

Application of Block Copolymeric Surface Modifier with Crosslinkable Units for Montmorillonite Nanocomposites

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ABSTRACT: Montmorillonite (MMT) of which the surface was modified with a block copolymer with crosslinkable units was incorporated into methacrylate-based composites as nanofiller to improve dimensional and mechanical properties. A bifunctional block copolymer containing 2-isocyanato ethyl methacrylate in one block and poly(vinyl pyridine) units in the other block was prepared as the block copolymeric surface modifier for MMT through controlled/"living" radical polymerization technique. Application of the modified MMT in 2,2-bis[4-(2-hydroxy-3-methacryloyl-oxy)phenyl]propane (bis-GMA) based composites showed that polymerization shrinkages of the composites decreased as the content of modified MMT increased. Compressive and flexural strengths of the composites were also improved in the presence of the modified MMT, which demonstrate the beneficial effect of the modified MMT as a nanofiller and IEM as a cocrosslinkable unit. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: controlled/"living" radical polymerization; functional block copolymers; montmorillonite; surface modifier

Received 28 January 2012; accepted 7 April 2012; published online

DOI: 10.1002/app.37856

INTRODUCTION

The improvement in dimensional stability and mechanical properties of composites reinforced by little amount of nanofillers is well known.^{1,2} However, nanoscale fillers typically aggregate because of strong interfiller van der Waals forces and thus may negate benefits associated with the nanoscopic dimensions of the fillers.³ Therefore, better spatial distribution of nanofillers in the resin matrix is one of the key requirements to obtain desirable properties of nanocomposites. A good dispersion of nanofillers can normally be ascertained through surface modification of nanofillers to enhance miscibility and interconnectivity of the nanofillers with polymer matrices.⁴ For successful surface modification of nanofillers, structural characteristics of surface modifiers should be finely tuned to afford favorable interaction between nanofillers and polymer host. Unfortunately, the choice of suitable surface modifier among commercially available products is often very limited because of few variations in structural and compositional characteristics. In addition, molecules that can afford steric repulsion between nanofillers, such as polymeric surface modifiers, are often desired especially when higher loading of nanofillers is targeted.⁵

One of the representative example of polymeric composite materials can be 2,2-bis[4-(2-hydroxy-3-methacryloyl-oxy)phenyl]propane (bis-GMA) based polymeric dental restorative composites (PDRC), which mainly consist of microscale inorganic fillers and polymer resin matrices. In addition to conventional PDRC, new compositions based on nanoscale fillers have continuously attracted considerable attentions.⁶ In reference to nanocomposites reinforced by montmorillonite (MMT) nanofiller, most of results reported that mechanical properties of the nanocomposites were significantly improved. More importantly, MMT is recognized as safe (GRAS) as a direct human food ingredient.⁷ Therefore, the incorporation of MMT to PDRC is expected to improve the clinical performances of PDRC such as mechanical and polymerization shrinkage properties to improve marginal adaptation and prevent recurrent caries.

The first report concerning the application of MMT to dental application has been reported by Atai et al.⁸ Their results suggested that the dispersion stability and microshear bond strength of dental adhesive were significantly improved by incorporation of 0.5 wt % of PMMA-graft-MMT in dental

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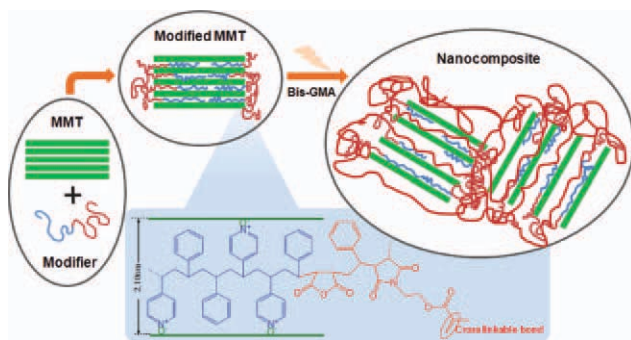


Figure 1. Schematic representation for the polymeric nanocomposite containing surface modified MMT with block copolymer capable of not only interacting with MMT layer surfaces but also being cocrosslinked with polymer matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adhesive. Considering the fact that PDRC contains not only dental adhesive but also microfillers, and the fact that network formation during photopolymerization of PDRC is very fast, monomer diffusion into clay galleries that would aid exfoliation is actually limited. Hence, the role of polymeric surface modifier is considered to be significantly important to incorporate the nanofiller successfully into PDRC system.

As mentioned earlier, this study aims at the preparation and application of polymeric surface modifier capable of not only interacting with MMT surfaces but also being cocrosslinked with composite matrix. Bis-GMA-based PDRC was used as a model composite matrix and a bifunctional block copolymer having 4-vinyl pyridine (4VP) units in one block and pendant methacrylate units in the other block was targeted as the surface modifier. Because 4VP units are capable of cation exchange reaction with Na^+ -MMT and methacrylate units are capable of cocrosslinking with bis-GMA-based resin matrix during curing process, the new block copolymer is expected to improve dispersability and interconnectivity of the modified MMT with the resin matrix (Figure 1).

EXPERIMENTAL

Materials

Styrene (St, 99%, Aldrich, St. Louis, MO) was purified by passing through alumina column to remove inhibitor. 4-Vinyl pyridine (4VP, 97%, Aldrich, St. Louis, MO) was dried over CaH_2 , followed by distilling under reduced pressure at 51°C before use. Both St and 4VP were stored in a freezer under nitrogen. 2-Isocyanato ethyl methacrylate (IEM, Showa Denko K.K, Tokyo, Japan), 2,2-azobis-isobutyronitrile (AIBN, 98%, Aldrich, St. Louis, MO), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 98%, Aldrich, St. Louis, MO), maleic anhydride (MAN, 99%, Aldrich, St. Louis, MO) were used as received. Sodium-montmorillonite (Na^+ -MMT, Cloisite[®] Na^+) was provided by Southern Clay Product (Gonzales, TX). Solvents were used without further purification. 2,2-Bis[4-(2-hydroxy-3-methacryloyl-oxy)phenyl]propane (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA), camphorquinone (CQ, 97%, used as a photoinitiator) and *N,N*-dimethyl aminoethyl methacrylate (DMA-EMA, as a photoactivator) were also obtained from

Aldrich (St. Louis, MO). Barium aluminum silicate glass filler (Ba-glass microfiller, average particle diameter = $1\ \mu\text{m}$, surface area = $1.5\ \text{m}^2/\text{g}$, Schott, Mainz, Germany) and colloidal silica filler (pyrogenic silica nanofiller, average particle diameter = $40\ \text{nm}$, surface area = $50\ \text{m}^2/\text{g}$, Degussa, Essen, Germany) were used as received. The inorganic fillers were treated with γ -methacryloxypropyltrimethoxy silane (γ -MPS, Aldrich, St. Louis, MO) before use.

Preparation of Poly(maleic anhydride-*co*-styrene)-*block*-Poly(styrene-*co*-4-vinyl pyridine) (MSP)

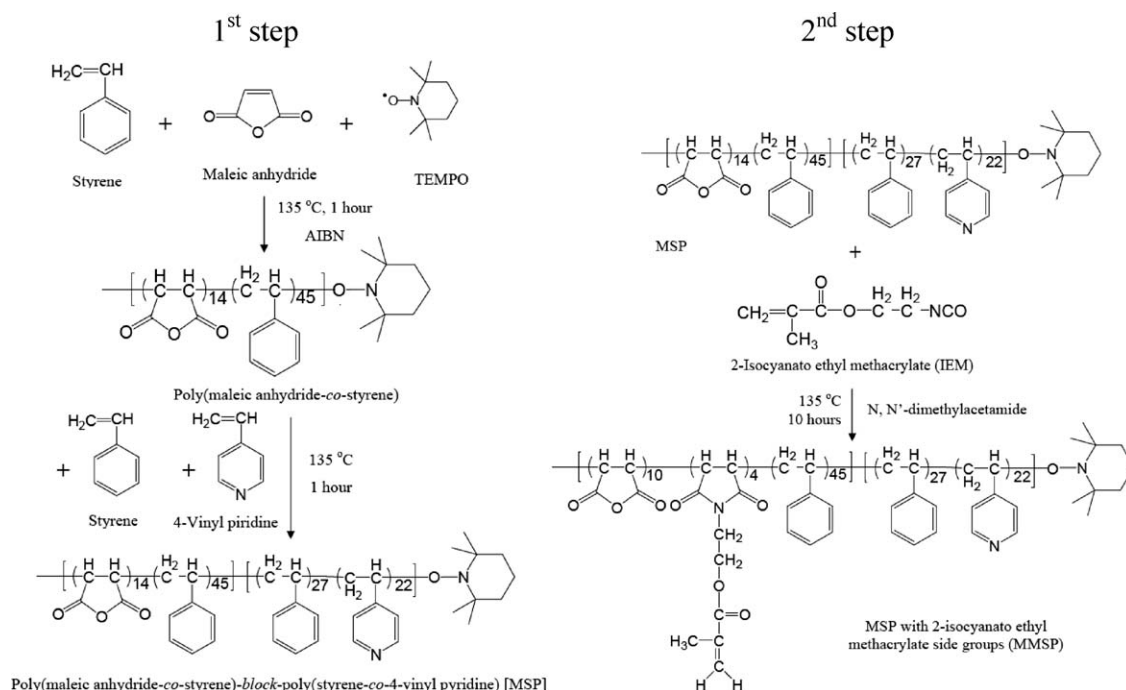
In a typical run, a mixture of MAN (14 g, 0.045 mol), AIBN (260 mg, 1.6 mmol), and TEMPO (630 mg, 3.8 mmol) was first charged in a dry Schlenk flask. The flask was sealed with a rubber septum, degassed and back-filled with nitrogen, followed by introduction of St (50 mL, 0.48 mol) and anisol (10% v/v of St) ($[\text{St}]:[\text{MAN}]:[\text{AIBN}]:[\text{TEMPO}] = 300 : 28 : 1 : 2.4$). The solution was stirred until the solids were completely dissolved. Three freeze-pump-thaw cycles were then performed, and the flask was refilled with nitrogen. An initial sample was collected and the reactor was immersed in an oil bath that was preset to a specific reaction temperature (135°C). Samples were taken out from the flask via syringe at timed intervals to allow kinetic data to be determined. Samples were diluted with tetrahydrofuran (THF) for analyses, such as gas chromatography (GC) and gel permeation chromatography (GPC). After 1 h, degassed 4VP (16.5 mL, 0.15 mol) was then injected ($[\text{St}]:[\text{MAN}]:[\text{4VP}]:[\text{AIBN}]:[\text{TEMPO}] = 300 : 28 : 100 : 1 : 2.4$). The reaction was continued for additional 1 h. After a certain polymerization time, the reactor was removed from the oil bath and cooled to room temperature. The viscous solution was diluted with THF and the polymer was recovered through the precipitation under hexane, followed by drying under vacuum at 60°C for 12 h ($M_n = 11,100\ \text{g/mol}$, $M_w/M_n = 1.60$).

Preparation of Poly(maleic anhydride-*co*-styrene)-*block*-Poly(styrene-*co*-4-vinyl pyridine) Anchored with 2-Isocyanato Ethyl Methacrylate (MMSP)

MSP (2 g, 2.5 mmol of MAN), *N,N*-dimethylacetamide (30 mL), and IEM (0.4 mL, 2.5 mmol) were placed in a 50 mL round bottom flask under nitrogen. The reactor was immersed in an oil bath that was preset to a specific reaction temperature (135°C). After the reaction time of 15 h, the reactor was removed from the oil bath and cooled to room temperature. The mixture was further diluted with THF and the polymers were recovered by precipitation under hexane followed by washing with fresh hexane and drying under vacuum at 60°C for 12 h.

Modification of Na^+ -MMT with IEM Functionalized Poly(maleic anhydride-*co*-styrene)-*block*-Poly(styrene-*co*-4-vinyl pyridine) (MMSP-MMT)

A typical procedure to modify MMT follows: MMSP (5 g) was completely dissolved in 45 mL of dimethylformamide (DMF) followed by the injection of HBr (0.5 mL, 11 mmol). The dispersion of Na^+ -MMT (2.91 g in 15.1 mL of distilled water) was then added slowly to the solution. The mixture was stirred vigorously at 70°C for 15 h with gradual addition of DMF. A white precipitate was then collected through centrifugation. The product was washed intensively with deionized water for several times. The product was collected through freeze-drying for 48



Scheme 1. Schematic representation for the preparation of polymeric surface modifier for MMT: 1st step, preparation of poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) (MSP); 2nd step, MSP with 2-isocyanato ethyl methacrylate side groups (MMSP).

h, affording MMSP-MMT. MSP-MMT was also prepared following similar procedures using MSP instead of MMSP.

Preparation of Composite Resin Containing Modified MMT

Experimental composite resins included 75 wt % of inorganic fillers, which consisted of 70 wt % silane-treated Ba-glass microfiller and 5 wt % pyrogenic silica nanofiller. Resin matrix was composed of 70 wt % of bis-GMA and 30 wt % of TEGDMA along with 0.5 wt % of photoinitiator (CQ) and 1.0 wt % of photoactivator (DMA-EMA). The composites mixtures with modified MMTs were produced through kneading of monomer matrix, filler and modified MMTs (MSP-MMT and MMSP-MMT) in appropriate proportions.

Characterization

Molecular weight and molecular weight distribution of polymer modifiers were determined by Shimadzu LC-20A GPC using PSS columns (styrogel HR 2, 4, 5) equipped with a Shimadzu LC-20AD solvent delivery unit and a Shimadzu RID-10A refractive index detector. THF was used as an eluent at the flow rate 1 mL/min. Linear polystyrene standards (641 g/mol~ 1.35×10^6 g/mol) were used for calibration. Conversion of monomer to polymer was determined using a Shimadzu GC 2010AF gas chromatograph equipped with a FID detector using a ValcoBond VB-wax 30 m column and anisole as an internal standard. The polymer modifiers were characterized by using Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet 380) and proton nuclear magnetic resonance measurement ($^1\text{H-NMR}$, 500 MHz Bruker Avance). For FTIR analysis, samples were dissolved in THF and then dropped on a KBr window, followed by drying under vacuum for 12 h. The spacing between MMT layers were determined by X-ray diffractometer (XRD, Rigaku) with Cu source ($\lambda = 0.154$ nm) through 2θ of 2 to 10° at a scan speed of $1^\circ/\text{min}$.

Thermogravimetric analysis (TGA) was performed to determine the composition of MMTs by using a TGA/SDTA 851 (Mettler Toledo) under nitrogen at a scanning rate of $10^\circ\text{C}/\text{min}$ from room temperature to 600°C . Morphologies of the nanocomposites were observed by using transmission electron microscope (TEM, CM200, Philips). The samples for TEM analyses were prepared by using an ultra-microtome (DMU3, Reichert, Australia) to afford specimens having the thickness of ~ 70 nm. The cytotoxicity of MMSP was also tested according to ISO10993.⁹ Compressive strengths of PDRC resins were determined following a standard method described in ISO 9917.^{10,11} Flexural strengths of composite resins were investigated following a test method described in ISO standard 4049 for polymer based filling restorative materials.^{12,13} Level of polymerization shrinkages were obtained by axial shrinkage method described in literatures.^{14,15} Measured mechanical values of five specimens were averaged and compared by using one-way ANOVA test and Tukey's multicomparison test at the significance level of 0.05.

RESULTS AND DISCUSSION

Schematic representation for the chemical procedures of block copolymer preparation is provided in Scheme 1. First, a convenient one-pot production of functionalized copolymer was conducted to afford poly(maleic anhydride-*co*-styrene) end-capped with 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (Scheme 1, first step). Maleic anhydride (MAN) tends to form charge transfer complex with styrene (St), leading to a copolymerization having alternating characteristics. In controlled/"living" radical polymerization, this alternating nature of copolymerization between MAN and St led to a preferential consumption of MAN at the beginning of the polymerization, forming MAN functionalized polystyrene block.^{16,17} In our experiment, MAN

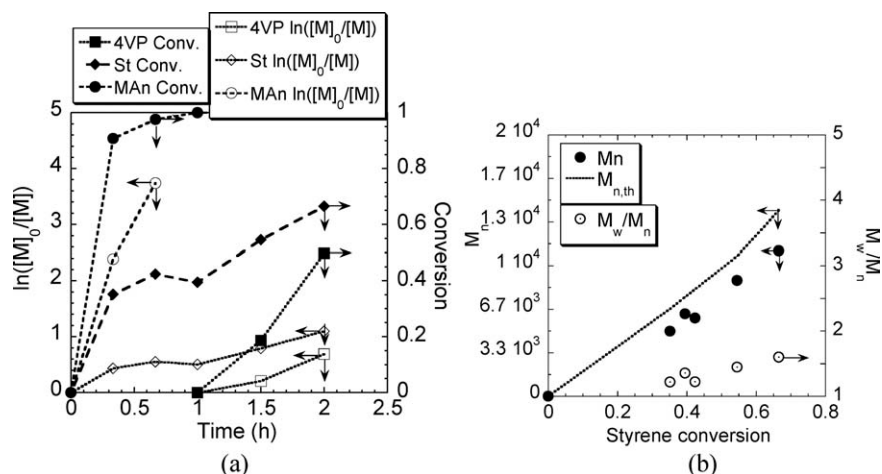


Figure 2. Kinetic plots (a) and evolution of M_n and M_w/M_n versus conversion of Styrene (b) for the copolymerization of styrene (St) with maleic anhydride (MAN) and 4-vinyl pyridine (4VP) at 135°C: Polymerization condition, [St]:[MAN]:[4VP]:[AIBN]:[TEMPO] = 300 : 28 : 100 : 1 : 2.4; for (a), conversion of MAN (○, ●), conversion of St (◇, ◆), conversion of 4VP (□, ■).

completely incorporated into polymer at the polymerization time of 40 min, where the conversion of St was 40% [Figure 2(a)]. Theoretically, this first block contained ~ 14 units of MAN, assuming that the initiation efficiency of AIBN was 1. The mole ratio of MAN to St in the first copolymer block calculated from the monomer conversions was ~ 1 to 3, indicating ~ 45 units of St in the first block. After MAN was completely consumed, 0.15 mol of 4VP monomer was added to the reactor, which led to a copolymerization between the remaining St and 4VP, forming poly(4-vinyl pyridine-*co*-styrene) second block (Scheme 1, first step). The conversion of 4-vinyl pyridine (4VP) between the polymerization times of 1 to 2 h was 50% [Figure 2(a)], indicating that the second block contained ~ 25 units of 4VP as summarized in Table I. Figure 2(b) represents the evolution of number-average molecular weight (M_n) and polydispersity indices (M_w/M_n) with St conversion. Relatively good agreements between theoretical and experimental molecular weights and a continuous increase of molecular weight with conversion clearly represented a successful formation of the block copolymers through controlled/"living" radical polymerization.

Structural characteristics of the block copolymer were determined by $^1\text{H-NMR}$ and FTIR spectroscopy. $^1\text{H-NMR}$ spectrum

Table I. Conversion of Monomers and the Composition of Poly(maleic anhydride-*co*-styrene)-*block*-Poly(styrene-*co*-4-vinyl pyridine) (MSP) Calculated from Various Methods^a

	Conversion (%) ^a	Composition		
		By GC number of units/chain	Mol fraction (%)	Number of units/chain
St	67	100	67	72
4VP	50	25	20	22
MA	100	14	13	14

^a Overall polymerization time was 2 h.

showed typical aromatic peaks originated from St and 4VP units around 6.3–8.5 ppm [Figure 3(a)]. Aliphatic proton peaks were also observed around 1.0–2.3 ppm, indicating successful formation of the block copolymers. Broad peaks around 3.0–4.0 ppm represented protons originated from MAN. The number of MAN in each polymer chain was calculated to be ~ 14 , which

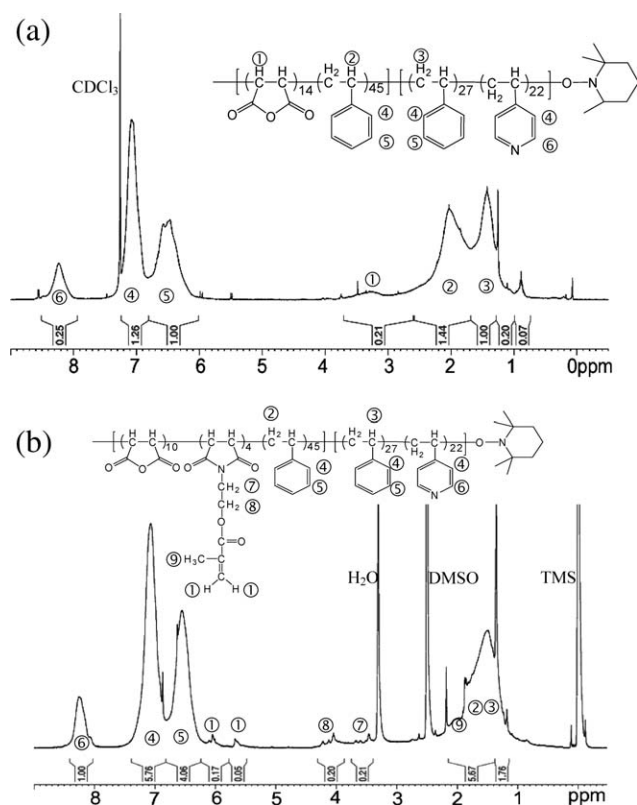


Figure 3. Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra of poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) (MSP, a) and MSP with 2-isocyanato ethyl methacrylate side groups (MMSP, b).

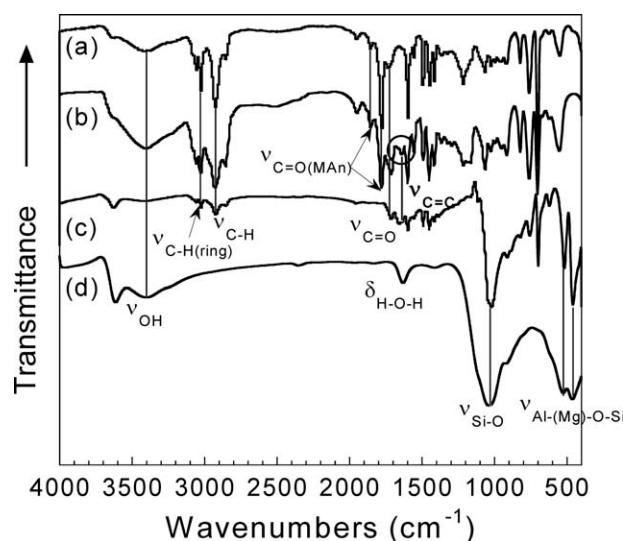


Figure 4. Fourier transform infrared (FTIR) spectra of poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) (MSP, a) and poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) with 2-isocyanato ethyl methacrylate pendant units (MMSP, b), MMT with polymeric surface modifier (MMSP-MMT, c), pristine MMT (Na^+ -MMT, d).

agreed well with that from the recipe. Monomer conversion and the composition of the copolymer were determined by GC and $^1\text{H-NMR}$, and were summarized in Table I.

Further characterization of the block copolymer was performed by FTIR [Figure 4(a)]. Aliphatic and aromatic C—H stretching vibration, methylene stretching vibrations and C=C ring stretching vibrations peaks in FTIR spectrum were observed around 700 cm^{-1} , 3050 cm^{-1} , $2930\text{--}2850\text{ cm}^{-1}$, and $1600\text{--}1560\text{ cm}^{-1}$, respectively. Those peaks further confirmed successful preparation of the copolymers. FTIR spectra of poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) (MSP) also exhibited double carbonyl peaks, one at 1780 cm^{-1} and the other at 1860 cm^{-1} representing asymmetric and symmetric carbonyl coupled stretching motion of anhydride group.¹⁸ Although carbonyl peaks around 1730 cm^{-1} was also observed indicating partial hydrolysis of anhydride to carboxylic acid, we believed that the carboxylic acid groups are not to afford a harm on the reaction with IEM, because IEM could still react with carboxylic acid.^{19,20} Broad O—H stretching peaks around 3500 cm^{-1} probably originated from this carboxylic acid units or absorbed water due to the presence of polar 4VP units.

Anhydride units in MSP were reacted with isocyanate in IEM to give imide linkage possibly through a seven membered polycycle intermediate with separation of carbon dioxide²¹ (Scheme 1, 2nd step). Because unreacted IEM was carefully washed out during the precipitation process under hexane, the signals appear at $\delta = 3.5\text{--}4.5$ and $5.5\text{--}6.2$ in $^1\text{H-NMR}$ spectrum [Figure 3(b)] belonged to protons in IEM units, confirming successful attachment of IEM onto block copolymer to afford crosslinkable block copolymer. From the calculation based on the peak areas in $^1\text{H-NMR}$ spectrum [Figure 3(b)], the number

of IEM units in each poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) chains was determined to be ~ 4 . In addition, the presence of the shoulder at 1640 cm^{-1} on FTIR [peak in circle, Figure 4(b)] which was ascribed to C=C double bond of IEM provided additional evidence for the successful preparation of poly(maleic anhydride-*co*-styrene)-*block*-poly(styrene-*co*-4-vinyl pyridine) anchored with 2-isocyanato ethyl methacrylate (MMSP).

The polymeric surface modifier (MMSP) was incorporated to MMT layers through solution process, where both high solubility of polymer and good dispersion of MMT are important. Swelling of MMT layers with water is probably an indispensable step to ascertain successful cation exchange.²² Therefore, solvent for the polymeric surface modifier should also exhibit high miscibility with water. In this study, solvent system consisted of water for swelling of MMT and DMF for dissolving the polymeric surface modifier. MMSP contains 4VP units, which permits facile formation of the onium salt in the presence of HBr. With the evolution of NaBr, the onium salt underwent cationic exchange reaction with Na^+ -MMT to afford MMT intercalated with MMSP.

After washing and drying steps, the modified MMT was subjected to FTIR analysis. Beside the typical stretching vibration peaks of pristine MMT [Figure 4(d)], stretching vibration peaks from MMSP in the modified MMT were also observed [Figure 4(c)]. Distinct IR bands associated with the symmetric and asymmetric stretching of C—H bands appeared at 2850 and 2920 cm^{-1} . Aromatic C—H bands appeared at 3020 and 3060 cm^{-1} . Interestingly, disappearance of carbonyl peak of MAN

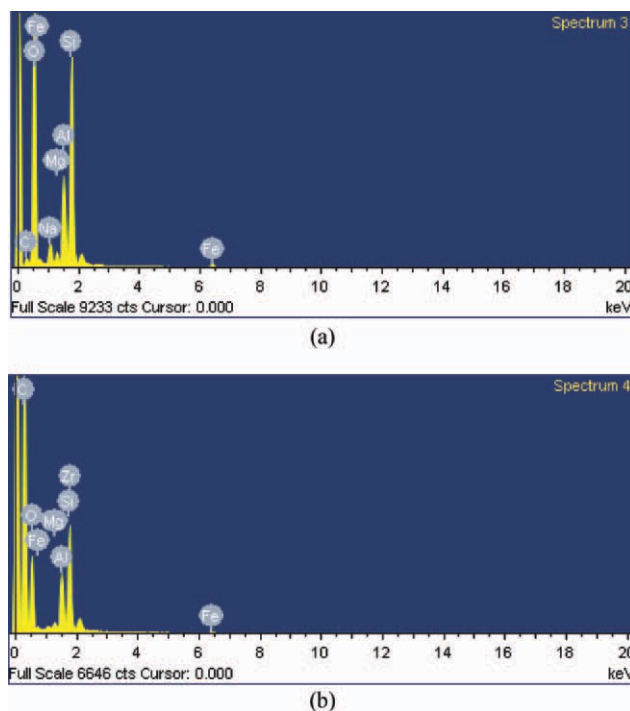


Figure 5. EDS spectrum of pristine MMT (Na^+ -MMT, a) and modified MMT (MMSP-MMT, b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Modification of Montmorillonite (MMT) with 2-Isocyanato Ethyl Methacrylate Functionalized Poly(maleic anhydride-*co*-styrene)-*block*-Poly(styrene-*co*-4-vinyl pyridine) (MMSP) and the Analytical Results of the Modified MMTs

Sample designation	Total amount of DMF added (mL)	MMSP concentration in recipe (mol/L)	Washing solvents	2θ ($^{\circ}$)	<i>d</i> -spacing (nm)	Amount of MMSP in MMSP-MMT (%) ^a
Na ⁺ -MMT	–	–	–	7.5	1.18	–
MMSP-MMT1	900	4.79×10^{-4}	DMF-W ^b	5.8	1.52	24
MMSP-MMT2	900	4.79×10^{-4}	W-W	5.8	1.52	31
MMSP-MMT3	60	5.84×10^{-3}	W-W	4.8	1.84	63

^a The amount of MMSP in the intercalation recipe was 63%, ^b W indicates deionized water.

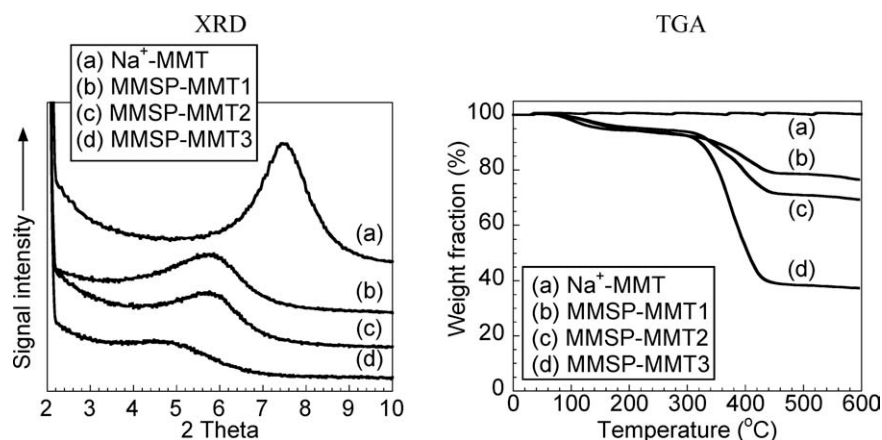
units was also observed on the spectra, suggesting that MAN may be hydrolyzed during the intercalation process and/or may interact with MMT layers as a compatibilizer.²³ C=C peak appeared at 1640 cm^{-1} as a shoulder confirmed the presence of the crosslinkable polymeric modifier in the modified MMT. Narrower in-plane vibration of Si–O bonding at 1046 cm^{-1} for the modified MMT indicated the delamination of silicate layers as observed by Ijdo et al.²⁴ Successful modification of MMT layers with the polymeric surface modifier was further confirmed by the disappearance of sodium atom along with the increase of carbon atom content from EDS spectrum (Figure 5).

Recent studies have revealed the effect of polymer-solvent, clay-solvent interactions on the intercalation procedures.²⁵ In our study, not only the amount of DMF used in intercalation process, but also solvent combinations used in washing steps were found to affect the degree of intercalation and composition of resulting MMT. The solvent combinations and the analytic results of the modified MMTs are summarized in Table II. The interlayer distance was used to measure the degree of intercalation of MMT layers. The interlayer distances were determined through XRD by calculations based on the Bragg equation $2d\sin\theta = n\lambda$, where n is the progression of diffraction. The compositions were determined by TGA [Figure 6(b)]. The weight loss around $100\text{--}180^{\circ}\text{C}$ in TGA curves probably originated from the evolution of remaining solvents such as DMF and water.

Na⁺-MMT exhibited 2θ of 7.5° , which corresponded to *d*-spacing of 1.18 nm. As MMT was modified with MMSP (MMSP-MMTs), the 2θ value shifted toward a lower 2θ region and the XRD intensities decreased (Figure 6). Lower 2θ values indicated effective modification of MMT and intercalation of MMSP chains into MMT layers. Weaker intensities of XRD peaks of MMSP-MMTs were probably originated from lowered content and exfoliation of MMT.²⁶

When DMF was used as a solvent in washing step (MMSP-MMT1 in Table II), the amount of MMSP in the modified MMT was 24%, which is significantly lower value than that in recipe, 63%. The lower content of MMSP indicated that unreacted MMSP, which is well soluble in DMF, was removed during the washing step. The replacement of DMF with deionized water in washing steps, which is a nonsolvent for MMSP, still afforded MMSP-MMT having similar *d*-spacing and composition (MMSP-MMT2 in Table II). This result suggested that deionized water still effectively removed free MMSP.

To increase the efficiency of intercalation, the concentration of MMSP in intercalation recipe increased 12 times as shown in MMSP-MMT3 in Table II. For MMSP-MMT3, the amount of MMSP in the modified MMT was almost identical to that in recipe, indicating that MMSP was almost completely intercalated into MMT layers resulting in the increased *d*-spacing of 1.52 to 1.84 nm.

**Figure 6.** X-ray diffractometer (XRD) patterns and thermogravimetric analyses (TGA) of polymer-layered silicate nanocomposites: Na⁺-MMT (a), MMSP-MMT 1 (b), MMSP-MMT 2 (c), and MMSP-MMT3 (d).

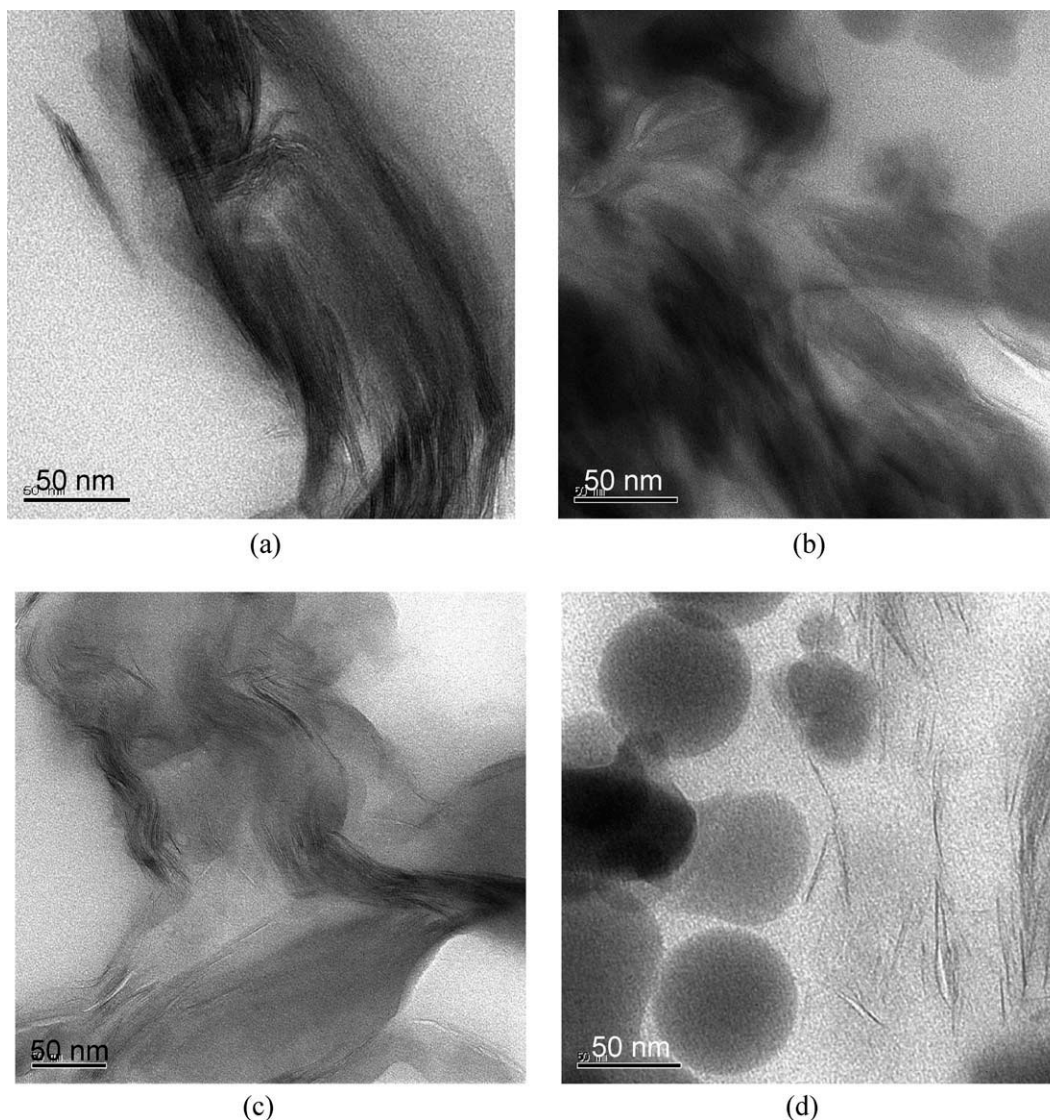


Figure 7. Transmission electron microscope (TEM) images of MMSP-MMT in polymeric dental restorative composite (PDRC): Na⁺-MMT in PDRC (a); Na⁺-MMT with fused silica in PDRC (b); MMSP-MMT2 in PDRC (c); MMSP-MMT2 with fused silica in PDRC (d). Scale bar 50 nm.

A “dimethacrylate crosslinker” by condensation of IEM with anhydride functionality was also reported previously.²⁷ IEM-based crosslinker have better wetting and mixing potential for adhesive and substrate and thus is more favorable for bonding. Different from the sedimentation of PDRC during mixing with Na⁺-MMT, no sedimentation was observed when PDRC was mixed with the modified MMT (with and without IEM). These behaviors suggested that the polymeric modifier turns the surface property of pristine MMT layers to more hydrophobic and chemically favorable to PDRC monomers. The modified surface property prevented the aggregation of PDRC and improved the dispersion stability of the MMTs. Our sedimentation observation is also consistent with the previous study of Atai.⁸ The degree of intercalation of nanoclay in PDRC system was also evaluated through TEM images. PDRC with modified MMT [MMSP-MMT2, Figure 7(c, d)] obviously exhibited intercalated or exfoliated features in comparison with stacked Na⁺-MMT [Figure 7(a, b)].

Because PDRC can inadvertently extrude and contact with soft and hard tissue and cause irritating, the biocompatibility or the toxicity is an important factor. In this study, the cytotoxicity of three different PDRC was examined according to The International Organization for Standardization, ISO 10993 (2009).⁹ The score and interpretation of the cytotoxic results was also interpreted based on ISO 10993-5:2009 (Table III). These results exhibited that significant difference between positive control group and MMSP-MMT sample, but no difference between the negative one and MMSP-MMT sample, indicating that the surface modified MMT (MMSP-MMT) nanofiller can be classified as a noncytotoxic material.

The effect of MMSP-MMT nanofillers on the properties of PDRCs was evaluated through several parameters such as polymerization shrinkage, compressive strength and flexural strength (Figure 8). For comparison, those of neat PDRC and PDRC with MSP-MMT were also tested. From the results from PDRC

Table III. Cytotoxicity Test of MMSP-MMT

Temp. (°C)	Time (h)	Negative control		Positive control		Test specimen			RI ^a	Interpretation
		Zone index	Lysis index	Zone index	Lysis index	Zone index	Lysis index			
37	72	0	0	3	5	0	0	0	0	Nontoxic
50	72	0	0	2	5	0	0	0	0	Nontoxic

^a Response index (RI) = zone index/lysis index.

with MMSP-MMT3 and MSP-MMT, the effect of the crosslinkable units (IEM) could be evaluated.

Polymerization shrinkages results of PDRCs in the presence of 0.1, 0.2, and 0.3 wt % of MMSP-MMT3 were 2.76 vol %, 2.73 vol %, and 2.69 vol %, respectively [Figure 8(a)]. The values were lower than that of neat PDRC, 2.91 vol % and decreased as the content of MMSP-MMT3 increased. The one-way ANOVA on the effect of the modified MMT indicated a significant difference ($P < 0.05$) on the polymerization shrinkage properties. These low polymerization shrinkage properties of PDRC in the presence of MMSP-MMT represent advantages of the system, because it can prevent secondary dental caries originated from inferior dimensional stability. The low polymerization shrinkages of PDRC/MMSP-MMT are obviously owing to the exfoliated and crosslinked nano-platelet of MMSP-MMT in matrix. In fact, PDRC with MSP-MMT, which was in lack of cross-linkable units (IEM), exhibited polymerization shrinkage properties superior to that of neat PDRC, but inferior to those of PDRC/MMSP-MMT. These results clearly demonstrated beneficial effect of IEM. FTIR spectroscopy was used to monitor the conversion of double bond with the content of MMT in PDRCs.²⁸ No significant difference was found between degree-of-conversions of the composites containing different amount of MMT (one-way ANOVA, $P > 0.05$). Because the degree-of-conversion was not affected by the amount of MMT in the PDRC, the differences of polymerization shrinkage was probably mainly caused by the presence of the modified MMT fillers.

Compressive strength properties of PDRC, PDRC/MMSP-MMT3, and PDRC/MSP-MMT are also shown in Figure 8(b). The values of PDRC/MMSP-MMT3 were significantly higher than that of PDRC and PDRC/MSP-MMT, which increased

with higher loading of MMSP-MMT3. The values of PDRC/MMSP-MMT were also higher than that of PDRC. Figure 8(c) also exhibit improved flexural strengths of PDRC/MMSP-MMT3 compared to that of neat PDRC and PDRC/MSP-MMT. The one-way ANOVA on the effect of the modified MMT indicated a significant difference ($P < 0.05$) on the compressive strength and flexural strength properties. These results clearly demonstrate beneficial effect of not only MMT but also IEM, affording superior properties as a PDRC.

CONCLUSION

MMT was incorporated into 2,2-bis[4-(2-hydroxy-3-methacryloyl-oxy)phenyl]propane (bis-GMA)-based resin matrix as nanofiller to improve dimensional and mechanical properties of the composite. A well-defined bifunctional block copolymer (2-isocyanato ethyl methacrylate functionalized poly(maleic anhydride-co-styrene)-*block*-poly(styrene-co-4-vinyl pyridine), MMSP) was prepared as a novel block polymeric surface modifier for MMT through nitroxide mediated polymerization technique. MMT was effectively modified with MMSP as evidenced by low 2θ values (as low as 4.8°), high interplatelet spacing (as high as 1.84 nm) and low intensities in XRD analyses. The content of MMSP in the modified MMT was as high as 63%, also suggesting successful modification of MMT with MMSP. Intercalated or even exfoliated features of MMT with increased interplatelet distances in the composite were also visually confirmed through transmission electron microscope (TEM) observations. Polymerization shrinkages of the composite decreased as the content of MMSP-MMT increased, which represent advantages of the system. Compressive and flexural strengths of PDRC were also significantly improved in the presence of MMSP-

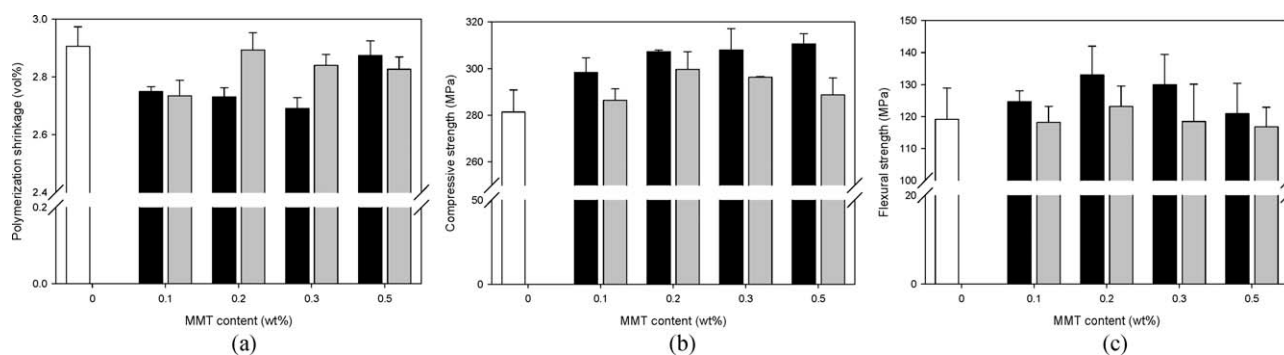


Figure 8. Polymerization shrinkages (a), compressive strengths (b), and flexural strengths (c) of polymeric dental restorative composite (PDRC) with different amount of MSP-MMT and MMSP-MMT3: White bar, neat PDRC; black bar, PDRC with MMSP-MMT3; gray bar, PDRC with MSP-MMT.

MMT, demonstrating beneficial effect of MMT and IEM in the composite.

ACKNOWLEDGMENTS

This work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials (10037176) funded by the Ministry of Knowledge Economy, Republic of Korea. This study was also supported by Technology Development Program for Materials & Components, Ministry of Knowledge Economy (grant number: 0701DG10271), Republic of Korea.

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