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SURFACE TREATMENT OF CARBON STEEL FOR GLUE JOINTS

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1. Introduction

Modern automotive industry increase using of nonferrous metals and plastic/composite materials. These constructions bring problems of jointing heterogeneous materials. Similar metallic materials are possible to joint by welding (MMA, TIG, MIG/MAG; spot welding). Jointing different metallic materials together by weld is possible by friction welding [1], [2], [3]. Friction welding and friction stir welding has been widely applied in the industry for joining aluminum and is expanding its application in joining steels [2]. But friction stir welding need expensive CNC technology and methodology is limited to using in joints accessible to large robotic arm.

Using of glue joints in transport means constructions is more than one hundred years old history. Casein-based glues had been used in wooden aircraft since 1917 [4]. During WWII was developed REDUX® technology for aluminum (aluminum/wood) joints. This technology based on phenol/formaldehyde and poly(vinyl formal) resin is used to present days in aircraft industry [4].

Automotive industry use lot of glues. In 1980 typical car used 12 kg of adhesives. In 1999 year it was about 50 kg and cars are stronger, lighter [5]. Using glue in transport means increase rapidly.

Application of glue joints is usually independent to metallic substrate material (adherend). Strength of metallic adherends glue joint is main function of adherend surface treatment. High strength glue joint usually need not expensive technology, there is necessary good surface pretreatment [6]. Surface pretreatment consist from several

steps that prepare metallic surface to connection to polymeric glue. Typical surface pretreatment steps of metals are:

- degrease,
- scale removing,
- modification of surface roughness,
- increasing of corrosion resistivity of surface,
- production of conversion layer,
- adhesion promoter or primer application.

Some metals and/or technology of o glue jointing enable consolidate or skip some surface treatment steps. Typical surface pretreatments of metallic surface for glue joints are recommend in standard ČSN EN 13887 [7].

Long term stability of glue joints is ensuring by environmentally stable glue and by stable (or corrosion resistant) layer(s) on metallic adherend. Typical degradation of plain carbon steels surface degradation is attack by moisture. Inhibiting of this surface degradation may be production of stable corrosion inhibiting layers. Typical corrosion protection layer on steels are stable oxide (e.g. blackening steels) or phosphates (e.g. parkerising, walterising) [6].

Weak boundary layers can originate from environment, adhesive or adherend, or a combination of any of the three. Weak boundary layers can occur in the adhesive or adherend that forms a weak attachment to the substrate. When failure takes place, it is the weak boundary layer that fails, although failure appears to take place at adhesive-adherend interface. [6]

For produce of strong, safe and light cars body is necessary to use stable glues. Glues must be resistant to degradation by environment. Glue layer must be impermeable for corrosion environment or, for (water) permeable, surface treatment of metal must provide sufficiently corrosion resistant layer (coating). For this reasons must be all combinations metal/glue tested not only for initial strength, but for corrosion resistivity and environment stability too. Strength of glue joint must not decrease below designed strength during service life of product. Failure of glue joint on bearing (primary) structure may produce fatal crash. For these reasons is necessary to know interaction between adherend and glue.

2. Experimental

Focus of study was plain carbon steel ČSN 11 373 (EN S235). Coupons of dimension 25x100x1 mm with different pretreatment were study. All coupons were degreased first by ethanol. Then was coupons blast by ceramic abrasive. Samples were chemically treated after degreasing and blasting. ´

Epoxy glue was 3M™ ScotchWeld™ DP490 and acrylate base glue Weicon RK-7000. Samples with cataphoretic paint were made by company Iveco Czech Republic, a.s. This cataphoretic paint is the same as basic anticorrosive paint on bus body.

Surface pretreatment was creating on sand blast surface or on cataphoretic paint respectively. Cataphoretic paint was hand hone by sand paper with grit P400. Sanded surface of steel was untreated or chemically treated respectively. Pretreating bath was mix from concentrate supply by Atotech CZ. Pretreatment preparation was made by two different systems. UniPrep PP is adhesion promoters contain no metals or acids, eliminate scale/sludge and drastically minimize waste treatment requirements. Interlox® Phosphate 2325 MCIZ is highly concentrated liquid phosphating compound for use by immersion phosphatizing methods. Interlox® Phosphate 2325 MCIZ produces a microcrystalline zinc-calcium phosphate coating. Both solutions were prepared by datasheet and surface treatment was creating by immersion described in datasheet.

Immediately after surface treatment was coupons glue together. Adhesive used was acrylate type Weicon RK-7000 or epoxy 3M´s SW DP490 respectively. Overlap of coupons was 15+3 mm, geometry of joint samples is in Fig. 1. Curing of glues was at room temperature at constant load 0.1 MPa.

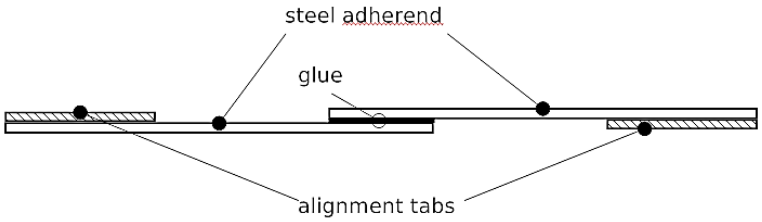

Figure 1 Single lap joints geometry

After curing of epoxy glue (1 week) was samples expose to corrosion environment. Corrosion test proceed in condensation chamber containing SO_2 for 200 hours exposure.

Determination of tensile lap shear strength of bonded assemblies was measured on testing machine ZD 10/90.

3. Results and Discussion

Tensile lap shear strength of bonded assemblies was measured before and after corrosion test. Results are summarized in Tab. 1 and Fig. 2. Testing of shear strength of corrosion unexposed samples show low adhesion strength of epoxy glue SW 490DP to surface phosphate by Interlox 2325. These low adherend adhesion still decreases after corrosion expose.

Strength of lap shear of epoxy glue/sanded steel and epoxy glue/sanded steel with UniPrep PP conversion coat was similar. Failure patterns of these glue joints were mixed adhesion/cohesion damage, dominant failure were cohesion.

Adhesion between epoxy and cataphoretic coat was higher than adhesion cataphoretic coat to steel. Cataphoretic coating show similar (low) adhesion to steel as epoxy glue to phosphatize steel.

Table 1 Tensile lap shear strength of bonded assemblies by epoxy glue SW 490DP

	sanded surface	sanded + UniPrep PP	sanded + Interlox 2325	cataphoretic
shear strength not exposed corrosion test [kPa]	19700	15700	8679	8761
shear strength after 200 h in corrosion chamber [kPa]	17067	17100	7184	7642

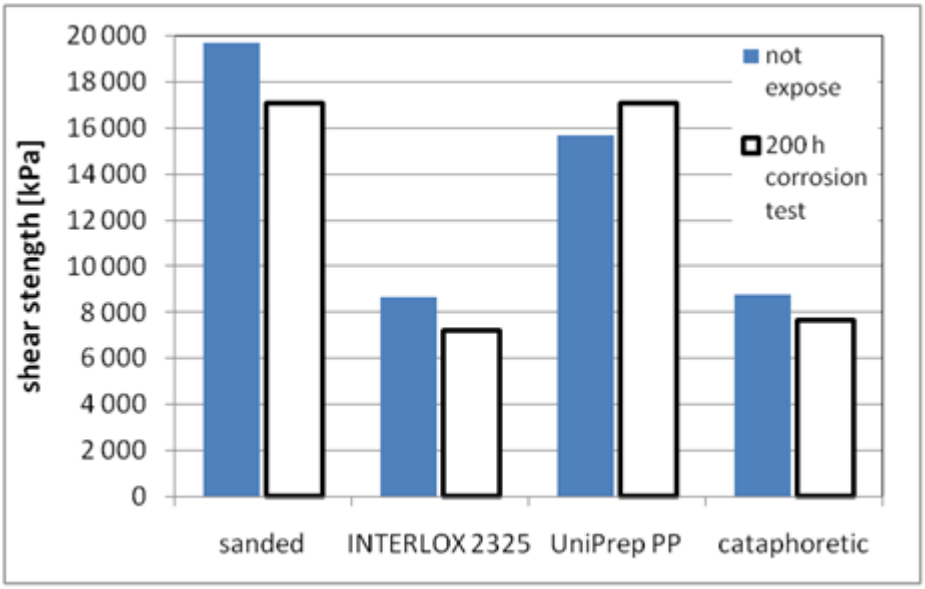

Figure 2 Tensile lap shear strength of bonded assemblies before and after corrosion test

Results of shear strength measurements show decreasing of strength of glue joints after corrosion agents except of surface treated by UniPrep PP adhesion promoter. Decreasing of glue joints strength after corrosion were probably relate to corrosion of interface steel/glue (adhesion layer). This assumption further similar macroscopic look of tested glue joints – look of fracture areas of tested samples was similar for unexposed and corrosion exposed samples.

Increasing of shear strength for UniPrep PP surface treating after corrosion test is probably due to better mechanic embedded on surface after corrosion exposition. Other reason for better shear strength of glue joint is plasticizing of epoxy glue by water. Shear strength of sanded only (chemically untreated) and UniPrep PP surface pretreatment after corrosion exposition are similar.

Single lap shear joint strength of glue joint glued by acrylate glue RK-7000 are given in Tab. 2 and Fig. 3. Strength of RK-7000 joints is in datasheet denote about 20 to 25 MPa. Results of strength for RK-7000 glue show single lap shear from 1867 kPa (for

blast only surface) to 16067 kPa (for surface etched in phosphoric acid). All samples of plain carbon steel joint by acrylate glue RK-7000 show big standard deviation of strength – more than 20% from average strength (except samples etched in phosphoric acid).

Table 2 Summary of single lap shear joint strength

glue/surface pretreatment	***τ_{sls} [kPa]***	***standard deviation s [kPa]***	***failure type****
RK-7000/blasting	1867	981	c
RK-7000/*UniPrep PP*	14933	3029	a+c
RK-7000/*INTERLOX 2325*	5074	2138	a
RK-7000/etching in H_3PO_4	16067	694	a
RK-7000/anodic oxidation	7259	5688	a
RK-7000/alkaline blackening	7239	2006	a+c
DP490/blasting	19730	295	c
DP490/*UniPrep PP*	15700	600	c
DP490/*INTERLOX 2325*	8679	635	a

**a = adhesive, c = cohesive*

Strength of DP490 is in datasheet denote for pretreated aluminum about 25 to 30 MPa. Results of single lap shear strength by epoxy glue DP490 on plain carbon steels show strength from 8679 to 19700 kPa for different surface pretreatment.

The best strength of prepared samples for acrylate glue RK-7000 was for coupons etched in phosphoric acid – about 16 MPa.

Samples of plain carbon steel joint by acrylate glue RK-7000 show big standard deviation of strength. This spread of strength is probably connected with high reactivity of acrylate glue. Due high chemical reactivity of acrylates starts oxidation of steel surface immediately after application of uncured glue to adherend. Result of steel oxidation is weak layer [6]. Presence of this oxidic layer (rust) at the interface of steel is itself mechanically weak. These oxidic layers do not provide adhesion, for this reason decrease carrying capacity of glue joint.

Prevention of production of weak layers (rust in this case) is creation of corrosion resistant layer(s) [6, 8]. Corrosion resistant layer provide corrosion protection but may produce conversion layer too. Main aim of conversion layer is provide good embedding of inorganic (ceramic) or polymeric layer to metal adherend. Conversion layer must provide excellent surface property for adhesion of glue. Conversion layer may have mechanical properties (thermal expansion, heat conductivity, strength) between property of adherend and glue for averaging of different properties of glue and adherend. Ideal pretreatment must provide all properties describe in this paragraph – corrosion protection, good adhesion to adherend, ideal substrate for glue.

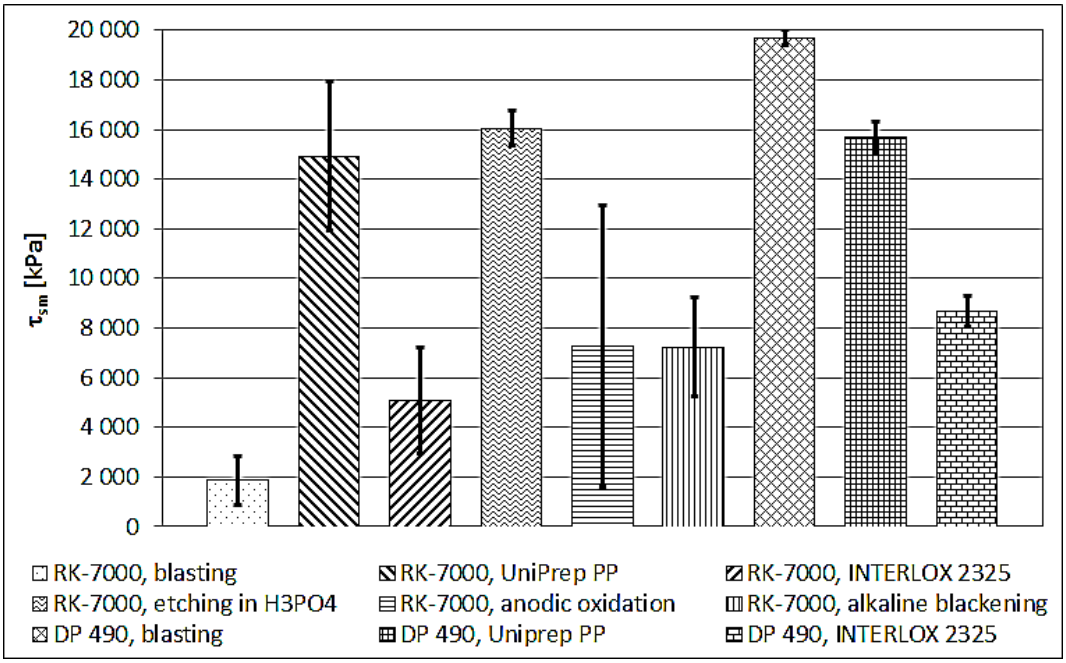

Figure 3 Single lap shear joint strength

Theoretically perfect property of surface pretreatment for plain carbon steels is phosphating. Phosphate compounds have slightly anticorrosion property and provide rough surface for mechanic interlocking of glue. For this reason was choosing the INTERLOX Phosphate 2325 MCIZ pretreatment for highly reactive (corrosive) acrylate glue. But strength of single lap shears of plain carbon steel coated by phosphates show low strength and high deviation of this strength. Low strength is probably connected to relatively large columnar crystals of phosphate. These columnar crystals probably provide too much rough relief for glue adhesion.

Phosphate conversion layer may provide good pretreatment of metals for glue joints. But for pretreatment of plain carbon steels is necessary choose phosphate pretreatment very carefully. In this time exist lots of phosphate coating (for organic painting surface pretreatment), but only several types is suitable for glue joint pretreatment, e.g. Bonderite 901-Pyrene 8-90 [8]. From experiments and [8] is possible to accept conclusion that for phosphate treatment of plain carbon steels is necessary use iron phosphate only (not manganese and/or zinc, calcium phosphate). For this reason for glue joints of plain carbon steels by acrylate glue is good pretreatment by phosphoric acid etching.

Other types of tested surface pretreatment not provide good pretreatment for acrylate glue. UniPrep PP adhesion promoter provides good embedding of acrylate glue, but do not provide corrosion protection against oxidation of steel surface by acrylate glue (high deviation of strength of glue joints). For this reason this surface pretreatment is not

acceptable for good, long term stability, glue joints. Other types of applied pretreatments – blasting only, anodic oxidation, alkaline blackening – not provide good glue joints. These surface pretreatments of carbon steel provide glue joint with low strength joints and high deviation of strength.

4. Conclusions

Conducted experiments show changing of shear strength of epoxy glue/steel bond after corrosion affects. Shear strength usually decrease after corrosion affect to bond. Strength of bond for epoxy glue/surface treated steel by UniPrep PP conversion coat show slightly increasing, but strength was similar as for sanded only steel/epoxy glue joints.

Results show that sufficient surface treatment is perfect cleaning and roughening of surface for joining by epoxy glue SW 490DP.

Acrylate glues provide high strength, impact resistant, residual elasticity glue joints [9]. These properties provide acrylate glue RK-7000 for corrosion resistant materials only. For plain carbon steel provide acrylate glue RK-7000 low strength and/or high deviation of strength of glue joints. In contrast of the high deviation of strength of acrylate glue was compare with low strength deviation of epoxy glue.

For plain carbon steel without surface pretreatment (grit blasting only) provide acrylate glue RK-7000 low strength adhesive joints with high deviation of strength. Similar low strength and high strength deviation show pretreatment of carbon steel by INTERLOX Phosphate 2325, anodic oxidation and alkaline blackening. Higher strength but high strength deviations show pretreatment by UniPrep PP adhesion promoter. For these reasons is necessary accept conclusion that above mentioned steel surface pretreatments are not suitable for adhesive joints glued by acrylate glue.

Good results of strength and relative small strength deviation of single lap glue joints show plain carbon surface etching by phosphoric acid. Etching of carbon steel by phosphoric acid provides conversion coating with good surface for embedding of glue and acceptable corrosion protection. This result is in correlation of [8] – pure iron phosphate (without other metals phosphates) provides acceptable pretreatment for glue joints.

Decreasing of single lap shear joint strength and/or increasing of strength deviation is explain due oxidation surface of carbon steel immediately after acrylate glue application. RK-7000 is high reactivity glue that oxidise steel surface and produce “rust” weak layer. These weak layers weaken loading capacity of glue joints.

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Resumé

PŘEDÚPRAVA UHLÍKOVÝCH OCELÍ PRO LEPNÉ SPOJE

Pavel ŠVANDA

Práce se zabývá zkoumáním pevnosti jednoduše přeplátovaných spojů z uhlíkových ocelí lepených epoxidovým a akrylátovým lepidlem. V případě nevhodné (nebo žádné) předúpravy povrchu uhlíkové oceli dochází ke snížení pevnosti lepených spojů. V práci je ukázán vliv předúpravy povrchu oceli před lepením epoxidovými lepidly na adhezní pevnost lepených spojů po korozním působení. Korozní působení bylo simulováno v kondenzační komoře s přítomností SO_2. Výsledky ukazují, že dokonalé očištění a zdrsnění povrchu je dostatečnou předúpravou pro lepené spoje lepené epoxidovými lepidly. Snížení pevnosti spojů lepených akrylátovým lepidlem je vysvětlováno tvorbou oxidických (korozních) vrstev. Tyto vrsvy působí jako tzv. slabé vrstvy, kde nedojde vytvoření pevného adhezního spojení mezi lepidlem a adherendem a tím dojde ke snížení únosnosti spoje. Jako vhodná předúprava bylo nalezeno leptání v kyselině fosforečné. Ostatní předúpravy nefosfátového typu a fosforečnany obsahující kationty manganaté a zinečnaté vykazovaly nedostačné vlastnosti požadované pro lepené spoje.

Summary

SURFACE TREATMENT OF CARBON STEEL FOR GLUE JOINTS

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Presented paper is devoted to the study of strength of adhesive joints glued by epoxide or acrylate glue. Plain carbon steel with different surface pretreatment was joined by glues and then was test single lap shear joint strength. In case of insufficient (or none) surface pretreated plain carbon steel decrease strength of these glue joints. The research indicated the influence of steel surface treatment before glue bonding with epoxy adhesives to adhesion strength of bonded joints after corrosion affects. Corrosion affects were simulated in the condensing chamber with the presence of SO_2. Results show that sufficient surface treatment for joining by epoxy glue is perfect cleaning and roughening of surface. Decrease strength of glue joints is explain by production of oxidic (corrosion) layers. These layers have an effect of weak layer. These weak layers decrease of loading capacity of glue joint. As suitable pretreatment was found etching in phosphoric acid.

Zusammenfassung

OBERFLÄCHENBEHANDLUNGEN AUS KOHLENSTOFFSTAHL FÜR KLEBEVERBINDUNGEN

Pavel ŠVANDA

Präsentiert Papier wird auf das Studium der Festigkeit von Klebeverbindungen von Epoxid- oder Acrylat-Kleber verklebt gewidmet. Plain Stahl mit unterschiedlichen Oberflächen Vorbehandlung wurde von Klebstoffen verbunden und dann war Test einzigen Überlappungsscherfestigkeit gemeinsame Stärke. Bei unzureichender (oder keine) oberflächenvorbehandelt reiner Kohlenstoffstahl Abnahme Stärke dieser Klebeverbindungen. Die Forschung zeigte den Einfluss der Stahl Oberflächenbehandlung vor Verleimung mit Epoxy-Klebstoffe Haftfestigkeit von Klebeverbindungen nach Korrosion betroffen sind. Korrosionsschutz beeinflusst wurden in der Kondensationskammer mit dem Vorhandensein von SO_2 simuliert. Die Ergebnisse zeigen, dass eine ausreichende Oberflächenbehandlung zum Verbinden von Epoxid-Kleber perfekte Reinigung und Aufrauen von Oberflächen ist. Verringern Stärke der Klebeverbindungen ist durch die Produktion von oxidischen (Korrosion) Schichten zu erklären. Diese Schichten haben die Wirkung schwach Schicht. Diese schwachen Schichten Abnahme der Tragfähigkeit der Klebefuge. Als geeignete Vorbehandlung wurde gefunden Ätzen in Phosphorsäure.