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PMMA/PC Blends: Effect of Mixing Conditions on Compatibility

Maurizio Penco,[*1] Luciana Sartore,[1] Stefania Della Sciucca,[1] Luca Di Landro,[2] Alberto D'Amore[3]*

Summary: In this work the effect of melt mixing condition and of a *trans*-esterification catalyst on miscibility of poly(methyl methacrylate) (PMMA)/polycarbonate of bisphenol A (PC) blends is studied. In particular, at high temperature chemical reactions between PMMA and PC phases can take place; these strongly change the compatibility in the blend and materials having single T_g can be obtained. FT-IR analyses, coupled with solvent extraction, suggest that a grafting reaction of PC on PMMA is involved. SEC and DSC data are consistent with spectroscopic results, and some decrement of the molar weight distribution (MWD) of PC phase is observed. On the other hand, the presence of a fraction of modified material having higher MWD of starting PMMA is also noticed. The single T_g characteristic of some materials has been confirmed by experimental data of structural relaxation performed by differential scanning calorimetry (DSC). These materials showed optical clarity and the morphological analysis performed by scanning electron microscopy (SEM) confirm the homogeneity of these materials.

Keywords: blends; miscibility; poly(methyl methacrylate); polycarbonate of bisphenol A; trans-esterification

Introduction

Among the studies on poly(methyl methacrylate) (PMMA) blends, the mixture PMMA and bisphenol A polycarbonate (PC) is one of most deeply studied polymer pairs. This may be attributed to the highest transparency of PMMA among the commercial plastics and to the excellent properties of PC (outstanding ductility, low water adsorption and high glass transition temperature (T_g)).

The phase behaviour of this blend system has been extensively investigated by various researchers [1–5] and it was found to depend on the method of preparation. For example, homogeneous blends can be obtained by casting from tetrahydrofuran (THF) at 46 °C,[6,7] while partially miscible or complete immiscible blends are obtained by melt mixing.[6,8] Moreover, the nature of the equilibrium phase behaviour is controversial: some researchers claimed that miscibility with a low critical solution temperature (*LCST*) exists [9]; others suggest that also an upper critical solution temperature (*UCST*) above the *LCST* exists.[10] If this is true, it is a very unusual and rare case for polymers. In fact debates and studies on this topic have therefore been intensive and the view of the thermodynamic origin of the *UCST* in PMMA/PC blends was later revised. Different types of chemical reactions between PMMA and PC have been suggested as being responsible for blend miscibility above 200 °C: PMMA unzipping,[11] the attack

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[1] Dipartimento di Chimica e Fisica per l'Ingegneria e per i Materiali. Università degli Studi di Brescia, Via Salotti 9, 25133 Brescia, Italy
E-mail: maurizio.penco@ing.unibs.it

[2] Dipartimento di Ingegneria Aerospaziale, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy

[3] Department of Aerospace and Mechanical Engineering, The second University of Naples-SUN, Via Roma 29, Aversa (CE), Italy

of PMMA macroradicals on PC chains,[12] *trans*-esterification of PMMA ester pendant group with PC [13] and termoxidative branching leading to graft copolymer which induces re-homogenization at high temperature.[14]

In this contest, clearly appears that the blend microstructure can be strongly affected by blending conditions as both immiscibility or high compatibility can occur. The object of this work is the evaluation of the effect of composition, mixing time and of a *trans*-esterification catalyst on PMMA/PC blends prepared by melt mixing with the goal of obtaining a single T_g material using short mixing time to limit degradation.

The chemical modifications of the blends were studied by infrared spectroscopy (FT-IR) combined with solvent extraction and by size exclusion chromatography (SEC). The glass transition behaviour of all blends was evaluate by differential scanning calorimetry (DSC), and the morphology with optical microscopy (OM) and scanning electron microscopy (SEM).

Experimental Part

Materials

Poly(methyl methacrylate) (PMMA) ($M_n = 59{,}700$ g/mol, $M_w = 92{,}000$ g/mol and $T_g = 114\,^\circ C$) and polycarbonate of bisphenol-A (PC) ($M_n = 40{,}200$ g/mol, $M_w = 74{,}500$ g/mol and $T_g = 150\,^\circ C$) were purchased from Aldrich and Co. (Milan, Italy) and used after drying in a vacuum oven at 80 °C for 48 hours. All the solvents and the tetrabutylammoniun tetraphenylborate (TBATPB) were purchased from Aldrich and Co. (Milan, Italy) and used as received.

Blends preparation

PMMA/PC blends were prepared by melt mixing in a discontinuous mixer (Brabender), equipped with a 60 cm^3 chamber. The temperature was set at 250 °C, the rotor speed at 60 rpm and the mixing time at 2 and/or 6 min. The compositions of the blends were 25/75, 50/50 and 75/25 wt-% PMMA/PC, with and without 1 wt-% of TBATPB, a *trans*-esterification catalyst.[15]

Methods

FT-IR spectroscopy (Jasco 5300, Japan) was used for investigating the chemical reaction between constituents; the ratio of C=O stretching bands ($PC_{C=O}/PMMA_{C=O}$) of the acetone-insoluble fraction was used to evaluate the taking place of *trans*-esterification reaction. FT-IR measurements were carried out on thin films cast onto a potassium bromide (KBr) disk. The acetone insoluble portion of the blends was first dissolved in chloroform and then cast onto KBr.

The molecular weights distributions (MWD) were determined by size exclusion chromatography (SEC); an Erma instrument equipped with Shodex KF columns and Knauer RI detector, with tetrahydrofuran (THF) as eluent (1ml/min), was used. The values of M_w and M_n were calculated relative to polystyrene standards (Polymer Laboratories, Shropshire U.K.).

Thermal analysis was performed in nitrogen atmosphere (50 ml/min) with a TA Instruments differential scanning calorimeter (DSC Q100, USA) on a sample of 7.5 ± 0.3 mg, employing a constant heating rate of 10 °C/min. The T_g is taken as the inflection point of the change in heat capacity with temperature on the second scan between 40–190 °C.

Annealing experiments were performed by heating ($q_h = 10\,^\circ C/min$) the samples above T_g at 190 °C, cooling ($q_c = -10\,^\circ C/min$) to the annealing temperature T_a ($T_a = T_g - 20\,^\circ C$ for all samples), holding at that temperature for various annealing times t_a (60–480 min), cooling with the programmed rate q_c to 60 °C and finally reheating at q_h through the T_g. The resulting curves were used to evaluate polymer-polymer miscibility.

The morphological analysis was carried out with optical microscopy (OM), instrument Labphot-2 bi Nikon, and scanning electron microscope (SEM), instrument

Stereo Scan 260 by Cambridge, on moulded sheets (thickness 1 to 2 mm) obtained by compression moulding at 210 °C and 35 bar.

Results and Discussion

PMMA/PC blends preparation

PMMA/PC blends having different composition, 25/75, 50/50 and 75/25 wt-% PMMA/PC respectively, were prepared at 250 °C with different mixing times to evaluate the effect of composition and chemical modification on the compatibility.

As reported in Table 1, after 2 minutes of mixing, all blends show two glass transition temperatures: a low T_g ($T_{g,l}$) and a high T_g ($T_{g,h}$) due to the PMMA and PC phases, respectively. It should be noticed that these values are shifted respect to the pure polymers in the direction of a compatibilization. In fact for all composition $T_{g,l}$ is always higher than the T_g of pure PMMA, and it increases with PC content; on the other hand, $T_{g,h}$ is always lower than the T_g of pure PC and it decreases if PC content decreases; a difference of about 20 °C between $T_{g,h}$ and $T_{g,l}$ is observed for all compositions.

The FT-IR analysis performed on the acetone-insoluble fraction of the Blends 1–3 (acetone is a good solvent for PMMA), shows the characteristic carboxyl stretching bands of PC at 1774 cm^{-1} and of PMMA at 1732 cm^{-1}, suggesting that some amount of PMMA-PC graft copolymer has been formed. [13,14] In Figure 1.a, the FT-IR spectrum of Blend 2 is shown.

The OM and SEM morphological analyses performed on Blends 1–3 highlight un-homogeneities in these materials. In Figure 2.a, the SEM micrograph of Blend 2 is reported.

The effect of a thermal treatment on blend miscibility was studied on Blend 2 performing heating cycles in DSC and the results are shown in Figure 3. The experiment consists of six subsequent scan at 10 °C/min each time increasing the end-run temperature from 190 °C to 280 °C (after each run the sample was quenched at 40 °C). It is interesting to note that until the third run the low and the high T_gs seems to be not effected by the thermal treatments. After the forth run, which means an end-run temperature of 250 °C, the $T_{g,h}$ decrease was observed while $T_{g,l}$ can be considered unaffected. Just after the fifth run, which means 280 °C as end-run temperature, a single T_g was observed. This let us to suppose that, being the temperature set at 250 °C, an increment of residence time in the mixer could give a similar result. In fact all the blends melt mixed for 6 min were characterized by a single glass transition temperature, as reported in Table 1, namely Blends 4–6. In particular, the T_g increase with PC content was observed but yellowed materials were obtained.

It should be underlined that the results that can be obtained with these mixing conditions (6 min at 250 °C and 60 rpm)

Table 1.
Composition and calorimetric data of PMMA/PC blends melt mixed at 250 °C and 60 rpm.

Blend	PC[a] (wt-%)	TBATPB (wt-%)	mixing time (min)	low T_g (°C)	high T_g (°C)
1	25	–	2	120	140
2	50	–	2	123	142
3	75	–	2	124	145
4	25	–	6	118	
5	50	–	6	123	
6	75	–	6	137	
7	25	1	2	119	
8	50	1	2	125	
9	75	1	2	129	
10	25	1	6	116	
11	50	1	6	122	
12	75	1	6	127	

[a] PC: $T_g = 150$ °C; PMMA: $T_g = 114$ °C.

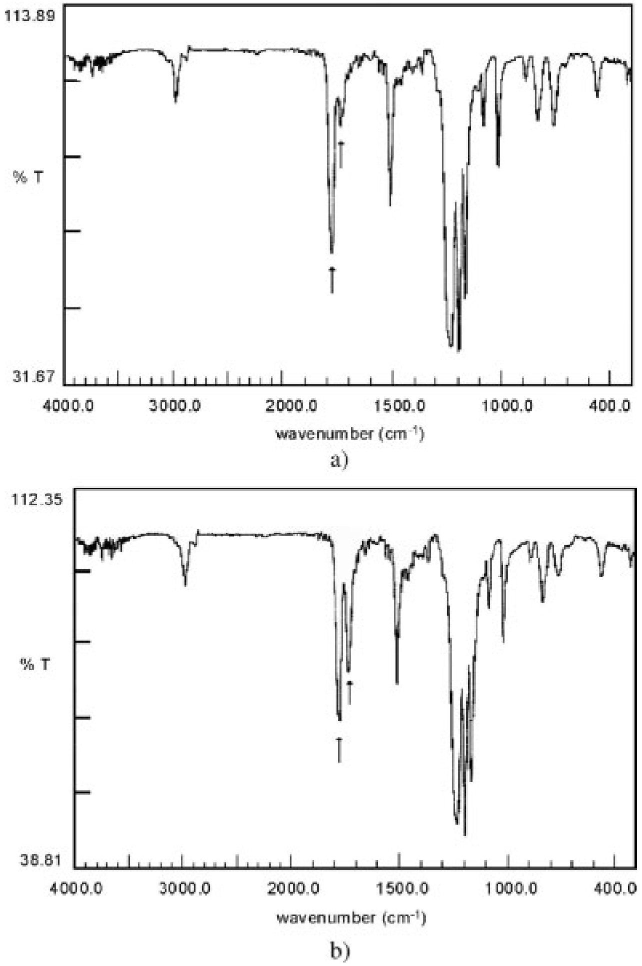


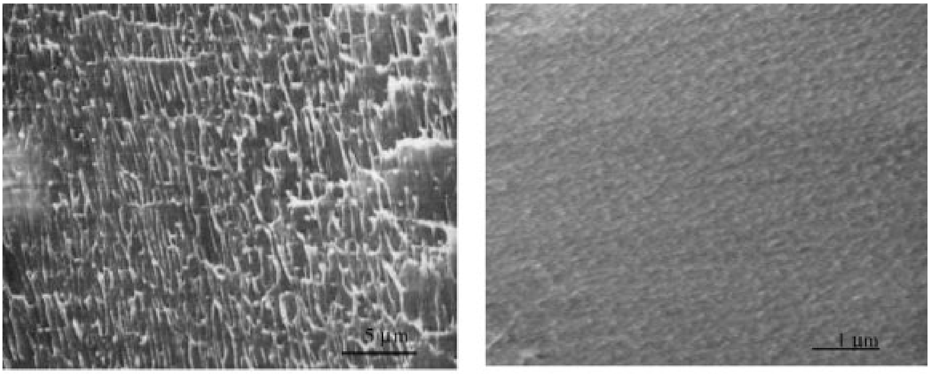
Figure 1.
FT-IR spectra of acetone-insoluble fraction of Blend 2 (a) and Blend 8 (b). Arrows indicate the C=O stretching bands at 1774 cm^{-1} and 1732 cm^{-1} of PC and PMMA, respectively.

strongly depend on the molecular weights of the starting polymers. In fact the thermograms reported in Figure 4 show that being the same the composition and the mixing conditions, when a higher PMMA molecular weight ($M_w =$ 300,000 g/mol) is used, the blend still exhibits two glass transition temperatures even after 6 min of mixing at 250 °C.

The development of a single T_g PMMA/PC blend could be interesting to produce high performance materials, but is essential to avoid or to reduce some main thermally induced degradation reactions; of course the use of long mixing times in not the adequate strategy for this purpose.

In principle, the grafting reaction due to the *trans*-esterification reaction between the ester pendant group of PMMA and the carbonate group of PC could be promoted also with short mixing times employing a specific catalyst.

In this contest, PMMA/PC blends with the addition of 1 wt-% of TBATPB, a *trans*-esterification catalyst, were prepared by melt mixing for 2 min and 6 min. As reported in Table 1, all samples, namely Blend 7–9 and Blend 10–12, show a

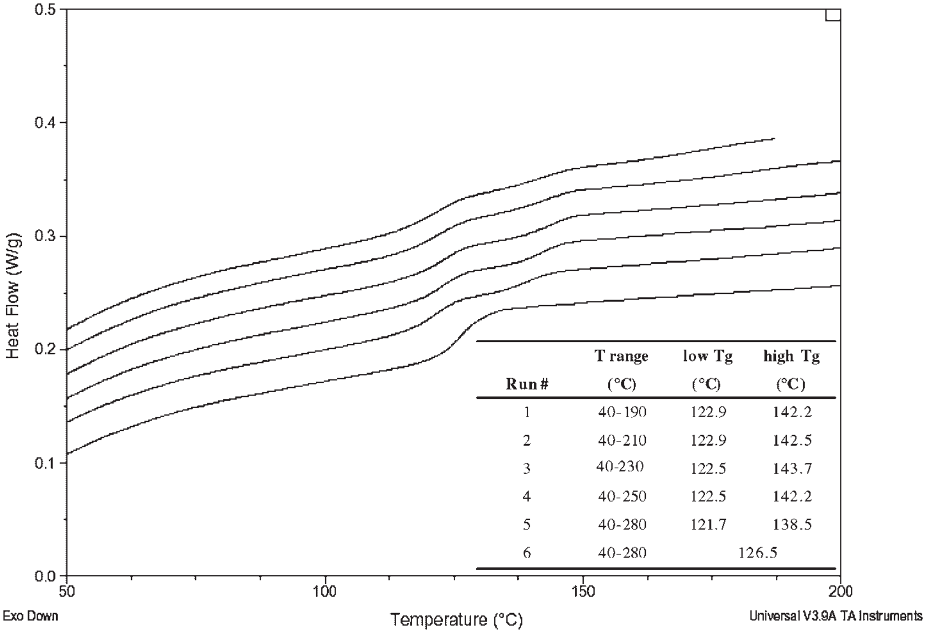


a) b)

Figure 2.
SEM micrographs of Blend 2 (a) and of Blend 8 (b).

single T_g which increases with the PC content; moreover, on going from 2 min to 6 min of mixing time, the T_g decrease is quite the same for each composition, but also in this case the blends obtained with longer mixing times are yellowed.

To have a further check of PMMA/PC miscibility, all the prepared blends characterized by a single T_g have been subjected to annealing experiments at 20 °C below T_g for annealing times ranging from 60 to 480 min. The single enthalpy recovery peaks observed are additional evidence that we have obtained miscible blends. In fact, it is known from literature that the enthalpy recovery peak can be used to



Run #	T range (°C)	low Tg (°C)	high Tg (°C)
1	40-190	122.9	142.2
2	40-210	122.9	142.5
3	40-230	122.5	143.7
4	40-250	122.5	142.2
5	40-280	121.7	138.5
6	40-280	126.5	

Figure 3.
Thermal treatment carried out on blend 2. The experiment consists of six subsequent scan at 10 °C/min each time increasing the end-run temperature from 190 °C to 280 °C. The table in the graph shows the temperature range of each cycle and the corresponding glass transitions observed.

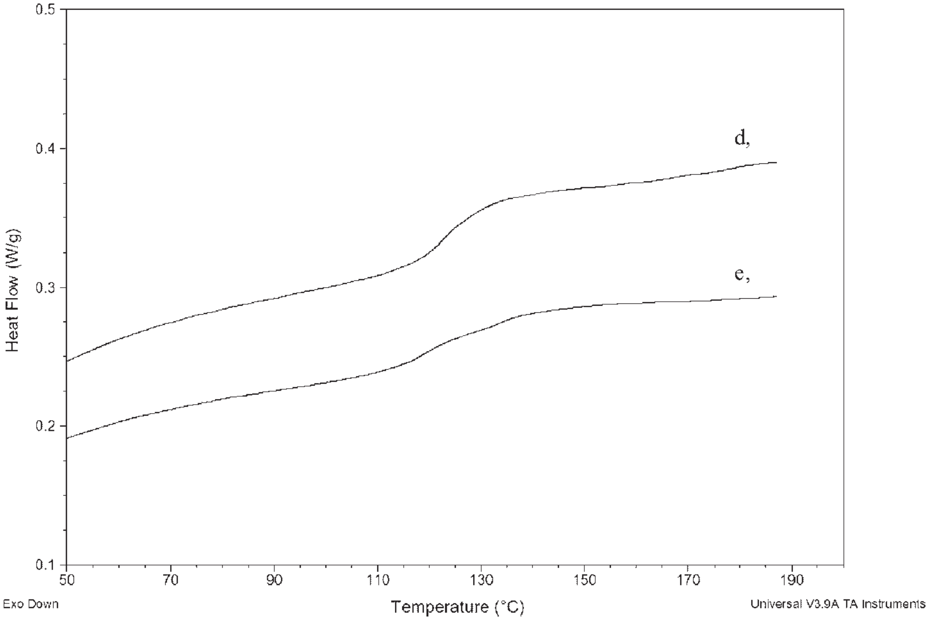


Figure 4.
DSC scans at 10 °C/min carried out on 50/50 PMMA/PC blends melt mixed at 250 °C and 60 rpm for 6 min. a) PMMA $M_n = 59{,}700$ g/mol; b) PMMA $M_n = 300{,}000$ g/mol.

determine polymer-polymer miscibility because each polymer has its own relaxation behaviour, manifested in the position and in the magnitude of the enthalpy recovery peak.[16] As example, in Figure 5 the annealing experiments carried out on Blend 5 (a) and Blend 8 (b) are reported: the enthalpy recovery peak observed have the characteristics of a single pure component.

The OM and SEM morphological analyses performed on Blends 7–9 confirm that these blends are homogeneous. In Figure 2.b the SEM micrograph of Blend 8 is reported.

To find evidence of ester-ester exchange reaction between PMMA and PC, a FT-IR analysis was carried out on the acetone-insoluble fraction of PMMA/PC blends melt mixed for 2 min with and without the catalyst. If *trans*-esterification occurs during the melt mixing, the blend becomes insoluble in the solvent. The unreacted PMMA was extracted by acetone and insoluble fraction was completely dissolved in chloroform and cast on KBr disk.

In Figure 1.a and 1.b are shown the FT-IR spectra of Blend 2 and Blend 8. The characteristics carboxyl stretching bands of PC and PMMA, respectively at 1774 cm^{-1} and 1732 cm^{-1}, are evident in both samples and the $PC_{C=O}/PMMA_{C=O}$ ratio goes from 3.1 for Blend 2 to 1.4 for Blend 8. These results indicate that *trans*-esterification already occurs at 2 minutes of mixing time and the catalyst addition acts effectively in the direction of increasing the *trans*-esterificated product. The acetone-insoluble fraction of the PMMA/PC physical mixture, without thermal treatment, shows the band at 1774 cm^{-1} only.

The Size Exclusion Chromatography (SEC) was used to evaluate the effect of the chemical reaction on the molecular weight distribution (MWD). In this case the blends melt mixed for 2 min with and without the catalyst and PMMA/PC physical mixture were taking into account.

The SEC traces reported in Figure 6.a are referred to Blend 2 and Blend 8 and show that, with respect to the physical mixture, the reaction shifts the maximum of

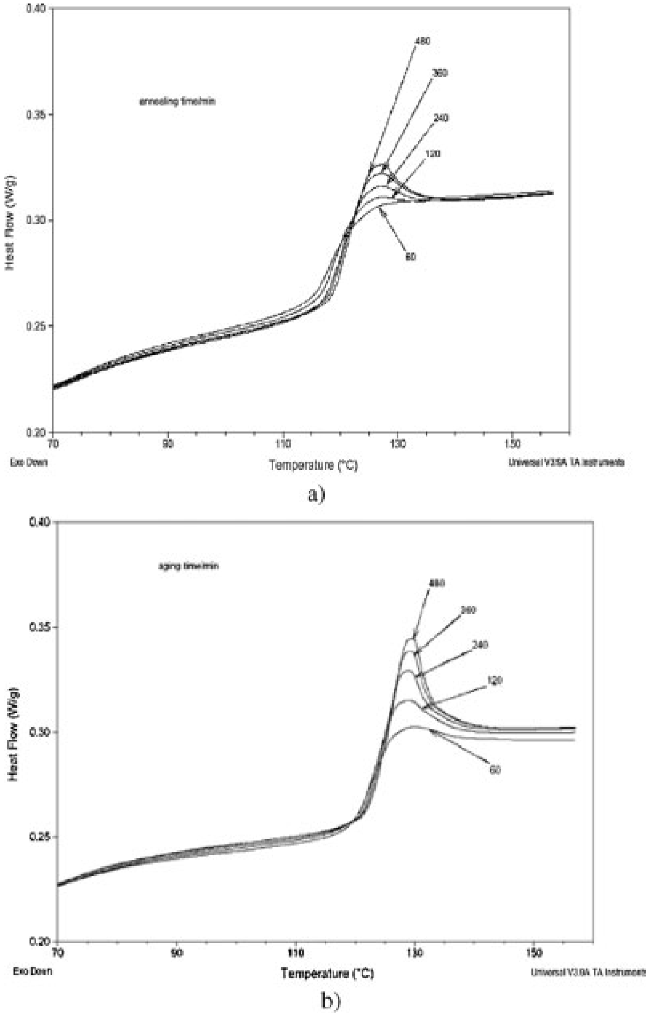


Figure 5.
DSC heating scans at 10 °C/min for a) Blend 5 and b) Blend 8 annealed at $T_a = T_g - 20$ °C for the times indicated on each curve.

the peak to higher elution times, which means to lower molecular weights, and wider distributions are obtained. This is more evident in the blend melt mixed with the catalyst and is related to the decrement of average molecular weight of PC during the reactive mixing; moreover the arrow in Figure 6.a highlights the appearance of PMMA peak. On the other hand, a small fraction of Blend 2 and Blend 8 gets out in order at lower elution times with respect to the physical mixture, suggesting an increment of PMMA molecular weight. This is definitely evident in the blends melt mixed with the catalyst for 6 min. In fact, as shown in Figure 6.b for Blend 11, there is a remarkable fraction of macromolecules at lower elution times with respect to the blend melt mixed with the catalyst for 2 min (in Figure 6.b Blend 8); moreover there is a further decrement of PC molecular weight and the PMMA peak is completely visible.

These results, that are the decrease of PC molecular weight and the increase of the molecular weight of a fraction of PMMA when the *trans*-esterification catalyst is

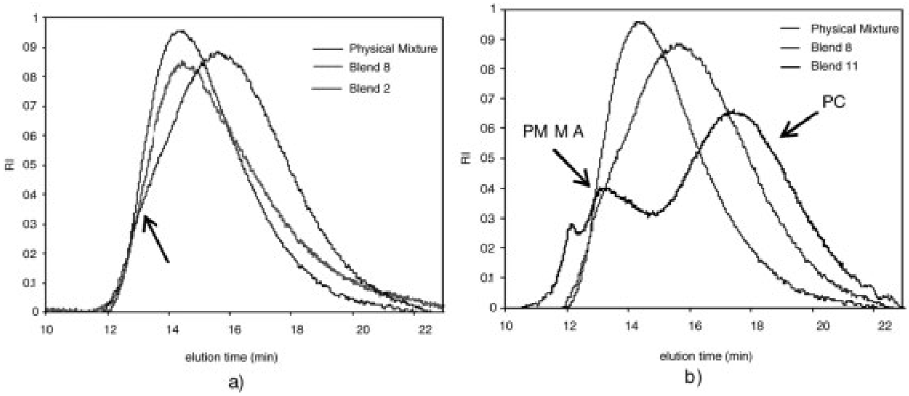


Figure 6.
a) SEC traces of Blend 2, Blend 8 and of PMMA/PC physical mixture; b) SEC traces of Blend 8, Blend 11 and PMMA/PC physical mixture.

used, are in accordance with the taking place of the *trans*-esterification reaction, even if at 250 °C also other reactions could be active.

Conclusions

According to the previous discussed results, the following conclusions can be drawn.

A single T_g PMMA/PC blend was obtained by reactive blending in a discontinuous mixer with short residence time and with the addition of a trans-esterification catalyst. The miscibility of this system was evaluated with conventional DSC analysis and confirmed by annealing experiments. Evidences of ester-ester exchange reaction were pointed out *via* FT-IR analysis and the consequent effects on the molecular weights distribution were shown with SEC.

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