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Membrane Permeability Properties of Dental Adhesive Films

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Abstract

This study evaluated the permeability properties of five experimental resin membranes that ranged from relatively hydrophobic to relatively hydrophilic to seal acid-etched dentin saturated with water or ethanol. The experimental resins (R1, R2, R3, R4 and R5) were evaluated as neat bonding agents or as solutions solvated with ethanol (70% resin/30% ethanol). The quality of dentin sealing by these experimental resins was expressed in terms of reflection coefficients calculated as the ratio of the effective osmotic pressure to the theoretical osmotic pressure of test solutions. The effective osmotic pressure produced across resin-bonded dentin was induced in hypertonic solutions (CaCl₂ or albumin) at zero hydrostatic pressure. The outward fluid flow induced by these solutions was brought to zero by applying an opposing negative hydrostatic pressure. The least hydrophilic resin blends, R1 and R2, exhibited significantly ($p < 0.05$) higher reflection coefficients than the most hydrophilic resins (R4 and R5) in both conditions of dentin saturation (water and ethanol). The reflection coefficients of neat resins were, in general, significantly higher when compared to their corresponding solvated versions in both conditions of dentin saturation. In dentin saturated with ethanol, bonding with neat or solvated resins, resulted in reflection coefficients that were significantly higher when compared to the results obtained in dentin saturated with water. Reflection coefficients of CaCl₂ (ca. 1×10^{-4}) were significantly lower ($p < 0.05$) than for albumin (ca. 3×10^{-2}). Application of hydrophobic resins may provide better sealing of acid-etched dentin if the substrate is saturated with ethanol, instead of water.

INTRODUCTION

Contemporary hydrophilic adhesives seem to attract water from hydrated dentin through apparently intact, polymerized adhesive layers. Absorbed water molecules are drawn through the adhesive where they become trapped at the interface of the adhesive and

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overlying composite if polymerization is delayed¹⁻³. Theoretically, the use of hydrophobic resins as dentin adhesives would alleviate water sorption seen in hydrophilic resins^{4,5}, thereby lowering adhesive permeability and improve the durability of resin-dentin bonds. However, the use of hydrophobic monomers is not effective because they are not miscible with water-saturated dentin. To solve this problem, we proposed to modify the wet bonding technique by saturating acid-etched dentin with ethanol, an excellent solvent for monomers, instead of water. Dentin saturated with ethanol permits infiltration of interfibrillar spaces with relatively hydrophobic monomers, producing bond strengths as high as those obtained when using hydrophilic monomers on water-saturated dentin⁶⁻⁸.

Osmosis is due to the diffusion of water across a semi-permeable membrane. Although resin-bonded dentin is permeable to water^{1, 3, 9-13}, little is known about the permeability of resin-bonded dentin to solutes. That is, it is not clear whether the resin-bonded dentin function as a true semi-permeable membrane that is permeable only to water molecules, or belong to the broader category of permeable membranes that permit both the passage of water and solute of different sizes. The latter include small ions, plasma proteins in dentinal fluid¹⁴ or even residual uncured monomers entrapped in polymerized resin. True semi-permeable membranes must exhibit high selectivity, or the ability to distinguish between water and solute molecules. This selectivity is defined by the reflection coefficient (σ) of a permeable membrane¹⁵⁻¹⁶. Membranes with $\sigma = 1$ are semi-permeable membranes that are exclusively permeable to water molecules. In such membranes all other solute molecules are "reflected" from the membrane surface (i.e. total reflection) back into the solution. Conversely, membranes with $\sigma = 0$ are non-selective in that they have pore sizes that are large enough to permit the passage of water and a wide range of solute molecules (i.e. the extent of reflection is not different from when there is no membrane). Membranes with values between "0" and "1" are partially-selective. They are permeable to water and solute molecules of definitive sizes (i.e. partial permeation), while larger solute molecules are "reflected" away from the membrane walls¹⁷⁻²⁰ (Fig.1A-C).

Osmotic pressure is defined as the hydrostatic pressure applied to "the solute solution" side of a semi-permeable membrane that is required to stop the osmotic water flow. Osmotic pressure gradients induce fluid movement due to the diffusion of water down its concentration gradient created by concentrated solute solutions. Osmotic pressure defined in this way are equilibrium values, that is, when there is no net fluid movement^{19,20}.

The magnitude of osmotic pressure is then given by the van't Hoff equation¹⁵:

$$\pi_t = \Delta c RT \quad (1)$$

Where: π_t = theoretical osmotic pressure of a solution in pascals (Pa);

Δc = chemical concentration differences of solutes (in osmoles/L) across the membrane;

R = gas constant in $\text{m}^3 \text{ Pa osmole}^{-1} \text{ }^\circ\text{K}^{-1}$ ($8.3145 \text{ m}^3 \text{ Pa osmole}^{-1} \text{ }^\circ\text{K}^{-1}$)

T = absolute temperature in $^\circ\text{K}$ ($298 \text{ }^\circ\text{K}$)

To the extent that the membrane is permeable to solute, the effective osmotic pressure exerted across the dental resin layers will be less than the theoretical pressure¹⁵⁻¹⁶. The degree to which solute permeation of the membrane lowers the effective osmotic gradient is expressed by the reflection coefficient. The reflection coefficient is defined as the ratio of the effective osmotic pressure/the theoretical osmotic pressure, and it is used to correct the van't Hoff equation using equation 2^{15,16}.

$$\pi_e = \sigma \Delta c RT \quad (2)$$

Where: π_e = effective osmotic pressure of a solute in pascals (Pa);

All other symbols are the same as in equation (1)

If no solute permeated the membrane, π_e would be equal to 1.0 and the effective osmotic pressure would equal the theoretical pressure. Solute permeation of the membrane is equal to $1 - \sigma$ ¹⁵. The reflection coefficient takes into account the ability of a membrane to restrict solute permeation. Thus, reflection coefficients (σ) are measures of the semi-permeability qualities of membranes²⁰. Based on these principles, the reflection coefficients of experimental resins with different degrees of hydrophilicity bonded to water- vs ethanol-saturated dentin were determined in this study. The null hypotheses are that the permeability of resin infiltrated into dentin matrices saturated with water vs ethanol are not different; and that the molecular size of solutes has no effect on reflection coefficients of resins bonded to dentin.

MATERIALS AND METHODS

Teeth preparation

One-hundred forty non-carious human third molars were collected after the patients' informed consent had been obtained under a protocol reviewed and approved by the Human Assurance Committee of the Medical College of Georgia. Crown segments were prepared by removing the occlusal enamel and roots of these teeth, using a slow-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water-cooling. The pulpal tissue was extracted with a pair of small forceps. Care was taken to avoid touching the predentin. Dentin surfaces were further abraded with 240-grit silicon carbide paper, until a remaining dentin thickness of 1 ± 0.2 mm was achieved from the ground surface to the highest pulp horn. The resulting crown segments were glued to Plexiglass slabs ($1.8 \times 1.8 \times 0.7$ cm) using cyanoacrylate (Zapit, Dental Ventures of America, Corona, CA, USA), which also covered the entire peripheral cementum. Each Plexiglass slab was penetrated by a short length of 18-gauge stainless steel tubing, which ended flush with its top. This tube permitted the pulp chamber and polyethylene tubing to be filled with water (Fig. 2) and to be connected to an automated flow-recording device (Flodec System, De Marco Engineering, Geneva, Switzerland) in the absence of any pulpal pressure.

When hypertonic test solutions were applied to the polymerized resin surfaces, their low water concentrations established a water concentration gradient from the pulp chamber, contain pure water, out the water water-filled dentinal tubules that are continuous with the pulp chamber, to the resin tags. Water seeped around resin tags and diffused across the resin films via nanoporosities to reach the test solutions (Fig. 2).

Bonding procedures

Five experimental comonomer resin blends (R1, R2, R3, R4, R5) were evaluated as potential primers and bonding components of dentin/enamel adhesive systems. These comonomer blends with different degrees of hydrophilicity were either used as bonding agents in the form of neat resins, or were solvated with absolute ethanol to produce primer solutions, each containing 30% ethanol/70% resin (v/v%). Their composition and relative hydrophilicity/hydrophobicity, expressed as a function of the Hoy's solubility parameters, are listed in Table I. Hoy's solubility parameters were calculated using commercially available software (Computer Chemistry Consultancy, www.compchemcons.com). This is done by summing the molar attraction values of all structures according to the method of Van Krevelen²¹.

The dentin surfaces of the crown segments were etched with 37% phosphoric acid gel (Etch 37, Bisco Inc., Schamburg, IL, USA) for 15 s, rinsed thoroughly with deionized water and

left moist until bonding. The latter was rendered visibly saturated with either deionized water or 100% ethanol. A single layer (approximately 20 μm thick) of neat or solvated resin was then applied to the acid-etched dentin, under constant agitation for 30 s. Solvent evaporation was not performed as preliminary gravimetric experiments showed that 30% ethanol/70% resin mixtures did not lose significant mass when exposed to a gentle air stream (unpublished data). Additionally, if air was blown on such a thin resin layer (20 μm), it could have resulted in the incorporation of air bubbles into the solvated comonomer mixtures prior to their curing and/or resulted in overthinning of the resin layer. A piece of Mylar film was placed over the top of the comonomer mixture (neat or solvated) to exclude oxygen. The adhesive was then light-cured for 20 s using a halogen light-curing unit (Optilux 500, Demetron/Kerr, Danbury, CT, USA) with a power output of 600 mW/cm^2 . Bonding was performed with the pulp chamber filled with water, but at zero hydrostatic pressure.

Reflection coefficient measurements

Equation 2 can be solved for the reflection coefficient (σ) as:

$$\sigma = \left(\frac{\pi_e}{\Delta c RT} \right) J_v = 0 \quad (3)$$

Where: σ = the reflection coefficient of permeant solutes (unitless)

π_e = effective osmotic pressure of a solute in pascals (Pa)

J = fluid flow ($\mu\text{L m}^{-2} \text{sec}^{-1}$)

All other symbols are the same as in equation (1)

Under conditions of zero fluid flow ($J_v = 0$), the negative hydrostatic pressure required to stop outward fluid flow is a direct measure of the effective osmotic pressure of the test solution.

The effective osmotic pressure of the test solutions was measured by covering the resin-bonded dentin surface of the crown segment with two drops (with approximately 0.1 mL) of a hypertonic test solution (i.e. 5.5 M CaCl_2 or 35% albumin) (Fig 1A–C). The measurement of outward fluid flow induced by each hypertonic test solution was performed using the Flodec device (Fig. 2, DeMarco Engineering, Geneva, Switzerland). As soon as an outward fluid flow was detected, the horizontal, water-filled polyethylene tubing connected to the left side of the Flodec (Fig. 2) was lowered below the height of the tooth, stepwise, until the outward fluid flow ceased. This negative hydrostatic pressure (P) necessary to create $J_v = 0$ was a direct measurement of the effective osmotic pressure (π_e) of the test solution (equation 3). This procedure required between 1–3 minutes for each test solution. Between test solutions, the resin-covered crown segment was immersed in 50 mL of water and the pulp chamber was rinsed multiple times with 10 mL of water to remove any solute from the resin and pulp chamber, respectively.

The theoretical osmotic pressures of the CaCl_2 solutions were measured by freezing point depression using a microOsmette instrument (Precision Instruments, Sudbury, MA, USA). Multiple 10-fold dilutions were made. After obtaining the osmolarities of the dilutions, the results were plotted against dilutions and extrapolated to zero dilution to obtain the osmolarities of the undiluted test solutions. The osmolarity of the 35% albumin solution was calculated because its osmolarity is so low. Thirty-five percent bovine albumin = 350 g/L / 68,000 g mole^{-1} = 0.0052 osmoles = 5.2 mOsm/kg .

Substituting these values into equation 1 gave theoretical osmotic pressures of 4.08×10^7 Pa for 5.5 M CaCl_2 and 1.263×10^3 Pa for 35% albumin.

Finally, the reflection coefficient was calculated by dividing effective osmotic pressure of the test solutions (the negative hydrostatic pressure required to stop outward osmotic-induced fluid flow in Pa) by their theoretical osmotic pressures in Pa.

Statistic analysis

The means and standard deviations of the negative pressures required to null osmotically-induced fluid flow and the reflection coefficients of resin-bonded dentin to CaCl_2 and albumin were separately analyzed by three-way ANOVA (type of resin, solvated or not, solvent for matrix) and Holm-Sidak multiple comparison tests. Data were transformed into $\log_n$ in order to obtain a normal distribution. Additionally, correlations between the reflection coefficients exhibited by resin-bonded dentin and the Hoy's solubility parameters of the polymerized neat and solvated resins were evaluated by means of linear regression analyses. Statistical significance was preset at $\alpha=0.05$.

RESULTS

The effective osmotic pressures developed by the test solutions (i.e. the negative hydrostatic pressure necessary to stop osmotically-induced fluid movement) are listed in Table II. Note that the highest effective osmotic pressures were produced by the most hydrophobic neat resin (R1) bonded to ethanol-saturated dentin, while the most hydrophilic neat resin (R5) gave the lowest effective osmotic pressures after bonding to water-saturated dentin. Within this ranking, whenever 30% ethanol/70% comonomer mixtures were used instead of neat versions, they tended to lower the effective osmotic pressures of the test solutions (R + E vs. R in Table II).

When these same comonomer mixtures were applied to ethanol-saturated dentin, they produced resin-dentin bonds that produced significantly higher ($p<0.05$) effective osmotic pressures using 5.5 M CaCl_2 or 35% albumin (Table II). Solvated versions of the resins also tended to give lower effective osmotic pressures compared to neat resins (Table II).

After converting the effective osmotic pressures in Table II from cm H_2O pressure to Pascals (by multiplying by 0.010197), they were divided in the theoretical osmotic pressures of the test solutions (4.08×10^7 Pa for 5.5 M CaCl_2 and 1.263×10^4 Pa for 35% albumin) to obtain the reflection coefficients of the resin-dentin bonds. These are listed in Table III for water-saturated dentin and in Table IV for ethanol-saturated dentin. Since the effective osmotic pressures expressed in cm H_2O in Table II were only divided by constants, the statistical significance and different groups in Tables III and IV are the same.

Weak correlations were observed when the reflection coefficients of neat or solvated resins bonded to water- or ethanol-saturated dentin were plotted against the Hoy's solubility parameter for dispersive forces (δ_d), regardless of the solute ($p=0.65 - 0.85$, regressions not shown). Conversely, the reflection coefficients of resins bonded to ethanol-saturated dentin, with solvated or neat resins, were strongly correlated with the Hoy's solubility parameters for H-bonding (δ_h) of resins R1 to R5, using either CaCl_2 (Fig. 3A,B) or albumin (Fig. 3C,D) ($p<0.001$). The neat and solvated versions of resins R1 to R5 bonded to water-saturated dentin exhibited reflection coefficients that also correlated well with their respective Hoy's solubility parameters for H-bonding (δ_h), when albumin was the hypertonic solution employed ($R^2 = 0.97$ for both, neat and solvated versions, $p<0.001$ - regressions not shown). Significant, but moderate correlations (i.e. $R^2 = 0.85 - 0.9$, $p<0.05$) were obtained when the reflection coefficients to CaCl_2 and albumin at water- or ethanol-saturated dentin,

bonded with solvated or neat resins, were plotted against the Hoy's solubility parameter for polar forces (δ_p , regressions not shown).

DISCUSSION

Calcium chloride produced effective osmotic pressures (in cm H₂O, Table II) that were 7–11 times larger than albumin in water-saturated dentin, even though the theoretical osmotic pressure for 5.5 M CaCl₂ was $(4.08 \times 10^7 \text{ Pa}/1.263 \times 10^4 \text{ Pa})$ 3230 times larger than that of albumin. This is because the molecular radius of calcium or chloride, estimated²² as one-tenth of the cube root of their molecular weights, is about 0.34 nm, while that of albumin is 4.08 nm. Polymer pore theory proposes that there are pores of different sizes in polymers that permit water vs. solute entry (Fig. 1A–C). Polymers with high selectivity for water over solutes (Fig. 1B) are used for reverse osmosis, where high hydrostatic pressures are used to separate pure water from salt solutions, since such membranes have reflection coefficients of 1.0. If polymer membranes are so permeable that they can not distinguish between water and solutes because their pores are so large (Fig. 1A), they would be unable to restrict water from solute. Thus, their reflection coefficients are near zero. All of the test resins had values of about 1×10^{-4} for calcium chloride which is near zero. As solute permeability is equal to $1 - \sigma$, the resin films were 99.9999% as permeable to calcium and chloride as they were to water. However, these same resin films were much less permeable to albumin compared to calcium chloride. In resins bonded to water-saturated dentin, albumin gave reflection coefficients as high as 0.088 for R1 to as low as 0.031 for R5 (Table III). However, when those same resins were bonded to ethanol-saturated dentin, the σ values for albumin were 0.215 for R1 and 0.044 for R5 (Table IV), values that were 2.4 to 1.4-fold higher than to water-saturated dentin, respectively. Albumin, being much larger than calcium or chloride, was restricted more in its permeability and would be considered to interact with the membrane in a manner shown in Fig. 1C. The higher σ values for albumin in bonds made to ethanol-saturated dentin suggest that the pores are smaller or more uniform than those made to water-saturated dentin. Neat resins 1 and 2 might undergo phase changes when placed on water-saturated dentin²³ but not on ethanol saturated dentin⁷.

It is the permeability of methacrylate-based resins to solutes that permits fluoride to diffuse out of resin matrices that contain fluoride compounds²⁴. Similarly, chlorhexidine can be slowly released from UDMA-TEGDMA resins because it can permeate through the resin matrix²⁵.

The osmotically-induced permeability of resin-bonded dentin to hypertonic solutions in this study provided evidence that leakage pathways within the hybrid layer and adhesive layer may permit not only water transport but also the permeation of small solutes across dentin. The results indicated that the permeability of resin-infiltrated acid-etched dentin was significantly lower when experimental hydrophobic resins were infiltrated into dentin matrices saturated with ethanol *versus* hydrophilic monomers infiltrating matrices saturated with water (Tables III and IV), which requires rejection of the first null hypothesis. The reflection coefficients of water- *vs* ethanol-saturated dentin bonded with experimental resins were significantly higher for large solutes (Tables III and IV), requiring rejection of the second null hypothesis.

Recent research has reported that many polymerized dental resins are permeable to water. It is thought that simplified “single-step” dental resins attract water that, in turn, swell the polymer network slightly, creating more space for bulk water movement^{3,12,26,27}. The former two studies were conducted using miniature impressions of polymerized resins to record microscopic water droplets that accumulated between the fast-setting hydrophobic polyvinyl siloxane impression material and the underlying permeable resin bonded to dentin.

The number and size of these tiny water droplets correlates well with the quantitative measures of bulk water movement across the resin¹². These reports show that most hydrophilic simplified “single-step” adhesives are far more permeable to water than more hydrophobic resins, but that most resins and resin tags are in general permeable to water²⁸. The presence of water-filled channels manifested as a linear array of connected nanometer-sized voids that span the full thickness of dental adhesives has been termed “water-trees”. These are commonly found in simplified single-step adhesives^{26,27–31}. Some authors have speculated that if these resin coatings are permeable to water, they may be permeable to bacterially-produced lactic acid and/or bacterial or salivary enzymes¹².

Biological membranes are spanned by protein channels or “pores” called aquaporins³² that permit single-file diffusion of water molecules across lipid membranes. However, when water is protonated to form a positively-charged hydronium ion, it is unable to cross biological membranes via aquaporin channels³³. Thus, molecular size and charge are very important determinants for biologic membranes transport. Similarly, in dental resin coatings, although they are many orders of magnitude thicker than biological membranes and the diffusion channels or pores are much larger, they behave as if they contain linear hydrophilic polymer domains that span the entire thickness of adhesive layers that are made up of mixtures of both hydrophilic and hydrophobic copolymers. The hydrophilic sites in these domains contain hydroxyl groups of HEMA or carboxylic acids in acidic methacrylate monomers such as 4-MET, BPDM, MAC-10 or phosphate-derivates such as phenyl-P or MDP³⁴. We speculate that water molecules that hydrogen bond to these polar groups permit water to permeate through hydrophilic resins by hopping from one bound water molecule to the next^{35,36} – the so-called “interaction theory” of water transport. As these water-filled channels are much larger than those in aquaporins, they may permit permeation of small ions such as calcium, chloride and fluoride²⁴. The fact that the K_{sp} value of these resin-dentin bonds to calcium chloride is 1×10^{-4} means (Table III) that these experimental resins bonded to dentin are 99.99 % as permeable to calcium chloride as they are to water. The presence of solutes such as calcium chloride in aqueous solution applied to resins lowers the water concentration of those solutions relative to the water concentration in dentinal fluids. This causes water to diffuse outward from dentin through permeable resins to where the water concentration is lower (i.e. into the calcium chloride). Large molecular compounds such as polyalkenoic acid polymers in some adhesives, polyacrylic acid in GICs, unreacted monomers or dextrans synthesized by plaque organisms may draw water from dentin through simplified adhesives. The rate of that fluid movement would be too low to cause dentin sensitivity, but it may contribute to the elution of non-polymerized adhesive monomers.

If the experimental resins used in this study were truly semipermeable, that is, permeable only to water, then both calcium chloride and albumin would have had reflection coefficients of $0.99 - 1.0$ ^{15,20}. The fact that calcium chloride produced reflection coefficients of 1×10^{-4} means that resins and their bonds to acid-etched dentin are very permeable to calcium and chloride. We previously reported reflection coefficients of calcium chloride to smear layer covered dentin of about 1.4×10^{-4} using a different technique¹⁶. It is interesting that the reflection coefficient values of calcium chloride to resin-bonded acid-etched dentin are similar to that of smear layer-covered dentin. In a recent comparison of the abilities of smear layer/smear plugs to seal dentin relative to resin/resin tags³⁷, the resins sealed dentin about as well as did smear layers. Apparently, the permeability of resins to large molecules like albumin (MW 68 kDa) is much lower than that of calcium chloride because albumin gave reflection coefficient values that were 28 to 581 times higher than those of calcium chloride (Tables III and IV). Similar values for calcium chloride to these same neat resins alone have been obtained indicating that they represent

intrinsic properties of the resins, not the bonded interface (Pashley, unpublished observations).

Dental resins should be regarded as being relatively permeable to water > ions > large molecules. Highly selective artificial membranes that are manufactured under stringent controls can perfectly discriminate between water and ions in salt-water, allowing only pure water to pass (Fig. 1B). This is the basis for reverse osmosis³⁸ purification of water. It is unlikely that such resins could be created on a wet dentin at room temperature in 30 seconds as is done during dentin bonding.

Positive correlations have been reported between the percentage of residual hydraulic conductance across resin-bonded dentin and the Hoy's solubility parameters δ_h and δ_p of resins R1 to R5, when they were applied on ethanol-saturated dentin³⁷. These results lead us to believe that differences in the hydrophilicity of each material may play an important role in determining the ability of polymers to permit water permeation. Interestingly, the present results corroborate this assumption, showing an inverse correlation between the Hoy's solubility parameters for H-bonding (δ_h) of resins R1 to R5 (neat or solvated) and the reflection coefficients of ethanol-saturated dentin bonded with these resins (Fig. 3A–D). The higher reflection coefficients (i.e. closer to 1) of resins bonded to acid-etched dentin saturated with ethanol compared to dentin saturated with water (Tables III and IV) suggest that either infiltration of resins or hybridization of the resin tags to the surrounding dentin was improved in ethanol-saturated dentin.

Thus, in addition to convective water movement across adhesives in response to a pulpal hydrostatic pressure gradient, water can diffuse across adhesives down osmotic gradients both before and after polymerization¹¹. Reflection coefficients express the fraction of the theoretical osmotic pressure that can be developed by a solute, for that “membrane”. Measurements of reflection coefficients of various molecules for various resins provide important information on the relative permeability of these diffusion barriers to water vs larger molecules. The fact that ethanol-saturated dentin provided higher reflection coefficients for calcium chloride and albumin (Table IV) indicates these resins are less porous than when they were applied to water-saturated dentin (Table III). The results of this study indicate that more research should be done to characterize the “sieving” features of dental adhesives for solutes of different molecular size and charge.

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Figure 1. Schematic of the degree of selectivity of membranes based on their reflection coefficients. **A.** Non-selective; **B.** Semi-permeable (permeable only to solvent molecules); **C.** Partial selectivity (permeable to molecules of solvent and solutes with a certain size).

Figure 2.

Schematic of apparatus used to measure osmotically-induced fluid flow across resin-bonded dentin at zero hydrostatic pressure and how flow was stopped by applying negative hydrostatic pressure (i.e. lowering outflow tubing). The schematic of the specimen shows cross-sectional appearances of crown segment, water-filled the pulp chamber and the microscopic dentinal tubules that were covered at the surface by experimental resins that, in turn, were covered with test solution.

Figure 3.

Correlations between the polymer Hoy's solubility parameters for hydrogen bonding forces (δ_h) and the respective reflection coefficients (σ) of ethanol-saturated dentin (ESD) bonded with neat (R) or solvated (R+E) resins when using CaCl_2 (A and B) or in (C and D).

Table I

Composition and Hoy's solubility parameters (J/cm^3)^{1/2} of polymerized neat (R) and solvated (R + E) experimental resins

Hoy's solubility parameters (J/cm^3) ^{1/2}						
Material	Composition	%	d	p	h	t
R1	Bis-GMA-E	70.00 (wt %)				
	TEGDMA	28.75 (wt %)	15.44	10.59	6.17	19.71
	CQ	0.25 (wt %)				
	EDMAB	1.00 (wt %)				
R2	Bis-GMA	70.00 (wt %)				
	TEGDMA	28.75 (wt %)	15.58	12.1	8.64	21.54
	CQ	0.25 (wt %)				
	EDMAB	1.00 (wt %)				
R3	Bis-GMA	70.00 (wt %)				
	HEMA	28.75 (wt %)	15.37	13.02	9.94	22.46
	CQ	0.25 (wt %)				
	EDMAB	1.00 (wt %)				
R4	Bis-GMA	40.00 (wt %)				
	TEGDMA	28.75 (wt %)				
	TCDM	30.00 (wt %)	16.21	12.61	9.3	22.55
	CQ	0.25 (wt %)				
R5	Bis-GMA	40.00 (wt %)				
	HEMA	28.75 (wt %)				
	2MP	30.00 (wt %)	15.76	14.37	10.75	23.88
	CQ	0.25 (wt %)				
R1 + E	EDMAB	1.00 (wt %)				
Solvated resins (Polymer)	R1	70.00 (v %)	14.59	10.76	10.32	20.86
	Ethanol	30.00 (v %)				

Hoy's solubility parameters (J/cm ³) ^{1/2}						
Material	Composition	%	d	p	h	t
R2 + E	R2	70.00 (v %)	14.69	11.82	12.05	22.38
	Ethanol	30.00 (v %)				
R3 + E	R3	70.00 (v %)	14.54	12.46	12.96	23.13
	Ethanol	30.00 (v %)				
R4 + E	R4	70.00 (v %)	15.13	12.18	12.51	23.1
	Ethanol	30.00 (v %)				
R5 + E	R5	70.00 (v %)	14.82	13.41	13.52	24.13
	Ethanol	30.00 (v %)				

Abbreviations: 2MP: Bis[2-(methacryloyloxy)ethyl] phosphate; Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; Bis-GMA-E: ethoxylated bisphenol A diglycidyl ether dimethacrylate; CQ: camphorquinone; EDMAB: ethyl N,N-dimethyl-4-aminobenzoate; HEMA: 2-hydroxyethyl methacrylate; TCDM: di(hydroxyethyl methacrylate) ester of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2dicarboxylic anhydride; TEGDMA: triethylene-glycol dimethacrylate; d: dispersion forces; d: dispersion forces; h: hydrogen bonding forces; p: polar forces; t: total cohesive energy density

Table II

Effective osmotic pressures produced by CaCl₂ or albumin across resin-bonded dentin previously saturated with water (WSD) or ethanol (ESD)

Resin	Effective Osmotic pressure (π) of CaCl ₂		Effective Osmotic pressure (π) of Albumin	
	WSD	ESD	WSD	ESD
R1	80.3 $\pm$ 13.0 ^c	154.2 $\pm$ 31.8 ^a	11.3 $\pm$ 0.7 ^C	27.7 $\pm$ 1.2 ^A
R1 + E	65.6 $\pm$ 1.5 ^{d,e}	128.1 $\pm$ 16.7 ^b	9.4 $\pm$ 0.5 ^D	16.7 $\pm$ 1.3 ^B
R2	73.8 $\pm$ 15.6 ^c	118.4 $\pm$ 17.3 ^b	7.8 $\pm$ 0.3 ^E	12.0 $\pm$ 0.6 ^C
R2 + E	63.9 $\pm$ 6.3 ^d	80.3 $\pm$ 7.34 ^c	5.9 $\pm$ 0.4 ^{F,G}	7.4 $\pm$ 0.6 ^E
R3	54.5 $\pm$ 11.2 ^f	75.1 $\pm$ 7.4 ^c	5.5 $\pm$ 0.6 ^G	7.0 $\pm$ 0.6 ^{E,F}
R3 + E	39.1 $\pm$ 4.6 ^h	55.2 $\pm$ 8.8 ^f	2.5 $\pm$ 0.1 ^K	3.0 $\pm$ 0.3 ^I
R4	63.4 $\pm$ 6.9 ^{d,e}	79.0 $\pm$ 5.2 ^c	6.2 $\pm$ 0.3 ^F	8.5 $\pm$ 0.4 ^D
R4 + E	46.9 $\pm$ 6.1 ^g	60.1 $\pm$ 5.1 ^e	3.4 $\pm$ 0.9 ^{I,J}	5.3 $\pm$ 0.3 ^G
R5	48.0 $\pm$ 5.7 ^g	58.1 $\pm$ 11.6 ^{e,f}	4.0 $\pm$ 0.3 ^H	5.8 $\pm$ 0.4 ^G
R5 + E	22.3 $\pm$ 0.7 ⁱ	37.6 $\pm$ 2.5 ^h	1.8 $\pm$ 0.1 ^L	3.2 $\pm$ 0.2 ^J

Data are expressed as Mean $\pm$ SD (in cm H₂O pressure); R= neat resins; R + E= solvated resins. n=8 in R1–R5 and n=6 in R1+E–R5+E.

Theoretical osmotic pressures were 4.08×10^7 Pa for CaCl₂ and 12,630 Pa for 35% albumin assuming a molecular weight at 68 kDa. Superscript different letters express statistical differences among groups within the same hypertonic solution (lower case letters to CaCl₂ and upper case letters to albumin). Comparisons among groups considering the two hypertonic solutions are not exhibited in this table. These values can be converted to Pa by multiplying by 0.010197.

Table III Reflection coefficient (unitless) of resin-bonded dentin saturated with water to CaCl₂ and albumin

Reflection coefficient of resin-bonded dentin saturated with water		
	CaCl ₂	Albumin
R1	0.00019 ± 0.000031 ^{a,B}	0.088 ± 0.0052 ^{a,A}
R1+E	0.00016 ± 0.000006 ^{b,B}	0.073 ± 0.0041 ^{b,A}
R2	0.00017 ± 0.000037 ^{a,B}	0.060 ± 0.0026 ^{c,A}
R2+E	0.00015 ± 0.000015 ^{b,B}	0.046 ± 0.0033 ^{d,e,A}
R3	0.00013 ± 0.000026 ^{c,B}	0.042 ± 0.0048 ^{e,A}
R3+E	0.00009 ± 0.000001 ^{e,B}	0.019 ± 0.0006 ^{h,A}
R4	0.00015 ± 0.000015 ^{b,B}	0.048 ± 0.0024 ^{d,A}
R4+E	0.00011 ± 0.000014 ^{d,B}	0.026 ± 0.0014 ^{g,A}
R5	0.00011 ± 0.000013 ^{d,B}	0.031 ± 0.0024 ^{f,A}
R5+E	0.00005 ± 0.000001 ^{f,B}	0.014 ± 0.0009 ^{i,A}

Data are expressed as Mean ± SD (unitless); n=8 in R1–R5 and n=6 in R1+E–R5+E. Different superscript upper (analysis per row) and lower (analysis per column) case letters express statistical differences among groups ($p < 0.05$).

Table IV Reflection coefficient (unitless) of resin-bonded dentin saturated with ethanol to CaCl_2 and albumin

Reflection coefficient of resin-bonded dentin saturated with ethanol		
	CaCl_2	Albumin
R1	$0.00037 \pm 0.000076^{\text{a},\text{B}}$	$0.215 \pm 0.009^{\text{a},\text{A}}$
R1+E	$0.00030 \pm 0.000040^{\text{b},\text{B}}$	$0.130 \pm 0.010^{\text{b},\text{A}}$
R2	$0.00028 \pm 0.000040^{\text{b},\text{B}}$	$0.093 \pm 0.004^{\text{c},\text{A}}$
R2+E	$0.00020 \pm 0.000017^{\text{c},\text{B}}$	$0.057 \pm 0.004^{\text{c},\text{A}}$
R3	$0.00018 \pm 0.000017^{\text{c},\text{B}}$	$0.054 \pm 0.004^{\text{c},\text{A}}$
R3+E	$0.00013 \pm 0.000021^{\text{c},\text{B}}$	$0.030 \pm 0.002^{\text{g},\text{A}}$
R4	$0.00019 \pm 0.000012^{\text{c},\text{B}}$	$0.066 \pm 0.003^{\text{d},\text{A}}$
R4+E	$0.00014 \pm 0.000012^{\text{d},\text{B}}$	$0.041 \pm 0.002^{\text{f},\text{A}}$
R5	$0.00014 \pm 0.000027^{\text{d},\text{e},\text{B}}$	$0.044 \pm 0.002^{\text{f},\text{A}}$
R5+E	$0.00009 \pm 0.000006^{\text{f},\text{B}}$	$0.025 \pm 0.001^{\text{h},\text{A}}$

Data are expressed as Mean $\pm$ SD (unitless); R= neat resins; R + E= solvated resins. n=8 in R1–R5 and n=6 in R1+E–R5+E. Different superscript upper (analysis per row) and lower (analysis per column) case letters express statistical differences among groups ($p < 0.05$).