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Author(s)	Hu, Xuesong; Lal, Jyotsana; Jiang, Zhang; Sinha, Sunil K.; Narayanan, Suresh; Sandy, Alec; Jiao, Xuesong; Lurio, Laurence B.
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Observation of a Low-viscosity Interface Between Immiscible Polymer Layers

Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL-60439, USA.
Xuesong Hu, Jyotsana Lal[2]
Department of Physics, University of California, San Diego, La Jolla, CA-92093, USA.
Zhang Jiang, Sunil K. Sinha[2]
Advanced Photon Source, Argonne National Laboratory, Argonne, IL-60439, USA.
Suresh Narayanan, Alec Sandy[2]
Department of Physics, Northern Illinois University, DeKalb, IL-60115, USA.
Xuesong Jiao, Laurence B. Lurio[2]

Abstract: X-ray Photon Correlation Spectroscopy (XPCS) was employed in a surface standing wave geometry in order to resolve the thermally diffusive in-plane dynamics at both the surface/vacuum (top) and polymer/polymer (bottom) interfaces of a thin Polystyrene (PS) film on top of Poly(4-bromo styrene) (PBrS) and supported on a Si substrate. The top vacuum interface shows two relaxation modes: one fast and one slow, while the buried polymer-polymer interface shows a single slow mode. The slow mode of the top interface is similar in magnitude and wavevector dependence to the single mode of the buried interface. The dynamics are consistent with a low-viscosity mixed layer between the PS and PBrS and coupling of the capillary wave fluctuations between this layer and the PS.

1 Introduction

Polymer/Polymer interfaces play an important role in the mechanical toughness of polymer blends, adhesion properties in coatings and co-extrusion of polymers. It has been reported that immiscible polymer blends can have viscosities lower than either of their components [1] and recent multilayer co-extrusion experiments indicate that the lower viscosity is due to interfacial slip [2]. Normally, interfaces between immiscible polymers exhibit poor adhesion [3] and this is attributed to weak entanglements between dissimilar polymers at an interface [4]. Dissipation within the interfacial regions can only be indirectly studied with bulk rheological measurements. Most results are in qualitative agreement with theories [4,5,6] that predict fewer chain entanglements near the interface between two immiscible polymers and thus a small interface width with lower viscosity. The lower viscosity at the interface explains slip on application of shear, however existing theories over-predict the slip effect [2]. Here we report on the development of a new technique, employing x-ray photon correlation spectroscopy [7] in a surface standing wave geometry [8,9], which provides a way to resolve the dynamics at buried polymer-polymer interface at nanoscale resolution both parallel and perpendicular to the interface.

2 Results and Discussion

In order to measure XPCS at a buried interface it is crucial to measure scattering from that interface alone, excluding possible scattering from the free surface or polymer-substrate interface. We have solved this problem by directing a coherent x-ray beam onto a polymer bilayer at grazing incidence so that a standing wave is set up in the sample. The phase of this standing wave can be adjusted to have a high intensity at the polymer-polymer interface and simultaneously a node at the polymer-air interface. In addition, at sufficiently grazing incidence angles, the x-rays do not penetrate to the substrate. Thus, the XPCS signal measured in this condition is an indication of the dynamics of the buried interface alone [8,9]. The sample we have chosen for this measurement is a polymer bilayer composed of a 100 nm polystyrene film on top of a 200 nm polybromostyrene film, supported on a Si substrate.
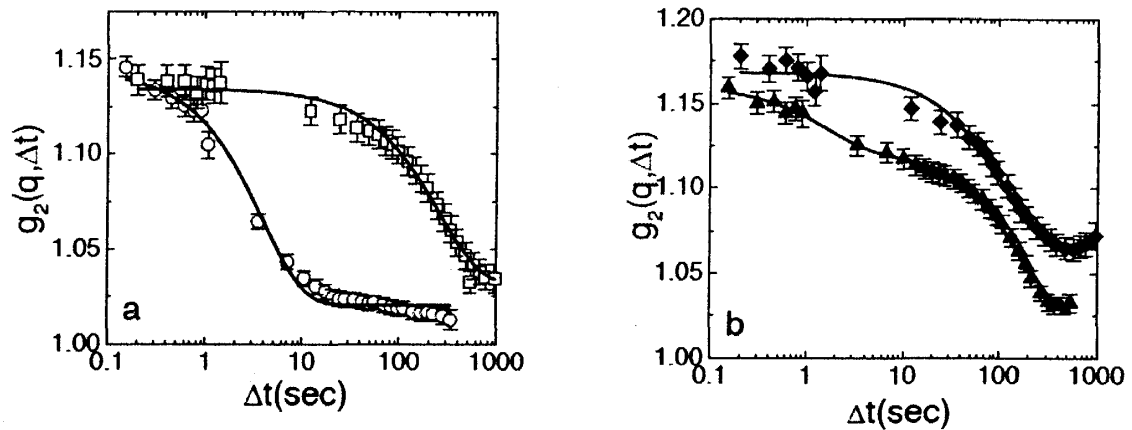
Figure 1: Auto-correlation functions from single and bilayer films at (a) 210°C (q=0.00405nm^{-1}) PS single layer(○) and PBrS single layer(□) (b)210°C (q =0.00430nm^{-1}) PS/PBrS top layer(▲) and PS/PBrS bottom layer(◆).

Figure 1b shows measured XPCS correlation functions for incident angles θ_{in} =0.140° and θ_{in}=0.180°, obtained from the PS/PBrS/Si film at 210°C. As can be seen from the Figure 1 at a fixed in-plane wavevector q=4.3 x 10^{-3}nm^{-1} [8, 9] the scattering at θ_{in} =0.140° is due entirely to the top PS interface, while the scattering at θ_{in}=0.180° is dominated by the buried interface. The solid lines in Figure 1 represent the best single or double exponential fits to the measured autocorrelation at fixed value of q, $g_2(t)$=1+$B\Sigma_i a_i$exp(-2t/τ_i), where B is the speckle contrast and τ_i is the relaxation time for equilibrium surface height fluctuations. The time constant for buried interface (θ_{in} =0.180°) is found to be significantly slower than that of the top surface(θ_{in} =0.140°). The data from top and buried interface of the bilayer is compared to single layers of equivalent thickness at the same temperature (Figure 1a). In conclusion, have implemented a method for measuring diffuse scattering from each of the interfaces within a polymer bilayer, and shown that it is possible to measure XPCS independently at each interface, this has been measured as function of film thickness, wavevector and temperature.

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