Environmental degradation aspects influencing coach-working one-component epoxy adhesives

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Abstract

Müller M., Valášek P., 2014. **Environmental degradation aspects influencing coach-working one-component epoxy adhesives**. Res. Agr. Eng., *60*: 37–43.

Degradation processes act on adhesive bonds behaviour in a negative way. The aim of experiments is to set the influence of liquid contaminants on strength changes of the adhesive bonds created with the adhesive used in the area of a coach-work construction. It is presumed according to a hypothesis that the adhesives applied in the construction of traffic and electricity means are resisting to liquid contaminants. The rain water, 33% solution of the rain-water and halite and the oil were used as the degradation mediums/environments. On the basis of evaluated experiments it can be said that resultant strength of the adhesive bonds decreases in the course of time at simultaneous affection of the environment. The measure of the strength decrease depends on specific conditions of the environment; however, it can be as much as 55%. The significant contaminant is the solution of the water and halite.

Keywords: adhesive bond strength; corrosion; diffusion; failure area; liquid contaminants

Degradation actions caused by the environment factors differ one from another according to the time of action. Most of the degradation processes lasts so long than the system reaches the balanced state that means the state when the degradation already does not pass through (Crocombe 1997; Messler 2004).

The adhesive bonds are liable to the liquid contaminants acting till given measure and this decreases their strength and subsequent functionality. The liquid contaminants acting on the hardened adhesive depends on the nature of these contaminants that means on their aggressiveness. However, it usually leads to a decomposition of adhesive – cohesive links which have a significant function for the adhesive bonds adhesion (Müller, Valášek 2012).

According to an analysis of various scientific works, a humidity acts on the adhesive bonds in the negative way. The negative effects show themselves by the adhesive bonds ageing causing the strength decrease and a change of the adhesive bond failure mechanism (Court et al. 2001). That means that namely liquid contaminants are a problem. The humidity stability of the adhesive bonds depends on the concentration of the liquid water at the interfacial zone between the adherent and adhesive. In most cases the adhesive link was broken from the periphery of the adhesive bonded area to the centre at the adhesive bonds (Crocombe et al. 2006).

Constructional adhesives used in the construction of automobiles and agricultural machines give the construction mass decrease and improve the technical life of the electricity means e.g. harvest-

Supported by the Technology Agency of the Czech Republic, Project No. TAČR TA01010192.

ing machine, tractor. The mass decrease of the agricultural machines significantly contributes to an elimination of the soil compacting at crossings after agricultural lands (Ansorge, Godwin 2007).

The advantage of constructional adhesive bonds applied at the coach-work production is the hardening process which runs through the course of the coach-work paint hardening.

The character and composition of the adhesives used for the coach-work construction are closely linked to the required bond function. In such way the adhesives can be divided into the adhesives sealing, reinforcing and of fortification.

Doyle and Pethrick (2009) dealt with this problem more detailed and they found out the influence of six various environments occurring in the air industry (rain-water, air petrol, hydraulic liquid, rust remover, solution of urea, and sea water) on the properties of bonds adhesive bonded by epoxy adhesives. Increased temperature 65°C was a complementary testing criterion. The results can be quantified as follows. Essential conclusions for the construction of traffic and electricity means used in the agriculture are above all the contaminations based on the urea, water and its solution with the salt. All environments behaved in a negative way for the strength values of the adhesive bonds. The adhesive bond strength decreased a number of tens percentages. The fall was distinguished for a progressive trend depending on the time. As Doyle and Petrick (2009) assumed at the salt water also the diffusion of the sea water showed itself which led to the strength loses. Alarming findings were also symptoms of the corrosion occurring in the failure area after ca 300 days. Another considerable negative phenomenon was the increase of the dispersion variance in measured data. This fact is undesirable from the constructional safety point of view. At the adhesive bonds exposed to the moisture for longer time the adhesive failure is more common (Crocombe et al. 2006; Doyle, Pethrick 2009; Müller et al. 2009; Müller, Valášek 2012). The absorption of the moisture by the adhesive influences significantly the measure of the adhesive bond failure during the process of the environmental degradation (Loh et al. 2003).

It was found out that the moisture diffuses into the adhesive bond along the ends of the adhesive layer. The moisture distribution into the profile of the adhesive layer causes according to the results the increase of the diffuse area which equalizes in the interval 2–6 mm from the edge at the adhesive bonds exposed to the degradation mediums (Crocombe et al. 2006).

The aim of experiments was to set the influence of liquid contaminants on the strength changes of the adhesive bonds. It is presumed according to the hypothesis that the adhesives applied in the construction of traffic and electricity means are resistant to the liquid contaminants.

MATERIAL AND METHODS

The basis of adhesive bonds 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) (Equivalent is BS 1465).

The one-component epoxy resins Betamate 1493 and Betamate 5103 from the DOW Automotive (Dow Europe GmbH, Freienbach, Switzerland) were used to describe the degradation process influencing the safety of constructional adhesive bonds. It was the adhesives Betamate 1493 and Betamate 5103 (both adhesives developed for coach – workshop). They are excellent adhesives used in the construction of the coach – work. However, these adhesives have never been tested to the degradation process of the liquid contaminants as it results from available data. Approximate shear strengths according to material cards are 29 MPa at the adhesive Betamate 1493 and 23 MPa at the adhesive Betamate 5103.

Laboratory tests were carried out using the standardized test specimens made according to the standard ČSN EN 1465 (dimensions 100 ± 0.25 × 25 ± 0.25 × 1.6 ± 0.1 mm and lapped length of 12.5 ± 0.25 mm) from the constructional plain carbon steel S235J0 (Ferona, Prague, Czech Republic). This steel was chosen on purpose in order to verify/prove a potential influence of the corrosion on the adhesive bond strength.

Ahead of bonding the surface of bonded specimens was blasted using the Al_2O_3 of F80 grain size. Using the profilograph Surftest 301 (Mitutoyo, Michigan, USA) following values were determined:

$Ra = 1.9 \pm 0.1$ μm, $Rz = 12.5 \pm 1.2$ μm

where:

Ra – the arithmetic mean of the departures of the profile from the mean line (μm)

Rz – the average of the maximum peak-to-valley length of five consecutive sampling lengths (μm)

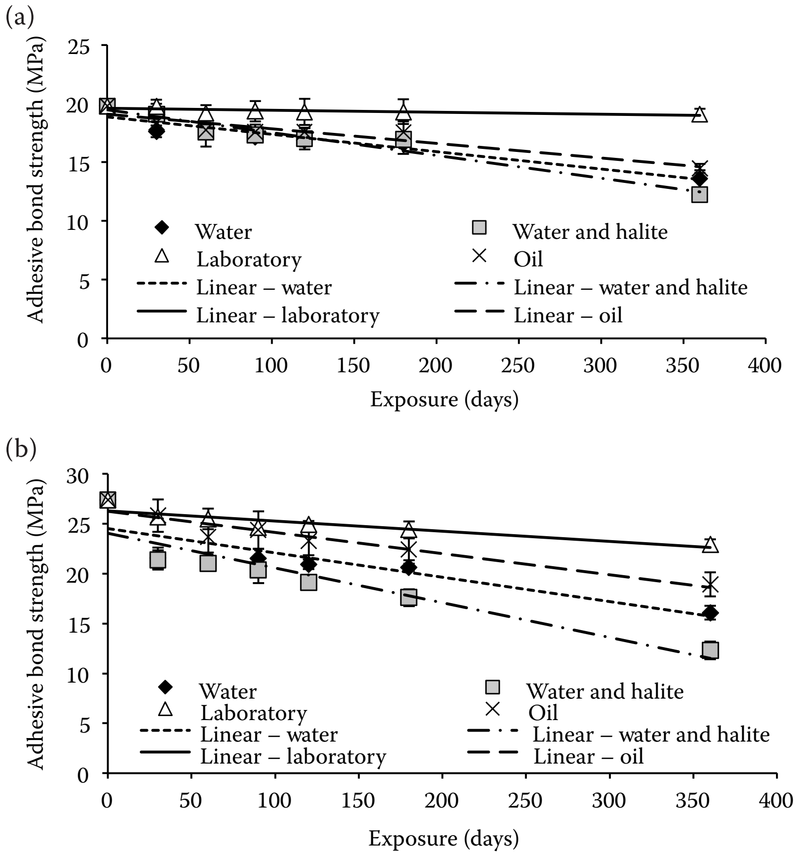

Fig. 1. Influence of environment/medium on adhesive bond strength (a) Betamate 5103 and (b) Betamate 1493

The bonding was carried out on a glass panel. On one steel specimen the adhesive was applied so that the whole surface in designated length (12.5 mm) was evenly coated. The adhesive layer thickness 139 ± 5 μm was secured by putting distance bodies in the adhesive bond. The adhesive real layer was measured by means of the stereoscopic microscope on cuts of the adhesive bonds.

Then the second specimen (sheet steel) was put to so that the overlapping of 12.5 mm was reached (according to the standard). The upper specimen was underlain using the sheet of equal thickness and the assessment was aligned according to the longitudinal axis. Then the assessment was loaded using the weight of 720 g. So created bond was left for 30 min in the laboratory drying – room at the temperature 180°C for hardening. After hardening, the marking of single assessments and placing in the relevant medium followed.

Following degradation environments/mediums were used: the rain-water, 33% solution of the rain-water, halite and the oil. By analysing the potential environments it was found out that the rain-water and in winter the solution of the water and halite are significant degradation mediums which have to be taken into regard.

The comparing standard was the laboratory environment with the temperature 22.7 ± 0.5°C and the relative humidity 45 ± 5%.

Degradation processes affecting the adhesive bonds were continuously evaluated after passing set time intervals: 30, 60, 90, 120, 180 and 360 days. Each cycle was terminated by a destructive testing of the adhesive bonds on the universal testing machine and by defining the failure type according to the ČSN ISO 10365 (1995).

RESULTS AND DISCUSSION

The decreasing trend of the adhesive bonds strength at both tested constructional adhesives was found out by the destructive testing of the adhesive bonds after passing set time intervals 30, 60, 90, 120, 180 and 360 days (Fig. 1).

From the experiment results an increased dispersion variance of the results was proved in the interval 0–360 days in accordance with the conclusions of Doyle and Pethrick (2009). This hypothesis was certified by the *F*-test when after a certain time of the degradation the disagreement of the dispersion variances of the statistical data sets was

Table 1. F Functional equations of linear functions and their coefficient of determination

Adhesive	Environment	Functional equations	R^2
Betamate 5103	laboratory	constant	–
	water	$y = -0.0148x + 18.861$	0.91
	water and halite	$y = -0.0194x + 19.467$	0.95
	oil	$y = -0.0124x + 19.097$	0.89
Betamate 1493	laboratory	$y = -0.0102x + 26.289$	0.83
	water	$y = -0.0244x + 24.516$	0.77
	water and halite	$y = -0.0348x + 24.044$	0.87
	oil	$y = -0.0212x + 26.248$	0.92

recorded at each environment. The results of dispersion variance are shown in Fig. 1 in the form of mistake line segments of the measured data set related to the arithmetical mean.

The trend of the failure area change is in accordance with the results of authors dealing with the degradation processes of adhesive bonds. First changes of the failure area occurred already after 30 days – from the cohesive failure, prospectively adhesive – cohesive failure to the adhesive one. It did not come to the change of the failure area regularly in this time interval. Next stage was the change of the failure area to the adhesive one.

In the Table 1 functional equations and coefficients of determination are stated describing relevant functions presented in Fig. 1 grasping the decrease of the adhesive bond strength in time at acting various environments. For the adhesive Betamate 5103 the agreement of mean values of the statistical data sets was certified by means of the T-test when the lowest probability of the agreement was $P = 0.09$ (H_0: $P > 0.05$) (H_0 – zero hypothesis). The tensile strength decrease was not proved under the laboratory conditions in given time interval of the degradation.

The failure areas of destroyed adhesive bonds placed in the degradation environments showed various types of the failure. In the first phase they showed identically the cohesive failure area, prospectively the adhesive cohesive failure. Further the failure type changed to the adhesive one.

Reason having the influence on the adhesive bonds strength decrease is the diffuse seepage of the degradation medium into the adhesive bond. The functional area, which means the overlapping area, was constantly lessened by this and so it came to the adhesive bonds strength decrease. So it came not only to the decrease of the cohesive strength by the humidity and chemical stuffs diffusion into the adhesive bonds but also to decrease of the adhesive adhesion (Fig. 2).

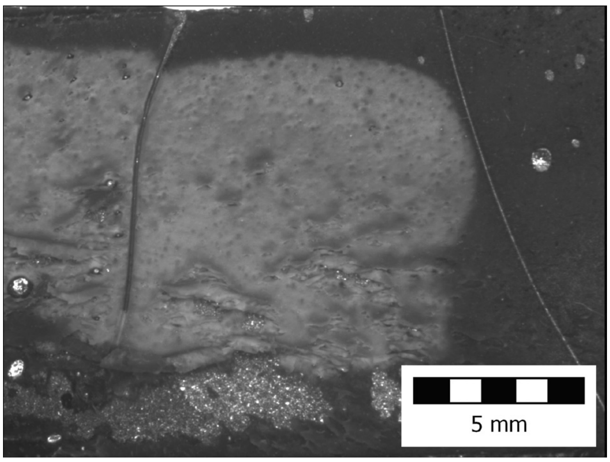

Fig. 2. Diffuse seepage in tested constructional adhesive Betamate 5103 – environment: rain-water

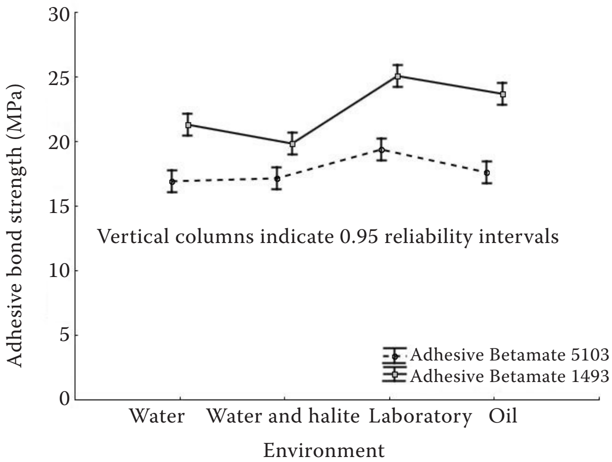

Fig. 3. Influence of environment on adhesive bond strength – arithmetical mean of values found out in intervals 30, 60, 90, 120, 180 and 360 days

Table. 2. Statistical comparison of mean values – Tukey's HSD test

Adhesive	Environment	Arithmetical mean (MPa)*	Agreement				
			1	2	3	4	5
Betamate 5103	water	16.95	****				
	water and halite	17.14	****				
	oil	17.61	****	****			
	laboratory	19.40		****	****		
Betamate 1493	water	19.87			****	****	
	water and halite	21.33				****	
	oil	23.70					****
	laboratory	25.06					****

*arithmetical mean of data found out in interval 30, 60, 90, 120, 180 and 360 days

On the basis of evaluating the carried out experiments it is possible to say that the resultant strength of the adhesive bonds decreases during the time at simultaneous affecting of the environment.

Fig. 3 shows the schematic presentation of the tensile shear strength results of adhesive bonds created by means of ANOVA by the lowest squares methods. The Tukey's HSD test was used for the statistical comparison of mean values. In the Table 2, single means are presented in the statistically homogeneous groups.

When comparing the mean values of the strength data sets the clear difference between used adhesives is visible. Betamate 5103 reaches higher tensile strength which certifies data stated in the technical documentation of the adhesives. From the carried out comparison of the tensile strength values for various environments (the value of the Tukey's HSD test – arithmetical mean of all values of the tensile strength in given time interval of the degradation) it is clear that the water, water solution of halite, oil and laboratory environment have the same influence on both adhesives from the tensile strength point of view. From the Fig. 4 a similar trend of both constructional adhesives is obvious in various environments.

Also the diffusion of the humidity and given medium, namely its chemical stuffs, into the adhesive causes the change of the failure type. The functional area, which means the overlapping area, is constantly decreased by this so it comes to the intense fall of the cohesive strength. By decreasing own cohesive strength and by decreasing the adhesion the destruction in the interface of the adhesive-adherent inevitably occurs which is shown itself by the adhesive failure area. These conclusions are

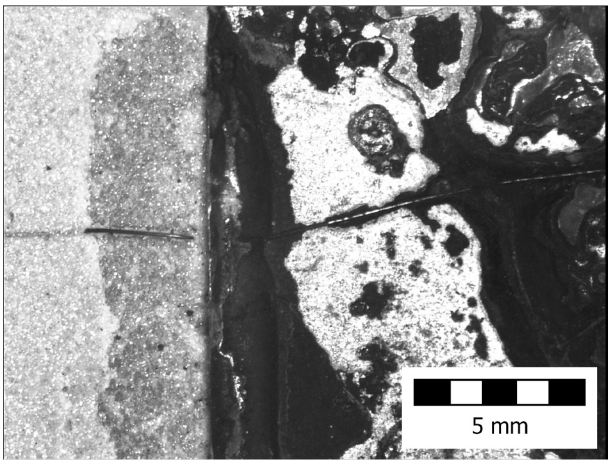

Fig. 4. Adhesive-cohesive failure area of adhesive bond and corrosive waste products outside adhesive bond

Fig. 5. Histogram of stratification of corrosive waste products size in the layer of adhesive

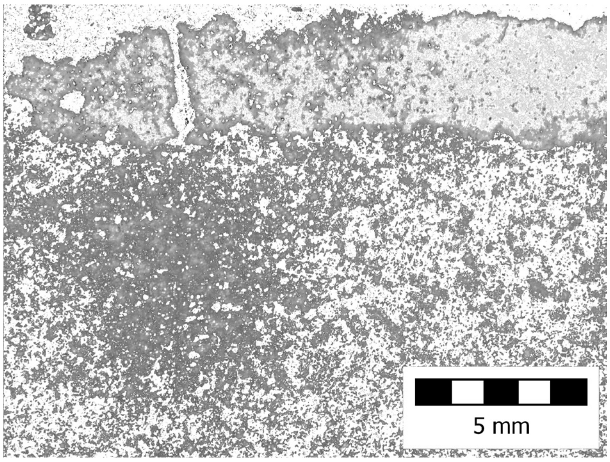

Fig. 6. Phase of corrosive waste products included in failure area of adhesive layer (corrosion – white colour)

supported by the research published by Davis and Bond (1999) who state that the main cause of the bond service time failure is the degradation of the interface between the adhesive and the adherent distinguished for the adhesive failure.

The cohesive failure area with the place of the fracture initiation (a wavy structure in the destroyed layer of the adhesive) caused by the deformation of adhesive bonded material owing to a bending moment is visible. The bending moment comes into being at loading the adhesive bond owing to an axial asymmetry of test specimens prepared according to the standard ČSN EN 1465 (2009).

The Fig. 4 shows the adhesive-cohesive failure area. It was found out by a picture analysis of the adhesive bond that the adhesive failure was caused by the deformation of the adherent and not by the degradation process. From the Fig. 4 the action of the bending moment at the adhesive bond loading is also visible which caused the initiation of the destruction. At the edge of the adhesive bond ca. 3–4.5 mm area of the adhesive failure occurred.

The influence of the degradation on the failure area change showed up only by the adhesive type which occurred at the adhesive bonds at least after minimum 90 days solely in the water bath and in the solution of the water with the halite. At other mediums (the oil, comparing standard – laboratory) the adhesive change of the failure area did not occur. At the test specimens placed in the water bath and in the solution of the water with halite the corrosion of the adhesive bonded material significantly showed itself.

The corrosive waste products were also found out from the failure area analysis in the layer of destroyed adhesive bond which means in the layer of the adhesive. The under-corrosion showed itself by local corrosive areas of sizes 56.02 ± 27.59 μm. The dispersion variance of the corrosive waste products size was huge. The size of the corrosive waste products analysed around the failure area is visible from the histogram (Fig. 5).

From the results of the picture analysis of the adhesive and the corrosive waste products phase 29.2% representation of the corrosion was found out (Fig. 6). From the results of the phase representation of the corrosive waste products in the failure area of the adhesive bond it is obvious that higher representation of the corrosive waste products (white place in the failure area) was in the places of the diffusion of the liquid contaminant. On the contrary, in the area of the adhesive bond which was not hit with the liquid contaminant there is a minimal representation of the corrosive waste products. From the Fig. 6 it is visible that the diffusion of the liquid contaminant runs through along the boundary of the distance wire delimitating the constant layer of the adhesive. This finding can work in the negative way on an acceleration of the degradation process which is connected with the strength losses.

Experiments results complete the statement of Crocombe et al. (2006) about the distribution of the moisture into the layer of the adhesive from the edge of adhesive bonds. Significant distribution means are also means delimitating the layer of the adhesive. Messler (2004) speaks more detailed about the means delimitating the even layer of the adhesive in his work.

From the experiments results it is obvious that liquid contaminants decrease the strength and by it also the service life of adhesive bonds. Essential constructional attribute of adhesive bonds application is a necessity to eliminate a contact of created adhesive bonds with the degradation environment in the form of liquid contaminants by constructional treatments and by a choice of technologic ways of the production limiting possibilities of an arise and acting of the corrosive agents, namely the long-term contamination of adhesive bonds.

CONCLUSIONS

On the basis of the carried out experiments it can be said that the resultant strength of adhesive bonds decreases during the time at simultaneous acting of the environment. The measure of the strength decrease depends on specific conditions of the environment. From the experiment results the hypothesis about the resistance of the coachwork one–component epoxy adhesives to the liquid contaminants was not certified.

These conclusions were set from the experiments:

– Under the laboratory conditions the mild decrease of the adhesive bonds strength of 3.75% was found out at the adhesive Betamate 5103 after 360 days. On the contrary, the considerable decrease of 16.25% occurred at the second adhesive Betamate 1493.
– At other degradation mediums the strength decrease was more considerable, as much as of 55%. The considerable fall of the adhesive bond strength occurred namely in the solution of the water and the halite.
– The change of the failure area from the cohesive to adhesive – cohesive was not primarily caused by the degradation process, but by the deformation of the adherent.
– Form the results it is visible that the corrosion of adhesive bonded materials (adherents) is not in most cases entirely definite factor having the influence on the adhesive bond strength. At the adhesive bonds where the corrosive waste products occurred in the layer of the adhesive the accelerated process of the adhesive bond strength decrease did not come on. The strength fall showed the linear trend.
– The liquid contaminants diffuse into the layer of the adhesive and they lessen the functional area of the overlapping acting on the transfer of the loading force.
– The strength fall of the adhesive bonds is not direct proportional to the dispersion variance of the results of measured values.

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Received for publication April 4, 2013
Accepted after corrections July 2, 2013

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