Polish Journal of Chemical Technology, 20, ***4,*** *26—31, 10.2478/pjct-2018-0050*

Influence of epoxy resin curing systems and aluminium surface modification on selected properties of adhesive joints

Małgorzata Szymiczek[1*], Błażej Chmielnicki[2]

[1] Silesian University of Technology, Institute of Theoretical and Applied Mechanics, Faculty of Mechanical Engineering, Konarskiego St. 18A, 43-410 Gliwice, Poland
[2]Institute for Engineering of Polymer Materials and Dyes, M. Skłodowskiej-Curie St. 55, 87-100 Toruń, Poland
**Corresponding author: e-mail: malgorzata.szymiczek@polsl.pl*

The aim of the present study was to investigate the effect of epoxy resin curing agents and aluminium surface modification on the properties of adhesive joints which were subjected to aging under thermal shock conditions. Composites containing reinforced aramid and carbon fibres with aluminium flat profiles (alloy Al 5754) were tested under shear conditions. Epoxy resin (Araldite LY 1564) with amine curing agents (Aradur 3486, Aradur 3487 and Aradur 3405) was used as a matrix. Composites were made using vacuum-assisted contact lamination. The degree of degradation was assessed on the basis of lap shear strength of adhesive joints in accordance with EN ISO 1465:2009. The research showed that epoxy composite samples based on Aradur 3405 (accelerated aliphatic polyamine) and sanded surface of aluminium presented the best lap shear adhesive strength, because this composite has the largest roughness. The hardness of the used adhesive is slightly increased with the cycle number.

Keywords: adhesive joints, composite materials, aging, surface modification.

INTRODUCTION

The significant advances in material engineering and increasing use of various materials in construction require fast, precise and tight and durable joint between them.

The use of composite polymeric materials in conjunction with light metal alloys in the automotive, aerospace or defence industries requires the development of an effective and quick joining method that will guaranty of high performance of the formers. Such systems are used under conditions, where high specific strength, different properties are important, and variable temperature conditions become of key importance. Appropriate design of the adhesive-bonded joint (chamfering the overlap ends) described by Kuczmaszewski[1] allows reduction of the coefficient of stress concentration and functional requirements to be met. Studies conducted by Czaplicki[2] and Godzimirski[3] showed that the strength of adhesive joints is influenced by characteristic of load (e.g. tension, flexural). The greatest strength is obtained in joints with double overlap joints, which is at least two times greater than that of plain overlap joint.

The important factor is choice of adhesive. For example, epoxy hardened by aromatic amine: m-phenylenediamine (MDF) are characterized high thermal, and chemical strength and electrical properties. Epoxy resins cured by aliphatic amines are characterized high mechanical and chemical resistance, but smaller thermal resistance and elasticity[4]. The ideal adhesive for such applications is one, in which adhesive flexibility and strength properties change along the length of the joint. Due to higher stresses on the edges of the overlap flexible adhesive should be used with stiff adhesive present in the middle of the joint[5].

Most of the strength criteria are limited to proper surface preparation, which depends on materials used in the joint and properties of the applied adhesive, and is determined to synergistic effects of specific adhesion, mechanical mechanisms and cohesion forces of the same adhesive[1, 5–9]. Various methods of surface modification of polymeric materials (e.g. laser, mechanical, chemical) and metalworking (e.g. chemical or electrochemical treatment, interlayers, mechanical, plasma atmosphere) are known[1, 7, 10–12]. Studies conducted by Rudawska have shown that the use of primers increases the strength and cataphoretic coating improves adhesive properties[13]. Abrahami et al.[14] demonstrated high initial adhesion without mechanical locking is obtained in the case of anodized aluminium, and regardless of the electrolyte type used during pre-treatment, stability of the joint is strongly dependent on chemical compounds formed on the modified surface.

During exploitation, adhesive-joints exposed to a number of different environmental conditions – UV radiation, water, heat, chemical factors and load, what is not sufficiently described in the literature[15–20]. Chemically cured, adhesive exhibits resistance to aggressive substances - petrol, oils, acids, bases and water, and the strength of the adhesive-joint is about 70% of the initial strength. Corrosion that occurs on the surface of such joints results in formation of oxides with no adhesion forces. Adhesive joints depend on interactions between the oxides[1]. The changes properties of joint materials are observed. Especially polymer materials are sensitive to degradation factors causing a decrease in their exploitation properties. Aging tests under thermal shock conditions of adhesive joints of epoxy composite – aluminium (materials with different thermal properties) are justified.

The aim of the present study was to evaluate the effect of aging under thermal shocks conditions, taking into account the curing system of the matrix used and the method of surface preparation. The evaluation criterion was lap shear strength and deformation measured in accordance with EN 1465:2009[21]. Shore D hardness was also used to measure the eventual changes in adhesive properties.

EXPERIMENTAL

Material

Aging and lap shear strength tests were performed on samples of adhesive joints (according to EN ISO 1465:2009), made of epoxy-carbon and aramid laminate and flat aluminium profiles. These are materials with different thermal expansion coefficients. The Al 5754 alloy has the value of thermal expansion coefficients: 23.7x10-6/K[22], density: 2.68 g/cm^3, young modulus: 70.5 GPa, tensile strength 150–200 MPa, Brinell hardness: 44 HB. Thermal expansion coefficients of aramid and carbon-epoxy composites are about 2.1 x 10^{-6}/K[23].

The matrix of the laminates contained Araldite LY 1564 epoxy resin (density: 1.1 g/cm^3, viscosity: 1200–1400 mPa×s, epoxy index (ISO 3001): 5.8–6.05 Eq/kg, epoxy equivalent: 170 g/equiv.) cured with amine curing agents with different characteristics (Aradur 3486, Aradur 3487 and Aradur 3405) – Table 1. The used curing agents differ viscosity and amine value, which affects the strength properties of the composites. The used curing agents differ viscosity and amine value, which affects the strength properties of the composites. Aradur 3405 is accelerated aliphatic polyamine and cured matrix characterise the higher properties – tensile strength, strain and Young modulus. The used materials are manufactured by Huntsman Advanced Materials.

Fabric reinforcements included aramide (173 g/m^2) and carbon (200 g/m^2) with fabric laid at 0^o/90^o (8 layers), which were jointed with flat aluminium profiles of 14–18% elongation and tensile strength of 190-200 MPa (Al 5754 alloy of type PA11).

Composite samples were made using the contact laminating method under vacuum of approx. 0.06 MPa, allowing for proper venting and removal of excess matrix.

Preparation of composite and aluminium samples

In order to ensure proper adhesion of the joint, the outer layer of the matrix was manually ground with P60 graduated sand paper (average grain size 269 mm), in such a way that the fibres were exposed but not damaged. Prepared surfaces of composite and surface topography of samples are shown in Fig. 1.

The surface of aluminium samples was prepared in three different ways:

– sanded down with P60 graduated sandpaper (average grain of average size 269 mm);

– anodizing with sulfuric acid and sealed with hot water,

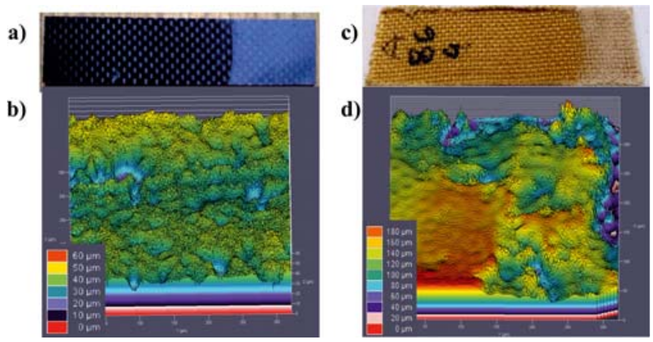

Figure 1. View of composite samples prepared with adhesive joints a) carbon-epoxy composite b) topography of carbon-epoxy composite surface c) aramid-epoxy composites and d) topography of carbon-epoxy composite surface

– etching in a bath including 5 g of chromium anhydride, 15 ml of sulfuric acid, density 1.83, distilled water to 100 ml (temperature 60^{o}C, time 20 min, the etched part length was 15 mm)[20].

Comparison of prepared surfaces and topography of aluminium is shown in Fig. 2–4. The study was conducted using the Zeiss LSM 5 Exciter confocal microscope. As can be seen in the topography maps shown (Fig. 2–4) the surfaces differ in roughness – Table 2.

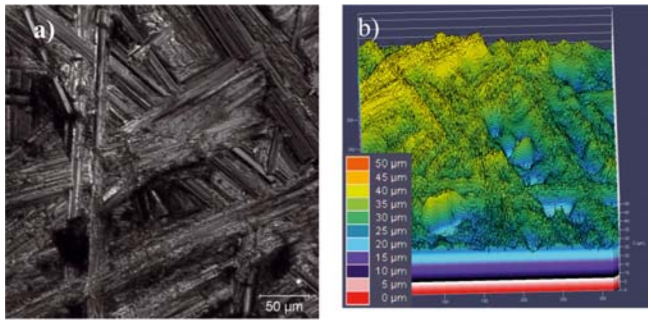

Figure 2. Microscopic image of sanded surface (a), surface topography (b)

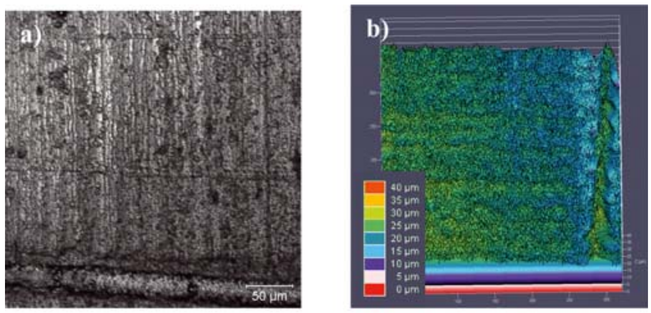

Figure 3. Microscopic photo of etched surface (a), surface topography (b)

Table 1. Properties of curing agents[24]

	Aradur 3486	Aradur 3487	Aradur 3405
Mix ratio for 100g matrix	34	41	35
Viscosity at 25 °C (ISO 12058-1) [mPa·s]	10–20	30–70	70–90
Density at 25 °C (ISO 1675) [g/cm^3]	0.94–0.95	0.98–1	0.95–1
Amine value (ISO 9702) [Eq/kg]	8.55–9.30	9.3–10.2	–
Pot life (100g at 23^{o}C) [min]	560–620	130–170	26–36
Gel time at 80^{o}C. [min]	33–43	18.25	5–11
Properties of curing matrix (15h. 50^{o}C)			
Tensile strength [MPa]	74–78	77–81	85–90
Strain at tensile strength [%]	4–4.2	3.9–4.1	4.4–4.9
Tensile modulus [MPa]	3100–3250	3200–3350	3500–3900
Flexural strength [MPa]	120–135	125–138	90–100
Strain at flexural strength [%]	5.2–5.6	5–5.4	2.2–2.6
Flexural modulus [MPa]	3100–3300	3200–3400	3800–4000

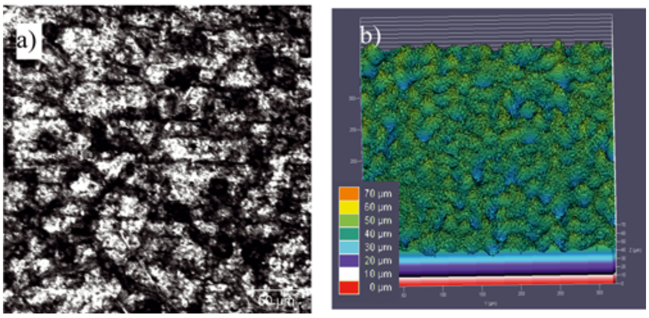

Figure 4. Microscope image of anodized surface (a), surface topography (b)

Table 2. Roughness surface

Type of Surface	Roughness R_a [μm]
Sanded aluminium flat	4.38
Etched aluminium flat	2.5
Anodized aluminium flat	3.1
Sanded carbon-epoxy composites	3.99
Sanded aramid-epoxy composites	27.6

Applied adhesive

Two-component epoxy adhesive cured at room temperature, intended for general purposes, was used for the tests. It is recommended for bonding elements with high conductivity. Its adhesive properties are presented in Table 3.

Table 3. Properties of epoxy adhesive

Properties	Epoxy adhesive
Mix ratio for 100g matrix	50 g curing agent
Pot life (25°C) [min]	165–255
Tensile strength [MPa]	52.6
Elongation at tensile strength [%]	2.9
Tensile modulus [MPa]	2420
Shore hardness D	83

The samples were degreased using a cleaning agent (Loctite 7063) and bonded with epoxy adhesive (properties presents in table 3). The curing time of adhesive joint was 48 h at 23°C. Figure 5 presents a view of the carbon-epoxy composite and etched flat aluminium profile prepared for bonding.

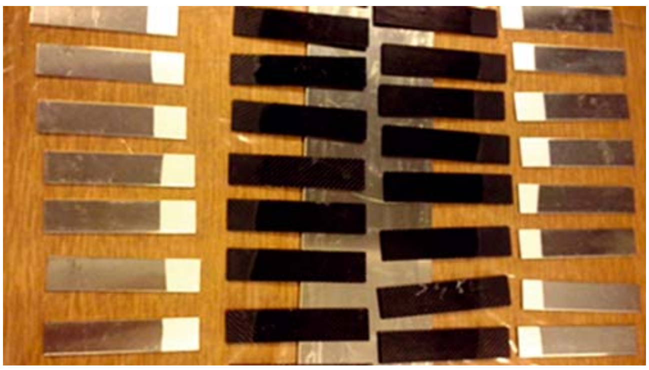

Figure 5. View of samples prepared for bonding

Aging tests

Prepared samples were conditioned in temperature 23°C, time 168h and next were subjected to aging under thermal shock conditions from –20°C to 130°C, hold exposure time 105 min, time of temperature changes was 30 min. The number of cycles was 10, 60, 120. Studies were conducted in the climatic test chamber ACS Discovery 650 in dry environment. Temperature changes correspond to the assumed extreme working conditions of the tested composites.

Mechanical properties

Lap shear strength and strain at break were determined according to EN 1465: 2009[21]. The study was conducted on a Zwick/Roell Z020 device. Testing speed of was 5 mm/min. Hardness of the aging and reference adhesives was determined in Shore D scale according to PN-EN ISO 868:2005[25]. Studies were carried out at each stage of aging and compared to the properties of reference samples.

RESULTS AND DISCUSSION

The results of lap shear strength (R_s) tests taking into account the curing agent used for matrix and type of surface preparation are shown in Fig. 6–8 (epoxy aramid-epoxy composite), Fig. 9–11 (epoxy-carbon composite). Results presented in Figures 7–11 are the arithmetic mean of five measurements. The dependence of lap shear strength of function of cycle number was described by the second-degree polynomial because it gave the best fit, as proved by high correlation coefficients. Descriptions in the charts mean: 3405 – Aradur 3405, 3486 – Aradur 3486, 3487 – Aradur 3487, a – anodized, t – etched, s – sanded.

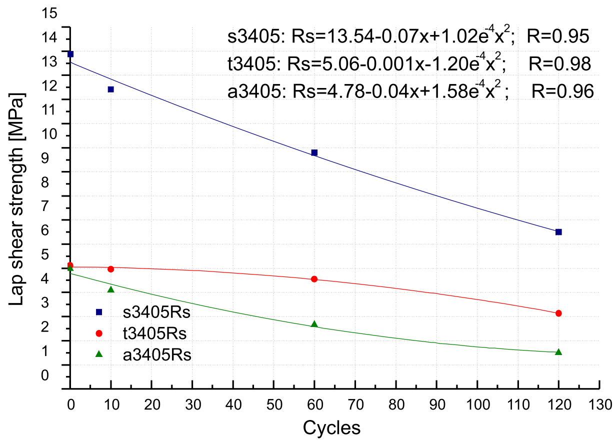

Figure 6. Lap shear strength of aramid-epoxy composite (with Aradur 3405) for different surfaces: a – anodized, t – etched, s – sanded

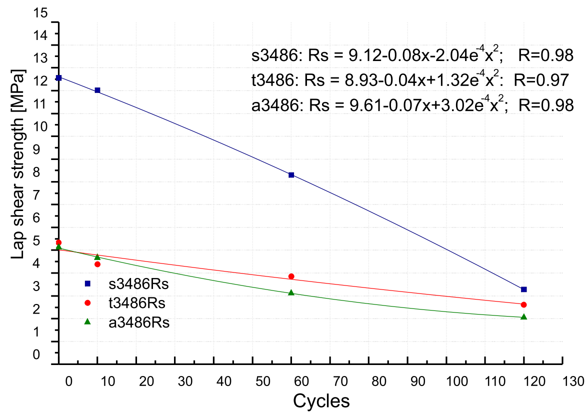

Figure 7. Lap shear strength of aramid-epoxy composite (with Aradur 3486) for different surfaces a – anodized, t – etched, s – sanded

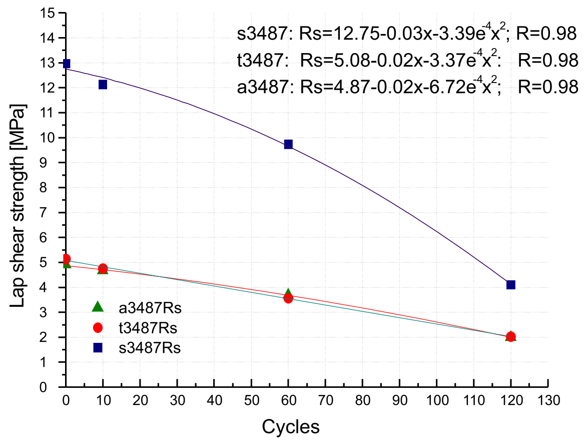

Figure 8. Lap shear strength of aramid-epoxy composite (with Aradur 3487) for different surfaces: a – anodized, t – etched, s – sanded

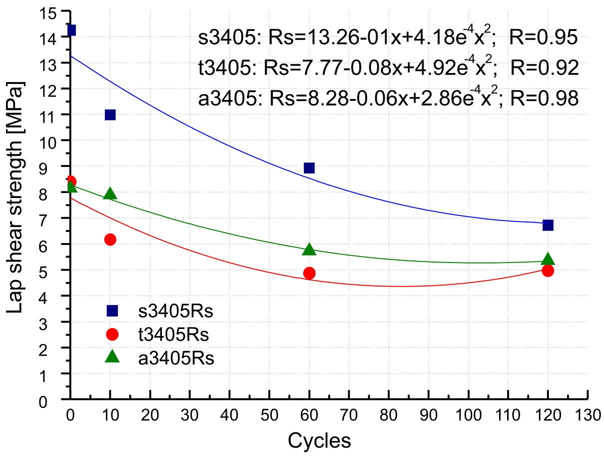

Figure 9. Lap shear strength of carbon-epoxy composite (with Aradur 3405) for different surfaces: a – anodized, t – etched, s – sanded

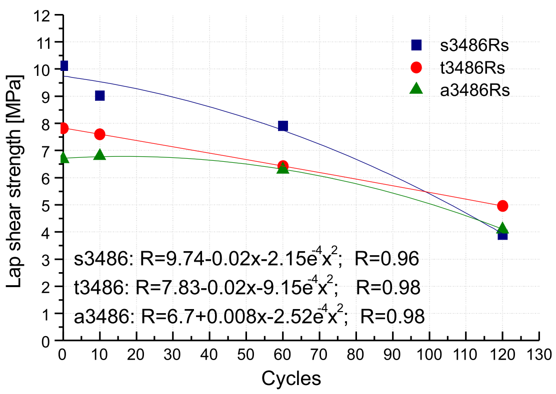

Figure 10. Lap shear strength of carbon-epoxy composite (with Aradur 3486) for different surfaces a – anodized, t – etched, s – sanded

Higher values of lap shear strength (Fig. 6–11) were observed for epoxy composites cured by using a alipphatic polyamine (Aradur 3405) compared to other amine curing agents used (Aradur 3486 and Aradur 3487). The highest values of lap shear strength were found in samples with sanded aluminium surface. This is especially noticeable in the case of aramid-epoxy composites, regardless of the type of curing agent used. In the case of amine-cured epoxy resin (Aradur 3486 and 3487) used on the matrix of carbon composites, the difference of lap shear strength observed between various types of surface treatment

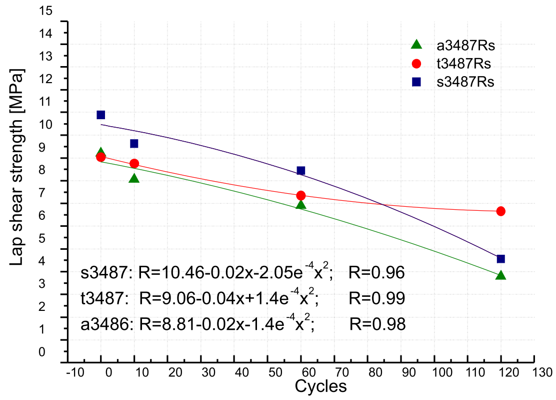

Figure 11. Lap shear strength of carbon-epoxy composite (with Aradur 3487) for different surfaces: a – anodized, t – etched, s –sanded

is not particularly significant, but samples with greater roughness of aluminium surface were characterized by the highest tensile strength. It can be concluded that mechanical adhesion is of greater importance in the tested area. The highest lap shear stress was observed for epoxy compounds applied with Aradur 3405 as the curing agent. It is a high viscosity hardener. Applying accelerated alipphatic polyamine for cured resin cause yield rapid and high degree of crosslinking of the resin. These composite samples (with Aradur 3405) were characterized by the highest roughness, because it was hardnesser and the sanding allowed for a larger surface developing than the composites cured Aradur 3486 and Aradur 3487. The use of Aradur 3405 allowed obtain high strength properties of aramid and carbon reinforced composite.

Fig. 12–14 presents the results of strain at break (e) on the aramid-epoxy composite. Fig. 15–17 shows the results of strain at break of carbon-epoxy composites. On the Figures 12–17 the same designations were used as on the Figures 7–11. The results (mean of five measurements) were approximated by a polynomial, and the correlation coefficients obtained showed a very good fit.

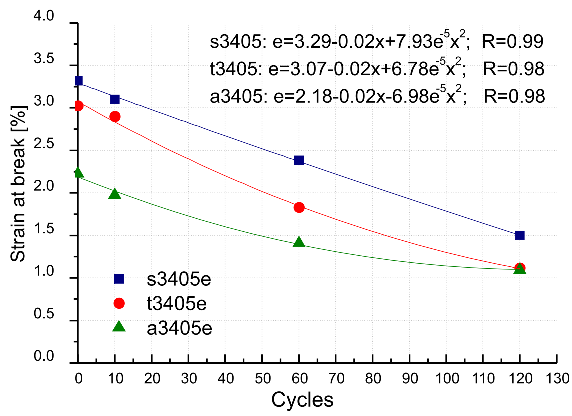

Figure 12. Strain at break of aramide-epoxy composite (with Aradur 3405) for different surfaces: a – anodized, t – etched, s – sanded

The results of failure strain at break (Fig. 12–17) evaluated for the adhesive in the lap shear strength test do not show a clear relationship between surface roughness and applied curing agent. This is a result of the adopted research methodology and the clearance

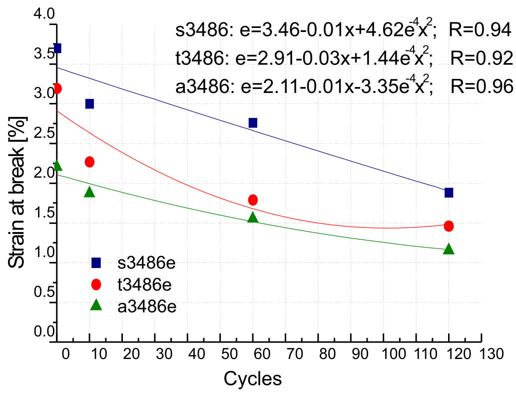

Figure 13. Strain at break of aramide-epoxy composite (with Aradur 3486) for different surfaces a – anodized, t – etched, s – sanded

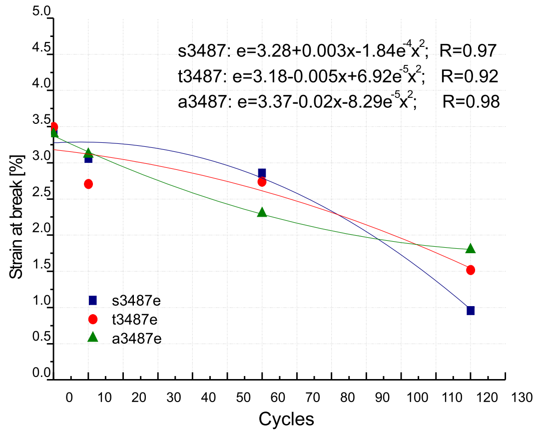

Figure 14 Strain at break of aramide-epoxy composite (with Aradur 3487) for different surfaces: a – anodized, t – etched, s – sanded

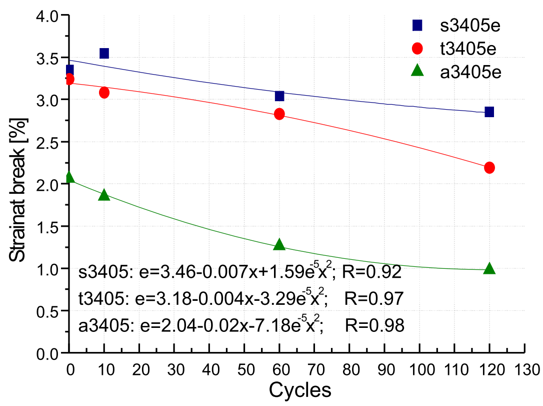

Figure 15. Strain at break of carbon-epoxy composite (with Aradur 3405) for different surfaces: a – anodized, t – etched, s – sanded

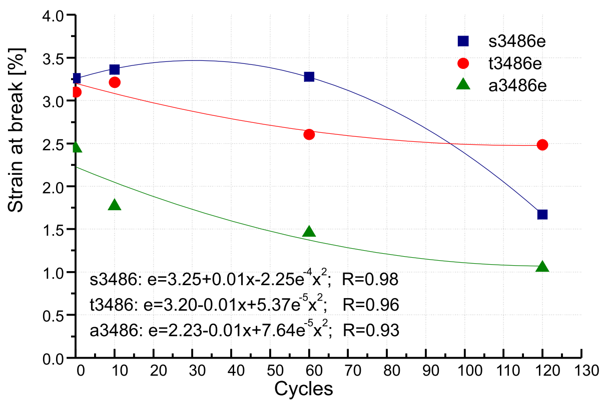

Figure 16. Strain at break of carbon-epoxy composite (with Aradur 3486) for different surfaces: a – anodized, t – etched, s – sanded

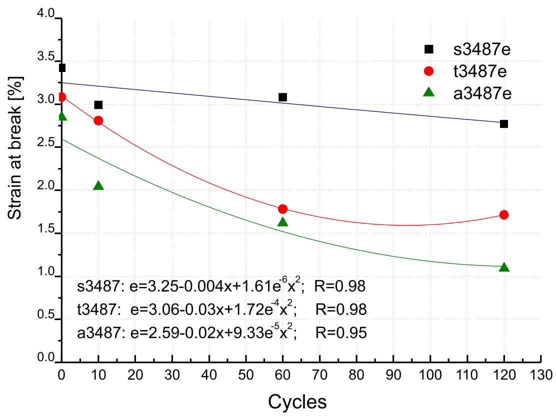

Figure 17. Strain at break of carbon-epoxy composite (with Aradur 3487) for different surfaces: a – anodized, t – etched, s – sanded

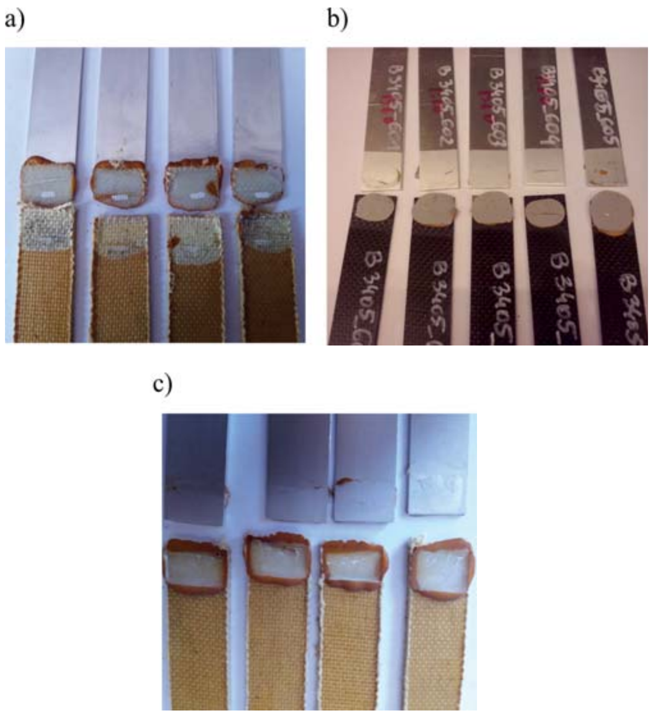

Figure 18. View of cohesive damage of composite for sanded surface of aluminium (a), adhesive damage on etched surface of aluminium (b), adhesive damage on anodized surface of aluminium (c)

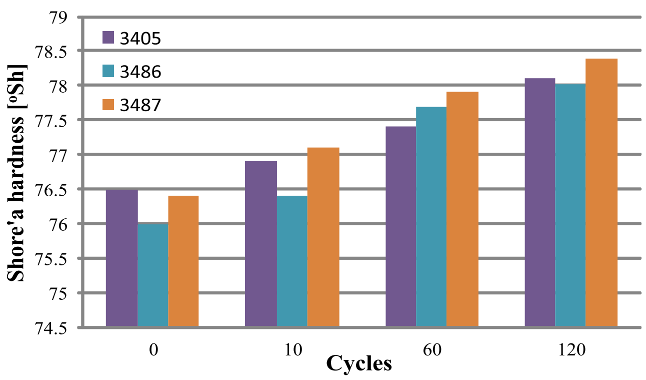

Figure 19. Hardness as function of the number of cycles

observed during tensile tests. We observed a decrease of the failure strain during aging.

Changes in lap shear strength and strain were described by the second-degree polynomials with very high correlation coefficients of 0.92–0.98. The developed function allows prediction with high probability behaviour of the tested material under determined exploitation conditions.

Adhesive damage was observed in most of the analysed adhesive joints during the study. Destruction of cohesive composite or adhesive on aluminium surface occurred for sanded samples, regardless of the type of curing agent and reinforcement (Fig. 18). In the case of etched and anodized aluminium, adhesive damage was caused by the flat aluminium profile – Fig. 18 b–c. Figure 18 illustrates selected examples of adhesive joint destruction.

Figure 19 shows the change of Shore D hardness as a function of the number of cycles, taking into account the curing agents used. Adhesive hardness increases with increasing number of cycles. This is caused by degradation, causing the epoxy resin to become stiff. The obtained results confirm a strain reduction. A colour change is observed, which is a visual indication of the aging process.

CONCLUSIONS

On the basis of obtained results, it can be concluded that:

The best lap shear strength properties, at each stage of the aging process, were shown by samples in which the matrix was cured using Aradur 3405. This is due to the surface preparation method used (sanded). Higher viscosity of the curing agent increases stiffness, warp hardness of the composite, which is important for sanded materials.

Larger differences in lap shear strength, taking into account the curing agent type, were observed for aramid-epoxy composites. In the case of carbon-epoxy composites, significant differences caused by the use of reinforcing fibres were not observed.

The hardness of the adhesive is slightly increased and the strain at break of the adhesive joint decreases. However, strain at break results were not reliable because the accepted methodology takes into account deformation of jointed materials.

The highest lap shear strength of the received adhesive joints was found for sanded surface of aluminium. Mechanical adhesion allows for increased roughness, which results in expansion of the adhesive surface. As the roughness increases, the lap shear strength is also increased.

LITERATURE CITED

1. Kuczmaszewski, J. *Fundamentals of metal-metal adhesive joint design*. Lublin University of Technology, Polish Academy of Sciences, Lublin, 2006.

2. Godzimirski, J. *Adhesive plastics. Application in repair of technical equipment*, WNT, Warsaw, 2010, (in Polish).

3. Czaplicki, J., Ćwikliński, J., Godzimirski, J. & Konar, P. *Adhesive plastics*. Transport and Communication Publishers, Warsaw, 1987, (in Polish).

4. Bereska, B., Iłakowska, J., Czaja, K. & Bereska, A. (2014) Hardeners for epoxy resins. *Przem. Chem. – Chemical Industry,* 93/4:443–448, DOI: dx.medra.org/10.12916/przemchem.2014.443.

5. da Silva, L.F.M. & Lopes, M.J.C.Q. (2009) Joint strength optimization by the mixed-adhesive technique. *Int. J. Adhes. Adhes.* 29(5): 509–514, DOI: 10.1016/j.ijadhadh.2008.09.009.

6. Banea, M.D. & Da Silva, L.F.M. (2009) Adhesively bonded joints in composite materials: an overview. *Proceedings of the Institution of Mechanical Engineers Part L: Journal of Materials: Design and Applications* 223(1), 1–18, DOI: 10.1243/14644207JMDA219.

7. Wingfield, J.R.J. (1993) Treatment of composite surfaces for adhesive bonding. *Int. J. Adhes. Adhes* 13, 3, 151–156. DOI 10.1016/0143-7496(93)90036-9.

8. Rudawska, A. Filipek, P. & Kowalska, B. (2016) The choosen issues of epoxy compounds modification. *Polymer Processing* 170(22), 91–99.

9. Szymańska, J., Kostrzewa, M., Bakar, M. & Białkowska, A. (2017) Study on adhesive properties and curing of reactive liquid rubbers toughened epoxy-clay ternary hybrid nanocomposites. *J. Polym. Eng*. – online 11.09.201. DOI: 10.1515/polyeng-2017-0099.

10. Palmieri, F.L. at al. (2015) Laser surface preparation of epoxy composites for secondary bonding: optimization of ablation depth. Composite Materials. SAMPE Baltimore Conference and Exhibition, Baltimore, USA, 18–21 May 2015.

11. Liston, E.M., Martinu, L. & Wertheimer, M.R. (1993) Plasma surface modification of polymers for improved adhesion: a critical review. *J. Adhes. Sci. Techno.* 7(10), 1091–1127. DOI: 10.1163/156856193X00600.

12. Rudawska, A., Reszka, M. & Warda, T. et al. (2016) Milling as a method of surface pre-treatment of steel for adhesive bonding. *J. Adhes. Sci. Technol.* 30(23), 2619–2636. DOI.org/10.1080/01694243.2016.1191585.

13. Rudawska, A., Bociąga, E. & Olewnik-Kruszkowska, E. (2017) The effect of primers on adhesive properties and strength of adhesive joints made with polyurethane adhesives. *J. Adhes. Sci. Technol.* 31(3), 327–344. doi.org/10.1080/01694243.2016.1215013.

14. Abrahami, T.S., Hauffman, T. & De Kok, J.M.M. et al. (2016) Effect of anodic aluminum oxide chemistry on adhesive bonding of epoxy. *J. Phys. Chem.: C* 120(35), 19670–19677. DOI: 10.1021/acs.jpcc.6b04957.

15. Martin, R. (2008) *Ageing of composites*. Cambridge: Woodhead Publishing Limited.

16. Harris B (2003) *Fatigue in composites*, Cambridge: Woodhead Publishing Limited.

17. Hu, H., Sun, C.T (2003) The equivalence of moisture and temperature in physical aging of polymeric composites. *J. Compos. Mater.* 37(10), 913–928. doi.org/10.1177/0021998303037010004.

18. Szymiczek, M., Rojek, M. & Wróbel, G. (2016) The influence of the ageing-fatigue degradation on the mechanical properties of glass-reinforced composites. *Pol. J. Chem.* 18(1), 113–119. doi.org/10.1515/pjct-2016-0017.

19. Wang, J., Ganga, Rao, H., Liang, R. & Liu, W. (2003) Durability and prediction models of fiber-reinforced polymer composites under various environmental conditions: A critical review. *J. Reinf. Plast. Compos.* 35(3), 179–211. doi.org/10.1177/0731684415610920.

20. Kuczmaszewski, J. & Kłonica, M. (2015) Comparative researches of shearing strength of single-lap adhesive bonded joints 316l steel after „thermal shock”. *Polymer Processing* 164(21), 125–130.

21. EN 1465:2009 (2009) Adhesives – Determination of tensile lap-shear strength of bonded assemblies.

22. Tabal Wholesale (2017) Sheets from aluminium alloys. Available at: http://hurtownia.tabal.pl/stop-5754-gatunek-pa11,262.html (accessed 10 June 2017).

23. Hull, D. & Clyne, T.W. (1996) *An introduction to composite materials*. Cambridge: Cambridge University Press.

24. Characteristic card of materials (HUNTSMANN).

25. PN-EN ISO 868:2005 (2005) – Plastics and ebonite — Determination of indentation hardness by means of a durometer (Shore hardness).