ELSEVIER

International Journal of Adhesion & Adhesives 20 (2000) 489–495

International Journal of Adhesion & Adhesives

Effects of microwave curing carbon doped epoxy adhesive-polycarbonate joints

Bambang Soesatyo[a], Aaron S. Blicblau[b,*], Elias Siores[c]

[a]School of Engineering and Science, Swinburne University of Technology, John Street, Hawthorn, Melbourne, Australia
[b]Swinburne University of Technology, John Street, Hawthorn, Melbourne, Australia
[c]Industrial Research Institute Swinburne (IRIS), Swinburne University of Technology, John Street, Hawthorn, Melbourne, Australia

Accepted 8 May 2000

Abstract

This paper reports on the effect of adding two types of carbon black; Vulcan 66 and Sterling, to epoxy adhesive in lap joint of polycarbonate sheet to improve the microwave curing characteristics. The maximum bond shear strength after a 30 s cure time was compared with the two carbon black types at various dopant concentrations. The addition of the Vulcan 66 carbon black resulted in the higher bond strength when compared to Sterling carbon. Microscopical analysis of the fractured joint was carried out using SEM, and residual stress was investigated with a polariscope. Raman spectra revealed changes in material characteristics resulting from microwave processing

1. Introduction

Joining materials to achieve high strength and functionality of design is a technique which has been utilised for thousands of years. Mechanical joining using non-metallic nails was used before the beginning of the bronze and iron ages to construct wooden structures both large and small. The advent of the metallic ages resulted in the development of mechanical joining processes using nails, screws, nuts and bolts, together with heat associated joining techniques employing brazing and welding [1,2]. Adhesive bonding is an alternate method by which materials can be joined to generate assemblies or structures without the use of mechanical fasteners, relying on the properties of the adhesive and the material which it joins (adherend). The use of adhesives as a joining medium has traditionally been used in a very demanding, load-bearing applications, for both metallic and non-metallic materials. Modern polymer technology has brought with it the necessity to join materials without mechanical fasteners yet which have high strengths. A large variety of high-strength polymeric adhesives has been developed since the beginning of the space age in the 1940s, encompassing both thermosetting and thermoplastic adhesives, e.g., anaerobic adhesives, epoxies, hot melt adhesives, cyanoacrylates, silicones and UV cured adhesives [3–5].

There has been a recent increase in the use of structural thermoplastic component or structures which are often manufactured by plastics moulding techniques. These are net-shape processes requiring little or no finishing. In some instances net shape processing is not possible, often when the structure is complex in detail or die costs are prohibitive due to the small number of components required. In these instances, components may be manufactured by cutting and shaping techniques with final assembly utilising high-performance adhesives for the achievement of structural characteristics. The use of epoxy adhesive for joining various types of thermosetting substrates, for both structural and non-structural applications has been given much attention recently, by taking advantages of the adhesive's high strength [5–7]. The achievement of high strength in epoxy adhesives is accomplished by the use of high temperature during curing (from approximately 120 to 185°C), extended curing times and where necessary the application of pressure to the join. Most epoxy adhesives available in the industrial market consist of various types, grades and formulations whose curing procedures are varied and may

* Corresponding author. Tel.: +61-3-9214-8372; fax: +61-3-9214-8264.
E-mail address: ablicblau@swin.edu.au (A.S. Blicblau).

0143-7496/00/$ - see front matter
PII: S0143-7496(00)00020-8

involve ultraviolet (UV), infrared (IR) or conventional (thermal) type oven curing. However, to obtain faster epoxy adhesive processing and curing times the use of microwave curing procedures has recently been investigated [8–11]. The faster curing times are due to the polar groups in the hardener component of epoxy adhesives which can be cured by microwaves without being destroyed.

To facilitate the fast heating of the epoxy adhesive, carbon black is added as a dopant to the adhesive. Without the addition of carbon black, heating of the epoxy adhesive under microwave radiation will be either difficult or impossible to achieve. Carbon black absorbs microwaves, and like polyaniline salts which are electrically conducting polymers [12], can enhance the absorbance of the microwave energy in the epoxy due to its high dielectric loss properties. The hardening of the adhesive will be due to cross-linking of the epoxy via the curing agent. The objective of this work was to study the effect of various carbon black concentrations (mixed into two different epoxy adhesives) on the joint strength of polycarbonate adherend in the form of a thin sheet.

2. Dielectric heating and microwave joining

Microwave joining occurs as a result of the interaction between an electromagnetic absorbent material and electromagnetic waves. An electromagnetic absorbent material, such as carbon black, mixed with an adhesive such as epoxy is placed at the interface of two sheets of polymers to be joined (adherend). Carbon black, has high loss dielectric properties, enabling it to couple well with the microwave energy. This facilitates the heating process by making the material conductive. It can store and convert the microwave energy into heat. By controlling the amount of carbon black dopant level the conductivity of the adhesive can be controlled, and hence the resulting strength of the cured joint can be controlled.

For material–microwave interactions in microwave processing, the material property of greatest importance is the permittivity complex (dielectric constant) ε^*, consisting of the storage dielectric constant, ε', effective loss dielectric constant, ε'' [13].

The relationship for the dielectric constant has a complex form as follows:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where by definition, ε^* is the permittivity complex of a dielectric or dielectric constant (i.e. doped epoxy adhesive), ε' the storage dielectric constant of doped epoxy adhesive — which indicates the ability of the adhesive to store energy as bound charges, ε'' the effective loss dielectric constant of doped epoxy adhesive which indicates the ability of the adhesive to lose energy as heat and j the coefficient of the imaginary part of a complex number.

The amount of power absorbed (P) by the adhesive greatly influences its curing and resulting bond strength and is dependent on both the permittivity and the loss tangent of the adhesives as follows:

$$P = \tfrac{1}{2}\varepsilon_0\varepsilon' \tan\delta E^2(\text{Watt m}^{-3}),$$

where ε_0 is the dielectric permittivity of free space, tan δ is the loss tangent, defined by ratio of ε'' (dielectric loss) ε' (dielectric constant) and E is the electric field strength.

Experimental work in microwave joining of thermoplastics using epoxy and other adhesives has been undertaken by a number of workers [10–15]. In one series of experiments, the determination of mechanical strength of bonds [14] was obtained using a mixture of 582 Epoxy adhesive with carbon black concentration ranging from 0.1 to 1.0 wt% for bonding glass fibre-reinforced (GFR) urethane adherend. In this experiment, a multimode microwave oven having $61 \times 61 \times 61$ cm cavity, was used to cure the epoxy adhesive. The maximum shear-bond strength results for all samples were between 2600 and 3000 psi (18 and 21 MPa). The major conclusion from that work was that microwave curing times were approximately $\frac{1}{3}$ to $\frac{1}{4}$ less than the curing times required by conventional thermal ovens to similarly achieve bond strengths of GFR urethane joints. But the optimum carbon black content which resulted in the highest and lowest bond strength was not detailed; only carbon black contents of 0.1 and 1.0 wt% were discussed. Using carbon (graphite) fibres in an epoxy matrix subjected to microwave curing [15] the interface temperature at the graphite epoxy boundary was found to change dramatically. The graphite acted as heat source causing some unidentified phenomena at the interface, within the epoxy which may have influenced the curing of the epoxy and associated shear strength of the composite. However, the use of microwaves for curing, especially with the addition of graphite fibres, was faster than conventional thermal heating techniques and resulted in superior adhesion. Further applications of carbon black doping involved the development of a conductive polymer [16]. In this case carbon black was added to high-impact polystyrene (HIPS) and styrene isoprene styrene (SIS) blend polymer.

3. Experimental

Thin single lap joints were prepared according to ASTM D3163 [17]. The substrate, or adherend, was polycarbonate sheet [18]. This is a transparent and tough thermoplastic often used as a replacement for glass. It has low dielectric loss properties and does not absorb microwave energy. The dimensions of the two samples of polycarbonate used to make the join were: length 101 mm, width 25.4 mm and thickness 1.5 mm. The join overlap was 10 mm resulting in a pre-cured

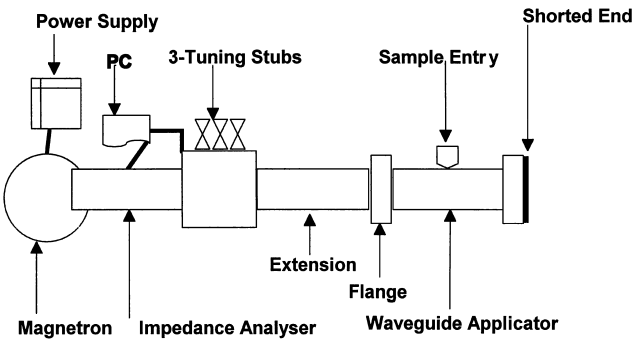


Fig. 1. Microwave unit set-up diagram.

254 mm^2 effective bond area. Emery paper and methanol solution were used for cleaning the mating adherend samples prior to adhesive bonding. Epoxy adhesive (C-Bond-245, a general purpose adhesive manufactured by Cuming Microwave Corporation, USA) was prepared in accordance with manufacturer's instruction, mixing part A (resin) and part B (hardener) in equal volumes using a 5 ml syringe. The mixture was prepared on a tray and had a pot life of approximately 2 h after mixing. Prior to curing, the join was prepared to a constant thickness (3.1 mm) by inserting it into a specially machined parallel slot aluminium jig (manufactured using a CNC lathe with an accuracy of machining of 0.0127 mm, according to ASTM guidelines).

A 6.0 kW single-mode microwave unit was used operating on a fixed frequency of 2.45 GHz as seen in Fig. 1. It consists of a magnetron as a microwave source; an impedance analyser for load matching; an automatic 3-stub-tuner, a personal computer with special data acquisition card to record the incident, absorbed and reflected microwave energy; a specially designed non-radiated slotted waveguide applicator to facilitate the joint for curing in during the microwave exposure; and a short end to terminate and turn back to create a standing wave pattern in the waveguide.

To compare the effect of using different varieties of dopant, two types of carbon black were used to dope the epoxy adhesive i.e. Vulcan 66 (high microwave activity) and Sterling (low microwave activity), supplied by Cabot Australia Pty. Ltd. It was assumed that the carbon black particles had uniform dimensions. Three different amount of carbon black, 0.1, 0.2 and 0.3 g were separately added to the epoxy adhesive to obtain carbon black concentrations of 0.05, 0.1, and 0.15 g/ml. For comparison, unmodified (i.e. no carbon black doping) epoxy joints were also examined.

The lap joints were mechanically tested using an Instron universal testing machine, model 4303. Microscopical analysis of the fractured joint was carried out using SEM and photo-stress methods and a polariscope was used to reveal residual stress in the adherend both before and after curing. Raman spectra analysis was performed on a number of samples to reveal any changes in the adhesive join material surface characteristics.

4. Results and discussion

The authors had previously conducted trials to obtain appropriate operating conditions for microwave processing of *C*-doped epoxy polymer joints [19]. In that work a series of epoxy/polycarbonate joints were exposed to microwave curing at 15, 30 and 45 s, where the input power was varied from 500 to 2250 W. The tensile bond strengths were found to be a maximum at 30 s irrespective of the input power level, for example, with 0.05 g/ml of Vulcan carbon black. Based on these results, the microwave energy exposure for the current work was chosen at an input power of 1000 W for 30 s. This was considered to be a conservative use of microwave power whilst achieving acceptable bond strengths.

The variation of bond strength with carbon black concentration is shown in Fig. 2. All results are an average of five test replications. The highest bond strengths ranged between 4.28 and 4.36 MPa for adhesive containing Vulcan 66 carbon black epoxy at a concentration range of 0.05–0.10 g/ml. The lowest strength, 3.08 MPa, was at a concentration of 0.15 g/ml Vulcan 66 carbon black. These results suggest that the optimum Vulcan carbon black ranged between 0.05 and 0.10 g/ml. For Sterling carbon black, the highest bond strength achieved was 3.26 MPa, at 0.10 g/ml concentration, whereas the lowest bond strength achieved was 2.28 MPa at 0.05 g/ml carbon black concentration. Tensile tests to determine bond strengths of samples of polycarbonate joins containing unmodified epoxy adhesive (i.e. containing no carbon black dopant) had very low or virtually zero strength after microwave curing.

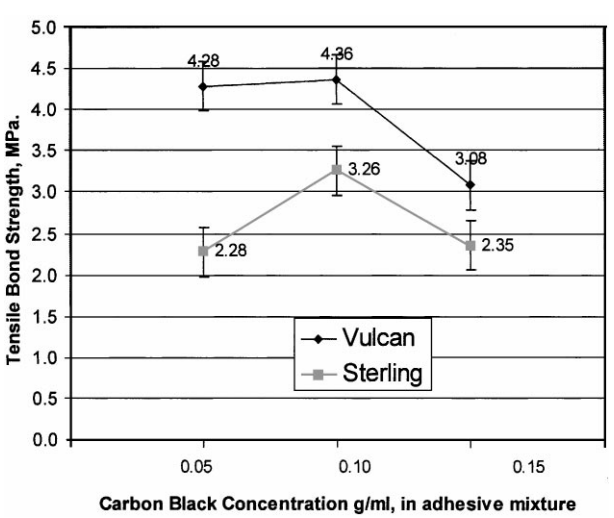


Fig. 2. Comparison of bond strengths using Vulcan 66 and Sterling carbon black doped epoxy adhesive.

These mechanical test results indicate that the use of high microwave activity carbon black, Vulcan 66, gives rise to high bond strengths when compared with the strengths obtained from the Sterling black. This Vulcan carbon black has a high-loss tangent which is associated with high microwave activity, i.e. an increase in the heat absorption in the join area and so may result in subsequent cure hardening of the adhesive, resulting in high bond strengths within the lap joint.

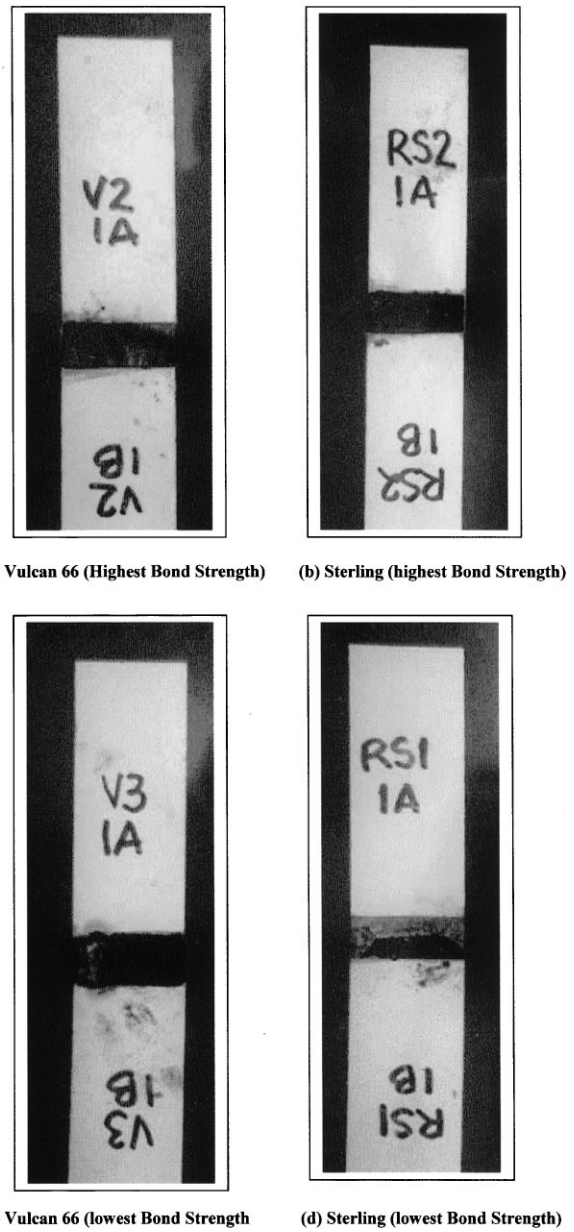
Examination of all failed sample surfaces indicated that the locus of failure occurred within the adhesive, and not the adherend. For both Vulcan and Sterling carbon black doping the strength variations of the joins may be an indication of a potential weakness at the interface since the surfaces of the thermoplastic adherend was subjected to a solvent–abrasion pretreatment.

Oven curing of unmodified (no carbon black) joints was performed at a range of temperatures and over a range of times. Five replications at each condition was performed. The temperatures ranged from RT (room temperature), to 50, 75, 100 and 150°C and curing times ranged from 24 h for room-temperature curing, to 30, 40, 50 and 60 min at the elevated temperatures. The maximum measured bond strength was found to be 5.58 MPa after 30 min exposure at 50°C. The epoxy manufacturer's data sheet for this particular adhesive suggested maximum bond strength of 20.7 MPa with a metallic substrate. However, the results are not easily comparable because of the different class of materials used for the adherend with both conventional thermal and microwave cure conditions.

Using a polariscope, Figs. 3(a)–(d) represent photostresses of the lap shear joint samples taken soon after microwave curing but before tensile testing was conducted. Shown in Figs. 3(a) and (d) are the joints which resulted in the highest bond strength of the doped Vulcan and Sterling epoxy adhesive, respectively. The photostress results show that the overlap joining area was dark-coloured which was due to carbon black in the adhesive mixture preventing the transmission of polarised light from its source through the polariscope down to the samples. The different light intensity level in these strips indicated that the substrates had different stress level prior to joining, suggesting the presence of residual stresses during the polycarbonate manufacturing process.

Figs. 3(c) and (d) are joints representing lowest bond strength with the doped Vulcan and Sterling epoxy adhesive, respectively. A red fringe pattern around the edges of the joint area indicates that this area had been subjected to the greater heat deposition and stress concentration as a result of the microwave absorption. The less uniformly distributed colours as indicated in Figs. 3(c) and (d) relate to the low bond strength joints.

Figs. 4(a)–(d) are scanning electron microphotographs (SEMs) of the fractured adhesive joint. Figs. 4(a) and (b)



(a) Vulcan 66 (Highest Bond Strength) (b) Sterling (highest Bond Strength)

(c) Vulcan 66 (lowest Bond Strength (d) Sterling (lowest Bond Strength)

Fig. 3. (a)–(d) Shows the photo stress distribution of the joint areas resulting in the highest and lowest bond strength of epoxy adhesive mixed with Vulcan 66 and Sterling carbon black.

are SEMs of the fractured sample showing the glue line, and the heat affected zone (HAZ), representing highest bond strength, using Vulcan 66 and Sterling carbon black, respectively. The glue line is seen on the right side of the HAZ in Fig. 4(a), as shown under 160 × magnification. The darkened HAZ in Fig. 4(a) indicated that carbon black (Vulcan 66) had diffused evenly in the HAZ, which gave rise to the highest recorded bond strength. Shown in Fig. 4(b) is the random diffusion of the carbon black (Sterling) in the HAZ. The glue line was not shown under 1000 × magnification, although at this magnification the carbon black distribution around the HAZ was

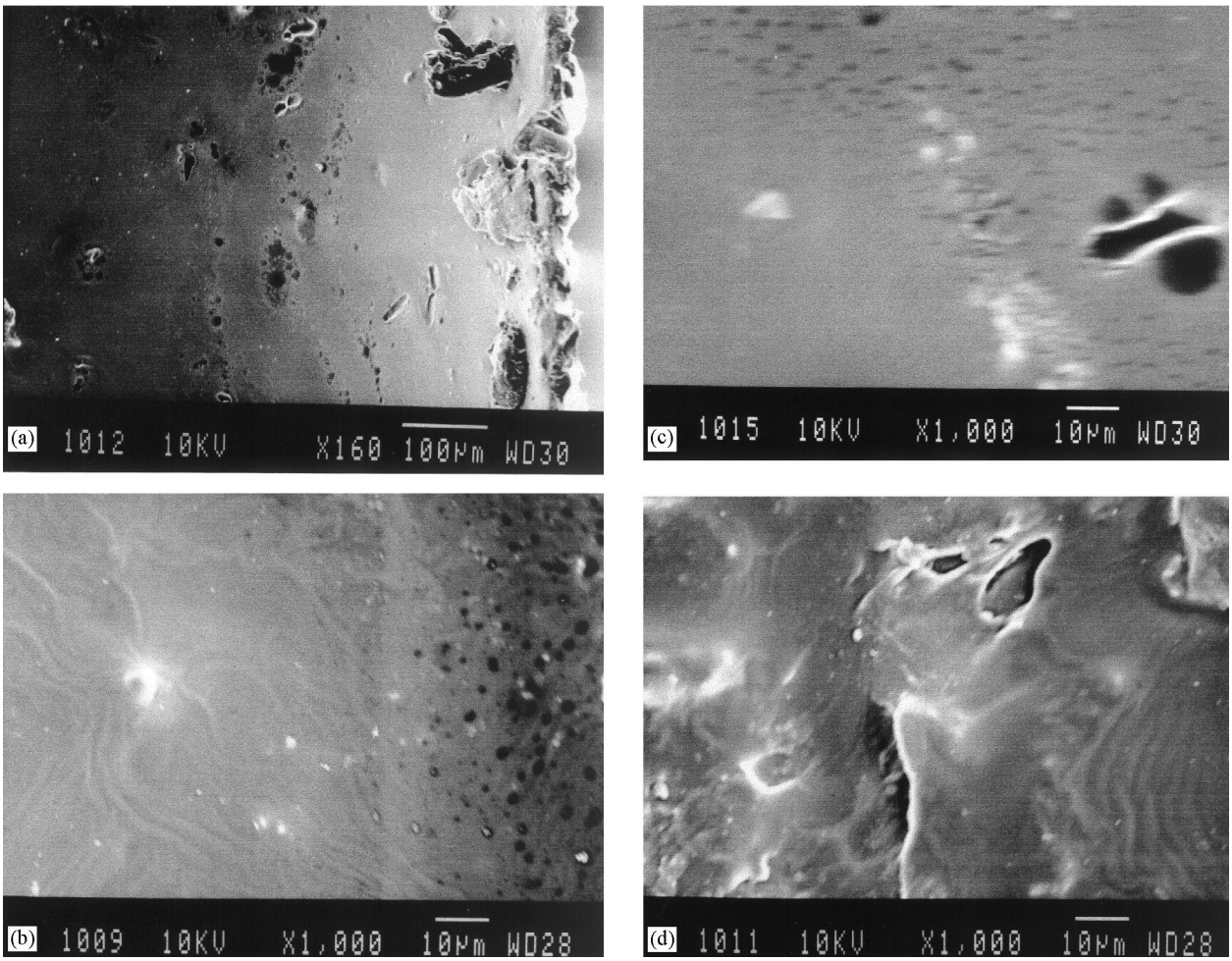


Fig. 4. (a)–(d) Shows scanning electron microscope of the highest and lowest bond strength fractured surface of the doped epoxy adhesive at different carbon black concentration for Sterling and Vulcan 66 carbon black.

seen. This is a result of heat being deposited in the HAZ from the microwave energy which was absorbed, allowing the curing process to create a strong joint.

Shown in Figs. 4(c) and (d) are SEMs of the HAZ of fractured joints with the lowest recorded strength. There is uneven distribution of carbon black, for both Vulcan 66 (Fig. 4(c)) and Sterling carbon black-doped epoxy (Fig. 4(d)) adhesive, respectively. This less uniformly carbon distribution in the joint may have led to low bond strengths. The large dark area in the middle right of the SEM image of Fig. 4(c) shows an accumulation of (Vulcan 66) carbon black. On the bottom right of Fig. 4(d) (Sterling), the SEM shows the HAZ in which a large accumulation of carbon black occurred at a certain area in the fractured joint, resulting in low bond strength. The inhomogeneous distribution of Carbon black suggests that the strength of the joints is adversely affected by the clustering effect of the carbon. This may result in a stress concentration within the joint, lowering its overall strength, or the carbon black may act as an inclusion so reducing the fracture toughness of the joint.

From each pair of joints, the locus of failure for all failed samples was within the adhesive. An adherend which contained the least amount of adhesive, was selected for Raman analysis from both Vulcan and Sterling doped adhesive samples. Figs. 5(a) and (b) show the comparison of Raman spectra analysed from the fractured surfaces of joints which recorded the highest and lowest bond strength based on the carbon Sterling doped epoxy adhesive, respectively. These two spectra show different trends from wavenumber shifts ranging from 500 cm^{-1} to approximately 1750 cm^{-1} indicating that both surfaces were chemically different. The different peak heights and locations indicate that the surface had undergone modifications after curing, as indicated by the different peaks.

Figs. 6(a) and (b) shows the comparison of the Raman spectra analysed from fractured surfaces of joints giving the highest and lowest bond strength based on the Vulcan 66 doped epoxy adhesive. From the wave number shifts ranging from 500 to approximately 1750 cm^{-1} the different peaks qualitatively indicate the different surface modifications resulting from the microwave heating.

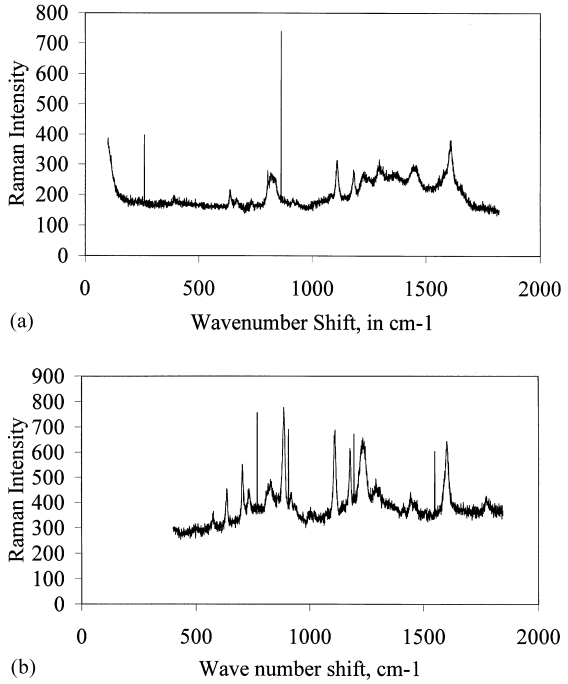


Fig. 5. (a) Raman spectra of the highest tensile bond strengths due to Sterling doping. (b) Raman spectra of the lowest tensile bond strengths due to Sterling doping.

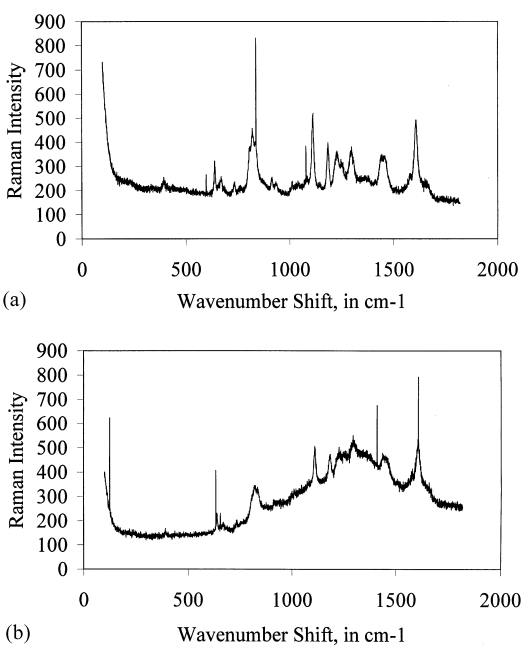


Fig. 6. (a) Raman spectra of the highest tensile bond strengths due to Vulcan doping. (b) Raman spectra of the lowest tensile bond strengths due to Vulcan doping.

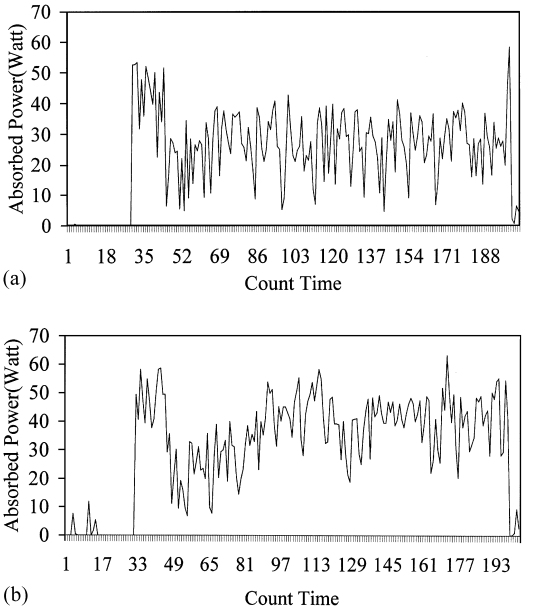


Fig. 7. (a) Absorbed power of the highest tensile bond strength of Sterling doped epoxy. (b) Absorbed power of the lowest tensile bond strength of Sterling doped epoxy.

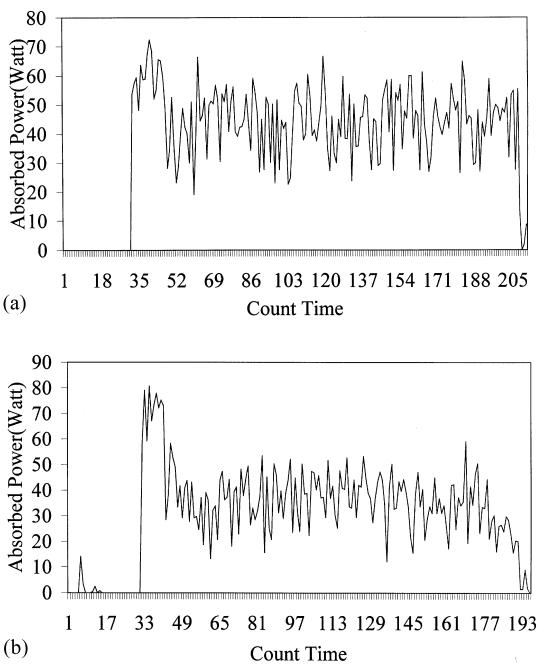


Fig. 8. (a) Absorbed power of the highest tensile bond strength of Vulcan 66-doped epoxy. (b) Absorbed power of the lowest tensile bond strength of Vulcan 66-doped epoxy.

Figs. 7(a), (b), 8(a) and (b) show the four different trends of the absorbed microwave power versus count time for Sterling and Vulcan doped epoxy adhesive, respectively. All joints were exposed for 30 s curing time at a power input of 1000 W. The level of microwave absorption in the joint were largely influenced by the permittivity and the loss tangent of the carbon-black-doped epoxy adhesive which enhanced the electrical conductivity [20,21].

5. Conclusion

Under the microwave curing and epoxy doping conditions used in this investigation, the addition in between 0.05 and 0.1 g/ml Vulcan 66 carbon black in the epoxy adhesive resulted in the highest bond strength when comparing to the addition of the same concentration of Sterling carbon black. For the Vulcan-doped epoxy adhesive the maximum bond strength was achieved at 4.36 MPa, whereas the maximum achievable bond strength of adding Sterling carbon black was 3.26 MPa at 0.1 g/ml C black concentrations. Moreover, conventional oven curing resulted in the highest bond strength, but at longer curing times than with microwaves. The use of microwave curing of carbon-doped epoxy adhesive polycarbonate joints is seen as a step in increasing the production process of these joints.

All microwave cured samples showed heat-affected zones at the joint overlap. For both Vulcan 66 and Sterling carbon black-doped epoxy adhesive joints, the high bond strength joints showed an even diffusion of carbon black whereas the lowest bond strengths showed an uneven distribution of carbon black.

Surface modification of the overlap occurred as indicated by the different trends and peaks of the Raman spectra.

References

[1] Brandon DG, Kaplan WD. Joining processes. New York: Wiley, 1997.
[2] Charles W. Tool and manufacturing engineers' handbook, 4th ed. vol. IV. Dearborn: Society of Manufacturing Engineers, 1987 [Chapter 11].
[3] Kinloch AJ. Adhesion and adhesives, science and technology, 1st ed. London: Chapman & Hall, 1984.
[4] Adams RD, Comyn J, Wake WC. Structural adhesive joints in engineering, 2nd ed. London: Chapman & Hall, 1997.
[5] Hartshorn SR. Structural adhesives: chemistry and technology. New York: Plenum Press, 1986.
[6] Ellis B. Chemistry and technology of epoxy resins. New York: Blackie Academic & Professional, 1993.
[7] Pocius AV. Adhesion and adhesives technology, an introduction. München, Germany: Carl Hanser Verlag, 1997.
[8] Boey FYC, Jacob J, Chia LHL, Proceedings of the First World Congress on Microwave Processing. OH, USA: American Ceramics Society, 1997. p. 417.
[9] Gourdenne AJ. Proceedings of the First World Congress on Microwave Processing. OH, USA: American Ceramics Society, 1997. p. 425.
[10] Groombridge A, Oloyede A, Siores E. Proceedings of the First World Congress on Microwave Processing, OH, USA: American Ceramics Society, 1997. p. 437.
[11] Yarlagadda PKDV, Chai TC. J Mater Process Technol 1998;74:199.
[12] Wu CY. 1997, http://www.joinplastics.eng.ohio-state.edu
[13] Decereau P. Microwave processing and engineering. England: Ellis Horwood VCH Verlagsgesell Schaft GmbH, 1986.
[14] Paulaukas MG, Meek TT, Warren CD. Proceedings of the Microwave Processing of Materials V, MRS Symposium, vol. 430. Pittsburg: MRS, 1996. p. 193.
[15] Agrawal R, Drzal L. J Adhesion 1989;29:63.
[16] Tchoudakov R. Polym. Eng Sci 1997;37(12):1928.
[17] ASTM D3163-96, ASTM, Pennsylvania, 1996.
[18] Timothy E. Chemical Market Reporter 1997;251(6):16.
[19] Soesatyo B, Blicblau A, Siores E. Proceedings of the 9th International Conference on Modern Materials and Technologies (CIMTEC 9), 1997, p. 515.
[20] Bouazizi A, Gourdenne A. Eur Polym J 1988;24(9):889.
[21] Ku HS, Siores E, Ball JAR, Horsfield. Proceedings of the 1998 Pacific Conference on Manufacturing. Brisbane: PCM Publisher, 1998. p. 68.