**

Table 1: Comparison of interfacial strength of blank/native stainless steel sample different wet coated stainless steel sample with epoxy resin

3.3 Optimisation of atmospheric plasma deposition technique

The influence of different deposition conditions of atmospheric plasma deposition technique on the interfacial strength of steel-epoxy hybrid is shown in table 2. From the result, it can be notice that interfacial strength is increased with lowering of the plasma power. At high plasma power, the plasma might be fragmenting the silane molecules or might be destroying its functionality. As a result lower interfacial strength was observed. Two different types of precursor, the pure silane and the pre-hydrolysed silane (APS+1% water) were studied. It was found that the most favourable precursor was pre-hydrolysed silane. In this study, the plasma treatment time and thickness of the coating were controlled by number of passes. Number of passes has a strong influence on the interface strength. It was found that with the increase of number of passes the interface strength decreases. A thicker and non uniform coating might rises at higher number of passes and as a result lower interfacial strength was obtained.

Type of sample	**Atmospheric plasma coating deposition**			**Condensation condition**	**Stress at break (MPa)**
	Type of precursor	Power (W)	Number of passes		
Silane surface treated sample	Pure APS	450	6	4 hr at 100°C	21.92±8.74
		200			36.17±2.29
	APS+1% water	200	6	4 hr at 100°C	37.94±5.58
			6	2 hr at 100°C	39.2±6.68
			10		34.23±5.64

Table 2: Comparison of interfacial strength of different atmospheric plasma coated sample with epoxy resin

4. Conclusions

The dolly testing is successfully optimised for thin plates. It can be concluded that the sample geometry has a strong influence on the final value of interfacial strength and the optimum configuration for very thin plates is dolly-plate-dolly symmetric configuration. Stainless steel surface is also successfully modified by silane treatment. It was observed that for both wet and atmospheric plasma deposition routes the deposition conditions strongly influence the interfacial strength. And they need to be controlled very precisely for the better performance of the steel-polymer hybrid systems. A strong improvement of interfacial strength upto 60 MPa of steel-epoxy system is observed after the surface modification of the stainless steel surface.

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