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Interpenetrating Polymer Networks (IPNs) in Dental Polymers and Composites

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Abstract

An interpenetrating polymer network (IPN) is a material containing two polymers, each in network form. In biomaterials used in dentistry, the IPN-like nanostructures are used in denture base polymers, denture teeth and fibre-reinforced composites. IPN structures provide the specific and desired properties for the resin system prior to and after polymerization. At adhesive interfaces, IPN polymers and composites provide good interfacial adhesion for adhering and veneering resin composites based on the so-called secondary-IPN bonding formation due to swelling of the IPN nanostructure. Good interfacial adhesion is a requirement for the success of modern adhesive dentistry.

Keywords

Interpenetrating polymer network, IPN, composites, biomaterials, fibre-reinforced composites

1. Introduction

Modern dentistry utilizes polymers and composites in dental treatments. The use of natural rubber and thereafter synthetic polymers as denture base polymers started in the 1860's. The introduction of a denture base polymer of poly(methyl methacrylate) (PMMA) occurred in the late 1930's [1]. Since then, the thermoplastic PMMA denture base polymer has been multiphasic, i.e., it has been made by mixing methylmethacrylate monomer liquid and PMMA beads. In free radical polymerization, the highly viscous resin dough formed the multiphase denture base polymer. The dough-like consistency enabled packing of the resin into the denture moulds and reduced polymerisation contraction of the resin. Since the introduction of cross-linking thermoset monomers in dentistry by Bowen [2], cross-linking dimethacrylate monomers became available also for monomer liquids of denture base resins and, thus, in multiphase denture base polymers. This can be considered the start of the use of IPN-like structures of various kinds in dentistry.

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Table 1.
Definitions of mixed polymers [3]

Name of mixture	Description
Polymer blend	One or more polymers are mixed together without a resulting strong chemical bonding between the phases, and in such a way that the phases be separated from each other
Graft polymer	Strong chemical bonding between some portion of polymer I and the end of polymer II
Copolymer	Strong chemical bonding of the end of polymer to the end of polymer II
Interpenetrating polymer network (IPN)	Polymers I and II are at least partially interlaced at molecular level but are not covalently bonded to each other, and cannot be separated unless chemical bonds are broken

IPNs were used for the first time in 1914 by Alysworth, who combined phenol-formaldehyde compositions with natural rubber and sulphur to make the first rubber-toughened plastic. By definition, an IPN is a combination of two or more polymers in network form that are synthesized in juxtaposition [3]. IPNs do not interpenetrate by chemical reactions on a molecular scale, but are composed of finely divided phases of 5–10 nm. IPNs differ from polymer blends which are less homogeneous in structure. They differ from copolymers which are based on chemical reactions of monomers and polymer backbones (Table 1). The rationale for using IPNs instead of homopolymers and copolymers is in the improved handling properties, toughness and mechanical interlocking at nanometer level of resin adhesives to IPN-like polymers and composites. The interlocking of resin adhesives to polymers and composites plays an important role in the clinical success of dental treatments carried out with composite resin restorations. The bonding of resin adhesives to a composite (particulate filler or fibre-reinforced composite) transfers stresses from the restoration to the teeth. Without adequate interlocking of materials, the loads and stresses debond the restoration and the treatment fails.

Currently, the IPN-like structures can be found in nanostructures in denture base polymers, denture teeth, fibre-reinforced composites (FRCs), and very recently, in the restorative composite resins [4–9] which are described and discussed in this review. Structurally, several adhesive interfaces between natural and synthetic biomaterials and adhesive resins by means of primers or coupling agents can also be considered IPNs. Examples of these are the dentine bonding hybrid layer and the silane coupling agent-promoted adhesive interphases between metal and ceramics and adhesive resins.

2. IPNs

There are several kinds of IPNs which differ in terms of structure. These include:

- sequential IPN

- gradient IPN
- thermoplastic IPN
- semi-IPN
- simultaneous IPN.

The dental IPN structures are semi-IPNs in which one or more polymers are cross-linked, and one or more polymers are linear or branched. More precisely, the IPNs belong to the group of non-covalent semi-IPNs where only one of the polymer systems is cross-linked, in contrast to non-covalent full IPNs in which the two separate polymers are independently cross-linked. Dimethacrylate monomers or multifunctional monomers and dendrimers form the cross-linked part of the semi-IPN, while the monofunctional MMA forms the non-cross-linked part of the semi-IPN system. In dental semi-IPNs, due to the fabrication processes of dental materials and devices, the MMA is first polymerized and then swelled and dissolved by the monomers of the cross-linker system, or with a separate solvent. In polymerization of the cross-linking monomers in the presence of swelled and dissolved polymer chains of the PMMA, a semi-IPN structure is formed. The components of current dental semi-IPNs are, therefore, not cross-linked from monomers as in the IPNs according to the definition of the IUPAC (International Union of Pure and Applied Chemistry). However, the dental IPNs fulfill the structural requirements of the IUPAC for the IPN, i.e., the IPN swells but does not dissolve into solvents, the two polymers are not phase separated, and the polymers are interlaced on a molecular level.

In dental IPNs, solid PMMA is often used in powder form in denture base resins and in porous polymer form in preimpregnated glass-fibre reinforcements [10]. Depending on the capability of dimethacrylate monomers like bisphenol-A-diglycidyldimethacrylate (bisGMA) or triethyleneglycol dimethacrylate (TEGDMA), or ethyleneglycol dimethacrylate (EGDMA) to swell and dissolve the PMMA, the contact wetting time of the liquid dimetharylate monomers, and the temperature, and the penetration depth of the cross-linking monomers into the PMMA, the semi-IPN varies. After polymerization, two or three of the following phases occur: cross-linked matrix, semi-IPN phase and linear polymer phase. Thus, the whole polymer is not necessarily a semi-IPN, but there are nano or microstructures of semi-IPNs in the polymer or composites.

Although the IUPAC Comission on Macromolecular Nomenclature has not given a statement on the nomenclature of IPNs, the above-mentioned semi-IPN made of bis-GMA and PMMA can be written as [3]

net-poly(methyl methacrylate)–*inter-net*-poly(bis-glycidyl-A-dimethacrylate),

which is a semi-IPN made of PMMA beads and bis-GMA monomer. If the cross-linking monomer system is diluted by another monomer, like TEGDMA, in order to achieve a copolymer for the cross-linked polymer, the semi-IPN is written as:

> *net*-poly(methyl methacrylate)–*inter-net*-copoly(bis-glycidyl-A-dimethacrylate)-triethyleneglycol dimethacrylate.

For IPN formation, certain requirements have to be fulfilled to differentiate the IPN from polymer blends. If the IPN is made of photopolymerizing dimethcarcylate monomers and monofunctional methacrylates, the polymerization could occur simultaneously, but without the formation of copolymer of the dimethacrylate and monomethahacrylate. Because of the generally known low reactivity of monofunctional methacrylates in photoinduced free radical polymerization, the monofunctional methacrylates first need to be prepolymerized by other means. By mixing polymerized monofunctional methacrylates and cross-linking dimethacrylates, a polymer blend is obviously formed, unless the cross-linking dimethacrylate monomers, or other solvents, swell and dissolve the monofunctional polymer, which results in molecular-level interlacing and IPN formation.

For interlacing, the solubility parameter of the solvent monomer should match the solubility parameter of the polymer phase. It was known hundreds of years ago by Paracelsus that *similia similibus solvuntur*, *like dissolves like*. Qualitatively, ‘like’ may be defined variously in terms of similar chemical groups or similar polarities in the molecular structure. Quantitatively, the solubility of one component in another is governed by the equation of free energy of mixing, and, as a result, there will be an increase in the entropy [11]. The solubility parameter of a polymer can be determined by swelling experiments or by measuring the intrinsic viscosity of the polymer in the solvents. Values for the solubility parameter can be calculated; the unit of solubility parameter (δ) is $(\text{cal/cm}^3)^{1/2}$. The solubility parameter for PMMA is 9.45 $(\text{cal/cm}^3)^{1/2}$, for MMA 8.8 $(\text{cal/cm}^3)^{1/2}$, for solvent tetrahydrofuran (THF): 9.1 $(\text{cal/cm}^3)^{1/2}$, and for solvent acetone 9.9 $(\text{cal/cm}^3)^{1/2}$. In comparison to these good solvents for PMMA, the solubility parameters of poor solvents for PMMA are water ($\delta = 23.4\ (\text{cal/cm}^3)^{1/2}$) and methanol ($\delta = 14.5\ (\text{cal/cm}^3)^{1/2}$).

A polymer dissolves in two stages. First, solvent molecules diffuse into the polymer, swelling it to a gel state. Then the gel gradually disintegrates and the molecules diffuse into the solvent-rich regions. Linear amorphous polymers can be fully dissolved whereas cross-linked polymers may reach the gel state but they do not dissolve. The concentration of the final solution depends on the relative proportions of polymer and solvent. The molecular size of the solvent needs to allow diffusion into the interchain spacing of the polymer, which in typical engineering polymers varies between 5 and 10 Å.

3. Denture Base Polymers and IPN Structure

Polymers used in baseplates of complete dentures and removable partial dentures, as well as in extension bases of metal framework removable partial dentures, are made of denture base polymers. Denture base polymers are mixed from PMMA powder (typically M_w 200 000, particle size: 50 μm) and methyl methacrylate monomer (MMA) liquid. The monomer system contains on average 10 wt% of cross-linking dimethacrylate monomers like EGDMA. Before polymerization, the MMA dissolves the PMMA beads only from the surface, or entire beads. The degree of dissolution or swelling depends on the contact wetting time with MMA in its liquid form, i.e., as a solvent capable of dissolving the PMMA beads. In heat-cured denture base resins, the dough time of 30–60 min allows PMMA beads to be almost fully dissolved by the monomers; whereas in autopolymerizing denture base resins, the polymerization reaction is initiated within a few minutes from mixing the powder and liquid, and putting the initiator and activator together. By rapid solidification of the monomers of the autopolymerizing resins, the penetration depth is limited to a few micrometres. However, in both cases, the monomer system containing the cross-linking agent partly or fully dissolves the linear PMMA beads and forms a semi-IPN structure once it is polymerized.

The semi-IPN structure of denture base polymers increases their creep resistance [12, 13]. In comparison with heat-cured and autopolymerized denture base polymers, the heat-cured polymers have higher mechanical strength and creep resistance than the autopolymerized polymers. The average critical strain values, which correlate with the ultimate failure values, were increased by adding cross-linking monomers to the denture base polymer. This demonstrates the effect of the semi-IPN structure in the interphase of the PMMA beads and the cross-linked matrix on improving mechanical strength. On the other hand, semi-IPN in the denture base polymer does not influence water sorption but increases the solvent resistance [14].

In repairs of fractured pieces of acrylic polymers of linear or semi-IPN type, the adhesion of new resin is also based on dissolving the pieces of denture base polymer by monomer systems of the repair acrylic resin. It has been shown that the wetting time of the acrylic surface with the repair resin is of importance for achieving the swelling and dissolving of the surface of the denture base resin [15]. A three-minute contact wetting time of the denture base polymer of semi-IPN type with the MMA-EGDMA monomer system results in durable adhesion of the repair resin to the pieces of denture base polymer. The bonding mechanism is called *secondary-IPN formation* to differentiate it from the semi-IPN structure of the actual substrate material. Requirements for the secondary-IPN formation are swelling of the substrate, and interlacing of the polymer chains of the repair resin and the old resin together. In this context, the MMA fulfills the requirements for a good solvent for PMMA.

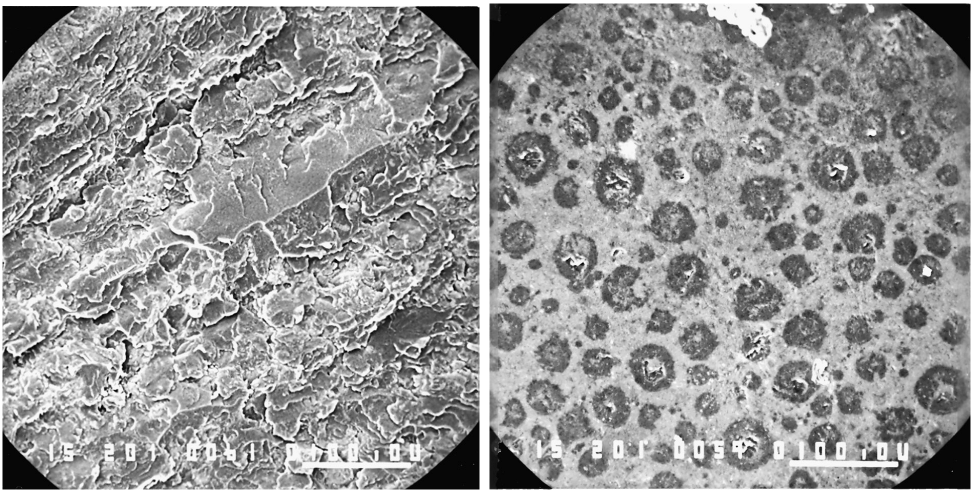
There are two kinds of denture base polymers classified according to the initiation of the polymerization reaction. These are heat-cured and autopolymerized denture base polymers. They differ in terms of the homogeneity of the semi-IPN structure and the quantity of residual monomers in the polymer. Heat-cured denture base polymers are more homogeneous due to the longer dough time of the powder–liquid mixture before polymerization than of the autopolymerized polymers. The PMMA beads in the denture base polymer are predominantly attached to the matrix by a semi-IPN layer. However, at higher temperatures (above 70°C) in the heat-cured denture base resins, the PMMA beads are also bonded to the matrix from MMA by chemical means involving unsaturated double bonds in the PMMA backbones after the termination stage of the polymerization reaction in manufacturing the beads. The quantity of residual monomers in the denture base polymer is around 0.2 wt% in heat-cured polymers and ca. 4 wt% in autopolymerized polymers [15]. Three factors, the homogeneity of the semi-IPN structure, the quantity of residual monomers in the denture base polymer and the polymerisation temperature have been shown to affect the formation of the secondary-IPN between the repair acrylic resin and the denture base polymer. Autopolymerized denture base polymers allow monomers of the repair acrylic resin to penetrate more deeply, thus forming a thicker secondary-IPN layer between the repair resin and the denture base polymer.

During swelling of the polymer surface, the diffusion of monomers takes place in two directions: the monomers of the repair resin to the polymer and *vice versa* [3]. The rate of diffusion of small molecules like MMA is faster than that of PMMA. If the polymer is glassy, like PMMA at room temperature or at mouth temperature, the MMA lowers the glass transition temperature (T_g) of the PMMA by a plasticizing action. The rate of diffusion is, therefore, related to the T_g of the polymer. A linear relationship exists between the time and rate of diffusion at temperatures below the T_g of a polymer [11].

The T_g value for heat-cured PMMA powder varies from 117°C to 122°C, whereas the T_g of the matrix between the PMMA beads varies from 97°C to 100°C [17]. The T_g of the autopolymerized PMMA is substantially lower, varying from 67°C to 78°C. Therefore, the swollen secondary-IPN layer is thicker in the autopolymerized denture base polymers than in the heat-cured polymers. This enables easier secondary-IPN bonding of repair acrylic resin to the denture base polymer in the case of autopolymerized denture base polymer than with heat-cured polymer. On the other hand, it needs to be emphasized that denture base polymers, regardless of whether they are heat-cured or autopolymerized, provide a good adhesive substrate for repair acrylic resins, which is not the case with cross-linked polymers and composites. Examples of cross-linked composites are composite dental fillings and prefabricated fibre-reinforced composite root-canal posts which do not allow secondary-IPN formation and, thus, adhere with difficulty to adhesive resins.

4. Denture Teeth and IPN Structure

The composition of acrylic resin polymer teeth is essentially poly(methyl methacrylate) beads and colour pigments in a cross-linked polymer matrix. There is a semi-IPN layer between the PMMA bead and the cross-linked matrix. The cross-linked polymer matrix of a good quality tooth is usually not evenly distributed in the tooth structure. For example, the gingival ridge-lap area may not be as highly cross-linked as the incisal or occlusal area of the tooth. The less cross-linked structure in the area of the ridge-lap facilitates better bonding of the polymer tooth to the denture base polymer by secondary-IPN formation. Moreover, the cores of the PMMA beads,



(a) (b)

Figure 1. SEM micrographs of fractured bonding surfaces of polymeric denture teeth that have been bonded to (a) a heat-cured denture base polymer and (b) to an autopolymerized denture base polymer. Note how the intact linear polymer phase in the centre of the PMMA bead into the denture base polymer has formed the secondary-IPN structure (Bar = 100 μm) [9].

which have not been affected by the monomers of the matrix, i.e., have not formed a semi-IPN structure, are appropriate sites for the denture base resin to bond. This was clearly demonstrated by a scanning electron microscopy study which showed good bonding of the denture base resin to the linear polymer cores of the PMMA beads of denture teeth (Fig. 1) [9].

The bonding of denture base resin to the denture teeth occurs *via* secondary-IPN formation. In the case of denture base polymer and tooth bonding, the polymerization activation temperature plays a significant role because of the relationship between the temperature and the rate of diffusion. It is known that heat-cured denture base polymers bond better to the denture teeth than autopolymerizing denture base polymers (Fig. 1). The activation of intiators of heat-cured resins occurs at temperatures above 75°C up to 100°C when the bezoyl and phenyl radicals are formed to initiate polymerization of the resin. On the other hand, activation of the radical formation from initiator benzoyl peroxide in autopolymerized denture base resins occurs at lower temperatures with the help of amine activators. Typically, the polymerization temperature is around 45°C.

It has been shown that the polymerization activation temperature affects the bonding of the denture base polymer to denture teeth. At higher temperatures, regardless of the type of denture base polymer (heat-cured or autopolymerized), the bond strengths are increased. This was shown to be due to the deeper penetration of the monomers of the denture base polymers into the denture teeth, showing thicker secondary-IPN layer formation, which resulted in the higher bond strength values.

The critical polymerization temperature to avoid adhesional failures between the denture base polymer and denture teeth is 55°C [9].

5. Fibre-Reinforced Composites and IPN Sturucture

One new group of non-metallic dental biomaterials is fibre-reinforced composites (FRCs) which were first tested as a reinforcement of denture bases in the early 1960's [18]. In principle, an FRC could even then have offered already a durable and tough tooth-coloured material for several applications by combining it with Bowen's resin. Because there were some problems in combining the resin systems with reinforcing fibres and there were difficulties in handling the FRC clinically and technically, the material was not made available until recently. Development of the FRCs with new types of resins systems and an understanding of the design principles behind the devices have led to the use of FRCs in a variety of disciplines and applications: in removable prosthodontics, restorative dentistry, periodontology, orthodontics, and in repairs of fractured porcelain veneers [19–29]. An FRC is a material combination of polymer matrix and reinforcing fibres. The fibres of the composite reinforce the phases when the load is applied to the composite. Load is transferred to be carried by the fibres. The reinforcing fibres can be continuous unidirectional (rovings), continuous bidirectional (weaves), continuous random oriented (mat), or short random-oriented fibres.

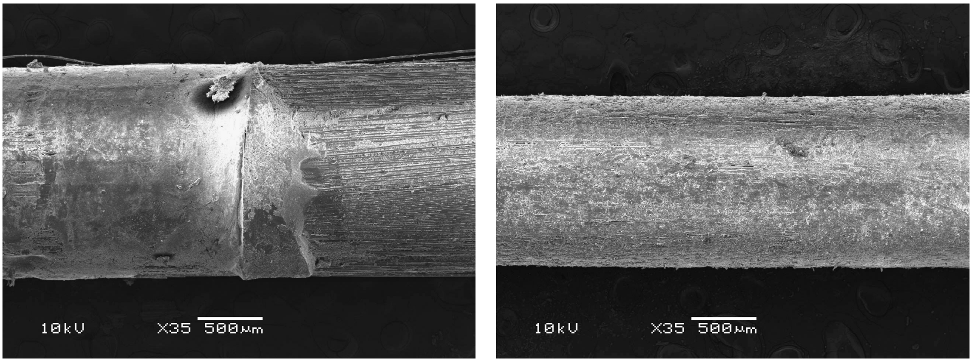
Of the many types of fibres, the clinically most suitable have been proved to be glass fibres which can be silanized and, thus, adhere well to the resin matrix of the FRC [30–32]. Glass fibres vary according to their composition, the most commonly used fibre being E-glass (electrical glass) which offers a chemically stable and durable glass in the pH range 4–11 [33].

In dental appliances of relatively small size, the quality of the load-bearing FRC substructure is important. For example, an FRC-reinforced root-canal–post system consists of dentine, composite resin cement, a core built-up composite resin and, as a load-bearing material, there is the FRC root-canal post. All these phases need to have adequate strength, and the phases need to adhere well to each other. By increasing the fibre quantity in the resin matrix, the strength of the FRC and the flexural modulus are increased. An important parameter responsible for the strength of the FRC is impregnation of the fibres with resin. Reinforcing fibres are difficult to impregnate with resin systems of high viscosity [34–36].

Such highly viscous resin systems are especially those made from a mixture of polymer powder and monomer liquid which are used in denture bases, provisionally fixed partial dentures, and removable orthodontic appliances, or those made of light-curing resins and particulate fillers. The resin impregnation of fibres by the manufacturers is recommended to ensure complete impregnation of the fibres by the resin in mechanically demanding dental applications. The complete impregnation of fibres by the resin allows the resin to come into contact with every fibre. If complete impregnation is not achieved due to the high viscosity or polymerisation shrinkage of the resin, the mechanical properties of FRC do not reach the optimal values as calculated by the laws of mixture.

Two types of resins, the cross-linked (thermoset) or linear (thermoplastic) polymer matrix, can be used in FRCs. The cross-linked matrix is formed from multifunctional or dimethacrylate resins, whereas monofunctional methacrylates form the linear (non-cross-linked) polymer matrix. There are also impregnation methods based on using a combination of thermoset and thermoplastic types of resins. The polymer matrix is multiphase in nature, and it is a semi-IPN having the cross-linked polymer and the linear polymer mixed together. The semi-IPN forms in the polymerization of the dimethacrylate monomers with swelled linear polymer poly(methyl methacrylate) (PMMA). The modulus of elasticity of the cross-linked polymer matrix FRC is higher than that of the semi-IPN or linear polymer matrix FRC [37–39]. On the other hand, linear and semi-IPN polymer matrices provide greater toughness than FRCs made of cross-linked thermosets. The semi-IPN polymer matrix of FRC provides benefits over the cross-linked dimethacrylate or epoxy-type of polymer matrices in handling properties and in the bonding of dental laboratory made restorations and root-canal posts to resin-luting cements and veneering composites [40]. Figure 2 shows the bonding of composite resin-luting cement to root-canal posts with a cross-linked or semi-IPN resin matrix.

The adhesion of particulate filler composite (PFC) resin (resin-luting cement, veneering composite) plays an important role in the load transfer from the surface of the device to the FRC framework and tooth. FRC as a bonding substrate contains different types of materials, from polymers to inorganic glass-fibre fillers and even particulate fillers. The internal adhesion of the FRC, influencing its cohesional strength, is based on the bonding of the fibres to the matrix polymer. In this respect, the most suitable fibres are of the OH-group containing glass and silica fibres which can be silanated to produce the adequate adhesion to the polymer matrix [30–32].



(a) (b)

Figure 2. SEM micrographs of the surface of an FRC root-canal post after being pushed out from the composite resin-luting cement. Post with (a) semi-IPN polymer matrix and (b) cross-linked matrix. Note good bonding of cement to semi-IPN post by secondary-IPN bonding mechanism and poor bonding to cross-linked post [40].

Less suitable fibres are ultra-high molecular weight polyethylene (UHMWP) fibres which have been proved to be difficult to adhere to resins even though the fibre surface has been activated with, e.g., various types of high energy treatments [41].

In bonding new resin to FRC, exposed fibres and polymer matrix are the substrates for adhesion. If the fibres of the FRC are exposed on the bonding surface, the adhesional properties of the fibres themselves play a role in adhering the adhesive resin and composite resin-luting cement to the FRC: glass fibres can be adhered to PFC (particulate filler composite) by silanation. Due to the cross-linked nature of the polymer matrix of most dental FRC materials, there are two possibilities to obtain adhesion of the PFC to the FRC. These are mechanical interlocking, and adhesion based on the ongoing polymerisation of the resin matrix of the FRC. If the FRC contains non-cross-linked polymer phases, i.e., they are made of thermoplastics or semi-IPN polymers, the adhesion can also be achieved *via* secondary-IPN formation by diffusion of the monomers of the new resin or resin composite into the non-cross-linked polymer matrix (Table 2) [6, 42]. This requires that the solubility parameter of the linear polymer is close to that of the monomer system of the PFR. In polymerisation of the resin, an adhesion bond based on a secondary-IPN structure is formed.

The adhesion of PFC to directly made (in patient's mouth) or chair-side-made FRC differs from that of FRC made indirectly in the dental laboratory. It is known that in the polymerisation of resins and resin-based composites or FRCs in air, a non-polymerised surface layer, the so-called oxygen inhibited layer, is formed

Table 2.
Summary of the bonding mechanisms for composite resin-luting cements to the FRC root-canal post

Type of post	Type of fibre	Type of polymer matrix	Bonding mechanism
Prefabricated	Carbon/graphite	Cross-linked	– Mechanical retention
Prefabricated	Glass or quartz	Cross-linked	– Mechanical retention – Silane-promoted adhesion
Individally formed (laboratory made)	UHMWP	Cross-linked	– Mechanical retention
Individually formed (laboratory made)	Glass or quartz	Cross-linked	– Mechanical retention – Silane-promoted adhesion
Individually formed (laboratory made)	Glass	Semi-IPN	– Mechanical retention – Silane-promoted adhesion – Secondary IPN adhesion
Individually formed (chair-side made)	UHMWP, Glass or quartz	Cross-linked Semi-IPN	– Mechanical retention – Silane-promoted adhesion – Secondary-IPN adhesion – Free radical polymerisation based adhesion

on the surface [43]. PFCs can adhere to this layer by free radical polymerization of the PFR and form a durable bond. However, with indirectly made restorations, old restorations and prefabricated FRC root-canal posts, a durable bond between new resins and the polymer matrices of the composites can be achieved by the introduction of a linear or semi-IPN polymer matrix into the polymer matrix of the composite [44, 45].

6. Conclusions

Interpenetrating polymer network (IPN) structures of two or more polymers are utilized in dental polymers and composites, although the processing of the IPNs may vary from that generally used in polymer chemistry. Interlaced polymers at the molecular level of dental IPNs provide increased toughness for the polymer and allow the bonding of additional resins to the IPN-containing polymer *via* a secondary-IPN mechanism, i.e., interlacing the polymeric materials together.

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