



A study of adhesion on stainless steel in an epoxy/dicyandiamide coating system: Influence of glass transition temperature on wet adhesion



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ABSTRACT

A coating was developed by controlling its glass transition temperature (T_g). This coating attained its highest T_g value in wet conditions (wet T_g) of higher than 100 °C, and maintained its adhesion on stainless steel even after immersion in boiling water. When this coating material was applied to a conventional two-component epoxy structural adhesive as a metallic primer, it improved the primer adhesion durability on the stainless steel sheet in water significantly, even if it was not chemically modified (without pretreatment). This indicated that a relative weak hydrogen bond between the hydroxyl group of the epoxy network and a surface hydroxyl group of the oxide layer of the stainless steel could be sufficient to prevent water penetration into the interface if the thermal mobility of the epoxy network is restrained. An investigation by X-ray photoelectron spectroscopy (XPS) indicated an interaction between a primer amino-group component and the metallic surface accompanied by proton transfer. However, the thermal mobility of the epoxy network could be the most important factor in its adhesion in wet conditions.

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1. Introduction

Adhesive bonding of metallic materials is now established as an indispensable industrial technology for the construction of airplanes and cars [1,2]. Nevertheless, several technological problems of strategic importance remain unsolved in this important industrial technology. The most important problem includes “loss of adhesive strength in the presence of humidity (wet adhesion)”. This unsolved problem is actually identical in nature to the problem of the adhesion of a corrosion protective coating layer to a metallic substrate in a humid environment [3].

It is well known that stainless steel exhibits inferior adhesion to organic coatings compared to other metals such as cold rolled steels or aluminum alloys due to the CrO₂ passivation layer present on its surface. Various types of pretreatment had been discussed to activate the surface of stainless steel, and several have been proposed and used in the aerospace industry (mechanical, chemical, and combination of mechanical and chemical) [4]. However, if these chemical pretreatment processes are employed, a residue

(smut) deposits on the surface. At the end of the process this residue needs to be removed by another chemical treatment, such as de-smutting. For this reason, the chemical pretreatment process is not attractive environmentally, and has prompted considerable interest in a more environmentally friendly and effective organic primer replacement.

In the last few decades, there have been several studies on organic primers (thin layer), for example the use of an aqueous solution of poly(acrylic acid) and electrolytic polymerization with triazinethiol compounds to improve adhesion in humid environments [5,6]. However, they mainly focused on the formation of strong (covalent or ionic) interactions between the stainless steel and the organic layer, and there are very few studies focusing on the physical properties of the organic primer, such as the glass transition temperature (T_g) [7].

Having examined the rate of water penetration into adhesive joints, it remains to consider the mechanism whereby it causes weakening. Water could influence the adhesive or the interface and in the case of permeable adherends changes in substrate properties could occur. Some of the processes which might occur would be reversible and so be accompanied by recovery in strength on removal of water but others would be irrecoverable. Gledhill has studied the durability of structural metallic adhesive joints,

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Table 1
Composition of investigated primer coatings (varnish).

Sample codes		A	B	C	D	E	F
Epoxy resin	Bis-phenol A	60	40	40	40	40	40
	Phenol-novolac	0	20	20	20	20	20
Curing agent	Dicyandiamide	5	5	5	5	5	5
Accelerator	Imidazole (Table 2)	No.1	No.1	No.2	No.3	No.4	No.5
Filler	SiO ₂	25	25	25	25	25	25
	TiO ₂	9	9	9	9	9	9

employing an epoxy adhesive, and also measured the diffusion coefficient and solubility of water in the bulk epoxy adhesive under the same environmental conditions, and he has suggested the rate of interface disbonding in these joints is controlled by the availability of water at the interface, which in turn is governed by diffusion of water through the adhesive [8]. The temperature T_g is defined as that at which there is an increase in the thermal expansion coefficient. The increase in the thermal expansion coefficient above T_g can be explained by the greater degree of freedom available to molecular segments. The larger volume between molecules gives more degree of freedom so that the same increase in temperature will give a greater increase in volume. In other words, a higher T_g restrains the mobility of polymer network and its bonding to metallic substrate can be stabilized.

In this study the influence of the T_g of the organic primer coating on the adhesion in a humid environment, especially in the critical condition (in boiling water), was investigated in an attempt to optimize the primer coating design. As a result of this investigation, a novel epoxy based primer coating was proposed, which did not lose its adhesion on stainless steel even after boiling water immersion.

2. Experiments

2.1. Materials

2.1.1. Primer coating

Table 1 shows a brief listing of the composition of the investigated primer coatings (varnish).

Epoxy resin (diglycidyl ether of bisphenol-A type and phenol-novolac type) supplied by Mitsubishi Chemical Co. was used as the main resin. Dicyandiamide (DICY) was used as a curing agent and it was also supplied by Mitsubishi Chemical Co. In order to optimize the T_g, imidazole curing accelerators were additionally used and they were supplied from Shikoku Kasei Co. The surface of stainless steel that has not received chemical treatment is very inert and has a low surface energy. In this case, inorganic fillers are required to control flow characteristics during curing. For this purpose, TiO₂ and SiO₂ fillers from Ishihara Industry Co. and Kinsei Matec Co., respectively were used as rheology control agents. Their compositions are listed in Table 1 and Table 2. All this materials were used without further purification.

Table 2
Chemical structure of imidazole accelerators.

Structure ^a	Triazine type		Alkyl imidazole type		
	No.1	No.2	No.3	No.4	No.5

^a Molecular weight: R1 < R2 < R3.

All formations are absolutely solvent free. They were mixed in a high-rotation homogenizer (Excel Auto Homogenizer by Nihon Seiki Kaisha Co.) at 10000 rpm for 20 min.

2.1.2. Primer application on stainless steel

The prepared varnish was applied to an austenite type stainless steel (C; 0.06, Ni; 8.89, Cr; 18.75, Si 0.54 Mn; 1.59, P; 0.03, S; 0.005 wt%, Fe; balance) with a drawdown rod applicator aiming for a thickness of 10 μm. In all cases, stainless steel sheets were firstly degreased using acetone before use. The primer-coated stainless steel sheets were baked and cured at 175 °C for 60 min in a convection oven.

2.2. Characterization

2.2.1. Determination of glass transition temperature (T_g)

Thermo mechanical analysis (TMA) was used with the penetration method to determine T_g in dry (dry T_g) and wet conditions (wet T_g). The T_g was determined by the temperature at which the highest penetration change was observed [7]. A cured coating film on Ni foil of 0.1 mm thickness was immersed in boiling water for 7 days, and consecutively its wet T_g was measured in TMA. The advantage of TMA analysis has the benefit that the T_g of a film on a substrate can be measured. A TMA4030SA (Bruker AXS) was employed for the TMA measurements under the conditions of 1.0 mm diameter of the probe top and 5 °C/minute temperature increase rate from 20 °C to 200 °C (5 °C/min.) under a nitrogen atmosphere.

2.2.2. Adhesion properties

2.2.2.1. Initial adhesion strength. These primer coated specimen were bonded (bonded area: 312.5 mm²) using epoxy/polyamide-amine adhesive (Scotch-Weld DP190G, designed for metal bonding) which was supplied by 3M Co. The thickness of the adhesive layer was controlled approximately to 150 μm after application. The adhesive was cured for 7 days at room temperature and then for 1 h at 100 °C, and single lap specimens were prepared. These specimens were drawn in an Autograph instrument manufactured by Shimadzu Co., and the maximum load required to break joints were recorded in accordance with JIS K6850. The adhesive (primer) residual area on the stainless surfaces was evaluated visually to determine the fracture mode, as either failure in cohesion or failure in adhesion. Fig. 1 shows illustrations of the typical fracture modes observed. Interfacial fracture between primer and adhesive was never observed.

2.2.2.2. Adhesion strength after boiling water immersion. The specimens were immersed in boiling water for 7 days to confirm the influence of water penetration on adhesion. The joints were removed from the boiling water and cooled down to room temper-

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