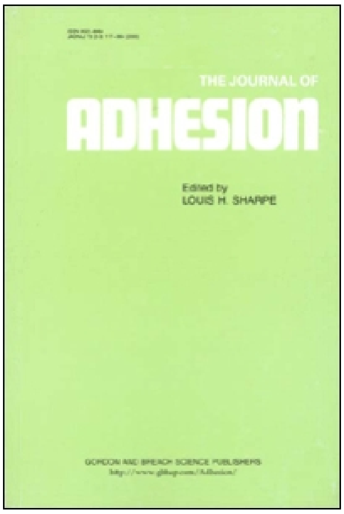
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Ageing of Adhesive Bonds with Various Surface Treatments, Part 2: Acrylic Modified Amine-Cured Epoxy Resin

Robert Comrie[a]; Stanley Affrossman[a]; Richard A. Pethrick[a]
[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

To cite this Article Comrie, Robert , Affrossman, Stanley and Pethrick, Richard A.(2005) 'Ageing of Adhesive Bonds with Various Surface Treatments, Part 2: Acrylic Modified Amine-Cured Epoxy Resin', The Journal of Adhesion, 81: 12, 1183 — 1197

To link to this Article: DOI: 10.1080/00218460500371723

URL: http://dx.doi.org/10.1080/00218460500371723

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 81:1183–1197, 2005
Copyright © Taylor & Francis Inc.
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460500371723

Taylor & Francis
Taylor & Francis Group

Ageing of Adhesive Bonds with Various Surface Treatments, Part 2: Acrylic Modified Amine–Cured Epoxy Resin

Robert Comrie
Stanley Affrossman
Richard A. Pethrick
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK

Ageing of adhesive-bonded aluminium–diglycidyl ether of bisphenol A based aliphatic amine–cured acrylic modified epoxy resin reinforced with fused silica exposed to 100% humidity and cycled between 42–48–42°C every hour is reported. Moisture uptake was followed using broadband dielectric measurements. It was found that the adhesive absorbs moisture very rapidly, the adhesive undergoes significant swelling, and there is a consequent reduction in strength consistent with plasticization of the matrix. The dielectric measurements parallel closely the changes occurring in the adhesive bond line and provide a nondestructive method for monitoring the changes in bond strength. The changes that occur are dominated by the effects of moisture on the adhesive, various pretreatments have little effect on the ageing process, and interfacial failure in this case does not make a significant contribution to the failure of these joints.

Keywords: Acrylic toughened resins; Dielectric measurements; Epoxy resins; Silica/silicon pretreatment; Titanium/zirconium pretreatment

INTRODUCTION

Adhesive bonding of aluminium structures plays an important role in the creation of aerospace and automobile structure [1]. In the previous article [2] the effects of moisture ingress into a series of joints produced with different pretreatments were reported. Surprisingly, the changes observed during ageing were fairly insensitive to the

Received 27 July 2004; in final form 22 August 2005.

Address correspondence to Richard A. Pethrick, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Thomas Graham Building, Glasgow, G1 1XL UK. E-mail: r.a.pethrick@strath.ac.uk

pretreatment and were dominated by the effects of plasticization on the adhesive resin, a dicyandiamide-cured epoxy reinforced with fumed silica [2]. The article demonstrated that for this system the dielectric method was able to monitor nondestructively the changes occurring in the adhesive joint. In the present article, a diglycidyl ether of bisphenol A–based, aliphatic amine–cured, epoxy resin reinforced with fused silica and toughened with acrylic resin particles is investigated. The aim of the study was to establish whether the dielectric method was also capable of monitoring this related but different resin system.

Choice of Adhesive

The addition and copolymerisation of acrylic monomers has been recently investigated as a route to producing toughened resins that have the advantage of being oil tolerant [3]. Poly(2-ethyl hexyl acrylate)s containing carboxyl and epoxy functions have been used to toughen aluminum silicate–filled epoxy resin cured with 4,4′-diaminodiphenyl methane [3]. The lap-shear strength of the filled epoxy resins is higher than that of unfilled ones. Analysis of adhesive failure surfaces by scanning electron microscopy (SEM) indicated the presence of a two-phase microstructure. A two-phase structure has also been observed in this type of resin over a broad range of composition [4]. Other types of acrylic have also been investigated, including methyl methacrylate (MMA) and copolymers of MMA and glycidyl methacrylate (GMA) [5]. When the mixture of the acrylic particles and the epoxy resin are heated, the particles are swollen with the epoxy resin and a soft gel is formed. Further heating promotes the cross-linking reaction and vitrification follows. Incorporation of 5 mol% of GMA showed the best enhancement of impact strength and adhesive property. Similar effects have been reported with other types of acrylic monomers [3–7]. When properly formulated, the acrylic modified epoxy resins-improve their fracture resistance. The initial adhesive mixture also has the advantage of being able to “wet out” substrates contaminated with oil.

Treatment of Substrate

The aluminium used in all the bonds studied in this article was subjected to an initial etch cleaning process. The aluminium sheet was exposed to a mixture of sulphuric acid and hydrofluoric acid in an nonionic surfactant. The sulphuric acid is employed to maintain acid conditions during the etching process and the nonionic surfactant ensures wetting of the aluminium and acts as a defoaming agent. The hydrofluoric acid reacts with aluminium to form salts, which remain in solution. The sheet is then washed prior to being pretreated and bonded.

Silica/Siloxane Pretreatment

A stable surface layer can be created using a silica/siloxane [8]. The silica/siloxane pretreatment system consists of silica particles dispersed within a silicate/siloxane matrix that is applied to the hot, previously anodised, substrate. The silicate particles produce a rough surface, enhancing the mechanical interlocking between the substrate and adhesive.

Non-Rinse Chrome Pretreatment

The surface is treated with a silica suspension deposited onto a partly reduced chromic acid mixture and produces films with a silica-rich surface and chromium-rich interfacial zone between the silica and the metal substrate [9]. The chromium-rich layer consists of a mixture of trivalent and hexavalent compounds. These compounds are formed as a consequence of the acid dissolution of the metallic substrate's oxide film, followed by the dissolution of the metal and precipitation of chromium hydroxides resulting from reduction of chromium ions [9]. Bond durability is enhanced by the production of a convoluted surface topography resulting from the presence of colloidal silica particulates that are bonded through silanol groups to the epoxide groups in the adhesive. Exposure of films containing Cr(VI) compounds to moisture releases ions, which react with the aluminium and stabilise the oxide layer.

Titanium/Zirconium (Ti/Zr) Pretreatment

The titanium/zirconium (Ti/Zr) pretreatment [10, 11] uses a mixture of polyacrylic acid and fluorozirconic (H_2ZrF_6), fluorotitanic (H_2TiF_6), and fluorosilicic acids (H_2SiF_6) in an aqueous solution. Hydrofluoric acid is added to provide a source of free fluoride, which dissolves the aluminium surface. The resultant rise in pH leads to precipitation of the coating mixture that is then heated to form a stable coating.

This study attempts to compare the changes that occur in the dielectric spectrum, during ageing of aluminium–epoxy bonded adhesives with the variation in the mechanical properties.

EXPERIMENTAL

Sample Preparation

Lap-shear joints were produced from 2.0-mm-gauge AA5754 aluminium alloy (typical composition, 96.15% Al, 0.10% Si, 0.20% Fe, 0.10% Cu, 0.25% Mn, 3.2% Mg) sheets, which were subjected to the pretreatments indicated previously. The joints consisted of 100 mm × 20 mm adherend with an overlap area of 10 mm × 20 mm and were bonded using a jig. The bond line thickness of the joint was 200 µm, controlled by the addition of 1% by weight of Ballotini glass spheres to the adhesive, and spring clips were used to achieve a constant pressure during cure. The adhesive was a diglycidyl ether of bisphenol A–based, amine-cured, epoxy resin. The adhesive contains an acrylic rubber toughening agent based on poly(2-ethyl hexyl acrylate) and a silicate-based inorganic filler. Curing conditions were 20 min at 170 °C. Fifteen joints were prepared for each of the pretreatments studied.

Ageing of Samples

A humidity cabinet that creates (100%) humidity, with the temperature cycling between 42–48–42 °C every hour, was used for ageing the joints [12]. The temperature cycling process is a standard procedure used by Alcan in assessment of the effects of aging on adhesive-bonded joints. The joints were initially examined dielectrically on a weekly basis, which was decreased to once every two months as the ageing progressed.

Dielectric Measurement Techniques

The joints were removed from the ageing bath, dried, and cooled to ambient temperature. The ends of the joints were abraded to remove the surface oxide so as to ensure that good electrical connection was achieved. Prior to ageing, the bond line thickness for each of the joints measured was determined by taking the average of several micrometer measurements across the bonded area of each joint and was found to be 0.17 mm ± 0.05 mm. Three joints were studied for each of the surface treatments investigated, and the data represent the average of these data. Measurements were performed using a Solatron, Hauts UK, 1250A Frequency Response Analyser (FRA), that generates frequencies between 10^{-3} Hz and 63 kHz. The high-frequency dielectric measurements were carried out using a Hewlett Packard HP8753A network analyser, Hewlett Packard, Queenferry, Scotland, UK; both methods used have been described previously [2].

Mechanical Testing

Tensile tests were carried out on batches of three joints using a cross-head displacement speed of 2.0 mm/min and a specimen grip length of 75 mm, with the maximum loads being recorded using an Instron Series IX Automated, Materials Testing System, Instron Ltd., High Wycombe, Buckinghamshire, UK.

Modes of Failure

The failure surfaces of the mechanical test pieces were scanned images using a Hewlett Packard 4 C high-resolution flatbed scanner. These images allowed visual assessment and differentiation between adhesive and cohesive failure.

RESULTS

Dielectric Studies, Low-Frequency Dielectric Results (0.01 Hz–63 kHz)

The variation of dielectric permittivity and loss with ageing time, Figure 1, indicates dramatic changes occur after only a relatively short time for two of the joint systems: the etched-only and the silica/siloxane systems. The titanium/zirconium (Ti/Zr) system and no-rinse chrome system exhibited very similar behaviour. The low-frequency feature is consistent with the material being phase separated. In phase-separated materials, the dielectric relaxation often shows a large loss feature at low frequency associated with the heterogeneous nature the material and ascribed to the so-called Maxwell Wagner Sillers loss processes [13–16]. Ionic conduction is a result of chloride, sodium, and hydrogen ions from the synthesis of epoxy resins using epichlorohydrin, and contaminants introduced with the silicate filler [16]. Normally, an epoxy resin, even when it contains a phase-separated structure, would be expected to have exhibited a much lower loss at low frequencies because the fully cured epoxy would inhibit the ion migration. However, because the acrylic is initially soluble in the epoxy resin, it will be retained as a plasticizer and residual monomer and will aid the ionic mobility by lowering the T_g of the epoxy resin.

After ageing for 8 days, a massive increase in both the dielectric permittivity and loss for the samples was observed, Figure 1, The water ingress drastically plasticises the adhesive and increases the mobility of the ions in the polymer matrix. The change in permittivity at 10 kHz with ageing time, Figure 2, shows there is an initial sharp rise in permittivity after only 8 days in the humidity ageing cabinet.

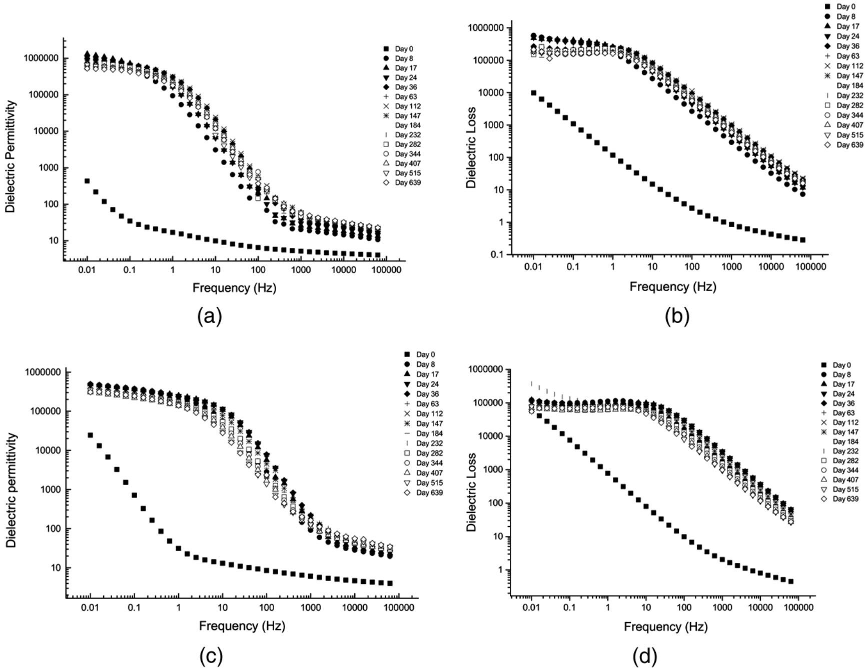
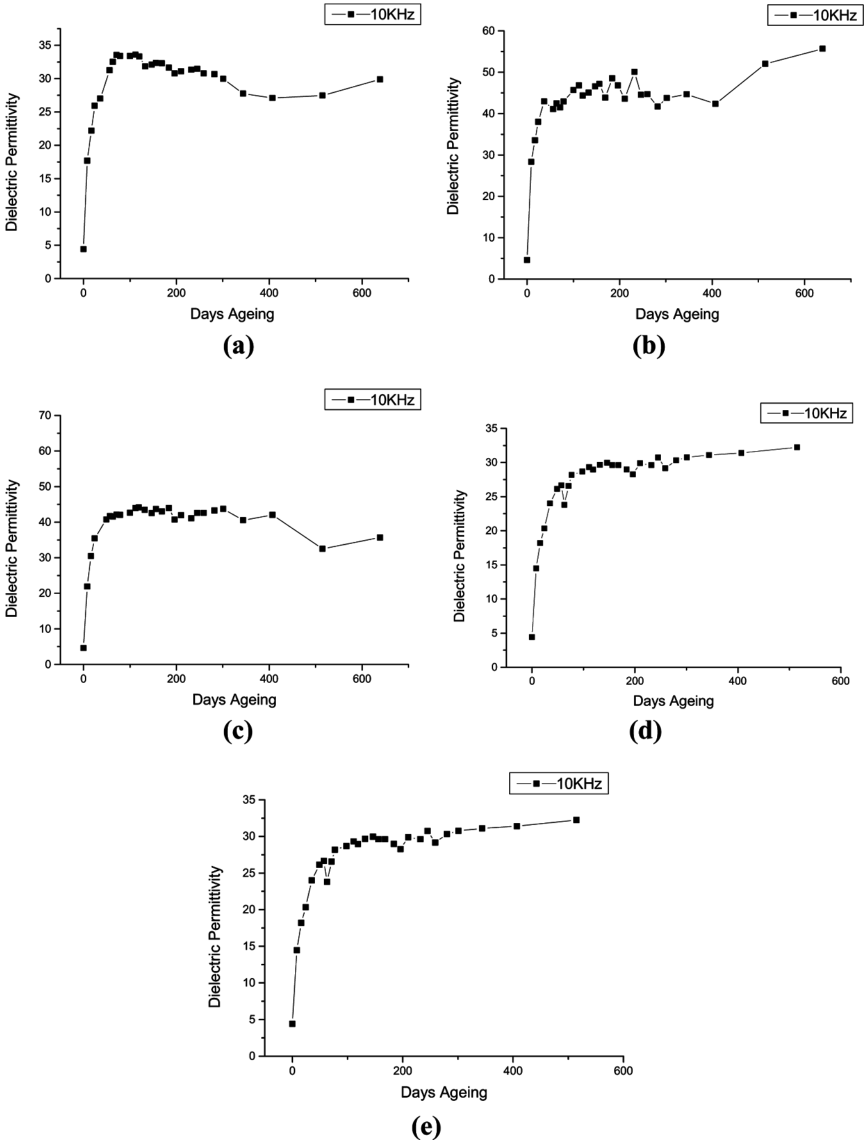


FIGURE 1 Low-frequency dielectric data for the etched-only system (a) dielectric permittivity and (b) dielectric loss; and the silica/siloxane system (c) dielectric permittivity and (d) dielectric loss.

After the samples have been aged for 70 days the permittivity begins to exhibit an almost constant value, indicating that the adhesive is becoming saturated with water. After approximately 100 days of ageing, the permittivity of the samples can be seen to drop in value, which can be attributed to a stress relaxation process occurring within the epoxy matrix and the creation of microvoids within the matrix. The lowering of the dielectric permittivity may be explained by the voids being created but not containing any moisture. Because the resin has been cured at 170 °C and then cooled to room temperature, it may be argued that the epoxy will contain stresses frozen within the matrix. Subsequent perturbation of the matrix, resulting from the ingress of water, may then result in stress relaxation and densification. Water then continues to enter the matrix, resulting in further plasticisation of the sample, indicated by increases in both the dielectric permittivity and loss of the sample [17]. The effects of thermal cycling have been discussed by many authors [18–26]; however, the work of Humfield and Dillard [27] shows the effects that thermal



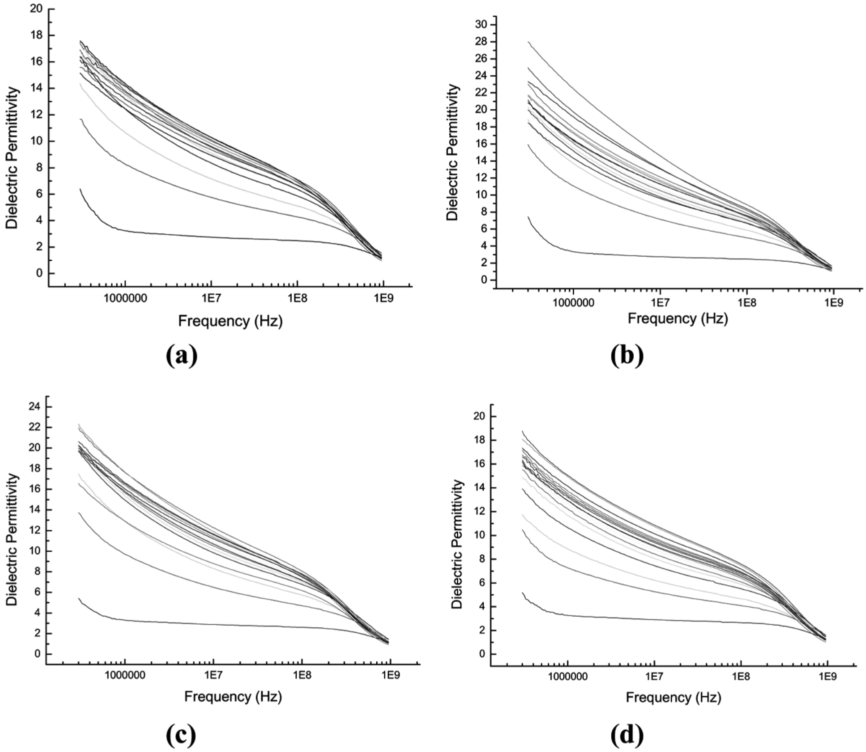
(a) (b) (c) (d) (e)

FIGURE 2 Variation of dielectric permittivity at 10 kHz *versus* ageing time for (a) the no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, (d) etched-only system, and (e) no-rinse chrome system.

cycling can have in the destabilisation of the adhesive–adherend interface. This type of mechanism could be operative with this adhesive [27]. The dielectric permittivity data at 10 kHz for the no-rinse chrome adhesive system indicates initial plasticisation due to the absorption of water. However, after about 80 days of ageing, the stress relaxation process occurs, leading to the densification of the adhesivg-and a decrease in the dielectric loss. Similar effects have been observed previously [18] and are associated with collapse of microvoids present within the adhesive upon curing.

High-Frequency Dielectric Results (300 kHz–13 GHz)

The variation of the high-frequency permittivity with ageing time in the humidity cabinet, Figure 3, indicated that the adhesive rapidly absorbs moisture across the whole dielectric spectrum. The initial permittivity values for the adhesive at 1 MHz range between 3.23 and 3.30 with an average value of 3.29. A sharp rise in permittivity observed within the first 10 days; can be attributed to a substantial increase in the concentration of "free" water residing in voids and microcavities within the epoxy resin. The mixing of the various components will be expected to incorporate air into the resin; therefore, voids may expected once the cure cycle has been completed, unless the cure is performed under vacuum. Absorption of moisture will allow these voids to be filled, and this will be observed as free water [18, 19]. In previous studies, it has been shown that conversion of interfacial oxide to hydroxide produces a dielectric feature, which is located at approximately 3 MHz. By monitoring the changes which occur at this frequency, it is possible to identify the point at which modification of the surface and, hence, the interface occurs. In previous studies [1], the point at which a marked change in the permittivity with time occurs correlated well with the observation of the failure mechanism changing from one of cohesive to adhesive failure. The change in permittivity at 3 MHz against ageing time, Figure 4, can be seen to peak after approximately 100 of days ageing and then plateau. This behaviour is indicative that the resin has reached its saturation level. If it is assumed that the permittivity change, $\Delta\varepsilon'$, between the dry and saturated state can be assigned to the water uptake, then dividing the change by 80.36, which is the permittivity for free water at 25 °C, allows the amount of moisture to be calculated. Applying this calculation to the no-rinse chrome system, a value of approximately 10.6% water is obtained, indicating the presence of a large amount of water within the epoxy. Similar results are obtained for the other systems. This calculation assumes that the total change is due to



(a) (b) (c) (d)

FIGURE 3 High-frequency dielectric permittivity results for (a) the no-rinse chrome system, (b) silica siloxane system, (c) titanium/zirconium (Ti/Zr) system, and (d) etched-only system.

moisture in the matrix and assumes that there has been no significant change in the surface oxide layer. If oxide-to-hydroxide conversion had occurred, then an additional loss peak would be expected, which was not observed. Throughout the ageing process the permittivity values for the joints can be seen to peak and trough occasionally; that can be associated with the stress relaxation processes occurring within the epoxy matrix. An example is the trough that can be observed in the permittivity values for the silica/siloxane system after 231 days ageing; this appears to indicate the densification of the sample due to the stress relaxation process. The increase in permittivity that can be observed after 231 days ageing may be associated with the occurrence of plasticisation of the adhesive. The densification process due to relaxation of the network is well known from ageing studies and is consistent with the model of Humfield and Dillard [27]. The data

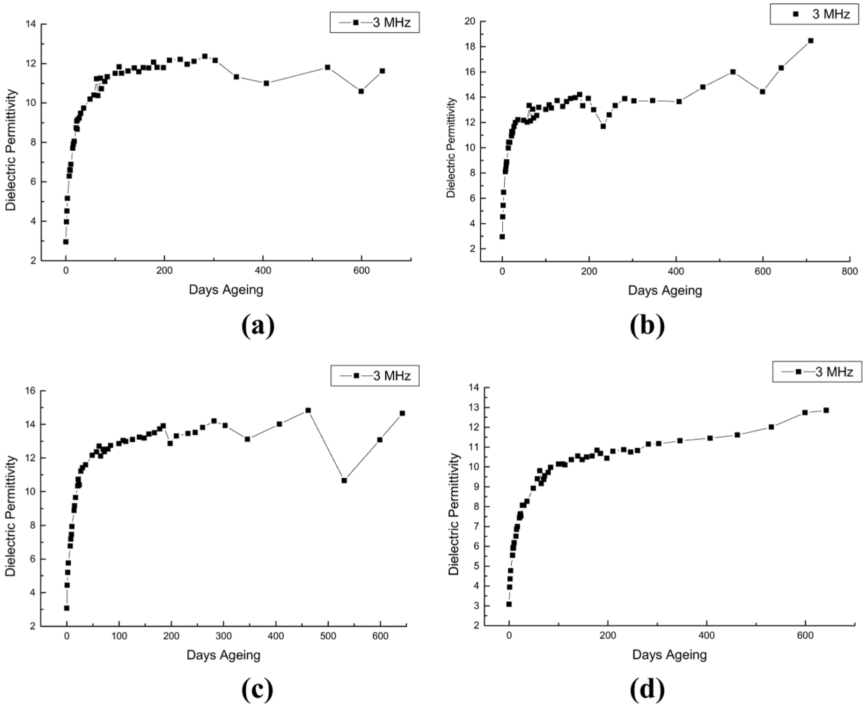


FIGURE 4 Dielectric permittivity at 3 MHz *versus* ageing time; (a) no-rinse chrome system, (b) silica/siloxane system, (c) titanium/zirconium (Ti/Zr) system, and (d) etched-only system.

appear to indicate that although the general shapes of the water-absorption profiles are similar, there are differences between the surface treatments. These differences are probably the effects of the moisture interacting with the surface, treatments and creating new dipole species that are adding to the strength of the relaxation. The apparent trough after the initial rise is consistent with been completed, unless the cure is performed under vacuum. Absorption of moisture will allow these voids to be filled, and this will be observed as free water [18, 19]. In previous studies, it has been shown that conversion of interfacial oxide to hydroxide produces a dielectric feature, which is located at approximately 3 MHz. By monitoring the changes which occur at this frequency, it is possible to identify the point at which modification of the surface and, hence, the interface occurs. In previous studies [1]. The point at which a marked change in the permittivity with time occurs correlated well with the observation of the failure mechanism changing from one of cohesive to adhesive failure. The change in permittivity at 3 MHz against ageing time, Figure 4, can be seen to peak after approximately 100 days of ageing and then plateau. This behaviour is indicative that the resin has reached its saturation level. If it is assumed that the permittivity change, $\Delta\varepsilon'$, between the dry and saturated state can be assigned to the water uptake, then dividing the change by 80.36, which is the permittivity for free water at 25 °C, allows the amount of moisture to be calculated. Applying this calculation to the no-rinse chrome system, a value of approximately 10.6% water is obtained, indicating the presence of a large amount of water within the epoxy. Similar results are obtained for the other systems. This calculation assumes that the total change is due to moisture in the matrix and assumes that there has been no significant change in the surface oxide layer. If oxide-to-hydroxide conversion had occurred, then an additional loss peak would be expected, which was not observed. Throughout the ageing process the permittiviry values for the joints can be seen to peak and trough occasionally; that can be associated with the stress relaxation processes occurring within the epoxy matrix. An example is the trough that can be observed in the permittivity values for the silica/siloxane loxane system after 231 days ageing; this appears to indicate the densification of the sample due to the stress relaxation process. The increase in permittivity that can be observed after 231 days ageing may be associated with the occurrence of plasticisation of the adhesive. The densification process due to relaxation of the network is well known from ageing studies and is consistent with the model of Humfield and Dillard [27]. The data appear to indicate that although the general shapes of the water-absorption profiles are similar, there are differences between the surface treatments. These differences are probably the effects of the moisture interacting with the surface treatments and creating new dipole species that are adding to the strength of the relaxation. The apparent trough after the initial rise is consistent with this idea; the moisture initially present as water on conversion to the surface-modified species may have a smaller dipolar strength that is reflected in a decrease in the amplitude of the dielectric permittivity. No distinct characteristic relaxation features were be detected that could be assigned to specific surface treatments.

Mechanical Tests

The mechanical testing results, Figure 5, show that after only 7 days in the humidity cabinet a dramatic reduction in the residual strength of the samples has occurred. For example, the strength of the

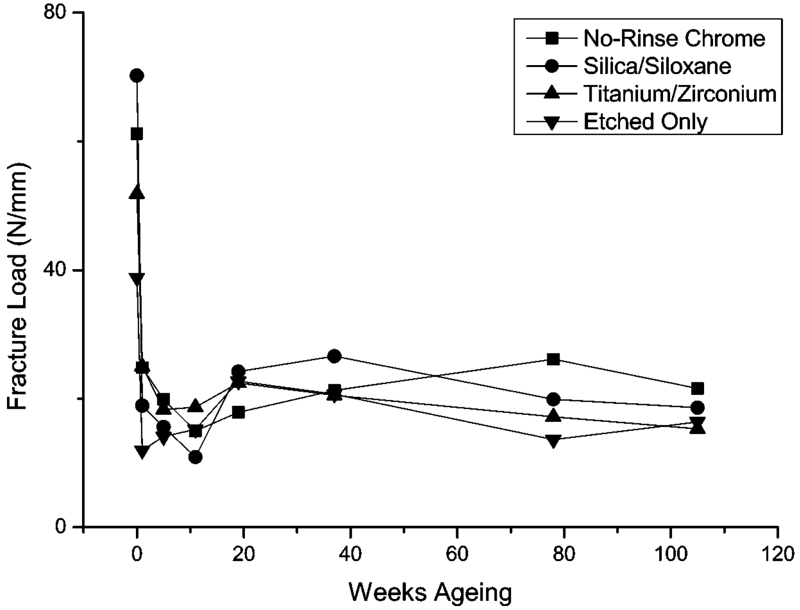


FIGURE 5 Lap-shear testing results for the low-strength adhesive systems.

silica/siloxane system has dropped by 73% during the initial week in the humidity cabinet. The results then plateau off for the remainder of the ageing period. The mechanical testing results mirror the water-uptake profiles obtained from the dielectric analysis of the samples. Because the samples failed cohesively throughout the ageing study, the loss in strength of the samples can be attributed to the adhesive being plasticised by the ingress of water.

Mechanical Testing Results of the Neutral Salt-Spray Samples

The mechanical testing results for joints aged at 43 °C in a 5% neutral salt spray are shown in Figure 6. The salt-spray test is, as its name implies, an ageing process in which the samples are subjected to a spray of water rather than the usual deionised environment. This test simulates the type of exposure encountered in an automobile situation. The dielectric results show that the ingress of water into adhesively bonded systems occurs very rapidly during the first 7 days of exposure, and this is mirrored by a 70% reduction in joint strength. Because the adhesive failed cohesively throughout the ageing period, the loss in joint strength can be attributed to the adhesive being

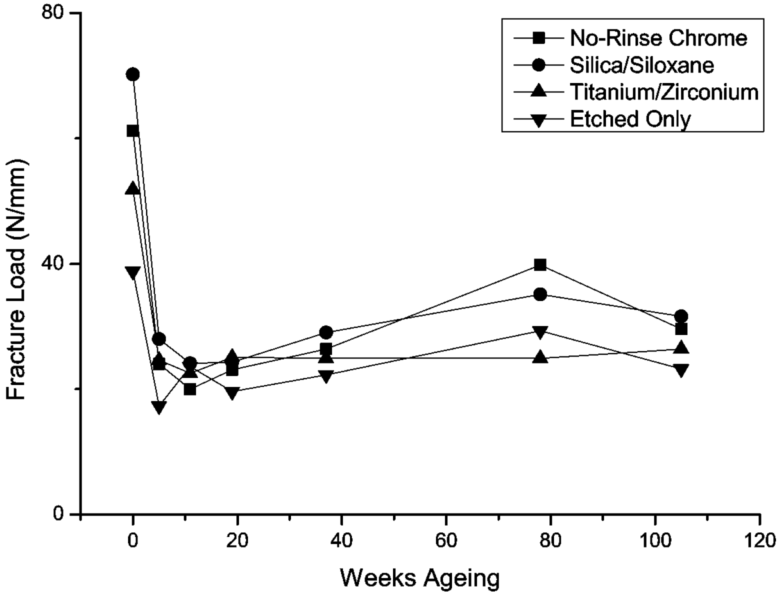


FIGURE 6 Lap-shear testing results for the low-strength adhesive systems aged under neutral salt-spray conditions.

plasticised by the ingress of moisture. The interesting observation from the mechanical testing is that the etched-only pretreatment exhibited as good long-term durability as the other pretreatment systems. This result implies that, provided the metal has been property cleaned, good bond durability can be achieved without the need for any further pretreatment.

The mechanical testing results show an initial dramatic decrease in strength, a 70% reduction in 7 days, throughout the remaining ageing period although the strength of the samples also appears to plateau off. For some of the samples, specifically the no-rinse chrome and silica/siloxane systems, the joints strength can be seen to recover partially as the ageing process proceeds, indicative of stress relaxation processes occurring, leading to densification of the resin and an increase in the mechanical properties of the resin.

DISCUSSION

The high-frequency dielectric data indicate that there is in this adhesive a significant amount of free water in the epoxy resin, and this is consistent with there being a significant microvoid content in the resin. Vapour pressure assisted void growth and cracking of polymeric films has been observed by others [20–22]. Under the combined action of thermal stress and high vapour pressure, the rate at which changes occur is related to the value of the T_g of the matrix, and both pre-existing and newly nucleated voids grow rapidly and coalesce. In extreme situations, vapour pressure alone could drive voids to grow and coalesce, and no additional external stimulus is required. Crack-growth resistance-curve calculations using these models show that high vapour pressure combined with high porosity can bring about severe reduction in the fracture toughness. In some cases, high vapour pressure accelerates void growth and coalescence, resulting in brittle-like interface delamination. The observed loss in strength is consistent with these observations and explains the connection between the high values of the dielectric permittivity and the loss in strength. The large MWS feature is consistent with the idea that the structure is phase separated and may have a significant void structure.

The effect of various pretreatments on the durability of adhesive bonded joints has been reported recently [25]. A chromate-free Ti-Zr–based pretreatment provided improved durability relative to an alkaline etch and deoxidation pretreatment, but was clearly inferior to chromating in terms of adhesion. It was observed that excessive Ti-Zr oxide deposition occurred in the vicinity of intermetallic alpha-Al(Fe,Mn)Si particles during pretreatment, which significantly reduced the performance of bonded joints during a wedge test. The usefulness of the dielectric measurements to monitor nondestructively the changes in mechanical properties once more is demonstrated.

CONCLUSIONS

The observation variation in the mechanical properties for the joints studied in this article are consistent with the dominant ageing process associated with plasticization of the resin matrix. The high-frequency dielectric data indicated that during the period of ageing reported here there were no significant changes occurring in the interfacial region for any of the pretreatments studied. The changes in the dielectric spectrum in the case of the silica-filled epoxy resin contains a dipolar contribution from the heterophase nature of the polymer matrix, which becomes evident upon hydration of the silica particles. The close similarity in the changes in the dielectric spectra for all the systems is consistent with plasticization being the dominant effect of water adsorption. The drop in the dielectric permittivity after prolonged periods of ageing is consistent with the formation of microvoids within the matrix. This study illustrates the type of molecular-scale information that is available through dielectric investigation.

ACKNOWLEDGEMENTS

One of us (R.C.) thanks Alcan for a studentship for the period of this research.

REFERENCES

[1] Kinloch, A. L., *Proc. Instn. Mech. Engrs.* **221**, 308–335 (1997).
[2] Comrie, R., Affrossman, S., Hayward, D., Pethrick, R. A., Zhou, Z., and Thompson, G. E., *J. Adhes.* **81**(12), XX–XX (2006).
[3] Kar, S., Gupta, D., and Banthia, A. K., *J. Adhes. Sci. Technol.* **16**(14), 1900–l914 (2002).
[4] Ratna, D. and Simon, G. P., *Polymer* **42**(18), 7739–7747 (2001).
[5] Ashida, T. and Ochi, M., *J. Adhes. Sci Technol.* **11**(4), 519–530 (1997).
[6] Pocius, A. V., Schultz, W. J., Thompson, W. L., and Adam, R. A., *J. Adhes.* **41**(1–4), 189–202 (1993).
[7] Riew, C. K., Siebert, A. R., Smith, R. W., Fernando, M., and Kinloch, A. J., *Advan. Chem. Ser.* **252**, 33–44 (1996).
[8] Hartman, N., European Patent 92905413.8-2103 (1997).
[9] Vussey, C. A., Albon, C., and Holker, K., U.S. Patent 3,706,603 (1972).
[10] Dollman, D. Y. and O'Grady, T. J., U.S. Patent 4,191,596 (1960).
[11] Packham, D. E. (Ed.) *Handbook of Adhesion* (Longman Scientific and Technical, Harlow, 1992).
[12] Personnel communication from Alcan.
[13] Pethrick, R. A., North, A. M., and Wilson, A. D., *Polymer* **19**, 913–922 (1978).
[14] Pethrick, R. A., North, A. M., and Wilson A. D., *Polymer* **19**, 923–930 (1978).
[15] Hayward, D., Pethrick, R. A., Siriwittayakorn T., *Macromolecules* **25**, 1480–1486 (1992).
[16] MacKinnon, A. J., Jenkins, S. D., McGrail, P. T., and Pethrick, R. A., *Polymer* **34**(15), 3252–3263 (1993).
[17] Hayward, D., Hollins, E., Johncock, P., McEwan, I., Pethrick, R. A., and Pollock, E. A. *Polymer* **38**(5), 1151 (1997).
[18] Mijovic, J. and Zhang, H., *Macromolecules* **36**(4), 1279–1288 (2003).
[19] Pethrick, R. A., Hollins, E. A., McEwan, I., MacKinnon, A. J., Hayward, D., Cannon, L. A., Jenkins, S. D., and McGrail, P. T., *Macromolecules* **29**(15), 5208–5214 (1996).
[20] Adams, R. D. and Wake, W. C., *Structural Adhesive Joints in Engineering* (Elsevier Applied Science Publications, London, 1984).
[21] Cheng, L. and Guo, T. F., *Interface Sci.* **11**(3), 277–290 (2003).
[22] Lunder, O., Lapique, F., Johnsen, B., and Nisancioglu, K., *Int. J. Adhes. Adhes.* **24**(2), 107–117 (2004).
[23] Cotter, J. L., in *Developments in Adhesives—1*, W. C. Wake (Ed.) (Applied Science Publishers, London, 1977), p. 1.
[24] Jethwa, J. K. and Kinloch, A. J., *J. Adhes.* **61**, 71–95 (1997).
[25] Kinloch, A. J., *Adhesion and Adhesives—Science and Technology* (Chapman and Hall, London, 1987), p. 302.
[26] Ahearn, J. S., in *Adhesion Aspects of Polymeric Coatings*, K. L. Mittal (Ed.) (Plenum Press, New York, l983).
[27] Humfeld, G. R. and Dillard, D. A., *J. Adhes.* **65**(1–4), 277–306 (1998).