

Effect of chromate conversion coatings with and without poly(acrylic acid) on the press formability, shearing properties and durability of galvanized steel laminates using poly(vinyl butyral) as core material

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A sandwiched type of electrogalvanized (EG) steel sheets bonded with poly(vinyl butyral) (PVB) was used to study the effect of chromate conversion coating on the interfacial bonding and bending formability of the laminate. It was found that a proper chromium passivation on the steel surface enhanced both initial tensile shearing strength (TSS) and the joint durability in the corrosive environment. The greatest TSS, i.e. 17.8 MPa, was measured for the chromated steel sheet with chromium content ranging 0.040–0.055 g/m². A good correlation between the TSS and the bending formability of the laminate was obtained. Poly(acrylic acid) (PAA) was also added in the chromate solutions and the complex conversion coating exhibited an improvement on the shearing properties of the EG steel sandwiches. The effect of PAA incorporated in the chromate coating on adhesion was dependent upon its concentration and molecular weight. The greatest TSS, i.e. 24.0 MPa, was measured by adding a proper amount of PAA with MW = 380,000 g/mol, approximately 8 wt %, in the chromate solution for EG surface coating. The possible mechanism of the enhancement of interfacial properties due to the incorporation of PAA will be discussed. © 1999 Kluwer Academic Publishers

1. Introduction

The vibration-damping steel sheet had become a commercially active product recently. It is usually produced as a sandwich form consisting of two steel faces and a viscoelastic polymer as a core layer. The damping property is mainly due to the viscoelastic layer that dissipates vibration energy [1, 2]. But only when the viscoelastic layer is sandwiched between the panels with sufficient degree of adhesion can vibration energy then be converted to heat due to shear deformation of the core [3]. On the other hand, if the interfacial strength is poor, delamination occurs during shape forming and the shape of bent laminate becomes defective. However, it was reported [4, 5] that a tensile shear strength greater than 12.0 MPa was necessary for a steel laminate to have bendability as good as a monolithic steel sheet. Hence, to improve interfacial strength is an important subject for the vibration-damping steel sheets or similar sandwiched structures.

A chemical conversion coating on steel sheet to modify the surface can significantly affect the interfacial bonding to a polymeric material and corrosion resistance of the joint. The most common treatment on steel or zinc is phosphating that unfortunately has been

reported [6, 7] to be a poor method from the aspect of adhesive bonding. On the other hand, a chromate conversion coating often helps the bondability for aluminum and its alloys [6–8]. Chromates inhibit the corrosion of most metals; the chromate ion oxidizes any exposed metal and thus repairs and reinforces the protection offered by the air-formed film. Chromate treatments producing a thickened and protective surface film have been developed for aluminum, magnesium and zinc. Just as zinc plating is almost always chromated, galvanized coatings that are not specifically intended being painted are usually chromated. Chromate is one of the best passivation and separation films ever invented; it is extensively used on stainless steel sheets in electrorecovery cells so that the plated coatings will peel right off. It is also used on all sorts of electroforms for making compact disks, vinyl records, and other precision stampers, so that the two surfaces will separate without a flight. However, chromating was seldom studied in the pretreatment of steel or zinc surfaces for the purpose of adhesion promotion.

Sugama *et al.* [8, 9] studied incorporation of poly-electrolyte resins in the phosphate solution and precipitating onto the steel surface to improve the bond

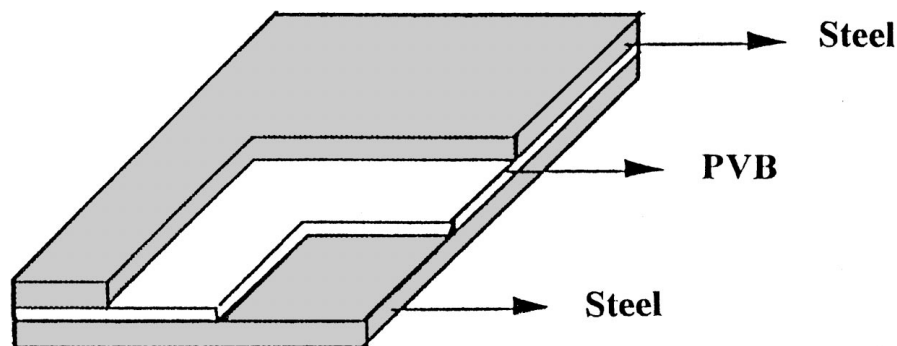


Figure 1 Construction of sandwiched steel panel.

durability. They studied, for example, the interfacial interaction of poly(acrylic acid) on oxidized metals such as iron orthophosphate dihydrate or zinc phosphate hydrate crystal which deposited on the metal surface. They concluded that incorporating polyelectrolytic resin in the phosphate solution resulted in enhanced wettability of the oxide layer by the electrolytic macromolecules, thereby increasing the mechanical interlocking bond forces.

The purpose of this study is to investigate the effect of chromate conversion coating on the interfacial properties, including bondability and durability, of the laminated steel sheets. The effect of incorporating poly(acrylic acid) into the chromate coating on the mechanical performances including press formability, shearing property were also studied.

2. Experimental

The polymer film with a thickness of $100\ \mu\text{m}$ was sandwiched between $0.5\ \text{mm}$ thick EG steel sheets, as shown in Fig. 1, with a laboratory press at a pressure of $8.0\ \text{MPa}$ and $180\ ^\circ\text{C}$ for 10 min. Polymer used as the viscoelastic core of the laminates was PVB containing free acid 0.05%, hydroxyl content 19–23% and butyral content 74–78%. Pretreatment procedures were carried out as following: alkaline cleaning, tap-water rinsing, distilled water rinsing, air drying, rinsing, chromating, then drying at $160\ ^\circ\text{C}$ for 30 min. The chromate solution consisted of sodium dichromate ($2\text{H}_2\text{O}$) 15% w/v and nitric acid (specific gravity = 1.42) 15% w/v. The immersion time was from 20 to 200 s at room temperature. The chromium content on the coated layer was measured by a X-ray fluorescence (XRF) analyzer. Laminated-assembly type of lap-shear, as shown in Fig. 2, was used to measure the tensile shearing strength by a universal Instron machine at a cross-head speed of $5\ \text{mm}/\text{min}$ for shearing apart. The residual shearing strengths after aging in a 5% NaCl salt-spray at $35\ ^\circ\text{C}$ for 200 to 1000 h were measured to compare the joint durabilities of the laminates. Square laminates measuring $90\ \text{mm}$ by $90\ \text{mm}$ were prepared for vertical bending tests. The line-marks were made at an interval of $1\ \text{mm}$ on the lateral sides of both steel layers as they were still bonded well. A punch radius of $6\ \text{mm}$ was used in the bending test. The difference of the distance displacements from the two skin-layers due to bending and delaminating was denoted as “discrepancy” and was measured as an indication of the bendability of the laminate.

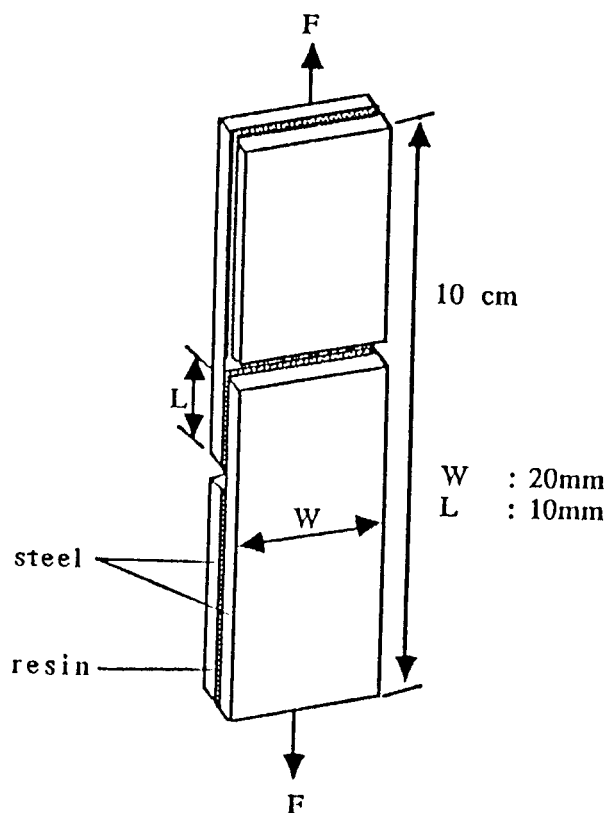


Figure 2 Methods of measuring adhesive shearing strength of steel laminate.

PAA with various molecular weights including 5.0×10^3 , 2.50×10^4 , 7.50×10^4 and $1.25 \times 10^6\ \text{g}/\text{mol}$ was added into the chromate solution, respectively. Ethylene glycol diglycidyl ether[1,2-bis(2,3-epoxypropoxy)ethane] was added into the complex chromate solutions as crosslinking agent for PAA if needed in some cases.

3. Results and discussion

3.1. Effect of chromate coating on TSS of the laminate

Chromium contents in the chromate coating from various immersion times were tabulated in Table I. The

TABLE I Relationship between coating weight of Cr and treatment time

Immersion time (s)	20	40	60	100	150	200
Coating wt. of Cr (g/m^2)	0.012	0.025	0.040	0.055	0.080	0.125

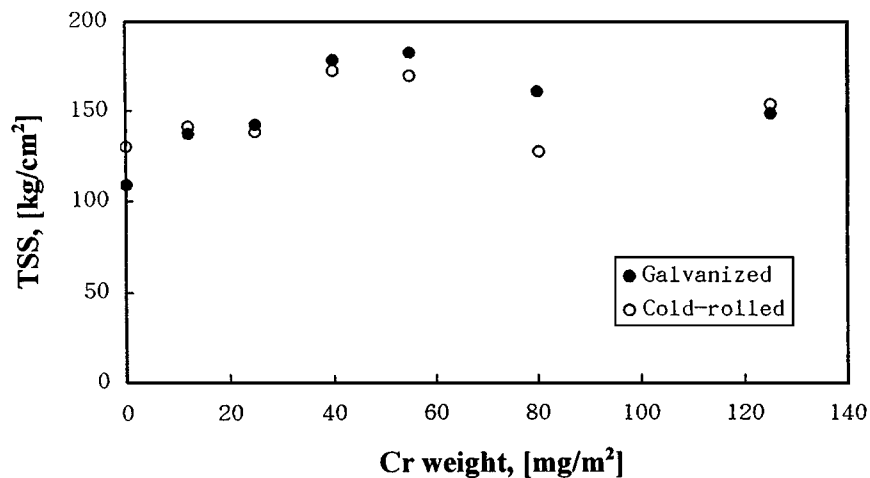


Figure 3 TSS measurements plotted against coating weight of Cr.

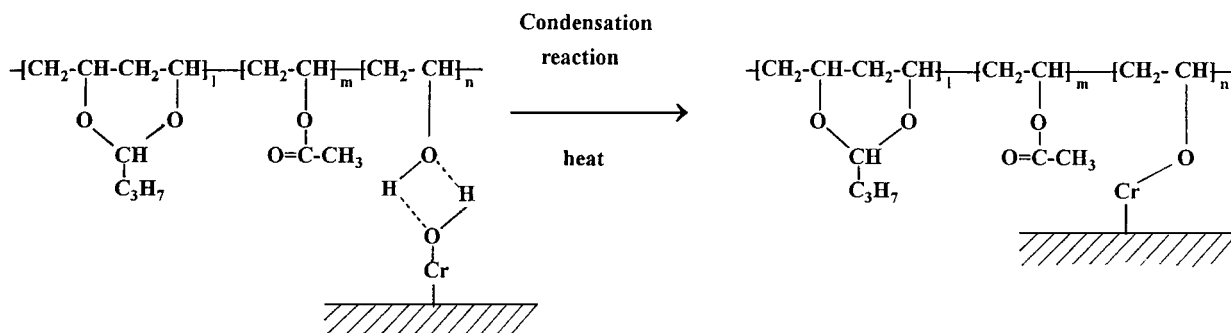


Figure 4 Condensation reaction of PVB and chromate layer.

quantitative analysis by XRF indicated that the average chromium contents on the surface coatings were 0.012, 0.025, 0.040, 0.055, 0.080 and 0.125 g/m², respectively. The effect of the chromium contents of the conversion coating on the adhesive bonding of the galvanized steel sheet is shown in Fig. 3. As can be seen, all solutions resulted in TSS greater than 12.0 MPa, a minimum shear strength for a sandwiched laminate to have bendability as good as monolithic steel sheet. A chromium content ranging 0.040–0.055 g/m² resulted in a highest TSS value as high as 18.2 MPa. On the other hand, higher chromium content resulted in poorer adhesive bonding. This may be ascribed to the weak adhering property for the thicker oxide layer. The adhesive strengths for the cold-rolled (CR) steel sheets were also measured for comparison and were plotted against chromium content in the same figure. As can be seen, a chromium content near 0.040–0.055 g/m² also resulted in the highest bonding strength. If the steel sheets were alkaline cleaned only and were not chromated, the CR laminates with TSS equal to 13.0 MPa was superior to the EG steel sheets which was measured with TSS equal to 10.9 MPa. This may be ascribed to the formation of zinc oxide as a weak boundary layer on the galvanized surface. However, the chromated CR steel sheets and the chromated EG steel sheets showed the similar shearing strengths to PVB. This demonstrates that the chromate layer forms firmly on the top layer of the substrate and plays a dominating role in adhesive bonding regardless of the steel type. The reason for adhesion enhancement due to chromating was thought to be the conversion of the original metallic surface into

a chromate oxide layer which offered hydroxyl groups for interfacial interactions with polar groups of the core resin. The dominant mechanism of adhesive bonding between the chromated surface and the core material is presumed as the chemical condensation reactions between the hydroxyl groups in the first monolayer of chromate oxide and hydroxyl groups of PVB, schematically shown in Fig. 4.

3.2. Effect of chromate coating on joint durability

The effect of chromate coating on the joint durability of EG laminate in an accelerated corrosion environment was studied by measuring its residual TSS after a salt-spray aging up to 1000 h and the results were plotted in Fig. 5. It was found that chromate coating helped in resisting joint deterioration from salt-spray aging. As can be seen, a chromated EG steel sheet with chromium content 0.055 g/m² declined from 18.2 to 16.2 MPa, deteriorating about 11%. On the other hand, the joint without chromate coating, declined from 10.9 to 7.3 MPa, i.e. it lost 33% of its initial joint strength. It was presumed that water molecules incorporated with joint bonds through the formation of hydrogen bonds, as shown in Fig. 6, and therefore depressed the opportunity of the replacement of chemical bonds. It is worthwhile to compare the durability of the CR steel laminate and the EG steel laminate and as can be seen that the EG steel showed better performance in joint durability. The joint strength of the CR steel laminate pretreated with chromate solution deteriorated about

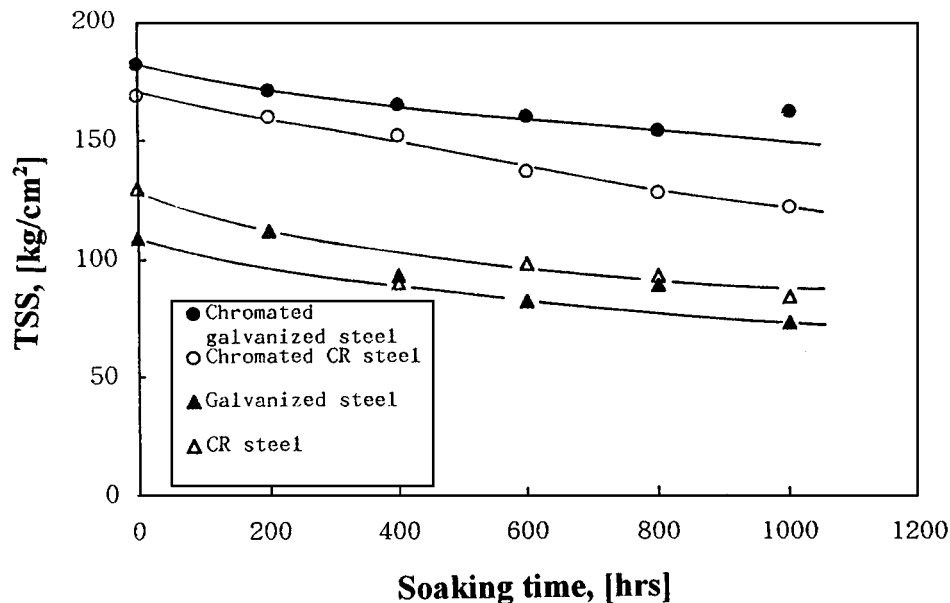


Figure 5 Residual TSS plotted against aging time.

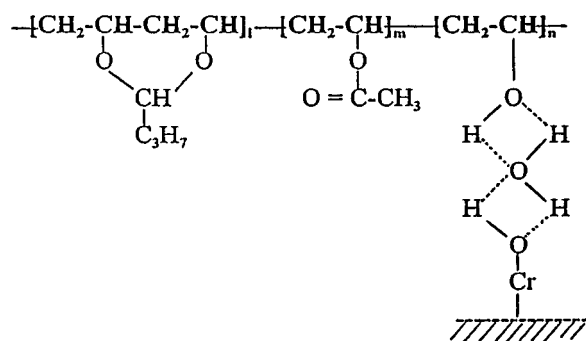


Figure 6 Water molecule incorporated with joint bond through the formation of hydrogen bond.

27.8% after salt-spray aging. The possible reason is the easy formation of the so-called white rust of zinc oxide on EG steel surface in a moisture-rich environment; this oxide layer acts as a weak boundary layer, if there is no protective barrier like the conversion coating, and hence decreases the joint durability. The laminates without chromate coating showed the same tendency for both types of steel laminates. Regarding durability, however, these results are opposite to the performances for monolithic CR and EG steel sheets, of which the latter is well known as much more durable steel.

3.3. Relationship of shear strength and bending formability of the laminate

Adhesion is an important factor to ensure the strength and reliability of the steel/polymer/steel laminate as a structural material. The relationships between the bonding strength and bending formability have been studied. Fig. 7 shows the discrepancies, from delamination due to vertical bending with a punch radius of 6 mm, against distance to the bending center for the galvanized steel laminates with various TSS values. The untreated EG steel with 10.9 MPa TSS exhibited serious slipping from the bending center all the way to bending end and showed a peak value of 0.21 mm at about a distance of 6 mm from the bending center. On the other hand, the

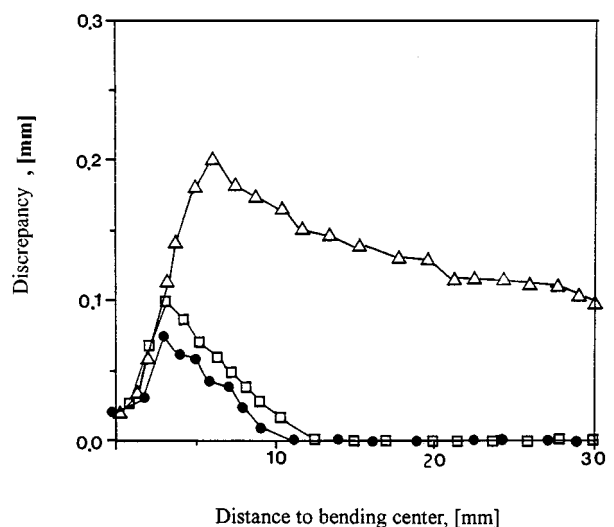


Figure 7 Discrepancy versus distance to bending center of the laminate (Δ) untreated EG steel (\square) chromated CR steel (\bullet) chromated EG steel.

discrepancy of the chromated EG steel laminate, with shear strength greater than 12.0 MPa, approached zero at a certain distance about 11 mm. The higher the TSS, the closer the zero-discrepancy point to the bending center and the lower the peak of distance discrepancy. For example, the chromated EG steel laminate with 18.2 MPa in TSS exhibits a peak value of 0.08 mm and the discrepancy disappears at 11.0 mm from the bending center. On the other hand, the chromated CR steel laminate with TSS equal to 14.2 MPa has a peak value of 0.10 mm at a distance of about 3 mm from the bending center and the zero-discrepancy at about 12 mm. Accordingly, the adhesive bonding strength is a significant factor for a sandwiched laminate in bending. A good consistence between TSS and distance discrepancy due to bending was obtained.

3.4. Effect of PAA in chromate layer on the adhesive bonding

Adding electrolyte resin into phosphate conversion coatings has recently sparked the scientists' interest

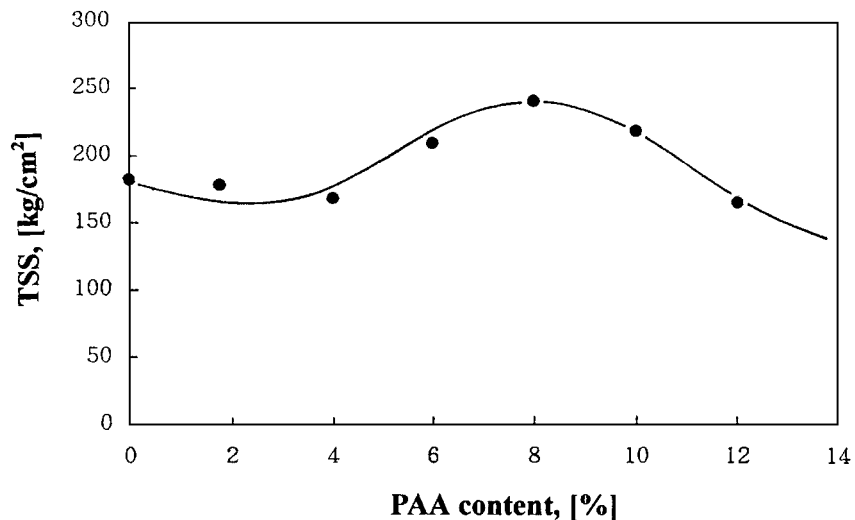


Figure 8 TSS measurement plotted against PAA (MW = 38,000) concentration in chromate solution.

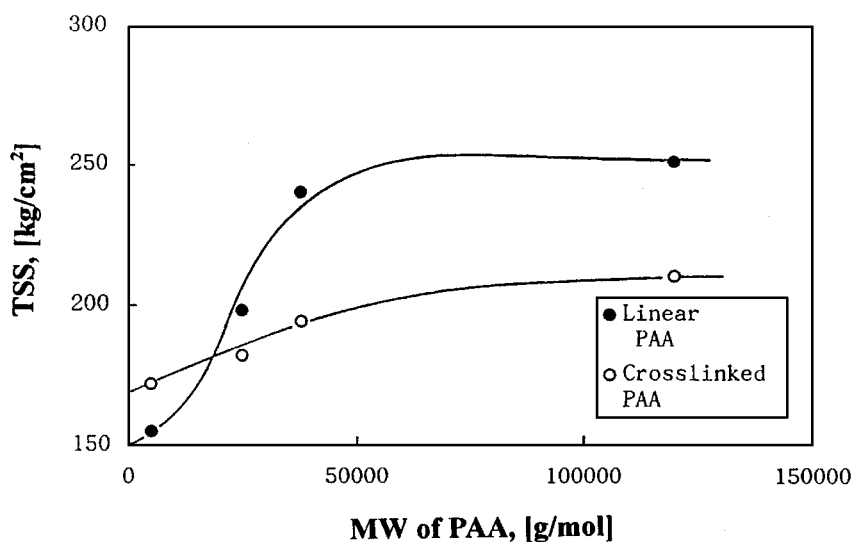


Figure 9 Effect of molecular weight of PAA on the lap shear strengths of the laminates.

[8–10] regarding better corrosion resistance and improved coating bendability. In this investigation, we added polyacrylic acid as a modifier for the chromate coating on the EG steel surface and the associated behaviors were compared. Polyacrylic acid of various MWs was added at various concentrations into the chromate solution. The effect of PAA content in the chromate solution used to pretreat the galvanized steel sheets on the lap shear strength of the laminate is shown in Fig. 8. An optimum content at about 8 wt % was found and enhanced 35% in TSS. In contrast, far away from this optimum content, the bonding strengths significantly decline. The possible mechanism for interfacial interaction will be discussed as follows. Some of carboxylic acid groups of PAA, precipitating simultaneously with the chromate conversion coating on steel surface, react with -OH groups on the metal oxide layer. On the other hand, some PAA chains not only diffusionally entangle with long chains of PVB resin—a core material of the laminate, but also chemically adsorb on the hydroxyl sites of the PVB resin. Some prerequisites must be fulfilled for macromolecules' entanglement. First, they must be linear chains. Second, they must

be high molecular weight or long chains. Therefore, two approaches were carried out to prove this hypothesis. In the first approach, 1.0 wt % of ethylene glycol diglycidyl ether[1,2-bis(2,3-epoxypropoxy)ethane] as a crosslinking agent of PAA was added into the chromate solutions. As heat was applied, a crosslinked network of PAA formed. This hot curable process for polyacrylic acid was well adopted in several patents [11, 12]. Consequently, TSS values, as shown in Fig. 9, were largely reduced due to the difficulty of molecular diffusion for entanglement. In the second approach, PAA with MW of only 5000 g/mol at the same weight ratio was added into the chromate solution for coating processes. It was found that the TSS value significantly declined again, as can be seen in Fig. 9. It is therefore believed that one of the effects of PAA on the bondability of the chromated steel laminate is ascribed to the degree of entanglement of PAA molecules with the long chains of the core resin of PVB. Accordingly, it is interpreted that only a proper amount of PAA with high enough MW incorporated into the chromate solution can molecularly entangle with the PVB chains for better bonding. An excessive concentration of PAA

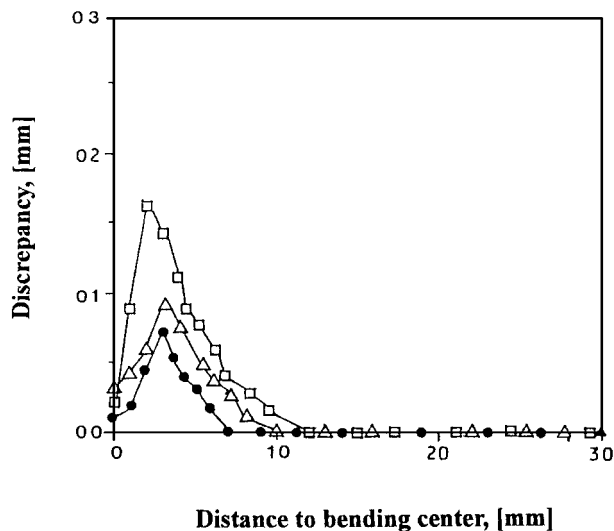


Figure 10 Discrepancy versus distance to bending center. PAA incorporated into chromate coating at a concentration of (Δ) 4 wt %, (\bullet) 8 wt %, (\square) 12 wt %.

not only occupies all the hydroxyl groups on the oxide layer but also forms weak boundary layer due to lack of reaction sites to bound the excessive PAA molecules. In contrast, too low concentration of PAA occupies partial hydroxyl groups but fails to form good entanglements.

Fig. 10 shows the bending discrepancy plotted against delamination distance of the laminates consisting of EG steel sheets pretreated with complex chromate coatings with various PAA loadings. It manifests a good adhesion was achieved by treating an EG steel with chromate coating incorporated with PAA.

4. Conclusions

1. A higher tensile shear strength resulted in a better bendability of the sandwiched laminate. Serious delamination occurred if TSS was lower than 12.0 MPa.

2. The chromate oxide layer instead of the intrinsic layer of the metal dominated the initial adhesive strength of the chromated steel sheet. The chromium content in the chromate coating had a great influence on the adhesive bonding with polymer and a good ad-

hesion of TSS equal to 17.8 MPa was obtained from a content ranging between 0.040–0.055 g/m².

3. Incorporation of polyacrylic acid in the chromate solutions coated on galvanized steel surface had a beneficial effect on the adhesive bonding of the steel laminate, depending upon the concentration of PAA and its molecular weight.

Approximately 8 wt % of PAA incorporated in the chromate solution resulted in a good adhesion of the laminate with TSS equal to 24.0 MPa.

Acknowledgements

The author wishes to thank Mr. C. H. Huang for his help with bending tests. The financial support from National Science Council of the Republic of China under grant NSC86-2221-E-224-022 is gratefully acknowledged.

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Received 19 August

and accepted 16 November 1998