Full Paper: Poly(methyl methacrylate) – polycaprolactone (PMMA/PCL) microheterogeneous beads were synthesized by suspension polymerization starting from methyl methacrylate (MMA) monomer and PCL, which was synthesized by ring-opening polymerization of ε-caprolactone using $ZnCl_2$ as initiator. The resulting polymer was fully characterized by ^{1}H and ^{13}C NMR, differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and dynamic mechanical thermal analysis (DMTA). The size distribution and morphology of the resulting beads were investigated by optical microscopy and scanning electron microscopy (SEM). Moreover, blends of PMMA beads and PCL in different proportions were prepared and the morphology of the films was examined by optical microscopy. The low compatibility between PMMA and PCL was clearly evidenced through these experiments.

SEM micrograph of PMMA/PCL beads containing 10.9% PCL (sample B).

Microheterogeneous polymer systems prepared by suspension polymerization of methyl methacrylate in the presence of poly(ε-caprolactone)

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Introduction

Bone cement, widely used in orthopedics for the fixation of joint prostheses, is mostly made by completing in situ the polymerization of methyl methacrylate (MMA), added with PMMA powder, spherical beads with diameters ranging from approximately 10 to 100 micrometers, and by using benzoyl peroxide and tertiary amines as catalyst. It was also reported the use of amines with low toxicity, such as dimethylaminobenzyl alcohol (DMOH).[1] The addition of PMMA to the monomer, usually in the weight ratio 2:1, is needed in order to reduce polymerization temperature and volume shrinkage occurring during polymerization, while adjusting the cement viscosity and reaction kinetics. PMMA beads, in fact, partially dissolve in the monomer, so that at the end the cement is a blend of poly(methyl methacrylate) beads included in a matrix of the newly-formed PMMA polymer. Beads content and size distribution plays a major role in the control of the cement reaction

kinetics and properties, and, in this sense, the suspension polymerization method leads to the fabrication of polymer particles with appropriate size and shape that contribute to form a uniform paste.

Although PMMA based bone cement has widespread use, the literature reports contrasting opinions about its responsibility in causing the failure of an implanted prosthesis, mainly in the case of hip prostheses.[2]

Efforts for improving the mechanical properties of bone cements have focused in different directions, enhancing existing cements rather than developing new cements. The modification of PMMA was tried for years. Some attempts were directed towards polyurethanes based on poly(ether glycol)s as modifiers.[3,4] The use of a lower modulus cement as matrix material based upon poly(ethyl methacrylate)[5] and poly(butyl methacrylate)[6] have been other alternative approaches to modify the properties of this material.

Tab. 1. Composition, average diameter, stirring rate and yield of the synthesized beads.

Sample	Initial solution	Average diameter (μm)	Stirring rate (rpm)	Yield [a] (%)	Composition [b] (wt.-%) PCL	Theoretical composition [c] (wt.-%) PCL
A	MMA	14.2 ± 8.6	600	60.0	–	–
B	MMA + 10% PCL	58.0 ± 28.6	600	86.7	10.9	9.1
C	MMA + 20% PCL	136.4 ± 63.8	600	99.8	16.8	16.7
D	MMA + 30% PCL	129.0 ± 83.5	600	99.9	23.5	23.1
E	MMA + 15% PCL	21.0 ± 11.1	1 000	45.4	16.6	13.1

[a] Value relative to beads production (in some cases lower than the polymerization yield because of the foam formation).
[b] Determined by NMR.
[c] Defined as weight of PCL by 100 g of beads.

Polycaprolactone (PCL), which has proven to be a good modifier of poly(vinyl chloride),[7] was investigated in the preparation of PCL/PMMA crosslinked polymers via concentrated emulsion polymerization method.[8]

It has been also reported the formation of crosslinked copolymers and semi-interpenetrating or interpenetrating polymer networks in reactive blends of PCL/MMA[9, 10] and PCL/PHEMA systems[11] by using peroxide initiators as radical source. In this paper, we present the synthesis and extensive characterization of PMMA/PCL microheterogeneous beads obtained by suspension polymerization. The morphology of the beads, visualized by scanning electron microscopy (SEM), is shown and discussed. Such beads could be of interest for the formulation of MMA based bone cements with improved toughness. This matter is being investigated at present.

Experimental part

Materials

ε-Caprolactone (Merck-Schuchardt) was distilled under vacuum, zinc chloride (Probus) was dried under vacuum during 24 h and toluene (Merck) was used as received. Methyl methacrylate 99% (MMA) was purchased from Acros Organics and used without removing the stabilizer, poly(vinyl alcohol) (PVA, ERT Spain) ($\overline{M}_n = 50\,000$, 99% hydrolyzed) was used as suspension agent and recrystallized benzoyl peroxide (BPO) from Fluka as radical initiator.

Synthesis of polycaprolactone

In a previous work we have reported the synthesis of PCL by ring-opening polymerization of ε-caprolactone, which was successfully performed by using ZnCl$_2$ as initiator in toluene solution.[12] Briefly, anhydrous ZnCl$_2$ was first dissolved in toluene under stirring and ε-caprolactone was then added, monomer/initiator mole ratio 60:1. The flask was immersed into a thermostated heating bath at the solvent boiling temperature (110 °C). The product was collected after 72 h and

the polymer was isolated by pouring into a excess of ethanol, filtered and exhaustive drying at vacuum (reaction yield = 97%). The resulting polymer showed a $\overline{M}_n = 45\,000$.

Preparation of PMMA-PCL beads and PMMA-PCL films

Different percentages of PCL (i.e., 10, 15, 20 and 30% wt/wt of monomer) were first dissolved in methyl methacrylate (50 g) under vigorous stirring. The initiator (1.5% wt/wt) was then dissolved in the mixture. Polymerization was carried out by suspension polymerization method in a 250 mL three neck flask fitted with a mechanical stirrer, nitrogen inlet and condenser. Distilled water 2% poly(vinyl alcohol) solution (100 mL) was first introduced into the reactor, as suspension agent, heated to 65 °C (reaction temperature), stirred at 600 rpm and flushed with nitrogen for 10 min. The reactive phase (MMA/PCL and initiator) was introduced into the reactor in a stepwise, the reaction was carried out at this temperature for 4 h, and then temperature was increased to 80 °C allowing the polymerization reaction to be completed after 2.5 h. The reaction product, spherical beads, was exhaustively washed with water and dried under vacuum for 24 h. Samples without PCL were also prepared. The stirring rate as well as the concentration of the suspension agent were also varied in order to investigate the effect of these parameters on the polymerization yield and final composition. Tab. 1 shows the experimental conditions, composition and yield of the synthesized beads.

PMMA/PCL blends were also prepared with a wide range of PCL content. Therefore, PMMA beads and PCL were dissolved in boiling dioxane, a mutual solvent. The resulting homogeneous solution was used to obtain films with different compositions of PCL (i.e., 0, 20, 40, 60, 80, 90 and 100%) by solvent casting onto glass plates. These films were dried at room temperature under vacuum to remove the residual solvent and ready to be examined by optical microscopy.

Methods

Differential scanning calorimetry (DSC) experiments were carried out in a Mettler DSC30 calorimeter equipped with a

controlled cooling accessory. Two scans were performed by using a 10 °C/min heating rate and a 320 °C/min cooling rate (quenching) between runs. Thermograms were obtained in the range −100 to 200 °C under nitrogen purge. The sample cell was previously calibrated with indium. The glass transition temperature (T_g) was taken at the onset of the transition.

^{1}H and ^{13}C NMR spectra were recorded in a Varian XLR-300 NMR spectrometer operating at 75.5 MHz for ^{13}C and 300 MHz for ^{1}H measurements. All spectra were obtained at room temperature from 5% (wt/v) CDCl$_3$ solutions for ^{1}H analysis and 25% (wt/v) for ^{13}C analysis, using in this case a delay time between pulses of 2 s.

Molecular weight distributions were determined by using a Perkin Elmer gel permeation chromatograph equipped with a refractive index detector series 200. A set of 10^4 Å, 10^3 Å and 500 Å, 300 × 7.5 mm i.d. PL-gel columns conditioned at 25 °C were used to elute the samples of 10 mg/mL concentration at 1 mL/minHPLC-grade chloroform flow rate. The weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights were determined using a calibration curve with polystyrene standards.

Dynamical mechanical thermal analysis (DMTA) was performed in a MKII instrument (Polymer Laboratories, UK). Single cantilever bending experiments were carried out in the range of −100 to 150 °C at the constant heating rate of 3 °C/min, the strain was 64 μm and the frequency was fixed at 1 Hz. In comparison, tests have been also performed on samples molded by using commercially available PMMA beads, and namely Plexidon M449, by Rohm, Germany (viscosity number 145–175 ml/g). Rectangular specimens 12 mm wide, 1.6 mm thick, and a span length of 12 mm were used. Optical and scanning electron micrographs were obtained by using an eclipse E400 optical Nikon microscope (using polarized light and dark field) and a scanning electron microscope (SEM) Cambridge 440 Leika Stereoscan, respectively. For SEM, specimens were gold coated prior to examination, and images recorded on a computer for further analysis. The size distribution of the microspheres was determined by measuring the average diameter of the particles by means of a camera Nikon FDX-35 coupled to the optical microscope. The size and size distribution data were averaged after determination of the parameters of up to 100 particles randomly distributed in different images.

Results and discussion

Beads characterization

PMMA based beads were synthesized by suspension polymerization as described in the *Experimental part*. Materials loaded with polycaprolactone from 0 to 30% wt/wt of monomer were prepared covering the range of compositions of practical interest. Higher PCL contents were hardly dissolved or remained insoluble in the monomer. The composition of the synthesized polymers was determined by ^{1}H NMR. Fig. 1 shows the spectra of PCL and samples A to D. The percentile composition of PMMA and PCL present in samples B, C and D was approximately the same as the theoretical one. This
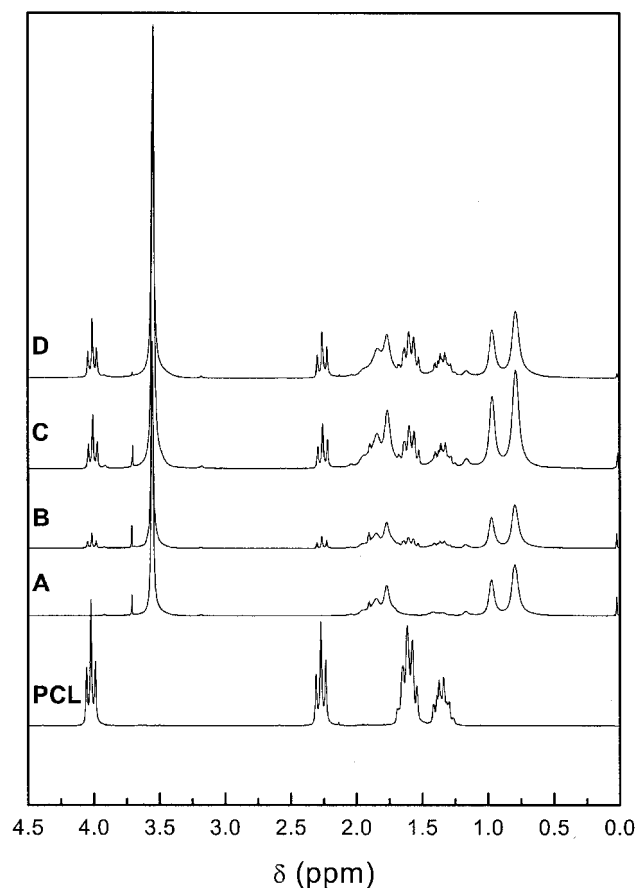

Fig. 1.   300 MHz ^{1}H NMR spectra of the synthesized polymers: samples A, B, C D, and PCL.

means that the incorporation of PCL into the beads was complete. The observation of signals of the monomer indicates the presence of a small amount of residual monomer which decreases with the PCL content. ^{13}C NMR spectra (not shown here) gave the typical signals of both polymers.

Molecular weight distributions measured by GPC are shown in Fig. 2. The chromatograms reveal a two-modal distribution, corresponding to both PMMA and PCL phases, confirming again the incorporation of the polycaprolactone to the PMMA matrix in the beads. The area under the PCL trace is in agreement with the amount of PCL incorporated into the beads, as determined by deconvolution and analysis of the two resulting curves. It was reported that PCL, in the presence of radicals, can be crosslinked. A very small fraction remained insoluble in CHCl$_3$ suggesting that a crosslinked graft copolymer could be produced by the formation of PCL macroradicals in the presence of the peroxide initiator and then given rise to grafted copolymers as it has been proposed in this reference. Moreover, when the peroxide concentration is increased (up to 40% wt/wt) the extension of the crosslinking reaction can be augmented, with a resulting decrease in crystallinity.[13]
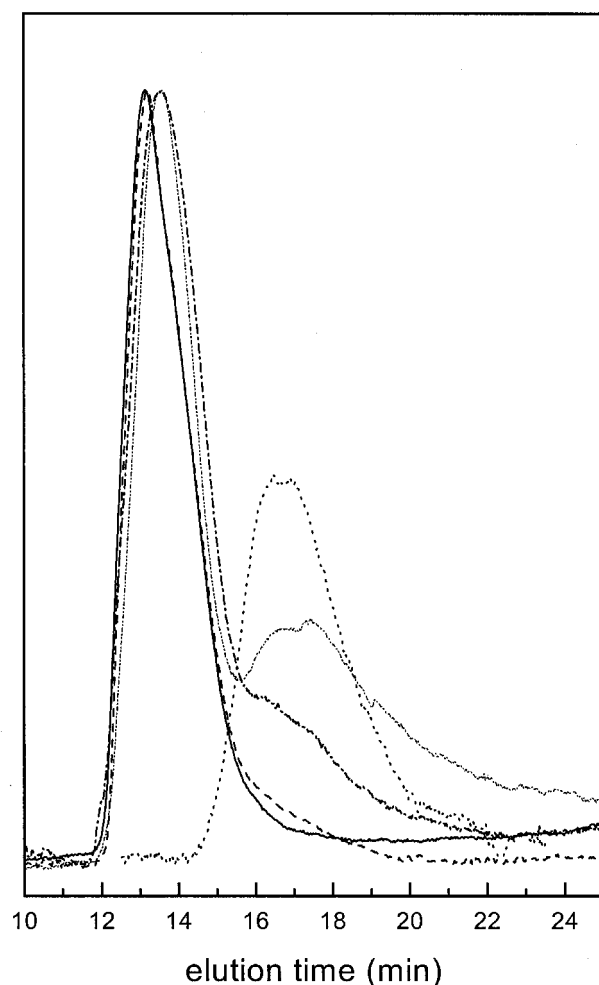
Fig. 2.   GPC chromatograms: (—) sample A; (- - -) sample B; (- · -) sample C; (- · · -) sample D; (· · ·) PCL.

Fig. 3.   Optical micrographs (× 40) and size distribution of samples A to E.

Fig. 3 shows optical micrographs of the different samples and its corresponding size distribution profiles. The average diameter of the beads clearly increases when PCL is incorporated. Moreover, there is a higher size dispersion when PCL load increases, leading in the case of sample D (30% of PCL) to a multimodal profile in the size distribution which is in agreement with the SEM analysis and could be related with the segregation of this two low compatible polymers. These bigger beads are not the most appropriate for the proposed use in the cement preparation but the size distribution can be adjusted by varying the stirring rate as it can be seen for sample E.

SEM pictures of the beads are reported in Fig. 4. Morphology patterns are quite complex, as a result of complexity of the MMA suspension polymerization and PCL melting-crystallization. In fact, the resulting morphology is the effect of several phenomena that occur in sequence, proceeding the MMA polymerization in presence of PCL. In the initial steps, droplets of the reactant solution of PCL in methyl methacrylate monomer are dispersed in the medium. As the polymerization proceeds, poly-
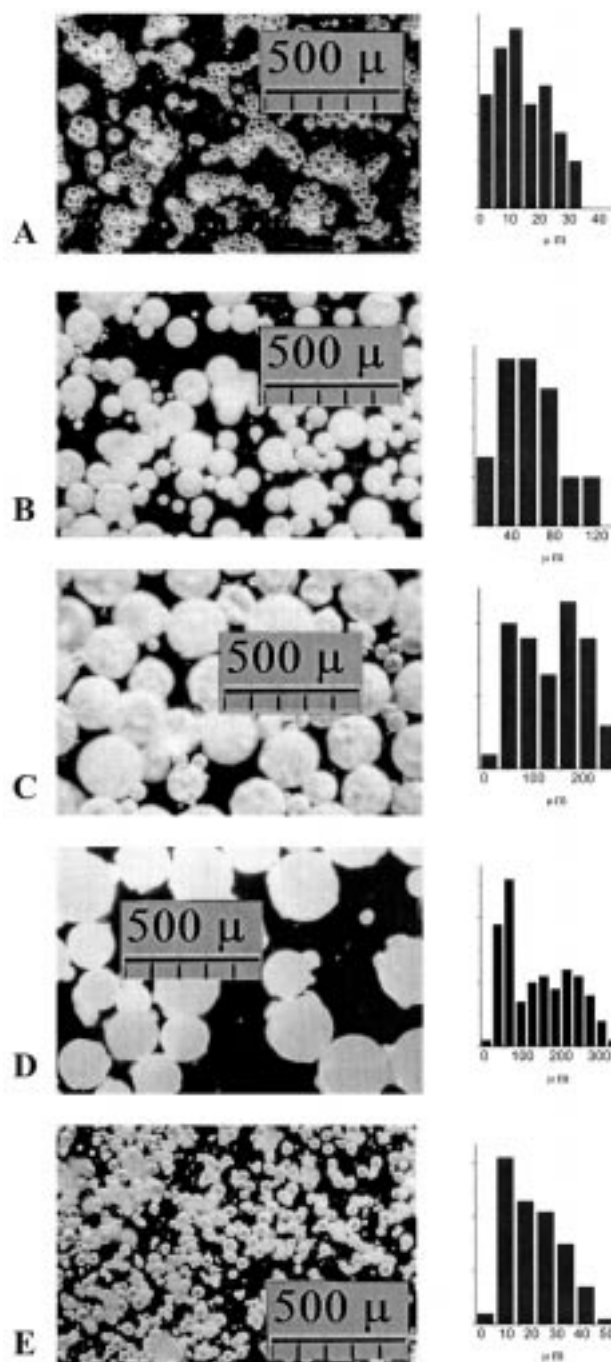
(methyl methacrylate) is formed and the homogeneous solution of MMA/PCL becomes a more concentrated solution of MMA/PCL/PMMA. The progress of the reaction gives a very concentrated solution of these three components and at a given ratio the PCL chains are not compatible with the polymerized PMMA chains giving rise to the segregation of the particles in microdomains. This is clearly shown in the SEM micrographs corresponding to samples B, C and D in Fig. 4. The result is
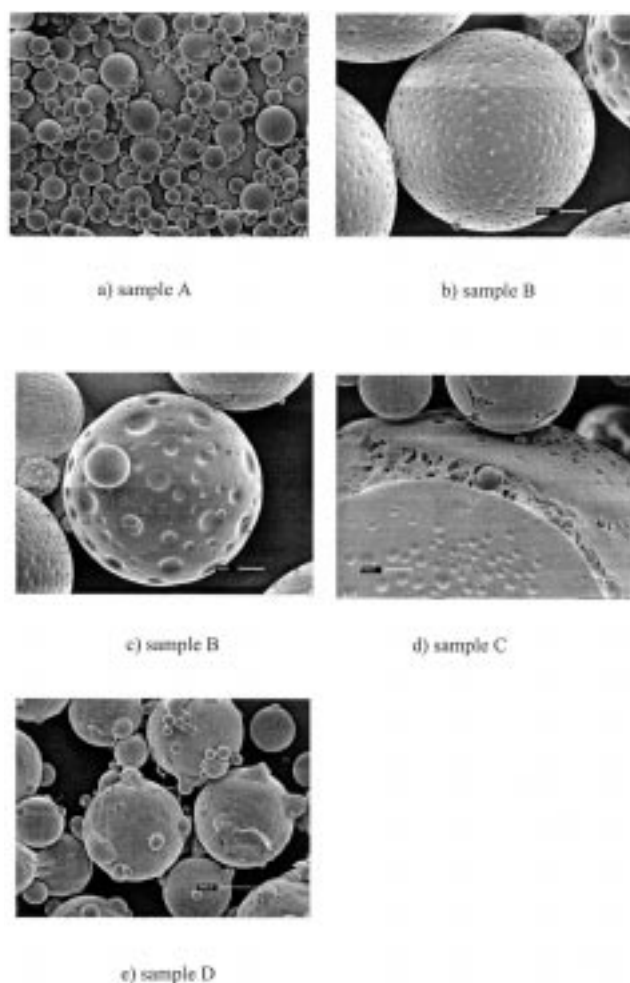
Fig. 4. SEM micrographs of beads: a) sample A; b) sample B; c) sample B; d) sample C; e) sample D.

Fig. 5. DSC thermograms (second run) of samples A, B, C, D, and PCL.

the formation of beads with a morphology determined by the presence of the PCL, which at the reaction temperature (65 °C) is beyond the melting point of the polymer. The interpretation and the description of this phenomenon would require a series of experiments quite complex and time consuming, that will be the object of a further publication.

Thermal properties

The microheterogeneous morphology of beads can be demonstrated by DSC and DMTA analysis. DSC thermograms showed an exotherm peak (at 120 °C) associated to the polymerization of the residual monomer. This peak was, of course, not observed in the second scan (Fig. 5). The melting heat (ΔH_m) of the PCL incorporated into the beads increased with the PCL content, whereas the melting temperature of PCL in the blend did not exhibit a significant difference compared to pure PCL. The degree of crystallinity (X_c) of PCL was calculated taking into account the value of 16.9 kJ/mol of repeating units com-
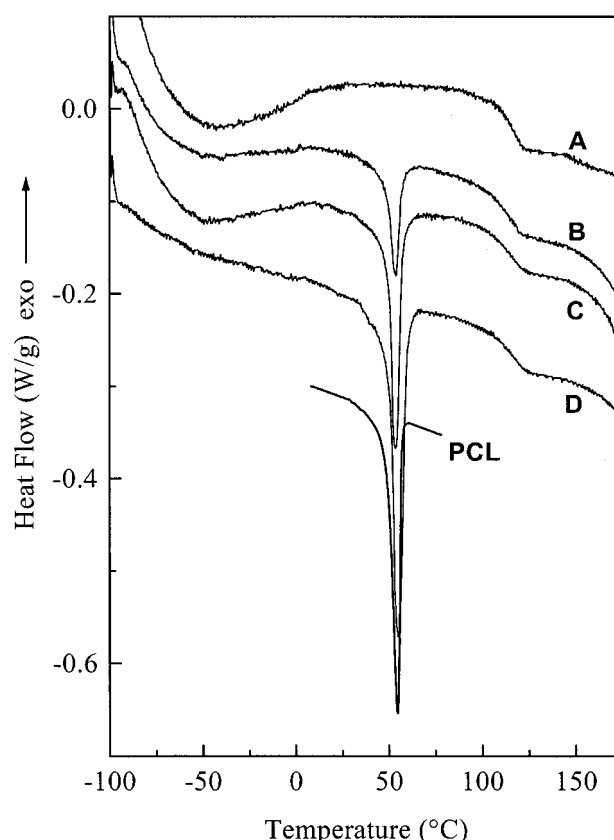
puted for 100% crystallinity reported for PCL.[14] As shown in Fig. 6, were the crystallinity degree of PCL in the blends is reported with respect to the pure PCL crystallinity, the value of X_c depends on the PCL content and slightly increases with it. The glass transition temperature (T_g) of the amorphous fraction of PCL was observable only for the pure polymer at −62 °C, while the T_g of PMMA was easily detectable at 107.6 °C for the pure polymer. The small decrease of the T_g values of the PMMA phase in samples containing PCL (B, C and D) is indicative of a very small compatibility with PCL, PMMA and PCL being segregated in two phases. In fact, the analysis of the T_g values is one of the most powerful criteria to check the compatibility of polymeric systems.

Dynamical mechanical thermal curves are shown in Fig. 7 and 8. The effect of the PCL incorporated in the beads is observed in the decreasing of the bending storage modulus (E') at the melting temperature of PCL phase and the presence of a slight transition visible at about −60 °C, associated to T_g of PCL (Fig. 7). These facts indicate that the molten PCL acts as a plasticizing phase in the glassy matrix of PMMA. The bending loss modulus (E'') curves (Fig. 8) show this effect more clearly with increasing PCL concentration. Commercial PMMA exhibited clear transitions at about 10 and 89.5 °C (if cal-
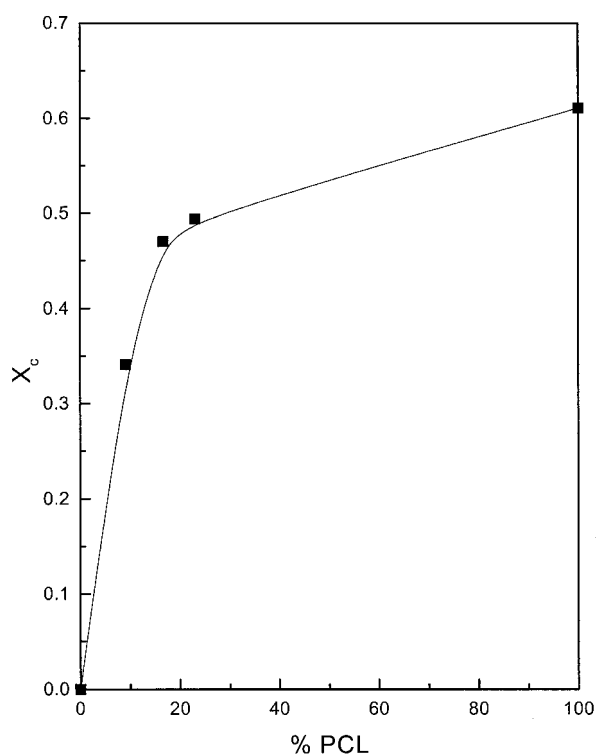
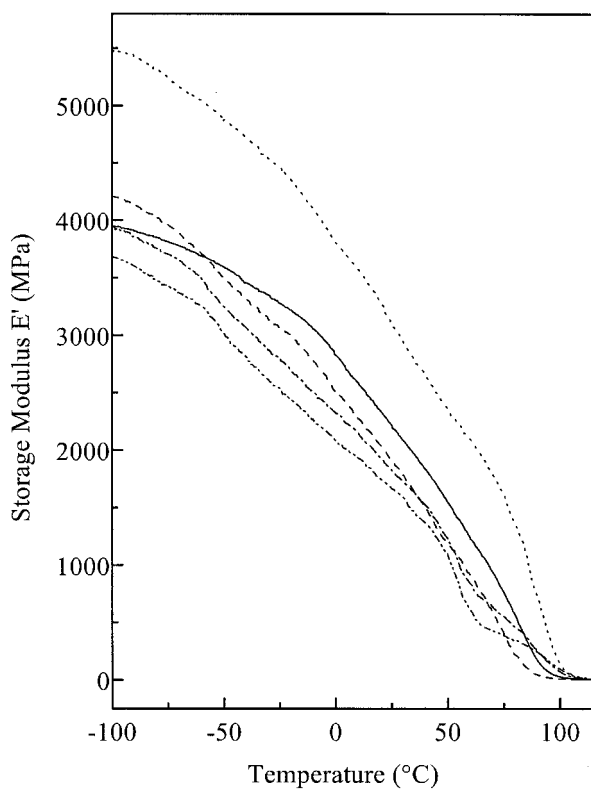Fig. 6. Crystallinity degree (X_c) of PCL as a function of PCL content.

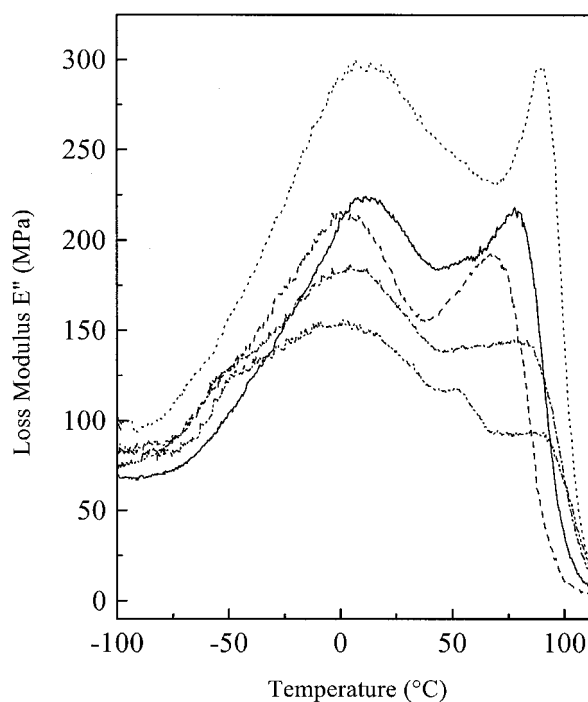Fig. 8. Bending loss modulus (E'') as a function of temperature: (· · ·) commercial PMMA; (—) sample A; (- - -) sample B; (- · -) sample C; (- · · -) sample D.
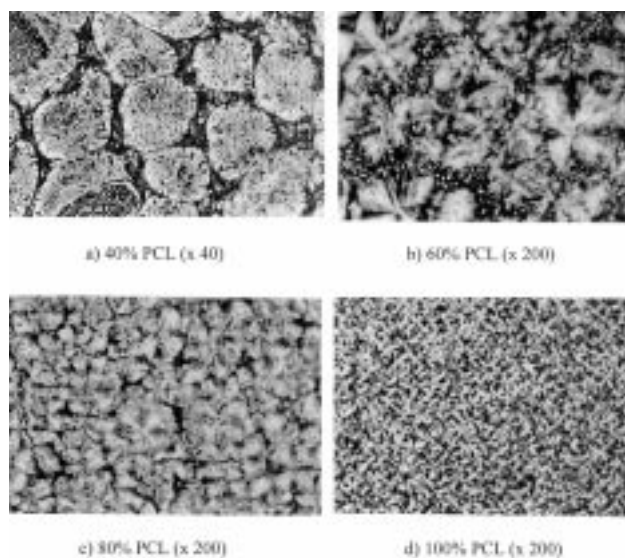

a) 40% PCL (× 40)   b) 60% PCL (× 200)

c) 80% PCL (× 200)   d) 100% PCL (× 200)

Fig. 9. Optical micrographs of films prepared from PMMA/ PCL blends: a) 40% PCL (× 40); b) 60% PCL (× 200); c) 80% PCL (× 200); d) 100% PCL (× 200).

Fig. 7. Bending storage modulus (E') as a function of temperature: (· · ·) commercial PMMA; (—) sample A; (- - - -) sample B; (- · -) sample C; (- · · -) sample D.

culated at E'' peaks), whereas our PMMA beads (sample A) displayed the same transitions being the second one at lower temperature (77.7 °C). Samples containing PCL, such as B and C, showed the presence of the above mentioned transitions. In particular, the lower glass transition temperature of the samples B, as detected by the E'' curve peak, could be the effect of mechanical plasticization due

to a more intimate distribution of liquid PCL (PCL melts during the test at around 60 °C) in the PMMA, depending on the initially more homogeneous distribution of the solid PCL within the blend; finally, in sample D a third transition, associated to the melting of PCL, is observed at 55.5 °C.

Morphology of blends

Finally, the low compatibility between PMMA and PCL was also visualized for the blends prepared starting from polymerized components. Optical micrographs clearly evidenced the morphology of the different PMMA/PCL blends (as seen in Fig. 9 a, b, and c). The blends exhibited PCL domains with a typical spherulitic structure immersed in a glassy matrix of PMMA. The spherulitic morphology of PCL is finally showed in Fig. 9 d.

Conclusions

We have obtained PMMA/PCL beads of controlled size and distribution by suspension polymerization of solutions of PCL in MMA using benzoyl peroxide as initiator. The increase in PCL component leads to a higher bead size and to a higher size dispersion. From DSC, GPC and DMTA experiments, we can conclude that the beads are formed by a microheterogeneous two phase system, evidencing the low compatibility of the two polymers. SEM analysis showed the complex structure of the beads, product of the nature of the polymerization conditions and components.

As this material is of interest as partial replacement of the solid phase in PMMA-based bone cement formulations, further studies are being carried out in this way.

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