Effects of adhesion on the effective Young's modulus in glass slide/glue laminates

Part I *Experiments*

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Bond-phase defects in laminates can affect the mechanical properties of laminate composites. In this study, the effects of adhesion area, number of glue spots, and bond thickness on the effective Young's modulus of adhered microscope glass slides have been investigated. Three different adhesive agents (super glue, epoxy cement, and epoxy resin) were used to explore the effect of bond-phase defects upon adhesion in laminates. The elastic moduli of single glass slides, unadhered glass slide pairs, glass slide/glue composite specimens and epoxy resin specimens were non-destructively determined by a sonic resonance technique. The change of Young's modulus of adhered glass slides was monitored while adhesion area per cent ranged from 0.35%–100%. Trends in the Young's moduli of glass slide/glue composite specimens have been analysed by a least-squares best-fit procedure to two empirical equations. Qualitative explanations for the observed trends are discussed in this paper.

1. Introduction

We have explored the use of elastic modulus measurements, in particular, to non-destructively assess the mechanical integrity of adhesive bonds in three-layer composites (a bond layer sandwiched between two matrix layers). Although it will not be treated in this study, the methods used here could probably be applied to *in situ* measurements of adhesive bond degradation, such as might be the case when the bond phase of a laminate composite degrades at high temperature.

As a model laminate composite specimen, we used two microscope glass slides bonded by three different types of adhesives: (1) super glue, (2) epoxy cement, and (3) epoxy resin. In order to obtain a range of bond integrities, the area fraction of the bond layer was varied from nearly 0% adhered area to 100% adhered area. We also sought to determine the extent to which the spatial distribution of the bond layer affected the modulus; thus specimens were fabricated having one, two, three, and five glue spots (Fig. 1). The large mismatch in Young's modulus between the glass and the bonding agent (the Young's modulus of the glass slides, was approximately 70 GPa while the Young's modulus of the bond phase was about 3 GPa) implies that the overall elastic modulus will decrease as the bond thickness increases. Thus we also determined the nature of the changes in the composite's elastic modulus as a function of the bond layer thickness. Thus, in this study we varied (1) the total adhesion area, (2) the spatial distribution of the bond layer (by varying the number of glue spots), and (3) the thickness of the glue bond (Fig. 1).

Microscope glass slides were selected for this study because microscope glass slides are (1) readily available, (2) relatively inexpensive, (3) easily used without additional dimensioning, grinding, or polishing, (4) comparatively uniform (in the as-received state) in terms of external slide dimensions and elastic moduli, and (5) brittle, which is important because the primary area of interest for the authors is ceramics and ceramic composites.

Glass slide/glue composite specimens having less than 100% adhesion area had glue spot(s) surrounded by unadhered regions on the glass slide surface (see Fig. A1b, Appendix 1) which are analogous to specimens having external cracks (see Fig. A1a, Appendix 1) or delamination cracks. In this sense, this study is related to the study of external-crack-induced changes of mechanical properties.

Kemeny and Cook [1] modelled an external crack as one which penetrates a solid, leaving only a single, unbroken internal ligament surrounded by a continuous, surface-breaking crack (often considered in fracture mechanics) in which the cracked area is small compared to the specimen cross-section (see Fig. A1a). The present study deals with specimens having planar unadhered regions (analogous to cracks) surrounding glue spots between two glass slides (see Fig. A1b). For specimens having one glue

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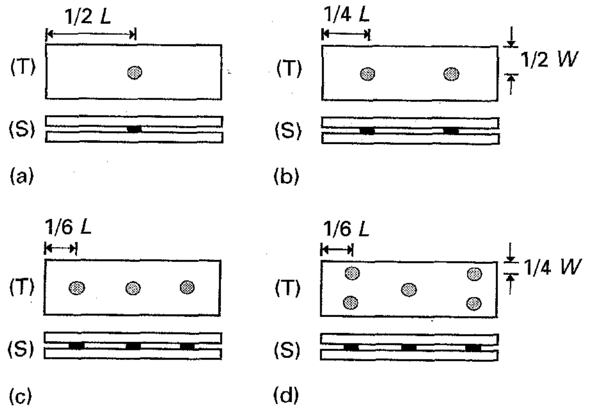

Figure 1 Schematic drawings of (a) one glue spot, (b) two glue spots, (c) three glue spots, and (d) five glue spots adhered composite specimens. T, top view of the composite specimen; S, side view; *L*, specimen length; *W* specimen width.

spot, the specimen geometry is roughly similar to that modelled by Kemeny and Cook (see Appendix 1).

However, Kemeny and Cook [1] assume a mechanical loading on their specimens that is considerably different from the loads experienced by the specimens in this study (Appendix 1). Thus, we shall not use Kemeny and Cook's model to analyse the elastic modulus data presented in Part I of this study. Instead, in Part II [2], we develop a semi-empirical model describing the elastic modulus of the laminate composite as a function of adhesion area, spatial distribution of the bond layer, and thickness of the glue bond.

2. Experimental procedure

2.1. Materials and preparation of specimens

Commercial microscope glass slides (model 2954-F, Sybron Corp.) with approximate dimensions 7.62 cm × 2.54 cm × 0.12 cm, were used to fabricate glass slide/glue composite specimens. In order to select appropriate adhesives for this study, we initially determined the change of mass of five different adhesives during a 92 h time period after the adhesives were applied to glass slides. The candidate adhesive materials were Sure Shot Super Glue® (Devcon Corp., Wood Dale, IL), Elmer's Epoxy Cement® (Borden Inc., Columbus, OH), Cement For Plastic Models® (The Testor Corp., Rockford, IL), Elmer's School Glue® (Borden Inc., Columbus, OH), and Quick Setting Epoxy Adhesive® (Super Glue Corp., Hollis, NY). A large time-dependent change of mass of adhesives makes exact measurements of specimen mass difficult and may result in errors in determining the elastic modulus (the calculation of elastic modulus involves the mass and dimensions of the specimen, as discussed in Section 2.3). As a result of the "mass stability" screening, the adhesives selected for this research were (1) Sure Shot Super Glue® (super glue), (2) Elmer's Epoxy Cement® (epoxy cement), and (3) Quick Setting Epoxy Adhesive® (epoxy resin).

To study the effects of adhesion area and number of glue spots; one, two, three, or five glue spots with differing adhesion areas were applied using a wood stick at pre-selected positions on one glass slide (Fig. 1). The super glue was applied directly to the glass slide, while the epoxy cement and the epoxy resin were applied after mixing the resin and hardener. Within a few seconds after applying adhesive on the first glass slide, a second glass slide was placed on the first glass slide. Pressures from about 20–120 N were applied to fix two glass slides in place, resulting in glass slide/glue composite specimens with a variety of adhesion areas and bond thicknesses (Fig. 1). Table I lists the adhesive type, number of glue spots per specimen, range of adhesion area, and glue bond thickness for the 168 glass slide/glue composite specimens included in this study.

Before measuring mass, thickness and Young's modulus of each glass slide/glue composite specimen, the glue bonds were allowed to set. Thus we used two criteria to determine the setting time for each type of adhesive. First, a shear force was applied to a glass slide/glue composite specimen. If the slides did not move with respect to one another due to the shear force, then the lack of shear was taken as one indication that the adhesive had set. Secondly, when the glue extruded from the edge of a glass slide/glue composite specimen was no longer sticky, then this was taken as another indication that the glue had cured. The setting time was 1 h for the super glue and about 24 h for the epoxy cement. For the epoxy resin the setting time varied depending on the ratio of resin and hardener in the epoxy. The setting time was about 4 h for the composition of 50% resin and 50% hardener, while it was about 2 days for the other compositions.

In this study, five epoxy resin specimens were fabricated with differing compositions of resin and hardener to determine the Young's modulus of epoxy resin. Also we wished to determine the extent to which experimental error in mixing the resin and hardener (from separate tubes for resin and hardener which were supplied) affects the Young's modulus of the resulting bond layer in the composite specimens. Thus we intentionally varied the resin-hardener proportions over a relatively large range and determined the Young's modulus of the epoxy resin specimens (Table II).

To fabricate an epoxy resin specimen of a pre-selected composition, the hardener was squeezed into a rectangular plastic mould (Fig. 2a). Then the resin and the hardener were mixed together using a wooden stick (Fig. 2b), resulting in an epoxy resin of relatively uniform composition (Fig. 2c). After mixing, the mould and the uncured epoxy resin were placed in a vacuum chamber (Fig. 2d). The chamber was then evacuated two or three times using a roughing pump, which eliminated the large bubbles present in the mixed epoxy. The setting time varied from specimen to specimen. After about 3 weeks, the three epoxy resin specimens having amounts of resin greater than 50% were cured. Then the plastic moulds of the three epoxy resin specimens were ground off by a belt grinder (Fig. 2e), resulting in three epoxy resin specimens composed of epoxy resin itself (Fig. 2f). The dimensions and mass of each epoxy resin specimen are

TABLE I Data for all of glass slide/glue composite specimens used in this study

Type of adhesive	Number of glue spots per specimen	Number of specimens	Range of adhesion area (%)	Bond thickness range (mm)
Super glue	1	28	2.6–79.4	0.010–0.030
	2	13	7.2–59.4	0.011–0.020
	3	24	0.35–89.0	0.010–0.021
	5	5	7.0–16.9	0.012–0.016
	[a]	8	96.1–99.5	0.007–0.020
Epoxy cement	1	10	0.84–77.9	0.010–0.179
	3	9	1.0–78.1	0.019–0.112
	[a]	1	93.8	0.111
Epoxy resin	3	55	2.2–88.3	0.036–0.370
	[a]	2	91.9–97.9	0.196–0.256
	[a]	13	100	0.075–0.305

[a]Number of glue spots of the specimens having adhesion areas greater than 90% cannot be distinguished.

TABLE II Experimentally obtained elastic moduli, densities and Poisson's ratios for cured epoxy resin compositions, compared with reference values

Composition (resin: hardener)	Elastic modulus (GPa)	Density ($g\,cm^{-3}$)	Poisson's ratio	Reference
50% : 50%	2.98	1.13	0.27	This study
65% : 35%	3.17	1.14	0.29	This study
80% : 20%	3.43	1.16	0.31	This study
[a]	2.7–4.1	[b]	0.34	[8]
[c]	3.0–6.0	1.1–1.4	0.38–0.4	[9]

[a]Specific compositions were not specified in [8] and [9], material listed as "cured epoxy resins."
[b]Mass density was not specified.
[c]Specific compositions were not specified, material listed as "epoxy resins."

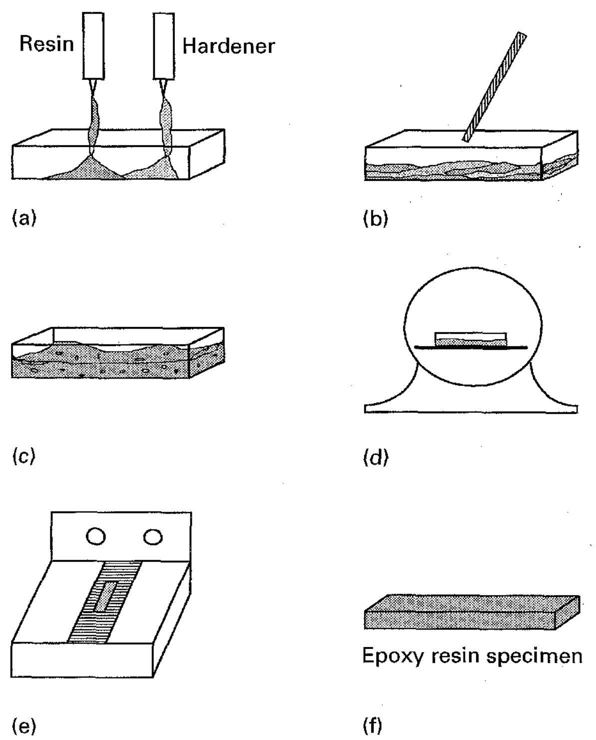

Figure 2 Schematic drawings showing the fabrication process for epoxy resin specimen: (a) squeezing resin and hardener into the mould, (b) mixing, (c) uncured epoxy resin containing pores, (d) removing pores by vacuuming, (e) grinding off the mould, and (f) the resulting epoxy resin specimen.

TABLE III Dimension and mass of each epoxy resin specimen used in this study

Composition resin : hardener	Dimensions, length × width × thickness (cm)	Mass (g)
50% : 50%	8.51 × 2.19 × 0.50	10.63
65% : 35%	8.90 × 2.05 × 0.46	9.57
80% : 20%	8.64 × 2.15 × 0.41	8.92

given in Table III. However, the other two epoxy resin specimens having compositions of 20% resin and 35% resin were not set even after 2 months, so that the two specimens were excluded from modulus measurements.

2.2. Measurements of bond thickness, mass, and adhesion area

Before gluing, the thickness of each glass slide was measured by a micrometer with an accuracy of ± 0.001 mm. After curing, the thickness of the glass slide/glue composite was measured using the same micrometer. Also, the mass of the glass slides and the cured composite specimens were measured by an electronic balance with an accuracy of ± 0.0001 g.

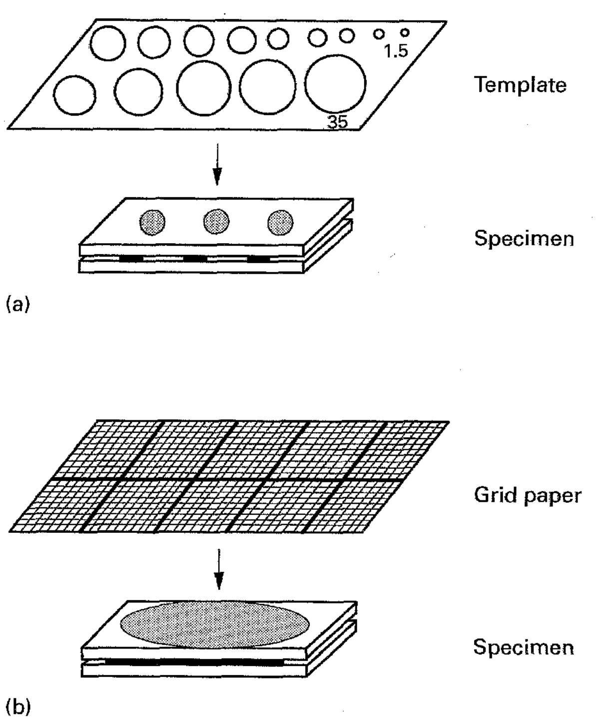

Figure 3 Schematic drawings showing two techniques used for measurement of adhesion area on the glass slide/glue composite specimens: (a) template method for small circular glue spots, (b) grid counting method for irregular glue spots.

The adhesion area of each glass slide/glue composite specimen was measured by one of two techniques, depending on the shape of the glued area for each specimen (Fig. 3). For small circular glue spots, a template having 41 circles of various sizes from 1.5–35 mm was used to measure the glued area fraction (Fig. 3a). The template was placed over each of the glass slide/glue composite specimen's glue spots. The size of each glue spot was determined from the template circle that most closely matched the glue spot diameter. However, for larger, irregularly shaped glue spots, the template method could no longer be applied. Instead, a grid counting method which employed translucent grid paper ruled into 3.175 mm (1/8 in) squares was used to determine the adhesion area (Fig. 3b). First, the grid paper was placed above a glass slide/glue composite specimen with a line traced along the edge of glued area. Then, the adhesion area fraction was calculated by counting the number of squares which covered the glued area.

2.3. Determination of elastic modulus

The sonic resonance apparatus (Fig. 4) includes a prismatic bar specimen suspended horizontally by cotton threads from a driver transducer and a pick-up transducer [3]. The driver transducer excites a mechanical resonance in the specimen. The pick-up transducer then converts the mechanical vibrations to a corresponding electrical signal, which is monitored by a digital voltmeter and an oscilloscope [3].

In order to determine the elastic modulus of the specimen, the vibrational modes of the specimen must be identified [4, 5]. The location of nodes and antinodes are unique to a specific vibrational mode

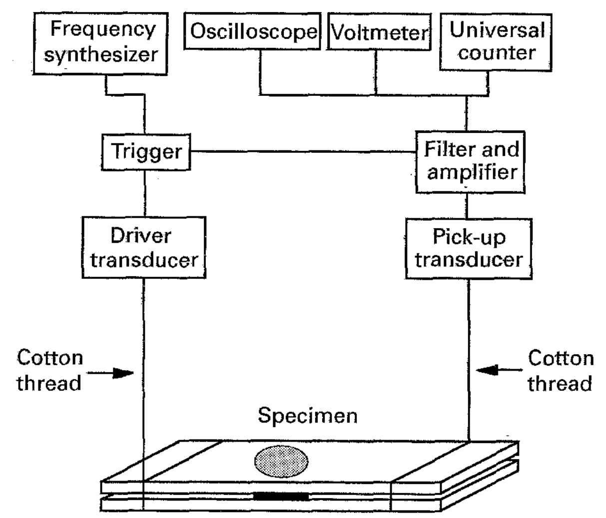

Figure 4 Block diagram of the sonic resonance apparatus for determining elastic modulus [3].

[4]. Thus, once the positions of the nodes and antinodes are known, then the vibrational mode is uniquely identified. In this study, the fundamental flexural vibration mode was used for Young's modulus determinations. The resonant mode identification was performed using a steel wire to probe for the locations of nodes and antinodes [4].

The fundamental flexural frequency, F_{flex}, of a given specimen was determined at room temperature in air. The elastic modulus, E, is related to F_{flex} by [3, 6, 7]

$$E = D\rho S_{\text{flex}} F_{\text{flex}}^2 \quad (1)$$

where ρ is the mass density of the material and S_{flex} is a shape factor. For the flexural vibration of prismatic bars, the constant $D = 0.94642$.

3. Results and discussion

The Young's modulus was measured for a total of 168 glass slide/adhesive composite specimens (Table I). Two different types of empirical equations were employed to interpret experimental results for the effects of adhesion on the effective elastic modulus, E, of a glass slide/glue composite specimen

$$E = E_{100}[1 - C_1 X^{C_2}] \quad (2)$$

$$E = E_{100}[1 - C_3 \exp(C_4 X)] \quad (3)$$

where X is the fractional unadhered area and C_1, C_2, C_3, and C_4 are least-squares fitting constants. E_{100} is the elastic modulus of specimens having an adhesion area of 100% (that is, $X = 0$). However, it was not always possible to produce composite specimens with an ideal 100% area coverage of adhesive. Working approximations of E_{100} were thus obtained by averaging the measured modulus for specimens having adhesion areas approaching 100%. For each adhesive type, Table IV lists the values of $\langle E_{100}(\text{exp}) \rangle$, which is the average of the experimentally determined moduli for high-adhesion-area specimens. In addition, Table IV gives the range of adhesion area for specimens used to obtain $\langle E_{100}(\text{exp}) \rangle$. The power-law equation (Equation 2) and the exponential candidate

TABLE IV E_{100} values used in Equations 2 and 3 for super glue, epoxy cement, and epoxy resin

Type of adhesive	Number of specimens averaged	Range of adhesion area (%)	$\langle E_{100}(\text{exp})\rangle$ (GPa)
Super glue	8	96.1–99.5	69.99
Epoxy cement	1	93.8	70.07
Epoxy resin	13	100	68.49
	1 (R1[a])	100	69.54
	3 (R2[a])	100	68.42
	2 (R3[a])	100	67.03

[a]Ranges of bond thickness; R1, 0.025–0.075 mm; R2, 0.125–0.175 mm; R3, 0.225–0.275 mm.

TABLE V Fitting constants, C_1, C_2, and correlation coefficient found for fitting the elastic modulus versus adhesion area data to Equation 2 (Figs 5–9). Except for the specimens adhered by one glue spot, correlation coefficients were similar for fitting to Equation 3 (exponential dependence on X). For specimens adhered by one glue spot, fitting to Equation 3 yielded a very poor fit.

Type of adhesive	Number of glue spots per specimen	C_1	C_2	Correlation coefficient
Super glue	1	0.7878	2.0959	0.99
	2	0.3585	4.9727	0.98
	3	0.4099	5.0131	0.98
	5	0.3323	5.0955	0.99
	2, 3, and 5	0.4102	5.7098	0.98
Epoxy cement	1	0.8000	1.4544	0.98
	3	0.4205	4.5380	0.98
Epoxy resin	3	0.4610	3.8187	0.97
	3 (R1[a])	0.4205	4.2041	0.99
	3 (R2[a])	0.5002	4.2619	0.99
	3 (R3[a])	0.5466	3.9076	0.99

[a]Ranges of bond thickness; R1, 0.025–0.075 mm; R2, 0.125–0.175 mm; R3, 0.225–0.275 mm.

equation (Equation 3) fit the multiple glue spot data quite well, with similar correlation coefficients ≥ 0.97 for each type of specimen (Table V). However, for the specimens adhered by one glue spot, Equation 3 yielded a relatively poorer fit (with correlation coefficients of 0.94 and 0.97 for epoxy cement and super glue adhered specimens, respectively) than Equation 2 (with correlation coefficients of 0.98 and 0.99). Both the multiple and single glue-spot groups of data can be described well by Equation 2 (Table IV). The least-squares best-fit curves corresponding to Equation 2 are shown with experimental results from modulus measurement in Figs 5–9.

3.1. Experimentally obtained elastic moduli of single glass slide, pairs of unadhered glass slides, and epoxy resin specimens

In this study, the average elastic modulus of the glass slides used to fabricate glass slide/glue composite specimens was 70.53 ± 0.32 GPa, as determined from sonic resonance modulus measurements of 140 individual glass slides. Also, sonic resonance measurements yielded an average elastic modulus of 20.04 ± 1.62 GPa for six different pairs of unadhered glass slides (Fig. 10b).

Three epoxy resin specimens of three different compositions of resin and hardener were fabricated to

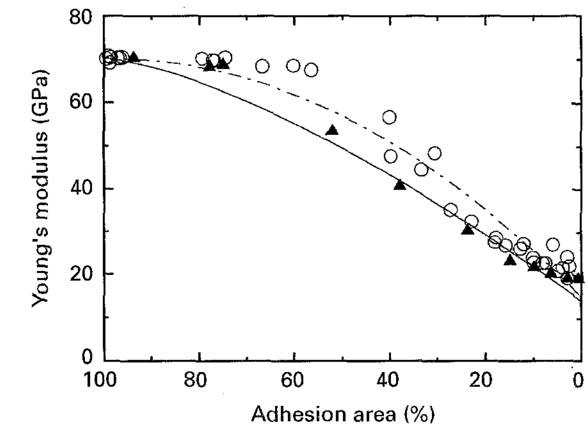

Figure 5 Comparison of Young's modulus for (○) super glue adhered specimens and (▲) epoxy cement adhered specimens for one glue spot as a function of adhesion area (%). The curves represent a least-squares best-fit to Equation 2.

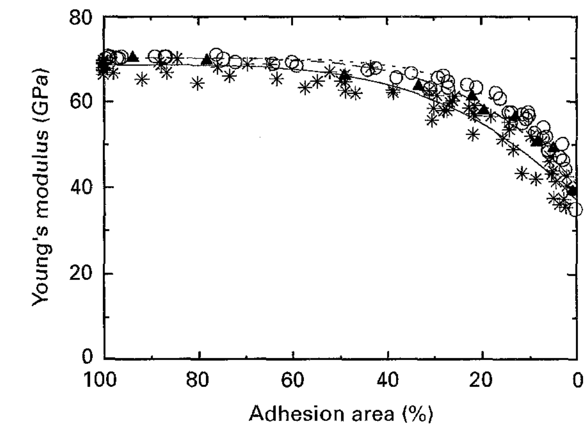

Figure 6 Young's modulus of (○) glass slide/super glue, (▲) glass slide/epoxy cement, and (*) glass slide/epoxy resin composite specimens having two or more glue spots as a function of adhesion area (%). The curves represent a least-squares best-fit to Equation 2.

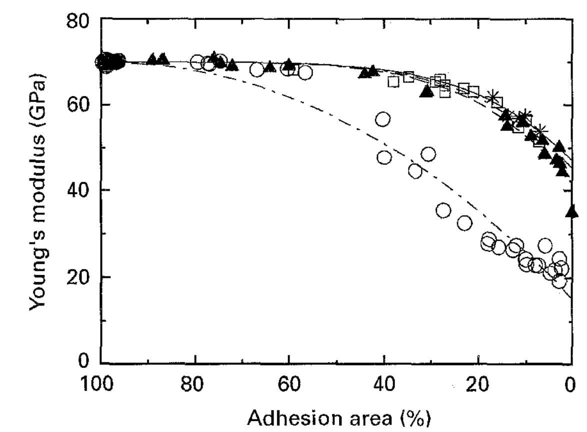

Figure 7 For a super glue bond layer, the effects of the adhesion area and the number of glue spots on Young's modulus as a function of adhesion area (%) (○) one glue spot, (□) two glue spots, (▲) three glue spots, (*) five glue spots. The curves represent a least-squares best-fit to Equation 2 [10].

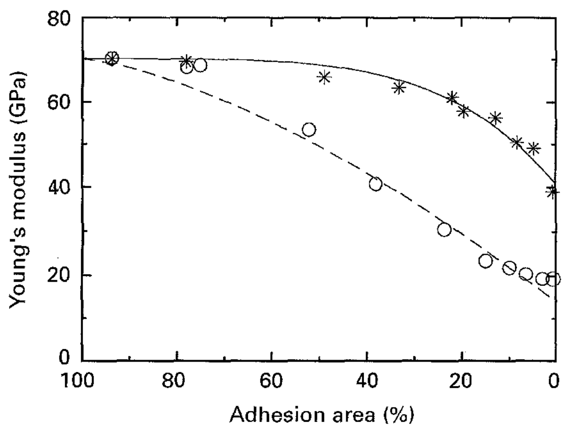

Figure 8 For an epoxy cement bond layer, the Young's modulus as a function of adhesion area (%) for specimens having (○) one and (*) three glue spots. The curves represent a least-squares best-fit to Equation 2 [10].

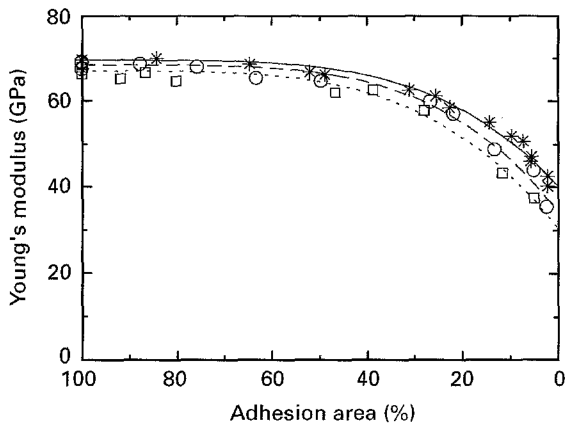

Figure 9 For an epoxy resin bond layer, the effect of glue bond thickness of epoxy resin on Young's modulus as a function of adhesion area (%) (*) 0.025–0.075 mm, (○) 0.125–0.175 mm, (□) 0.225–0.275 mm. The curves represent a least-squares best-fit to Equation 2 [10].

determine the elastic modulus, density, and Poisson's ratio of the epoxy resin itself (Table II). The experimental values of Young's moduli and densities obtained in this study were comparable to moduli, density, and Poisson's ratio values in the literature (Table III) [8, 9]. As the fraction of resin in the epoxy resin composition increased from 50% to 80%, the Young's modulus of the epoxy resin increased from 2.98 GPa to 3.43 GPa. The modulus of the epoxy resin is relatively insensitive to small changes in the hardener–resin proportions. Therefore, small experimental errors in mixing the resin and hardener components should have little effect on the modulus of the composite specimens. Also, for the particular modulus values for the glass slides and the glue bond layers, a model for the effective Young's modulus of the glass slide/glue composites predicts a relatively weak dependence on the modulus of the bond layer (Section 2.2, Part II [2]). A composition of 50% hardener and 50% resin was subsequently used to fabricate a total of 70 epoxy resin adhered specimens with varying adhesion areas (Section 3.2).

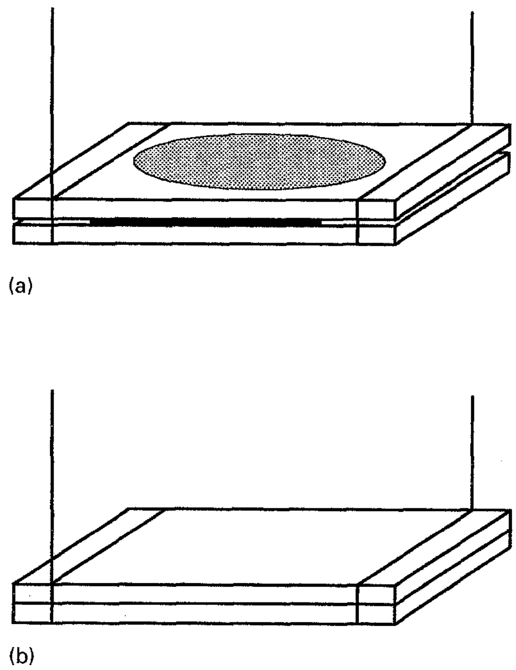

Figure 10 Glass slides suspended by cotton threads (a) with glue bond, (b) with no glue at the interface between the two glass slides.

3.2. The effect of adhesion area and spatial distribution of bond phase on elastic modulus

For the discussion of the effective Young's modulus, two adhesion area regimes will be considered: (1) from 100% to 70%, and (2) from 70%–0%. These two adhesion area regimes show different behaviours of modulus versus adhesion area.

For every one of the glass slide/glue composite specimens, including each of the three bond types and each of the spatial patterns for bond-phase distribution (Fig. 1), the effective modulus was relatively constant at approximately 70 GPa for adhesion areas ranging from roughly 70%–100% (Figs 5–9) [10]. It should be noted that, for adhesion areas above about 90%, the final geometry of the bond-phase was indistinguishable when one, two, three, or five glue spots were initially applied to fabricate the composite specimens (Table I). For the epoxy resin specimens adhered by three glue spots (Fig. 9), however, there is a systematic decrease in Young's modulus as the thickness of the bond phase increases, and this decrease is apparent for the adhesion area range from 70–100%, as well as for lower values of adhesion area [10]. Bond-thickness effects will be discussed further in the next section.

For the adhesion area range from 70%–0%, there is a striking difference (Figs 7 and 8, and shown schematically in Fig. 11) in the behaviour of the Young's modulus between those specimens adhered by a single glue spot and those specimens adhered by multiple glue spots (two, three, and five in this study) [10]. For one glue spot the effective Young's modulus decreases continuously as the adhesion area decreases beyond about 70%, approaching 20 GPa as the adhesion area approaches 0% (Figs 7, 8, 11) [10].

The effective Young's moduli of two, three, and five glue-spot adhered composite specimens decreases slowly as the adhesion area decreases from 70% to 40% (Figs 7, 8, 11) [10]. However, for adhesion areas less than 40% Young's moduli decrease relatively rapidly. When the adhesion area approaches 0% for the multiple glue spot adhered specimens, the measured Young's modulus ranges from about 35–50 GPa, depending on the adhesive type, number of glue spots, and bond thickness (Figs 6–9).

For a given adhesion area fraction, A, $E_{MS}(A)$ and $E_{1S}(A)$ represent the modulus for glass slide/adhesive specimens with multiple (two or more) glue spots and a single glue spot, respectively. The quantity $E_{MS}(A) - E_{1S}(A)$ for the epoxy cement adhered composite specimens is greater than $E_{MS}(A) - E_{1S}(A)$ for the super glue adhered composite specimens over the entire range of A (Fig. 12), which reflects the more rapid decrease in the effective Young's modulus of epoxy cement adhered specimens having one glue spot compared to the effective Young's modulus of super glue adhered composite specimens having one glue spot (Figs 5–8 and 12). Also, $E_{MS}(A) - E_{1S}(A)$ reaches a maximum of 28 GPa at around 10% adhesion area for the glass slide/super glue composites and a maximum of 30 GPa at about 15% adhesion area for the glass slide/epoxy cement composites, although the two curves converge when 0% adhesion area is approached (Fig. 12).

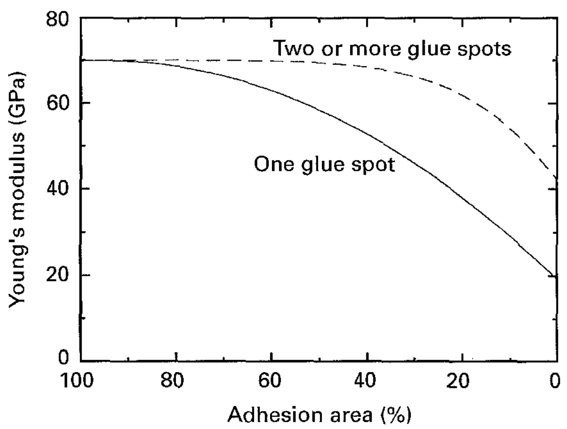

Figure 11 Schematic illustration of Young's modulus versus adhesion area (%) for one glue spot and two or more glue spot adhered glass slide/glue composite specimens.

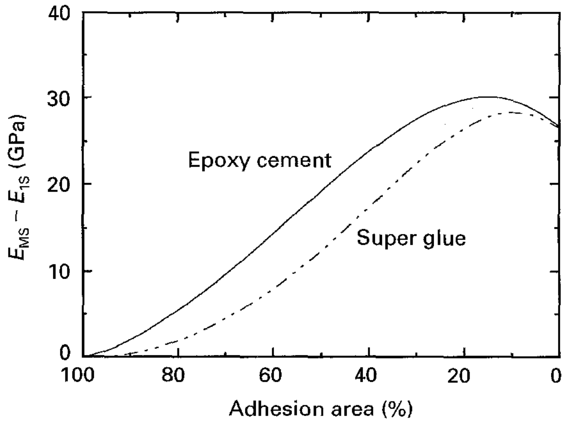

Figure 12 Difference between the Young's modulus, E_{1S}, of one glue spot adhered composite and the Young's modulus, E_{MS}, of multiple (two or more) glue spot adhered composite as a function of adhesion area (%).

3.3. The effect of glue bond thickness on elastic modulus

In order to explore the effect of the glue bond thickness on the Young's modulus, the data for the super glue and the epoxy resin adhered composite specimens were classified according to glue bond thickness ranges. For the super glue adhered specimens having two or more glue spots, the selected data subsets corresponded to bond thickness ranges of 0.010–0.012, 0.019–0.021, and 0.028–0.030 mm. For the epoxy resin adhered specimens, the selected bond thickness ranges were 0.025–0.075, 0.125–0.175, and 0.225–0.275 mm. For both the super glue and the epoxy resin adhered specimens, the data subsets were intentionally chosen to be "disjoint". For example, for the epoxy resin bond thickness data, the consecutive data intervals of 0.025–0.075 and 0.125–0.175 mm have an intentional "gap" in the data for the bond thickness interval 0.075–0.125 mm.

For the glass slides adhered by the epoxy resin, as the glue bond thickness increased from 0.025 mm to 0.275 mm, the effective Young's modulus decreased from about 70 GPa to roughly 67 GPa for 100% adhesion area. Near to 0% adhesion area, the Young's modulus decreased by up to 10 GPa (Fig. 9) [10].

A glue bond thickness effect was not obvious for the glass slide/super glue composites. This weak dependence of Young's modulus on the glue bond thickness likely results from the fact that the super glue bonds were relatively thin and that the super glue bond thickness spanned a maximum of only a factor of 3 in bond thickness (bonds for super glue adhered specimens ranged from 0.010–0.030 mm). In contrast to the super glue bond layers, the epoxy resin bonds were much thicker and the bond thicknesses varied by more than a factor of 10 (the epoxy resin bond thicknesses were from 0.025–0.275 mm).

For the glass slide/epoxy resin composite specimens, the observed decrease in the effective Young's modulus with increasing bond thickness can be explained qualitatively in terms of the relative difference between the Young's modulus of the glass slides (70.53 GPa) and the epoxy resin (3 GPa) (see Section 3.1). Recall that the glass slide/glue composites employed in this study are essentially a "sandwich" structure, with the bond layer sandwiched between two glass slides (Fig. 1). For specimens having a fixed adhesion area, as the bond thickness increases the fraction of the low-modulus phase in the structure increases. Thus, the overall effective modulus of the laminate composites can be predicted to decrease as the bond layer thickness increases, which agrees with experimental observations.

However, if the porosity of the bond layer changes as a function of the bond layer thickness, then the elastic modulus of the epoxy resin bond layer itself will depend on the bond thickness (Appendix 2). However, for the 13 epoxy resin adhered composite specimens having 100% adhesion area (Table I), the volume fraction porosity is independent of the bond thickness (Appendix 2). Therefore, the experimentally observed trend that the overall elastic modulus of the glass slide/epoxy resin composites decreases as the bond thickness increases, apparently does not depend on porosity within the bond phase, because no systematic changes in bond-phase porosity occur as a function of bond thickness.

Part II [2] of this study treats quantitative models for the effect of thickness on the effective Young's modulus, including a rule of mixtures model, a dynamic beam vibration model. In addition, a semiempirical model for the effective elastic modulus of a laminate composite as a function of adhesion area, bond thickness, and spatial distribution of the bond phase is developed in Part II [2] of this study.

4. Conclusion

Glass slide/glue composite specimens were fabricated to investigate effects of adhesion on the effective Young's modulus of glass slides adhered by three different types of adhesives: (1) super glue, (2) epoxy cement, and (3) epoxy resin. The sonic resonance technique was used to determine the Young's moduli of individual glass slides, unadhered glass slide pairs, glass slide/glue composite specimens, and epoxy resin specimens. Composite specimens adhered by two or more glue spots showed very similar trends in the effective Young's modulus as a function of adhesion area (Figs 6–9).

Composite specimens adhered by one glue spot showed a lower effective Young's modulus over the entire adhesion area range than specimens adhered by multiple glue spots (Figs 7, 8, and 11). The Young's modulus difference between one glue spot and multiple glue spots adhered specimens increased from approximately 0 GPa at 100% adhesion area to about 30 GPa at about 10% adhesion area (Figs 11 and 12).

The dependence of the Young's modulus on adhesion area (Figs 5–9) was described well by an empirical power law equation (Equation 2), which has two free parameters that were determined by a least-squares technique. Also, for the epoxy resin specimens, a trend of decreasing Young's modulus with increasing bond thickness was observed. In Part II [2], we first consider the thickness dependence of layers having 100% adhesion area in terms of known models that can be applied to laminate composites, such as the rule of mixtures and dynamic beam vibration models. The failure of both the ROM and dynamic modulus models to describe the thickness data leads us to propose a semiempirical equation, which is then extended to describe the adhesion area dependence of elastic modulus, as well as bond thickness, in a single expression (Section 2.2, Part II [2]).

Appendix 1. External crack model and qualitative explanation for the dependence of the effective Young's modulus on adhesion area

Kemeny and Cook [1] introduced an "external crack" model to estimate the effect of strongly interacting cracks which are very common in rocks having a high crack density. From considering increase in strain energy due to the presence of the cracks, Kemeny and Cook estimated the effective Young's modulus for a linear elastic, isotropic and homogeneous body containing a random distribution of N external cracks with a mean crack length squared $\langle c^2 \rangle$ and a mean external crack contact length squared $\langle a^2 \rangle$ (Fig. A1a) [1]. For a two-dimensional body of area, A, effective Young's modulus, $\bar{E}$, and intrinsic Young's modulus, E, the Kemeny and Cook model [1] gives

$$\frac{\bar{E}}{E} = \left\{1 + \frac{8}{\pi} m \ln\left[\left(1 + \frac{1}{n}\right)(1 - \nu^2)\right]\right\}^{-1} \quad \text{(A1)}$$

where $m = N\bar{c}^2/A$ is the crack density parameter, $\bar{c}$ is the effective crack length ($\bar{c}^2 = \langle c^2 \rangle / N$), $n = \bar{a}/\bar{c}$ is the external crack shape parameter which characterizes the relative amount of contact per unit area, and $\bar{a}$ is the effective external crack contact length ($\bar{a}^2 = \langle a^2 \rangle / N$).

From Equation A1, as the crack density approaches infinity, the effective Young's modulus approaches zero [1]. When the crack density, m, is held constant, the effective Young's modulus decreases with the decrease of the relative crack contact area, n [1].

The dependence of the effective Young's modulus on adhesion area might be qualitatively explained with the external crack concept (Fig. A1a and b). In the current study, the glass slide/glue composite specimens were fabricated with glue spots surrounded by unadhered regions. The unadhered regions are similar to external cracks.

For a tensile specimen having external cracks (Fig. A1a), the overall Young's modulus decreases with decreasing crack contact area, $2a$ [1]. Similarly,

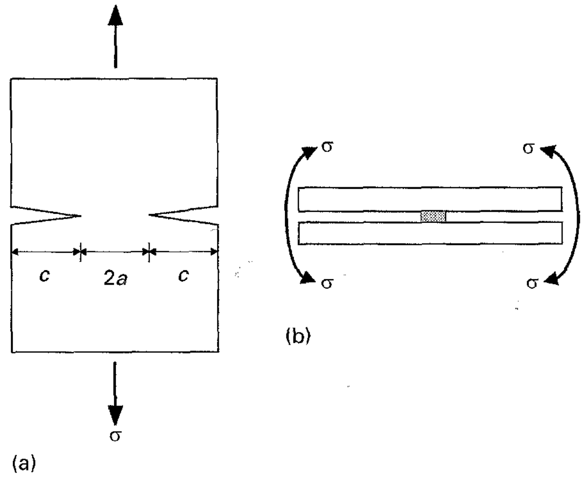

Figure A1 (a) External cracks under uniaxial loading [1], (b) schematics drawing of one glue spot adhered glass slide/glue composite specimen undergoing vibrational motion.

the effective Young's modulus of a glass slide/glue composite specimen decreases with decreasing adhesion area (Fig. A1b), as observed in this study. However, in our study, two glass slides of nearly equal thickness are joined by an adhesive. Thus if the adhesion area is less than 100%, the unadhered regions of the glass slide/glue composite specimens are at the mid-plane of the specimen in our study (Fig. A1b). During the elastic modulus measurements (Section 2.3) the specimens undergo flexural vibration under free–free boundary conditions (Fig. 4 and schematically in Fig. A1b). On the other hand, the model specimen with external cracks undergoes a uniaxial tension applied along the longitudinal direction (Fig. A1a). Thus, while the Kemeny and Cook model does describe physical systems that are somewhat similar to our specimens, the specimen loading assumed by Kemeny and Cook and the loads experienced by our specimens were sufficiently different that the Kemeny and Cook model was not used in this study.

Appendix 2. Pore diameter and volume fraction porosity measurements in epoxy resin specimens and in the epoxy resin bond layers of composite specimens

In general, the elastic modulus of a solid decreases as the volume fraction porosity increases [11, 12]. For ceramics [12] the relationship between the elastic modulus, E, and the volume fraction porosity, ρ, is given by

$$E = E_0(1 - b\rho) \quad \text{(A2)}$$

where E_0 is Young's modulus of the theoretically dense material, b is a non-dimensional empirical constant. In many cases, $b \cong 2.0$. For this study, we assume Equation A2 also holds for the epoxy resin, which will allow us to estimate the relative change in modulus induced by porosity changes (see below, *Epoxy resin specimens*).

If the volume fraction porosity of the bond phase changes as the bond thickness increases, then the elastic modulus of the bond phase itself would depend on the bond thickness. Such an interdependence of bond thickness and bond-phase moduli would complicate and confuse the relationship between the bond thickness and the overall elastic moduli, as discussed in Section 3.3 and Part II Section 2.1 [2]. This appendix discusses measurements of volume fraction porosity and pore diameter as a function of bond thickness for the glass slide/epoxy resin composites.

Of the three adhesive agents used in this study (super glue, epoxy resin and epoxy cement), the epoxy resin and the epoxy cement were mixtures of two initially separate components (a hardener and a resin). While the super glue and epoxy cement were relatively pore-free when applied as a bond layer in the glass slide/glue composites, the required mixing of the epoxy resin generated small bubbles which became pores in the cured epoxy resin. Thus we measured the pore diameter and the porosity for both: (1) the three epoxy resin specimens listed in Table II and III and (2) the epoxy resin bond phase for the 13 glass slide/epoxy resin composite specimens having a 100% adhesion area (Table I). An optical-image analysis system (Leco Neophot-21 Image Analysis System, Leco Corporation, St Joseph, MI) was used to determine the average pore diameter and the effective volume porosity for epoxy resin specimens and the epoxy resin bonded specimens.

Epoxy resin bond-phase measurements

The pore diameters varied from about 15 ~ 250 μm, although the image analyser neglected pores with diameters less than about 15 μm. Thus, the analysis presented here is for pores exceeding 15μm in diameter.

The pores were non-uniformly distributed within the volume of the epoxy resin bond phase. At a magnification of 40 (which was used for all measurements described in this study) and a depth of field of about 300 μm (which is close to or greater than the thickness of bond phase, Table VI), approximately 1–12 pores were visible in the image analyser's field of view (approximately 1800 μm by 1800 μm).

The average pore diameter and the bond-phase porosity were determined from measurements on ten randomly selected locations on each specimen (Table VI). The average pore diameter, which was between 40 and 55 μm for 8 of the 13 specimens, was not correlated with the thickness of the epoxy resin bond layer (Table VI). The overall average pore size for the 13 epoxy resin bonded specimens was 50.1 μm, as calculated from the average pore size of the individual specimens. The mean volume fraction porosity of the epoxy resin bond layer was between 0.06% and 0.45%

TABLE VI Average pore size and porosity of 13 glass slide/epoxy resin composite specimens having 100% adhesion area. For each specimen, the average pore size was calculated on the basis of 10 randomly selected locations on the specimen

Bond layer thickness (mm)	Average pore size (μm)	Average porosity (%)	Bond layer thickness (mm)	Average pore size (μm)	Average porosity (%)
0.075	38.8 ± 12.5	0.06 ± 0.02	0.163	52.2 ± 23.5	0.06 ± 0.08
0.088	41.1 ± 22.3	0.07 ± 0.09	0.205	46.8 ± 19.6	0.17 ± 0.07
0.09	46.4 ± 20.7	0.10 ± 0.08	0.227	59.5 ± 34.2	0.43 ± 0.37
0.09	58.3 ± 35.5	0.36 ± 0.38	0.247	55.5 ± 32.8	0.25 ± 0.25
0.116	54.8 ± 23.5	0.21 ± 0.17	0.279	58.4 ± 39.5	0.45 ± 0.44
0.145	48.3 ± 37.1	0.08 ± 0.11	0.305	47.5 ± 22.8	0.12 ± 0.08
0.153	43.5 ± 21.0	0.10 ± 0.10			

for the 13 composite specimens included in this study, as listed in Table VI (for 10 of the 13 specimens, the mean volume fraction porosity was between 0.06% and 0.25%). The overall average porosity was 0.19% as calculated from the porosity values of the 13 individual specimens. The large standard deviations associated with the mean volume fraction porosities (Table VI) are indicative of the variations in porosity for the ten random sites for which porosity data were taken for each specimen.

Thus neither the pore size nor the volume fraction porosity seem to be correlated with the thickness of the epoxy resin bond layer for the glass/epoxy resin composites. The porosity data for the 13 specimens was fit to the linear equation

$$P = D_1 + D_2 t_b \quad \text{(A3)}$$

where P is the porosity in per cent and t_b is the thickness of the epoxy resin bond in millimeters. A least-squares fit of the data to Equation A3 gave fitting constants D_1 and D_2 values of 0.060 and 0.777, respectively, with a correlation coefficient of 0.43 (Fig. A2). While the fit to Equation A3 is very poor for the porosity versus bond thickness data, the scatter in the data (Fig. A2) indicates that a poor regression fit also would result if other functional forms for the porosity–bond thickness relation had been used.

Epoxy resin specimens

In addition to the bond phase in glass slide/epoxy resin composites, measurements of the volume fraction porosity and the pore diameter were performed on the three epoxy resin specimens fabricated in this study (Section 2.1). The elastic moduli of these bulk epoxy resin specimens were used to estimate the moduli of the bond phase in glass slide/epoxy resin composites. As will be discussed in this section, the volume fraction porosity of epoxy resin specimens is very similar to the porosity of the bond phase in the epoxy resin adhered glass slide composites. Thus it is reasonable to estimate the epoxy resin bond-phase modulus based on the modulus of the bulk epoxy resin specimens.

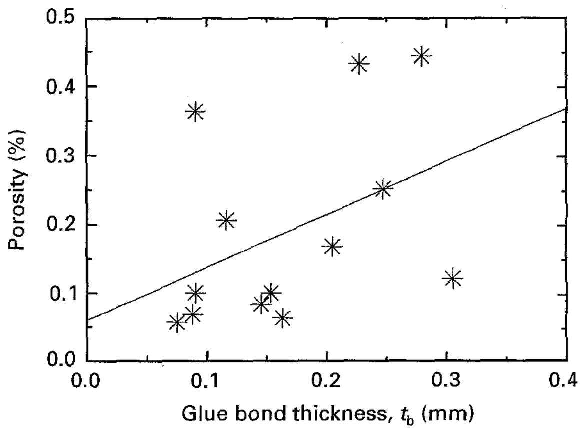

Figure A2 A plot of the volume fraction porosity versus the glue bond thickness for the 13 epoxy resin adhered composite specimens having 100% adhesion area.

Using a low-speed diamond saw, a thin section approximately 21 mm × 5 mm × 1 mm was cut from the end of each of the three epoxy resin specimens (Table II and III). After cutting, the specimens were ground using 600 grit abrasive paper, resulting in thin sections about 300 μm thick which matches the depth of field for the optical microscope under magnification of 40. The same image analysis system was used to determine the average pore diameter and volume porosity of each of the specimens. As in the measurements on the epoxy resin bond phase of the composite specimens, the pores were non-uniformly distributed in the epoxy resin, thus the mean pore diameter and the volume fraction porosity were computed based on five randomly selected locations on each of the epoxy resin thin sections. However, the optical contrast for the pore–resin interfaces within the epoxy resin thin sections was lower than the optical contrast for the epoxy resin bond-phase measurements. As a result of the lower optical contrast for the thin sections, the image analyser software underestimated the actual pore diameters for the epoxy resin thin section specimens. Therefore, for the epoxy resin thin section specimens the relative pore diameters were measured directly from the image analyser screen using a ruler and then the diameter data were converted to actual diameters and volume fraction porosities (Table VII). As the amount of the resin changed from 50% to 80%, both the pore diameter and the volume fraction porosity decreased (Table VII).

The epoxy resin bond phase within the glass slide/epoxy resin composites used in this study were composed of 50% resin and 50% hardener (Section 2.1). The volume fraction porosity determined for the epoxy resin specimen having 50% resin and 50% hardener was 0.81% (Table VII), which is not significantly different from 0.19% (Table VII), the average volume fraction porosity in the bond phase determined from the 13 glass slide/epoxy resin specimens. To estimate the relative difference in elastic moduli induced by this small difference in porosity, we differentiate Equation A2 with respect to ρ to obtain

$$\frac{d(E/E_0)}{d\rho} = -b \quad \text{(A4)}$$

or, in terms of finite differences

$$\Delta(E/E_0) = -b\Delta\rho \quad \text{(A5)}$$

Thus, from Equation A5, the elastic modulus of the epoxy resin bond phase within a glass slide/epoxy

TABLE VII Average pore size and porosity determined from thin sections of three epoxy resin specimens used in this study. For each thin section specimen, the average pore size was calculated on the basis of five randomly selected locations on the specimen

Composition (resin: hardener)	Average pore size (μm)	Average porosity (%)
50%:50%	117.6 ± 36.3	0.81 ± 0.42
65%:35%	53.1 ± 28.2	0.22 ± 0.12
80%:20%	42.7 ± 20.0	0.04 ± 0.21

resin specimen should be within about 1% of the modulus of the bulk epoxy resin specimen. Based on this assumption obtained from the porosity measurements, in Part II of this study [2], the modulus value determined from the epoxy resin specimen having 50% resin and 50% hardener is used to obtain a model for a glass slide/glue composite specimen.

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Received 15 September and accepted 25 October 1995