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PMMA-grafted nanoclay as novel filler for dental adhesives

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ABSTRACT

Objective. The aim of this study was to investigate the benefits of incorporation of poly(methyl methacrylate)-grafted-nanoclay on the bond strength of an experimental one-bottle dentin bonding system. The effect of the modification on the stability of the nanoparticle dispersion in the dilute adhesive was also studied.

Materials and methods. Poly(methyl methacrylate) was grafted onto the pristine Na-MMT nanoclay (Cloisite® Na⁺) through the free radical polymerization of methyl methacrylate in an aqueous media in the presence of ammonium persulfate as initiator. A reactive surfactant (AMPS) was also used in the reaction recipe to provide active sites on the surface of the nanoclay. The grafting polymerization reaction was carried out at 70 °C. The PMMA-g-nanoclay was then coagulated in methanol and filtered. The resulting PMMA-g-nanoclay was characterized using FTIR, TGA, X-ray diffraction (XRD) and particle size distribution analysis. The modified nanoclay was added to an experimental dentin bonding system as filler and the morphology of the nanoclay layers in the adhesive matrix was studied using TEM and XRD. Shear bond strength of the adhesives containing different filler contents was tested on the caries-free extracted human premolar teeth. The mode of failure was studied by scanning electron microscopy. The stability of the nanoclay dispersion in the dilute adhesive was also studied using a separation analyzer. The results were then statistically analyzed and compared.

Results. The grafting of poly(methylmethacrylate) onto the nanoclay was confirmed and the results revealed a partially exfoliated structure for the PMMA-g-nanoclay. Incorporation of the modified nanoclay provided a dentin bonding system with higher shear bond strength. The dispersion stability of the modified nanoparticles in the dilute adhesive was also increased more than 40 times in comparison with the pristine nanoclay.

Significance. The grafting modification provided nanoclay particles with higher dispersion stability than pristine Na-MMT nanoclay in a dilute dentin bonding system. Incorporation of the modified nanoclay into the bonding system provided higher shear bond strength. The finding would be beneficial in producing nano-filler containing adhesive systems.

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1. Introduction

The role of dental adhesives in a restoration is to provide a good bonding between the filling materials and tooth

structure [1–3]. Bonding to enamel is considered satisfactory, but due to the dynamic nature of dentin, adhesion to this wet substrate is much more complex [4]. Dentin is a hydrated biological composite, including 70% inorganic

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material, 18% organic matrix and 12% water [5,6]. It contains dentinal tubules, extending through its thickness, which are surrounded by highly mineralized peritubular dentin in the crown and fluid flows in the tubules in a direction to outside [7,8]. Further more, filling of the dentin tubules by smear layer when dentin is cut or ground, make the formation of a reliable adhesion more complicated [9,10]. Failure in obtaining a satisfactory interfacial bond between the resin restoration and dentin substrate causes marginal leakage, marginal discoloration, post-operative sensitivity, secondary caries and a pulpal pathology [11,12].

The bonding mechanism of recent dentin bonding agents is based on the penetration of ambiphilic molecules into the acid-etched dentin [13,14]. Penetration of dentin bonding monomers is facilitated by water chasing solvents such as ethanol and/or acetone to obtain a direct contact of resin with the collagen fibers, which results in the hybrid layer which is a mixed zone of polymerized resin and entangled collagen fibrils [15–18]. Therefore, a micro-mechanical retention between resin and dentin surface is formed [8–10]. At the resin–dentin interface, the adhesive layer has the lowest elastic modulus among the components of the bonded complex [11,12]. When the occlusal loading exceeds the inherent strength of the adhesive, defects or cracks may occur at the low-modulus layer leading to the failure of restoration [16–18].

It has been shown that the incorporation of fillers into the adhesives would increase the mechanical properties of the adhesive layer [19–21]. The enhancement in mechanical properties produced by small amounts of nano-fillers is well known. Montmorillonite is a nanoclay which occurs in nature as plate-like particles called platelets with an average platelets thickness of 1 nm and length and width of up to 1 μm . The high aspect ratio of 200–1000 of nanoclay platelets has been effectively used to improve the tensile and compression moduli of polymeric systems [22–24]. Therefore, the incorporation of nanoclay into the dental adhesives may be a solution to overcome the lower mechanical properties of the adhesive layer. Addition of nanoclay to dental adhesive, on the other hand, accompanies with the problem of rapid sedimentation of particles due to the dilute characteristic of the adhesives and higher density of the clay.

As grafting is an effective method to give especial functionality to the surface of nanoparticles [25], in this study the surface of pristine Na-MMT nanoclay was modified through the graft polymerization using methyl methacrylate monomer. The grafted nanoclay was then characterized and its dispersion stability in an experimental dilute adhesive was investigated. The shear bond strength of a dentin bonding system containing different percentages of the PMMA-g-nanoclay was also studied.

2. Experimental

2.1. Materials

2-Hydroxyethyl ethyl methacrylate (HEMA), camphorquinone (CQ), and 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (TMPTMA), acetone, ethanol and methanol were purchased from Merck (Germany). Tetrahydrofuran

(THF), *N,N'*-dimethyl aminoethyl methacrylate (DMAEMA) and *tert*-dodecyl mercaptan (TDM) were obtained from Fluka (Germany). 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (Bis-GMA) was kindly supplied by Röhm (Degussa group, Germany). Cloisite® Na⁺ was obtained from Southern Clays Product, Inc. (USA). 2-Acrylamido-2-methyl-1-propane-sulfonic (AMPS) acid, ammonium persulfate and aluminum sulfate were purchased from Sigma–Aldrich (Germany).

2.2. Methods

2.2.1. Graft polymerization of methyl methacrylate onto the surface of nanoclay platelets

A 0.5 wt.% dispersion of nanoclay in water was prepared in a 1 l jacketed glass reactor. The temperature was held at 50 °C for 12 h while acute stirring. Aqueous solutions containing 2.5 g AMPS, as reactive surfactant, and 2 g ammonium persulfate, as polymerization initiator were added to the clay dispersion. 50 ml methyl methacrylate monomer and 2 ml TDM as chain transfer agent were then added to the reaction medium. The temperature was increased to 70 °C while stirring. The polymerization reaction was completed in 1 h. The product was then coagulated by dropping the reaction mixture to 1 l methanol containing 5 wt.% aluminum sulfate. The precipitate was vacuum-filtered, washed several times with distilled water until a constant conductivity of the effluent, measured with a conductivity meter (JENWAY 4010, UK), was reached. Finally, the filtrate was washed with ethanol to remove the unreacted monomers and vacuum dried at room temperature for 24 h. The product was then Soxhlet-extracted for 72 h using THF as solvent to remove the unbond homopolymer (PMMA) produced during the polymerization reaction. The purified PMMA-g-nanoclay was vacuum dried and powdered using a ball mill (PM100, Retch, Germany), passed through a 400 mesh (ASTM) sieve and used as filler.

2.2.2. Characterization of the PMMA-grafted nanoclays

The pristine Na-MMT and PMMA-grafted nanoclay were analyzed by FTIR spectroscopy (EQUINOX 55, Bruker, Germany) at a resolution of 4 cm^{-1} and 32 scans in the range of 4000–400 cm^{-1} using KBr disc technique. Thermogravimetric analysis of the pristine Na-MMT, PMMA-g-nanoclay and pure PMMA was performed (TGA-1500, Polymer Laboratories, UK) from room temperature to 600 °C at a heating rate of 10 °C/min and under N₂ atmosphere. X-ray diffraction patterns of pristine Na-MMT and PMMA-g-nanoclay were collected in the range of $2\theta = 2\text{--}10$ and step size of 0.02, using a Philips X-ray diffractometer (Philips, X'pert, Netherlands) with copper target, $\lambda = 1.55414 \text{ \AA}$ operating at a voltage of 40 kV and a current of 40 mA at the rate of 2°/min. The d_{001} spacing was calculated according to the Bragg's equation: $n\lambda = 2d \sin \theta$.

2.2.3. Preparation of adhesives

The adhesive was prepared according to the recipe shown in Table 1. Pristine Na-MMT and PMMA-g-nanoclays were added to the adhesive in 0.2, 0.5, 1, 2 and 5 wt.%. The fillers were well dispersed in the adhesive solution by ultra sonication using a probe sonication apparatus (Sonoplus UW2200, Bandelin, Germany) for 3 min. The stability of the dispersions

Table 1 – Recipe of the experimental dentin bonding

Materials	% Weight
Bis[4-(2-hydroxy-3-methacryloyl oxyproxy)phenyl] propane (Bis-GMA)	9
2-Hydroxy ethyl methacrylate (HEMA)	29
Acetone	37
Ethanol	17
2-Ethyl-2-(hydroxymethyl)-1,3-propandiol trimethacrylate (TMPTMA)	7
Camphorquinone (CQ)	0.5 ^a
N,N'-Dimethyl aminoethyl methacrylate (DMAEMA)	0.5 ^a

^a The photoinitiator and activator were added after sonication to prevent un-wanted polymerization before applying the adhesive.

was investigated by a separation analyzer (LUMiReader® 416.1, LUM, Germany) working with visible light and intensities of 25% and tilt of 0, for 12 h including 256 intervals. The particle size distribution of the nanoclay dispersions were analyzed using laser light scattering (SEM633, SEMAtech, France) with the wavelength of 632–8 nm, angle of 90° and experiment duration of 120 s. The dispersions were diluted to a concentration of 0.05 wt.% before analysis.

2.2.4. Measurement of degree of conversion

Small amount of the adhesives containing 0.5 wt.% CQ and 0.5 wt.% DMAEMA as photoinitiator system were placed on a polyethylene film. The solvent of adhesive was gently evaporated for 10 s applying a low-pressure air stream and a second film was placed on it to form a very thin layer. The sandwich was placed into the FTIR spectrometer's sample holder and the absorbance peaks obtained by transmission mode of FTIR. The samples were then light cured for 40 s using a dental light source with an irradiance of circa 600 mW/cm² (Demetron, SDS Kerr, Germany) and the peaks were measured for the cured samples. The degree of conversion (DC%) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm⁻¹) against internal reference of aromatic C...C (peak at 1608 cm⁻¹) before and after curing of the specimen. The degree of conversion was then calculated as follows:

$$DC\% = \left(1 - \frac{(1638 \text{ cm}^{-1}/1608 \text{ cm}^{-1})\text{peak area after curing}}{(1638 \text{ cm}^{-1}/1608 \text{ cm}^{-1})\text{peak area before curing}} \right) \times 100$$

2.2.5. Transmission and scanning electron microscopies (TEM and SEM)

Adhesive samples containing 1 wt.% pristine Na-MMT and PMMA-g-nanoclay were solvent evaporated and light cured in a mold. An ultra-microtome (DMU3, Reichert, Austria) was used to prepare approximately 70 nm thick samples. A Philips TEM (CM200, FEG, Netherlands) was used for TEM observations. The composite–dentin interface was observed using SEM (TESCAN, VEGAII, XMU, Czech Republic) to study the mode of failure.

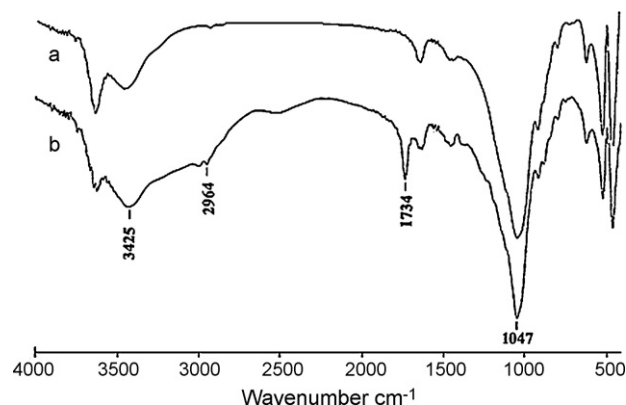


Fig. 1 – FTIR spectrums of (a) pristine Na-MMT nanoclay and (b) PMMA-g-nanoclay.

2.2.6. Specimen preparation for microshear bond test

A total of 49 caries-free extracted human premolars were used in this *in vitro* study. The teeth were washed under running water immediately after extraction and stored in formaldehyde 10% for maximum 3 months. A week before the test, the surfaces of crowns and roots were cleaned from any hard and soft tissues. The teeth were randomly divided into seven groups. The occlusal enamel mass removed using a trimmer (Dentaurim, Germany). A dentin slice (approximately 3.0 mm thick) was prepared by cutting perpendicular to the long axis of each tooth from the middle coronal region using double face diamond disk of a slow-speed sectioning machine (DEMCO, E 96-230, USA) under water coolant. The occlusal surfaces of slices were ground with silicon carbide paper 320 and 600 grit (Soft Flex, Germany) to prepare a flat and homogeneous smear layer. In groups 1–6, teeth were etched with a 35% phosphoric acid solution (3M ESPE, USA) for 15 s and rinsed with water jet spray for 15 s. To avoid over drying, a paper tissue was used to dry the dentin surface (blot drying). The bonding agents containing 0, 0.2, 0.5, 1, 2 and 5 wt.% PMMA-g-nanoclay were applied on the dentin surface by a brush and their solvent were gently evaporated for 5 s under directed low-pressure air stream. In group 7 a commercially available dentin bonding (SingleBond®, 3M ESPE, USA) was applied on the surface of each slice following the manufacturer's instruc-

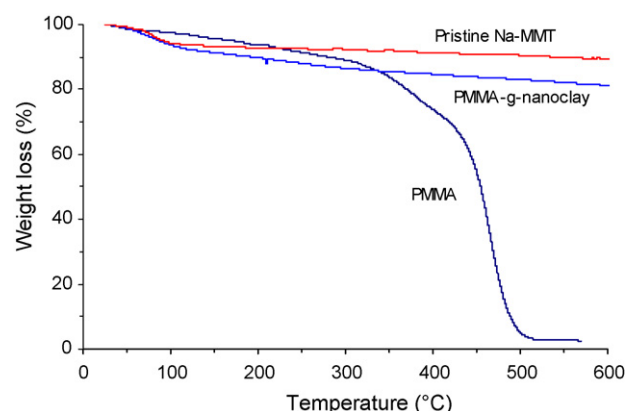


Fig. 2 – TGA thermograms of PMMA, PMMA-g-nanoclay and pristine Na-MMT nanoclay.

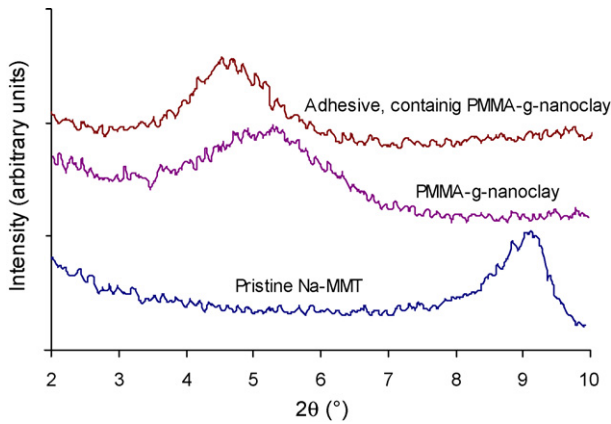


Fig. 3 – XRD patterns of pristine Na-MMT, PMMA-g-nanoclay, and adhesive containing 1 wt.% PMMA-g-nanoclay.

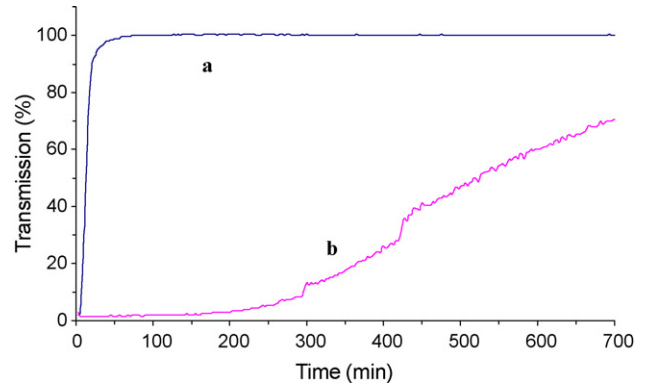


Fig. 5 – Separation analysis; transmission (%) vs. time at the height of 28 mm of LUMi Reader® tube for the adhesive containing: (a) 1 wt.% pristine Na-MMT sonicated for 3 min (total test duration: 5 min). (b) 1 wt.% PMMA-g-nanoclay sonicated for 3 min (total test duration: 12 h).

tion. Prior to light-curing, two cylinders (internal diameter: 0.75 mm, height: 1.0 mm) of Microbore Tygon® Tubing (USA) were placed on the dentin surface. After 10 s irradiation, each tube was carefully filled with resin composite (Clearfil AP-X, Kuraray, Japan) and light cured for 40 s. The specimens were then stored in dionized water at room temperature for 1 h

and the Tygon® tubes around the composite cylinders were removed by gently cutting the tube using a surgery blade, providing 14 composite cylinders for microshear test (each measurement was considered separately to increase the number of samples per group). Having stored for 24 h in water at

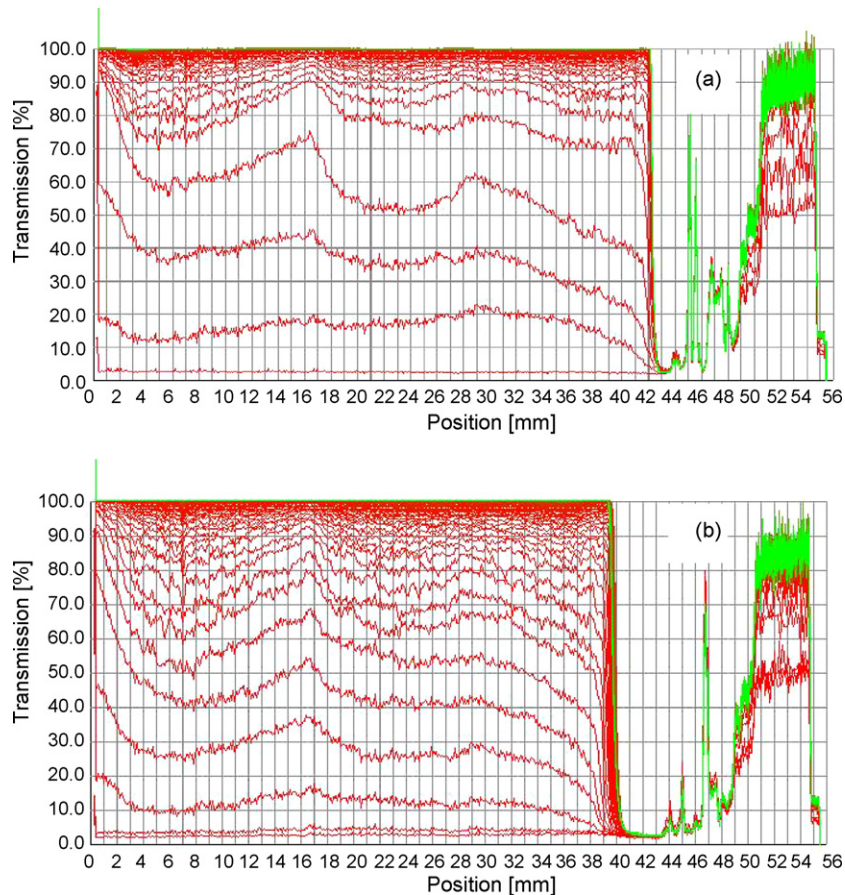


Fig. 4 – Separation analysis in LUMi Reader®. Sedimentation behavior of the adhesive containing: (a) 1 wt.% pristine Na-MMT sonicated for 3 min (total test duration: 5 min). (b) 1 wt.% PMMA-g-nanoclay sonicated for 3 min (total test duration: 12 h).

37 °C, each specimen was adhered to the testing apparatus with a cyanoacrylate adhesive. A thin wire (diameter 0.2 mm) was looped around each composite cylinder, so that the wire was in contact with the lower half-circle of the cylinder and the tooth surface. Pulling up the wire, a shear force was applied to each specimen at a cross-head speed of 1 mm/min using a universal testing machine (SMT 20, Santam, Iran) until failure occurred [26]. The microshear bond strength was then calculated by dividing the force at break by the composite–dentin interface area.

2.2.7. Statistical analysis

The results were analyzed and compared using one-way ANOVA and the Tukey test at the significance level of 0.05.

The reported values are the average of 14 measurements for microshear bond strength and three measurements for degree of conversion.

3. Results

Fig. 1 shows the FTIR spectra of the pristine Na-MMT and PMMA-g-nanoclay illustrating the characteristic peaks of PMMA which confirm the grafting reaction. Fig. 2 shows the TGA curves of the pristine Na-MMT, PMMA-g-nanoclay, and neat poly(methyl methacrylate), which was synthesized in the same conditions as the graft polymerization. Considering the ash content of neat PMMA in the thermo-

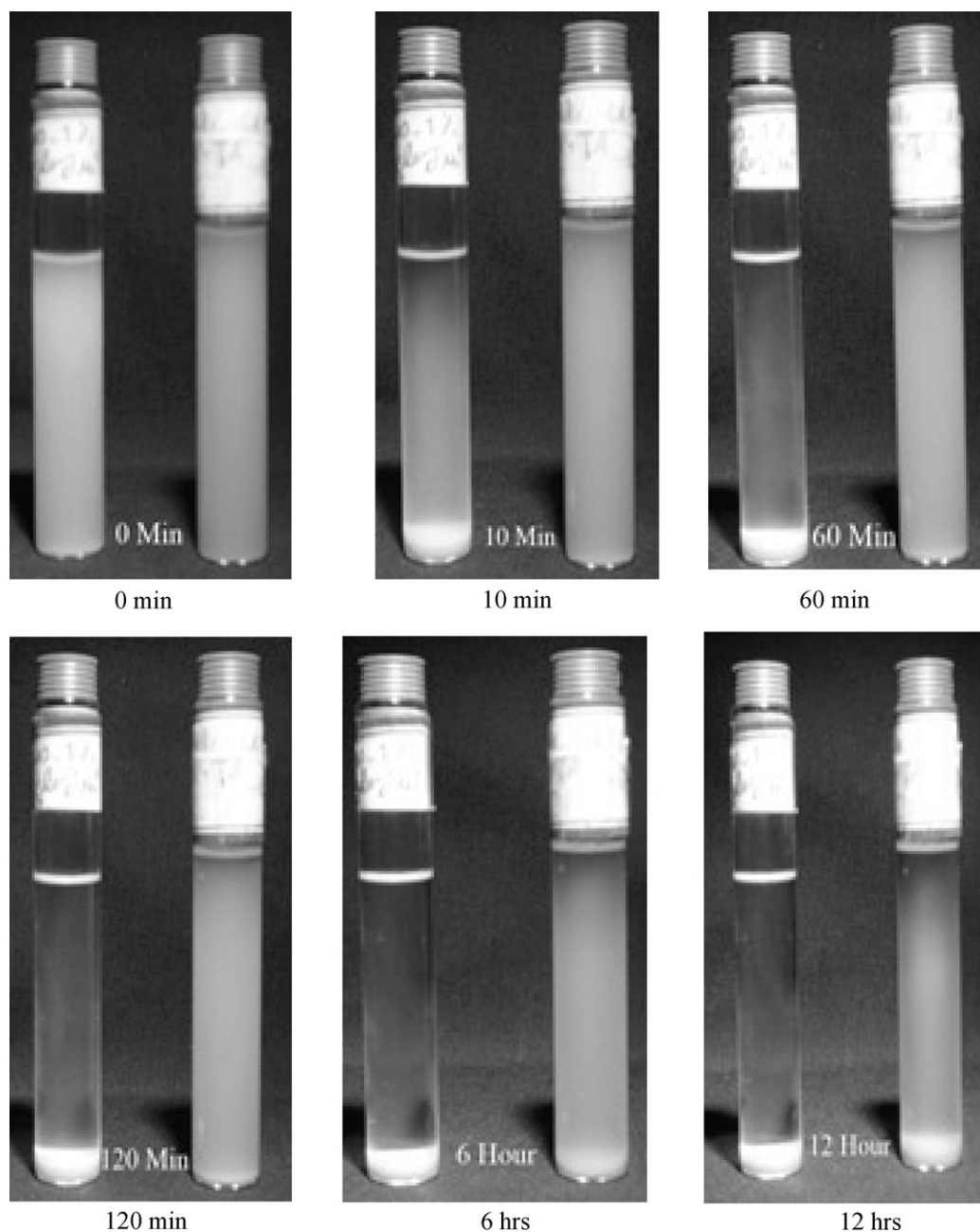


Fig. 6 – Visual observations of sedimentation of nanoclay in the adhesive solutions containing 1 wt.% pristine NA-MMT (left tube) and 1 wt.% PMMA-g-nanoclay (right tube).

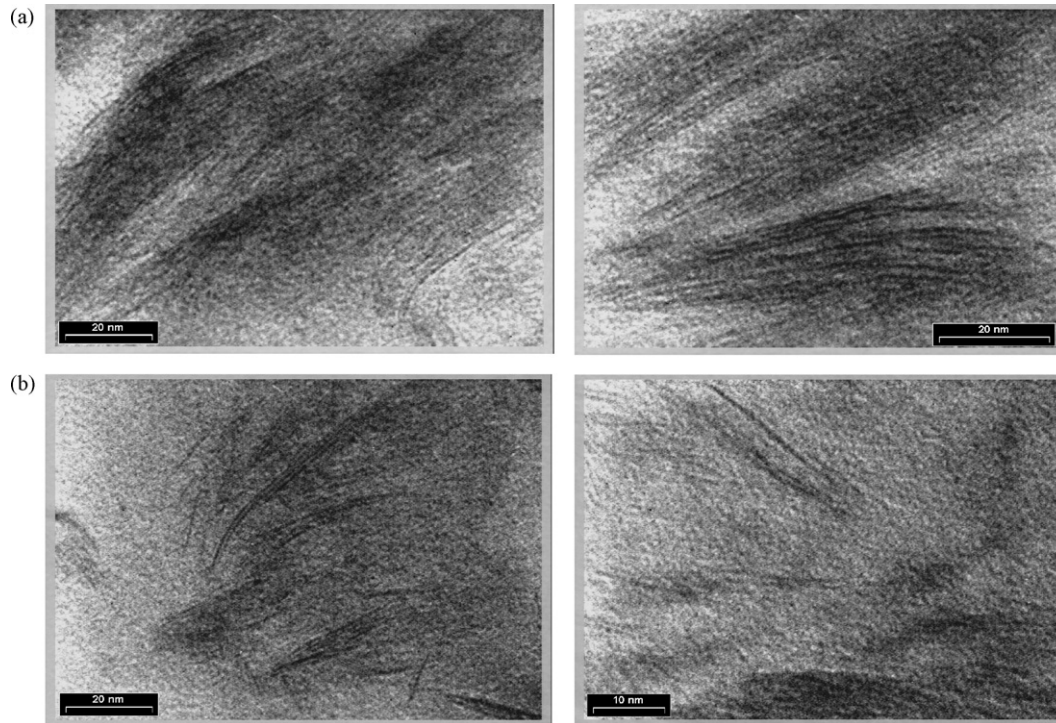


Fig. 7 – TEM micrographs of the adhesive containing: (a) 1 wt.% PMMA-g-nanoclay showing partially delaminated clay platelets and (b) 1 wt.% pristine Na-MMT showing well-stacked nanoclay platelets.

gravimetric analysis (≈ 2.6 wt.% at 550°C), the grafted PMMA was obtained about 14%. Fig. 3 illustrates the X-ray diffraction (XRD) patterns of pristine Na-MMT, PMMA-g-nanoclay, and the cured adhesive containing 1 wt.% PMMA-g-nanoclay. It shows that in the case of PMMA-g-nanoclay, the peak has been broadened and also shifted towards lower angles, which is an indication of the lower regularity and larger basal spacing as a result of the intercalation of PMMA chains into the clay galleries. The XRD pattern of the adhesive containing PMMA-g-nanoclay shows even more improvement. Figs. 4 and 5 illustrate the separation analysis results which show the sedimentation behavior of the nanoparticles in the adhesives. The sedimentation of the adhesive containing 1 wt.% pristine Na-MMT (left tube) and 1 wt.% PMMA-g-nanoclay (right tube) was also visually observed and compared (Fig. 6). The figure confirms that the stability of the dispersion containing modified nanoclay has significantly been improved. Fig. 7 shows the TEM images of light cured adhesive containing 1% pristine Na-MMT (a) and PMMA-g-nanoclay (b) which is an indication of partially exfoliation of the PMMA-g-nanoclay in the adhesive system. Fig. 8 shows the microshear bond strength of the adhesives containing different percentages of PMMA-g-nanoclay. It reveals a significant increase ($p < 0.05$) in the microshear bond strength of the adhesive containing 0.5 wt.% PMMA-g-nanoclay. The failure modes of the shear bond test are illustrated in Fig. 9. The figure shows mixed and adhesive failures for the adhesives containing 0.5 and 5 wt.% PMMA-g-nanoclay, respectively. The failure mode of the adhesive containing 0.5 wt.% PMMA-g-nanoclay was mostly mixed

and for the other groups was mostly adhesive from the dentin–adhesive interface (the other groups have not been illustrated here).

Measurement of degree of conversion revealed that the DC% values of the adhesives were in the range of 74–79% and there was no significant difference between the DC% of the adhesives with different filler contents and the SingleBond® ($p < 0.05$).

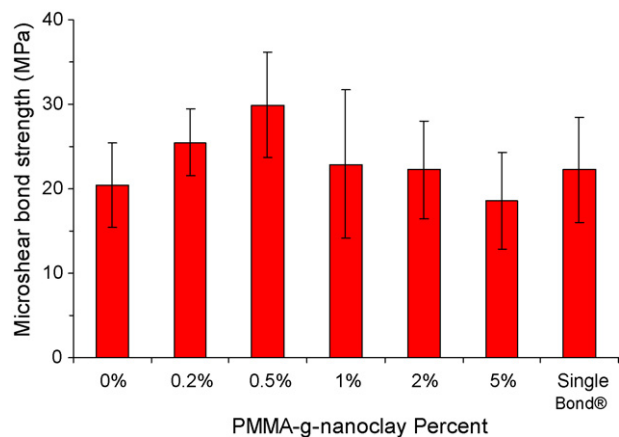


Fig. 8 – Microshear bond strength of the adhesives containing different percentages of PMMA-g-nanoclay. SingleBond® (3M ESPE, USA) is a commercially available dentin bonding agent.

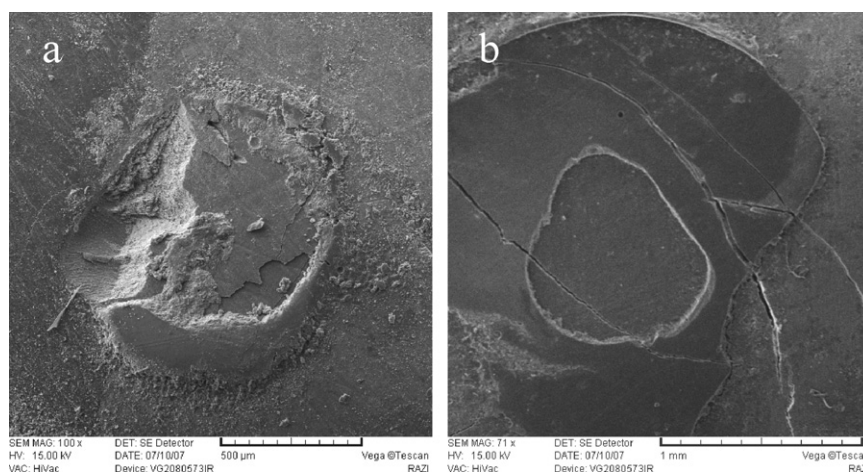


Fig. 9 – SEM of the composite–dentin interface showing the failure mode of the adhesive layer: (a) mixed failure in adhesive containing 0.5 wt.% PMMA-g-nanoclay and (b) adhesive failure in adhesive containing 5 wt.% PMMA-g-nanoclay.

4. Discussion

The grafting of PMMA on the Cloisite® Na⁺ was carried out in aqueous solution. The pristine Na-MMT was dispersed in water in the presence of a reactive surfactant, AMPS, which has amido and sulfonic acid groups in its structure. It has been suggested that the AMPS molecule is capable of being exchanged with Na⁺ counter ion in the pristine nanoclay structure through its amido group, providing active sites for free radical polymerization via the acrylate end groups of AMPS [27–29]. Polymerization of methyl methacrylate monomers in the presence of nanoclay platelets, AMPS, and a water soluble free radical initiator, ammonium persulfate, leads to both graft polymerization involving the acrylate groups of AMPS, and homopolymerization in aqueous phase. Therefore, the reaction product is a mixture of PMMA-g-nanoclay and PMMA homopolymers. Having Soxhlet extracted with THF for 72 h for completely removal of the PMMA homopolymers, the remained, PMMA-g-nanoclay, was characterized using different analytical techniques.

The grafting of PMMA on the pristine Na-MMT was confirmed by FTIR spectroscopy. Fig. 1 shows the appearance of two characteristic peaks at 1736 and 2955 cm⁻¹ which are assigned to carbonyl group and stretching vibration of C–H in PMMA structure, respectively [30]. The percent of grafted PMMA according to the thermogravimetric analysis data (Fig. 2) is about 14 wt.%. As the PMMA-g-nanoclay was Soxhlet extracted for 72 h with THF, which is a good solvent for PMMA, the weight loss in the grafted clay is due to the degradation of the bonded PMMA polymer chains. The weight loss around 100 °C (Fig. 2) is due to the loss of unbound water. The TGA also shows that there is no sharp weight loss for degradation of PMMA in the grafted clay, which is probably due to the thermal stabilization effect of nanoclay on the polymer [31].

Comparison of the XRD patterns (Fig. 3) shows that the peak position from $2\theta = 9.11^\circ$, corresponding to an interlayer spacing of $d_{001} = 9.70 \text{ \AA}$ for pristine Na-MMT, is shifted to $2\theta = 5.33^\circ$, representing an interlayer spacing of $d_{001} = 16.56 \text{ \AA}$, for PMMA-g-nanoclay. This increase in the basal spacing is

due to the intercalation of PMMA chains into the clay galleries, because, the grafted poly(methylmethacrylate) chains prevent the clay sheets to stack up after removing from the aqueous grafting reaction medium. When PMMA-g-nanoclay is incorporated into the dilute adhesive, due to the solvating power of the solvent (acetone), PMMA chains in the clay galleries swell and allow diffusion of the adhesive monomers into the clay layers. Removing the solvent and curing the adhesive leaves additional organic components between the layers and results in increased basal spacing. As shown in Fig. 3 the peak position for the cured nanocomposite adhesive is shifted to $2\theta = 4.53^\circ$ corresponding to an interlayer spacing of $d_{001} = 19.48 \text{ \AA}$ which recommends an intercalated structure. In addition, slightly broadening of the peak in comparison to that of the pristine Na-MMT, could be an evidence to the partially exfoliation of the nanoclay, which is further confirmed by the TEM observations. TEM images of the adhesive containing 1 wt.% PMMA-g-nanoclay is shown in Fig. 7b. The results reveal a partially exfoliated or intercalated-exfoliated structure, that confirms the findings of XRD. Where as, the TEM micrographs of the adhesive containing 1 wt.% pristine Na-MMT (Fig. 7a) show the well-stacked nanoclay platelets.

Dispersion analysis of the adhesives containing different concentrations of the modified nano-particles showed a significant increase in the sedimentation time of the particles through the dilute solution of the bonding system. Figs. 4 and 5 show the LumiReader® dispersion analysis which represent the sedimentation behavior of the specimen containing 1 wt.% of the pristine Na-MMT and treated nanoclay filler (the behavior was observed for all nanoclay percents and the figures are typical). Visual observations also show the higher stability of the dispersion when the nanoclay is modified (Fig. 6). In this experimental bonding system acetone is a good solvent for PMMA, therefore polymer chains, grafted onto the nanoclay surface, swell and force the nanoclay platelets to separate from each other which results in decreasing the overall density of the filler particles. The lower density of the particles leads to an increase in the sedimentation time.

The ultimate goal of a dental bonding system is providing a strong and stable bond between the restoration and

tooth substrate. Microshear test is one of the accepted methods in measuring the strength of the bond between dentin substrate and composite restoration [32]. As the bonded surface in this method is very small (approximately 0.5 mm²), it would allow testing many specimens on a single surface of sectioned dentin and provides an almost pure shear on the area which force is applied. The method is also considered as a rapid method [32,33]. The microshear test results which are presented in Fig. 8 show a significant increase in the bond strength of the adhesive containing 0.5 wt.% PMMA-g-nanoclay ($p < 0.05$). It has been reported that the addition of filler to adhesives leads to increase in mechanical properties and bond strength [16,19,21]. Incorporation of fillers into an adhesive causes an increase in its elastic modulus providing a layer with an elastic modulus between dentin and restoration. This intermediate layer, together with the resin-impregnated dentin, act as an elastic buffer which offers the resin–dentin interface a sufficient strain capacity to accommodate both the composite and dentin [14].

Fig. 8 also shows that the bond strength increases to an optimum level (0.5 wt.%) and then gradually decreases with the increase of filler content. The decrease in the shear bond strength is due to the agglomeration of the nano-particles at higher filler contents. The accumulation of filler agglomerates on the top of the etched dentin substrate may prevent the penetration of the adhesive resin monomers into the dentinal tubules and hybrid layer [16,19]. The higher viscosity of the adhesive at higher filler content is also another factor to reduce the penetration of adhesive and consequently decrease the micromechanical retention which is a key factor in the bond strength of dental adhesives.

Scanning electron microscopy of the shear bond test area (Fig. 9) shows that the failure mode at 0.5 wt.% filler content is mostly mixed failure. As it is observed, dentin has been broken out after the shear test which confirms the strong adhesion at this filler content.

Mechanical properties of the adhesives are strongly affected by the degree of conversion (DC%). Therefore, the shear bond strength should preferably be compared in the same degree of conversion. DC% measurements showed that there is no significant difference between the DC% of the specimens containing different percentages of PMMA-g-nanoclay ($p > 0.05$). It confirms that the results obtained for the shear bond strengths are solely due to the incorporation of filler into the adhesive system.

5. Conclusion

A pristine Na-MMT nanoclay (Cloisite® Na⁺) was modified by graft polymerization of poly(methyl methacrylate) onto the surface of the clay platelets. The grafted nanoclay was characterized using FTIR, TGA and XRD techniques. The modified nanoclay was dispersed in an experimental dental adhesive and the dispersion stability was shown to be improved more than 40 times with respect to the pristine nanoclay. XRD and TEM studies on the adhesive containing modified nanoclay showed a partially exfoliated structure for the nanocomposite. Incorporation of 0.5 wt.% PMMA-g-nanoclay to the experimental dental adhe-

sive resulted in a significant increase in microshear bond strength.

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