Effects of Ingredients on Thermal and Mechanical Properties of Acrylic Bone Cements

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ABSTRACT: There is a very delicate relation between the amounts of all the ingredients present in the cement composition and the properties of the product. In this study, homogeneous poly(methyl methacrylate) (PMMA) microspheres were prepared by suspension polymerization technique, and used in cement formulations. Various acrylic cements with different compositions were prepared by using PMMA microspheres, methyl methacrylate (MMA) monomer, radiopaque agent of barium sulfate ($BaSO_4$), inorganic particles of hydroxyapatite (HA), initiator and chain stopping agent of 1-dodecyl mercaptan (DDM). The effects of these additives on mechanical and thermal properties of the resultant cements were examined. Addition of 8% HA relative to the solid parts caused an increase in both tensile and compressive strengths from 20.40 to 25.20 MPa, and from 84.04 to 89.57 MPa, respectively, while curing temperature was decreased about 3 degrees. Chain stopping agent of DDM caused a sharp decrease about 30 degrees in the curing temperature. Radiopaque agent of barium sulfate caused inverse effect on mechanical and thermal properties. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 4077–4084, 2009

Key words: bone cement; acrylic; PMMA microsphere; hydroxyapatite

INTRODUCTION

Bone cements are used in dentistry and orthopedics to fill the cavities, to design artificial crowns, and to fix implanted prosthesis into the required places of the hard tissue. When placed in between the implant and the bone, they transfer and distribute the applied load and increase the load-carrying capacity of the prosthesis/cement/bone system with the help of mechanical bonding. Despite all their advantages, bone cements have several drawbacks such as insufficient mechanical properties, high exothermic polymerization temperature, release of monomer to the environmental tissue, and loosening of implant. Therefore, intense studies are carried out to improve the properties. All commercially available acrylic cements are prepared by mixing liquid and solid powder components. The compositions of powder and liquid parts may have some variations but in general the powder part contains poly(methyl methacrylate) polymer (PMMA) or PMMA-based copolymers, benzoyl peroxide (BPO) initiator, radiopacifier,[1,2] and sometimes antibiotics.[3,4] The liquid part includes methyl methacrylate (MMA) monomer, *N*,*N*-dimethyl-p-toluidine (DMPT) accelerator, hydroquinone (HQ) inhibitor to prevent premature polymerization and sometimes a crosslinking agent such as ethylene glycol dimethacrylate (EGDMA). To have a proper bone cement, all the chemicals should be added in definite amounts with precise ratios among each other.

After mixing the powder and liquid parts, some physical events and chemical reactions take place. Physical events are solvation of polymer and BPO in the liquid, diffusion of liquid into the powder part, polymer–polymer diffusion from the liquid to the solid phase, and monomer evaporation from the mixture. Chemical reactions are creation of radicals from initiator, radical formations on monomers, and propagation of polymerization reaction. The polymerization is a very rapid and exothermic reaction and reaches completion in approximately 10–15 min where the cement sets.[5] Nearly 544 j/g heat releases during the polymerization reaction, and this gives rise to local temperature with a maximum value ranging from 80°C to 124°C.[6] The elevated temperature may cause tissue necrosis at the bone–cement interface and subsequently induce implant loosening. It has been reported that the extent of bone necrosis depends on temperature rise and the period tissue exposed to this temperature.[7]

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During daily activities bone cements are exposed to tensile, compressive, and shear forces in the body, therefore suitable bone cement should have high mechanical strength to endure these applied loads. Cement breakdown and failure limit the lifetime and lead to revision of the implant. The tensile and compression strength values for the commercially available cements are about 20 MPa and 80 MPa range, respectively. To improve mechanical properties, hydroxyapatite (HA),[8,9] chitosan,[10] titanium wires,[11] various polymeric fibers[12] such as poly(ethylene),[13] carbon,[14] Kevlar,[12] and PMMA[15] are added to the cement formulations. However, reinforced cements are still under examination since addition of other ingredients may cause an increase in the viscosity of bone cement and therefore decreases its workability and deliverability.

It is known that calcium phosphate with a Ca : P ratio of 1.0 to 2.0 is biocompatible and HA ($Ca_{10}(PO_4)_6(OH)_2$) is a ceramic with Ca : P ratio of 1.67 having a composition similar to natural bone. Its surface is highly reactive and lead to favorable attachment of bone cells having osseoconductive and osseoinductive effects.[9,16] Therefore, it is believed that addition of HA into bone cements would be advantageous to increase biocompatibility and strength as well as setting characteristics and curing temperature of PMMA cements.[17–19]

The purpose of this study is to prepare new formulations for acrylic bone cements with enhanced thermal and mechanical properties by using the homogenously synthesized PMMA microspheres and the other additives such as HA, 1-dodecyl mercaptan (DDM), and barium sulfate.

EXPERIMENTAL

Materials

In the synthesis of PMMA microspheres, MMA monomer (Acros Organics, USA), poly(vinyl alcohol) (PVA, M_W = 88.000, Acros Organics, USA), BPO (Sigma-Aldrich Chemie, Germany), technical grade ethanol (Tekel Sincan Organize Sanayi, Turkey), and distilled water were used. The other chemicals used in cement preparation were HA (Riedel-de Haën A.G., Germany), barium sulfate ($BaSO_4$, Merck, Germany), DMPT (Sigma-Aldrich Chemie, Germany), and DDM (Acros Organics, USA). All chemicals, except MMA, were used as obtained without further purification. MMA was washed with 10 wt % aqueous sodium hydroxide (J. T. Baker, Holland) solution to remove the inhibitor before use.

PMMA microsphere preparation

PMMA microspheres were prepared by suspension polymerization of MMA. The polymerization of MMA was carried out in ethanol/water (50/50 v/v) media by using BPO as initiator and PVA as stabilizer. For this purpose, BPO initiator was dissolved in MMA monomer to prepare a solution with 10 mg/mL concentration and nitrogen gas was purged through the solution for 15 min to exclude air. On the other hand, equal volumes of distilled water and ethanol (80 mL each) were mixed and aqueous PVA solution (24 mL, 5% w/v) were mixed in a 500 mL round bottom two necked flask fitted with a nitrogen inlet and condenser. Nitrogen gas was bubbled through the solution for 15 min. Then monomer solution was added to the flask and nitrogen was bubbled for 15 more minutes. The polymerization reaction was carried out at 70°C for 6 h and nitrogen gas was bubbled through the solution during all process to exclude air from the medium to prevent its inhibition effect on the polymerization. The formed PMMA microspheres were filtered, washed with water, and alcohol and then dried in vacuum oven. The amounts of the materials used in microsphere preparation are given in Table I.

TABLE I
Materials Used in Polymerization

Materials	Amount (mL)	Amount (g)	wt %
MMA	16	15.04	8.2
Ethanol	80	63.2	34.4
H_2O	104	104	56.6
PVA	–	1.2	0.7
BPO	–	0.16	0.1

PMMA microsphere characterization

Scanning electron microscopy analysis

Topographic shapes and average particle size and size distributions of PMMA microspheres were examined by Scanning Electron Microscopy (SEM) (JEOL, JSM-6400, NORAN Instruments, Tokyo, Japan).

Particle size analysis

The average particle size and size distribution analysis of PMMA microspheres was carried out by means of Zeta Sizer (Malvern Nano ZS90, UK). Distilled water was used as a dispersant and the analysis was performed at 25°C.

Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of PMMA microspheres were recorded by using KBr pellets on a FTIR spectrometer (Perkin Elmer 1600 Series FTIR, USA) in the range of 700 to 4000 cm^{-1}.

TABLE II
Bone Cement Compositions

	Powder part		Liquid part
Sample[a]	HA (wt %)	$BaSO_4$ (wt %)	DDM (wt %)
BC	0	0	0
H4	4	0	0
H8	8	0	0
B13	0	13	0
H8B13	8	13	0
H8B13D1	8	13	1
H8B13D2	8	13	2
H8B13D3	8	13	3

[a] PMMA/MMA = 4 g/6 mL.
BPO = 45 mg; DMPT = 56 μL.

Nuclear magnetic resonance spectroscopy

Solid state ^{13}C-nuclear magnetic resonance (NMR) spectra of PMMA microspheres were obtained by using cross polarization-magic angle spinning (CP/MAS.DD) on a Bruker Superconducting FT.NMR Spectrometer Avance TM 300 MHz WB, Germany. High power Ultrashield superconducting magnet with 4 mm MAS probe was operated at a carbon frequency of 75.38 MHz and proton frequency of 299.77 MHz.

Bone cement preparation

Bone cement is a two-component system and it is obtained by mixing the liquid and the powder parts for 2–3 minutes until a homogenous dough was formed. Liquid part was prepared by mixing MMA monomer and DMPT accelerator and also various amounts of DDM relative to the amount of monomer was added to some compositions as chain stopping agent. Powder part consisted of PMMA polymer and BPO initiator. Moreover, powder part of some compositions included various amounts of HA and $BaSO_4$. All bone cements were prepared by hand mixing. Specimens were allowed to cure for 1 h at room temperature. For each preparation, 6 mL MMA monomer was used for 4 g PMMA polymer and this ratio was kept constant. In addition, in all experiments 45 mg BPO initiator and 56 μL DMPT accelerator were used. Different compositions were prepared by adding various amounts of HA, DDM, and $BaSO_4$ as shown in Table II.

Bone cement characterization

Tension and compression tests were performed to examine mechanical properties of the prepared bone cement samples. Mechanical tests were performed by using LLoyd® LRX 5K (LLoyd Instruments Limited, Fareham, Hampshire, UK) testing machine with a cell load of 5000 Newton at room temperature.

Tension tests

In the preparation of the tension test samples, the cement dough was rolled on a polyethylene surface, cut in dog bone shape and kept in saline solution in a temperature-controlled water bath for 24 h at 37 ± 1°C before mechanical tests. Dog bone shaped samples having approximately 5 × 0.5 × 0.5 cm^3 dimensions were used for tension tests. Tension was applied with a cross-head speed of 1 mm/min at room temperature. For each sample at least five specimens were tested and the average values were obtained.

Compression tests

Samples were prepared by pressing the soft dough in a stainless steel mold which has 56 holes with diameters of 6 mm as described previously.[19] Tests were performed with a cross-head speed of 25 mm/min at room temperature. For each sample at least eight specimens were tested and their average values were obtained.

Thermal analysis

The maximum curing temperatures of bone cements were measured by a "Thermocouple Input Module" (SuperLogics, USA). The temperature measurement experiments were performed at 23 ± 2°C. J-type thermocouple wires were cut into equal pieces of 5 cm and one end was electrically welded to form a thermocouple junction. The cement dough was prepared and rounded to give a spherical shape with a radius of ~ 15 mm. Then the welded end of the thermocouple used as temperature sensor was placed in the center of the dough. The other end was connected to a data acquisition device controlled by a computer. The temperature was recorded for 1200 s with a 1 data per second record rate. Temperature versus time graphs showing the exothermic temperature changes were obtained for each sample. A typical curve is given in Figure 1.

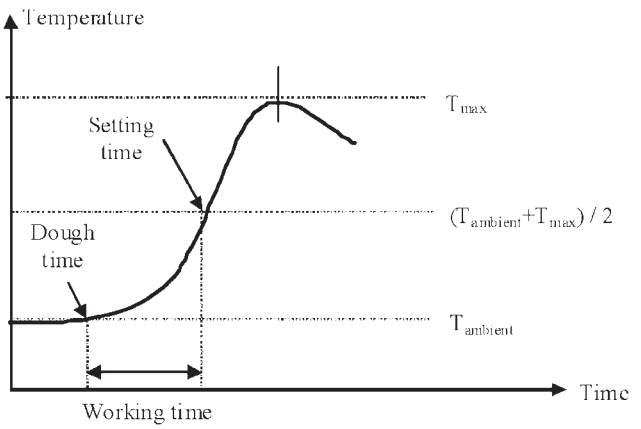

Figure 1 Typical temperature versus time graph.

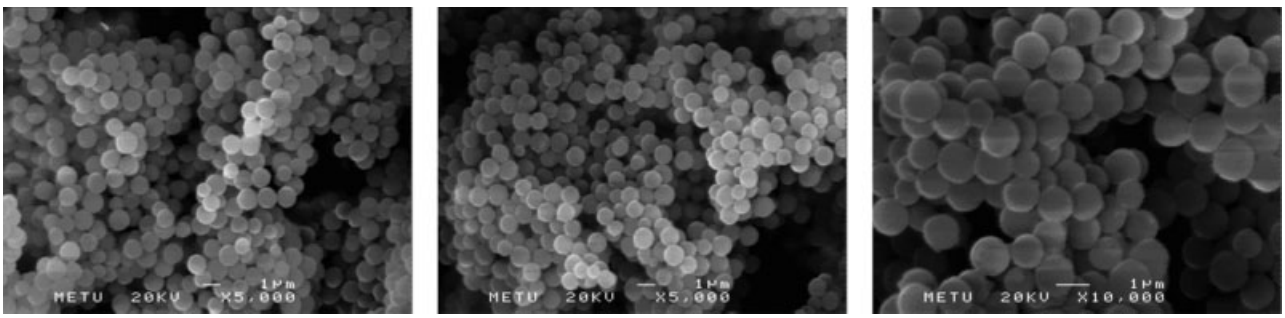

Figure 2 Scanning electron micrographs of PMMA microspheres.

Peak temperature was the maximum temperature reached during the polymerization. Setting time of bone cement was defined as the time when the temperature rise was at halfway point between the maximum temperature and the ambient temperature.[5] Setting temperature can be calculated by using the following equation:

$$T_{\text{setting}} = (T_{\text{ambient}} + T_{\max})/2$$

RESULTS AND DISCUSSION

SEM analysis

Scanning electron micrographs of the prepared PMMA microspheres are shown in Figure 2. It was observed that PMMA particles were very homogenous and monodisperse with perfect spherical shape. The average particle size was approximately 1 μm. These prepared monodisperse particles were used in the preparation of bone cements.

Particle size of PMMA microspheres

The particle size of PMMA microspheres was obtained by Zeta Sizer. During the experiments, distilled water was used as a dispersant and average particle size was found to be 1.0 μm. The size distribution is given in Figure 3. About 25% of the particles were below 1.0 μm.

FTIR results

The IR spectrum of the prepared PMMA microspheres is shown in Figure 4. The sharp intense peak seen at 1731 cm^{-1} can be identified as C=O stretching vibrations in the pendant group (—$COOCH_3$) of PMMA. Absorption bands in the range of 1500–700 cm^{-1} come from the following vibration modes: the C—O (ester bond) stretching vibration (1064–1242 cm^{-1}), C—H bending vibration (1450–1388 cm^{-1}), CH_2 rocking vibration (810 and 752 cm^{-1}). The broad peak from 2845 to 2998 cm^{-1} is due to the presence of C-H stretching vibrations. It can be concluded that the prepared PMMA microspheres demonstrate the characteristic peaks of pure polymer of PMMA. Disappearance of peak at 1650 cm^{-1} that corresponds to terminal methylene group of the MMA monomer showed the complete polymerization of vinyl group.

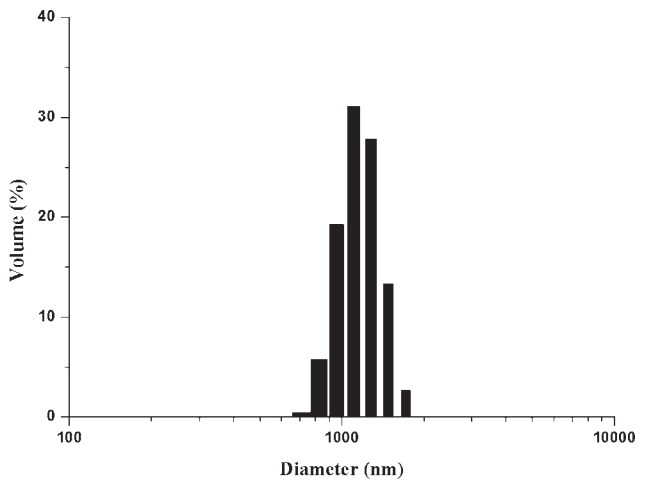

Figure 3 Particle size distribution of PMMA microspheres.

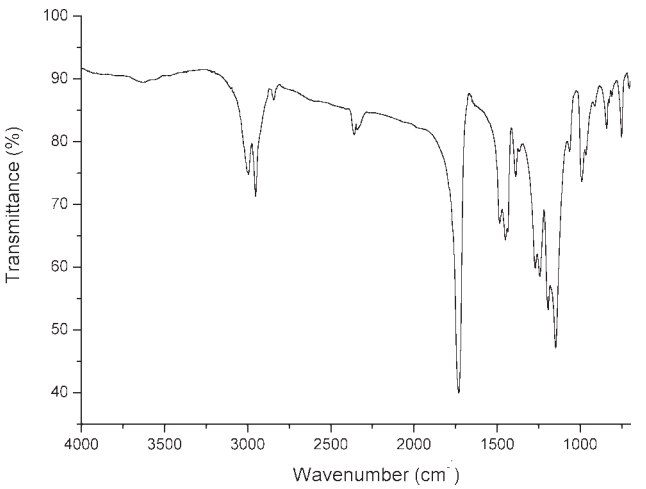

Figure 4 FTIR spectra of PMMA microspheres.

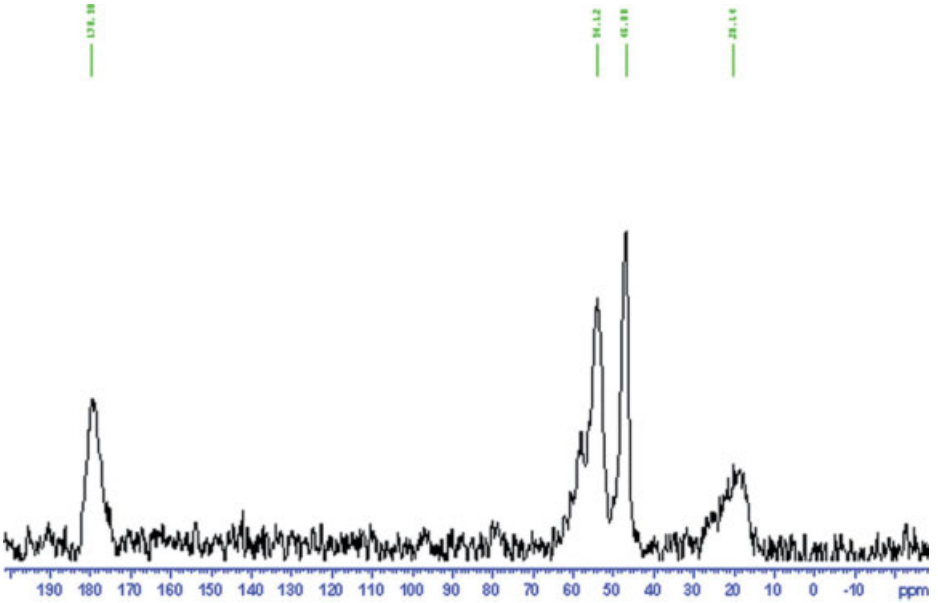

Figure 5 ^{13}C-NMR spectra of PMMA microspheres. [Color figure can be viewed in the online issue, which is available at www. interscience. wiley.com.]

^{13}C-NMR

^{13}C-NMR spectra of PMMA microspheres are shown in Figure 5. The main characteristics of the ^{13}C-NMR spectra of the PMMA microspheres are the peaks corresponding to the methyl carbon (CH_3—) at 17–21 ppm, the methoxy carbon (CH_3O—) at 51.27 ppm, the quarternary carbon (C_α) around 45 ppm, the methylene carbon (—$C_\beta H_2$—) between 52–58 ppm and the carbonyl carbon groups (—C=O) at 176.9 ppm. It can be concluded from ^{13}C-NMR spectrum MMA monomer completely polymerized to PMMA, otherwise, a peak around 110–150 ppm would be observed due to terminal methylene groups of the MMA monomer.

Tensile properties

Mechanical properties of the prepared bone cements were examined and all results obtained in this study are summarized in Table III. For the samples prepared as control (BC) without adding any ingredient, the ultimate tensile strength (UTS) and tensile elastic modulus (E_T) values were found as 20.40 MPa and 0.46 GPa, respectively. Addition of HA caused an increase in UTS and it was found as 24.87 MPa and 25.20 MPa when HA content was increased to 4% (H4) and 8% (H8), respectively. Addition of HA also caused slight increase in elastic modulus from 0.46 GPa to 0.47 GPa and 0.49 GPa for the same samples. This increase can be explained with the stiffer structure of HA in the polymeric matrix. The presence of inorganic HA particles enhance tensile strength and elastic modulus values compared to cement that has no HA particles.

On the other hand, addition of $BaSO_4$ (13%) caused a decrease in E_T. When BC and B13 samples are compared, $BaSO_4$ addition into the bone cement did not cause a significant change in tensile strength but approximately 10.87% decrease in tensile elastic

TABLE III
Tensile and Compressive Properties of Prepared Bone Cement Samples

	Tensile properties		Compressive properties	
Samples	UTS (MPa)	E_T (GPa)	UCS (MPa)	E_C (GPa)
BC	20.40 ± 2.53	0.46 ± 0.04	84.04 ± 2.91	0.54 ± 0.03
H4	24.87 ± 3.14	0.47 ± 0.03	87.77 ± 1.86	0.57 ± 0.03
H8	25.20 ± 2.34	0.49 ± 0.01	89.57 ± 2.44	0.59 ± 0.03
B13	20.20 ± 2.43	0.41 ± 0.02	80.35 ± 1.71	0.57 ± 0.02
H8B13	20.64 ± 2.47	0.44 ± 0.03	78.83 ± 1.75	0.59 ± 0.01
H8B13D1	18.25 ± 1.33	0.56 ± 0.05	86.90 ± 4.50	0.62 ± 0.02
H8B13D2	17.84 ± 1.77	0.40 ± 0.02	93.01 ± 3.59	0.59 ± 0.01
H8B13D3	15.28 ± 0.56	0.39 ± 0.05	82.16 ± 3.78	0.58 ± 0.06

modulus. These decreases are expected since radiopaque materials have significant effects on the mechanical properties depending on their size and morphology. It was reported that small barium sulfate particles do not provide mechanical anchorage with the cement matrix and tended to form agglomerates causing phase segregation and therefore led to a decrease in mechanical properties.[20,21] When HA containing samples, H8 and H8B13, are compared, a significant decrease in UTS value from 25.20 MPa to 20.64 MPa, and in E_T values from 0.49 GPa to 0.44 GPa were observed. In H8B13 bone cement composition, the total amount of inorganic part is higher when compared to other compositions, this may cause phase separation and therefore cause a decrease in mechanical properties.

Chain stopping agents, such as thiols and phenols, are highly reactive and have the ability to scavenge radicals by H–atom abstraction. In free radical polymerization when a chain stopping agent is added to the polymerization composition, a growing macroradical abstracts a hydrogen atom from the chain transfer agent giving a terminated polymer chain and a new initiating radical, which adds to the monomer giving a new propagating species. Therefore, chain stopping agent decreases chain length and so the polymer molecular weight.[22] Therefore, addition of the chain transfer agent of DDM affects mechanical properties since it causes formation of shorter PMMA chains. DDM also controls the kinetic of polymerization reaction and therefore the maximum curing temperature. Addition of 1% (H8B13D1), 2% (H8B13D2), and 3% (H8B13D3) of DDM caused a decrease in the tensile strength from 20.64 MPa (for H8B13) down to 18.25 MPa, 17.84 MPa, and 15.28 MPa, respectively. H8B13D1 samples containing 1% DDM demonstrated the maximum tensile elastic modulus (0.56 GPa) among all the prepared compositions.

Compressive properties

The average ultimate compressive strength (UCS) and compressive elastic modulus (E_C) values of the prepared bone cements are given in Table III.

Addition of 4% and 8% HA increased the UCS from 84.04 MPa to 87.77 MPa and 89.57 MPa, respectively. In addition, elastic modulus of the cement was also increased from 0.54 GPa to 0.57 GPa and 0.59 GPa for the same samples. These increases are expected since inorganic and solid HA particles act as load carrier component against compressive forces.

On the other hand, addition of $BaSO_4$ decreased UCS about 4.39% from 84.04 MPa (BC) to 80.35 MPa (B13) and compressive elastic modulus increased about 5.56% from 0.54 GPa to 0.57 GPa.

The similar decrease in UCS was also observed for the samples containing both HA and $BaSO_4$. When H8 and H8B13 samples are compared, a decrease in UCS from 89.57 MPa to 78.83 MPa was observed. For these samples, almost no change in E_C values was detected. The UCS values of DDM containing samples were found higher than that of similar compositions prepared without DDM (H8B13). Addition of 1% DDM (H8B13D1) increased UCS from 78.83 MPa to 86.90 MPa. When 2% DDM was added, UCS value increased up to 93.01 MPa (H8B13D2), which is the highest for all the prepared compositions. However, further addition of DDM caused a decrease (H8B13D3). Compressive elastic modulus was also first increased from 0.59 GPa to 0.62 GPa with addition of 1% DDM, but then decreased with further additions of DDM. These results are expected since DDM gives some softness to the hard PMMA matrix and therefore increase the strength against higher compression forces. But extra additions may cause very short chains and cause a decrease in the strength against compression forces. It was observed that all the prepared bone cements fulfilled the minimum compressive strength of 70 MPa requirement specified by ASTM F-451.

Curing temperature

The polymerization of MMA in a PMMA system is highly exothermic reaction and leads to an increase in local temperature. In this study, PMMA microspheres prepared homogenously by suspension polymerization having approximately 1 μm size were used. Curing temperatures were found to be in the range of 71–101°C. It is known that the maximum temperature reached during polymerization increases with decreasing polymer-to-monomer ratio. In this study, powder to monomer ratio was fixed as 0.7. Maximum temperatures and setting times of the prepared bone cements are given in Table IV.

The maximum curing temperature for BC sample was found as 101.78°C. This value decreased about 3 degrees on addition of HA up to 8%. Although the drop of the temperature is not very high, still it can be concluded that HA particles were acted as a heat sink and caused a reduction in temperature. On the other hand, addition of $BaSO_4$ (B13) did not cause any significant difference when BC and B13 samples and when H8 and H8B13 samples were compared. Addition of the chain stopping agent DDM caused a significant drop in the maximum curing temperature from 96.83°C to 71.35°C. It can be concluded as the presence of chain stopping agents control the polymerization reaction and prevent the highly exothermic reaction causing a decrease in the chain length of newly formed PMMA.

TABLE IV
Thermal Properties of the Prepared Bone Cement Samples

Samples	Thermal properties	
	T_{max} (°C)	$t_{setting}$ (s)
BC	101.78 ± 0.20	409 ± 35
H4	98.52 ± 4.24	362 ± 31
H8	97.97 ± 3.55	327 ± 14
B13	102.24 ± 3.45	356 ± 9
H8B13	96.83 ± 7.56	361 ± 26
H8B13D1	91.80 ± 0.11	434 ± 4
H8B13D2	78.38 ± 2.46	472 ± 3
H8B13D3	71.35 ± 3.69	550 ± 48

When setting times were examined, it was observed that with the addition of HA, setting time shortened about 20.05% from 409 s to 327 s (Table IV). However, addition of DDM extended the setting time from 361 s to 550 s (Table IV). As mentioned before, DDM controls polymerization reaction by retarding polymerization rate so decreases maximum curing temperature and lengthens the setting time for bone cement.

CONCLUSIONS

Acrylic bone cements are commonly used in dental and orthopedic applications. It was previously reported that presence of HA in bone cement composition increases the biocompatibility of the acrylic bone cement.[18] In this study, it was also observed that presence of HA increased both tensile and compressive strengths. UCS values increased from 84.04 MPa to 89.57 MPa and ultimate tensile strength values increased from 20.40 MPa to 25.20 MPa with addition of 8% HA. Moreover, HA addition reduced curing temperature from 101.78°C to 97.97°C since it achieved a heat sink property by absorbing the released heat. Presence of radiopaque materials has significant effects on the mechanical properties of bone cements depending on their size and morphology. It was observed that addition of 13% $BaSO_4$ led to a reduction in both compressive and tensile strength without a significant change in curing temperature.

For different commercially available acrylic bone cements, it is given that, tensile strength and compressive strength values vary in the range of 22.0–49.2 MPa and 72.6–117 MPa, respectively, depending on the composition, presence of inorganic additives, as well as molding and mixing techniques. The cements in this study all were prepared by hand mixing in the same way, and the effects of the added ingredients were compared. The mechanical properties improved with addition of HA, but decreased with addition of DDM, as expected. Mechanical properties could be enhanced more if the vacuum mixing would apply.

The novelty of the present study is the use of homogeneous micron size PMMA particles (which were synthesized in our labs at size of 1 μm) for the cement preparation and the use of chain stopping agents (DDM). It is thought that these very proper spherical particles would homogeneously distribute in the cement mixture and enhance the mechanical properties while the cement sets, and DDM existing in the medium would decrease the amount of the released heat by controlling the polymerization process. It was observed that the mechanical properties were quite acceptable for the bare samples (prepared without addition of HA, or DDM) and found as 20.40 MPa for tension and 84.04 MPa for compression strengths. Addition of 2% DDM into the formulations decreased the curing temperature from 101°C to 78°C. In this way, controlling the polymerization rate and preventing the damage of high temperatures to the neighboring tissues would be possible. Presence of DDM also extended the setting time of the cement so that the surgeon would have more time for the application of the cement. On the other hand, presence of HA enhanced the mechanical properties by increasing the tension and compression strength, as well as biocompatibility of the prepared cements.

Compressive strength values of all the prepared bone cements were found in the range of 78.83 MPa and 93.01 MPa. Values higher than 70 MPa are in acceptable range due to the requirement specified by ASTM F-451. Although tensile strengths of H8B13D2 and H8B13D3 samples were found to be lower when compared to other compositions, their compressive strength values are all above the required minimum value and their curing temperatures are quite low than that of the other bone cement samples. Therefore, H8B13D2 and H8B13D3 compositions can be considered as candidates for further studies and *in vivo* applications.

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