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Curing Characteristics of Urethane-Dimethacrylate Homopolymers and Their Composites for Potential Application in Bone Cement †

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Abstract: The polymerization of methacrylate compositions used in bone cement is often accompanied by a strong exothermic effect. The polymerizing mass heats up to very high temperatures at the cement application site, irritating the adjacent tissues and even cell death. On the other hand, a bone cement composition should have the optimal curing time, which should be long enough to allow for proper preparation of the cement and short enough to prevent leaking of the cement out of the restoration place. Therefore, new compositions are being sought to reduce the curing temperature of bone cement and maintain a sufficiently long curing time. Our proposal is based on using five homopolymers obtained by polymerizing urethane-dimethacrylates. These were composed of diisocyanate cores: toluene 2,4 diisocyanate (TDI), isophorone diisocyanate (IPDI), 4,4′-methylenebis(cyclohexyl isocyanate) (CHMDI), and di-, tri-, and tetraethylene glycol monomethacrylate wings (DEGMMA, TEGMMA, TTEGMMA, respectively). The following monomers were obtained: DEGMMA/CHMDI, TEGMMA/IPDI, TEGMMA/TDI, TEGMMA/CHMDI, and TTEGMMA/CHMDI. Neat homopolymers as well as their composites with barium sulfate and hydroxyapatite were tested for curing temperature and time. Almost all of the proposed systems were characterized by appropriate values of both parameters. The presence of fillers positively affected the studied parameters by lowering the polymerization temperature and time.

Keywords: bone cement; urethane-dimethacrylates; homopolymers; composites; polymerization parameters

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1. Introduction

The development of poly(methyl methacrylate) (PMMA)-based bone cements (PMMA-BCs) by Charnley in 1958 revolutionized orthopedic surgical technologies [1]. Since then, they have been widely used to stabilize hip and knee implants as well as bone fillers [2]. They consist of two phases: solid and liquid. A solid phase contains powdered PMMA, a polymerization initiator, inorganic fillers, and sometimes antibacterial additives such as antibiotics. A liquid phase consists of methyl methacrylate (MMA), a polymerization accelerator, and stabilizer [1]. The frequency of PMMA-BC application arises from their functional properties (good mechanical and physicochemical properties, high injection ability), ease of handling, good primary fixation between bone and cement, and economic reasons [3,4]. However, the main concern is that the polymerization of MMA is a strongly exothermic process, resulting in an increase in the temperature of tissue adjacent to the application site of PMMA-BCs. The highest curing temperature (T_c) recorded for the PMMA-BCs was 120 °C [5]. This value significantly exceeded the value of 90 °C, which is the maximum T_c specified for this type of material [6]. It is also worth mentioning that such high polymerization temperatures can cause the necrosis of bone tissue (the temperature at

which the necrosis of bone tissue begins is 50 °C) [7]. Bone cements should also have the optimal curing time (t_c). It should be long enough to ensure the proper preparation of the material and short enough to prevent its leaking out of the restoration place. According to the ISO 5833:2002 standard, a t_c from 3 to 5 min is recommended for PMMA-BCs [6]. Therefore, the development of new compositions characterized by low T_c and suitable t_c is one of the current trends in designing bone cements based on methacrylates.

The novel generation of bone cements is based on dimethacrylates. The first commercially available bone cement based on dimethacrylates was Cortoss ® (Stryker, Kalamazoo, MI, USA). It consisted of bisphenol A glycerolate dimethacrylate (Bis-GMA), ethoxylated Bis-GMA derivative (Bis-EMA), and triethylene glycol dimethacrylate (TEGDMA). Compared to the PMMA-BCs, it has lower T_c and more suitable mechanical and physicochemical performance. However, it contains the bisphenol A moieties that can release from the material to the human organism and thus disrupt hormonal balance and negatively affect the immune, reproductive, and neuroendocrine systems [8].

Our proposal was based on using homopolymers obtained by the polymerization of urethane-dimethacrylate derivatives (UDMAs) as alternatives for the currently used dimethacrylates. They are composed of diisocyanate cores: toluene 2,4 diisocyanate (TDI), isophorone diisocyanate (IPDI), 4,4′-methylenebis(cyclohexyl isocyanate) (CHMDI), and di-, tri-, and tetraethylene glycol monomethacrylate wings (DEGMMA, TEGMMA, TTEGMMA, respectively). These are abbreviated as DEGMMA/CHMDI, TEGMMA/CHMDI, TTEGMMA/CHMDI, TEGMMA/IPDI, and TEGMMA/TDI (Figure 1).

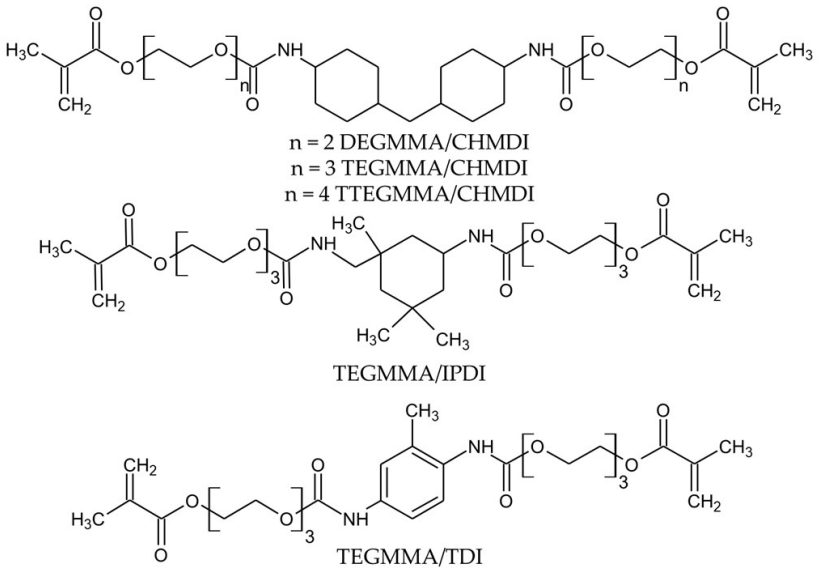


Figure 1. Chemical structure of the dimethacrylate monomers used in this study.

Monomers used in this study were selected from the group of 24 urethane-dimethacrylates described in the literature [9]. The selection was made on the basis of the properties of monomers and their corresponding polymers: (i) liquid state of monomers; (ii) low monomer viscosity, suitable for application with the use of a syringe; (iii) polymer glass transition temperature higher than 40 °C; (iv) polymer modulus lower than 3000 MPa; (v) degree of double bond conversion in polymer higher than 50%; and (vi) polymer water sorption lower than 40 $\mu g/mm^3$.

Monomers and their compositions with 10 wt.% hydroxyapatite and 20 wt.% barium sulfate were cured via low-temperature polymerization. The obtained cured materials were tested for curing temperature and time.

2. Materials and Methods

2.1. Chemicals and Reagents

Urethane-dimethacrylate derivatives: DEGMMA/CHMDI, TEGMMA/CHMDI, TTEGMMA/CHMDI, TEGMMA/IPDI, and TEGMMA/TDI were obtained from oligoethylene glycol dimethacrylates (OEGMMA) and diisocyanates according to the procedure described in [10]. OEGMMAs: DEGMMA, TEGMMA, and TTEGMMA were synthesized by transesterification of MMA (methyl methacrylate, Acros Organics, Geel, Belgium) with respectively: DEG (diethylene glycol), TEG (triethylene glycol), and TTEG (tetraethylene glycol) (all purchased from Acros Organics, Geel, Belgium) according to the procedure described in [10]. $BaSO_4$ (barium sulfate), BPO (benzoyl peroxide), DMPT (N,N-dimethyl-p-toluidine), HA (hydroxyapatite), PTZ (phenothiazine), and diisocyanates: CHMDI (4,4′-methylenebis(cyclohexyl isocyanate), IPDI (isophorne diisocyanate), TDI (toluene 2,4 diisocyanate) were purchased from Sigma-Aldrich (St. Louise, MO, USA) and used as received.

2.2. Curing Procedure

Homopolymers were obtained through low-temperature polymerization. Polymerization was performed in a glass test tube with the use of BPO (polymerization initiator) and DMPT (polymerization accelerator) in a weight ratio specified for each monomer (Table 1). Composites were obtained by the polymerization of a homogeneous mixture of monomers with 20 wt.% $BaSO_4$ and 10 wt.% HA, with the use of the same BPO/DMPT ratios as for the neat homopolymers.

Table 1. Weight ratios of BPO and DMPT used for the low-temperature polymerization.

Monomer	BPO (wt.%)	DMPT (wt.%)
DEGMMA/CHMDI	0.5	0.15
TEGMMA/CHMDI	0.6	0.15
TTEGMMA/CHMDI	0.6	0.15
TEGMMA/IPDI	1.1	0.2
TEGMMA/TDI	0.4	0.15

2.3. Curing Temperature and Time

Curing temperature (T_c) and time (t_c) were determined by utilizing a waterproof, highly accurate thermometer Elmetron PT-400 (Elmetron, Zabrze, Poland). The temperature during curing was checked every 10 s. The measurement started soon after the introduction of DMPT into the monomer system containing BPO and inorganic fillers (in case of composites).

T_c was calculated according to the equation:

$$T_c(^{\circ}\mathrm{C}) = \frac{T_0 - T_{max}}{2}, \quad (1)$$

where T_0 is the initial temperature of monomer composition (°C); $T_{\max}$ is the maximum curing temperature (°C). t_c was taken from the graph T = f(t) for T_c.

The relationship between the polymerization time (t) and temperature (T) for neat homopolymers and their corresponding composites are shown in Figure 2.

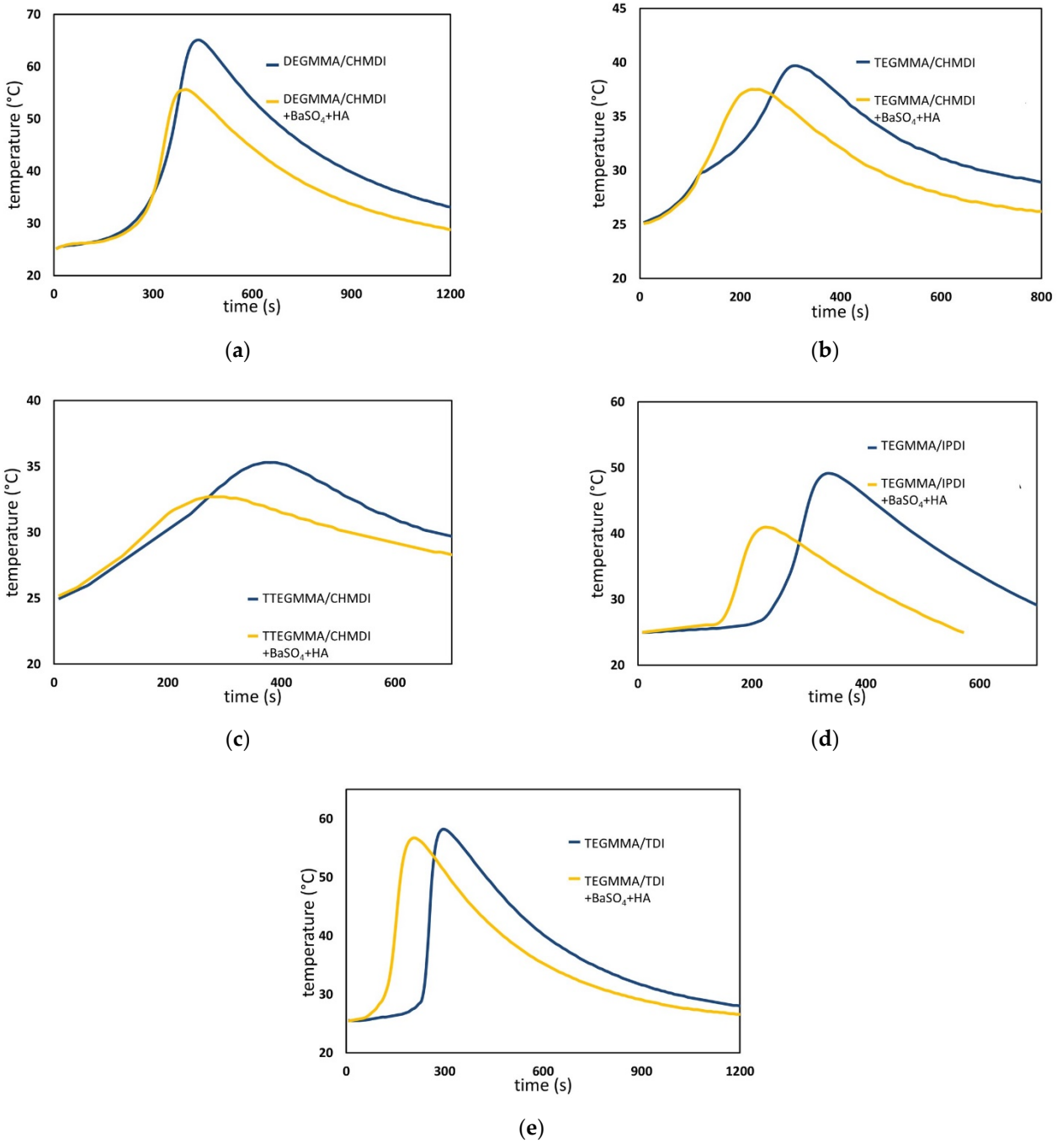
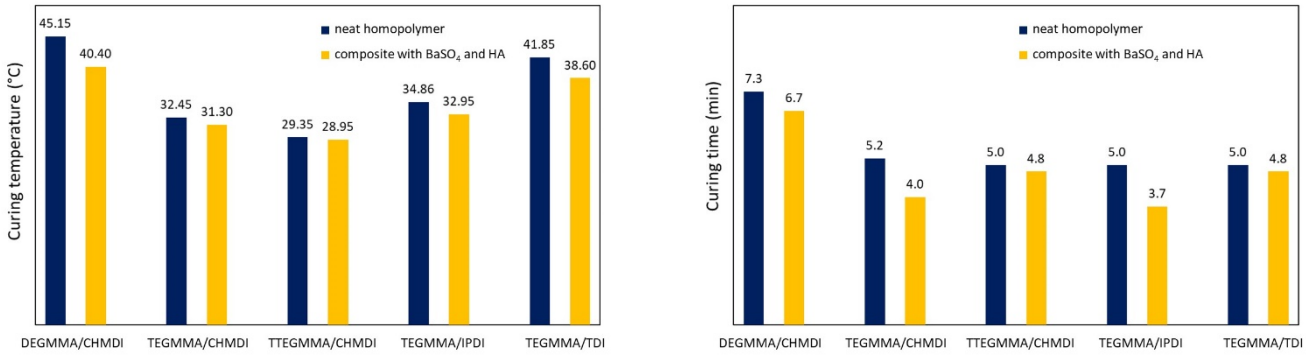


Figure 2. Relationship between the polymerization time and temperature for (**a**) DEGMMA/CHMDI; (**b**) TEGMMA/CHMDI; (**c**) TTEGMMA/CHMDI; (**d**) TEGMMA/IPDI; (**e**) TEGMMA/TDI and their composites with $BaSO_4$ and HA.

3. Results

In this work, five UDMAs synthesized according to the procedure described in [10] and their compositions with 20 wt.% $BaSO_4$, and 10 wt.% HA were subjected to low-temperature polymerization. Neat homopolymers and composites were tested for their T_c and t_c. Obtained results are shown in Figure 3a,b, respectively.



(**a**) (**b**)

Figure 3. The (**a**) curing temperature and (**b**) curing time of the studied neat homopolymers and their corresponding composites with $BaSO_4$ and HA.

The T_c of neat homopolymers ranged from 29.35 to 45.15 °C. The highest T_c was recorded for the DEGMMA/CHMDI, whereas the lowest T_c was recorded for TTEGMMA/CHMDI. Within the neat homopolymers with the CHMDI core, the T_c decreased with the lengthening of the oligooxyethylene chains. The T_c of the composites ranged from 28.95 to 41.85 °C and was lower than the T_c of the corresponding neat homopolymers. The highest T_c was recorded for the DEGMMA/CHMDI-based composite, whereas the lowest T_c was recorded for the TTEGMMA/CHMDI-based composite.

The t_c of the neat homopolymers ranged from 5.0 to 7.3 min. The highest t_c was recorded for DEGMMA/CHMDI, whereas the lowest t_c was recorded for three homopolymers: TTEGMMA/CHMDI, TEGMMA/IPDI, and TEGMMA/TDI. Within the homopolymers with the CHMDI core, the t_c decreased with the lengthening of the oligooxyethylene chains. The t_c of composites ranged from 3.7 to 6.7 min and was lower than the t_c of the corresponding neat homopolymers. The highest t_c was recorded for the DEGMMA/CHMDI-based composite, whereas the lowest t_c was recorded for the TEGMMA/IPDI-based composite.

4. Discussion

The main concern regarding the application of PMMA-BCs is their high polymerization temperature. Therefore, they can irritate adjacent tissues or even cause cell necrosis. For this reason, alternative methacrylate monomers are being sought, which can offer a bone cement with a low polymerization temperature.

In this study, five UDMA homopolymers and their composites with 20 wt.% $BaSO_4$, and 10 wt.% HA were checked for their polymerization temperature and time to verify the possibility of using them as bone cements. Homopolymers and their corresponding composites were obtained by low-temperature polymerization utilizing the BPO/DMPT initiating system.

All UDMA monomers were characterized by T_c lower than 90 °C, which means that they fulfilled the requirements for bone cements, according to ISO 5833:2002 standard [6]. The DEGMMA/CHMDI neat homopolymer showed the highest T_c of 45.15 °C. It implies that the polymerization of the tested UDMAs will not cause morphological bone tissue damage and cell necrosis, which occur at 47 and 50 °C, respectively [11]. The enrichment of UDMAs with inorganic fillers in each case caused a decrease in the T_c value. The greatest difference of 10.52% was observed for DEGMMA/CHMDI, whereas the lowest difference of 1.36% was observed for TTEGMMA/CHMDI. The highest T_c observed for the studied composites was slightly higher than the temperature inside the human body, which suggests that their polymerization would not have any adverse effects on the adjacent tissues.

According to the ISO 5833:2002 standard [6], bone cement should have a t_c within the range of 3 to 5 min. Almost all of the tested UDMAs met this requirement. TTEGMMA/CHMDI, TEGMMA/IPDI, and TEGMMA/TDI fell within the upper limit of the recommended scope as they were characterized by a t_c of 5 min. DEGMMA/CHMDI and TEGMMA/CHMDI were characterized by longer t_c, however, only DEGMMA/CHMDI significantly exceeded the acceptable value. The differences between the t_c and maximum t_c specified for bone cements were 46 and 4%, respectively. Similar to T_c, the enrichment of UDMAs with inorganic fillers in each case caused a decrease in t_c. The greatest difference of 26.00% was observed for TEGMMA/IPDI, whereas the lowest difference of 4.00% was observed for TTEGMMA/CHMDI and TEGMMA/TDI. Concerning the ISO 5833:2002 standard, all composites were characterized by appropriate t_c, except for the DEGMMA/CHMDI-based composite, which had a significantly higher t_c.

5. Conclusions

All proposed UDMA systems were characterized by appropriate values of T_c, which were significantly lower than that specified by the ISO standard. Obtained values were also lower than the temperature of cell necrosis, implying that their polymerization will not negatively affect the adjacent tissues. Almost all systems were characterized by suitable t_c, except for DEGMMA/CHMDI and TEGMMA/CHMDI, which had a t_c longer than 5 min. The presence of inorganic fillers positively affected the studied parameters by lowering the T_c and t_c. After their introduction, only the DEGMMA/CHMDI-based composite did not fulfill the requirements for bone cement due to incorrect t_c.

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