



ELSEVIER

Applied Surface Science 203–204 (2003) 556–560

applied
surface science

www.elsevier.com/locate/apsusc

Surface evolution of polycarbonate/polyethylene terephthalate blends induced by thermal treatments

A. Licciardello^{a,*}, A. Auditore^a, F. Samperi^b, C. Puglisi^b

^a*Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 6, 95125 Catania, Italy*

^b*ICTMP, Consiglio Nazionale delle Ricerche, V.le A. Doria 6, 95125 Catania, Italy*

Abstract

Bisphenol-A polycarbonate (PC) and polyethyleneterephthalate (PET) blends are known to undergo, upon thermal treatment (melt mixing), exchange reactions leading to the formation of copolymers having a final structure that is also affected by consecutive reactions involving CO₂ and ethylene carbonate losses. In this work we followed the evolution of the surface composition of this system during the melt mixing at 270 °C, both with and without catalysts, by means of time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The static SIMS spectra obtained at different treatment times show the appearance of peaks related to newly formed structures and also the modification of the relative intensities of peaks characteristic of both the initial constituents of the blend. From the variation of the relative intensities of peaks related to the bisphenol-A unit of PC and to the phthalate structure of PET, it is shown that after the first stages of melt mixing the surface is PC enriched and that with the progressive formation of a random copolymer the phthalate units increase their concentration at the surface of the system. Hence, as final result of the melt mixing process, the surface composition tends to reflect the relative amount of the repeating units in the bulk.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: ToF-SIMS; Polymer blends; Melt mixing

1. Introduction

The study of the chemical reactions occurring in polymer blends during thermal treatments continues to attract a certain interest, especially in connection with their influence in the miscibility of the system. Indeed such reactions can be an attractive and low cost route for the preparation of materials with controlled chemical and/or mechanical properties. In particular, reactions occurring in polyester/polycarbonate systems have been subject to extensive studies [1,2]. In the

case of blends of bisphenol-A polycarbonate (PC) and polyethyleneterephthalate (PET), detailed information on the results of the thermal reaction is available, obtained by various techniques including IR, NMR and direct pyrolysis MS [1–3]. It is known from such studies that thermal treatment induces exchange (transesterification) reactions, that lead to the formation of copolymers with a final structure that is also affected by parallel decomposition reactions, mainly loss of carbon dioxide and ethylene carbonate (EC) [1]. It is also known that at relatively low processing temperatures (270 °C) the addition of a catalyst is needed in order to obtain a reasonable reaction rate. As to the surface of these systems after thermal treatment, little information is available on the effect of the thermally

* Corresponding author. Tel.: +39-0957385086;
fax: +39-095580138.
E-mail address: alicciar@unict.it (A. Licciardello).

induced reactions in terms of surface composition and chemical structure. Among the surface techniques suitable for such investigation, time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is one of the most powerful and well-recognized tools for the study of polymer surfaces, and has been already successfully applied to the study of polymer blend systems [4–6]. In the present paper the surface evolution caused by thermal processing of equimolar PC/PET polymer blends has been investigated by means of ToF-SIMS.

2. Experimental

Equimolar mixtures of commercially available (Polymer Scientific Products) PET (approximately MW 35,000) and bisphenol-A polycarbonate (MW 25,000) were melt mixed at 270 °C under nitrogen flow in a Brabender mixer for various treatment times with and without the addition of a transesterification catalyst, namely $\text{Ti}(\text{O}i\text{Bu})_4$. The sample mixed for

2 min without catalyst is considered as the “zero time” PC/PET blend, also referred in the following as the “physical mixture”. Samples suitable for surface analysis were prepared by press molding the reacted mixtures between two aluminium foils in order to obtain 0.5–1 mm thick plates. The aluminium foil was peeled-off just before the ToF-SIMS measurement. The method allows to obtain a reproducible surface [5]. ToF-SIMS spectra were obtained in static mode with a ToF-SIMS IV spectrometer (ION-ToF), by using a pulsed $^{69}\text{Ga}^+$ ion beam (25 keV, ~ 0.5 pA) or an Ar^+ beam (10 keV, ~ 0.5 pA) rastered over a $300 \times 300 \mu\text{m}^2$ area. Primary ion fluence was kept $< 3 \times 10^{11}$ ions cm^{-2} . Surface charge compensation was accomplished by pulsed low energy electron flood.

3. Results and discussion

The melt mixing of the PC/PET blends causes the occurrence of transesterification and consecutive

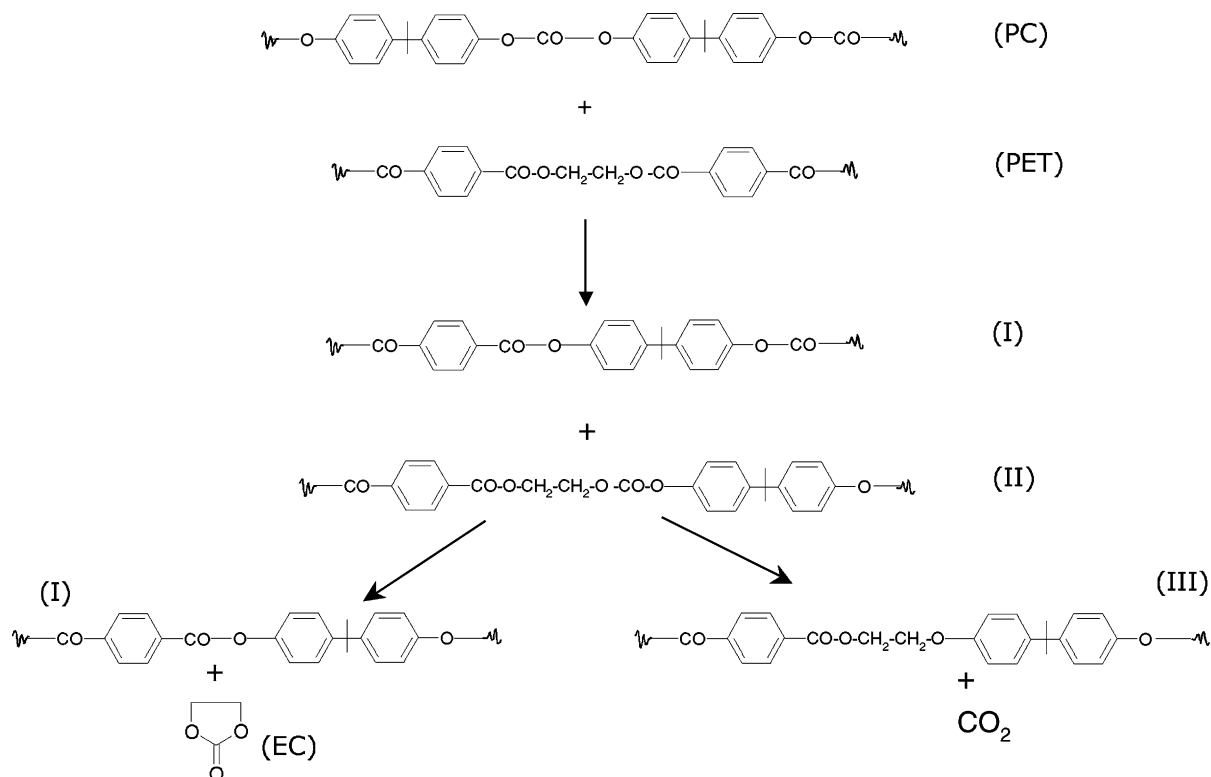


Fig. 1. Scheme of the reactions occurring in the PC-PET blend during melt mixing.

decomposition reactions, that cause the formation of a three component random copolymer, according to the well known mechanism [1] illustrated in Fig. 1. In the present work we show that these processes, in addition, give rise to sensible changes of surface composition, as reflected by the modification of ToF-SIMS spectra, that change both in terms of relative intensities and of appearance of peaks not present in the homopolymers composing the physical mixture.

Fig. 2 reports the positive static SIMS spectra of two samples treated for different times in the presence of catalyst (Fig. 2b and c), together with the spectra of pure PC (Fig. 2a) and PET (Fig. 2d). For the sake of brevity only two treatment times are reported in the figure although, for the catalysed system, measurements at six different treatment times (up to 60 min) have been performed. Some relevant peaks are labelled in the spectra of the homopolymers and of one of the reacted blends. All the spectra of the thermally treated samples are dominated by the presence of peaks pertaining to the initial homopolymers,

such as those at m/z 104, 148, 149, 191, 193 (PET) and 115, 135, 165 (PC). However, the reacted mixtures exhibit the presence of new peaks, in particular m/z 359, 387, 403, 447, 491. Such peaks, as suggested by the structures proposed in Fig. 3 are pertaining to fragments containing both the bisphenol-A and the phthalate structures, so that they give the indication that intermolecular exchange reactions occurred. From the spectra it also appears that the relative intensities of both the homopolymer- and PC-PET copolymer-related structures change with the treatment time. Actually, the intensities of the copolymer-related structures appear to exhibit a complex trend, and its interpretation is not easy due to the difficulty in obtaining a proper intensity normalization, also in consideration of the low peak intensities. A discussion of the intensity trends of the copolymer-related peaks will be published elsewhere. By contrast, the interpretation of the behaviour of the intense peaks related to the repeating units present in the system appears more straightforward.

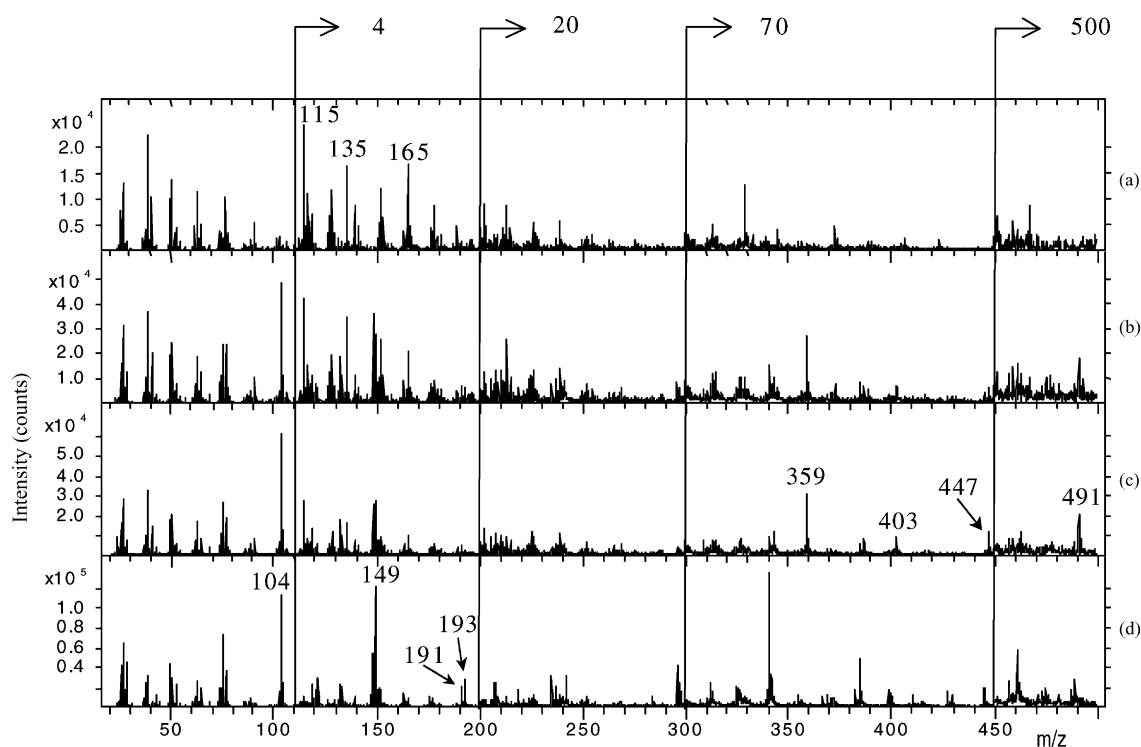


Fig. 2. Positive ToF-SIMS spectra of: (a) pure PC; (b) and (c) PC/PET blend after 10 and 60 min of melt mixing at 270 °C, respectively; (d) pure PET.

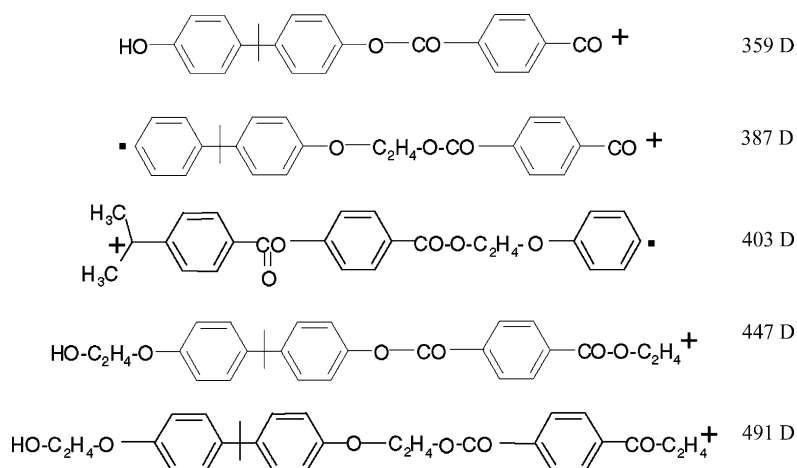


Fig. 3. Proposed structures of some fragment ions characteristic of the spectra of the melt mixed blend.

Fig. 4 presents the evolution of the intensity ratio between m/z 135 and m/z 104, that probe the presence at the surface of segments containing bisphenol-A and phthalate units respectively. In the absence of matrix effects and for an uniform mixture, one would expect

that such ratio should not change, since the relative concentration of the two units in the system is not affected by the transesterification reaction nor by the CO_2 and EC losses. What is actually found is a steep increase of such ratio on going from the unreacted

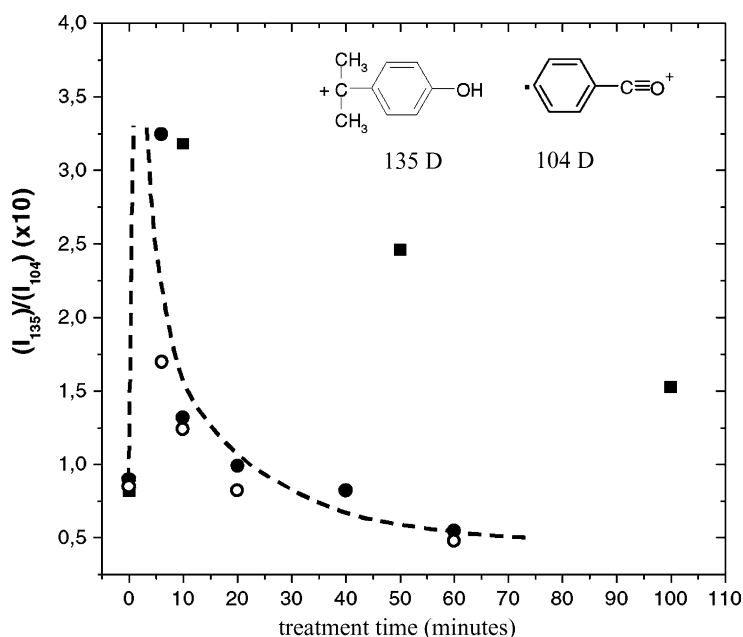


Fig. 4. Intensity ratio of peaks at 135 and 104 D as a function of melt mixing time at 270 °C. Squares refer to the uncatylsed system, circles to the catalysed one. Solid symbols: 25 keV Ga^+ primary ions, open circles: 10 keV Ar^+ ions. The dashed line following the points pertaining to the catalysed system has been drawn as a guide to the eye.

mixture to that treated for 6 min, and a subsequent decrease of the ratio as the treatment time increases. The mixture treated for 60 min, for which the reaction can be considered complete [1], shows a ratio that is similar to that of the physical mixture. It is to be noted that the same behaviour and the same relative intensities are found by using Ga^+ or Ar^+ primary ions. On the same figure, for comparison, the data for the blend prepared without catalyst are reported. For such samples we observe a similar sudden increase of the ratio followed by a decrease that is much less steep than in the catalyst-containing system, with the sample treated for 100 min exhibiting a ratio that is similar to that pertaining to the catalysed system after a treatment time between 6 and 10 min. Since the exchange reactions occur much slowly, also in agreement with data for the bulk [2], the composition of the sample melt mixed for 10 min without catalyst is very similar to that of the physical mixture. This suggests that the initial increase of the 135/104 intensity ratio is due to a surface enrichment of the blend with the PC phase, provided that a sufficient time at high temperature is given to the system in order to allow the rearrangement of the macromolecular chains. Indeed one can hypothesize that the in “zero mixing time” system the surface has, for statistical reasons, the same composition of the bulk. As the system is allowed to rearrange, due to the melt mixing at high temperature, the surface is enriched with the lower free energy phase, which is thought to be PC. When the exchange reactions start to occur, a block PC-PET copolymer is formed, but its structure tends to become random as the exchange reaction progresses. It is expected that in a block copolymer system the surface can be enriched with the lower free energy segments similarly to what occurs in the mixture of the homopolymers. The randomization will increasingly prevent such

phase separation so that the surface of a completely random copolymer is expected to have the same composition of the bulk, and this is reflected by the progressive decrease of the 135/104 intensity ratio as the melt mixing time increases. Such picture could appear quite oversimplified, because of the presence of consecutive degradation reactions (CO_2 and EC loss, see Fig. 1(I)) that cause the final structure of the system to be different from that of the simple PC-PET copolymer that would be formed if exchange reactions only have occurred. However, we must note that the molar ratio of the bisphenol-A and terephthalate units remains unchanged, so that the above outlined explanation has to be considered basically correct.

Acknowledgements

CNR (Rome) is gratefully acknowledged for partial financial support.

References

- [1] G. Montaudo, C. Puglisi, F. Samperi, in: S. Fakirov (Ed.), *Transreactions in Condensation Polymers*, Wiley, New York, 1999, p. 159 and references therein.
- [2] F. Pilati, M. Fiorini, C. Berti, in: S. Fakirov (Ed.), *Transreactions in Condensation Polymers*, Wiley, New York, 1999, p. 79 and references therein.
- [3] P. Godard, J.M. Dekominck, V. Devlesaner, J. Devaux, *J. Polym. Sci., Polym. Chem. Edn.* 24 (1986) 3301–3315.
- [4] X. Vanden Eynde, P. Bertrand, *Appl. Surf. Sci.* 141 (1999) 1–20.
- [5] A. Licciardello, C. Puglisi, D. Lipinsky, E. Niehuis, A. Benninghoven, in: A. Benninghoven, et al. (Eds.), *Secondary Ion Mass Spectrometry SIMS X*, Wiley, Chichester, 1997, pp. 711–714.
- [6] P. Brant, A. Karim, J.F. Douglas, F.S. Bates, *Macromolecules* 29 (1996) 5628–5634.