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Thin films of polymer blends: surface treatment and theoretical modeling

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Abstract

This work deals with the theoretical modeling, surface characterization, and excimer laser surface modification of thin films of polymer blends. The compounds considered in this study are bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) mixed in various mass ratios. The surface morphology of these blends and the influence of laser irradiation are investigated by means of atomic force microscopy. In parallel, the interactions occurring at the molecular level between the two polymers are modeled theoretically in order to provide information in the context of their miscibility. On one hand, we use the Hartree–Fock semiempirical Austin Model One method to obtain detailed geometrical structures for short oligomers. On the other hand, a molecular mechanics technique provides further information on PC and PMMA chains at the surface.

1. Introduction

The success of polymers as biomaterials is mainly related to their wide range of mechanical properties, transformation processes and their low cost [1]. One of the major parameters characterizing the quality of a biopolymer is its compatibility with living tissues. The biocompatibility of polymeric biomaterials is determined largely by specific interactions between proteins adsorbed onto the polymer surface and receptors on the surface of cells [1]. On that basis, surface modification of polymers towards improved

biocompatibility is of particular interest; a number of chemical approaches have been used towards these ends [2]. Along the same line, the creation of heterogeneities on the polymer surface at the subcellular and the cellular scale can enhance specific interactions with living tissues, because they can induce local gathering of cellular receptors.

In this paper we present a specific approach for the creation of such heterogeneities based on the excimer laser surface modification of thin films of polymer blends. Different immiscible polymers can be combined into a single material leading to a complete phase separation in the solid state. Such blends are microscopically heterogeneous; they are therefore good candidates to improve the interactions with living systems. The UV-pulsed laser treatment

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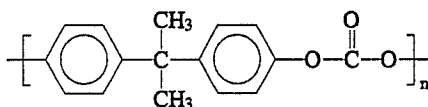
of these blends is expected to induce local changes in the roughness of the polymer surface, dependent on the way the two polymers absorb the radiation at the near surface. In particular, the ablative photodecomposition process [3–5] is of great interest because it leads to physical modifications of the morphology of polymer surfaces.

The compounds considered in this study are bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA) mixed in various mass ratios. Both are biocompatible polymers. The surface morphology of the PC–PMMA blends is investigated by means of atomic force microscopy (AFM), optical microscopy and profilometry before and after the laser treatment.

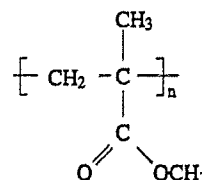
It is important to notice that the morphology of thin films of these blends is strongly dependent on the interactions occurring at the molecular level at the interfaces between the two phases. In this context, we have also focused on the modeling of these interfaces, following two theoretical approaches. On one hand, we use the Hartree–Fock semiempirical Austin Model One (AM1) [6] quantum chemical method to obtain detailed geometrical structures for oligomers. On the other hand, a molecular mechanics technique [7,8] provides further information on the conformation of PC and PMMA chains in the blend.

2. Experimental and theoretical procedures

Bisphenol-A polycarbonate (LEXAN 141 – General Electric; weight average molar mass $M_w = 34577$, polydispersity = 1.46) and poly(methyl methacrylate) (OROGLAS V825 – Rohm and Haas; $M_w = 55727$, polydispersity = 1.26) were used in this study:



Bisphenol-A polycarbonate



Poly(methyl methacrylate)

The blends were prepared by dissolving various mixtures of PC and PMMA with different mass ratios in CH_2Cl_2 at a total polymer concentration of 5 wt%. Thin films of the blends were cast on silicon substrates at room temperature. This yields transparent films with an average thickness of 3 μm , as determined by profilometry measurements (Sloan Dektak 3030ST). Blends were prepared with the following PMMA/PC concentrations: 100/0, 95/5, 90/10, 85/15, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 25/75, 20/80, 10/90, 5/95, 0/100.

The phase separation behaviour in the different compositions and the effect of the laser treatment were observed with an optical microscope working in the reflection mode (Leitz Wetzlar Orthoplan).

Laser irradiation was carried out using a KrF (248 nm) Lambda Physik LPX 100 excimer laser in air. The fluence was selected by adjusting the distance between a lens and the sample. The irradiation consisted of five 30 ns pulses at 1 Hz (the energy per pulse being kept constant). Experimental conditions for the laser treatment of blends were determined from a series of measurements on the pristine polymers investigated as reference samples.

The surface roughness of the laser-irradiated polymer films was analyzed by atomic force microscopy (AFM) in air (Nanoscope III, 100 μm triangular cantilever, wide legs, constant spring = 0.58 N/m). The largest scan area was $1 \times 1 \mu\text{m}$ (head type A). We also followed the surface modifications induced by the laser irradiation using optical microscopy and profilometry.

At the theoretical level, we performed quantum-chemical calculations on short oligomers of PC and PMMA. The molecular geometries of these oligomers were fully optimized with the AM1 method implemented in the MOPAC 93 package, running on an IBM RISC 6000 workstation. The oligomers were

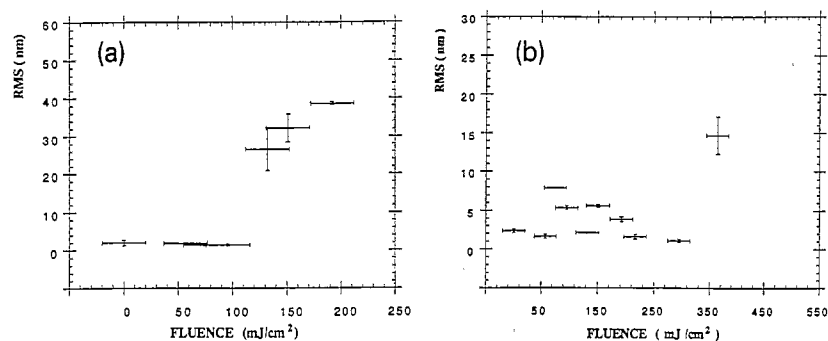


Fig. 1. Dependence of the AFM-determined root-mean-square (RMS) surface roughness of irradiated PC (a) and PMMA (b) on fluence (mJ/cm^2).

also investigated with the Polygraf molecular mechanics package running on a Silicon Graphics 4D35TG workstation. Clusters made of one PC and one PMMA oligomer were also studied at the molecular mechanics level.

3. Experimental results

Pure PC and PMMA were first irradiated at increasing fluences in order to determine their ablation threshold. Fig. 1 shows the dependence of the root-mean-square (RMS) surface roughness with fluence (mJ/cm^2). The RMS roughness has been calculated from typical $600 \times 600 \text{ nm}$ AFM images. It dramatically increases at fluences close to $100 \text{ mJ}/\text{cm}^2$ for pure PC while for PMMA, the increase in surface roughness occurs above $350 \text{ mJ}/\text{cm}^2$; these results indicate that ablative processes have taken place

[9–11]. The AFM results show the evolution of the roughness as a function of fluence. While the surface of the untreated samples is very smooth and shows no damage (RMS roughness $\sim 4\text{--}5 \text{ nm}$), fluences above the ablation threshold induce dramatic changes in the surface topography. As a consequence, the roughness is strongly increased (RMS roughness $15\text{--}20 \text{ nm}$). The optical microscopy photographs of PC irradiated at $124 \text{ mJ}/\text{cm}^2$ clearly confirm the evolution of the surface morphology, whereas for pure PMMA no changes were observed in the morphology after the same treatment.

Based on the study of the pure compounds, polymer blends of PC and PMMA were investigated. Optical microscopy on the untreated blends (Fig. 2a) shows that such mixtures consist of two phases with microscopic domains whose size is strongly dependent on the blend composition and the preparation process. Infra-red microscopy measurements show

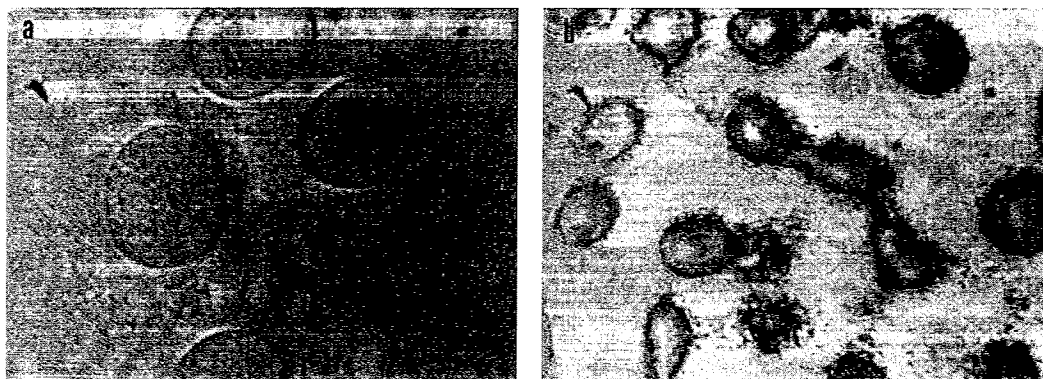


Fig. 2. Optical micrographs of the PC/PMMA blend (70/30) untreated (a) and irradiated at a fluence of $124 \text{ mJ}/\text{cm}^2$ (b); picture size: $240 \mu\text{m} \times 170 \mu\text{m}$.

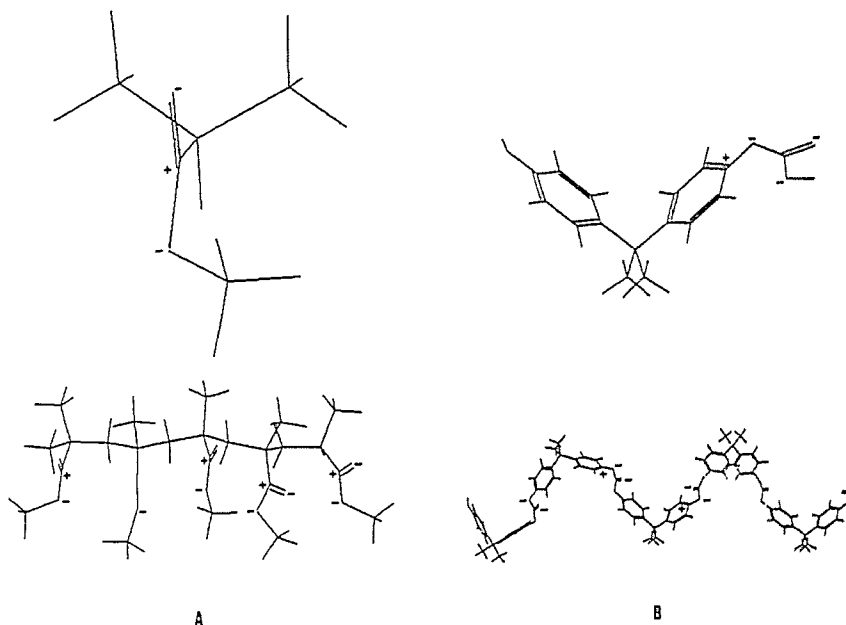


Fig. 3. Molecular structure and charge distribution of the PMMA monomer and pentamer (a) and the PC monomer and pentamer (b).

that the nodules consist mostly of the minority polymer while the matrix is made of the majority polymer, as expected. However, we observe that there can be small amounts of PMMA in the PC nodules, probably because the two polymers are not completely immiscible. All the blends received 5 pulses with a fluence of 124 mJ/cm^2 , for which we have observed significant ablation for PC and no changes for PMMA.

Upon irradiation, the surface of the films appears to be modified (Fig. 2b). The affected areas are most probably PC-rich regions where the ablative photodecomposition process takes place. The AFM images of the treated surfaces are consistent with these optical micrographs. We observe that in some areas the RMS roughness is much higher than in untreated films (20 versus 5 nm) while in other areas of the same samples, the roughness has not changed (~ 5

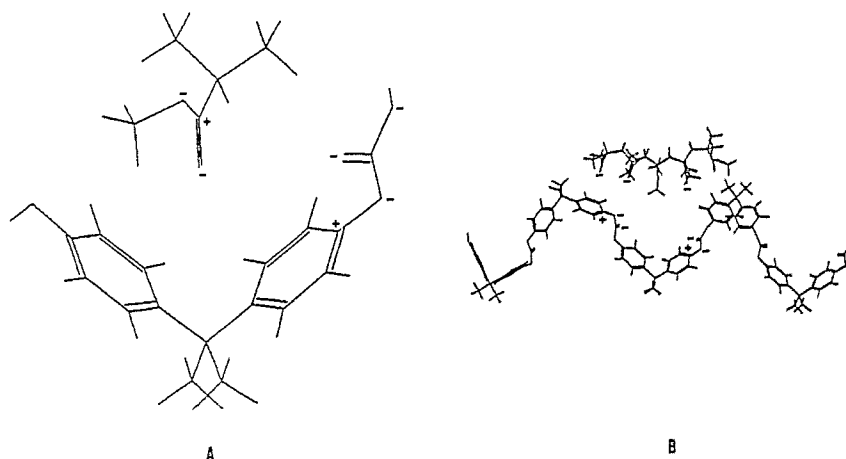


Fig. 4. Molecular structure and charge distribution of the PC monomer/PMMA monomer cluster (a) and the PC pentamer/PMMA pentamer cluster (b).

nm). This is a clear indication that photoablation has occurred locally on the surface.

4. Theoretical results

We first optimize separately short oligomers of the two polymers. The molecular structure and charge distribution are displayed in Fig. 3 for a few selected oligomers. As expected, the oxygen atoms in PMMA exhibit a negative character while the carbon atom of the carboxylic function is positive. The methyl group attached to the oxygen atom also shows a small negative character. PC oligomers have a region with electron deficiency around the aromatic carbon linked to the carbonate group, while a negative character is localized on the oxygen atoms and on the methyl groups. These results therefore suggest that favourable interactions between the oxygen atom of PMMA and the phenyl rings of PC can take place.

The optimized structures of PC/PMMA clusters are displayed in Fig. 4. We consider here the PC monomer (PC01) interacting with the PMMA monomer to a trimer (PMMA01 to PMMA03). The first cluster (PC01/PMMA01) is found to be 16.5 kcal/mol more stable than the separated species. In that case, we observe that the oxygen atom of the carbonyl group of PMMA lies 3.02 Å from a carbon atom of the aromatic ring. We also find an interaction between one hydrogen atom of the methyl ester group and the doubly-bound oxygen of the carbonate function. The PC01/PMMA02 complex also shows an interaction between the oxygen atoms of the carbonyl groups of PMMA and the phenyl rings of PC. This leads to a standard heat of formation of 92.0 kcal/mol, which is 25.5 kcal/mol more stable than the separated molecules. The minimum distance between the oxygen atom and the carbon atom of the aromatic ring is again around 3 Å. The cluster between the PC monomer and the PMMA trimer is 38.9 kcal/mol more stable than the isolated oligomers.

We then optimize the geometry of complexes formed by the pentamer of PC (PC05) with the monomer and with the pentamer of PMMA (PMMA01 and PMMA05). For the first cluster we obtain an energy gain of 13.5 kcal/mol. This could be explained by the interaction between the oxygen

atom of the PMMA monomer with the aromatic ring while the O–CH₃ group is in interaction with the carbonyl function on the carbonate group. Finally, the complex formed by pentamers of PC and PMMA presents a standard heat of formation which is 28.2 kcal/mol more stable than the separated molecules. Again, we notice an interaction between the doubly-bound oxygen of the PMMA species and the phenyl ring. An interaction between the hydrogens of the methyl group of one cell of PC and the oxygen of the PMMA carbonyl also appears.

5. Conclusions

It has been shown that polymer blends of PC and PMMA can be specifically patterned by excimer laser irradiation. AFM measurements and optical microscopy observations demonstrate the selectivity of the ablation process in the case of PC/PMMA polymer blends.

The theoretical results indicate that the main interaction occurring in the investigated clusters takes place between the carbonyl group of PMMA and the aromatic rings of PC. Other interactions also occur between hydrogens and electronegative atoms. We can also notice that all the PC/PMMA complexes studied in this work are more stable than the separated oligomers.

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