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Network structure in epoxy aluminium bonds after mechanical treatment

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Abstract

Mechanical pretreatment is the oldest and most common technique for improving the performance of adhesive metal bonds. But it is poorly understood, how mechanical pretreatment affects the surface state of the metal adherend and how in turn the pretreated surface influences the properties of the applied adhesive or the whole joint, respectively. This paper describes how mechanical pretreatment by blasting with alumina grit or with glass beads changes the topography and the chemical state of an aluminium adherend. For an epoxy adhesive different network structures evolve in joints of the pretreated aluminium adherend. These network structures are referred to the chemical states of the pretreated adherend. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In order to improve the performance of adhesive metal bonds the adherends are chemically or mechanically pretreated. Chemical pretreatment is widely used but often criticised for ecological and economical reasons. In order to obtain good properties for aluminium–epoxy bonds sophisticated and sometimes toxic pretreatments are used. Their replacement by mechanical pretreatment is of great technical interest as it is ecologically less critical. Mechanical pretreatment is the oldest and most common technique for improving the performance of adhesive metal bonds [1,2]. But it is poorly understood, how mechanical pretreatment affects the surface state of the metal adherend and how in turn the pretreated surface influences the properties of the applied adhesive or the whole joint, respectively. The most frequent explanation refers to mechanical interlocking between adhesive and roughened substrate as a major source for improved mechanical strength [3]. However, recent studies show that the efficiency of this technique does not obey these established explanations [4,5]. Further, it has to be assumed that within a bondline the zone which dominates the compound behaviour is not directly to be found on the metal surface but rather in the interface–near polymer region, the so called interphase [6]. Moreover, it is discussed in literature [7–9] that the performance of the bond could be influenced by the network structure of the adhesive. This has been shown experimentally for a model epoxy in [10,11] for the first time.

This paper investigates the effect of mechanical pretreatment by blasting with alumina grit or with glass beads on the surface state of an aluminium adherend and how in turn these pretreated surfaces influence the formation of the network structure in bonds with an epoxy adhesive system.

2. Experimental

2.1. Characterisation of the pretreated aluminium adherends

2.1.1. Samples

For the investigation an aluminium alloy with 3% Mg (AlMg3, EN–AW 5754) is used as adherend. Three

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different surface states are prepared by the following treatment procedures:

The 'reference state' of the aluminium is set by consecutive ultrasonic cleaning in acetone for 15 min at room temperature, etching in 1 M aqueous NaOH for 10 min at room temperature, neutralisation in 3.54 M aqueous HNO_3 for 1 min at room temperature, thorough rinsing in distilled H_2O and drying in air for 30 min at 100°C.

Both blasted states of the aluminium are set by pressure air blasting the 'reference state' with alumina grit or with glass beads. The alumina grit (corundum grit) is sized 125–250 μm and consists almost completely of Al_2O_3 (99.6 wt%). The glass beads are 100–200 μm in diameter and contain mainly SiO_2, Na_2O and traces of CaO, MgO, Al_2O_3 and Fe_2O_3. Blasting is performed perpendicular to the substrate surface at 6 bar blasting pressure for 10 s. The distance between nozzle and substrate is 10 cm. Under these conditions the resulting joint strength with an epoxy adhesive is proved to be independent on the processing parameters [12,13].

2.1.2. Experiment

The surface topography of the samples is depicted by scanning electron microscopy (SEM, CamScan 44 FE, primary electron energy 15 keV, working distance 21 mm, corresponding lateral resolution ≈ 10 nm).

The element composition of the near-surface layer of the aluminium (information depth ca. 1–2 μm) is studied by energy dispersive X-ray (EDX) spectrometry which is coupled to the SEM. The spectrometer comprises a Link ISIS Series 300 Microanalysis System, Link Pentafet detector and an ATW thin layer window. It is operated with a primary electron energy of 15 keV, a working distance of 31 mm, a resolution for local spot analysis or for element scanning mode of about 10 nm and an energy resolution of 136 eV for Mn at 5.895 keV.

The very top surface region of the aluminium is studied by scanning auger microscopy (SAM) and by core level X-ray photoelectron spectroscopy (XPS) which have both an information depth of less than 10 nm (SAM, Perkin Elmer PHI 660, primary electron energy 5 keV, lateral resolution ca. 350 nm, scanned sample area 560×400 μm. XPS, ESCALAB 220i-XL, vacuum generators, monochrome Al Kα, analysing spot diameter 600 μm). SAM is used to depict the element distribution at the surface. XPS spectra are recorded for element analysis (CAE = 70 eV, step = 500 meV) and with high-energy resolution (CAE = 10 eV, step = 40 meV) in order to get insight into the chemical state of the major elements at the surface. Therefore, the spectra are analysed by suitable peak fitting procedures (software Peak-Fit from Jandel Scientific). After subtracting a linear background, the lowest possible number of Gaussian lines is used with a free fit of position, peak heights and line widths.

2.1.3. Results and discussion

Each kind of pretreatment alters the topography of the aluminium surface in a specific way. Etching dissolves some layer of the metal and causes etch pits of about 1–10 μm size which cover the surface completely (Fig. 1a). This indicates that the chemical treatment removes the original surface material from the alloy. The chemical attack also uncovers inclusions of impurities. The blasted surfaces are much rougher than the etched samples. Blasting with alumina grit (Fig. 1b) causes micro-milling thus removing the upper material layer which results in a groovy structure on the 10 μm-scale. The glass beads (Fig. 1c) produce imprints which give evidence to the hammer-like treatment of the aluminium surface but no significant removal of material is established. The rims of these imprints contain cracks and flake-like parts.

The alloy itself contains inclusions of iron oxide and silicon oxide that are uncovered by the chemical etching. Tight-sticking fragments of both blasting materials are found in the aluminium surface. Apart from this also the chemical state of the aluminium is changed significantly (for more details see [14]). As usual for real surfaces, a thin carbonaceous contamination layer covers all samples. Additionally, absorbed water and hydroxyl groups are found on the aluminium oxide. Any adhesive has to replace these surface layers in order to provide proper adhesion to the oxide. One surprising result is that the oxide itself is not in all cases Al_2O_3. Al_2O_3 is only found for the etched surface whereas $Al_2O_{2.87}$ and $Al_2O_{1.3}$ are found 1 day after blasting with glass beads and alumina grit, respectively. Hence, not all Al atoms possess their maximum degree of oxidation (+3) in the blasted surfaces. These Al atoms are expected to be very reactive. This view is supported by the post-oxidation observed on the aluminium blasted with glass beads. It is important to note that on the aluminia grit blasted surfaces these states decay slowly for many days. It is expected that these stable but reactive sites may influence the network formation of an applied epoxy adhesive.

2.2. Characterisation of thin epoxy films on pretreated aluminium ('open bonds')

2.2.1. Samples

For the investigation a room temperature curing epoxy system is used. The adhesive consists of the diglycidylether of bisphenol A (DGEBA) and the curing agent diethylene triamine (DETA) (Fig. 2). These components are mixed in a mass ratio of DGEBA: DETA = 100:14 for 5 min at 55°C. Straight after mixing the epoxy system is cooled down to room temperature and dissolved in methylethyl ketone (MEK) in a ratio of 1.14 g epoxy system to 4 ml MEK in order to reduce the viscosity of the adhesive for the film preparation. The

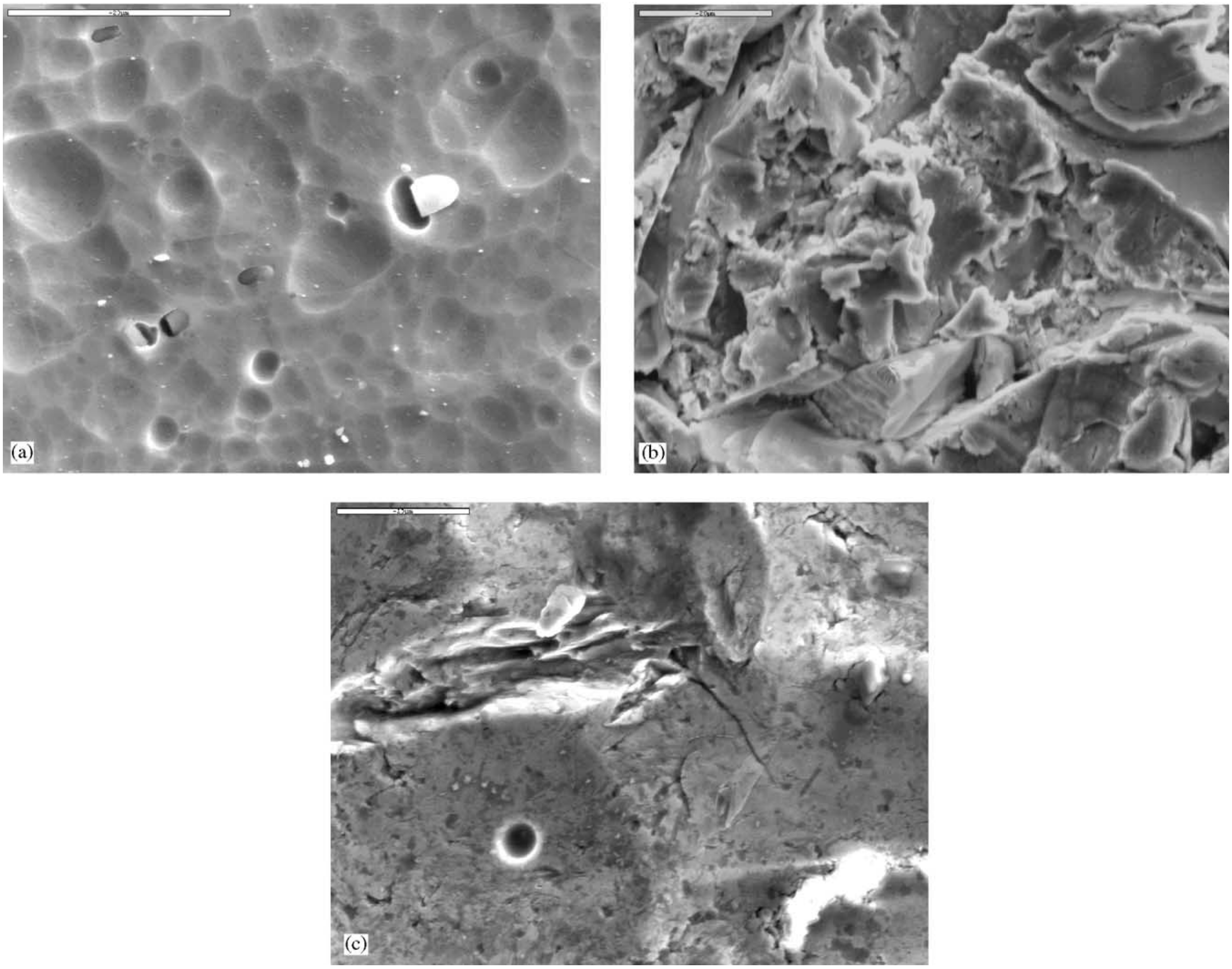

Fig. 1. SEM micrographs (secondary electrons) of the aluminium surface: (a) after chemical pretreatment, (b) after blasting with aluminia grit, (c) after blasting with glass beads. Scale bar 20 μm.

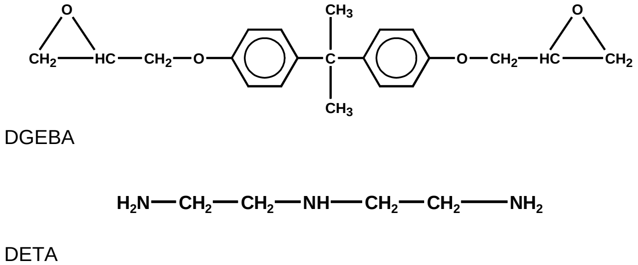

Fig. 2. Chemical structure of the epoxy system components.

solution is applied by spin-coating (5000 min^{-1}, 10 s) on the freshly pretreated aluminium substrates. The resulting thin epoxy films ('open bond') have a thickness of about 2 μm. The solvent MEK evaporates completely off the 'open bonds' within a couple of minutes as shown by infrared external reflection absorption spectroscopy (IR-ERAS).

2.2.2. Experiment

During the curing reaction at room temperature the oxirane rings of the DGEBA are consumed by reacting with the primary and the secondary amine groups of the DETA. This links both kinds of molecules. In this connection, secondary amines are formed by the reaction of primary amines with oxirane rings and tertiary amines result from the reaction of secondary amines, respectively. The reactivity of primary amines is the highest. In both cases a hydroxyl group is formed. Only at elevated temperatures, the hydroxyl group reacts with an oxirane ring forming an ether group. The route and the speed of these reactions are not surely known. As a consequence, the consumption of epoxy groups is used as a measure for the reaction progress in this investigation. For the given mixing ratio all oxirane rings can be consumed by the primary and secondary amines. In the course of the curing process continuous molecule growth takes place, oligomers and

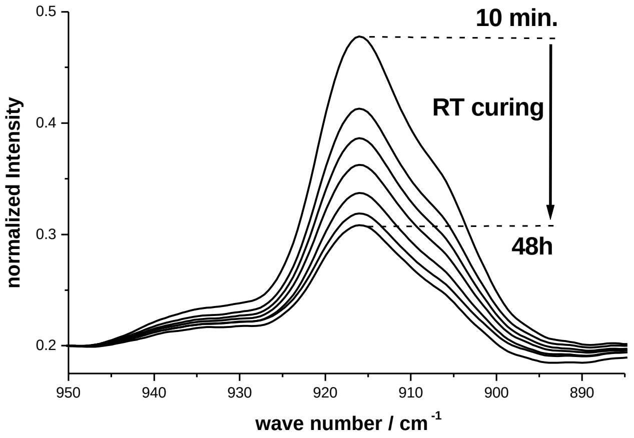

Fig. 3. Intensity of the epoxy band at 915 cm^{-1} during room temperature curing for the 'reference state'.

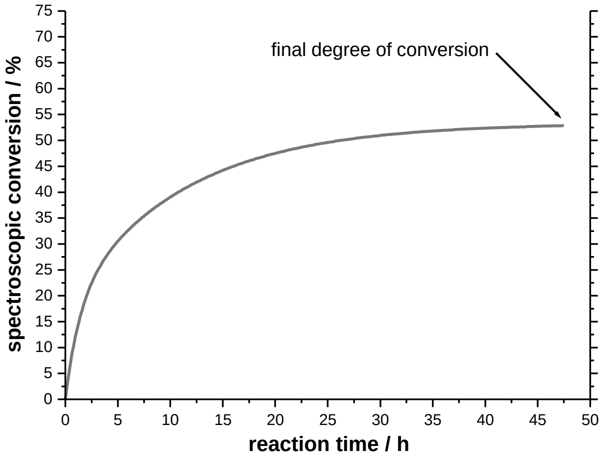

Fig. 4. Spectroscopic conversion of epoxy groups at room temperature as a function of curing time for the 'reference state'.

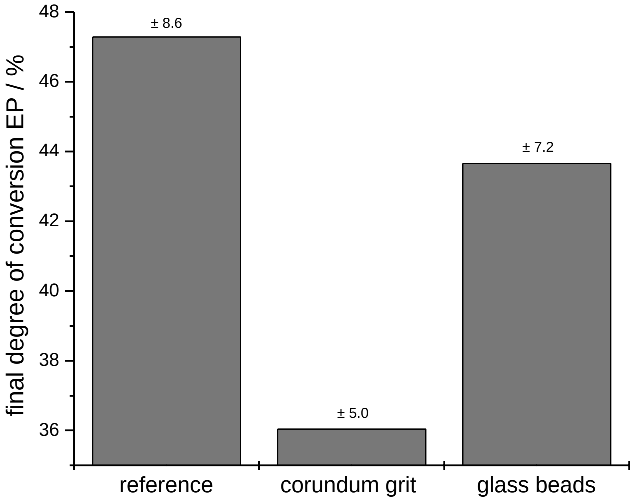

Fig. 5. Final degree of conversion of epoxy groups for 2 μm films on the aluminium in dependence of pretreatment.

macromolecules are formed. This decreases the molecular mobility in the epoxy system which in turn results in an increasing glass transition temperature. Oligomers and macromolecules form the epoxy network.

The curing reaction of the thin adhesive films on the pretreated aluminium at room temperature is studied by IR-ERAS (Bruker 66v, reflection unit: Harrick Seagull, *p*-polarised light, incidence angle 60°, purge gas: dry air). The conversion of epoxy groups as a function of reaction time is derived from the decay of the oxirane band at 915 cm^{-1} with curing time t_c. Fig. 3 provides an example for the 'reference state'). The peak height $I_{EP}(t_c)$ serves as a spectroscopic measure of oxirane concentration. The spectroscopic degree of conversion X_{EP} is calculated by

$$X_{EP}(t_c) = 1 - \frac{I_{EP}(t_c)}{I_{EP}(t_c = 0)}.$$

Fig. 4 shows the results for the 'reference state'. The final degree of conversion of the epoxy system on the aluminium after 48 h is evaluated in dependence of the pretreatment. As a consequence of vitrification which takes place after about 90 min (measured by modulated DSC), the curing reaction nearly ceases after 48 h due to the lack of molecular mobility. Hence, the curing reaction is incomplete (compare also Fig. 4) and the epoxy adhesive is in the glassy state (T_g= 53°C as measured by DSC).

2.2.3. Results and discussion

The final degree of conversion on the blasted aluminium is lower than on the etched samples (Fig. 5). Moreover, extremely low values are obtained on the alumina-blasted surfaces.

For this behaviour two reasons are suggested which both refer to the surface state of the substrates.

First, as discussed in literature [15–18], there is a preferential adsorption for DETA on the aluminium surface. This suggestion is additionally supported by the chemical surface state of the alumina-blasted substrate where $Al_2O_{1.3}$ is found. Hence, Al sites with a deficit of electron density must be available. On the other hand, the nitrogen atoms in the DETA can act as electron donors for appropriate partners. As a consequence, DETA could chemisorb on the oxide. The immobilised DETA molecules are not fully available in the curing reaction. However, the number of amine molecules in the chemisorption layer is much too low to explain the strong decrease of X_{EP} for the pretreated surfaces with respect to the bulk (Fig. 5). Hence, as a second mechanism, the epoxy system tends to demix gradually into a DETA rich phase on the aluminium. Now, another part of the DETA is not available for regular curing. In the corresponding DGEBA enriched phase less oxirane rings are converted which leads to the different X_{EP} values observed for the different pretreatments. Interestingly, the final degree of conversion correlates with the ranking of the degree of oxidation in the oxides.

The different degrees of conversion should exert an influence on the molecular mobility of the adhesive in the bondline. This is studied by DES.

2.3. Characterisation of epoxy aluminium bonds ('sandwich bond')

2.3.1. Samples

For DES measurements epoxy aluminium bonds ('sandwich bonds') are prepared (Fig. 6). The freshly pretreated aluminium adherends sized $25 \times 25 \times 1.5\,\text{mm}^3$ are contacted with a copper wire. The bondline thickness is set to 25 µm or 100 µm by Teflon spacers. Room temperature curing of the sandwich bonds is performed at 23°C for 48 h in dry air.

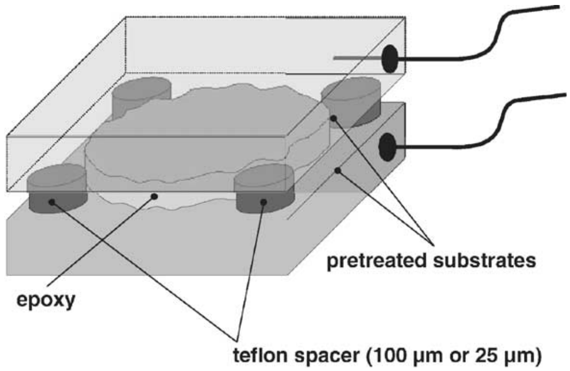

Fig. 6. Experimental set-up for DES measurement on epoxy aluminium bonds.

2.3.2. Experiment

The 'sandwich bonds' are contacted to a dielectric spectrometer (Novocontrol Broadband Dielectric Converter BDC with a Stanford Research Systems Lock-In Amplifier SR 810). The dielectric behaviour of the adhesive in the bondline is investigated as a function of frequency of the applied electric field and temperature. The room temperature cured samples are characterised in the glassy state (T_g= 53°C) from −60°C to +20°C and in a frequency range from 10^{-2} to 10^6 Hz. As for all polymers, the dielectric behaviour is described by the dielectric function $\hat{\varepsilon}(f, T) = \varepsilon'(f, T) - i\varepsilon''(f, T)$, where ε' is the permeability and ε'' is the dielectric loss. $\hat{\varepsilon}(f, T)$ describes to what extent the permanent dipoles in the epoxy network contribute to the dielectric behaviour as a function of frequency and temperature. In this context, any dipole orientation in the epoxy network involves local molecular motions. Consequently, $\hat{\varepsilon}(f, T)$ is associated with the molecular mobility in the epoxy network [19]. In this way the 25 µm bonds reflect the molecular mobility of a more interface-near network, whereas the 100 µm bonds represent a more bulk-like behaviour.

A secondary relaxation is found for ε'' as a function of frequency (Fig. 7 as example for the 'reference state'). This relaxation is attributed to the local molecular mobility in the glassy epoxy network. For increasing temperature this secondary relaxation systematically shifts to higher frequencies. As the most important characteristic, the maximum frequency f_{max} of this relaxation is determined by an appropriate Havriliak–Negami function [20]. The maximum frequency relates to the most prominent relaxation time τ_{max} by

$$\tau_{max} = \frac{1}{f_{max}}.$$

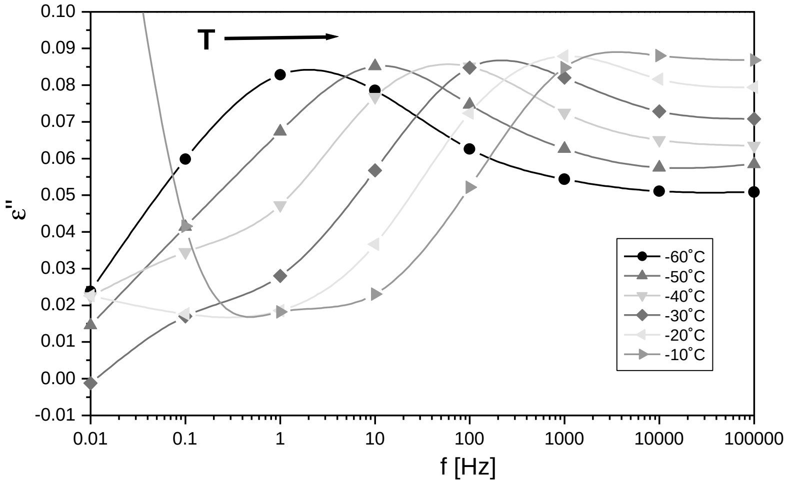

Fig. 7. Dielectric loss ε'' of the epoxy system in the glassy state as a function of frequency and temperature for the 'reference state'.

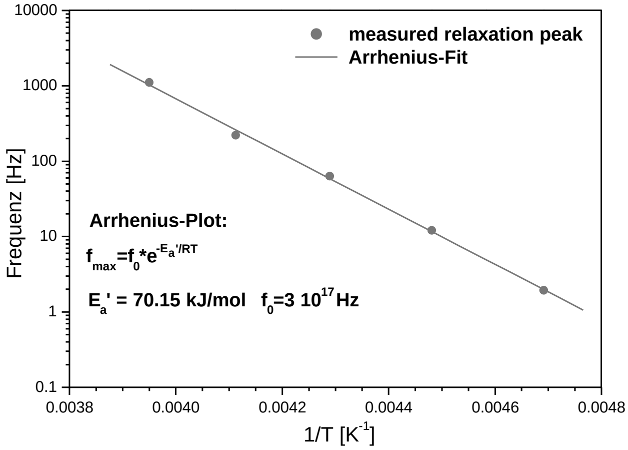

Fig. 8. Arrhenius plot for the frequency location of the secondary relaxation peak maxima versus the inverse temperature (‘reference state’).

An Arrhenius plot is applied in order to derive the apparent activation energy E'_A for the involved molecular motions (Fig. 8). This quantity is a certain mean value for the energy barrier of the molecular motions in the given relaxation. In other words, E'_A can be regarded as a measure for the local molecular mobility in the epoxy network. A low E'_A value corresponds to a high local molecular mobility or to a low local molecular stiffness, respectively.

2.3.3. *Results and discussion*

The DES results show that for the joints with 25 μm bondline thickness, the local molecular mobility of the epoxy network between the blasted samples is increased as compared to the reference (Fig. 9). In this context, the local molecular mobility of the epoxy network on the alumina-blasted samples is significantly lower than of the glass-blasted samples.

The increased mobility in the near-interphase region on both blasted aluminium substrates correlates to the low degree of epoxy conversion observed by IR-spectroscopy. This relation is evident as for a low degree of conversion-less network structure like chemical links, mashes and bulky side groups are built up which hinder the local mobility. Surprisingly, for the alumina-blasted substrates this consideration contrasts the relatively low local mobility in combination with the extremely low degree of conversion in the near-interface region. It is concluded that the epoxy network in this region must be locally hindered in some way. For this local hindrance two reasons are suggested:

First, the above discussed preferential adsorption of amine groups of the DETA on the aluminium leads to a pronounced chemisorption of DETA via electron donor–acceptor interaction. Consequently, a dense packing is expected in the first molecule layer. Fig. 10 illustrates this situation on a crude schematic level. The proceeding curing reaction results in a chain-like growth of epoxy structures on the chemisorbed DETA. It is convincing that this dense packed near-interface layer should have a high molecular stiffness. With increasing distance from the aluminium the packing of polymer chains decreases (Fig. 10), which in turn leads to a growing molecular mobility.

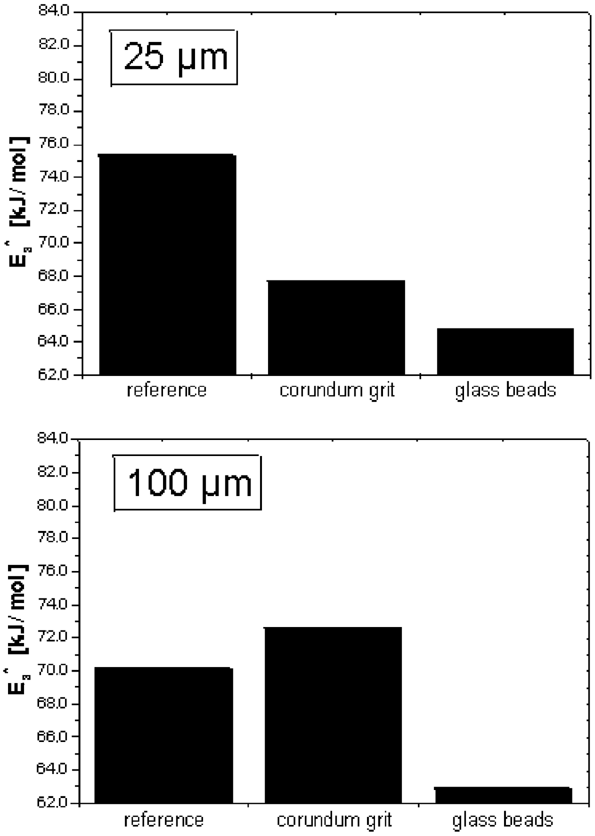

Fig. 9. Activation energy E'_A for the secondary relaxations in dependence of the bondline thickness of room temperature cured epoxy between pretreated aluminium.

Second reason, the alumina-blasted substrate catalyses the reaction of the epoxy groups with the secondary amine groups. In this way, many chemical links are formed which lead to a high crosslinking density in the epoxy network resulting in a low molecular mobility (not depicted in Fig. 10).

For the joints with 100 μm bondline thickness, which ought to reflect a bulk-like behaviour, one should expect a levelling of the mobility towards the values of the reference. However, the experimental results contradict this view (Fig. 9). Blasting with alumina grit leads to an epoxy network with a significantly low mobility. In contrast, a network with the highest mobility is found between the glass-blasted substrates.

Summarising all mobility data, a schematic sketch can be drawn for the gradients of molecular mobility in the epoxy networks perpendicular to the differently

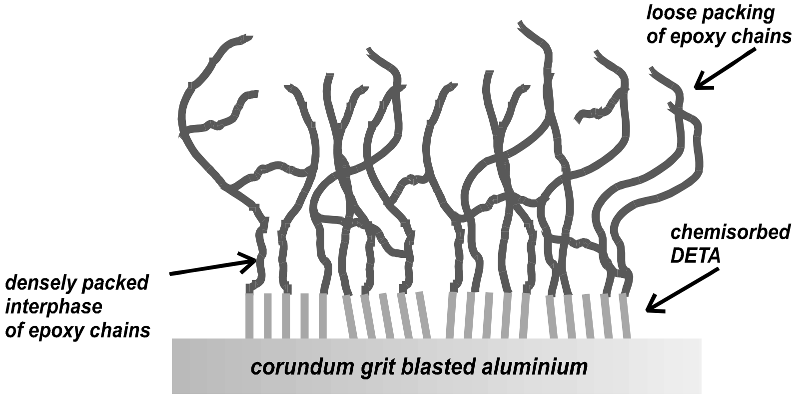

Fig. 10. Schematic description of the near-interface structure of the epoxy network as a consequence of preferential adsorption of primary DETA amine groups.

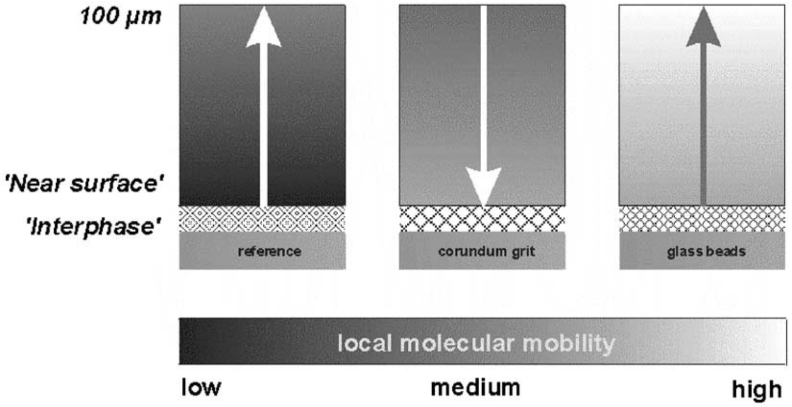

Fig. 11. Schematic description of the network structures between the treated aluminium adherends after room temperature curing.

pretreated aluminium surfaces (Fig. 11). In addition, the various degrees of epoxy consumption discussed above are indicated as hatched zones (the higher the degree of consumption the more dense the hatching). The local mobility of the network structure in the reference state significantly decreases towards the substrate. The crosslinking density in the interphase is the highest of all samples. On the alumina-blasted substrates, a network structure is detected which has an increased local stiffness in the bulk phase compared to the reference and which gains in mobility towards the substrate. The crosslinking density in the interphase is low as compared to the reference. On the glass-blasted substrates a network with the highest local mobility in the bulk phase is formed which slightly decreases towards the substrate. A medium crosslinking density is observed.

3. Conclusion

The pretreatment of the aluminium by blasting with alumina grit or with glass beads changes both, the topography and more important, the chemical state of the metal surface. Surprisingly, after pretreatment the oxide is not in all cases Al_2O_3. Al_2O_3 is only found for the etched surface, whereas $Al_2O_{2.87}$ and $Al_2O_{1.3}$ are found 1 day after blasting with glass beads and alumina grit, respectively. Hence, not all Al atoms possess their maximum degree of oxidation (+3) in the blasted surfaces. These Al atoms are expected to be very reactive due to their deficit of electron density.

These induced chemical surface states are found to influence the curing reaction of the epoxy system. Different degrees of conversion of epoxy groups are measured on the pretreated substrates. Interestingly, the final degree of conversion correlates with the ranking of the degree of oxidation in the oxides. For this behaviour it is suggested that a preferential adsorption for DETA takes place on the blasted aluminium surface. As a second mechanism, the epoxy system tends to demix gradually into a DETA-rich phase on the aluminium.

In the bondline of the pretreated substrates different epoxy network structures are formed which differ in their local molecular mobility. These network structures are inhomogeneous as they possess a mobility gradient perpendicular to the substrate surface (compare Fig. 11). With respect to the extremely low epoxy conversion, a low molecular mobility of the epoxy adhesive is found for the near-interface region on the alumina-blasted surfaces. It is assumed that the curing reaction is locally catalysed or that even the epoxy attaches to a chemisorbed layer of the amine-curing agent.

It is convincing that the different network structures in turn should exert an effect on the mechanical properties and on the ageing behaviour of the epoxy aluminium bonds. This is illustrated in a supplementary investigation with joints prepared of the same sample system [5,6].

In conclusion, for the investigated system it is shown that the effect of mechanical treatment for metal bonding is very complex and comprises topological changes and changes in the chemical surface state of the adherends. Surprisingly, the pretreated surface not only influences the formation of the network structure in the near-interphase region but also far from the substrate.

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References

[1] Guy D. Engineered materials handbook, adhesives and sealants. Metals Park: ASM International; 1999. p. 236–75.

[2] Habenicht G. Kleben: Grundlagen, Technologie, Anwendungen. Berlin: Springer; 1997. p. 495–507.

[3] Critchlow GW, Brewis DM. Review of surface pretreatments for aluminium alloys. Int J Adhesion Adhesives 1996;16:255–75.

[4] Brockmann W, Emrich S. Model studies of the influence of enlarged surface areas due to increased adherend macroroughness on the adhesive strength and long-term-durability of aluminium–epoxide joints. Conference Proceedings EURADH 2000 Lyon, France.

[5] Neeb T, Brockmann W. Network structure induced by mechanical treatment and their influence on the mechanical properties of epoxide bonds. Conference Proceedings WCARP-II, Orlando, USA, 2002.

[6] Neeb T, Bockenheimer C, Brockmann W, Possart W, Valeske B. Surface modification of metals by mechanical pretreatment. Conference Proceedings 23rd Annual Meeting of the Adhesion Society, Myrtle Beach, SC, USA, 2000.

[7] Lin CJ, Bell JP. The effect of polymer network structure upon the bond strength of epoxy–aluminium joints. J Appl Polym Sci 1972;16:1721–33.

[8] Dillard DA. Engineered materials handbook, adhesives and sealants. Metals Park: ASM International; 1999. p. 313–24.

[9] Safavi-Ardebili V, Sinclair AN, Spelt JK. Experimental investigation of the interphase in an epoxy–aluminium system. J Adhesion 1997;62:93–111.

[10] Possart W, Bockenheimer C, Valeske B, Wehlack C, Neurohr H, Brockmann W, Neeb T, Emrich S. DFG Research Report, Br 435/17-1/17-2, 2001.

[11] Bockenheimer C, Possart W, Valeske B. Network structure in epoxy aluminium bonds after mechanical pretreatment. Conference Proceedings WCARP-II, Orlando, USA, 2002.

[12] Neeb T. Adhäsionsmechanismen an mechanisch vorbehandelten Metalloberflächen. Thesis. Kaiserslautern University, Germany, 1999.

[13] Valeske B, Brockmann W, Neeb T, Possart W. Adhesive bonding on mechanically treated metal surfaces. Conference Proceedings EURADH 1998, Garmisch-Partenkirchen.

[14] Possart W, Bockenheimer C, Valeske B, Neeb T. The state of metal surfaces after blasting treatment—part I: technical aluminium. Surf Inter Anal, submitted for publication.

[15] Affrossman S, Brown NMD, Pethrick VK, Sharma VK, Turner RJ. Appl Surf Sci 1983;16:469–73.

[16] Boerio FJ, Chen SL. Appl Spectrosc 1979;33(2):121–6.

[17] Comyn J, Horley CC, Oxley DP, Pritchard RG, Tegg SL. J Adhesion 1981;12:171.

[18] Dillingham RG, Boerio FJ. J Adhesion 1987;24:315–35.

[19] Batzer H. PolymereWerkstoffe, Band 1: Chemie und Physik. Stuttgart: Georg Thieme Verlag; 1985. p. 384–440.

[20] Runt JP, Fitzgerald JJ. Dielectric spectroscopy of polymeric materials. Washington: ACS; 1997. p. 397–398.