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The semi-interpenetrating polymer network matrix of fiber-reinforced composite and its effect on the surface adhesive properties

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This aim of this study was to examine the effect of further-impregnation time of polymer pre-impregnated fiber-reinforcement on polymer matrix structure of the fiber-reinforced composite (FRC) used in dental applications. In addition, shear bond strength between the FRC and veneering composite after various length of further-impregnation was studied. Polymethyl methacrylate (PMMA) pre-impregnated glass fiber-reinforcement was further-impregnated with a diacrylate monomer resin by using five lengths of further-impregnation from 10 min to 24 h. The test specimens ($n = 5$) from each five groups were treated with the solvent tetrahydrofuran and examined with a scanning electron microscope (SEM) to determinate the existence of linear PMMA in the polymer matrix of the FRC. The same lengths of further-impregnation were used to form an adhesive substrate for veneering composite and to measure the shear bond strength ($n = 8$). The SEM examination showed that linear PMMA-polymer and cross-linked diacrylate polymer formed two independent networks for the polymer matrix of FRC. The highest mean shear bond strength value (18.7 ± 2.9 MPa) was achieved when the fiber reinforcement was further-impregnated for 24 h. The shortest further-impregnation, 10 min, resulted in the lowest mean shear bond strength (12.7 ± 2.9 MPa). A correlation between increased shear bond strength and longer further-impregnation was found (0.689, $p < 0.001$). The results revealed that linear PMMA network of the polymer matrix of the FRC remained in the structure regardless of the various lengths of the further-impregnation with diacrylate resin.

Introduction

A degree of impregnation of fiber-reinforcements used in dental applications affects properties of the fiber-reinforced composite (FRC). The impregnation is effective then when the reinforced polymer is into contact with the surface of every fiber trough the whole FRC. In the case of an incomplete impregnation, there are voids in the polymer matrix of FRC, which can be seen for instance in the scanning electron microscopic (SEM) examination [1]. If the impregnation of the FRC is not complete, the mechanical properties such as flexural strength and modulus of the FRC remain far from theoretically calculated values [2]. It has also been reported that the voids caused by an incomplete impregnation of the fibers increase the water sorption of the FRC, which plays an important role in long-term stability of FRC dental appliances in an aqueous environment such as in the oral cavity [3]. Furthermore, high water sorption of the FRC might lead the hydrolytic degradation of polysiloxane network of the FRC and thus reduce the mechanical properties of the FRC [4–6]. In addition, low degree of impregnation can cause discoloration of the FRC due to penetration of oral microbes into the voids of poorly impregnated FRC [7]. It has been also shown that the voids of poorly impregnated FRCs were oxygen reserves, which allowed oxygen to inhibit radical polymerization of the used acrylic resin inside the FRC [7, 8].

Well-impregnated fibers have been shown to increase the mechanical properties of the FRC [5, 9]. The complete degree of impregnation of the FRC can be obtained easier if the fiber-reinforcement is pre-impregnated either with polymer [8], with monomer [10], or with a combination of these [11]. However, the pre-impregnation of the fibers does not only affect the degree of impregnation but it also affects the adhesive properties of the finally polymerized FRC. In dental applications, the FRC framework is veneered with particulate filler composite, and thus, the strength of the FRC-veneering composite structure is also dependent on the adhesion

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TABLE I Materials used in the study

Brand	Code	Type	Manufacturer	Lot no.
StickNet	SN	Fiber-reinforcement	StickTech Ltd., Turku, Finland	1990324-W-0032
Sinfony activator*	SA	Low viscosity resin	ESPE Dental-Medizin GmbH & Co., Seefeld, Germany	033 44609
Sinfony dentin D/A1**	SD	Veneering composite	ESPE Dental-Medizin GmbH & Co., Seefeld, Germany	008 FW0061325
PalaPress Vario	—	PMMA powder	Heraeus Kulzer GmbH, Wehrheim, Germany	012109
PalaPress Vario	—	MMA liquid	Heraeus Kulzer GmbH, Wehrheim, Germany	010985
Tetrahydrofuran	THF	Tetrahydrofuran	Merck KGaA, Darmstadt, Germany	19971003

* ((octahydro-4,7-methano-1H-indenediyl)*bis*(methylene)diacrylate) > 90 wt %.

** ((octahydro-4,7-methano-1H-indenediyl)*bis*(methylene)diacrylate) 10–30 wt % + fillers.

between the framework and veneering composite. When a composite resin luting cement is adhered to FRC framework, the adequate adhesion of the cement to the FRD framework is also needed.

If the fiber products are pre-impregnated with a light-polymerizable bifunctional acrylate or methacrylate monomers the polymer matrix of FRC is highly cross-linked in nature. In this case, the bond between the finally polymerized and the new veneering or cement composite resin can be based only on free radical polymerization between the substrate and the new resin. This kind of polymerization takes place if there are unreacted pendant functional groups with carbon–carbon double bonds in the polymer backbone on the surface of FRC substrate. It has been found that the greatest reactivity of the substrate to the formation of covalent bonding exists on the surface during the first 24 h after polymerization [12]. Therefore, it can be assumed that the adequate chemical bonding of bifunctional acrylate or methacrylate impregnated FRC to the new resin cannot be obtained if this kind of FRC substrate is older than 24 h, which is often the situation with normal dental laboratory delivery times of dental appliances.

When the fibers are preimpregnated with porous linear polymer of polymethyl methacrylate (PMMA) and further-impregnated with bifunctional acrylate or methacrylate monomers the bonding of the FRC substrate to an overlying composite can be based on free radical polymerization and on interdiffusion of the monomers of the new resin. The bonding based on the interdiffusion of the monomers can be obtained if the polymer matrix of the substrate is linear polymer such as PMMA or if the polymer matrix of the substrate is a multiphase polymer such as semi-Interpenetrating Polymer Network (semi-IPN) containing linear polymer, and if the monomers of the new resin have a dissolving capability, i.e. similar solubility parameter to the linear polymer phase of the substrate [11, 13–16]. In the semi-IPN polymer the linear phases and the cross-linked polymer network are not bonded chemically together as a single network like they are in the case of a typical copolymer [16]. This independency of the networks of semi-IPN polymer is a crucial property when an adequate bonding based on the monomer interdiffusion is a demand. If the both polymers are in a single network as in the case of typical copolymer, the linear polymers phases cannot be dissolved and thus, the bonding based on the interdiffusion of the monomers cannot take be obtained.

As it is known, the composites with pure linear polymer matrixes allowing the bonding based on the interdiffusion of the monomers are seldom used in dentistry. In addition, the semi-IPN structures are successfully used in acrylic resin polymer teeth and denture base polymer [14, 16]. However, even it has been showed that IPN can be successfully used in removable dentistry, there are no published reports illustrating the existence of linear polymer network in finally cured polymer matrix of FRC, allowing the bonding based on the interdiffusion as described above. Furthermore, there is no information available how various lengths of further-impregnation with bifunctional monomers affect the bonding between the FRC substrate and veneering composite resin.

The aim of this study was to investigate the effect of various lengths of further-impregnation of polymer pre-impregnated fiber-reinforcement on the polymer matrix structure of the FRC and the solubility of the PMMA phase. In addition, shear bond strength between the FRC and veneering composite resin was studied to establish the surface adhesion properties of FRC.

Materials and methods

The materials used in this study are listed in Table I. The porous PMMA pre-impregnated woven glass fiber-reinforcement prepreg StickNet was further-impregnated with a low viscosity diacrylate monomer system (Sinfony activator) (for the chemical structure see Fig. 1) by using five different lengths of further-impregnation (10, 60 min, 2, 5 and 24 h). The further-impregnated StickNet-laminates (10×10 mm, thickness: 0.06 mm)

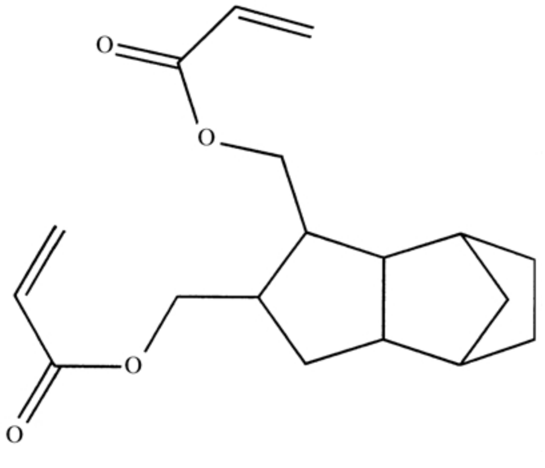

Figure 1 The chemical structure of the low viscosity diacrylate monomer system Sinfony activator (octahydro-4,7-methano-1H-indenediyl)*bis*(methylene)diacrylate). Molecule contains two functional diacrylate groups and an indenediyl group.

($n = 5$) were compared to polymer pre-impregnated StickNet-laminate (control) to find out if the different lengths of further-impregnation had an effect on the structure of the polymer matrix of FRC. Before light-curing, the excess of the resin was gently removed from laminates by using compressed air. The laminates were light-cured with dental light-curing unit for 40 s and the final polymerization was completed in the dental laboratory light-curing oven for 5 min. The polymerized laminates were stored in the desiccator at 37 °C for 48 h before measuring the weight of the laminates (Mettler Toledo AT261 Delta Range, Mettler-Toledo GmbH, Greifensee, Switzerland). The laminates were placed in the solvent tetrahydrofuran (THF) at room temperature for 48 h to remove linear PMMA network from the polymer matrix of the laminates. After removal of PMMA of the THF-treated laminates they were weighted and the soluble PMMA content as a percentage by weight was calculated. In addition, THF-treated laminates and one untreated laminate were examined with a SEM (JSM-5500, JEOL Ltd., Akishima-City, Tokyo, Japan) to determine the differences of the polymer matrices of the laminates.

To manufacture the adhesive substrates for shear bond strength test the further-impregnated fibers (10, 60 min, 2, 5 and 24 h) were placed into the retentively formed cavity of autopolymerizing denture base polymer (PalaPress Vario), surrounded by a metal cylinder. The fibers was covered with a transparent mylar sheet and initially polymerized with a hand-piece light-curing unit (Elipar, ESPE Dental-Medizin GmbH & Co., Seefeld, Germany) using wave length between 380 and 520 nm with the light intensity for 40 s. The final polymerization of the substrates was accomplished in a light-curing oven (Liculite, Dentsply, Dreieich, Germany) for 5 min where the temperature rose up to 85 °C. After the final polymerization the substrates were wet ground with 1200 grit (FEPA) silicon carbide grinding paper. The substrates were cleaned in distilled water in an ultrasonic cleaning device (Quantrex 90, L&R Ultrasonics, NJ) for 15 min. The cleaned substrates were conditioned in a desiccator at room temperature for 7 days. After conditioning of the cleaned substrates the flow viscosity veneering composite resin (Sinfony dentin) was applied on the substrate surface by using a translucent tubular polyethylene mold with an inner diameter of 3.6 mm as described earlier [17]. After which the resin was light cured with the hand-piece light-curing unit for 40 s. The final polymerization of the new resin was completed in the light-curing oven for 5 min. The polymerized test specimens were stored in a desiccator at room temperature for 7 days before testing the samples. There were eight test specimens ($n = 8$) prepared for each five groups.

To measure the shear bond strength of new resin to FRC substrate, the test specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville engineering Inc., San Ramon, CA, USA) of the universal testing machine (Lloyd LRX, Lloyd Instruments Ltd., Fareham, UK). The specimens were loaded at a crosshead speed of 1.0 mm/min and the shear force was applied until the load dropped to 50% of maximum force [17]. Statistical analysis of the results was carried out with one-way analysis of variances (ANOVA) and Dunnett's *post-hoc* test with a significance level of 0.05 (Statistical Package for Social Science, SPSS Inc., Chicago, Ill., USA). Regression analysis was performed to establish the correlation between the further-impregnation and shear bond strength.

Results

The mean values of soluble PMMA content as percentage by weight (wt %) varied from 7.07 to 8.16 wt % (Table II). ANOVA did not show differences of values for quantity of soluble PMMA wt % between different groups ($p > 0.05$). SEM examinations showed signs of existed PMMA phases in polymer matrix (Fig. 2(a)–(e)). The isles of existed PMMA phases were larger in size at FRC surface that had been further-impregnated for 10 or 60 min than in those further-impregnated for 2 or 5 h. After 24 h further-impregnation, the FRC surface was covered with a cross-linked polymer layer (Fig. 2(e)). The examination of inner structure of polymer matrix revealed the porous structure of PMMA pre-impregnation polymer of used FRC (Fig. 3(a) and the cross-linked polymer phases of the further-impregnation resin (Fig. 3(b)).

The highest mean shear bond strength (18.7 ± 2.9 MPa) was achieved when the fiber-reinforcement was further-impregnated 24 h (Fig. 4). The shortest further-impregnation, 10 min, resulted the lowest mean shear bond strength (12.7 ± 2.9 MPa) (Fig. 4). A correlation between increase of shear bond strength and prolonged further-impregnation time was found ($r = 0.689$, $p < 0.001$) (Fig. 4). Dunnett's T3 multiple comparison between different groups revealed differences between the shear bond strengths of the 24 h further-impregnated group and the other groups (Table III).

Discussion

This study demonstrated the effect of various lengths of further-impregnation of polymer pre-impregnated glass fiber-reinforced prepreg by diacrylate monomers on structure and solubility of polymer matrix of FRC. Furthermore, the influence of further-impregnation on shear bond strength between FRC substrate and veneering composite resin was investigated.

The study showed signs of existence of semi-IPN in polymer matrix of FRC after all further-impregnation times used in the study. Differences were observed between the semi-IPN structures of different groups in SEM micrographs by using THF dissolving technique to remove linear PMMA phases (Fig. 2(a)–(e)) and by comparing the SEM micrographs of the StickNet-prepreg with linear PMMA network (Fig. 3(a)) to further-impregnated laminate containing cross-linked diacrylate network only (Fig. 3(b)). The surface irregularities of FRC substrate were largest when fiber-reinforcement was further-impregnated for 10 and 60 min (Fig. 2(a) and (b)). By prolonging the further-impregnation time, the surface irregularities became smaller in size and after being further-impregnated for 24 h, the FRC substrate surface seemed to contain only a regular looking and

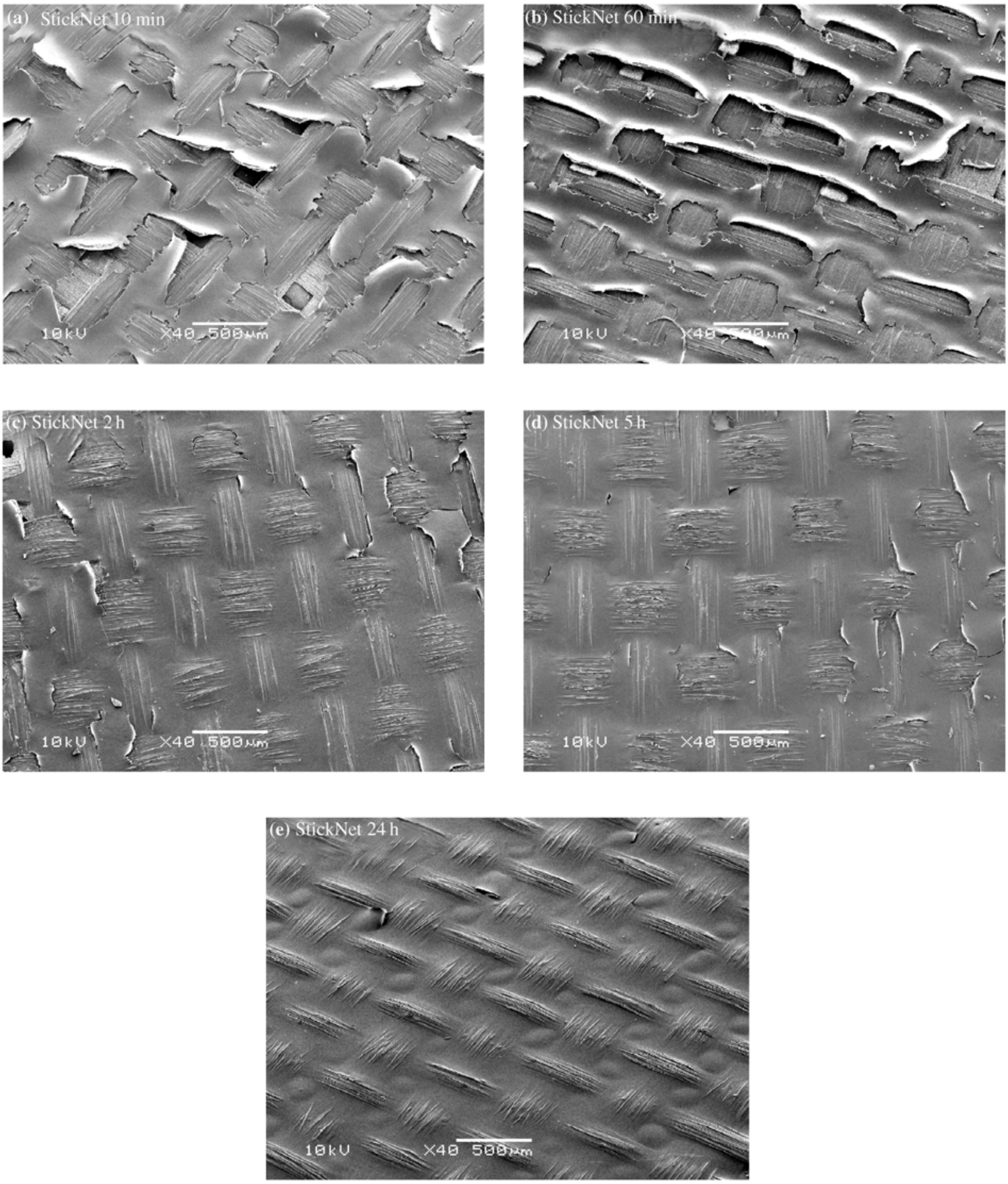

Figure 2 (a)–(e) Micrographs of further-impregnated StickNet-laminates (a) 10 min, (b) 60 min, (c) 2 h, (d) 5 h, and (e) 24 h after removing the linear PMMA phases by using THF dissolving technique. Original magnification × 40.

most homogeneous surface (Fig. 2(e)). After 24 h further-impregnation the outer most layer of homogeneous FRC surface was a cross-linked diacrylate as examined on a micrometer scale. If the further-impregnation time was less than 2 h, the diacrylate seemed to form after polymerization only a thin layer of PMMA-diacrylate semi-IPN, whereas the inner structure of polymer matrix of FRC was only PMMA. When the PMMA network was dissolved with the THF, the thin layer of PMMA-diacrylate semi-IPN at the FRC surface was broken especially from those areas where unimpregnated PMMA phases were the thickest as seen in Fig. 2(a) and (b). Thus, it seemed that the degree of penetration of Sinfony activator-diacrylate into the porous PMMA structure of StickNet-prepreg was dependent on the length of further-impregnation.

On the other hand, the total quantity of soluble PMMA remained at same level (Table II) although the further-impregnation was influenced. Therefore, it seemed that despite the monomers of the used diacrylate penetrated better into the porous PMMA structure of StickNet-prepreg after the prolonged further-impregnation, the monomers of the used resin did not effectively dissolve the PMMA phase. If the monomers had dissolved the PMMA phase entirely, the PMMA phase would be separated and surrounded all over by cross-linked network and therefore, dissolving of PMMA after polymerization would have been impossible. The finding that the mean quantity of soluble PMMA remained unchanged in all groups indicates that two independent polymer networks quite likely existed in FRC laminates despite the variation of further-impregnation. This finding might have a great importance for a nanometer scale IPN bonding, which is a bonding mechanism between based on interdiffusion of the monomers.

When the monomers of the new resins (veneering composite or composite luting cement) swell the soluble phases like PMMA of the semi-IPN polymer matrix of FRC substrate, this allows a penetration of the new resins into swelled phases of polymer matrix. During the polymerization, the monomers of new resin locks into the swelled PMMA phases of the FRC substrate zone and IPN bonding results. This kind of bonding phenomenon cannot take place, if the substrate does not include a soluble linear network like PMMA network. Thus, the finding of retained soluble PMMA phases in the examined FRC laminates supports the earlier findings of good bonding of PMMA preimpregnated FRC composite, such as fixed partial dentures, to composite resin luting cements [13, 18].

The IPN bonding mechanism has successfully been used in dentistry for decades. The repairs of multiphase denture base polymers and bonding of polymeric denture teeth to the denture base polymers have shown to been based on IPN bonding [14]. The depth of IPN bonding depends on solubility parameters of the resin and substrate and the polymerization temperature of denture base resin, which affects the bond of the polymeric denture tooth to the denture base polymer [12, 17]. On the other hand, the time for diffusion of monomer solvents to the linear polymer structure also affects bond strengths [14, 20–22]. In the present study, the polymerization temperature and time of veneering composite resin monomers to diffuse into the FRC substrate was equal in all of the test groups of the shear bond strength measurement. In spite of this, the bond strength values showed variation in the different groups (Fig. 4). Therefore, it needs to be discussed, how different further-impregnation times of StickNet-prepregs can affect the shear bond strength between FRC substrate and the veneering composite.

The difference between the prolonged further-impregnation time, which resulted in a more homogeneous multiphase polymer matrix and the increased shear bond strength cannot be explained by differences in IPN bond formation between the FRC substrate and used veneering composite because the polymerization temperature and time of the veneering composite resin monomers to diffuse into the SN-substrate was equal in the all test groups. However, the prolonged further-impregnation time with the diacrylate monomers might dissolve the most outer layer of the PMMA phases of the StickNet-prepreg at a nanometer scale and distributed then a stronger PMMA-diacrylate semi-IPN structure after polymerization. To verify this hypothesis, further investigations are needed. The other reasons for the correlation between the prolonged further-impregnation time and the increased shear bond strength is most certainly the good penetration of the Sinfony activators-monomers into the StickNet-laminate due to the prolonged further-impregnation. After 24 h further-impregnation and polymerization of the fiber-reinforcement the polymer matrix of the FRC is a combination of strong cross-linked network and a linear network in form that can be considered as the semi-IPN. The cross-linked network and the glass-fibers strengthen the linear PMMA network that the monomers of veneering composite swells when IPN bond is formed. If the strengthening of the network by the cross-linked polymer is not complete through the whole FRC structure the cohesive strength of polymer matrix decreases and shear bond strength can remain at lower level. Therefore, it can be concluded that the complete impregnation of the FRC has also an effect

TABLE III Dunnett's T3 multiple comparison between the groups

Group	Significance
StickNet 10 min	
60 min	0.865
2 h	0.479
5 h	0.252
24 h	0.003
StickNet 60 min	
10 min	0.865
2 h	0.967
5 h	0.639
24 h	0.008
StickNet 2 h	
10 min	0.479
60 min	0.967
5 h	1.000
24 h	0.022
StickNet 5 h	
10 min	0.252
60 min	0.639
2 h	1.000
24 h	0.039
StickNet 24 h	
10 min	0.003
60 min	0.008
2 h	0.022
5 h	0.039

TABLE II Mean values of soluble PMMA content (wt %) of StickNet-laminates with different further-impregnation times. Means compared by one-way ANOVA

Group	Mean (wt %)	Std. Deviation (wt %)	*n*	*F* value	df	Sig.
StickNet 10 min	7.25	1.41	5			
StickNet 60 min	7.68	1.55	5			
StickNet 2 h	7.07	0.84	5			
StickNet 5 h	6.27	3.02	5			
StickNet 24 h	7.7	1.38	5	0.517	4	0.724

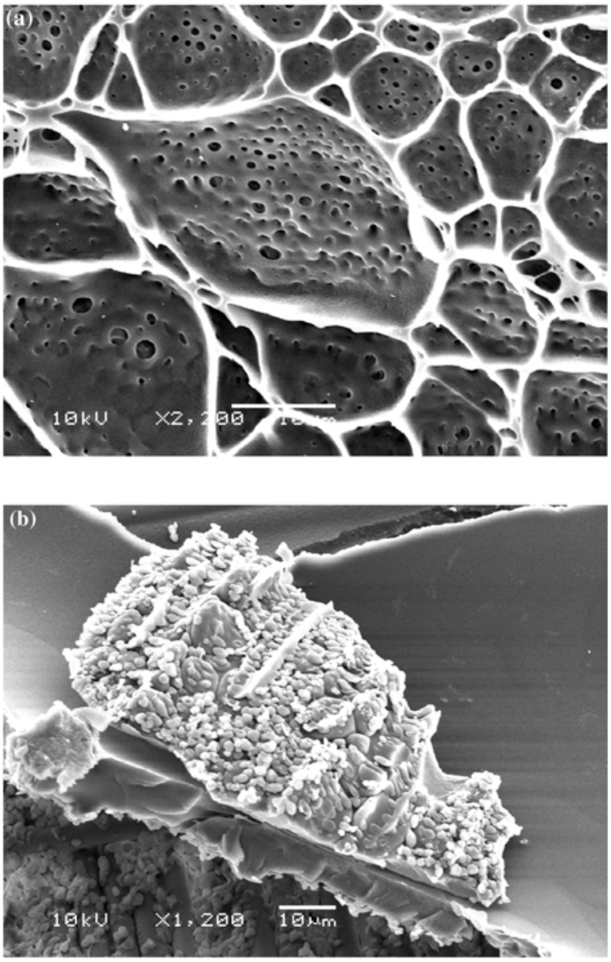

Figure 3 (a) Micrograph of porous structure of PMMA preimpregnated StickNet-prepreg. Original magnification × 2200. (b) Micrograph of StickNet-laminate after 2 h further-impregnation and removing the linear PMMA phases by using THF dissolving technique. Original magnification × 1200.

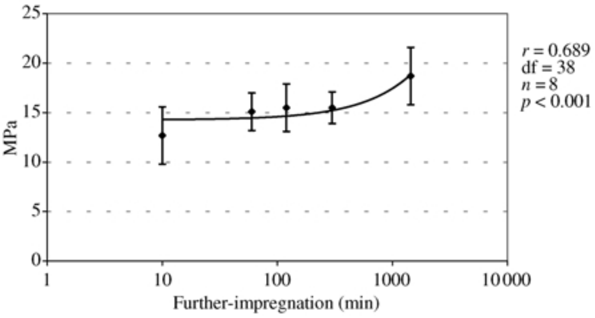

Figure 4 Further-impregnation time of StickNet-prepreg plotted to mean shear bond strengths of veneering composite to FRC substrates.

on the shear bond strength of the FRC substrate to the veneering composite.

However, it is not only the polymer matrix, which influences the bond strength between FRC material and composites. The surface pattern of FRC substrate can influence the bond strengths as well as the bonding of the polymer matrix to the fibers. As a background for this discussion, it should be emphasized that the glass fibers of StickNet-prepregs were silanized with the methacrylate/acrylate functional silane for adhesion to the polymer matrix. Furthermore, it should be noted, that the linear preimpregnation polymer is not bonded chemically to the fibers. The chemical reaction between reactive functional groups of silane based polysiloxane network occurs when polymerization of the resins used in further-impregnation takes place. Thus, the more homogeneous the semi-IPN structure exists between the fibers, the larger is the reaction surface between further-impregnation resin and the fibers. This results in better adhesion of the glass fibers to the polymer matrix, which most likely also improves integrity of IPN interphase between FRC substrate and veneering composite, and increases the bond strength.

It should also be noted that according to an earlier study the high bond strengths are related to specific FRC materials and intermediate resins [11, 17]. In the present study no special intermediate resin was used although the low viscosity of veneering composite Sinfony could be considered to behave as an intermediate resin. According to manufacturer's information the Sinfony activator-monomer system contains over 90% by weight of monomer (octahydro-4,7-methano-1H-indenediyl)*bis* (methylene)diacrylate), which is also the same monomer used in SD-veneering composite. This molecule contains two diacrylate functional groups and an indenediyl group (Fig. 1). The existence of indenediyl group increases rigidity of the molecule, which may have influenced both the dissolving capability of Sinfony activator-monomer system to linear PMMA and at the depth of the IPN bonding of the veneering composite and StickNet-substrate. Advantages of Sinfony activator-monomer system are its low polymerization shrinkage and its hydrophobic middle part (indenediyl) (Fig. 1), which retains the water sorption of composite at a low level. These properties are beneficial in FRC structures where high accuracy and mechanical properties are needed [23]. On the other hand, an alternative monomer system with different chemical compositions might result in equally homogeneous semi-IPN also in shorter further-impregnation times. However, too effective PMMA dissolving capability of the further-impregnation resin may lead to situation, in which the PMMA phases of polymer matrix of FRC are swelled and mixed with further-impregnation resin so homogeneously that the independent polymer networks of the semi-IPN do not anymore exist. Whether this has an influence on behavior as adhesive substrate or not, requires further investigation. Also, the monomeric composition of the veneering composite resin with regard to solubility parameter requires further investigations.

Conclusion

Within the limits of this study, the following conclusions were made:

1. PMMA pre-impregnated StickNet reinforcement and polymerized diacrylate momomer system of Sinfony activator formed a multiphase polymer matrix for FRC, which was considered to be a semi-IPN structure.
2. There was a correlation between the prolonged further-impregnation time of StickNet reinforcement and the increased shear bond strength values of StickNet FRC to veneering composite.

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