DOI: 10.1002/masy.200750315

Preparation and Characterization of Bone Cements Incorporated with Montmorillonite

Soon Yong Kwon,[1] *Sung Soo Kim*[*2]

Summary: Bone cements incorporated with montmorillonite (MMT) were prepared in an attempt to improve their mechanical properties. The cements were characterized using particle size analysis, gel permeation chromatography, viscosity measurements, unreacted monomer analysis, X-ray diffraction, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and mechanical properties. The average particle size and molecular weight of the PMMA powders used were 47 μm and 100,000 g/mol, respectively. The incorporation of MMT led to an increase in viscosity of the bone cement but did not severely affect its setting temperature or the amount of residual monomer. Regardless of the MMT mixing methods used, in this case MMT being mixing in liquid and powder components, sodium MMT (SMMT) was not well dispersed in the bone cements, which was believed to be due to its hydrophilicity. Organophilic MMT (OMMT) was better dispersed in the liquid component than in the powder component. The compressive and tensile strength of the bone cement containing the OMMT mixed into the liquid component were significantly higher than those of the bone cement without MMT ($p < 0.05$).

Keywords: biomaterials; mechanical properties; nanocomposites; nanoparticles

Introduction

Self-curing acrylic bone cements have been widely used in dentistry and orthopedic surgery as filling agents and for the fixation of joint prostheses.[1] However, they have some disadvantages such as weak mechanical properties, high polymerization exotherm, shrinkage and the release of the unreacted monomer. Many studies have been carried out to overcome some of these disadvantages,[2–7] and some improvements in mixing and dispensing techniques have been achieved. However, the composition of the bone cements is generally unchanged.

Montmorillonite (MMT) whose chemical composition is $Na_{1/3}(Al_{5/3}Mg_{1/3})Si_4O_{10}(OH)_2$ is a natural smectite clay consisting of stacked silicate sheets, with a typical thickness of 1 nm and a typical diameter ranging between 20 and 1000 nm. Polymer composites with MMT have been studied extensively in an attempt to improve the physical properties of polymer materials since the Toyota research group first reported the excellent thermal and mechanical properties of nylon-6/MMT nanocomposites.[8–11] The improvements in the thermal and mechanical properties of the polymer/MMT nanocomposites were significantly higher than those achieved in traditional filled polymers.[12]

Many methods have been used in the preparation of PMMA-MMT nanocomposites, including solution mixing,[13,14] melt blending,[15] and *in situ* polymerization.[16] However, there are usually very strong electrostatic interactions between silicate layers through cations, which make it

---

[1] Department of Orthopedic Surgery, Catholic University Medical College, 62 Yeoido, Yeoung deong po, Seoul, Korea

[2] Advanced Materials division, Korea Research Institute of Chemical Technology, 100 Jang dong, Yusong, Daejon 305-600, Korea
Fax: (+82) 42-861-4151
E-mail: sskim@krict.re.kr

extremely difficult to achieve complete exfoliation of the layers. It was reported that this difficulty could be overcome by replacing such cations with some organic ammonium salts.[17,18] Such organic ammonium cations reduce the hydrophilic property of the silicate layers and enhance the affinity between the silicates and the polymer matrix.

This paper reports the effects of incorporating MMT in the acrylic bone cements on their mechanical strength. In addition, the effects of two MMT-mixing methods, mixing in the liquid component or mixing in the powder component, on the handling characteristics of the cements were compared.

Materials and Methods

Materials

The sodium montmorillonite (Cloisite® Na^+, SMMT) and the organophilic montmorillonite (Cloisite® 25A, OMMT) used in this work were commercial products provided as free-flowing powder by Southern Clay Products (Gonzales, Texas). The OMMT contained 0.95 meq/g of dimethyl hydrogenated tallow 2-ehtyl-hexyl ammonium as an organophilc modifier. The SMMT and OMMT were dried thoroughly before being mixed with the other ingredients. Methyl methacrylate (MMA) was purchased from Junsei chemicals (Tokyo, Japan). Benzoyl peroxide (BPO), as an initiator, and N,N-dimethyl-*p*-toluidine, as an polymerization accelerant, were obtained from Aldrich Chemicals (St. Louis, Missouri). Polyvinyl pyrrolidone (PVP, $M_n = 1{,}300{,}000$ g/mol) (Acros Organics, Geel, Belgium) was used as a suspension stabilizer.

Suspension Polymerization of PMMA Powders

The PMMA powders were prepared by suspension polymerization carried out in a 2l baffled round flask equipped with a 2-bladed Teflon impeller and a digital controller to manage the stirring rate and temperature. Two grams of BPO was dissolved in the MMA monomer (100 g). The monomer was added slowly to the reactor containing a 0.2% PVP aqueous solution (1000 ml) as the dispersion medium with a stirring speed of 800rpm in at 80 °C for 8 hours. The polymer powders were obtained by centrifugation and were washed thoroughly several times with distilled water, and then dried in a vacuum oven at 60°C. Sieved PMMA powders with a particle size of ≤ 250 μm were used for the preparation of bone cements.

Sample Preparations

Five groups of test specimens with varying amounts of MMT (i.e. 0.5, 1, and 2 wt%) were prepared using the PMMA powders and MMT, as shown in Table 1. In the SMMT-P and OMMT-P groups, the polymer powder (PMMA + BPO) was first mixed with MMT (SMMT and OMMT, respectively), and the resulting powder mixture was then mixed with the monomer solution at room temperature. In the SMMT-L and OMMT-L groups, the plain polymer powder (PMMA + BPO) was mixed with the monomer liquid mixture containing various amounts of MMT (i.e. 0.5, 1, and 2 wt%) at room temperature. The control cement was prepared using the PMMA powders without SMMT and OMMT.

Material Characterization

The PMMA and MMT particles used in this work were characterized using particle size analysis, gel permeation chromatography (GPC), and scanning electron microscopy (SEM). The particle size and distribution of the PMMA and MMT particles were measured using a particle size analyzer (BI-DCP, Brookhaven instruments Ltd.). The composition of the commercially available CMW1 original bone cement (DePuy International Ltd., Blackpool, England) was chosen as a reference. GPC (Waters 2690, Malva Ltd.) was used to determine the molecular weight of the prepared PMMA particles. The surface of the gold-coated test specimens was

Table 1.
Chemical composition of the bone cements.

	MMT (%)	Powder components			Liquid components		
		PMMA (g)	BPO (g)	MMT (g)	MMA (ml)	NDPT (ml)	MMT (g)
Control	0	97.75	2.25	–	49.59	0.41	–
SMMT-P	0.5	97.5	2	0.5(S)	49.59	0.41	–
	1	97	2	1(S)	49.59	0.41	–
	2	96	2	2(S)	49.59	0.41	–
SMMT-L	0.5	97.75	2	–	49.34	0.41	0.25(S)
	1	97.75	2	–	49.09	0.41	0.5(S)
	2	97.75	2	–	48.59	0.41	1(S)
OMMT-P	0.5	97.5	2	0.5(O)	49.59	0.41	–
	1	97	2	1(O)	49.59	0.41	–
	2	96	2	2(O)	49.59	0.41	–
OMMT-L	0.5	97.75	2	–	49.34	0.41	0.25(O)
	1	97.75	2	–	49.09	0.41	0.5(O)
	2	97.75	2	–	48.59	0.41	1(O)

*(S) = sodium montmorillonite; (O) = organophilic montmorillonite.

observed using SEM (Philips XL30s FEG) at an accelerating voltage of 20 kV.

The dispersion of MMT in the bone cement was confirmed by X-ray diffraction (XRD, D/MAX-IIIB, Rigaku Corp.), which was equipped with a rotating-anode generator system using Cu-Kα radiation in the 2θ range of 1-10°, and transmission electron microscopy (TEM, JEM-2010, JEOL Ltd.) at an acceleration voltage of 120 kV.

Setting Temperature and Time

The 3 replicate measurements of the setting temperature and time for each cement group were performed using a temperature measuring equipment (Yokogawa MV200, Yokogawa electronic Corp.) and J-type thermocouple wires with one end being electrically welded to form a thermocouple junction. In the setting temperature measurements, the welded end of the thermocouple was used as temperature sensor and dipped into the center of bone cement dough (15 g) in a 50 ml Teflon beaker. The other end was connected to the temperature measuring equipment. The time at 1 minute after which the powder and liquid components were first mixed was taken as t = 0. The setting curve was monitored and used to determine the setting temperature and time. The setting temperature was determined as follows:

$$T_{set} = (T_{max} + T_{ambient})/2$$

where T_{set} is the setting temperature in °C, T_{max} is the maximum temperature and $T_{ambient}$ is the ambient temperature, $23 \pm 1\,^{\circ}$C.

Dynamic Viscosity

A rheometric dynamic spectrometer (Rheometrics RDA-III, Rheometric scientific^{TM}) in dynamic oscillation mode with a parallel plate configuration was used to measure rheological characteristics as a function of time. The bone cement components were added together in a PTFE beaker, at which point the timer was started. The components were mixed manually with a spatula for approximately 60 s and 5 g of the cement was then loaded into the rheometer. The plates were brought together and, after the excess cement had been removed, the rheometer was started. The rheometer was used in dynamic oscillation mode at a frequency of 5 Hz and at a temperature of 27 °C. The diameter of the upper plate was 25 mm and the gap between the plates was 2 mm. The instrument was used in a 5% constant strain mode. The dynamic viscosity measurements were made on a single sample of each cement group.

Mechanical Properties

The compression tests were carried out on cylindrical specimens, 6mm in diameter and 12 mm in height, from each subgroup. The cylindrical cement specimens were prepared by the above-mentioned. The compression test was carried out using the ASTM F451-86 recommendations. The compression load was applied along the axis (Universal testing machine, Instron 4482) using a crosshead speed of 20 mm/min ($n = 8$ per group). The tensile tests were carried out at a cross-head speed of 1 mm/min in accordance with ASTM D638-01 ($n = 8$ per group).

Results

Characteristics of MMT and PMMA Powders

Figure 1 shows the particle size distribution of the SMMT and OMMT powders. The average particle sizes of SMMT and OMMT were 33 and 17 μm, respectively, and 80% of the SMMT and OMMT particles were 15∼54 and 6∼29 μm, respectively. The particle sizes were larger than that of fully dispersed MMT (20∼1000 nm), suggesting that the particles were aggregated by electrostatic interaction. The particle size of OMMT was smaller than that of SMMT because the strength of electrostatic interaction of OMMT might be reduced by incorporating the organic ammonium compounds.

The average particle size of the prepared PMMA was 47 μm and the particle sizes of 80% of the prepared PMMA and reference (CMW1) samples were approximately 40∼60 μm (Figure 1). Figure 2 shows SEM images of the polymerized PMMA and CMW1 powders. Both powders were spherical and not aggregated. The shape and aggregation of the PMMA powders might assist in trapping air while mixing the bone cement. The particles with the spherical shape entrap presumably less air bubbles than those with the irregular shape because of the smooth surface. The molecular weight (M_n) and polydispersity of the prepared PMMA powders were 100,000 g/mol and 2.60, respectively, which were higher than the 43,000 g/mol (M_n) and the polydispersity (2.24) of the commercial cement (CMW1).

Setting Temperature and Time

The exothermal behaviors during the setting of the test groups showed a similar trend (data not shown). All the groups had

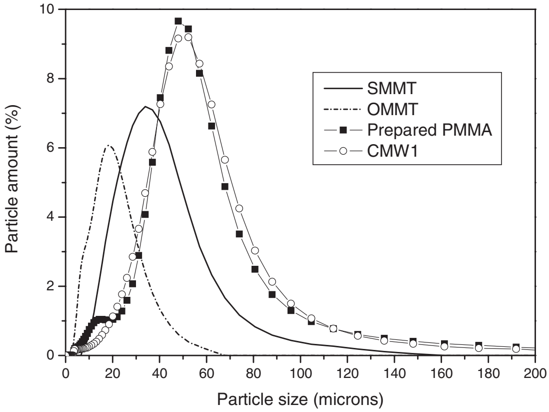

Figure 1.
Particle size distribution of powders of montmorillonite (SMMT and OMMT), prepared PMMA and CMW1 original bone cement.

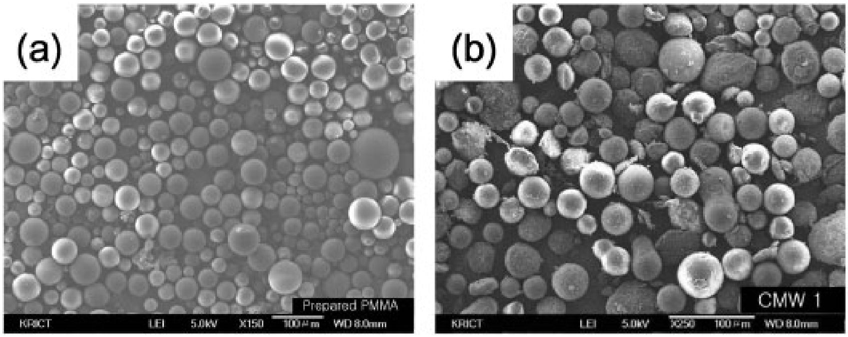

Figure 2.
SEM images of the prepared PMMA (a) and CMW1 (b) powders.

a similar setting temperature and time with $p > 0.05$ according to the Student's *t*-test, where p is the level of significance. In terms of the mean value, the setting temperatures at 1% concentration of all groups decreased slightly to 57.4 ± 2.9 for SMMT-P, 57.6 ± 0.8 for SMMT-L, 57.6 ± 3.0 for OMMT-P, and 56.1 ± 1.7 °C for OMMT-L, compared with the control cement (59.1 ± 3.5 °C).

Dynamic Viscosity

Figure 3 shows the changes in the dynamic viscosity of dough stages of the bone cements with time. The dynamic viscosity of the MMT-incorporated cement was higher than that of the control PMMA cement, when compared at the same time. The dynamic viscosity of the OMMT-L cement was the highest of the test cements compared at the same time. An abrupt increase in the dynamic viscosity of the control PMMA cement was observed between 300~350 sec. Abrupt increases in the dynamic viscosity of the MMT-incorporated bone cements were shown earlier than in that of the control PMMA cement. This increase occurred

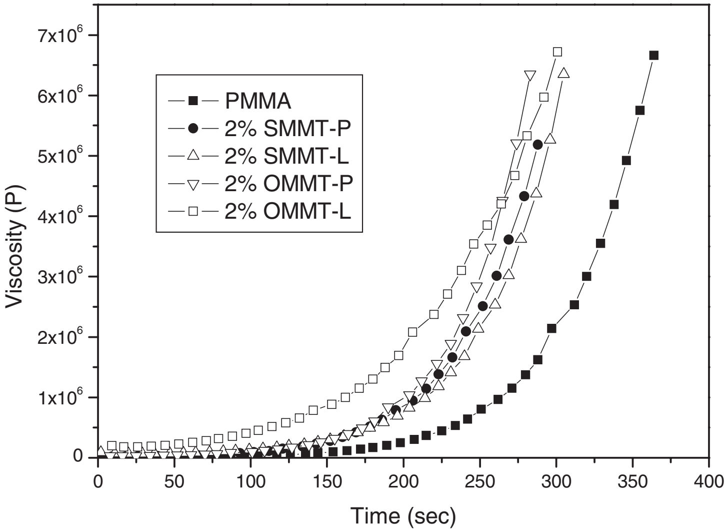

Figure 3.
Dynamic viscosity as a function of time for the control (PMMA) and bone cements incorporated with 2% sodium (SMMT) and organophilic (OMMT) montmorillonite.

earlier in the OMMT-L cement (180~230 sec) than in the other MMT-incorporated cements (220~270 sec).

XRD

Figure 4 shows the XRD patterns of sodium (SMMT) and organophilic (OMMT) montmorillonite, MMT/MMA monomer mixtures (SMMT/MMA and OMMT/MMA) and the corresponding bone cements (SMMT-P, SMMT-L, OMMT-P, and OMMT-L) ranging from 1 to 10°. The mean interlayer spacing of the (001) plane for the OMMT was estimated to be 2.112 nm, which was larger than that of SMMT (1.193 nm). The interlayer spacing in the monomer mixtures, SMMT/MMA and OMMT/MMA, was 1.701 and 3.889 nm, respectively, suggesting that the monomer molecules were intercalated into the interlayer space of the MMT. The spacing of SMMT-P was 1.525 nm but that of SMMT-L was not observed. The spacing of OMMT-P and OMMT-L was 3.785 and 2.848 nm, respectively.

TEM

Figure 5 shows TEM micrographs of the bone cements (control, SMMT-P, SMMT-L, OMMT-P, and OMMT-L). In the control, no inorganic particles were observed. In SMMT-P and SMMT-L, many aggregated MMT particles were observed regardless of the mixing methods. Less aggregated MMT particles were found in the OMMT-P and OMMT-L. The particles in OMMT-L were more dispersed than those in the OMMT-P.

Mechanical Properties

The mechanical properties such as the compressive and tensile strength of the bone cements mixed with up to 2 wt% of MMT were examined. The results were shown in Figure 6 and 7. Samples with more than 2 wt% MMT were not examined because the viscosity of the cements was too high. The measured compressive strength of the control bone cement without MMT was 110.1 ± 2.0 MPa, which is higher than that of the commercial cement (CMW, 91.7 ± 2.5 MPa).[19] In the SMMT group cements, the addition of SMMT caused an increase in compressive strength except for the SMMT-L cement containing 0.5 wt% of the SMMT (Figure 6). The compressive strengths of the SMMT-P cement containing 0.5 wt% SMMT and the SMMT-L cements containing 1.0 and 2.0 wt% SMMT were significantly higher than the control cement ($p < 0.05$). However, the increase in the compressive strength was generally not proportional to the amount of MMT incorporated. A comparison of the bone cements containing the same amount of SMMT revealed significantly higher compressive strengths in the bone cements containing the SMMT mixed into the liquid

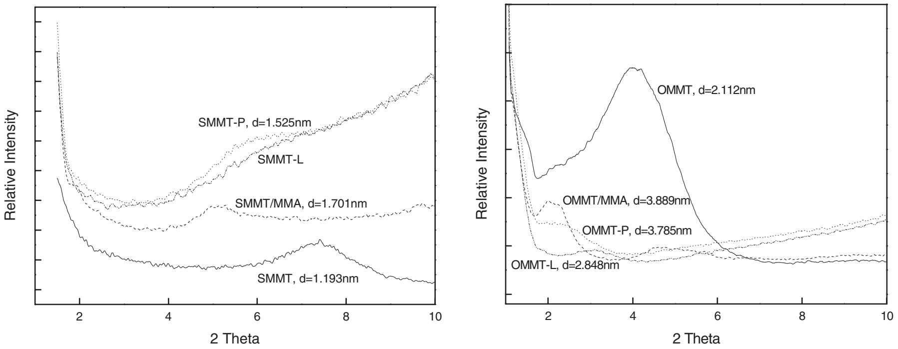

Figure 4.

XRD patterns of sodium (SMMT) and organophilic (OMMT) montmorillonite and the corresponding bone cements (SMMT-P, SMMT-L, OMMT-P, and OMMT-L).

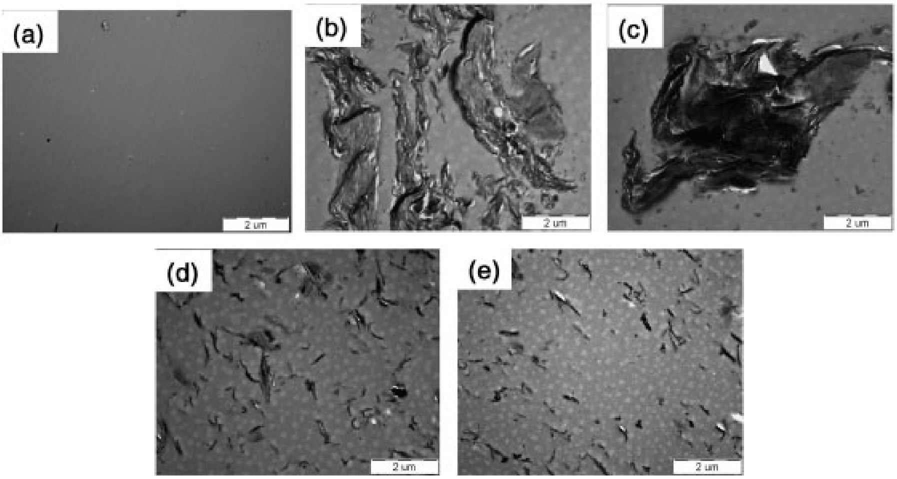

Figure 5.
TEM images of the bone cements: control (a), SMMT-P (b), SMMT-L (c), OMMT-P (d), and OMMT-L (e).

component (SMMT-L) than those of the bone cements containing the SMMT mixed into the powder component (SMMT-P) ($p < 0.05$), with the exception of the cement containing 0.5 wt% SMMT. The addition of OMMT decreased the compressive strength of the OMMT-P group cements. However, the compressive strength considerably improved in the OMMT-L group cements, compared with the control cement ($p < 0.05$). The compressive strengths of the OMMT-L group cements were not significantly different from those of the SMMT-L group cements.

The measured tensile strength of the control bone cement without MMT was 22.3 ± 3.8 MPa, which is lower than that of the commercial cement (CMW, 28.9 ± 1.6 MPa).[19] The addition of MMT caused an increase in the tensile strength except for the OMMT-P cements containing 1.0 and 2.0 wt% OMMT (Figure 7). The tensile strength of the SMMT-L and OMMT-L cements was significantly higher than that

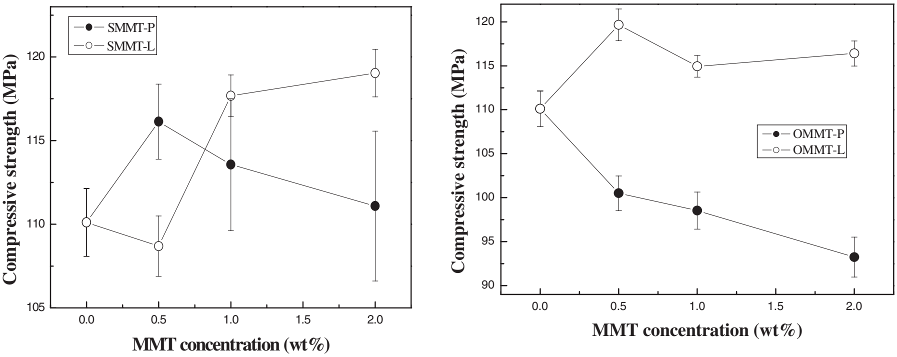

Figure 6.
The changes in the compressive strength according to the method of MMT addition (results are the mean ± standard deviation; n = 8).

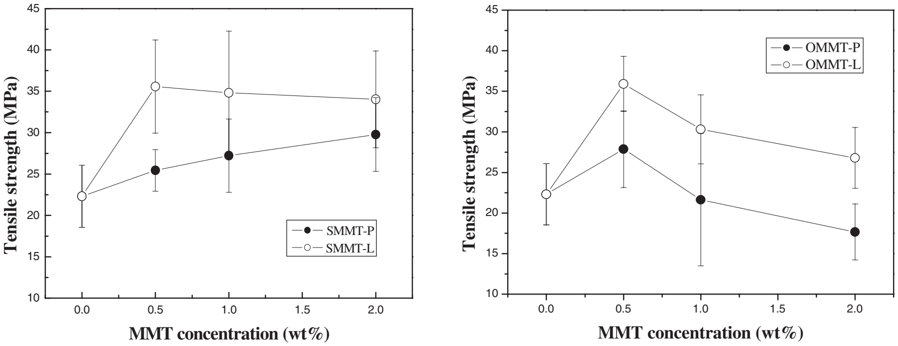

Figure 7.
The changes in the tensile strength according to the method of MMT addition (results are the mean ± standard deviation; $n = 8$).

of the control cement without MMT ($p < 0.05$). The SMMT-L group showed a slight decrease after achieving the maximum improvement in tensile strength at 0.5% MMT, while the tensile strength of the SMMT-P group increased monotonously. The addition of SMMT caused an increase in tensile strength in the SMMT containing cements, regardless of the mixing methods. At similar MMT concentrations, the tensile strengths of the bone cements containing 0.5 and 1.0 wt% SMMT mixed into the liquid component (SMMT-L) were significantly higher than those of the bone cements containing the SMMT mixed into the powder component (SMMT-P) ($p < 0.05$). In the OMMT-P cements, the change in the tensile strength as a result of the OMMT addition showed a similar trend to that of the OMMT-L group. This means that the OMMT groups showed a decrease after achieving the maximum improvement in tensile strength at 0.5%. Similar to the SMMT groups, the tensile strengths of the bone cements containing the OMMT mixed into the liquid component (OMMT-L) was significantly higher than those of the bone cements containing the OMMT mixed into the powder component (OMMT-P) when the tensile strength was compared at each MMT concentration ($p < 0.05$). The tensile strengths of the OMMT-L group cements were not significantly different from those of SMMT-L group cements ($p > 0.05$).

Discussion

MMT was incorporated into PMMA bone cement to increase its mechanical properties, such as compressive and tensile strength. Two different MMT-mixing methods, mixing in the liquid component and mixing in the powder component, were studied to examine the effect of the mixing method on the mechanical and handling properties of MMT-incorporated bone cements.

The important handling properties of bone cement are the setting temperature and time of the dough stage in the bone cement. According to observations of the exothermal behaviors of the dough stage of the bone cements, the addition of MMT had almost no effect on the setting temperature and time of the bone cements. The increase in temperature during setting is attributed to the polymerization heat of MMA monomers. Therefore, the incorporation of MMT does not affect the polymerization of the bone cement.

Another important handling property of bone cement is the viscosity change in the dough stage. The increase in the bone cement viscosity during setting was generally attributed to the dissolution of polymer particles in the monomer and the polymerization of the monomers. The dynamic viscosity measurements showed that the addition of MMT led to an increased viscosity because the shear moduli of test cements were presumably increased by the MMT particles. The abrupt increase in dynamic viscosity is attributed to the self-accelerating polymerization of MMA monomers. The earlier appearance of the abrupt increase in the dynamic viscosity of the MMT-incorporated cements compared to that of the control PMMA cement is also caused by increasing the shear moduli as a result of the MMT addition. Moreover, among the test cements, the earliest appearance of the abrupt increase in the dynamic viscosity in the OMMT-L cement may result from the highest contribution of OMMT to increase shear moduli because the OMMT mixed in the liquid component is most dispersed.

The XRD analysis can measure the mean interlayer spacing of the (001) plane for the MMT. The mean interlayer spacing of the OMMT was larger than that of the SMMT. The ion exchange of the ammonium organic compounds presumably increased the spacing. The large space can ease the intercalation of MMA monomers into the space. The mean interlayer spacing increased in the MMA monomer but decreased after polymerization. The decrease in the interlayer distance of the bone cements was likely caused by volume shrinkage as a result of polymerization, compared with those of the monomer mixtures (SMMT/MMA and OMMT/MMA). The spacing of the MMT in the OMMT cements was larger than that of the MMT in the SMMT cements, which indicated that the PMMA molecules in the OMMT cements were more intercalated into the interlayer space of the MMT.

TEM micrographs showed that many aggregated MMT particles were observed in bone cements with SMMT, compared with those with OMMT. SMMT may not be compatible with PMMA polymers due to its hydrophilic characteristics. In the OMMT cements, the OMMT particles mixed in the liquid component were more dispersed than those in the powder component. When the OMMT particles mix in the powder component, the OMMT particles contact MMA monomers very briefly because they only meet at the dough stage of the bone cement. Therefore, the OMMT particles were less dispersed.

The mechanical properties, such as the compressive and tensile strength, of the bone cements were examined to characterize the effects of MMT addition and its mixing methods. The compressive and tensile strength were generally enhanced when the MMT was mixed in the liquid component. The compressive and tensile strength of bone cement containing OMMT mixed into the liquid component were significantly higher than those of bone cement without MMT. Overall, the compressive and tensile strength of bone cement containing MMT mixed into the liquid component were considerably higher than those of bone cement with MMT mixed into the powder component.

Although TEM revealed a remarkable difference in the dispersion in the SMMT and OMMT groups, the compressive and tensile strength of bone cement containing OMMT were not significantly higher than those of bone cement containing SMMT when the MMT was mixed in the liquid component. Moreover MMA monomers were more intercalated into OMMT than SMMT according to the XRD analysis. Therefore, the compressive and tensile strength do not appear to be dependent on MMT dispersion, monomer intercalation, and the chemical nature of the MMT.

When the MMT is mixed in the powder component, the MMT contacts MMA monomers very briefly because they only meet at the dough stage of the bone cement. In this mixing method, MMA monomers may not soak the MMT particles completely, thus generating many air bubbles and voids. These defects may lead to decreases in the mechanical properties. However, the MMT mixed in the liquid component is substantially soaked by MMA monomers because of the longer contact time. Fewer defects are generated; therefore the mechanical properties of bone cement containing MMT mixed into the liquid component were generally higher than those of bone cement containing MMT mixed into the powder component.

[1] J. Charney, *J. Bone. Jt. Surg.* **1960**, *43B*, 28.

[2] K. Serbetci, F. Korkusuz, *Polymer Testing* **2004**, *23*, 145.

[3] M. Abboud, S. Vol, E. Duguet, *J. Mater. Sci: Mater. Med.* **2000**, *11*, 295.

[4] M. Stańczyk, B. van Rietbergen, *J. Biomech.* **2004**, *37*, 1803.

[5] S. Y. Kwon, Y. S. Kim, Y. K. Woo, S. S. Kim, J. B. Park, *Biomed. Mater. Eng.* **1997**, *7*, 129.

[6] R. G. Carrodeguas, B. V. Lasa, J. S. R. Barrio, *J. Biomed. Mater. Res. Part B: Appl. Biomater.* **2004**, *68B*, 94.

[7] B. Pascual, B. Vázquez, M. Gurruchaga, I. Goñi, M. P. Ginebra, F. J. Gil, J. A. Planell, B. Levenfeld, J. S. Román, *Biomaterials* **1996**, *17*, 509.

[8] K. Yasue, S. Katahira, M. Yoshikawa, K. Fujimoto, in: "*Polymer-clay nanocomposites*", T. J. Pinnavaia, G. W. Beall, Eds., J. Wiley & Sons, New York **2001**, p. 111.

[9] S. Bandyopadhyay, A. J. Hsieh, E. P. Giannels, in: "*Polymer Nanocomposites*", R. Krishnamoorti, R. A. Vaia, Eds., American Chemical Society, Washington **2002**, p. 15.

[10] N. Moussaif, G. Groeninckx, *Polymer* **2003**, *44*, 7899.

[11] G. Kickelbick, *Prog. Polym. Sci.* **2003**, *28*, 83.

[12] S. S. Ray, M. Okamoto, *Prog. Polym. Sci.* **2003**, *28*, 1539.

[13] D. C. Lee, L. W. Jang, *J. Appl. Polym. Sci.* **1996**, *61*, 1117.

[14] M. Okamoto, S. Morita, H. Taguchi, Y. H. Kim, T. Kotaka, H. Tateyama, *Polymer* **2000**, *41*, 3887.

[15] A. Tabtiang, S. Lumlong, R. A. Venables, *Eur. Polym. J.* **2000**, *36*, 2559.

[16] M. Okamoto, S. Morita, Y. H. Kim, T. Kotaka, H. Tateyama, *Polymer* **2001**, *42*, 1201.

[17] L. B. Aglietto, G. Ruggeri, F. Ciardelli, *Polymer* **1994**, *35*, 3296.

[18] M. Alexandre, P. Dubois, *Mater. Sci. Eng: R: Reports* **2000**, *28*, 1.

[19] S. S. Haas, G. M. Brauer, G. Dickson, *J. Bone Jt. Surg.* **1975**, *57A*, 380.