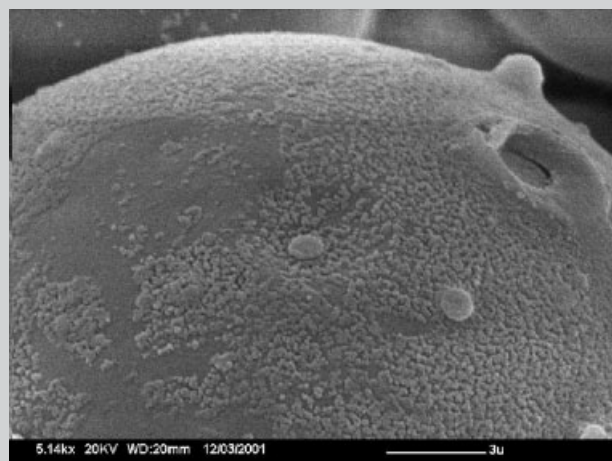


Full Paper: Poly(methyl methacrylate)-poly(ϵ -caprolactone) (PMMA/PCL) microparticles were synthesized by suspension polymerization of methyl methacrylate in the presence of PCL. The incorporation of a small amount of a macromonomer, methacryloyl-terminated PCL (M-PCL), into the reaction mixture, led to the formation of grafted systems, namely PMMA-g-PCL/PCL. The synthesis of the macromonomer and its characterization by nuclear magnetic spectroscopy (^1H NMR) is described. The role of M-PCL as an effective compatibilizing agent in the composite was investigated. PMMA/PCL and PMMA-g-PCL/PCL composites were fully characterized by ^1H NMR, gel permeation chromatography (GPC) and thermal analysis, including thermogravimetric analysis (TGA), conventional differential scanning calorimetry (DSC), modulated DSC (MDSC) and dynamic mechanical thermal analysis (DMTA). Finally, the morphology of the prepared systems was investigated by scanning electron microscopy (SEM). The addition of compatibilizing agent led the formation of a more homogeneous microcomposite with improved mechanical properties.



SEM picture of PMMA-g-PCL/PCL composite surface.

Microcomposites of Poly(ϵ -caprolactone) and Poly(methyl methacrylate) Prepared by Suspension Polymerization in the Presence of Poly(ϵ -caprolactone) Macromonomer

Gustavo A. Abraham,¹ Kemal Kesenci,² Luca Fambri,² Claudio Migliaresi,² Alberto Gallardo,¹ Julio San Román*¹

¹ Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Fax: +34 91 564 4853; E-mail: ictsr@ictp.csic.es, ictsr04@ictp.csic.es

² Dipartimento di Ingegneria dei Materiali, Università di Trento, Via Mesiano 77, 38050 Trento, Italy

Keywords: compatibilization; composites; graft copolymers; microstructure

Introduction

In a previous paper, we reported the synthesis of microheterogeneous polymer systems prepared by suspension polymerization of methyl methacrylate (MMA) in the presence of poly(ϵ -caprolactone) (PCL),^[1] along with its characterization by several techniques. Crosslinked graft copolymers produced by the formation of PCL macroradicals in the presence of the initiator were observed in some cases.^[1,2] The morphology of the beads, as observed by SEM, was quite complex. MMA suspension polymerization conditions and the presence of the PCL, which at the reaction temperature (65 °C) is beyond its melting point, are important factors that determined the resulting morphol-

ogy. During the course of the free radical polymerization, at a given conversion degree, the PCL chains are not compatible with the polymerized PMMA chains, giving rise to the segregation of the particles in microdomains. This is the main fact that defines the final morphology and microheterogeneity of the beads.

PMMA and PCL have two different degradation rates, PMMA is almost a not biodegradable polymer and PCL is a biodegradable polyester. In addition, both are roughly incompatible polymers. Although PCL in the presence of radicals can be crosslinked, the introduction of functionalised PCL chains in the polymerization of methyl methacrylate and PCL mixtures can provide an interesting way to get more homogeneous polymeric composites.

In this paper, we report on the synthesis and extensive characterization of PMMA/PCL microheterogeneous beads obtained by suspension polymerization with and without the addition of a macromonomer, methacryloyl-terminated PCL (M-PCL), as compatibilizing agent. The synthesis and characterization of M-PCL by ^1H NMR spectroscopy is described. In order to evaluate the effect of the addition of M-PCL in the initial reactive mixture, the resulting polymers were extensively characterized by several techniques including ^1H NMR, gel permeation chromatography (GPC), and thermal analysis (TGA, DSC, modulated DSC and DMTA). The surface morphology of the beads, visualized by scanning electron microscopy (SEM), is shown and discussed.

Experimental Part

Materials

ϵ -Caprolactone (Merck-Schuchardt), methacryloyl chloride (Acros Organics) were distilled under vacuum before use. Zinc chloride (Probus) was dried under vacuum. Methyl methacrylate (MMA, Merck) was used as received, poly(vinyl alcohol), PVA (ERT Spain) ($\bar{M}_n = 50\,000$, 99% hydrolyzed) was used as suspension agent and benzoyl peroxide, BPO (Fluka) was recrystallized from methanol at room temperature and used as free radical initiator. Other reagents were extra pure grade and were used as purchased.

Synthesis of PCL and the Macromonomer

The ring-opening polymerization (ROP) of ϵ -caprolactone in the presence of numerous catalysts to obtain high molecular weight polyesters has been widely investigated.^[3,4] In this work, PCL was synthesized by ROP of ϵ -caprolactone using ZnCl_2 as initiator in toluene solution, following a procedure reported previously.^[5]

In order to synthesize a PCL-based macromonomer, a PCL oligomer O-PCL, was synthesized by direct thermal polycondensation without using catalyst following the procedure described by Fukuzaki et al.^[6] Briefly, aqueous solution of ϵ -caprolactone (80 wt.-%) was charged into a glass ampoule and then nitrogen gas was bubbled into the solution at a controlled flow rate of $200\text{ ml} \cdot \text{min}^{-1}$. The ampoule was immersed in a silicone-oil bath maintained at 200°C being the solution under reflux during 2.5 h. The water was removed from the solution by closing the refrigerator coupled to the ampoule, allowing the polymerization reaction to carry out during 21 h. The polymer was purified by dissolution in dichloromethane and precipitation in a large excess of ethanol to remove the residual monomer. Afterward, the solid was filtered and exhaustive dried under high vacuum (10^{-3} mmHg) during 24 h at room temperature. The reaction yield was 89%.

A suitable amount of PCL oligomer was dissolved in dichloromethane. Then a calculated amount of triethylamine, in stoichiometric ratio to hydroxyl groups, was added to the solution under stirring. A large excess of freshly distilled methacryloyl chloride in a dichloromethane solution was

added dropwise to the flask. The mixture was stirred in an ice bath and then 10 h at room temperature. The triethylammonium hydrochloride by-product, that remains suspended as a white powder, was removed by filtration. The unreacted acid halide was neutralized by washing the solution three times with sodium hydroxide solution. The organic phase was finally concentrated and precipitated in a large amount of cold ethanol. After filtration, the methacryloyl-terminated PCL, called M-PCL thereafter, was extensively dried under high vacuum at room temperature for 1 day.

Preparation of PMMA/PCL with and without Addition of Macromonomer

The PMMA/PCL beads were obtained by suspension polymerization method following the experimental conditions previously reported.^[1] Briefly, a predetermined amount of PCL (10 wt.-%) was dissolved in MMA under vigorous stirring. The initiator, BPO, was then dissolved in the mixture (1.5 wt.-%). A 2 wt.-% PVA solution in distilled water was first introduced into the reactor, heated to 65°C and flushed with nitrogen for 10 min under stirring at 600 rpm. Then, the reactive phase was poured into the reactor in a stepwise and a temperature program of 4 h at 65°C and 2.5 h at 80°C . The product was exhaustively washed with distilled water and dried under vacuum for 24 h. The yield of PMMA/PCL beads was 88%.

The same procedure was followed for the preparation of systems containing macromonomer. In that case, M-PCL (2 wt.-%) was dissolved in the mixture MMA/BPO/PCL, and the resulting solution was polymerized and dried as mentioned above. The yield of this reaction was 70%.

Characterization of the Synthesized Polymers and Composites

All the polymers and composite systems were fully characterized by different techniques. Proton nuclear magnetic resonance (^1H NMR) spectra were performed in a Varian XLR-300 NMR spectrometer operating at 300 MHz and room temperature from 5% (wt./v) CDCl_3 solutions.

The weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights were determined by using a Perkin Elmer gel permeation chromatograph (GPC) equipped with a refractive index detector series 200. A set of 10^4 , 10^3 and 500 \AA , PL-gel columns conditioned at 25°C were used to elute the samples of 10 mg/mL concentration at 1 mL/min HPLC-grade chloroform flow rate. The values were calculated by means of a calibration curve with polystyrene standards.

Thermal Analysis was performed by several techniques including thermogravimetric analysis (TGA), conventional differential scanning calorimetry (DSC), modulated DSC (MDSC) and dynamic mechanical thermal analysis (DMTA).

The thermal degradation behavior of the particles was studied by using a thermogravimetric analyzer (Mettler TG50). All samples were heated from 30 to 500°C at a heating rate of 10 K/min under a nitrogen flow of 100 mL/min. Degradation percentages, onset temperatures and thermal degradation rates were evaluated.

Conventional DSC was performed in a Mettler DSC30 with three scan (heating-cooling-heating) at 10 K/min in the range

30–120 °C under nitrogen flow of 100 ml/min. The temperature and enthalpy calibrations were performed using indium. The glass transition temperature (T_g) was taken as the inflection point of the transition. On the other hand, MDSC measurements were performed on a TA Instruments 2920 DSC with MDSC option and cooling system, nitrogen was used as purge gas and indium was used for calibration. Standard modulation conditions used in the experiments were an amplitude of 1 °C and a period of 60 s. Samples with mass from 8 to 9 mg (or 7 mg for conventional DSC) in sealed aluminium pans were heated at 3 K/min from –80 to 150 °C.

The dynamic mechanical behavior of thick composite samples (12 × 10 × 3 mm) was analyzed using a dynamical mechanical thermal analyzer (Polymer Laboratories Ltd., model Mk II, USA) operated in the dual cantilever bending mode (dynamic displacement 64 μm, frequency 1 Hz) with a heating rate of 3 K/min in the temperature range going from 25 to 110 °C. Samples were prepared by compression moulding at 175 °C for about 15 min and then by cooling the mould in water.

Finally, the morphology of the particles was observed with a Cambridge Stereoscan 200 scanning electron microscope with an accelerating voltage of 20 kV.

Results and Discussion

PCL and PCL Macromonomer

In order to determine the chemical structure of PCL, O-PCL and M-PCL, ^1H NMR spectra were recorded. In the case of PCL, the observation of a triplet at 3.5 ppm was ascribed to a methylene endgroup capped with a chloride atom. This fact was previously attributed to the transference of a chlorine atom to the end chain which occurs during the ROP with zinc chloride by a coordination-insertion mechanism.^[5]

On the other hand, PCL oligomer exhibited a signal at 3.62 ppm which was assigned to the $\text{CH}_2\text{-OH}$ end group, as shown in Figure 1. After derivatization with trifluoroacetic anhydride this signal shifted downfield to 4.3 ppm confirm-

ing the assignation of the end group. The presence of a hydroxyl end group allowed the formation of a macromonomer by reaction with methacryloyl chloride. The resulting methacryloyl-terminated PCL, M-PCL, displayed two signals at 5.51 and 6.05 ppm corresponding to vinyl protons of the methacryloyl end group and a peak at 1.90 ppm assigned to the α -methyl protons (see Figure 1). The signal of $\text{CH}_2\text{-OH}$ end group at 3.62 ppm did not appear, evidencing that virtually all the hydroxyl end groups were converted to methacrylic end groups.

The average molecular weight values were determined by GPC. PCL exhibited a $\bar{M}_n = 45\,000$ and a polydispersity index (\bar{M}_w/\bar{M}_n) = 1.6. On the other hand, the macromonomer obtained from the PCL oligomer displayed a \bar{M}_n value of 6 000 and a polydispersity of 1.5.

Chemical Composition of the Microcomposite Systems

The theoretical composition of both samples is almost similar (89.1/10.9 for PMMA/PCL and 89.2/10.8 for PMMA-g-PCL/PCL). The composition of PMMA/PCL beads determined by ^1H NMR was 89/11 (wt.-%) whereas for the PMMA-g-PCL/PCL composite was 64/36, where 36% corresponds to the total amount of PCL. Although the composition in the first case was approximately the same that the theoretical one, a PCL-enrichment was observed in the case of PMMA-g-PCL/PCL sample. The GPC chromatograms of the composites (not shown here) revealed a two-modal distribution, corresponding to PMMA and PCL phases.

Thermal Analysis

The degradation of PMMA has been studied for many years and it is well known that the thermal degradation proceeds by chain scission and unzipping mechanism, giving a very high yield of monomer.^[7] The details of the degradation have been elucidated by Kashiwagi and Manring,^[8,9] who demonstrated that the degradation is initiated mainly at end chain unsaturations and weak links such as head-to-head linkages.

Thermogravimetric curves are shown in Figure 2. The results indicate that the thermal behavior of PMMA/PCL and PMMA-g-PCL/PCL is complex. In both cases, a continuous weight loss starting at 150 °C was observed, and at least three thermal events occurred. The first thermal process observed in the thermogravimetric curves is related to the low molecular weight components at 160 °C and involve a 10% wt. According to Figure 2, second thermal degradation occurred between 250 and 367 °C, with weight losses of 27 and 32% wt. for PMMA/PCL and PMMA-g-PCL/PCL, respectively. The third thermal degradation occurred between 367 and 450 °C, with weight losses of 63 and 58% wt., respectively. The temperature values and

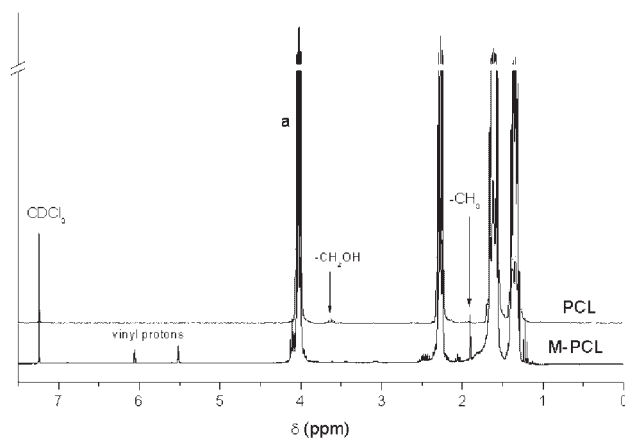


Figure 1. ^1H NMR spectra of PCL oligomer and methacryloyl-terminated PCL (M-PCL).

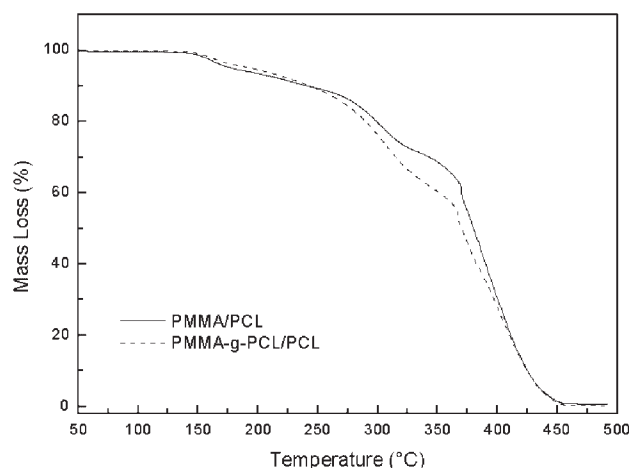


Figure 2. Thermogravimetric curves of PMMA/PCL and PMMA-g-PCL/PCL composites.

the percentage of volatilized material after each stage depends on the composition of the beads, and only small differences were found in these analysis.

Calorimetric Analysis

DSC results of first and second runs (after quenching) are summarized in Table 1. A single endothermic peak associated to PCL phase was detected along with a secondary transition assigned to PMMA.

On the other hand, Modulated DSC (MDSC), a modern technique which provides not only the same information as conventional DSC, but also provides unique information not available from conventional DSC increasing the understanding of complex transitions in materials, was used.^[10] In MDSC a sinusoidal modulation is overlaid on the conventional linear heating or cooling ramp to yield a heating profile in which the average sample temperature continuously changes with time but not in a linear fashion. In this way, MDSC determines the total heat flow and simple calculations are used to separate the total heat flow into its heat capacity (reversible) and kinetic (not reversible) components.

MDSC thermograms of Figure 3 display the heat flow and its reversible component versus temperature for the studied materials. Heating curves from -80 to 150 °C were denoted as traces **h** and the following cooling curves were denoted as traces **c**. Heat flow curves of PCL and M-PCL (Figure 3a and 3b) clearly show the melting and crystallization from melt during the cooling. PCL and M-PCL behave similarly, with temperatures that are however slightly different both for melting and crystallization.

Data of Table 2 indicate some differences in the heat flow MDSC results that should be noticed and are consistent with the different purity and molecular weight of PCL. According to its higher purity and molecular weight PCL presents both slightly higher melting and lower crystallization temperature than the observed for M-PCL, as well as lower melting and crystallization enthalpies. It is also worth noting the small endothermic peak centered at about 41 °C having an enthalpy of about 2.8 J/g, that should correspond to the melting of less ordered, hence less perfect, crystalline regions. Moreover, heat flow curves of both PCL/PMMA blends exhibited a double melting peaks, as for PCL. The lower temperature peak was however bigger and sharper, indicating the blending affected the PCL crystallizations and provoked the formation of higher amounts of less ordered crystalline regions. Data of Table 2 also show that melting temperature of the main melting peak of PCL phase decreases for both PMMA/PCL blends, with a larger dropping in the case of the graft copolymer blend, as result of a further reduction in the structure ordering. Taking into account the relative percentages of PCL in the blends, 11% and 36%, the corresponding normalized melting enthalpy resulted almost the same of pure PCL in the case of PMMA/PCL (97.3 J/g), and about one fifth in the case of PMMA-g-PCL/PCL (21.7 J/g). This could be explained as an effect of partial miscibility of the two polymers, that seems is also the reason of the glass transition temperature decrease of PMMA from about 114 to 108 °C, due to the presence of grafted PCL that would act as compatibilizer.

During heating above the glass transition temperature, in the case of the heat flow curve all the blends showed a small but wide exothermic peak at about 130 °C. This non-reversible energy is attributable to the reaction of unreacted

Table 1. Heat flow data of DSC analysis.

Sample	1 st Heating		Cooling	2 nd Heating	
	T_{m1} (ΔH_1) ^{a)}	T_g ^{b)}		T_{m2} (ΔH_2) ^{a)}	T_g
	°C (J/g)	°C		°C (J/g)	°C
PMMA/PCL	59 (10.4)	≥ 115	29.5 (6.5)	54 (7.9)	108
PMMA-g-PCL/PCL	56 (8.8)	110	3.3 (3.0)	55 (7.8)	107

a) Temperature and enthalpy of the melting peaks.

b) Glass transition temperature.

c) Temperature and enthalpy of the crystallization peaks.

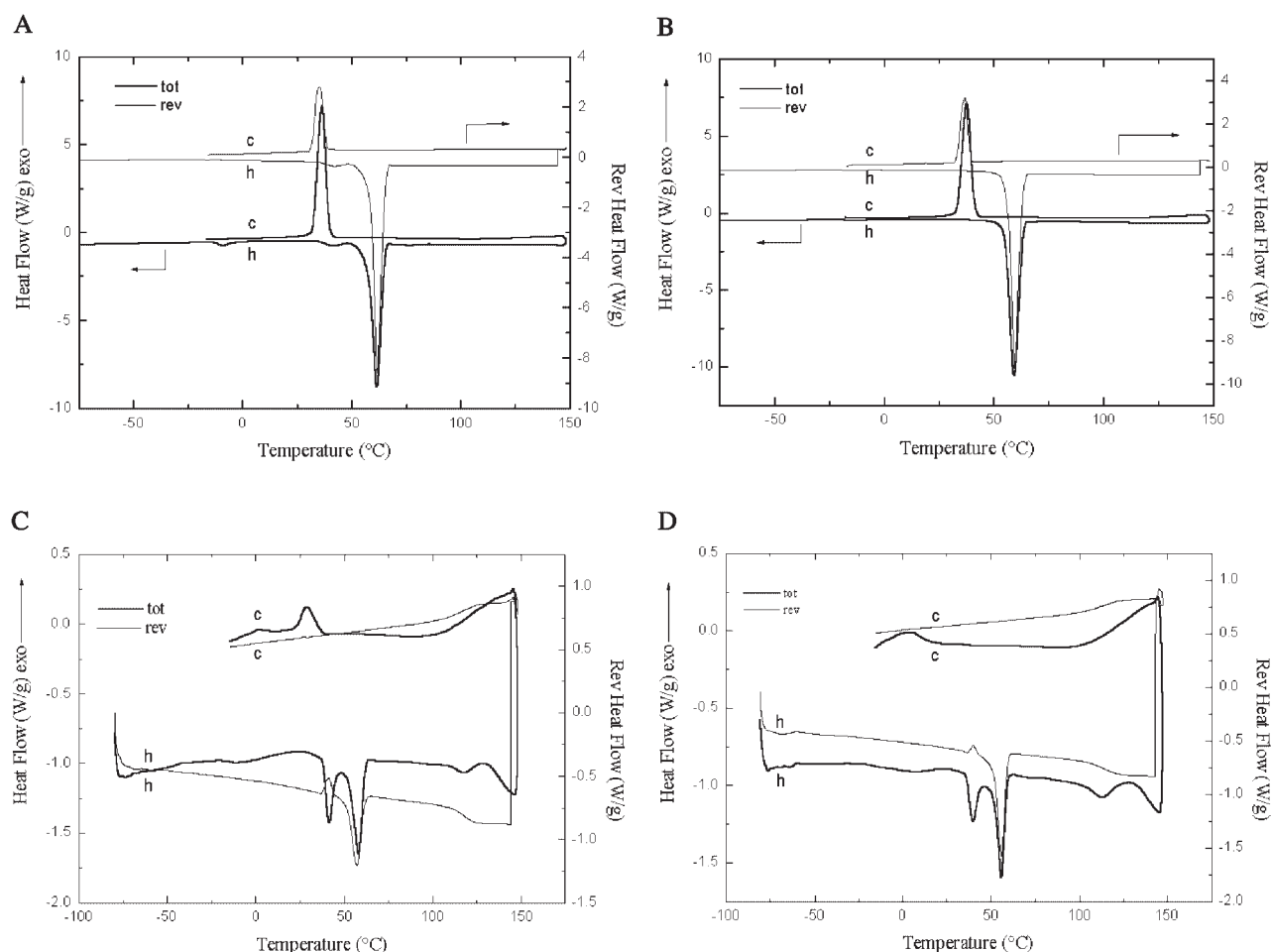


Figure 3. MDSC curves showing the total heat flow (—) and the reversible heat flow component (—). The letters h and c indicate heating and cooling traces. (a) PCL; (b) M-PCL; (c) PMMA/PCL composite; (d) PMMA-g-PCL/PCL composite.

MMA residual monomer in the beads. During cooling after the heating cycle, the curves of PMMA/PCL and PMMA-g-PCL/PCL exhibited again one exothermic peak, indicating the PCL crystallization. This crystallization peak was shifted to lower temperatures (about ten and thirty degrees lower

for PMMA/PCL and PMMA-g-PCL/PCL blends, respectively) with respect to that observed at about 37 °C in the pure PCL or M-PCL. The large decrease of both crystallization temperature and enthalpy, confirms that PMMA, and much more grafted PMMA, hindered in some extent the

Table 2. Heat flow data of MDSC curves.

Sample	Heating				Cooling
	$T_{m1} (\Delta H_1)^a$	$T_{m2} (\Delta H_2)^b$	T_g^c	$T_p (\Delta H_p)^d$	$T_c (\Delta H_c)^e$
	°C (J/g)	°C (J/g)	°C	°C (J/g)	°C (J/g)
PCL	41.3 (2.8)	61.5 (98.0)	—	—	36.4 (78.0)
M-PCL	—	59.1 (122.1)	—	—	37.6 (84.7)
PMMA/PCL	41.3 (5.5)	58.2 (9.6)	114.4	130.4 (3.5)	28.9 (3.7)
PMMA-g-PCL/PCL	39.7 (3.9)	56.1 (7.8)	108.3	128.6 (3.3)	5.6 (1.8)

a) Temperature and enthalpy of the secondary melting peaks.

b) Temperature and enthalpy of the main melting peaks.

c) Glass transition temperature.

d) Temperature and enthalpy of the residual MMA polymerization.

e) Temperature and enthalpy of the crystallization peaks.

PCL crystallization. Moreover the reader should note that crystallization peaks of PCL in the blends are less visible because of the less amount of material involved.

The reversible heat curves run similarly, but with values for the melting and crystallization enthalpies that are different from the previous ones, this being due to the meaning that the technique associates to the word "reversible". Reversibility is in fact evaluated within the applied temperature modulation, and phenomena that occur with different kinetics but are thermodynamically reversible display apparent different reversible components. A speculation on the curve behavior could suggest that melting is less heat flow rate dependent than cooling.

MDSC curves of PMMA/PCL and PMMA-g-PCL/PCL blends present a singular aspect that was not so well detected by the not reported conventional DSC experiments, i.e. two well distinct melting peak occurring during the heating at 40 and 60 °C, respectively. Differences between the traditional DSC curves (not shown here) where the melting peak is unique with a small shoulder, and the Figure 3c and 3d reported MDSC curves, are attributable to the different adopted heating rate, equal to 3 K/min in MDSC and to 10 °C in DSC, but mainly to the different response of the material to a continuous heating or cooling (DSC) and a modulated heating or cooling (MDSC). The difference existing between the two techniques is analogous to the one that could be applied by performing static stress-strain test (i.e. by straining a sample at a constant strain rate) or a dynamic stress-strain test (i.e. by superimposing to the constant strain increase a strain modulation). The results in this case would be evidently different, due to viscoelasticity dependent effects, and hence, to kinetic relaxation phenomena.

From the above reported results, it could be deduced that PCL assumed two different crystalline morphologies when blended with PMMA. In this case the higher temperature peak, consistently with the results on pure PCL, could account for the melting of the PCL that is completely segregated in microdomains from PMMA, while the lower temperature peak could express the melting of less perfect crystals that are formed by PCL chains in some extent hindered by the PMMA molecules to which are interconnected. This explanation appears to agree with the transitions that the technique said to be reversible, that is also reported in Figure 3c and 3d. Instead of the lower temperature endothermic peak, the reversible heat curves displayed, in fact, a small exothermic peak, both for PMMA/PCL (1.3 J/g at 41.0 °C) and PMMA-g-PCL/PCL blends (0.5 J/g at 39.7 °C). This peak could measure recrystallizations of part of the PCL chains free to rearrange forward the more stable crystalline form after the lower temperature melting. It is worth noting that crystallization of PCL in the blend during cooling from 150 °C at 3 K/min reached only 24% and 15% of the initial crystallinity of the as produced PMMA/PCL and PMMA-g-PCL/PCL powder, respectively.

Moreover, reversible heat flow put very well in evidence the glass transition temperature that is a typical reversible signal, both in the heating and in the cooling stage. In this latter case, T_g values of PMMA at 117.2 and 110.8 °C were obtained for PMMA/PCL and PMMA-g-PCL/PCL systems, respectively. That observation confirm the effect of the grafted copolymer, as previously observed in the glass transition temperature measured in the heat flow data of the heating curve (Table 2).

Dynamic Mechanical Thermal Analysis

Curves of the storage modulus, E' , versus temperature are shown in Figure 4 and clearly indicate the higher mechanical properties of the compatibilizer added PMMA/PCL blends (curve B). Dynamic mechanical analysis data however did not confirm the double transition that was detected at about 40 and 60 °C from the calorimetric studies. This fact could be due to differences among samples, i.e. as produced powder for DSC and a compression moulded specimen, for the DMTA, induced by the moulding process. For both samples, i.e. PMMA/PCL and PMMA-g-PCL/PCL, the storage modulus almost continuously decreased with temperature, reaching an apparent very low plateau above about 60 °C. It is clear that the stiffness of the samples after this temperature is dominated by the PCL physical state, i.e. the samples became very flexible after the PCL has molten. Moreover, the curve did not display the attended PMMA glass transition. These facts suggest that, after melting, PCL acted as a liquid plasticizer, or, from another point of view, that the PMMA was the reinforcing phase of a PCL matrix. In both cases mechanical stiffness of the samples was assured by the PCL consistence, hence the samples stiffness dropped after the PCL melting, reaching low values, too low for being correctly measured by the DMTA apparatus. This is the reason for which the system did not detect the expected PMMA glass transition. A DSC

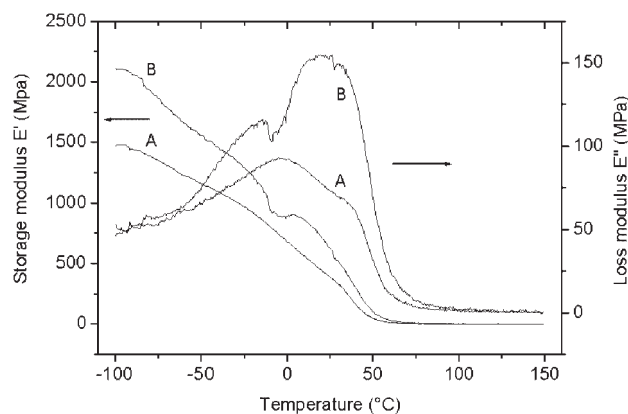


Figure 4. Storage modulus (E') and Loss Modulus as a function of temperature. (A) PMMA/PCL composite; (B) PMMA-g-PCL/PCL composite.

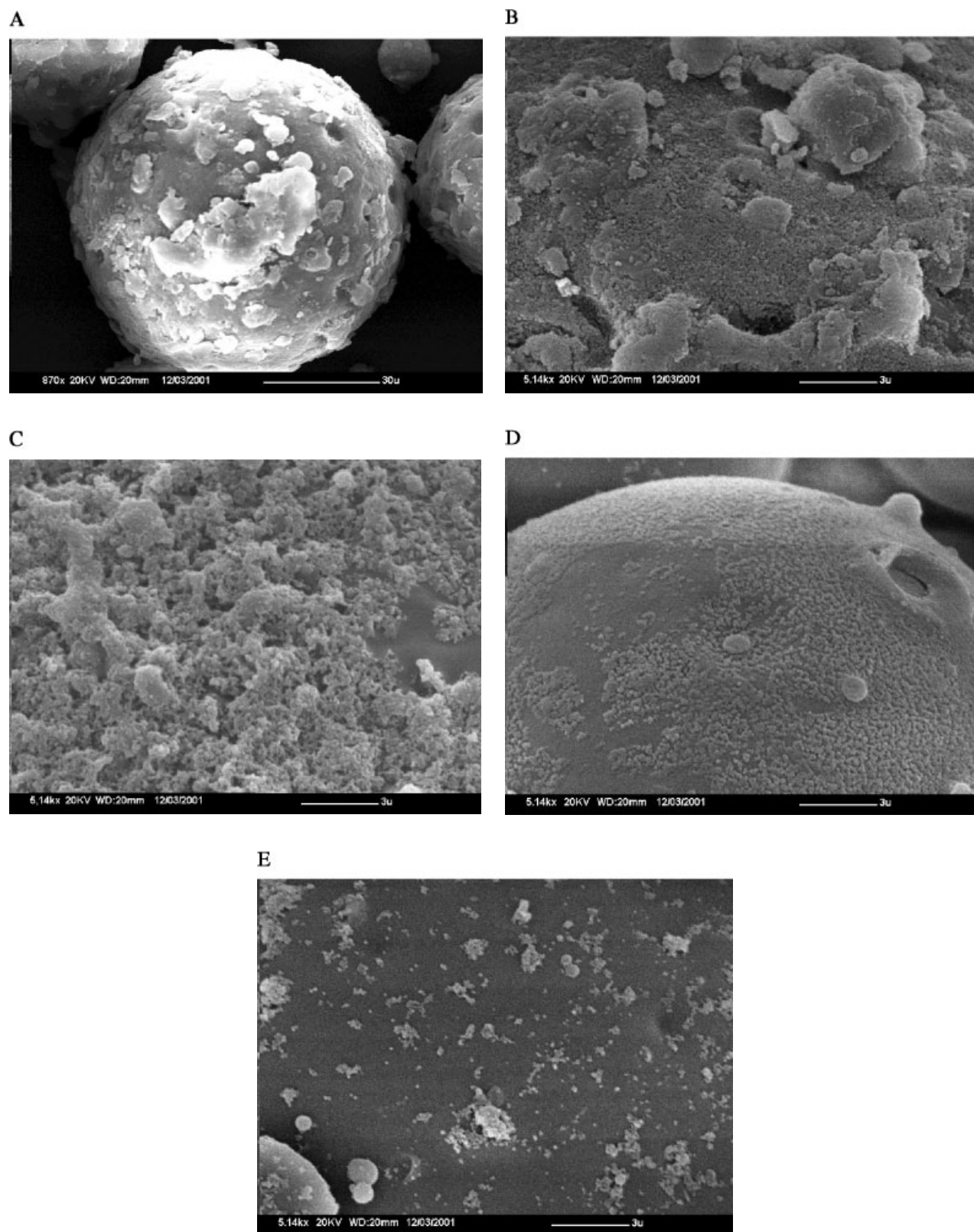


Figure 5. SEM pictures: (a) PMMA/PCL beads; (b) PMMA/PCL composite surface; (c) surface of PMMA/PCL composite after treatment with 0.1 N H₂SO₄; (d) PMMA-g-PCL/PCL composite surface; (e) SEM micrograph of the PMMA-g-PCL/PCL composite surface after treatment with 0.1 N H₂SO₄.

performed on the same specimen after the DMTA runs regularly registered the T_g value of PMMA.

A more accurate examination of the E' and E'' curves point the attention on the shoulders and on the peaks that appear along the curves in the temperature range -50 to 50°C . Referring to the loss modulus curves, the peaks could be attributed to PMMA β -relaxation and to the PCL melting, respectively.^[11] The β -relaxation of PMMA has been extensively analyzed by Heijboer^[12,13] and Struik^[14] and it was clearly assigned to the motions of an entire side group around the bond, joining it to the chain backbone. They confirmed, from DMTA experiments performed at 1 Hz, that the loss modulus peak seen at 10°C corresponds to the mechanical β -relaxation. In our case, the relaxation peak is shifted to -10°C , which could be explained taking into consideration the plasticizing effect of the graft copolymer. The difference in the attributed β -relaxation signal between the PMMA/PCL and PMMA-g-PCL/PCL samples could be due to the presence of the compatibilizer that could interfere with the lateral groups PMMA mobility. The difference in the height of the E'' melting peaks well agrees with the specimen composition, i.e. 11 and 36% of PCL in the blend samples without and with compatibilizer, respectively.

Surface Morphology

Relatively concentrated or semi-diluted sulfuric acid solutions attack PCL chains whereas PMMA chains are not sensitive at least during a period of time of one month. SEM pictures before and after treatment with $0.1\text{ N H}_2\text{SO}_4$ solution are shown in Figure 5a to 5e. From the comparison of Figure 5b and 5c with Figure 5d and 5e, it is clear that the addition of compatibilizing agent led to a highly homogeneous surface structure. The surface treatment allowed a more efficient elimination of the PCL in the case of the grafted blend while in absence of compatibilizer a clear phase separation between PMMA and PCL occurred.

Conclusions

Two microheterogeneous systems were prepared by suspension polymerization of MMA in the presence of PCL. The addition of methacryloyl-terminated PCL allowed the formation of grafted species PMMA-g-PCL/PCL that were well characterized from a thermal and mechanical point of view.

MDSC curves of these blends presented singular aspects that were not so well detected by the not reported conventional DSC experiments. Thus, it could be considered

that PCL assumed two different crystalline conformations when blended with PMMA. DMTA results clearly indicate the higher mechanical properties of the compatibilizer added PMMA/PCL blends. The addition of compatibilizing agent led to the formation of more homogeneous surface structure as visualized by SEM.

Acknowledgement: G.A. Abraham thanks *Ministerio de Educación y Cultura of Spain* which provided grant for his stay in Spain. Financial support from the *Comisión Interministerial de Ciencia y Tecnología, CICYT (MAT 2001-1618)* is also gratefully acknowledged.

Received: March 15, 2002

Revised: May 16, 2002

Accepted: June 7, 2002

- [1] G. A. Abraham, A. Gallardo, A. Motta, C. Migliaresi, J. San Román, *Macromol. Mater. Eng.* **2000**, 282, 44.
- [2] P. Jarret, C. V. Benedict, J. P. Bell, J. A. Cameron, S. J. Huang, in: "*Polymers as Biomaterials*", S. W. Shalaby, A. S. Hoffman, B. D. Ratner, T. A. Horbett, Eds., Plenum, New York 1985, p. 181.
- [3] A. Löfgren, A.-C. Albertsson, P. Dubois, R. J. Jérôme, *J. Mater. Sci., Rev. Macromol. Chem. Phys.* **1995**, C35(3), 379.
- [4] D. B. Johns, R. W. Lenz, A. Luecke, in: "*Ring-Opening Polymerization*", Vol. 1, K. J. Ivin, T. Saegusa, Eds., Elsevier, London 1984, p. 461.
- [5] G. A. Abraham, A. Gallardo, A. E. Lozano, J. San Román, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 1355.
- [6] H. Fukuzaki, M. Yoshida, M. Asano, K. Minoru, *Polymer* **1990**, 31, 2006.
- [7] C. F. Cullis, M. M. Hirschler, "*The combustion of organic polymers*", Clarendon, Oxford 1981, p. 117.
- [8] T. Kashiwagi, T. Harita, J. E. Brown, *Macromolecules* **1985**, 18, 131.
- [9] L. E. Manring, *Macromolecules* **1988**, 21, 528.
- [10] TA Instruments Inc., thermal analysis review.
- [11] N. G. McCrum, B. E. Read, G. Williams, in: "*Anelastic and Dielectric Effects in Polymeric Solids*", Dover Publications, Inc., New York 1991.
- [12] J. Heijboer, "Molecular origin of relaxations in Polymers", in: *The glass transition and the nature of the glassy state*, Vol. 279, New York Academy of Science, New York 1976, p. 104.
- [13] J. Heijboer, "Mechanical properties and molecular structure of organic polymers", in: *Physics of non-crystalline solids*, J. A. Prins, Ed., North Holland Publishing, Amsterdam 1965, p. 231.
- [14] L. C. E. Struik, "*Physical aging in amorphous polymers and other materials*", Elsevier, Amsterdam 1978, p. 26.