J Mater Sci: Mater Med (2006) 17:1219–1226
DOI 10.1007/s10856-006-0595-7

Effect of microencapsulated phase change materials on the thermo-mechanical properties of poly(methyl-methacrylate) based biomaterials

Roberto De Santis · Veronica Ambrogi · Cosimo Carfagna · Luigi Ambrosio · Luigi Nicolais

Received: 29 August 2005 / Accepted: 4 January 2006

Abstract Microencapsulated paraffin based phase change material (PCM) have been incorporated into Poly(methyl-methacrylate) (PMMA) matrix in order to enhance the thermo-mechanical properties. Calorimetric and mechanical analyses are carried out and the thermo regulating potential of PMMA/PCM composites is investigated. Results indicate that the PCM phase has a negligible effect on the glass transition temperature of the PMMA matrix, and the thermal regulating capability spans around body temperature absorbing or releasing a thermal energy up to 30 J/g. One of the effect of the PCM phase into the cement is the reduction of the peak temperature developed during the exothermal reaction.

Introduction

PMMA is the most common acrylic polymer used for biomedical applications. PMMA, combined with other polymers and additives, constitutes a very versatile material for *in vivo* applications regarding hard tissue substitute. In fact, bone reconstruction in the arthoplasty, vertebroplasty and maxillo-facial surgeries is often provided through PMMA [1–5]. Nevertheless, the relevance of this polymer, chosen to design partially degradable scaffolds for tissue engineering and drug delivery structures, is well known [6–11].

R. De Santis (✉) · L. Ambrosio · L. Nicolais
IMCB-CNR Institute of Composite and Biomedical Materials—National Research Council, Piazzale Tecchio 80, 80125 Naples, Italy
e-mail: rosantis@unina.it

V. Ambrogi · C. Carfagna
DIMP Department of Materials and Production Engineering, University of Naples Federico II, Piazzale Tecchio 80, 80125 Naples, Italy

From a technological point of view, PMMA is extensively used as injectable material (i.e. the bone cement fixation technique), however, 3D PMMA design recently have shown the potential of processes through both the subtractive (top-down) and additive (bottom-up) material production techniques [12, 13].

Resins based on self-polymerizing PMMA often consist of a solid powder represented by PMMA or related copolymer beads and a liquid monomer phase (MMA) [14–18] which are mixed right before the application. The powder phase has the main function of reducing shrinkage and temperature peaks during the polymerisation process. In bone cements the powder/liquid ratio is typically 2/1 and the kinetics of the free radical reaction polymerization is regulated by the concentrations of the initiator (e.g. benzoyl peroxide, BPO) and the activator (e.g. *N*, *N*-dimethyl-*p*-toluidine, DMPT) which are present in the solid and liquid phases respectively [19–21].

Several additives are used in order to functionalise this biomedical polymer. Radio-opacifier (e.g. barium sulphate or zirconium dioxide) is added to the solid phase in order to differentiate bone tissue from the cement through radiographic analyses [22]. Antibiotic (e.g. gentamicin) loading is suggested in order to improve the resistance to septic loosening, and is particularly indicated for revisions of infected joints [23, 24]. The introduction of a bioactive phase (e.g. hydroxyapatite) in the PMMA matrix is suggested in order to enhance the quality of the bone-cement bulk and interface properties [25, 26], while the use of a self-reinforced PMMA composite is proposed in order to improve the mechanical bulk properties of the cement [27]. Again, an increase of the mechanical properties is obtained by using cross-linked PMMA beads [28].

Poly(ε-caprolactone) (PCL) is a biodegradable hydrophobic polyester which has been frequently incorporated in

PMMA to design materials for both environmental and biomedical applications [29, 30]. Crosslinked copolymers and semi-interpenetrating networks in reactive blends of PCL/MMA and PCL/poly(Hydroxyethyilmetacrylate) systems have been reported [31, 32]. A low compatibility between PMMA and PCL in PMMA/PCL blends has also been suggested [30]. These partially degradable materials have been broadly investigated to engineer materials for bioactive bone cements, scaffolds and drug delivery systems [10, 34–36].

The thermal regulating capability [37], that is the absorption or the release of heat during the process of phase change of PMMA/PCL, is nonetheless important, especially when regarding the injected applications (i.e. bone cements) and their *in situ* polymerisation. The temperature increase of both the material and the surrounding hosting tissue due to the exothermal reaction may have detrimental effects on cells. PCL is expected to play a significant role in reducing the temperature of polymerising PMMA by taking the advantage from the energy absorbed in the melting phase change [33]. However, paraffin based phase change materials (PCM) are particularly attractive for this thermal purpose [37–39] since their heat of fusion is higher than PCL. Paraffin PCM is chemically inert, it is classified as a non polar liquid, therefore it does not mix with water or alcohols. Paraffins melt without segregation of components and display no supercooling, thus they do not require thickening and nucleating agents. Moreover, these PCM can be designed in order to match the thermal requirement according to the specific application; the melting point and the heat of fusion can be varied over a wide range simply by tailoring the chain length and ratio of hydrocarbons into the mixture.

Microencapsulation of PCM in polyester resin have recently gained popularity in the building and textile engineering allowing the design of materials with enhanced thermal energy storage capability [40]. The microencapsulation of paraffin based PCM has several advantages: the increase of the heat transfer area, the reduction of the reactivity towards the external environment and a better control of the volume variation as the phase change occurs [41]. Thermal cyclic tests also show that the geometrical profile and energy storage capacity of encapsulated paraffin is stable even after 1000 cycles of operation [40]. These PCM show low corrosion and toxicity over an adequate chemical stability up to 250°C.

In this report the effects of microencapsulated paraffin based PCM on the thermal and mechanical properties of PMMA/PCM composites are investigated and compared to PMMA/PCL formulations. The advantages of loading PMMA with materials which show the capability to storage and release thermal energy around body temperature are spotlighted.

Materials and methods

Table 1 reports the % composition by weight of the investigated PMMA/PCM composites.

The control group is the composition of the commercial bone cement PalamedG® (Biomet Merk, Germany). In group 1–4 microencapsulated PCM (Thermasorb TY95®, Frisby Technologies, Inc., Advance, NC) are finely mixed with the cement powder. The weights of constituent materials have been measured using a Mettler AE240 balance (Mettler Toledo, Highstown, USA) and reported in Table 1. Basically Group 1, Group 2 and Group 3 composition have been obtained by adding 10%, 20% and 30% by weight of PCM to the cement powder respectively.

Calorimetric properties are measured using a differential scanning calorimeter (DSC) TA 2920 (TA Instruments, New Castle, Canada). The polymerisation of PMMA and PMMA composites listed in Table 1 is carried out in the DSC chamber through an isothermal conditioning at 20°C for 1 hour, hence heating and cooling dynamic scans are executed between 0°C and 180°C at a rate of 10°C/min. Materials are gently hand mixed for 5min before pouring in the DSC capsule. Five specimen have been used for each sample depicted in Table 1.

Non-isothermal tests are carried out using a closed cylindrical poly(tetrafluoroethylene) reactor with an inner diameter of 40 mm and a thickness of 15 mm. About 20 g of

Table 1 %ww composition of the investigated cements. Group 1, Group 2 and Group 3 composition have been obtained by adding 10%, 20% and 30% by weight of PCM to the cement powder respectively

	Control	Group 1	Group 2	Group 3	Group 4
Powder					
PMMA beads	60.09	56.14	52.67	49.60	42.07
Zirconium dioxide	8.29	7.74	7.26	6.84	5.80
BPO	0.69	0.65	0.60	0.57	0.48
Gentamicin sulphate	1.44	1.35	1.27	1.19	1.01
PCM	–	6.58	12.35	17.47	21.15
Liquid					
MMA	28.88	26.98	25.32	23.84	28.88
DMPT	0.60	0.56	0.52	0.49	0.60
Chlorophylin	$6{\cdot}10^{-4}$	$6{\cdot}10^{-4}$	$5{\cdot}10^{-4}$	$5{\cdot}10^{-4}$	$6{\cdot}10^{-4}$

dough material is poured into the reactor and the temperature in the middle point is measured using *K*-type thermocouples, the 6B11 conditioners (National Instruments Corp.) and the Lab View 7.1 software. Temperature is acquired at a rate of 1pt/sec. Two replicates have been carry out for the Control, Group 1, Group 2 and Group 3 samples.

Mechanical testing is performed using the three point bending method according to ASTM-D790. The Enduratec ELF3200 (Bose Corp., USA) electromagnetic dynamometer is adopted in the displacement control mode set at 1mm/min. Test are carried out at room temperature.

Each bone cement dough depicted in Table 1 is poured into moulds of rectangular cross section (125 × 50 × 2.5 mm) and a pressure of 0.02 MPa is maintained during PMMA curing. PMMA sheets are kept at room temperature for 24 h to allow full polymerization and then machined into 25 × 50 × 2.5 mm specimens with a low speed diamond wheel saw (Isomet, Buehler Ltd., Illinois, USA) cooled by chilled water. Specimens are mechanically tested after 1 month of conditioning at room temperature in a dry environment in order to allow the release of unreacted monomer. Seven specimens have been tested for each sample depicted in Table 1. The results are analyzed using the one-way Anova variance test.

Results

The isothermal polymerisation at 20°C of Group 1–4 composites (see Table 1) suggests that the effect of the PCM amount is a slight decrease of exothermal energy and setting time. The lower BPO/DMPT ratio (group 4 specimens) has produced a delay up to 20 min of the setting process.

By comparing the first and second temperature scans, performed immediately after the isothermal polymerisation at 20°C, the exothermal reaction due to the unreacted monomer is always well detectable for every specimen. Thus the polymerisation process does not reach the completion through an isotherm curing at 20°C for 60 min. In Fig. 1 the control and Group 3 samples first and second scan are reported as an example. The plain cement (control group) develops an exothermal energy of 27.1 J/g mean value which results apparently higher than the energy measured for each PMMA/PCM composite.

The phase change of the microencapsulated paraffin material is shown through Figs. 1 to 3, where a well detectable melting process occurs during a temperature interval centred at about 37°C. The melting heat of PCM is 166 J/g (Fig. 2) which results higher than that of PCL (about 54 J/g). During the first temperature scan the temperature interval in which

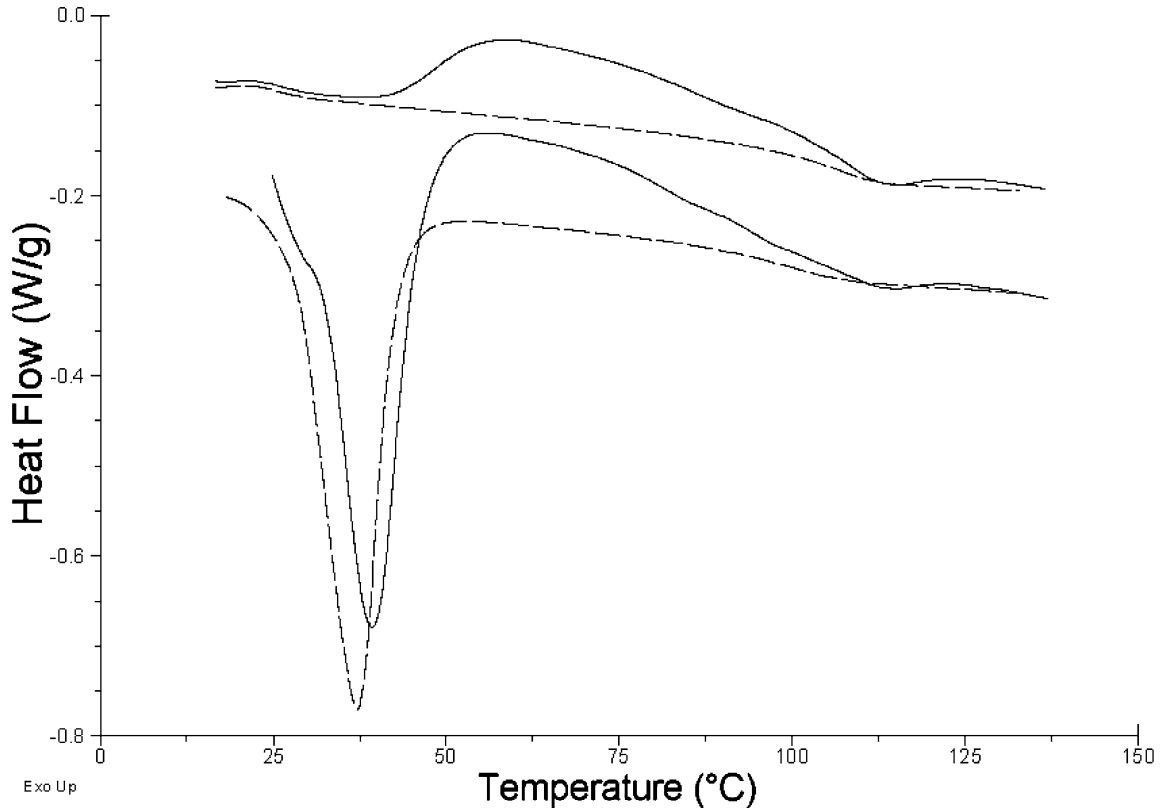

Fig. 1 First (—) and second (--) temperature scans for the control (upper curves) and Group 3 (lower curves) samples. The PCM melting and the exothermal reaction due to the unreacted monomer are well detectable

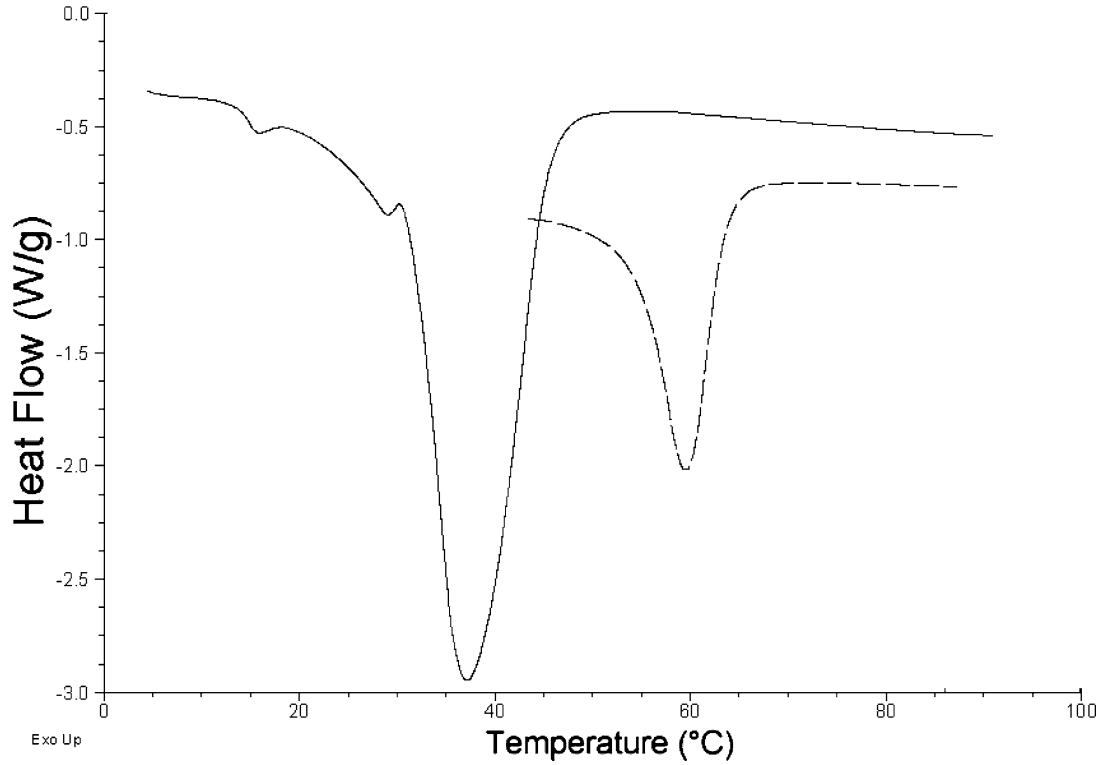

Fig. 2 First temperature scan of PCM (—) and PCL (--). The melting heat of PCM is higher than PCL by a factor of 3

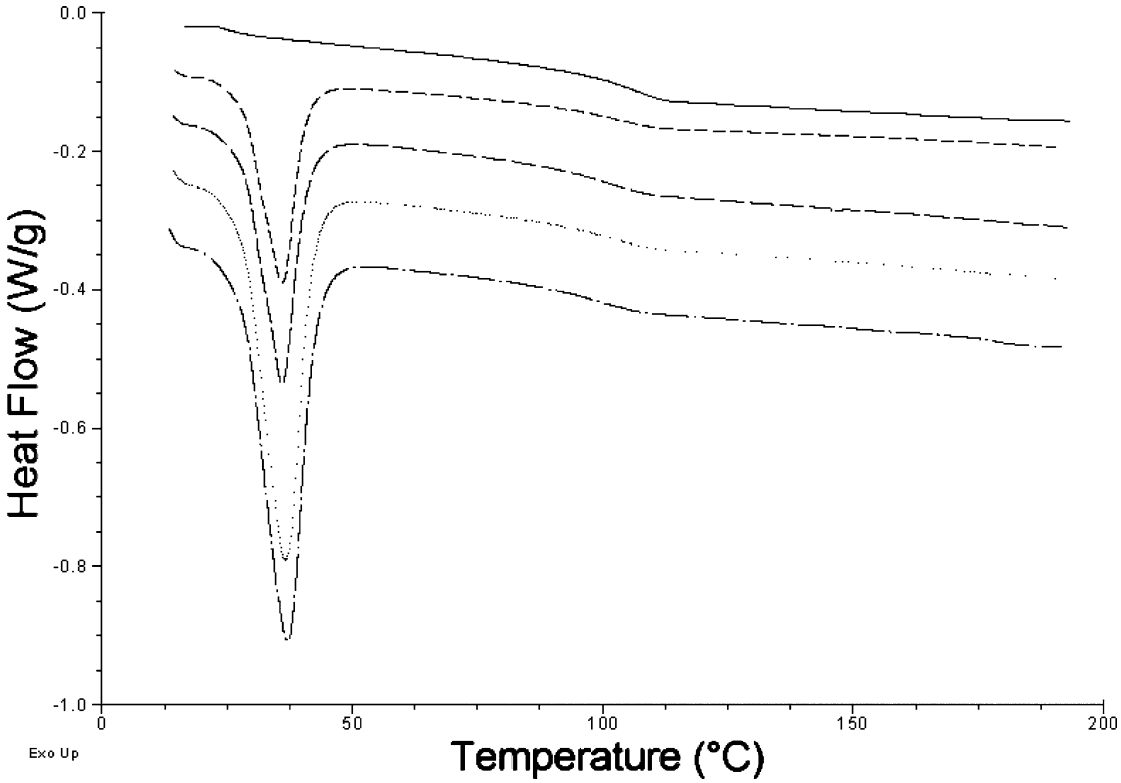

Fig. 3 Second temperature scan of PMMA Control (—) and PMMA/PCM composites: Group 1 (---), Group 2 (— —), Group 3 (· · · ·) and Group 4 (— -). The capability of the PMMA/PCM composites to absorb or release thermal energy is enhanced by the increase of the PCM amount. A small variations of the Tg with the amount of PCM is found

Table 2 Calorimetric properties measured in the second temperature scan. The thermal regulating capability spans around body temperature absorbing or releasing a thermal energy up to 30 J/g. A small variations of the Tg with the amount of PCM is found

	Melting temperature (°C)	Heat of fusion (J/g)	Glass transition (°C)
PCL	54	50	
PCM	37.1	150	
Control	–	–	110.6
Group 1	36.5	10	108.9
Group 2	36.1	18	107.7
Group 3	36.6	27	107.5
Group 4	36.4	30	108.0

the endothermic heat flow takes place (Fig. 1) is slightly shifted to values lower than those obtained during the second scan (Figs. 1 and 3). Also, the second temperature scan of each composite specimens (Figs. 1 and 3) suggests that the temperature at which the heat flow reaches the maximum is lower than that measured for the plain PCM (Fig. 2).

The effect of the PCM phase on the calorimetric properties of the PMMA/PCM composites are depicted from Fig. 3, and the calorimetric DSC measurements of the investigated materials are listed in Table 2. The capability of the PMMA/PCM composites to absorb or release thermal energy is enhanced by the increase of the PCM amount with an almost proportional rule at least up to 30%ww of PCM (Fig. 3 and Table 2).

The PCM phase has a negligible effect on the glass transition temperature (Tg) which ever is its amount (Fig. 3 and Table 2), thus suggesting an incompatibility between PCM and PMMA.

The exothermal reaction of the investigated cement formulations is shown in Fig. 4. The starting temperature of the control group is slightly higher than the other groups, suggesting that the polymerisation reaction is already started after 2 min (mixing duration of the powder and the reactive monomer solution). A significant delay in the polymerisation process ($p < 0.01$) and a significant reduction of the peak bulk temperature ($p < 0.05$) are found by increasing the amount of PCM.

The mechanical properties in bending are depicted through Fig. 5 and Table 3. Experimental results for the plain cement of the Young's elastic modulus (E) and the stress and strain values of the maximum point (Fig. 3) are consistent

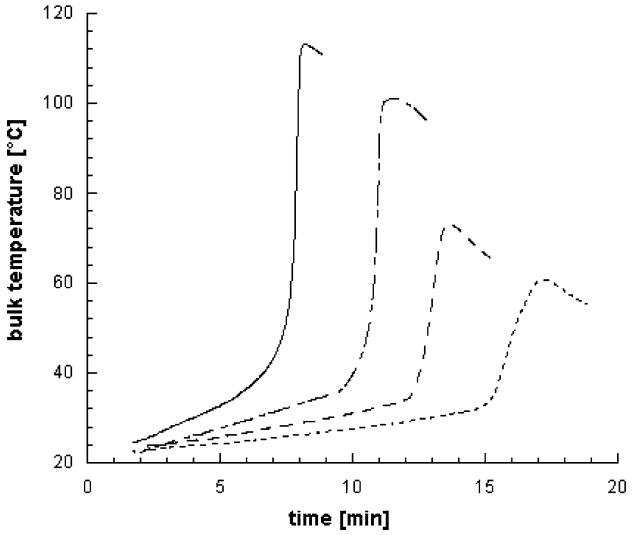

Fig. 4 Exothermal reation of of PMMA Control (—) and PMMA/PCM composites: Group 1 (— -), Group 2 (---) and Group 3 (· · · ·). By increasing the PCM amount a decrease of the temperature peak in the bulk of the cement is found. Particularly this reduction is 50% for Group 3 specimens

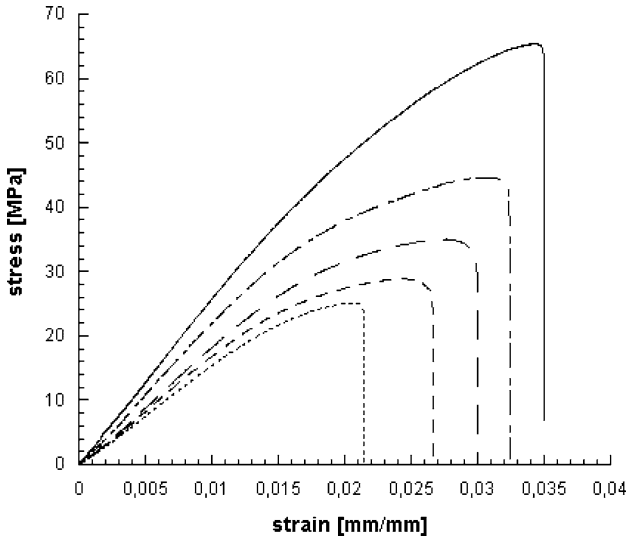

Fig. 5 Three point bending behvior: Control (—), Group 1 (— -), Group 2 (— —), Group 3(----) and Group 4 (· · · ·). The reduction of the bending properties is more marked for the maximum stress, this weakening effect may be related to the encreased brittlness due to an encreased porosity of the material

Table 3 Mean values and standard deviations of the mechanical properties in bending E is the Young's modulus, σ_{max} and ε_{max} are the maximum stress and strain respectively

	E (GPa)	σ_{max} (MPa)	ε_{max} (mm/mm)%
Control	2.61 (0.16)	66.1 (1.4)	3.50 (0.08)
Group 1	2.25 (0.12)	44.7 (2.5)	3.20 (0.18)
Group 2	1.95 (0.08)	35.5 (1.8)	2.72 (0.09)
Group 3	1.79 (0.07)	30.5 (1.7)	2.45 (0.10)
Group 4	1.58 (0.06)	24.8 (1.6)	2.02 (0.09)

with the bending modulus and strength reported for the same cement stressed by using the 4-point bending test [14]. A decrease of all the mechanical properties is found by increasing the PCM amount, and the difference between the mean values is always statistically significant ($p < 0.01$).

An almost linear trend *vs* PCM amount is found for the Young's modulus and the maximum strain (the correlation coefficient being 0.99), however the rate of decrease of the maximum strain is higher than that of the Young's modulus. Instead, a logarithmic trend is found to be more appropriate to describe the maximum stress behaviour. Therefore, PCM amount lower as 10% mainly decrease the bending strength rather than the elastic modulus.

Discussions

Partial replacement of the solid or liquid phase of materials like bone cements is the main tool available to researchers focused on the enhancement of the thermo-mechanical performances of PMMA based biomaterials through a material design.

Although the main feature of PCL is its bio-degradability capability, PCL is also attractive because it shows good mechanical properties and an easy miscibility with many engineering polymers.

Thermal necrosis due to the *in situ* polymerisation is a potential drawback of bone cements and injected methacrylate based materials [43]. PCL, when used as PMMA modifier, is also expected to reduce the temperature during the *in situ* setting [33]. Data based on measurements using non-isothermal polymerisation [43, 44] through the same reactor used in this study suggests that the reduction of the temperature may be up to 10% by adding 20%ww of PCL to the monomer reactive solution [45]. This capability being related to the phase change of PCL; the physical state of the material will gradually change from solid to liquid with the absorption of heat, while the temperature stays constant until all the solid PCL phase is melted. Thus, the energy of this endothermic process delays and compensates the heat developed during the polymerisation of the PMMA phase.

The capability of PCM materials to absorb or to release thermal energy, as shown by the microencapsulated paraffin used in this report, is of course more interesting. In fact, the melting heat of PCM is higher than PCL (Fig. 2) by a factor of 3, thus smaller amounts of PCM are required in order to lower the temperature peaks during the PMMA polymerisation process. Figure 4 clearly shows the effect of the PCM melting phase during the first stage of polymerisation up to 40°C; the slope of the time-temperature profile decreases by increasing the amount of PCM. This effect is due to the heat absorbed by the PCM and to the reduced diffusion capability of the monomer in the presence of small PCM particle size with relatively large surface area. By increasing the PCM amount a decrease of the temperature peak in the bulk of the cement is found. Particularly this reduction is 50% for Group 3 specimens. Thus, in clinical trials, the lower exotherm will benefit the biocompatibility of the cement. However, a balance needs to be found between the desired thermal effect of PCM (Fig. 4) and the mechanical properties (Fig. 5) according to the specific application of the cement.

Another advantage of the PCM is that the melting temperature of PCM can be varied between –60°C and 80°C, thus providing a thermo-regulating capability over a wide range. In this report the melting point of the microencapsulated PCM is centred at about 37°C. This choice is based on a thermo-regulating effect designed around body temperature which would prevent thermal shocks of the hosting tissues whatever if the PMMA/PCM is used as bone cement or as a scaffold. In fact, the material is designed in order to absorb energy from the environment if a heating process takes place, while releasing energy in a cooling process in which the heat flow exothermal peak is centred at about 25°C. Thus the material is active against heating (i.e. exothermal polymerisation of PMMA, thermal shocks, inflammatory response of the hosting tissue) and cooling of the implanted biomaterial. The thermal regulating capability spans around body temperature absorbing or releasing a thermal energy up to 30 J/g. Therefore, a thermal comfort effect of the implanted material is available for the hosting tissue in the same fashion by which PCM modified textile and clothing provide to the skin [37].

The small variations of the Tg as PCL or PCM is added in the liquid phase or solid phase respectively (Fig. 3 and Table 2) imply an incompatibility between PMMA, PCL and PCM. This result has already been reported for PMMA/PCL blends [30] where a phase segregation between the materials has been suggested.

The first temperature scan of every cement composition clearly indicate the presence of unreacted monomer into the material. The drastic effect of MMA on both the mechanical [15] and the biocompatibility [24, 46] properties of *in situ* polymerised cements is another very well known drawback.

By comparing the first and second temperature scan of PMMA/PCM specimens a small change of the melting temperature of the PCM phase is also evident (Figs. 1 and 3). Moreover, an apparent lower melting heat of fusion is measured during the first temperature scan. These variations are mainly due to a compensation effect on the total heat flow provided by the residual MMA esothermal reaction (not-reversible) which is already active before the PCM phase change ends. On the other hand, the values for the exothermal heat measured for the PMMA/PCM specimens (Fig. 1) are apparently lower than those measured for the control group

specimen during the first temperature scan; this effect can be ascribed to the energy absorption of the PCM phase during the esothermal heat developed by the unreacted MMA phase. Thus, further research is needed in order to assess the effects of PCM on the polymerisation degree of the PMMA matrix; the total heat flow measurements need to be separated into its reversible (PCM melting heat) and not-reversible (the kinetic reaction) components [47].

Mechanical results clearly show that a reduction of the bending properties is obtained by adding an amount of micro-encapsulated PCM higher than 10%ww to the cement powder. The decrease is more marked for the maximum stress, this weakening effect may be related to the increased brittleness due to an increased porosity of the material. In fact, the poor chemical and physical interaction between the PMMA matrix and the PCM beads (shown through the calorimetric analysis) and the volume expansion of the PCM phase [48, 49] as the polymerisation process of PMMA takes place and the subsequent shrinkage during cooling, contribute to form a void loaded structure. The notch effect of voids due to the air trapped in the setting phase of bone cements is notorious [46].

On the other hand, it is remarkable that the geometrical constraint of the polymerisation process related to injected applications is not based on the free volume condition; mechanical specimens have been obtained through constant stress (pressure) condition, while in clinical trials the bone's boundary walls limit the volumetric change. The shrinkage effect of bone cements and denture acrylic based filling materials on the interface properties with hard tissues (e.g. residual stress and gap) have been largely documented [50, 51]. Therefore, the expansion of the PCM phase is likely to be overcame in order to compensate the shrinkage of *in situ* setting cements and thus enhancing the mechanical interface properties.

Conclusions

PCL and paraffin based PCM can be successfully implemented into PMMA to form composite materials for biomedical application with enhanced thermal properties.

The endothermal effect can be conveniently used to reduce the temperature peaks due to the exothermal polymerization of PMMA. Thus, the materials are particularly interesting for *in situ* setting of PMMA. By using micro-encapsulated PCM with a melting and freezing phase changes positioned above and below the body temperature, it is possible to provide the function of being active against the effects due to thermal shocks.

These materials are particularly attractive for the design of scaffolds characterised by enhanced thermal regulating capability and interface mechanical properties.

Acknowledgments Mr. Rodolfo Morra and Dr. Antonio Gloria are acknowledged for the mechanical measurements and Mario De Angioletti for the calorimetric measurements. The authors also wish to thank Prof. Dante Ronca for the material supply and for useful discussions. The financial support of CRdC of regione Campania and the Cluster C/26 project "biomateriali in funzione applicativa" are gratefully acknowledged.

References

1. C. MIGLIARESI and L. NICOLAIS, *Int. J. Artif. Organs* **3** (1980) 114.
2. E. W. MORSHER and D. WIRZ, *Acta Orthop. Belg*. **68** (2002) 1.
3. K. SUN and M. A. K. LIEBSCHNER, *Annals Biom. Eng*. **32** (2004) 77.
4. R. GARCIA, B. VAZQUEZ and J. SAN ROMAN, *J. Biomed. Mat. Res Part B:Appl. Biomat.* **68** (2004) 94.
5. L. CHIARINI, S. FIGURELLI, G. POLLASTRI, E. TORCIA, F. FERRARI, M. ALBANESE and P. F. NOCINI, *J. Cranio-Maxillofacial Surg.* **32** (2004) 5.
6. J. KOST and R. LANGER, *Adv. Drug Deliv. Rev.* **46** (2001) 125.
7. A. S. HOFFMAN, *ibid.* **43** (2002) 3.
8. I. ESPIGARES, C. ELVIRA, J. F. MANO, B. VAZQUEZ, J. S. ROMAN and R. L. REIS, *Biomaterials* **23** (2002) 1883.
9. T. V. CLEYNENBREUGEL, H. V. OOSTERWYCK and J. V. SLOTEN, *J. Mat. Sci. Mat. Med.* **13** (2002) 1245.
10. J. A. MENDEZ, M. R. AGUILAR, G. A. ABRAHAM, B. VAZQUEZ, M. DALBY, L. DI SILVIO and J. S. ROMAN, *J. Biomed. Mat. Res.* **62** (2002) 299.
11. A. STREUBEL, J. SIEPMANN and R. BODMEIER, *Int. J. Pharm.* **241** (2002) 279.
12. J. L. SANCHEZ, G. GUY, J. A. VAN KAN, T. OSIPOWICZ and F. WATT, *Nucl. Instr. Meth. Phys. Res.* B **158** (1999) 185.
13. R. DE SANTIS, F. SARRACINO, F. MOLLICA, P. A. NETTI, L. AMBROSIO and L. NICOLAIS, *Comp. Sci. Tech.* **64** (2004) 861.
14. K. D. KUHN, in "Bone Cements" (Spinger-Verlag, Heidelberg, 2000).
15. R. DE SANTIS, F. MOLLICA, D. RONCA, L. AMBROSIO and L. NICOLAIS, *J. Mat. Sci. Mat. Med.* **14** (2003) 83.
16. N. J. DUNNE and J. F. ORR, *ibid.* **13** (2002) 17.
17. E. J. HARPER and W. BONFIELD, *J. Biom. Mat. Res.* **53** (2000) 605.
18. S. M. KENNY and M. BUGGY, *J. Mat. Sci. Mat. Med.* **14** (2003) 923.
19. J. A. BURDICK, A. J. PETERSON and K. S. ANSETH, *Biomaterials* **22** (2001) 1779.
20. N. J. DUNNE and J. F. ORR, *ibid.* **22** (2001) 1819–1826.
21. D. F. FERRAR and J. ROSE, *ibid.* **22** (2001) 3005.
22. M. P. GINEBRA, L. ALBUIXECH, E. F. BARRAGAN, C. APARICIO, F. J. GIL, J. SAN ROMAN, B. VAZQUEZ and J. A. PLANELL, *ibid.* **23** (2002) 1873.
23. R. P. DEL REAL, S. PADILLA and M. VALLET-REGI, *J. Biomed. Mat. Res*. **52** (2000) 1.
24. C. V. RAGEL and M. VELLET-REGI, *ibid.* **51** (2000) 424.
25. M. J. DALBY, L. DI SILVIO, E. J. HARPER and W. BONFIELD, *Biomaterials* **22** (2001) 1739.

26. L. F. BOESEL, M. H. V. FERNANDES and R. L. REIS, *J. Biomed. Mat. Res. Part B: Appl. Biomaterials*. **70** (2004) 368.
27. J. L. GILBERT, D. S. NEY and E. P. LAUTENSCHLAGER, *Biomaterials* **16** (1995) 1043.
28. C. I. VALLO, G. A. ABRAHAM, T. R. CUADRADO and J. S. ROMAN, *J. Biomed. Mat. Res. Part B: Appl. Biomaterials*. **70** (2004) 407.
29. M. F. KOENIG and S. J. HUANG, *Polymer* **36** (1995) 1877.
30. S. J. HUANG, M. F. KOENIG and M. HUANG, in "Biodegradable polymers and packaging," edited by C. Ching, D. L. Kaplan and E. L. Thomas (Technomic, Lancaster, PA, 1993) p. 97.
31. P. A. DAVIS, S. J. HUANG, L. AMBROSIO, L. NICOLAIS and D. RONCA, "A Biodegradable Composite Artificial Tendon", *J. Mat. Sci. Mat. Med*. **3** (1992) 359.
32. G. PELUSO, O. PETILLO, J. M. ANDERSON, L. AMBROSIO, L. NICOLAIS, M. A. B. MELONE, F. O. ESCHENBACH and S. J. HUANG, *J. Biomed. Mat. Res.* **34** (1997) 327.
33. G. A. ABRAHAM, A. GALLARDO, A. MOTTA, C. MIGLIARESI and J. S. ROMAN, *Macromol. Mater. Eng.* **282** (2000) 44.
34. G. A. ABRAHAM, A. GALLARDO, J. SAN ROMAN, A. F. MAYORALAS, M. ZURITA and J. VAQUERO. J, *J. Biomed. Mat. Res.* **64** (2003) 638.
35. J. A. MENDEZ, G. A. ABRAHAM, M. FERNANDEZ, B. VAZQUEZ and J. S. ROMAN, *ibid.* **61** (2002) 66.
36. G. A. ABRAHAM, C. I. VALLO, J. S. ROMAN and T. R. CUADRADO, *J. Biomed. Mat. Res. Part B: Appl. Biomat*. **70** (2004) 340.
37. B. YING, Y. KWOK, Y. LI, Q. ZHU and C. YEUNG, *Polymer Test.* **23** (2004) 541.
38. U. STRITIH, *Energy Build*. **35** (2003) 1097.
39. B. HE and F. SETTERWALL, *Energy Conv. and Manag*. **43** (2002) 1709.
40. M. N. A. HAWLADER, M. S. UDDIN and H. J. ZHU, *Int. J. Energy Res.* **26** (2002) 159.
41. M. M. FARID, A. M. KHUDHAIR, S. A. K. RAZACK and S. AL-HALLAJ, *Energy Conv. Manag.* **45** (2004) 1597.
42. C. LI, J. MASON and D. YAKIMICKI, *J. Mat. Sci. Mat. Med.* **15** (2004) 85.
43. A. MAFFEZZOLI, D. RONCA, G. GUIDA, I. POCHINI and L. NICOLAIS, *ibid.* **8** (1997) 75.
44. A. BORZACCHIELLO, L. AMBROSIO, L. NICOLAIS, E. J.HARPER, K. E.TANNER and W. BONFIELD, *ibid.* **9** (1998) 317.
45. R. DE SANTIS, V. AMBROGI, C. CARFAGNA, L. AMBROSIO and L. NICOLAIS, in "Proceeding of the 10th International Conference on Polymers in Medicine and Surgery" (Cambridge, Sept. 2004).
46. G. LEWIS, *J. Biomed. Mat. Res.* **38** (1997) 155.
47. G. A. ABRAHAM, K. KESENCI, L.FAMBRI, C. MIGLIARESI, A. GALLARDO and J. SAN ROMAN, *Macromol. Mater. Eng.* **287** (2002) 938.
48. H. BO, E. M. GUSTAFSSON and F. SETTERWALL, *Energy* **24** (1999) 1015.
49. Z. GU, H. LIU and Y. LI, *Apll. Therm. Eng.* **24** (2004) 2511.
50. A. M. AHMED, W. PAK, D.L. BURKE and J. MILLER, *J. Biomech. Eng.* **104** (1982) 21.
51. A. B. LENNON and P. J. PRENDERGAST, *J. Biomech.* **35** (2002) 311.