Evidence of glass transition in thin films of maleic anhydride derivatives: Effect of the surfactant coadsorption

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Received 24 April 2008
Published online: 7 July 2008 – © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2008

Abstract. The glass transition temperature of poly (maleic anhydride-alt-1-octadecen) and poly (styrene-co-maleic anhydride) cumene-terminated thin films has been measured by mechanical relaxation of Langmuir films of these polymers. The dynamical properties show glass-like features (non-Arrhenius relaxation times and non-Debye mechanical response) interpreted by the coupling model. The glass transition temperature values determined by a mechanical relaxation experiment (step-compression) agree very well with those obtained by surface potential measurements. It is found that the glass transition temperature values in thin films decrease by about 100 K as compared with those corresponding to the bulk polymers. The coadsorption of the water-insoluble surfactant DODAB decreases the glass transition temperature.

PACS. 68.15.+e Liquid thin films

1 Introduction

The thin polymer films are widely used in technological applications such as adhesives, optical or protective coatings, and biosensors [1]. In addition, these films with thickness of nanometers provide an ideal sample geometry for studying the effects of one-dimensional confinement on the structure and dynamics of polymer molecules.

The properties of polymers near the interface differ substantially from those of polymer molecules in the bulk. Thus, when the polymer molecules are confined to dimensions ranging from the size of the individual monomers to the overall size of the molecule, the motion of the molecules can be significantly different than in bulk. To probe the effect of the confinement on the dynamical properties of polymeric thin films, a variety of experimental geometries such as polymers intercalated into layered silicates [2], polymers in nanometer pores [3] and thin polymer films [4] have been studied in recent years. Thin films with thickness of the order of the radius of gyration show a decrease in the glass transition temperature with decreasing film thickness [5]. Several methods have been used to determine the glass transition temperature in these films. One of the most common techniques uses ellipsometry to determine the variation of the film thickness with temperature [5–9]. Brillouin light scattering [10] (BLS) has also been used to obtain $T_g$; however, the time required to carry out the experiment is a limiting factor of this technique. Recent works show that surface quasielastic light scattering [11] and mechanical relaxation (step-compression method) [12] of Langmuir monolayers of glass-forming films are accurate techniques to obtain the glass transition temperature [11,12].

All the experimental results evidence that the surface plays the most important role in the glass transition temperature depression in thin films. However, several basic questions still remain to be answered. One of these questions is the correlation between the molecular structure of polymers at the interface and the $T_g$ values. Some models concluded that the higher chain mobility at the interface is the main reason of the $T_g$ depression [13–15]; in contrast, other studies attribute this fact to intrinsic effects [16]. To study the effect of the polymer structure on the $T_g$, we obtain the equilibrium and the dynamic properties of monolayers of two different maleic anhydride derivatives, poly (maleic anhydride-alt-1-octadecen) and poly (styrene-co-maleic anhydride) cumene terminated. On the other hand, mixtures of surfactants and polymers play an important role on the stabilization of colloids such as emulsions or foams and are also used on the fabrication of multilayer films. The properties of polymer-surfactant mixtures in solution have been extensively studied [17]; however, the surface properties of polymer-surfactant monolayers have been much less studied [18–24]. Therefore, in the last part of the paper we analyze the effect of the addition of the water-insoluble cationic surfactant dodecyldimethylammonium bromide on both the equilibrium and the dynamical properties of polymer monolayers.
The polymer molecules poly (maleic anhydride-alt-1-octadecen), PMAO ($M_r = 40$ kDa) and poly (styrene-co-maleic anhydride) cumene terminated, PS-b-MA, ($M_r = 1.9$ kDa) were from Sigma-Aldrich, see Figure 1. The polymers were used as received without further purification. The polymer molecular weights were provided by the manufacturer. In the case of poly (styrene-co-maleic anhydride) cumene terminated the styrene composition provided by Sigma-Aldrich was 75% w:w. The glass transition temperature of the bulk polymers of were determined using DSC measurements. The $T_g$ value of PMAO (398 K) agrees with the that provided by the manufacturer and the value found for PS-b-MA was 393 K. The calorimetric measurements were carried out at a 20 K min$^{-1}$ heating rate in a Mettler Stare DSC instrument. The calibration of temperature and $C_p$ and the $T_g$ determination were carried out using the methodology published elsewhere [25].

Dioctadecyl dimethyl ammonium bromide surfactant, DODAB, and Chloroform (PAI, filtered) used to prepare the spreading solutions were from Sigma-Aldrich.

**Spreading techniques**

Two different techniques of spreading have been used to study mixed monolayers. One of these techniques uses the spreading of both surfactant and polymer previously mixed, co-spreading. In this case a stock solution of a given composition containing the two components was prepared in chloroform. The solution was spread on the water surface using a Hamilton micro-syringe.

In the separated spreading the two components were separately dissolved in pure chloroform and the solutions were spread separately on the interface. To test the effect of the spreading order on the monolayer properties, we change the order of the addition of each component. Thus if the DODAB solution was first spread a few minutes later, after equilibration of the surfactant monolayer, the solution of polymer was added.

**Langmuir trough**

The monolayers were performed on a computer-controlled Teflon Langmuir mini-trough (KSV, Finland). The surface pressure was measured with a Pt-Wilhelmy plate connected to an electrobalance. The temperature control of water in the trough was carried out by flowing thermostated water through jackets at the bottom of the trough. The water temperature was controlled by means of thermostat/cryostat Lauda Ecoline RE-106. The temperature near the surface was measured with a calibrated sensor from KSV.

In order to confirm the stability of the monolayer, two different forms for preparing the monolayers were used. In the first one the surface concentration was changed by subsequent additions of the polymer solutions on the liquid/air interface. The surface pressure was continuously monitored, and the equilibrium value was taken when the surface pressure $\Pi$ had remained constant for at least 10 min. In the second way, the monolayers were symmetrically compressed by moving two barriers under computer control after the spreading of the polymer solution. The maximum barrier speed was 5 mm/min. The spreading solutions were prepared on chloroform (0.35 mg ml$^{-1}$ for PMAO and 1.00 mg ml$^{-1}$ for PS-b-MA, respectively) by weight using an analytical balance precise to ±0.01 mg.

The relaxation experiments were performed on the Langmuir trough by the step-compression method [12]. The barriers were moved after the desired surface concentration has been reached and the equilibrium value of $\Pi$ obtained. In these experiments the area change, $\Delta A$, was kept below 5% of the total area in order to ensure that the system remained in the linear regime. The time necessary to make the compression was slightly less than 2 s. Readings of $\Pi$ at constant intervals of 1 s were taken until the equilibrium $\Pi$-value corresponding to the final area was reached. The relaxation curve is accepted only if the initial and final values of surface pressure for a given compression agree with those corresponding to equilibrium.

**Brewster angle microscopy (BAM)**

The BAM images were taken using an Optrel BAM 3000 from KSV. The microscope uses a helium-neon laser of 10 mW (632.8 nm) and a digital camera model Kam Pro-02 (768 \times 494 pixels) from EHD.

**Surface potential measurements**

The surface potential $\Delta V$ was measured in the Teflon Langmuir minitrough (KSV, Finland). A Kelvin probe.