Degradation medium of agrocomplex – adhesive bonded joints interaction

M. Müller, P. Valášek

Department of Material Science and Manufacturing Technology, Faculty of Engineering, Czech University of Life Sciences Prague, Prague, Czech Republic

Abstract

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Research of degradation medium occurring in agrocomplex at the current interaction with bonded joints strength and lifetime is desired owing to the possibilities of bonding applications in this dynamically developing field. The bonding technology is used in construction of machines, lines and devices of agriculture, forestry and food industry. Among the perspectives of bonding technologies the adhesive bonding can be considered thanks to its predominant pluses. At the bonding technology or more precisely adhesive bonding technology application the limits must be characterized, which occur in the process of application in the concrete medium. On the basis of characteristics and analyses the countermeasures eliminating the negative factors can be taken. Published results set themselves the goal to know degradation processes taking place in bonded joints contemporarily with taking account of adhesive/adherend interaction with accent on application in agriculture. Experimentally found results confirm the presumption of a significant portion of the adhesive layer on the adhesive bond strength decrease in the practice due to the degradation processes.

Keywords: liquid contaminants; bonding method; cyclic degradation; bond strength; bond lifetime

Adhesive bonding technology is carried out in cases when it is necessary to join materials (adherends) or at renovations at contemporarily taking account of economic and technological factors compared with other joining methods.

By the bonded joints analysis Messler (2004) found out four main reasons of failure, among which he classified "operation medium conducting to degradation of adhesive or of adhesive/adherend boundary".

The external medium factors act especially by the temperature or humidity changes, possible contact with water, chemicals and by atmospheric corrosion. These factors can be considered as uninfluenceable, but their effect is relatively significant. Therefore it cannot be expected that the bonded joint will keep its properties during the whole moral or physical lifetime of bonded assemblies.

To determine limits of a concrete application of bonding technology it is necessary to analyse specific degradation conditions affecting the bonded joint during its whole or partial lifetime. In the worldwide bench mark the degradation processes cause significant material and economical losses. On the one hand various climatic changes have a different effect on products (Herák et al. 2008), on the other hand there are different specific degradation media which occur in the concrete field of human activity, as e.g. specific media of agricultural, forestry and food branches. Owing to the influence

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of degradation media the change of colour, viscosity, hardness and the loss of cohesive and adhesive strength can occur. The knowledge of condition of the occurring degradation and the means of the joints protection are very valuable from the view of users (Ducháček 2006; Müller et al. 2009).

There is no doubt about harmful effects of neighbouring medium on the bonded joint (Kinloch 1987). The main problem is to determine which part of the joint is affected by the neighbouring medium, whether the adhesive, adhesive/adherend boundary or adherend (Court et al. 2001). If the affected part of the joint cannot be identified, the joint failure cannot be prevented (Kinloch, Osiyemi 1993; Kinloch et al. 2000).

Crocombe (1997) found out that bonded joints degradation depends on the adherend and adhesive types, adherend surface preparation, stress configuration and curing conditions.

Today no technique of bonded joint creation is accessible, which can foresee the degradation of bonded joints by media. Most experience of joints failure come from mechanical characteristics and fracture surfaces research. Armstrong (1997) and Davis and Bond (1999) state that the main reason of the joint failure is the degradation of the boundary between adhesive and adherend. Studies of Gledhill and Kinloch (1974) and Aglan et al. (1999) also showed that owing to ageing often the change in a way of joint failure occurs. The main change occurs from the cohesion failure (adhesive as well as adherend) to the failure in boundary, so called adhesive failure (Gledhill, Kinloch 1974; Aglan et al. 1999).

Sargent (2005) and Gerald and Pethrick (2009) claim that changes of medium can have effect on both the way how the adhesive physical properties are changing in time and on the strength in the boundary between adhesive and adherend.

The reduction of the initial and failure strengths is caused by the adhesive curing effect in the area near of the joint boundary owing to the change of adhesive mechanical properties. The change of failure mechanism is the proof, as mentioned in Court et al. (2001).

The exposure of bonded joints to water, extreme temperatures or chemicals can influence the joint failure process by the adhesive and/or joint weakening (Rushforth et al. 2004; Nolting 2008). Colak et al. (2009) claims that the liquid contaminants as fuels and antifreezes are of the analogous tendency. Contaminants attack the adhesive/adherend bond and destroy the joint integrity. The join can be attacked also by next chemical media (e.g. degreasers) (Sonawala, Spontak 1996), to which bonded joints are resistant only ca. 30 days.

Bonded joints exposed to "natural environment" conditions are attacked by many degradation factors. The influence of heat, humidity, atmospheric oxygen, ozone and microorganisms is outstanding (Ducháček 2006).

Generally all above mentioned authors agree with the assertion that the bonded joints behaviour depends on a row of factors and each adhesive/adherend system must be specifically examined on the basis of laboratory experiments. By the analysis of current scientific knowledge and of conclusions presented in references it is evident that from the long-term point of view the bonded joint properties are influenced by operational conditions and also by related degradation processes.

Authors occupying themselves with the bonded joint degradation are concentrated primarily on degradation processes, which affect and influence the bonded joint as whole, i.e. as the set adherend/adhesive. This orientation works on the assumption that the bonded joint strength is influenced by degradation processes and above all by the properties of adherend/adhesive boundary. The results of these researches, as the authors state, are considerably influenced by specialization and by adhesive use in concrete applications.

But the present well-known research of degradation processes in the field of bonding technology feels the lack of information about this influence. By the partial and contemporarily total view on the degradation process influence it comes to the elimination, eventually quantification of the share of the adherend and adhesive influence. On the basis of this knowledge it will be possible to deduce relevant measures which prevent or minimize the degradation process influence. The primary aim is to define the interaction portion of layers of the adherend, the adhesive and the adhesive forces, and secondary regarding the liquid contaminants occurring in the agriculture.

MATERIAL AND METHODS

Bonded joints, test assemblies and their interaction are the research subject. The basis of bonded joints laboratory testing was the determination of the tensile lap-shear strength of rigid-to-rigid bonded assemblies according to the standard ČSN EN 1465:2009. For the objective evaluation of laboratory experiments and to obtain further knowledge about measured data sets the numerical and graphical statistical characteristics were used. Single influences were analysed on the basis of laboratory experiments carried out according to the relevant standards using the test samples having demanded shapes and sizes.

The mastering of injection/casting of the adhesive in prepared moulds, which meet the standard ČSN EN 3167:2004 was the substantial step. Moulds for casting were made from Lukopren N using ready models. Injection of the ready composite mixture was carried out using the syringe of 20 ml volume.

Within the solution the laboratory experiments were carried out using samples prepared according to the standards ČSN EN 1465:2009 and ČSN ISO 10365:1995. The shear stress of lapped assemblies belongs to the most frequently applied test methods of bonded joints destructive testing, which is directly successive and utilizable by the processing sphere. The test assemblies are prepared by bonding of two adherends of dimensions 100 ± 0.25 × 25 ± 0.25 × 1.6 ± 0.1 mm and lapped length of 12.5 ± 0.25 mm. The bonded material was the steel S235J0.

After the bonded joint failure the maximum force is read, real lapping length measured and failure type determined according to ČSN ISO 10365:1995. Then the overlapped surface S [Eq. (1)] and bonded joint strength τ [Eq. (2)] are calculated.

$$S = L_u \times b \quad (1)$$

where:
S – bonded joint surface (mm^2)
L_u – overlapping length (mm)
b – overlapping width (mm)

$$\tau = \frac{F}{S} \quad (2)$$

where:
τ – bonded joint lap-shear strength (MPa)
F – acting force (N)
S – bonded joint surface (mm^2)

The failure surface will be qualitatively and quantitatively evaluated using the image analysis.

The tested assemblies for the tensile properties determination according to the standard ČSN ISO 527-1:1997 were prepared according to the standard ČSN EN ISO 3167:2004. By the destructive testing the tensile strength σ_M was determined. The tensile strength σ_M calculation was carried out using the Eq. (3):

$$\sigma_M = \frac{F}{A} \quad (3)$$

where:
σ_M – tensile strength (MPa)
F – acting force (N)
A – initial cross section of the test sample (width × thickness) (mm^2)

At defining the comparative strength according to Moor, it is possible to transform the state of stress theory; tensile strength σ_M in the reduced lap-shear strength τ_{red} according to the Eq. (4) (Müller, Herák 2010)

$$\tau_{red} = 0.5 \times \sigma_M \quad (4)$$

where:
τ_{red} – reduced lap-shear strength (MPa)
σ_M – tensile strength (MPa)

The hardness was measured using the Shore D method according to the ČSN EN ISO 868:2003. The test samples were of dimensions 25 × 25 × 17 mm. The use of the Shore A method was not possible with regard to the measured values over 90.

Occurring degradation processes were related to the given medium at the current time. In the test program the test bodies made in accordance with the above mentioned standards were used. The experiments were oriented on the specification of the degradation medium influence and on the course of degradation processes, which affect substantially the adhesives and bonded joints mechanical properties during the whole lifetime.

At experiments oriented on the degradation medium influence the bonded joints were exposed to water bath, solution of the Cererit mineral fertilizer, water salt solution and diesel oil.

Testing adhesive bonded and hardened samples were dipped into 33.3% solution of the Cererit fertilizer–water salt solution. The degree of the degradation potential is influenced by the content of oxygen and other aggressive gases, amount and type of dissolved salt, presence of organic substances and microorganisms, pH, temperature, speed of flowing and contents of hard particles. Namely admixtures are responsible for the course of corrosive reactions in water, which water always contains in various rates under natural as well as under operation conditions (Novák 2002).

The Cererit fertilizer is a multi-component NPK chloride-free fertilizer with magnesium and trace elements (boron, molybdenum, copper and

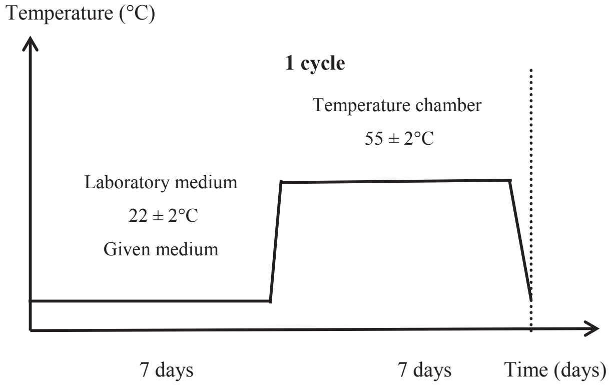

Fig. 1. Transformational diagram of the bonded joints testing at the exposure to different media

zinc) used for the basic fertilizing. The chemical characterization of Cererit is following: 10.0% $Ca(H_2PO_4)_2$, 12.0% $CaSO_4$, 30.0% $(NH_4)_2SO_4$, 22.0% K_2SO_4, 12.5% $NH_4H_2PO_4$, 0.8% $AlPO_4{\cdot}2H_2O$, 0.8% $(NH_4)_2SiF_6$, 6% $MgSO_4$ (Cererit 2001). The influence of the salt solution on degradation process depends on the concentration. The corrosion aggressively rises with increasing concentration of salt in the water solution (till given limit). The degradation process is caused namely by chlorides because they accelerate the uniform corrosion and they also cause the rise of the paint and slot corrosion. The sour solution comes into being by dissolving the salt, its aggression corresponds to the acid solution (Novák 2002).

Single runs of tested assemblies were left in the relevant degradation medium during the graded time interval of 15, 25 and 50 days. Nowadays the experiments are going on.

The second direction of the experimental research oriented on the degradation process influence was the cyclic exposure to the given medium, according to the standard ČSN EN ISO 9142:2004. The bonded joints were exposed for four cycles, namely to the bonded assemblies dipping in the given medium during 7 days and subsequently to the placing into the chamber tempered to 55 ± 2°C during 7 days. The transformational diagram (Fig. 1) demonstrates the one cycle course.

RESULTS AND DISCUSSION

In literary sources different limits of the "optimal adhesive layer thickness" are stated. But all authors agree with the fact that at the optimal adhesive layer thickness exceeding the bonded joint strength a decrease occurs.

At their experiments the authors (Brožek, Müller 2004; Müller, Chotěborský 2007) determined that the lapped single-shear joint strength increases from the very thin layer thickness to the optimum, when the joint strength is the highest. At the next adhesive layer thickness increase the joint strength decreases. It is caused by the effect of the interface area adhesive/adherend reinforcing influence, when the higher adhesive forces occur compared to the cohesive forces inside the adhesive. The laboratory experiments results specify clearly the bonded joint strength decrease after reaching the maximum. At the comparative tests of 8 epoxy adhesives the bonded joints reached their maximum in the range of 0.1 to 0.2 mm adhesive layer

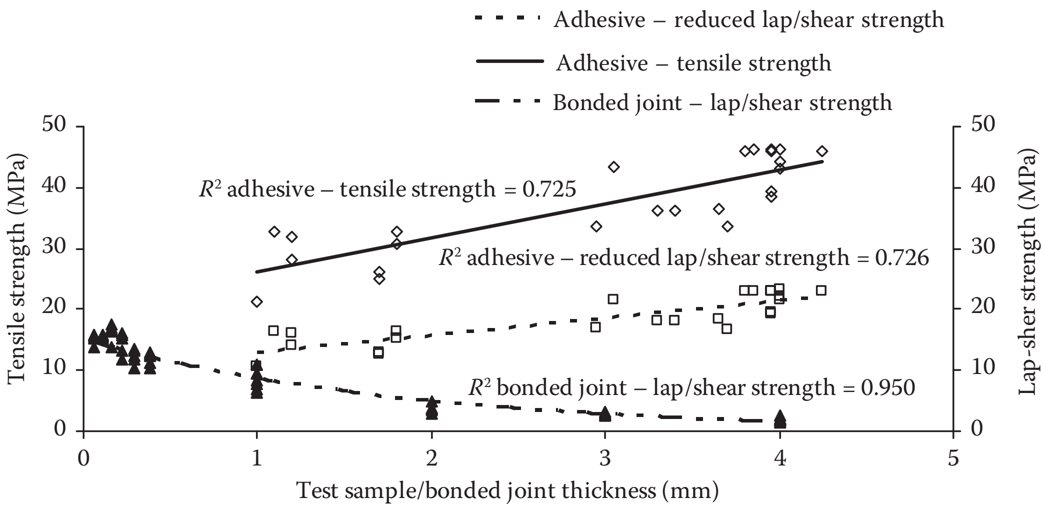

Fig. 2. Influence of tested sample and bonded joint thickness on the strength

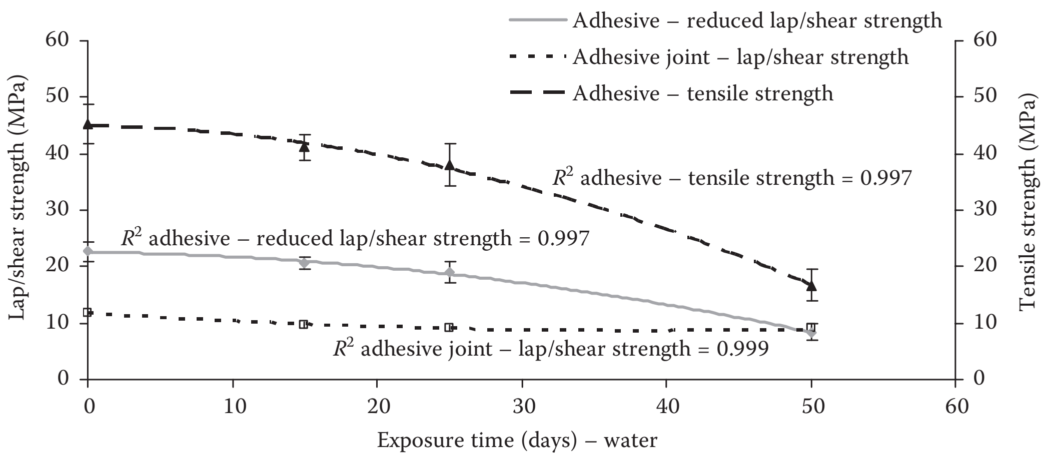

Fig. 3. Influence of degradation medium on the bonded joint and adhesive strength

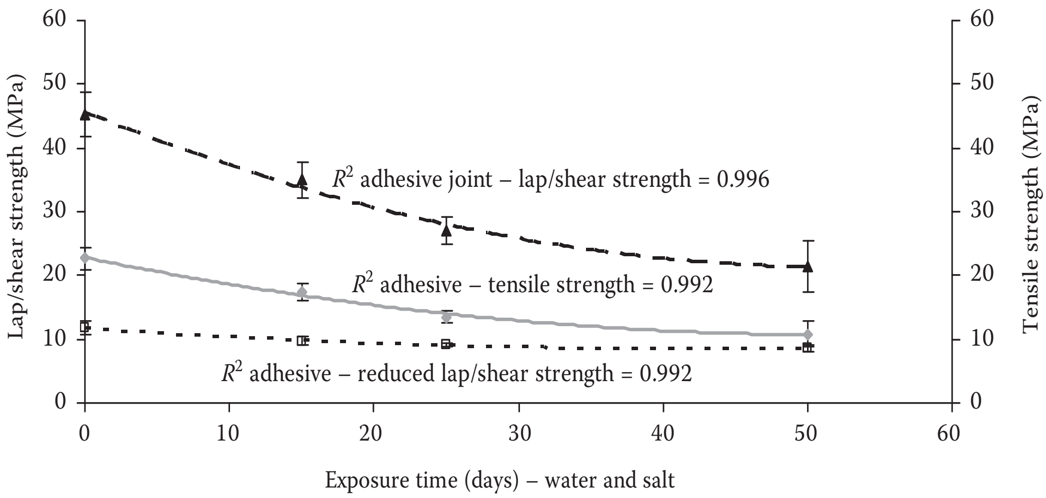

Fig. 4. Influence of degradation medium on the bonded joint and adhesive strength

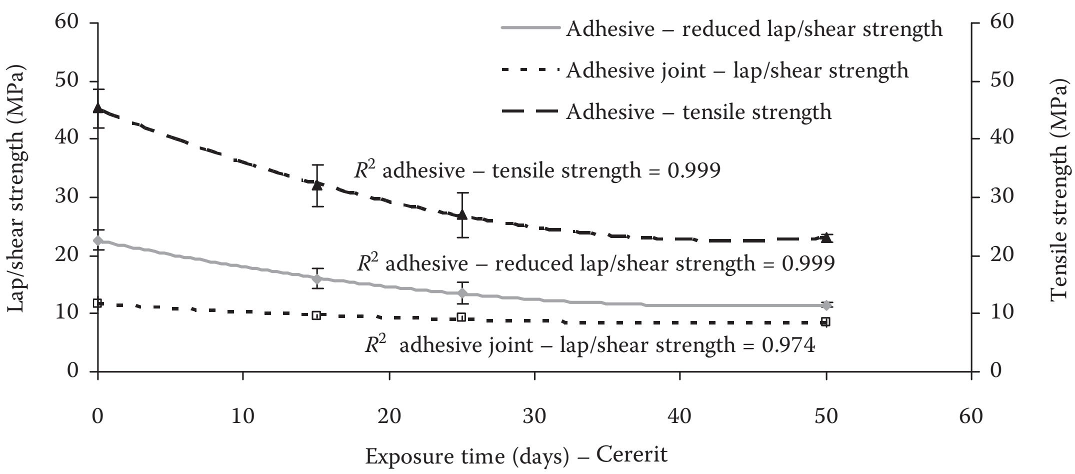

Fig. 5. Influence of degradation medium on the bonded joint and adhesive strength

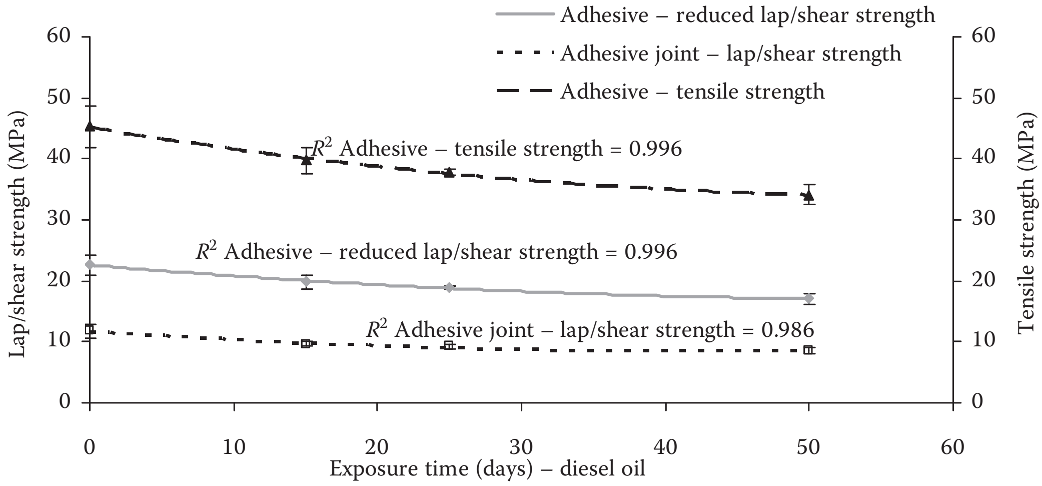

Fig. 6. Influence of degradation medium on the bonded joint and adhesive strength

thickness. At three epoxy adhesives after exceeding 0.3 mm, cohesive fracture surface changed to the adhesive or combined adhesive/cohesive.

Müller and Chotěborský (2007) reported an evident decrease of the bonded joint strength up to 36% at the unsuitable adhesive layer thickness.

At the single lapped bonded joint the influence of the increasing adhesive layer thickness is simultaneously affected by the increasing ratio of the bending moment, which shows itself by the strength decrease. This negative influence was eliminated by casting the test samples. In this way the two-component epoxy adhesive Lepox was tested (in the foregoing experiments marked by "L").

The flat test samples were cast in thickness from 1 to 4 mm. It was not possible to cast smaller thickness. From the results presented in Fig. 2 the adhesive strength decrease with increasing thickness is evident. This trend is quite opposite compared with the bonded joint, where the interaction between adherend and adhesive occurs.

From the above mentioned results it follows that the determination of the adherend/adhesive boundary unambiguous interaction on the basis of bonded joint strength is impossible.

Results of the bonded joints applied in relevant degradation medium are evident from Figs 3–6. The functional dependence is expressed by the polynomial function of the second degree. The function type is derived from the correlation field, which consists of points on the intersection of the dependent and independent variables. In the graph mentioned points are the arithmetic means of the given runs, where the standard deviations are stated, too. For the correct evaluation it is also important to determine the determination index R^2 of the given dependence using the correlation analysis.

According to the functional dependence the common characteristic of the degradation medium is a considerable decrease of single joints strength, which is evident from Figs 3–6. The considerable strength decrease occurred at the flat samples exposed for a certain period to the given medium. Diffusion seepage of the given degradation medium occurred in the cross section of test samples.

Analogically the same principles were noticed at the bonded joints. The functional surface, i.e. the lap length, became incessantly smaller and in this way the bonded joints strength rapidly decreased. So the cohesion strength decreased not only by the humidity and chemical substances diffusion in bonded joints, but also the adhesion decrease occurred.

On the basis of experiments carried out it is possible to say that the final strength of bonded joints during the time and at the contemporary ambient medium influence decreases. The strength decrease rate depends on specific conditions of the ambient medium. But the sufficient finding is the fact that the more expressive strength decrease occurs at the cast samples from the adhesive. This fact confirms the assumption of the substantial adhesive layer thickness influence on the bonded joint strength decrease owing to the degradation processes in practice.

The strength decrease of bonded joints and cast test samples from the adhesive were not considerably different at samples exposed to diesel oil. The

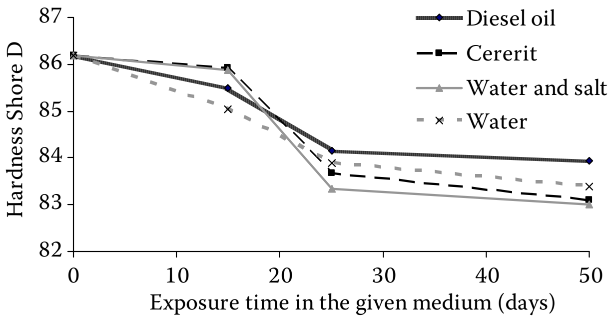

Fig. 7. Influence of degradation medium on the Shore D adhesive hardness

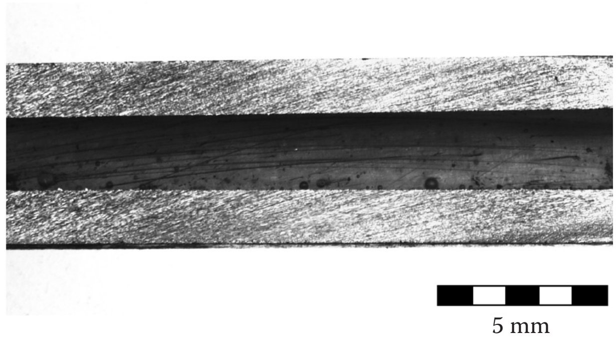

Fig. 8. Cross-section of the bonded joint

average strength decrease after 50 days of exposure ranges from 23.5 to 24.5%. The considerable differences occurred at other media. The average strength decrease ranged from 24 to 28%. At the cast samples from adhesive the strength decrease was more considerable. It ranged from 42 to 63%.

With the adhesive strength decrease the mild hardness decrease was connected. The results are evident from the line graph (Fig. 7). The turning point of the hardness decrease occurred after 15 days of exposure in the given medium. After 50 days the average hardness decrease ranged from 2.6 to 3.7%. The considerable hardness decrease was determined at the water–salt and water–Cererit media. The swelling and adhesive softening connected with it was the reason of the gradual hardness decrease.

In Fig. 8 the cross sections of the bonded joint are presented. The failure surface with the diffuse seepage of the given medium into the bonded joint can be seen.

The bonded joints exposed to the degradation process of the given medium and to the increased temperature are evident in Fig. 9. The samples are marked as "cycle". In Fig. 9 the final values of bonded joints exposed for 50 days to the given medium are presented. Compared with the etalon "0 days exposure" the bonded joint final strength decrease is evident. At the degradation process in the form of the alternative dipping in the given medium and drying, the average strength decrease is by 2.6% smaller compared with the direct contact with the given medium during the whole exposure time.

The corrosion influence was studied on the basis of the bonded joints surface examination and on the basis of material weight loss evaluation. The bonded material (steel S235J0)/bonded joint decline showed itself by its weight loss and by the

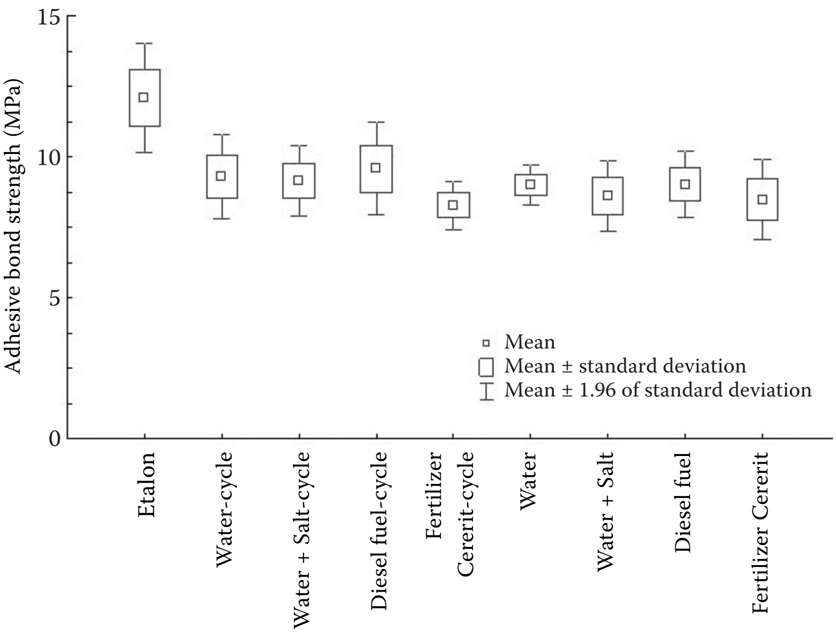

Fig. 9. Influence of degradation medium on the bonded joint strength

change of appearance. The highest weight losses of bonded samples came at the exposure to the Cererit fertilizer and to the solution of water and salt.

CONCLUSIONS

On the basis of evaluation of the experiments carried out it is possible to say that the bonded joints final strength decreases with the time together with the influence of surrounding medium. The strength decrease rate depends on specific conditions of the surrounding medium.

Experimental results determined at four media confirm the assertion of Kinloch (1987) and Court et al. (2001) about the negative and harmful effect of a surrounding medium on the bonded joint.

Environment/media influencing the bonded joints are significant components acting on the joints long-term quality and strength. Often the spontaneous destruction of bonded joints occurs already after a very short time of the exposure to degradation media. This dangerous phenomenon should lead to the prevention/elimination of the access of the mentioned degradation media to bonded joints, or to the limitation of their time of influence.

From the results it is evident that corrosion is mostly not fully unambiguous factor influencing the bonded joint strength. Yet, the assumption was confirmed that the adherend corrosion can cause a cohesive failure and change to the adhesive one; in this way the bonded joint strength secondarily decreases. Also Messler (2004) reached the similar assertion when he stated that mostly the corrosion of adherend or in the adhesive/adherend boundary contributes to the joint degradation and related strength decrease.

The adhesive saturation with humidity (given medium) causes lower joint strength and especially lower adhesive strength. The experiments carried out with the tensile strength test samples specified clearly a significant adhesive participation on the strength decrease of the complete bonded joint.

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Corresponding author:

assoc. prof. Ing. Miroslav Müller, Ph.D., Czech University of Life Sciences Prague,
Faculty of Engineering, Department of Material Science and Manufacturing Technology,
Kamýcká 129, 165 21 Prague-Suchdol, Czech Republic
phone: + 420 224 383 261, fax: + 420 234 381 828, e-mail: muller@tf.czu.cz