Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2543–2549

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fractographic analysis of epoxy coated glass

Tamer El-Sayed *, Russell J. Hand

Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK

Received 15 October 2011; received in revised form 8 November 2011; accepted 9 November 2011
Available online 18 November 2011

Abstract

Epoxy based surface coatings can be used to increase glass strength. Epoxy coated samples have been tested in bending and a detailed fractographic analysis of the resultant fracture surfaces has been conducted in order to more fully understand the strengthening mechanism. The fractographic analysis was conducted on samples coated using different emulsion concentrations and crack sizes. The fractographic analysis of the tested samples showed that increasing the emulsion concentration increased the amount of epoxy that infiltrated the cracks. It also showed that the type of the fracture varies with the change of the crack filling and the crack dimensions. The results confirmed that these epoxy coatings were capable of healing small cracks.
© 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: D. Glass; C. Fracture; Epoxy; Coating; Fractography

1. Introduction

The practical strength of glass articles is normally only a small fraction of its theoretical strength. It is well known that the strength of glass can be temporarily increased by surface etching techniques that remove flaws; however subsequent handling results in the re-introduction of the flaws [1,2]. Increases in glass strength can also be achieved by the introduction of controlled compressive stresses that have to be overcome before a crack can propagate through techniques such as thermal and chemical tempering. However these methodologies either impracticable or too expensive to apply to bulk container glass production [3].

Surface coatings are one of the more promising techniques used for glass strengthening. In principle such surface coatings can either increase the strength of a glass article by healing the pre-existing surface cracks or prevent further strength reductions by protecting the glass surface from future contact damage. There are two main categories for surface coating depending on the coating material. The first is hard coating, and in which the coating elastic modulus and hardness either match or are greater than that of the glass. The second is a flexible polymeric coating, and in which the coating elastic modulus and hardness are very low compared with that of glass. Epoxy resins based systems are examples of the latter type of system.

Several studies have attempted to explain how relatively flexible surface coatings can result in significant strength increases. It is generally accepted that penetration of the cracks by the coating is important but beyond this there is disagreement as to how this leads to strengthening. Recently the work of Fowkes et al. [4] and El-Sayed and Hand [5] has shown, through numerical and analytical modelling, that a soft coating layer inside a crack can heal that crack. The aim of the current work is to complement these theoretical studies into the strengthening mechanism of epoxy coated glass by undertaking a fractographic analysis of the coated samples and to link the results to the FE models [5,6].

2. Experimental

The glass samples used in this work were microscope slides that had been sectioned into 2 halves, each ~38 mm × 26 mm × 1.04 mm. In line with previous studies [see, for example 7] controlled defects were created in the middle of the glass slides using Vickers indentation. A CV model 4300-AAT Vickers hardness tester was used. Either a 1, 2.5, 5 or 10 kg load 10 s were used for indentation. The samples were left for a week after indentation to allow the sub-critical crack growth to saturate [8,9].

* Corresponding author. Present address: Department of Mechanical Design Engineering, Faculty of Engineering – Mataria, Helwan University, Egypt. Tel.: +20 1122154762.

E-mail address: tamer1_9@yahoo.com (T. El-Sayed).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.11.025

To remove any remaining residual stress some of the samples were annealed after one week. For annealing the samples were heated at 2 °C/min up to 560 °C, held 2 h and then cooled at 2 °C/min to room temperature.

The coatings were prepared by mixing a commercial blend of bisphenol A and F epoxy resin (Huntsman, Araldite 340-2) with polyamidoamine hardener (Huntsman, Ardur 340) using a motor driven paddle. Separately trimethoxy [3-(oxyran-2-ylmethoxy) propyl] silane (Dow Corning Z6040) was mixed with distilled water for 2 h. The two mixtures were then gradually mixed together. The percentage weight of epoxy to hardener was taken as 1:1.7 as recommended by Whittle [9]. Table 1 lists the weight ratios used to give the different emulsion concentrations (EC) studied in this work. The samples were coated by dipping in the coating solution. After dipping the samples were hung vertically and allowed to dry for 15 min in air before heating in a furnace at 200 °C for 15 min.

The fracture strengths of the coated samples were measured using 4 point bending on a Hounsfield model H100KS universal testing machine. A force transducer (model SM-100N-457) with capacity 1000 N was attached to Hounsfield testing machine to measure the applied load. The inner (l_i) and outer (l_o) loading spans were 6 and 20 mm and the loading rate was 0.5 mm/min. After fracture the failure stress was calculated using [6]

$$\sigma_f = \frac{3F(l_o - l_i)}{2bh^2} \quad (1)$$

where F was the measured load at failure; h and b the specimen thickness and specimen width (~1.04 mm and ~26 mm respectively) which were measured using vernier calipers. After fracture the crack depth was measured from the fracture surfaces using a Polyvar Met optical microscope. Axivision 4.7 was used to digitally capture the microscope images. For each test condition 10 samples were tested.

3. Results

In this work the effect of changing the emulsion concentration and the effect and the effect of changing the crack size were investigated.

3.1. Effect of coating emulsion concentration on crack filling

The strength experimental results showed that the emulsion concentration has an important role in strengthening of the glass [5]. The amount of the coating infiltrated the median crack was studied by acquiring optical microscope images of the fracture surfaces of the different coated samples. The samples used for this purpose were cured at room temperature in order to reduce interfacial strength and thus to encourage the crack to go through the median crack symmetric plane as shown in Fig. 1.

The fractured samples were captured using an optical microscope at the different emulsion concentrations as shown in Fig. 2a–h. The images were processed in order to evaluate the ratio of the epoxy filled area to the crack surface area at the different EC values. At least three samples were used to evaluate the epoxy filling percentage at each EC value. Fig. 1 shows an enlargement of two of the eight micrographs shown in Fig. 2a–h. The coating area inside the crack was calculated roughly using Digimizer software. This software enables the measurement of any selected area in the figure after adjusting the scale. The coated areas were selected and the software was used to calculate its area and then divided by the crack area (which was calculated the same way) to obtain the coating filling ratio. The calculated coating filling ratio was plotted versus the epoxy emulsion concentration as shown in

Table 1
List of the weight ratios for the different emulsion concentrations.

Emulsion concentration % (EC)	Epoxy/g	Hardener/g	Silane/g	Water/g
6.2	2.8	4.7	1.9	120
12.5	5.5	9.4	1.9	120
24	10.6	18.0	1.9	120
37.5	16.5	28.2	1.9	120
45	19.8	33.8	1.9	120
55	24.8	42.3	1.9	120

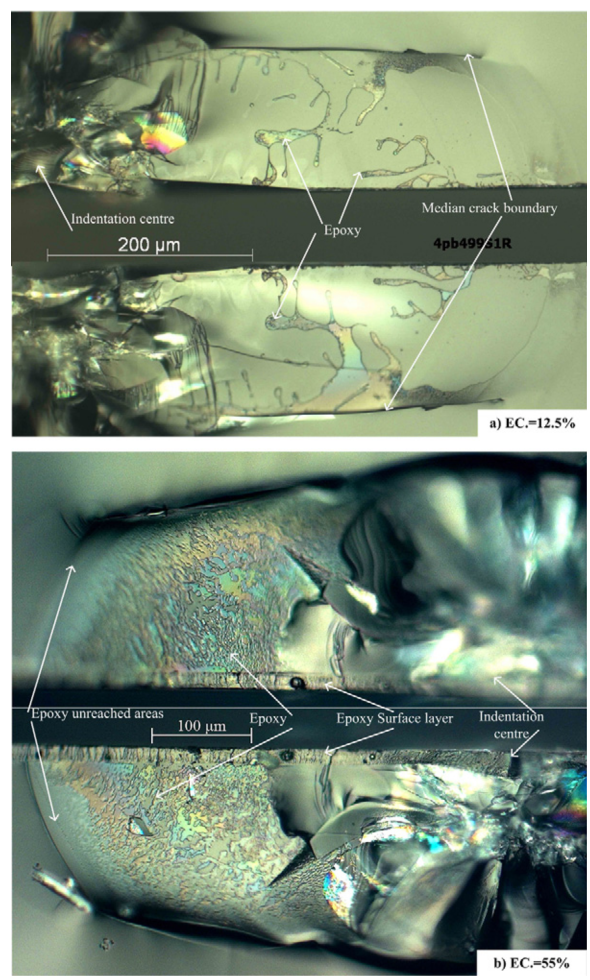

Fig. 1. Enlargement for two of the optical microscope images in the previous figure at epoxy emulsion concentration (EC) = (a) 12.5% and (b) 55%.

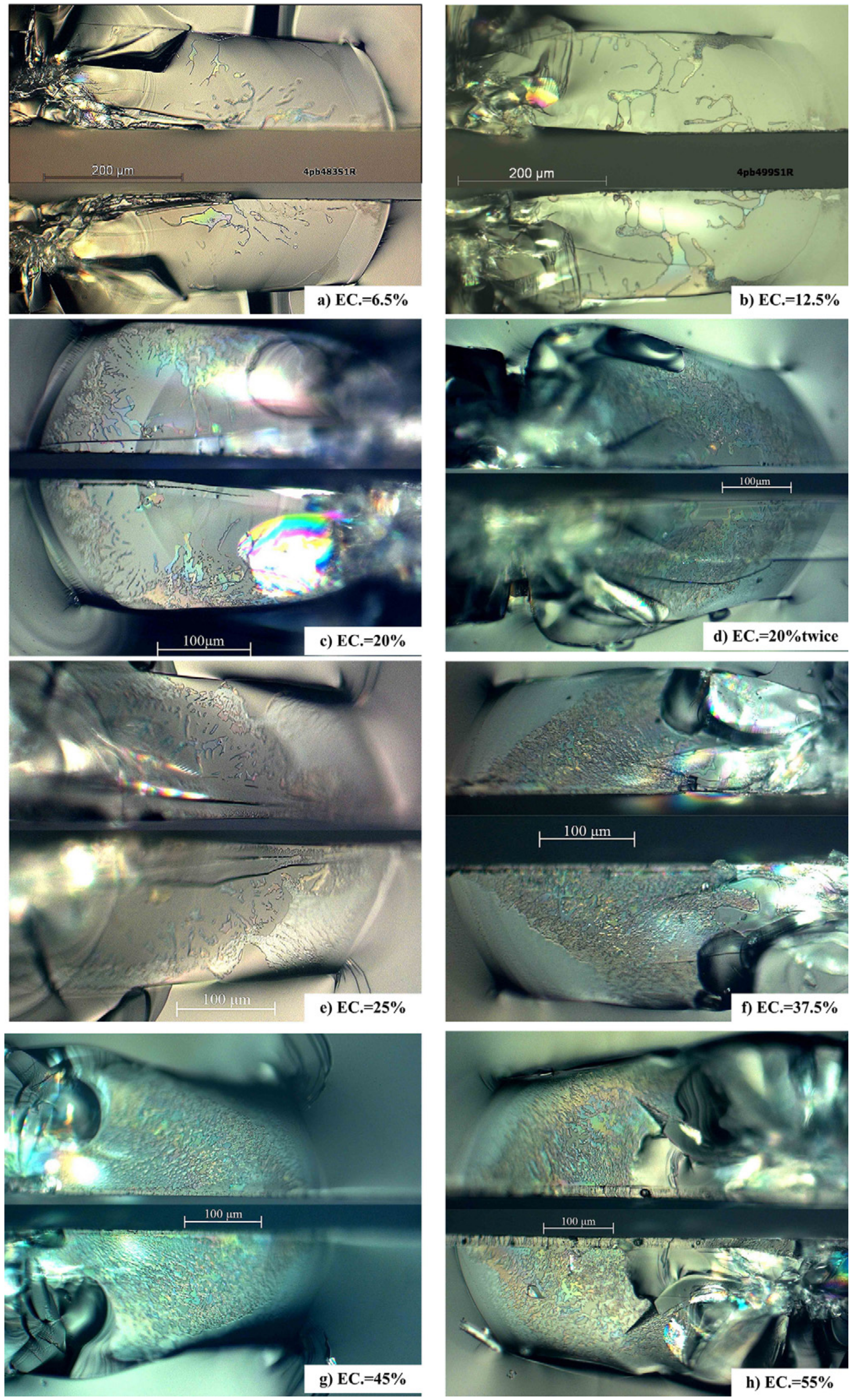

Fig. 2. Optical microscope images for coated cracks fracture surfaces using different epoxy emulsion concentrations.

Fig. 3. The captured optical microscope images Figs. 1a, b and 2a–h and the results shown in Fig. 3 indicate that increasing the coating EC results in an increase in the amount of the epoxy which infiltrates the median crack up to an epoxy coating EC value of approximately 35%. Subsequently, the amount of the epoxy infiltration stabilizes despite the increase of epoxy coating EC and up to 55%, which was the maximum value studied during the current work.

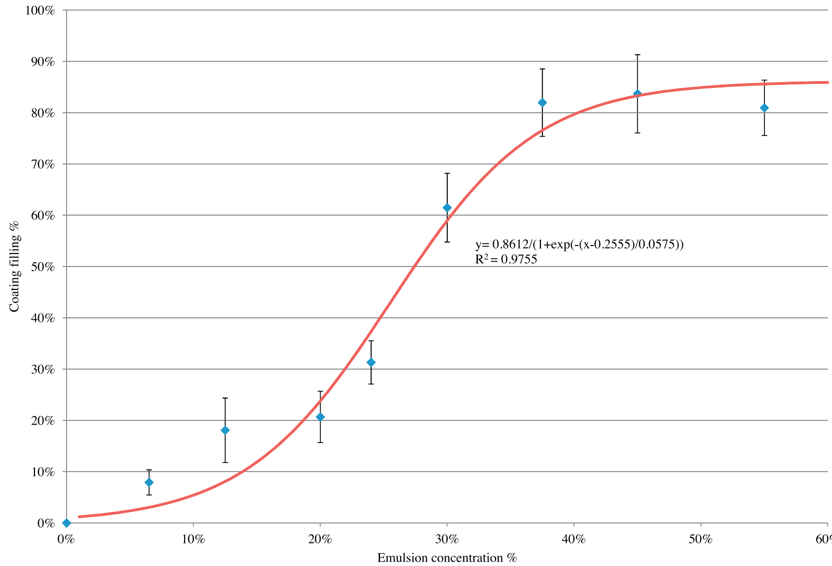

Fig. 3. Amount of crack filled with coating versus coating emulsion concentration.

3.2. *Fractographic analysis of coated samples with different EC values*

The samples were classified as to whether the fracture surface misses the controlled defect site or the fracture surface goes through the controlled defect site.

In the case of the fracture surface missing the controlled defect site, the fracture origin can be an edge defect or an internal inclusion. In this type of fracture, the indentation crack is considered as healed. The term heal here is not absolute, but it indicates that the coating was able to minimize the effect of the controlled defect so that the coated sample fractured from another defect elsewhere. If there were no other edge or internal defect in the glass sample, the sample would have fractured from the filled crack at higher stress.

In the second category, the fracture surface runs through the controlled defect. The fracture surface of these samples goes through diamond indentation imprint and it may follow the median crack symmetric plane or not. The fracture of these samples is classified into three types in terms of how or whether the fracture surface follows the symmetric plane of the median crack.

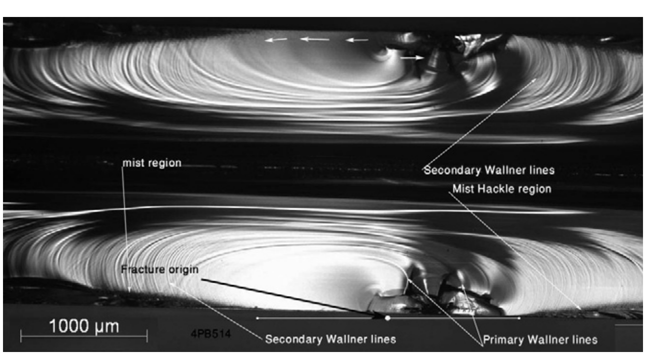

Fig. 4. Fractography of cracked coated sample tested in 4 pb test section view for the fracture surface.

In the first type of fracture, the fracture surface follows the median crack plane on both sides of the indent as shown in Figs. 4 and 5a and b. Since the amount of the coating and its distribution in the right and left sides of median cracks is not perfectly symmetrical, the crack starts growing from the weaker side. Fig. 5a shows that the amount of the coating in the left side is smaller than in the right side which means that the cracks start from the left side as shown in the figure. The white arrows in the top of Fig. 4 show the direction of crack growth.

Fig. 4 shows that the crack starts to grow from the left side of the crack. When the crack front encounters the right side of the crack primary Wallner lines are created as shown in Fig. 4 bottom right. Increasing the stress at the crack tip increases the crack velocity. When the crack velocity reaches higher speeds mist and hackle regions develop. As the crack front further grows and meets the mist and hackle region, secondary Wallner lines are created [10].

In the second type of fracture, the fracture surface follows the median crack plane on one side of the indent and misses the median crack plane on the other side as shown in Figs. 6 and 7. Fig. 7a shows a case where the fracture surface goes through nearly 80% of the left side of the median crack and then deviates from median crack plane (Fig. 7b bottom centre). On the right side of the crack, the fracture surface did not go through the median crack but follows a different plane as shown in Fig. 7b (top centre). The reason for that is that the amount of the coating infiltrated to this side of the crack was sufficient to close it under the current fracture stress.

The distribution of the Wallner lines shown in Fig. 6 indicates that the fracture originates from nearly the centre with a tiny shift towards the left side of the crack. Comparing this position with the plan view in Fig. 7b we find that this is the location of the edge of diamond imprint notch. The white arrows in Fig. 6 (bottom) show the direction of crack front growth.

In most of the fractured samples with epoxy coating EC values of 12.5% and 20%, the fracture origin is from the right or

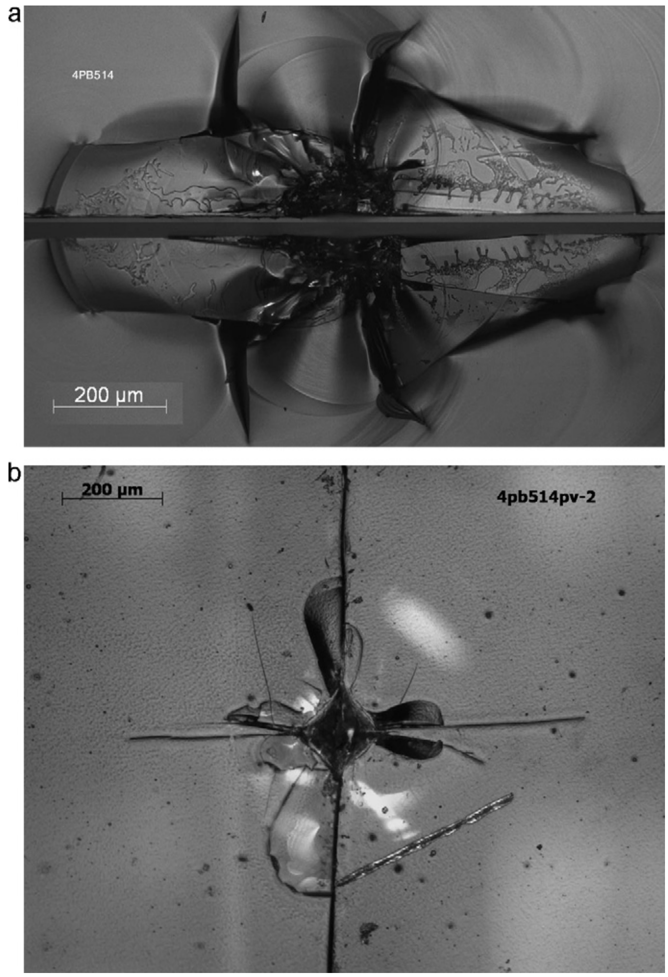

Fig. 5. Fractography of cracked coated sample tested in 4 point bending test. (a) close-up of the crack surface. (b) Plan view of the fracture crack.

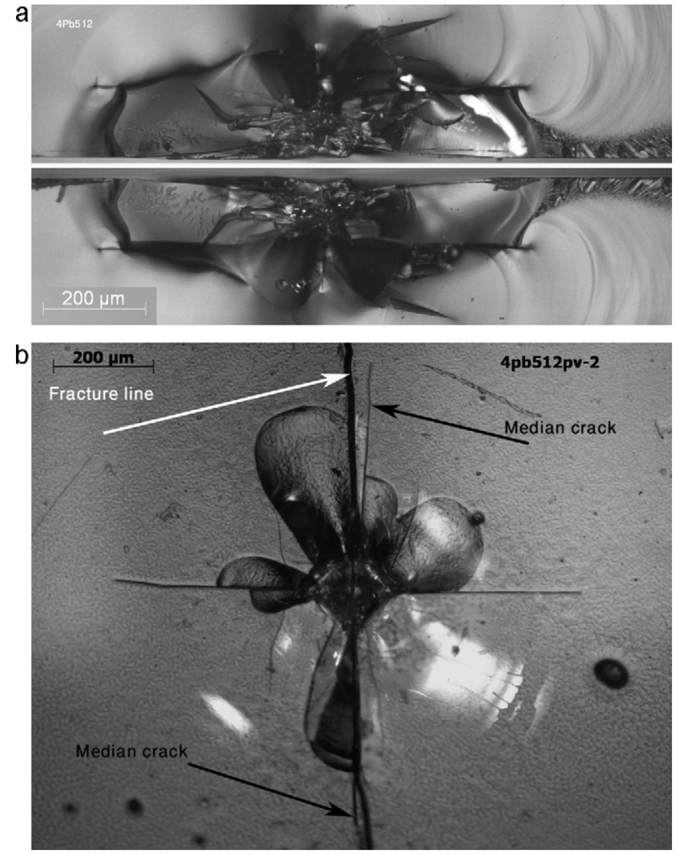

Fig. 7. Fractography of cracked coated sample tested in four-point bending. (a) Enlarged sectional view the crack surface. (b) Plan view of the fracture crack.

left crack tip, but there are a few cases where the crack grows from the middle as shown in Fig. 8.

In the third type, the fracture surface runs across the indentation site but it does not follow the median crack plane at all. An example of this type of fracture is shown in Figs. 9 and 10. Fig. 9 shows the fracture surface of one of the samples coated with epoxy EC = 37.5%. The fracture stress for this sample was 125 MPa which happens to be the same value as the average fracture stress of the as-received glass. The distance between the left and right mist and hackle starting point is very small which reflects the high fracture stress [see, for example, 10,11,12]. The left and right secondary Wallner lines indicate the direction of crack growth. Fig. 9 the position of the mist and hackle region and the direction of the secondary Wallner lines indicate that the fracture originates from the middle of the crack, i.e. the fracture starts from indentation diamond imprint. The crack front then propagated towards the right and the left as indicated by the white arrows in Fig. 9.

Fig. 10a is a plan view of the sample shown in Fig. 9 after indentation and before fracture whereas Fig. 10b shows a plan view of the same sample after coating and fracture in four-point bending. Fig. 10c is an overview of the view shown in Fig. 10b.

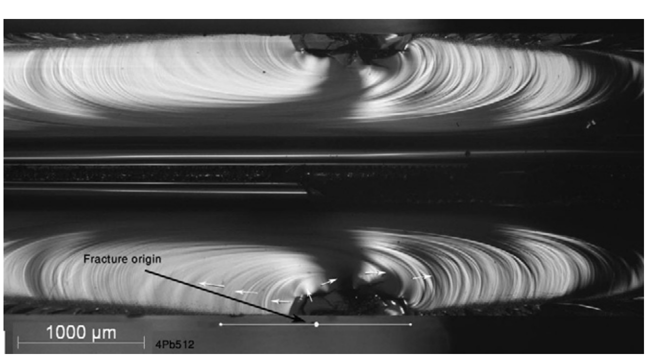

Fig. 6. Fractography of cracked coated sample tested in 4 point bending. (a) Section view of the fracture surface.

Fig. 8. Sectional view for the fracture surface of cracked coated sample tested in four-point bending. The figure shows that crack origin is nearly the middle of the median crack.

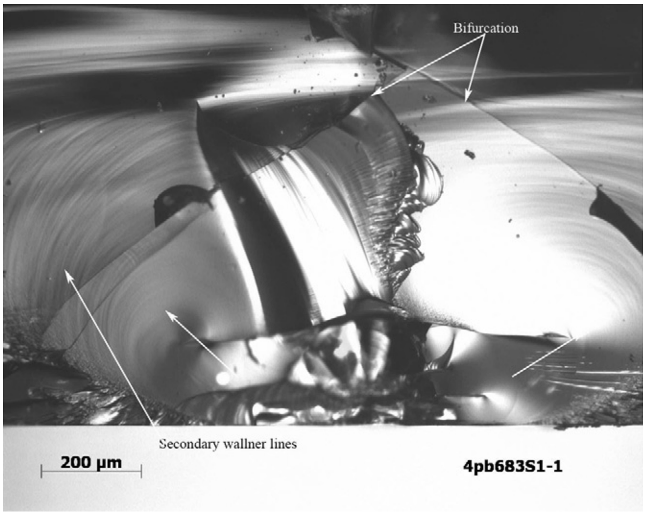

Fig. 9. Fractography of cracked coated sample with epoxy EC = 37.5%. The fracture surface did not go along the median crack plane. The fracture stress for this sample is 125 MPa.

It also shows the location of bifurcation of the sample. Fig. 10shows that the fracture does not start from an edge defect and rather starts from the controlled defect site. It also shows clearly how the fracture surface misses the median crack plane and the fracture line goes through the top notch edge of the diamond imprint Fig. 11.

From the fractographic analysis of the samples broken in the same manner as that shown in Fig. 10 we can conclude that the epoxy infiltrated to the median crack can produce a closure stress sufficient to heal the median crack. On the other hand, the plastic deformation around the indent produces a local stress concentration which results in fracture starting from the indentation controlled defect site.

4. Discussion

4.1. Fractographic analysis for different emulsion concentrations

The fracture types of the coated samples prepared using different epoxy emulsion concentrations are summarized in Table 2. All the samples listed in Table 2 were indented using a 10 kg indentation load. The fractured samples at each epoxy EC were classified according to their fracture type.

The results shown in Table 2 indicate that at lower epoxy emulsion concentrations the fracture surface tends to follow the complete median crack. Increasing the epoxy EC reduces the tendency of the fracture surface to follow the median crack. This can be explained by the fact that increasing the emulsion concentration results in an increase in the amount of epoxy infiltrating the median crack which results in higher closure stress over the crack surfaces. This stress can sometimes heal the median crack as shown in the fracture results of the samples coated with epoxy EC = 12.5% and 20% in Table 2. Further increase in the emulsion concentration to 30% results in fracture surfaces that do not go through the median at all

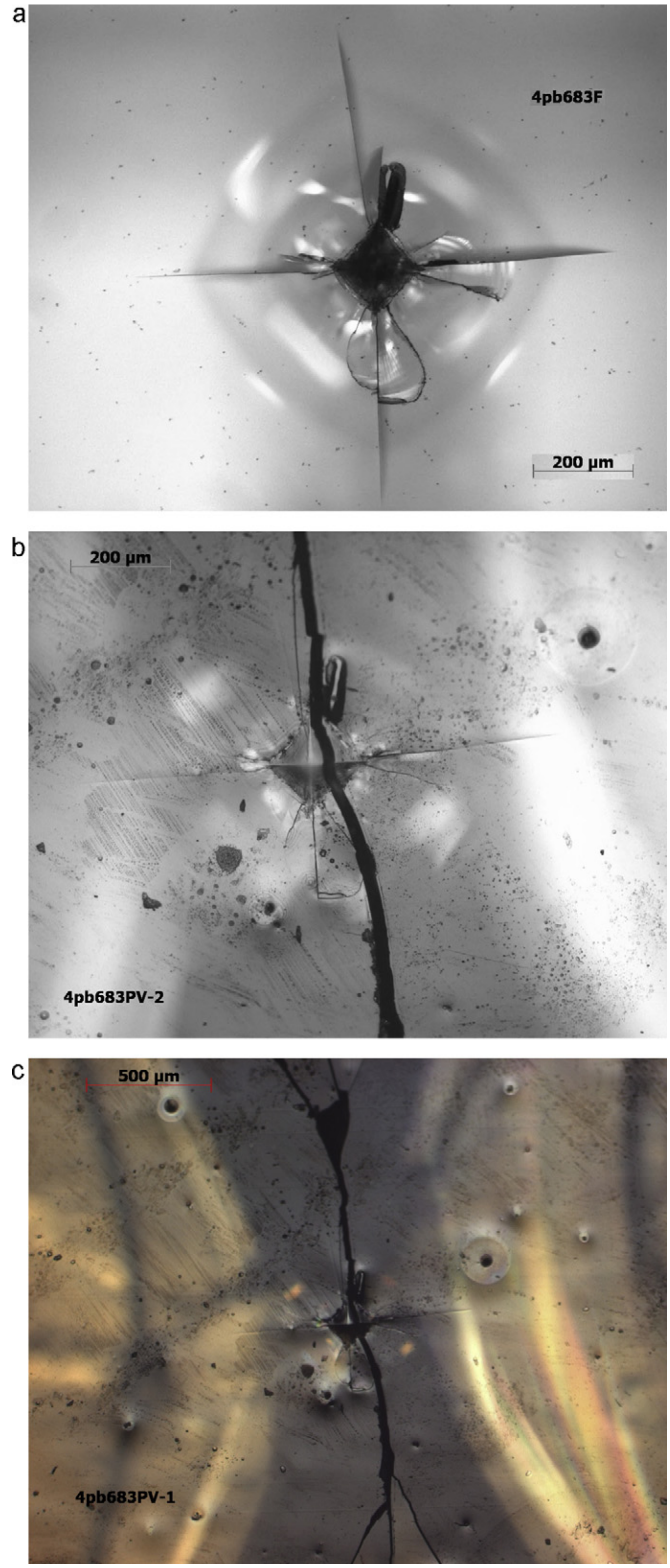

Fig. 10. Plan view for the same sample in Fig. 9. (a) Before coating and fracture, (b) after coating and fracture of the sample and (c) zoom-out to the view in (b).

appearing. Table 2 shows that at EC of 37.5%, 45% and 55% this latter type of fracture is the dominant fracture mode. In addition, some samples fractured from their edges. From these results it can be concluded that the epoxy which infiltrated the

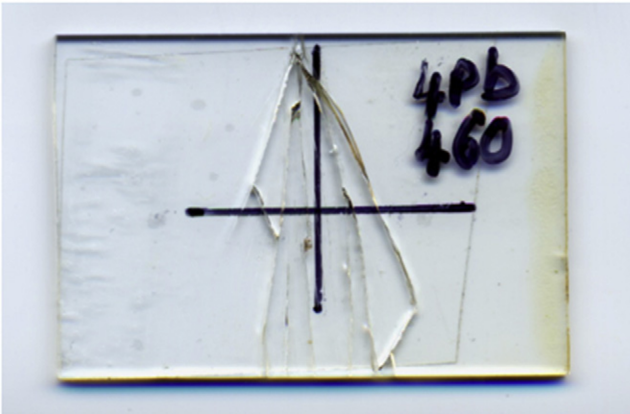

Fig. 11. Fracture sample after indenting using 1 kg and coated using epoxy EC 20% twice.

Table 2
Fracture type ratio at the different coating EC.

EC	Fracture type			
	Median crack both sides %	Median crack one side %	Controlled defect but not median crack %	Side fracture %
6.50%	78	22		
12.50%	70	30		
20%	44	56		
20% twice	21	47	26	5
30%	30	20	50	
37.50%		18	71	11
45%		30	60	10
55%		20	60	20

median crack when using EC of 37.5%, 45% and 55% is sufficient to heal the median crack.

4.2. Fractographic analysis of a small controlled defect

In this section the fracture of cracked coated samples is investigated. The controlled defects for these samples were created using a Vickers indentation load of 1 kg. A coating with epoxy EC of 45% was used because this EC showed the best results of strengthening samples indented by 10 kg indentation load. Also, a coating with epoxy EC 20% was used on some 1 kg indented samples and these samples were dipped twice.

The fracture stress results of the samples which coated using epoxy EC 20% and dipped twice; and epoxy EC 45% showed an increase in the average strength to 133 ± 23 MPa and 139 ± 13 MPa respectively which are higher than the as-received glass strength. The fracture surface of 80% of the 20% EC double coated samples and 60% of the 45% EC coated samples did not go through the controlled defect, which indicates that, the effect of both the median crack and the indentation imprint were healed for most of these samples as shown in Fig. 1.

5. Conclusions

Increasing the emulsion concentration results in an increase in the amount of the epoxy infiltrated into the median crack up to EC of approximately 37%. From EC of 37% and up to EC 55% the amount of the coating that infiltrates the crack fluctuates slightly.

Fractography of the coated cracked samples after 4 point bend testing showed different types of fracture. The facture surface goes through the indentation site in most of the samples. The fracture is classified into three types. The first type the fracture follows the median crack plane on both sides of the indentation. In the second type, the fracture surface follows the median crack plane on one side of the indent. In the third type the fracture surface did not follow the median crack at all.

The first type is the dominant at lower epoxy EC values. The third type is the dominant type of fracture when the amount of the coating infiltrating the median crack is sufficient to close it under the applied load. These conditions were achieved at an EC of 37% and 45% and 55%.

The fractography of the coated samples showed that a coating prepared with epoxy EC 20% dipped twice or a coating prepared with an epoxy EC 45% is sufficient to heal a small controlled defect created using 1 kg Vickers indentation.

References

[1] B.R. Proctor, The effects of hydrofluoric acid etching on the strength of glasses, Physics and Chemistry of Glasses 3 (1) (1962) 7–27.
[2] E.K. Pavelchek, R.H. Doremus, Fracture strength of soda-lime glass after etching, Journal of Materials Science 9 (11) (1974) 1803–1808.
[3] G. René, Ion exchange for glass strengthening, Materials Science and Engineering B 149 (2) (2008) 159–165.
[4] N. Fowkes, J.A. Teixeira de Freitas, R. Stacey, Crack repair using an elastic filler, Journal of the Mechanics and Physics of Solids 56 (9) (2008) 2749–2758.
[5] T. El-Sayed, R.J. Hand, Modelling the strengthening of glass using epoxy based coatings, Journal of the European Ceramic Society 31 (15) (2011) 2783–2791.
[6] T.A.E. Elsayed, Modelling the strengthening of glass using epoxy based coatings, Ph.D., University of Sheffield, 2010.
[7] R.J. Hand, F.H. Wang, B. Ellis, A.B. Seddon, Hydrolytic durability of silane primed epoxy coatings on silicate glasses, Physics and Chemistry of Glasses 39 (6) (1998) 305–310.
[8] F.H. Wang, The strengthening of glass with epoxy resin and ormosil-polymeric coatings, Ph.D., University of Sheffield, 1996.
[9] B.R. Whittle, Water-based epoxy resin coatings for the strengthening of flat glass edges, Ph.D., University of Sheffield, 2002.
[10] G.D. Quinn, Fractography of Ceramics and Glasses, National Institute of Standards and Technology, Washington, 2007.
[11] J.J. Mecholsky, Quantitative fractographic analysis of fracture origins in glass, Fractography of Glass (1994) 37–73.
[12] N. Shinkai, Fracture and fractography of flat glass, in: R.C. Bradt, R.E. Tressler (Eds.), Fractography of Glass,, Plenum Press, New York, 1994, pp. 253–297.