Effects of Various Additives on the Performance of Bis-GMA/Barium Glass Powder Composites

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ABSTRACT: The effects of various additives on the performance of 2,2′-bis[4-(methacryloxy-2-hydroxy-propoxy)-phenyl]-propane (Bis-GMA)/barium glass powder (Ba) composites were examined. Bis-GMA/Ba composites were manufactured by curing with visible light to measure various mechanical properties. The diametral tensile strengths (DTS) of Bis-GMA/Ba composites were the primary focus of this investigation. The main additives used were trimethylolpropyltrimethacrylate (TMPT), 1,4-bis-(tri-methoxysilylethyl) benzene (BTB), and cationic styryl silane. These additives were applied as both integral blends and aqueous pretreatments. Besides the DTS, Vickers hardness of cured matrix resins and the viscosity of composite pastes were measured to study the properties of the matrix resins and the processibility of the composites, respectively. Integral blends showed similar processibility to aqueous pretreatments. The addition of TMPT to the matrix resins increased Vickers hardness of integral blend systems as a result of its trimethacrylate functional group. BTB was useful in increasing the wet DTS of Bis-GMA/silane–treated Ba composites. STS was effective in improving the performance of Bis-GMA/Ba composites in the cases of both the integral blends and aqueous pretreatments. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1085–1092, 2000

Key words: Bis-GMA/Ba composites; diametral tensile strength (DTS); integral blends; aqueous pretreatments; additives

INTRODUCTION

Dental restorative composites have been successfully used in various fields of dental materials.[1–3] They commonly consist of dimethacrylate functional resins and inorganic fillers. The resin widely usedis2,2′-bis[4-(methacryloxy-2-hydroxy-propoxy)-phenyl]-propane (Bis-GMA) and barium glass powder is used as the main inorganic filler. Because of Bis-GMA's high viscosity and filler loading, it used to be blended with low viscous diluents [e.g., triethyleneglycoldimethacrylate (TEGDMA)]. Such diluents may play an important role in the processibility and mechanical properties of Bis-GMA/Ba

composites. In addition, silane-coupling agents have been applied to improve the interfacial strength between matrix and filler, and to lower the viscosity of the composite pastes. Therefore, various diluents and silane-coupling agents have been employed to promote the mechanical properties and processibility of Bis-GMA/Ba composites.[4,5]

The ways to apply the silane coupling agents on the inorganic surface can be divided into three categories: aqueous pretreatments, nonaqueous blends, and integral blends.[6] In the case of aqueous pretreatments, fillers are pretreated with prehydrolyzed silane coupling agents before mixing with matrix. On the other hand, integral blends have an advantage that the processing procedure can be simplified using neat fillers, that is, separate hydrolysis of silane-coupling agents and drying procedure are not required. Silane-coupling

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Table I   Chemicals Used in This Study and Their Experimental Codes

Name	Experimental Code
2,2′-bis[4-(Methacryloxy-2-hydroxy-propoxy)-phenyl]-propane (Bis-GMA)	B
Triethyleneglycoldimethacrylate (TEGDMA)	T
γ-Methacryloxypropyltrimethoxy silane (MPS)	M
N-[2-(Vinylbenzylamino)-ethyl]-3-aminopropyl-trimethoxysilane (cationic styryl silane, STS)	S
N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AAPS)	A
Trimethylolpropyltrimethacrylate (TMPT)	TT
1,4-bis-(tri-Methoxysilylethyl)benzene (BTB)	BB

agents are blended with matrix as additives. In this case, the composition of matrix resins and the types of silane-coupling agents mutually affect the various properties of composites.

As an extreme case, Venhoven and associates[7] used the silane-coupling agents, not only as couplers between matrix and filler, but also as diluents. γ-Methacryloyloxy propyl trimethoxy silane (MPS), the representative silane-coupling agent for this system, was used as a kind of integral blend instead of TEGDMA. However, the mechanical properties of integral blends were inferior to those of aqueous pretreatments. Insufficient crosslinking resulting from monomethacrylate functional group and incomplete hydrolysis of MPS might be the reasons for the poor mechanical properties. Therefore, if MPS is used instead of diluents, the increment of crosslinking of methacrylate or hydroxyl groups is required to improve the mechanical properties of integral blend systems. It can be achieved using various additives (e.g., amino silanes), trimethacrylate functional diluents, and hexamethoxy silanes. Amino groups in amino silanes are known to be catalysts for the condensation reaction of hydroxyl groups.[6] Trimethacrylate functional diluents increase the crosslinking of matrix through the reaction of methacrylate groups, and hexamethoxy silanes through the reaction of hydroxyl groups. These additives also affect the crosslinking of hydroxyl groups or carbon double bonds of MPS on the filler surface. A few studies have investigated such effects of these additives on the various properties of dental restorative composites, but information about these is very limited.[5,7]

In this study, integral blends and aqueous pretreatments were simultaneously applied and compared, to investigate the function of the additives in Bis-GMA/Ba composite systems. In the case of integral blends, various additives were used as diluents instead of TEGDMA. The effects of these diluents, including MPS, on the performance of Bis-GMA/Ba composites were studied in this investigation. In aqueous pretreatments, they were applied on the filler surface as mixed systems with MPS. Tensile strength is closely related to the mechanical properties of matrix resins and the interfacial properties of composites.[8,9] Therefore, it is adopted as a main characteristic property in this research. The processibility of Bis-GMA/Ba composites was investigated by examining the viscosity of composite pastes. Hardness of matrix was also measured to study the effect of the additives on the mechanical properties of matrix resins. Consequently, the main purpose of the present work is to investigate the effects of various additives on the performance of Bis-GMA/Ba composites.

EXPERIMENTAL

Materials

Bis-GMA was used as a matrix resin and TEGDMA as a diluent. The matrix resins were supplied from Shin-Nakamura Chemical Company (Japan). The matrix resins were cured, using the visible light curing system, containing camphorquinone as a photosensitizer and dimethylaminoethylmethacrylate as an amine-reducing agent. The filler used was barium glass powder (Ba, H-MAF1) supplied from Hansol Corporation (Korea). All chemicals used in this study are presented and coded in Table I. The molecular structures of MPS and the main additives are illustrated in Figure 1. MPS is the main silane-coupling agent used for filler surface treatment. BTB has hexamethoxy groups, which impart crosslink-
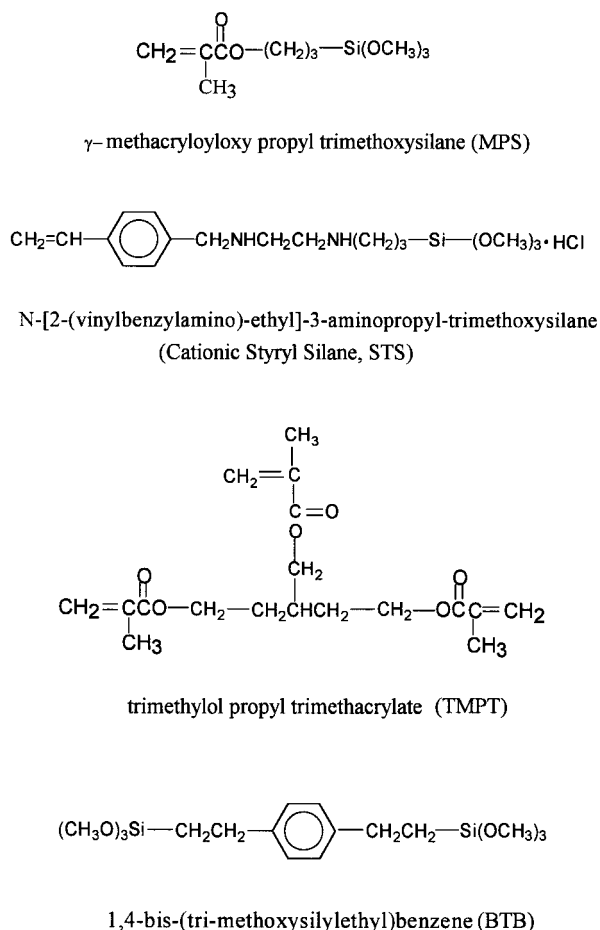
γ– methacryloyloxy propyl trimethoxysilane (MPS)

N-[2-(vinylbenzylamino)-ethyl]-3-aminopropyl-trimethoxysilane
(Cationic Styryl Silane, STS)

trimethylol propyl trimethacrylate (TMPT)

1,4-bis-(tri-methoxysilylethyl)benzene (BTB)

Figure 1   Molecular structures of MPS and main additives.

ing ability. Cationic styryl silane (STS) is one of the amino-functional silanes. All silanes were supplied from Korea Dow Corning Chemical Company (Korea). TMPT (SR350, Sartomer) was used as a trimethacrylate diluent.

Sample Preparation

The aqueous pretreatments were performed by the following procedure. The filler surface was treated with aqueous solution of silanes or the mixture of silanes and additives. Silanes were prehydrolyzed in aqueous solution of 70 wt % ethanol/30 wt % deionized water (pH = 3.5) for 1 h. Concentration of silane solution was fixed to 5 wt % based on Ba. Fillers were mixed with hydrolyzed silane solution, and then dried for over 20 days in hood at room temperature. Aqueous-pretreated or untreated fillers were used, and their content was fixed to 75 wt %. Bis-GMA and various diluents or additives were mixed to make

the matrix resin. The additives in Table I were used as diluents to perform the integral blending. In the case of silane-coupling agents, unhydrolyzed ones were mixed with matrix resins. The weight ratio of Bis-GMA and diluents in matrix resins was fixed to 60/40 (w/w), which is commonly used in commercial dental composites. Fillers and matrix resins were thoroughly mixed with mortar to fabricate composite pastes, and then cured in a Teflon-coated metal mold by visible light system to fabricate dental restorative composites. Both sides of the samples were cured for 40 s with a visible light–curing unit, the 3M Company's XL-1000 (energy output, 530 mW/cm^2). It had a visible light range of 400 to 500 nm and a maximum peak near 470 nm wavelength (blue light).

Measurements

Because of easy evaluation and small specimen size, diametral tensile strength (DTS) has been used primarily to measure the tensile strength of dental composites.[10–12] DTS was measured according to the American Dental Association's Specification No. 27: compressive loading on cylinder type specimen (6 × 3 mm) using a universal testing machine at 1 cm/min crosshead speed.[13] DTS was calculated as

$$\text{DTS} = \frac{2P}{DT}$$

where P is load at fracture (N); D, diameter (m); and T, thickness (m).

The Instron 4202 universal testing machine was used in DTS measurements, at a load cell of 1000 kg. To test the wet DTS of Bis-GMA/Ba composites, samples were stored in boiling water for 1 day before testing. In this case, however, heat as well as water simultaneously affects the DTS. Therefore, before being stored in boiling water, samples for wet DTS test were stored at 100°C in a convection oven for 1 day to eliminate the effect of heat and leave only the effect of water. Samples for dry DTS test were also stored at 100°C in a convection oven for 1 day before testing, to be accurately compared with the wet DTS. Vickers hardness was adopted to study the properties of matrix resins. Testing the specification for Vickers hardness was followed by ASTM E384-89. An AVK-CO Vickers hardness tester was used (Akash Co., Japan), in which the load was 1 kg and contact time was 15 s. The viscosity
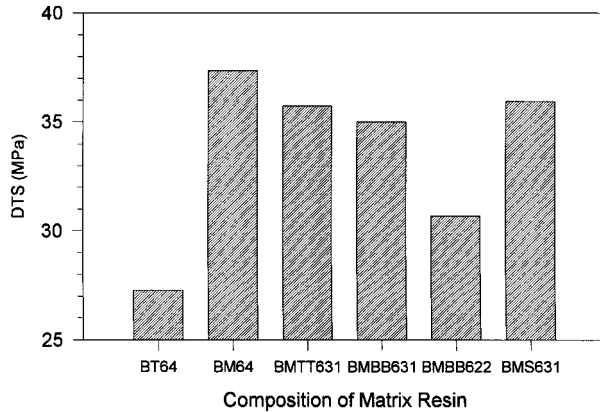
Figure 2 Dry diametral tensile strength of Bis-GMA/neat Ba composites.

of Bis-GMA/Ba composite pastes was measured to investigate the processibility of the Bis-GMA/Ba composites. A Rheometrics Mechanical Spectrometer (RMS-800, Rheometrics Corporation) was used to obtain the viscosity of composite pastes. All data were obtained in parallel-plate mode. The testing temperature was fixed to 30°C.

RESULTS AND DISCUSSION

Figure 2 represents the dry DTS of Bis-GMA/neat Ba composites. Experimental codes in this figure indicate the composition of matrix. For example, the matrix of BMTT631 is composed of 60 wt % of Bis-GMA, 30 wt % of MPS, and 10 wt % of TMPT. Dry DTS of BM64 is the highest but that of BT64 is the lowest. These results are attributed to MPS concentration in matrix. BM64 has 40 wt % of MPS in matrix but BT64 contains no MPS; that is, dry DTS of Bis-GMA/neat Ba composites increases with increasing MPS concentration in matrix. BMBB631, BMBB622, and BMTT631, in which other additives as well as MPS are included, show lower dry DTS than BM64. This means that MPS, having both methacrylate and methoxy groups, is an efficient coupling agent between Bis-GMA and neat Ba. However, BTB and TMPT, which have only one functional group such as a methoxy or methacrylate group, do not efficiently couple Bis-GMA and neat Ba. Consequently, MPS concentration in matrix is the most important factor contributing to the increase in the tensile strength of Bis-GMA/neat Ba composites.

This result can be confirmed by Figure 3, which shows a comparison of the dry DTS of integral blends with that of aqueous pretreatments. Dry DTS of integral blends (BM) increases with increasing MPS concentration, and approaches that of BT64a (aqueous-pretreated with MPS). Methoxy groups of silane-coupling agents can be sufficiently hydrolyzed to hydroxyl groups by the surface water of fillers.[6] MPS (especially those that are hydrolyzed) in matrix resins can increase the interfacial strength and filler dispersion of Bis-GMA/neat Ba composites, but reduce the mechanical properties of the matrix resins resulting from insufficient crosslinking and unreacted methoxy or hydroxyl groups. Therefore, Figure 3 indicates that the improvement of interfacial strength and filler dispersion, rather than the deterioration of matrix properties, by MPS predominantly affects the dry DTS of Bis-GMA/neat Ba composites. However, an excess increase of MPS concentration is practically undesirable, because MPS in matrix resin causes lower wet tensile strength and inferior hardness of matrix, discussed later.

Figure 4 shows the shear viscosity of Bis-GMA/Ba composite pastes. In this figure, the viscosity of BM64 and BMS631 (integral blends) is compared with that of BT64a (aqueous pretreatments). It can be expected that integral blends usually show higher viscosity than aqueous pretreatments and that their higher viscosity results in poor processibility. As expected, the viscosity of BM64, measured immediately after mixing of composite pastes, is higher than that of BT64a. However, the viscosity of BM64, measured 24 h after mixing, is lower than that of BM64 mea-
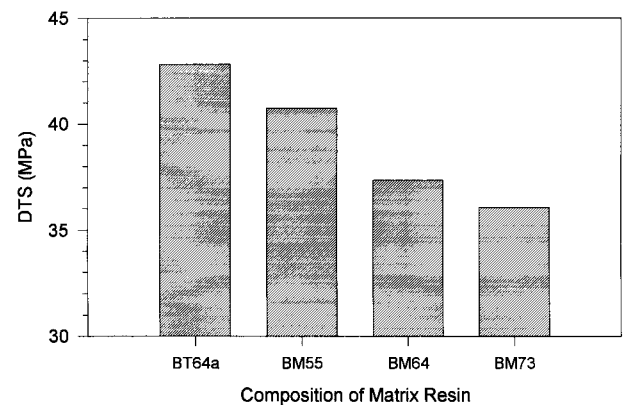

Figure 3 Comparison between dry diametral tensile strengths of integral blends and aqueous pretreatments (a, aqueous pretreatment).
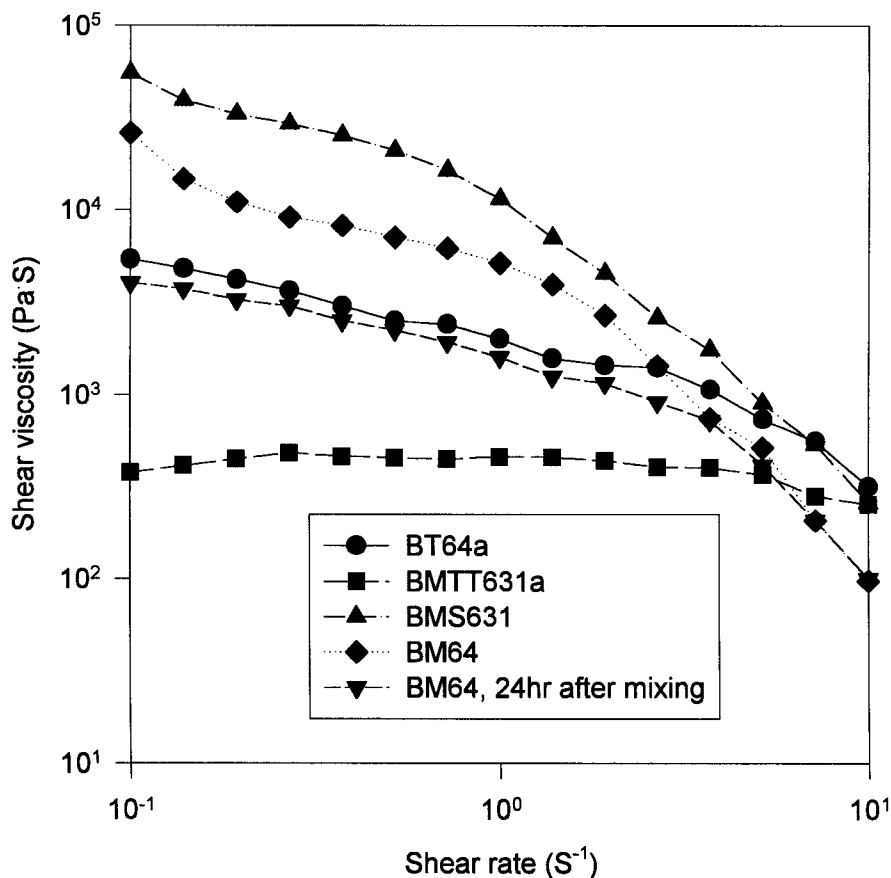
Figure 4   Shear viscosity of Bis-GMA/Ba composite pastes (a, aqueous pretreatment).

sured immediately after mixing, and even slightly lower than that of BT64a. It takes some time to sufficiently hydrolyze MPS at interface with the surface water of Ba. These hydrolyzed MPS seem to promote the dispersion of Ba in matrix through the physical interaction (e.g., hydrogen bonding) between hydroxyl groups of MPS and Ba.

Integral blends (BM64 and BMS631) show characteristic high-shear thinning; that is, they exhibit a higher viscosity dependence on shear rate than aqueous pretreatments (BT64a and BMTT631a). High-shear thinning also implies the incomplete dispersion of neat Ba in integral blends. Dispersion of neat Ba in matrix can be promoted by shearing the composite pastes at a high rate, as shown by the lower viscosity of BM64 and BMS631 at high-shear rates in Figure 4. Consequently, high shear of mixing is required to improve the dispersion of neat Ba in integral blends.

Figure 5 represents the dry DTS of Bis-GMA composites, in which silane-treated fillers are used. BMTT631 exhibits the highest DTS. This

result can be explained as follows. First, the tri-methacrylate functional group of TMPT in BMTT631 compensates, to some extent, for the insufficient crosslinking caused by the mono-methacrylate functional group of MPS. Figure 6 illustrates the Vickers hardness of various un-
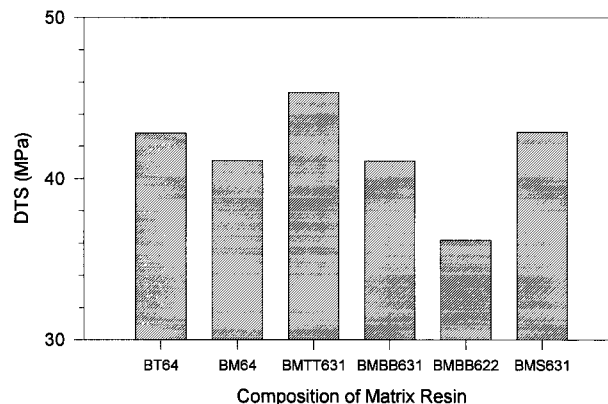

Figure 5   Dry diametral tensile strengths of Bis-GMA/silane–treated Ba composites.
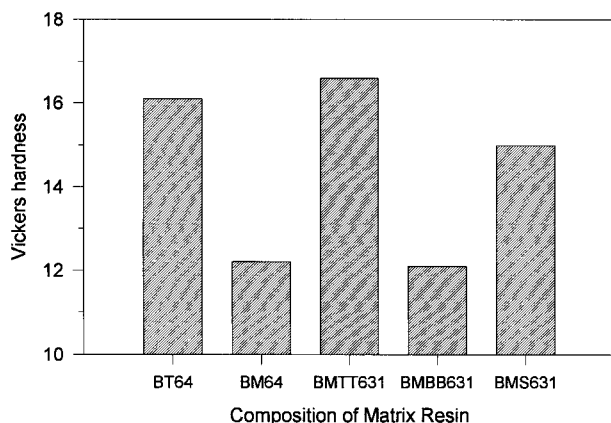
Figure 6 Vickers hardness of various unfilled matrix resins.

filled matrix resins. BMTT631 shows greater hardness than BM64 and even slightly greater hardness than BT64. This demonstrates that TMPT offsets the insufficient crosslinking of matrix. Accordingly, BMTT631 shows higher DTS than BM64, resulting from its improved crosslinking of matrix. Second, MPS in matrix is very compatible with the surface of MPS-treated fillers, which enhances the dispersion between matrix resins and fillers. This can be proved by the result shown in Figure 4: BMTT631a shows lower shear viscosity than BT64a. The tensile strength of filled systems is influenced not only by the interfacial strength between matrices and fillers, but also by the dispersion of filler particles in matrix. Consequently, improved dispersion of Ba increases the DTS of BMTT.

In contrast to TMPT, the addition of BTB to matrix decreases the DTS of integral blend systems. As shown in Figure 5, the DTS of BMBB decreases with increasing the concentration of BTB (BMBB631 and BMBB622). This may be a result of the different reaction types of TMPT and BTB: physical bonding of BTB with matrix is weaker than chemical bonding between methacrylate groups of TMPT and matrix. This can be proved by the hardness data. Figure 6 shows Vickers hardness of various unfilled matrices. BMTT631 represents the highest Vickers hardness, which accounts for TMPT's strong bonding in matrix resins. On the contrary, addition of BTB makes no difference in Vickers hardness, which indicates weak bonding of BTB with matrix. Methoxy groups of BTB in matrix also influence the interfacial strength of Bis-GMA/silane–treated

Ba composites. As the concentration of methoxy groups in matrix increases or that of methacrylate groups decreases, the portion of physical bonding at the interface between matrix and surface-treated Ba increases and, in turn, interfacial strength between them is reduced. Accordingly, BTB in matrix acts to decrease the DTS of Bis-GMA/silane–treated Ba composites.

Wet DTS of integral blends and BT64 is represented in Figure 7. As stated before, in the case of silane-treated fillers, it is inferior to that of BT64, a result of the hydrophilicity of MPS. Unreacted methoxy or hydroxyl groups of MPS in matrix resins increase the hydrophilicity of integral-blended matrix resins and then decrease the wet DTS of integral blends. BMTT631 shows slightly higher wet DTS than BM64, because the hydrophilicity of BMTT631 is reduced, but crosslinking of BMTT631 is increased, by TMPT. Wet DTS of Bis-GMA/neat Ba composites is somewhat different from that of the silane-treated case. As shown in Figure 7, wet DTS of integral blends is superior to that of BT. This indicates that the improvement of interfacial strength by MPS in matrix, rather than the increment of hydrophilicity of matrix, has much more influence on the wet DTS of Bis-GMA/neat Ba composites.

DTS of various mixed-silane systems is illustrated in Figure 8. The mixed-silane system of MPS and STS (M + S) shows the best dry and wet DTS, a result of the amino group of STS. Amine acts as a catalyst for the condensation of silanol groups, which is illustrated in Figures 4, 6, and 9. In Figure 4, the viscosity of BMS631 is higher than that of BM64. In addition, in Figure 6, Vick-
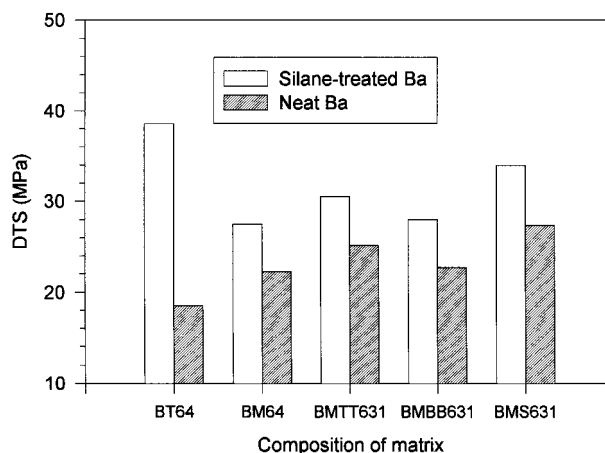

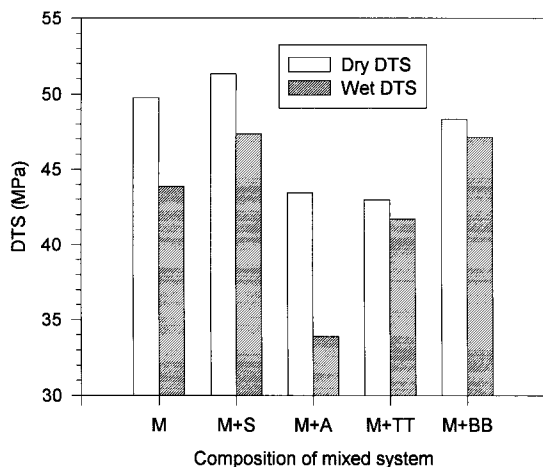**Figure 7** Wet diametral tensile strengths of Bis-GMA/Ba composites.

Figure 8 Diametral tensile strengths of various mixed silane systems.

ers hardness of BMS631 matrix is higher than that of BM64 and even almost equal to that of BT64. These results indirectly demonstrate the ability of STS as a catalyst for silanol condensation. It can be more directly shown by the results presented in Figure 9, in which OH stretching bands of hydrolyzed MPS and MPS/STS (mole ratio, 6/1) are compared. Addition of STS causes the reduction of OH peak intensity resulting from the condensation of OH. Its catalytic effect on the condensation of hydroxyl groups increases the DTS of Bis-GMA/silane–treated Ba composites. STS also demonstrates reactivity with matrix by vinyl group. These amino and vinyl groups of STS may improve the DTS of Bis-GMA/Ba composites. In the case in which STS is applied as integral blends (BMS631 in Figs. 2, 5, and 6), the results of DTS indicate that STS also plays the same role as in the case of aqueous pretreatments, that is, BMS631 shows good performance. As shown in Figure 7, in the case of silane-treated Ba, wet DTS of BMS631 approaches that of BT64. Condensation of hydroxyl groups in matrix produces a siloxane bond, and then reduces the hydrophilicity of the BMS631 matrix. Consequently, condensation of hydroxyl groups, catalyzed by STS, increases the wet DTS of BMS631; however, the result of the mixed-silane system of MPS and AAPS (M + A) is opposite from that of M + S. This is according to the different functional groups of AAPS and STS; that is, AAPS has no carbon double bond, whereas STS contains one vinyl group. In addition, the amine of AAPS, not reacted with matrix through carbon double bonds,

more efficiently increases the hydrophilicity of interphase than the reacted amine of STS.[6]

In Figure 8, the mixed-silane system of MPS and BTB (M + BB) shows good wet DTS, similar to that of MPS and STS (M + S). On the contrary, the DTS of MPS and TMPT (M + TT) is inferior to that of M + S, M + BB, and even MPS alone. Both TMPT and BTB increase the crosslinking of MPS on the filler surface. However, TMPT demonstrates no reactivity with the surface hydroxyl groups of Ba, and then drops the interfacial strength between MPS and Ba. In contrast to TMPT, BTB acts as a coupler between MPS themselves or between MPS and Ba. Consequently, filler surface–treating agents should have hydroxyl groups to promote the tensile strength of Bis-GMA/Ba composites. On the surface of fillers, the crosslinking of hydroxyl groups of BTB is required to improve wet DTS. On the other hand, in the matrix resin, addition of TMPT efficiently increases the DTS, through the crosslinking reaction of carbon double bonds. STS have the functions of both BTB on the filler surface and TMPT in the matrix.

CONCLUSIONS

The effects of various additives on the performance of Bis-GMA/Ba composites were investigated, with TMPT, BTB, and STS considered as
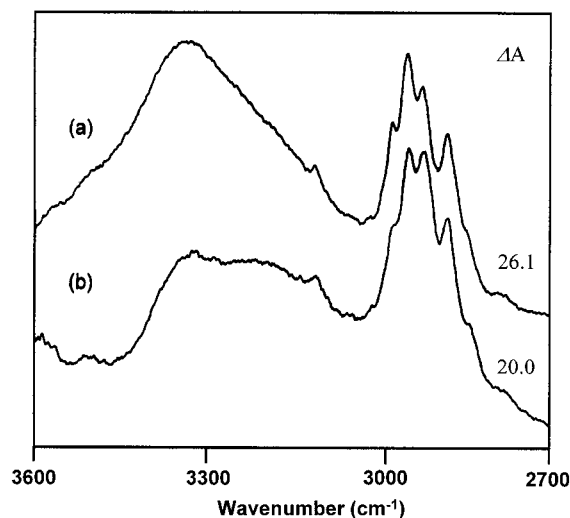

Figure 9 Transmission spectra of hydrolyzed silane coupling agents: (a) MPS alone, (b) MPS/STS (mole ratio, 6/1).

the additives that primarily affect performance. TMPT was an effective crosslinking additive to increase the DTS of integral blends, but not a good coupling agent to increase the DTS of aqueous pretreatments. In contrast to TMPT, BTB was not successfully used as a crosslinking additive, but acted as an efficient coupling agent to increase the wet DTS of Bis-GMA/Ba composites. STS served as a successful additive to both the integral blends and aqueous pretreatments, which resulted from the catalytic effect of amine groups. Integral blends exhibited greater viscosity than aqueous pretreatments immediately after mixing. One day after mixing, however, integral blends showed similar viscosity and processibility to aqueous pretreatments. In a comparison between neat and surface-treated Ba fillers, the improvement of interfacial strength and dispersion between fillers and matrices were needed to increase the performance of Bis-GMA/neat Ba composites, whereas the crosslinking of matrix by the crosslinking additives was required to promote the DTS of Bis-GMA/silane–treated Ba composites.

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