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Research on influence of cyclic degradation process on changes of structural adhesive bonds mechanical properties

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Abstract. The paper deals with an influence of a cyclic degradation process on changes of a shear tensile strength of single lap-shear adhesive bonds and their elongation according to ČSN EN ISO 9142. Five one-component structural adhesives used in a construction of car body works were used within the research. The degradation of adhesive bonds is a significant factor which influences a quality and a service life of adhesive bonds exposed to environment. A main requirement in production companies is not only reaching satisfactory initial mechanical properties but namely ensuring a reliability and a safety of adhesive bonds during their usage.
These reasons show a great importance of adhesive bonds tests either directly in the operating environment or by a simulation of operating conditions in laboratories. The degradation process of adhesive bonds worsens mechanical properties of not only the bond itself but also of the bonded material. This process is progressing and it is usually permanent and irreversible. It is a change of mechanical and physical properties which can endanger a safety and a reliability of parts, prospectively of the whole equipment. It can leads up to a complete failure of its function in the extreme case. A temperature, a moisture, a direct contact with water and chemicals or an atmospheric corrosion belong among the most serious degradation agents. It is important to take into regard time of the processes influence at the same time which can act either independently or concurrently when their effects grow stronger.
From that reason the adhesive bonds were exposed to the cyclic degradation process according to the standard ČSN EN ISO 9142. Subsequently, the adhesive bonds mechanical properties were tested on universal testing machine and by means of SEM analysis (TESCAN MIRA 3).
Results of mechanical tests proved a fall of the shear tensile strength of single lap-shear adhesive bonds after 42 cycles of the degradation process of 12.8 to 21.7%. The bond strength fall was gradual and it showed a linear trend at some adhesives. Other adhesives showed a significant fall after the exposition to the degradation process after which the strength fall stabilized.

Key words: shear tensile strength, elongation, temperature, moisture, SEM, automotive, ageing process.

INTRODUCTION

The main advantages of adhesive bonding in comparison with other joining are better load distribution, reducing stress concentrations, increasing fatigue resistance, corrosion resistance, weight savings and the ability to join different materials. In these reasons are adhesive bonding technics used in the automotive, aerospace, electronic industries (Baldan, 2004; Crocombe et al., 2006).

The disadvantages of adhesive bonds are various resistance at combination of aggressive environment and mechanical loading. The main conditions of aggressive environment are moisture and variable temperature. The various temperature can influence mechanical strength of adhesive bonds. The heat degradation on epoxy adhesive affect also elongation and strain at strength on shear test (Goda et al., 2010; Bar-Cohen, 2014).

There is a require for development on adhesive bonds and adhesive able to resist high and low temperature conditions. This requirement is for structural adhesives challenging because they are mostly polymer-based, which has a relatively low resistance to high temperature. However, there is a combination of adhesives in the chemistry development which allow the adhesive bonding in extreme temperature, e.g. vulcanizing silicones, high-temperature epoxies and ceramic-based adhesives (Marques et al., 2015; Qin et al., 2018; Yang et al., 2019).

The subject of this paper is an influence of a cyclic degradation process on changes of a shear tensile strength of single lap-shear adhesive bonds and their elongation. In general is known that mechanical properties deteriorate during degradation process but the exactly value is not established. For these reason was the degradation process followed in this research. In the research were examined a structural adhesive used in in a construction of car body works. The adhesive bonds of car body are exposed to wide span of temperature condition. A temperature, a moisture, a direct contact with water and chemicals or an atmospheric corrosion belong among the most serious degradation agents. For these reasons is degradation of adhesive bonds a significant factor which influences a quality and a service life of adhesive bonds exposed to environment. A main requirement for automotive production is not only reaching satisfactory initial mechanical properties but namely ensuring a reliability and a safety of adhesive bonds during their usage (Müller et al., 2014; Müller and Valášek, 2014; Sousa et al., 2018).

Temperature variations are the most important environmental factors which influence the tensility of adhesive bonds. Degradation effect is caused by exposure to extreme temperatures on the adhesive and the adherends. The thermal cycles also caused the eventually difference between the coefficients of thermal expansion of the adherends and the adhesive. This process between adhesive and adherend can caused creating the micro-cracks at the interfaces of adhesive layer or even delamination of adhesive bond (Marques et al., 2015).

In the research was used cyclic degradation process to simulate exposition of a car body in a real environment condition. Car body is exposed to increasing a decreasing temperature cycles in long time span. For these reasons are also important the time of exposition of adhesive bonds. It is needed to take into regard time of the processes influence at the same time which can act either independently or concurrently when their effects grow stronger. All these parameters of exposition influence mechanical properties of not only adhesive bonds itself but also of the bonded material. This process is progressing, and it is usually permanent and irreversible. The changes of mechanical and physical properties can a safety and a reliability of parts, prospectively of the whole equipment. This can lead up to a complete failure of its function in the extreme case.

The aim of this research is to study influence of cyclic degradation process on mechanical properties of single lap-shear structural adhesive bonds.

MATERIALS AND METHODS

Single lap-shear bonds were created by five one-component structural adhesive with filler. The filler is supply in adhesive from manufacture of one component adhesive. For research were tested type of adhesive Betamate 1496F, Betamate 5103-3, Betamate 1440G, Betamate 1040 and Sika Power 492 (E) used in car body construction (Table 1.). These adhesives were chosen because they are commonly used in automotive.

Table 1. The tested one component adhesive with designation for research, product name and standard curing

Designation for research	Product name of adhesive	Standard curing
A	Betamate 1496F	180 °C/30 min
B	Betamate 5103-3	180 °C/30 min
C	Betamate 1440G	180 °C/30 min
D	Betamate 1040	180 °C/30 min
E	Sika Power 492	< 220°C

Adherend for bonds was used carbon steel S235J0 of thickness 1.5 ± 0.1 mm and dimensions 100 x 25 mm. The bonded surface of adherend was sandblasted by Garnet MESH 80 (ČSN ISO 8501-1) and degreased by an acetone (ČSN EN 13887). The roughness of sandblasted surface was measured on R_a = 1.76 ± 0.18 µm, R_z 11.22 ± 0.84 µm by portable profilometer Mitutoyo Surftest 301. The overlap length of bonds was 12.5 ± 0.25 mm.

The cyclic degradation process was performed in a laboratory programmable chamber MKF240 (ISO 483) of the firm Binder (Fig. 1) according to the standard ČSN EN ISO 9142 (Adhesives - Guide to the selection of standard laboratory ageing conditions for testing bonded joints) in the cycles D from the standard. The single lap-shear bonds were exposed in degradation cycle, which contains two phases. The bonds in first phases was exposed to the increased temperature 70 ± 2 °C and the relative moisture 90% for the time 16 hours, subsequently a gradual cooling to the temperature -40 ± 3 °C and staying 3 hours at this temperature. The bonds in second phases were exposed again to the increased temperature 70 ± 2 °C at the relatively moisture 50% for 16 hours and staying for the 5 hours at this temperature. The quantity of degradation cycles were split in 14, 28 and 42 cycles.

Figure 1. The laboratory programmable chamber MKF240 of the firm Binder.

After cyclic degradation process were single lap-shear bonds loaded to analyse their mechanical properties. Mechanical properties of single lap-shear bonds were measured on universal testing machine LabTest 5.50ST at loading speed 2 mm·min^{-1} with evaluation software Test&Motion. As mechanical properties were studied shear tensile strength and elongation according to ČSN EN 1465.

The disruptions of single lap-shear bonds were examined according to ČSN ISO 10365. The interaction of one-component structural adhesive was followed up by scanning electron microscope TESCAN MIRA 3 GMX (SEM) in nitrogen vacuum with acceleration voltage (HV) of 10 kV at a distance approx. 15.5 mm.

The measured values were processed by statistical analysis *Anova F-test* (Analysis of Variance). The difference between values was compared by p-values. The null hypothesis H_0 for no statistically significant difference on median values was set to $p > 0.05$.

RESULTS AND DISCUSSION

On Fig. 2 is apparently, that increasing number of cycles influence decreasing shear tensile strength of the adhesive bond. The tensile lap shear strength meet the materials lists of adhesives in 0 cycles of degradation process. The largest decrease of shear tensile strength occurred at 42 cycles for all tested adhesive. The largest decrease of shear tensile strength between 0 and 42 cycles has occurred on adhesive C and up to 22.4%. The least decrease shear tensile strength between 0 and 42 cycles has occurred on adhesive B and up to 12.8%. The largest shear tensile strength was 20.92 ± 0.63 MPa at 42 cycles on adhesive E and contrariwise the least strength was 17.13 ± 1.07 MPa on adhesive B. From Fig. 2 is there noticeable linear decrease of shear tensile strength according to number of degradation cycles on some type of adhesives. The largest linear accordance is on adhesive D with reliability value $R^2 = 0.97$. This value shows Table 2, there are listed reliability values (R^2) and trend equation (τ) of adhesives.

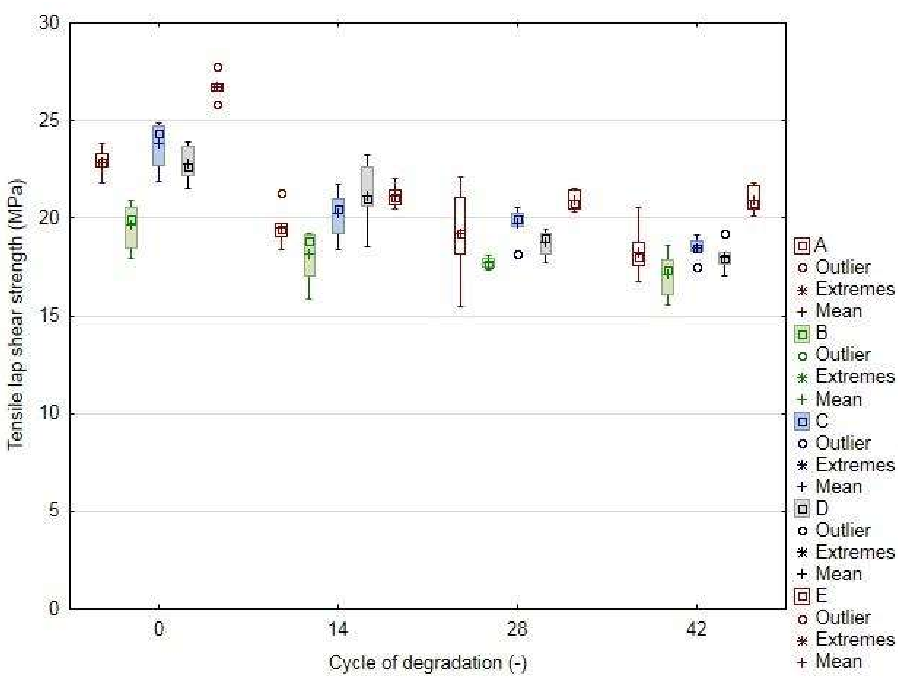

Figure 2. Accordance of degradation cycles on shear tensile strength of adhesive bond.

Table 2. The reliability values R2, trend equation τ and *p–parameter* of statistical test *ANOVA* for accordance of degradation cycles on shear tensile strength of adhesive bond

Adhesive	Reliability value R^2	Trend equation τ (NC – number of cycle)	p - parameter
A	0.83	$\tau_A = -0.1009\mathrm{NC} + 22.093$	0.0002
B	0.92	$\tau_B = -0.0571\mathrm{NC} + 19.354$	0.0046
C	0.87	$\tau_C = -0.1176\mathrm{NC} + 23.023$	0.0000
D	0.97	$\tau_D = -0.1990\mathrm{NC} + 22.673$	0.0000
E	0.63	$\tau_E = -0.1264\mathrm{NC} + 25.074$	0.0000

The statistical testing of influence of degradation cycles on shear tensile strength at significance level *0.05* confirm, that there is statistical inhomogeneous group, i.e. there is significant difference between measured values ($p < 0.05$). Hypothesis H_0 was rejected and was confirm the number of degradation cycles on shear tensile strength of adhesive bonds.

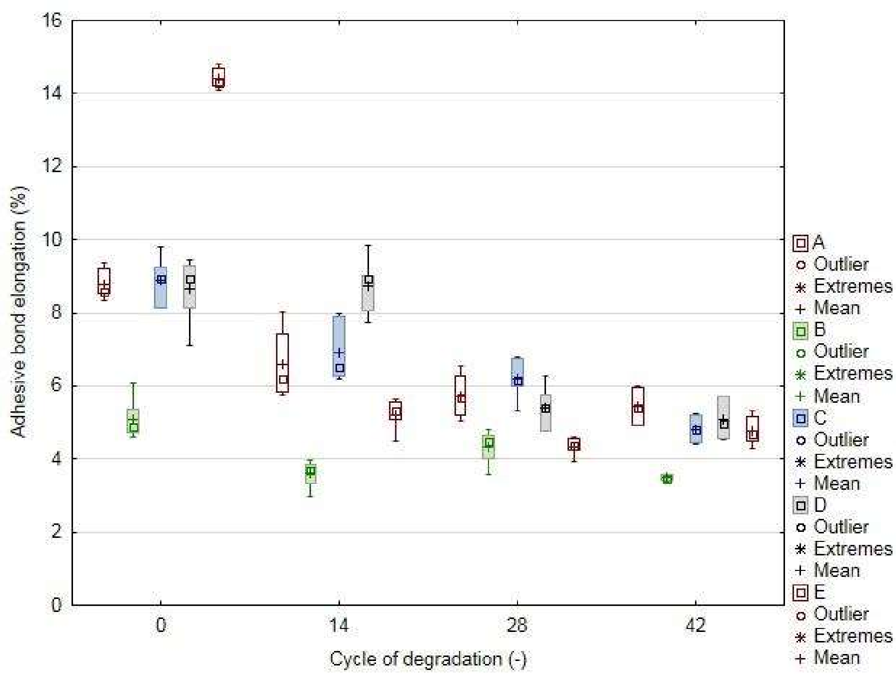

Figure 3. Accordance of degradation cycles on adhesive bond elongation of adhesive bond.

On Fig. 3 is apparently, that elongation decrease with increasing number of degradation cycles. The adhesive bond elongation meet the materials lists of adhesives in 0 cycles of degradation process. This effect is given by lower tensility of tested adhesive after degradation process. The results show, that the largest elongation 5.43 ± 0.47% happens at 42 cycles on adhesive A. The least elongation 3.48 ± 0.42% was on adhesive B. On adhesive D was elongation increased up to 1.25% at 14 degradation cycles against no degradation exposition adhesive bonds and elongation increase up to 0.1% at 42 degradation cycles on adhesive E. The largest elongation happens at all tested adhesive between 0 and 14 degradation cycles and on average 13.02 ± 5.23%. Between other degradation cycles was average elongation 3.28 ± 2.85%.

The significant decrease of elongation up to 21% happened on adhesive E between 0 and 14 degradation cycles. This was caused by influence of degradation process, i.e. adhesive lose own tensility. On Fig. 3 is apparently, that elongation decrease in accordance to degradation cycles was linear on some type of adhesive. The largest linear accordance between degradation cycles was on adhesive C with reliability value $R^2 = 0.97$. This value shows Table 3, there are listed reliability values (R^2) and trend equation (ε) of adhesives.

Table 3. The reliability values R^2, trend equation ε and *p–parameter* of statistical test *ANOVA* for accordance of degradation cycles on elongation of adhesive bond

Adhesive	Reliability value R^2	Trend equation ε (NC – number of cycle)	p - parameter
A	0.86	$\varepsilon_A = -0.0775\mathrm{NC} + 8.2565$	0.0000
B	0.50	$\varepsilon_B = -0.0292\mathrm{NC} + 4.7390$	0.0000
C	0.97	$\varepsilon_C = -0.0918\mathrm{NC} + 8.6298$	0.0000
D	0.82	$\varepsilon_D = -1.0050\mathrm{NC} + 9.0778$	0.0000
E	0.63	$\varepsilon_E = -0.2124\mathrm{NC} + 11.644$	0.0000

The statistical testing of influence of degradation cycles on adhesive bond elongation at significance level *0.05* confirm, that there is statistical inhomogeneous group, i.e. there is significant difference between measured values ($p < 0.05$). Hypothesis H_0 was rejected and was confirm the number of degradation cycles on adhesive bond elongation of adhesive bonds.

Tested adhesive points out the failure type SCF (special cohesive failure – ISO 10365) on steel bonded surface. Exposition process of degradation cycles did not change the type of fracture surface.

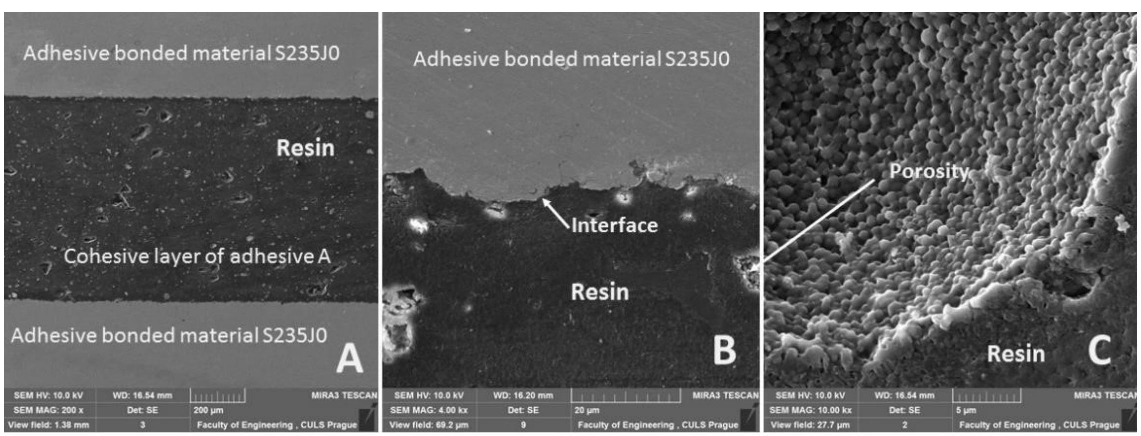

Figure 4. SEM images of cut through of adhesive bond A (SE detector, 10 kV): A: cut through of adhesive bond (MAG 200 x), B: adhesive layer interaction and bonded material (MAG 4000 x), C: porosity inside of adhesive layer (MAG 10000 x).

On the Fig. 4. and Fig. 5. is apparently sample of cut through on adhesive A and D. The figures present the adhesive layer and its interaction with bonded material. The Fig. 4, A. and Fig. 5, A. present overall view on cut through of adhesive layer. The Fig. 4, B and Fig. 5, B. show good interaction between adhesive and bonded material, i.

e. good wettability of adhesive and bonded material. From Fig. 5, B. is evident good interaction between resin and filler (filler in adhesive is supply in adhesive from manufacture of one component adhesive). The adhesive contains higher part of porosity, which is presented on Fig. 4, B and 4, C.

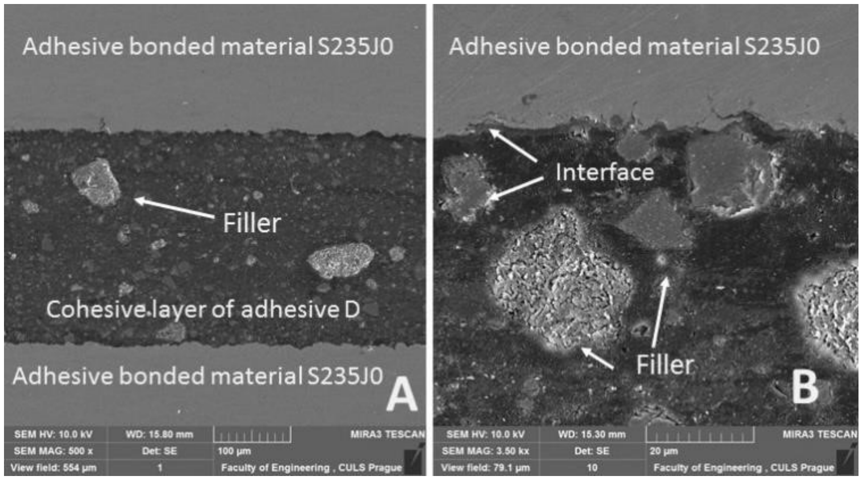

Figure 5. SEM images of cut through of adhesive bond A (SE detector, 10 kV): A: cut through of adhesive bond – one component epoxide containing filler (MAG 500 x), B: adhesive layer interaction, bonded material and filler (MAG 3500 x).

The research results of other authors confirm negative influence of different environment or mediums on quality of adhesive bond (Court et al., 2001; Doyle & Pethrick, 2009).

CONCLUSIONS

Results of mechanical tests proved a fall of the shear tensile strength of single lap-shear adhesive bonds after 42 cycles of the degradation process of 12.8 to 21.7%. The bond strength fall was gradual, and it showed a linear trend at some adhesives. Other adhesives showed a significant fall after the exposition to the degradation process after which the strength fall stabilized. The results classify the selected adhesives and their practical usage in degradation environment. The results also give the possibility to calculate the lifetime by the trend equation τ and ε.

The above conclusion from research results of on influence of cyclic degradation process on changes of structural adhesive bonds mechanical properties:

- In accordance on increasing number of degradation cycles decrease shear tensile strength of adhesive bond.
- The largest shear tensile strength 20.92 ± 0.63 MPa at 42 degradation cycles on adhesive E.
- The least shear tensile strength 17.13 ± 1.07 MPa at 42 degradation cycles on adhesive B.
- The influence of degradation cycles in accordance to shear tensile strength on adhesive bond was confirm at significance level *0.05*, i.e. hypothesis H_0 was rejected ($p < 0.05$).

- In accordance on increasing number of degradation cycles decrease elongation of adhesive bond, which is cause lower tensility of tested adhesive.
- The largest average elongation 13.02 ± 5.23% between 0 and 14 degradation cycles.
- The influence of degradation cycles in accordance to elongation on adhesive bond was confirm at significance level *0.05*, i.e. hypothesis H_0 was rejected ($p < 0.05$).
- Exposition process of degradation cycles did not change the type of fracture surface.

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