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Deformation Behavior of Triblock Copolymers Based on Polystyrene: An FT-IR Spectroscopy Study

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Summary: The effect of the long range order and thermal treatment on the micromechanical deformation of two triblock copolymers was investigated, i.e. polystyrene-*b*-polybutadiene-*b*-polycaprolactone (SBC) triblock copolymer with PS as the matrix and PCL cylindrical domains and a SBS triblock copolymers with 75 wt% of styrene. FTIR spectroscopy revealed information about the molecular orientation upon deformation of the separate components in the triblock copolymers. Films of SBC possess a higher ductility when the semi-crystalline PCL cylindrical microdomains are quenched. In this case, the deformation proceeds via cavitation of the PCL domains and subsequent shear yielding. Long range order of the cylinders leads to embrittlement since crazes formation and crack propagation can proceed along the cylindrical axis. For the SBS triblock copolymers, a morphological transition from lamellar to short rod cylindrical microdomains was obtained by changing the casting solvent from toluene to MEK, while macroscopic orientation could be achieved by compression molding in a channel die. The toluene cast films were ductile and deformed in a homogeneous way. The MEK cast films behaved brittle as a result of crazing. Loading parallel to the lamellae results in yielding by propagation of a stable macroscopic neck.

Keywords: block copolymers; deformation; FT-IR spectroscopy

Introduction

Polystyrene suffers from brittle fracture by catastrophic strain localization in the form of crazes. Considering the network density, the intrinsic toughness of PS is expected to be higher than polycarbonate, which deforms via shear yielding[1]. Crazing or shear yielding results from intrinsic strain softening and strain hardening. PS suffers from strong strain softening in combination with limited strain hardening, giving rise to an extreme localization of stress during deformation by crazing. To obtain a more ductile material, localization of stress has to be prevented, so that the high intrinsic ductility can be transferred to the macroscopic level. A

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possible way is introducing sub-micron particles, which can be done in several ways. One could make use of chemically-induced phase separation to reach the desired morphology[2]. Maximum toughness is expected when an easily cavitating modifier is blended with the glassy polymer matrix, which will support strain hardening. The required morphology cannot be achieved by melt blending routes, so we have used self-assembly of block copolymers. In the self-assembly process, the corresponding monomer is polymerized in the presence of block copolymers[3]. This results in a thermoplastic matrix filled with small rubbery particles. Our results on the morphology development showed that for a large number of systems with block copolymers based on hydrogenated PEB, undesired macro-phase separation occurs during the polymerization, resulting in a PS-rich phase, and block copolymer-rich phase, having a structure similar to the characteristic micro-phase structure of the block-copolymer itself[3]. Suppression of macro-phase separation can be realized by introducing intermolecular hydrogen bonding between the matrix material and the shell block, but this leads to partially or fully miscible systems. Therefore, we focused on two types of triblock copolymers with a high content of PS, which forms the glassy matrix, with special emphasis on the role of cavitation and the transition from crazing to shear yielding. The first block copolymer is polystyrene-*b*-polybutadiene-*b*-polycaprolactone (SBC) triblock copolymer, with a crystalline PCL-block. The second block is a poly(styrene-*b*-butadiene-*b*-styrene) (SBS) triblock copolymer with a polystyrene content of 75 wt%.

In this paper, the local deformation behavior will be presented and discussed as studied by in-situ FT-IR spectroscopy experiments during tensile testing.

Experimental

Materials

The SBC triblock copolymer used in this study was obtained from Prof. Balsamo (University of Caracas, Venezuela). The details of the synthesis are described elsewhere[4] together with the composition and molecular weight (distribution).

The SBS triblock copolymer was obtained from Kraton Polymers (Kraton^{TM} D-1401P). The copolymer has a composition of 75 wt% styrene and 25 wt% polybutadiene and a total molecular weight of 91 kg/mol (M_w/M_n =1.72) as determined by SEC.

Sample preparation

For the SBC triblock copolymer, the order/disorder transition is far above the glass transition temperature of PS; thus, the triblock copolymer is well segregated before the PS matrix vitrifies. Films of 0.2 mm thickness were obtained by a slow casting process at room temperature from 5 wt% toluene solutions. The samples were dried for 5 days under vacuum at 80°C. For further equilibration, the dry films were annealed at 140°C for two hours under a nitrogen atmosphere. The samples were subsequently slowly cooled at room temperature. Another set of samples was compression molded at 170°C and immediately quenched in cold water. Some of the samples underwent an additional quenching step in liquid nitrogen.

The SBS samples were prepared by compression molding at 160°C and by solvent casting from toluene and MEK. The solutions (5 wt%) were dried in F_2-coated glass dishes, such that the dried films had a final thickness of 0.2 mm. The solvent was slowly evaporated in air at room temperature for 6 days. The samples were then dried under vacuum for 48 hrs at 60°C, followed by 24 hrs at 110°C. Orientation of the triblock copolymer films was achieved by elongational flow in a channel die. The mould was first covered with silicon oil to promote elongational flow and prevent shear flow. The mould was heated up to 140°C and solvent cast films were compression molded to 100 bars for 5 minutes. After compression molding, the mold was kept in the machine which was allowed to cool slowly at room temperature.

FTIR spectroscopy

To investigate the molecular orientation of the individual components, polymer films were elongated using a simple, hand driven stretcher. Infrared (IR) spectra were recorded from the stretched sample using a BioRad UMA 500 microscope that is coupled to a BioRad FTS 6000 spectrometer. A wire grid polarizer was placed in the infrared beam in front of and behind the sample in front of the MCT detector to record spectra with the radiation polarized parallel and perpendicular to the stretching direction. In the transmission mode a rectangular aperture was used to adjust the illuminated sample area to approximately 30x30 µm. IR spectra were recorded with a resolution of 2 cm^{-1} co-adding 100 scans. For the SBS materials, which were measured in transmission mode, dog-bone shaped samples were machined from the oriented films, perpendicular and parallel to the orientation direction. Attenuated Total Reflection (ATR) spectra were recorded using the slide-on ATR accessory of the UMA 500 IR microscope which has a Si crystal. In this case the rectangular aperture was adjusted to an area of 100x100 μm.

Results and Discussion

SBC triblock copolymer

In this study FTIR spectrometry is used to gain additional information about the specific orientation upon deformation of every component in the SBC triblock copolymer which is successively quenched in water and liquid nitrogen. Since the quenched samples were not sufficiently thin to measure in transmission mode, ATR-FTIR is used.

The theoretical description of the determination of the molecular orientation using polarized light ATR-FTIR spectroscopy was given by Flournoy[5]. By means of this method, it is possible to study the orientation at the surface of a polymer film. There are four configurations possible, between the polarization directions of the radiation and the sample, which can be used to measure the optical constants κ_x, κ_y, and κ_z for the three dimensions. The x-axis is the axis of orientation, the y-axis is perpendicular to the x-axis, and the z-axis is orthogonal to x and y. The following equations for the reflectivity (R) can be derived for the four configurations:

Transverse Electric wave

x ⊥ plane of incidence: $\ln R_x^{TE} = \alpha\kappa_x$

x // plane of incidence: $\ln R_y^{TE} = \alpha\kappa_y$

Transverse magnetic wave

x ⊥ plane of incidence: $\ln R_x^{TM} = \beta\kappa_y - \gamma\kappa_z$

x // plane of incidence: $\ln R_y^{TM} = \beta\kappa_x - \gamma\kappa_z$

The parameters α, β and γ are constants representing the refractive indices of crystal and sample. The dichroic ratio in the x-y plane, $D = \kappa_x/\kappa_y$, can be calculated from the reflectivity (R_x and R_y). These values can be obtained by recording spectra using the TE wave while rotating the sample 0° and 90°. One of the main problems encountered in studies with polarized light with the ATR accessory is the reproduction of the experimental conditions when the sample is rotated 90°. The removal and remounting of the sample with the ATR crystal may give a difference in contact area, which leads to different attenuation factors in the spectra. This makes the comparison of the spectra, necessary to determine the dichroic ratio, difficult. Solutions to circumvent these problems are (i) the identification of an absorption band which does not have dichroism, and (ii) the use of a clamp which holds both the sample and the ATR crystal and which can be rotated 90°. The latter solution is not possible when using the ATR objective of our FTIR microscope, as the crystal is in a fixed position. Also the selection of absorption band which is not sensitive for orientation was not possible. However, by carefully making contact between crystal and polymer avoiding high pressure and applying the same contact area we were able to record spectra which were comparable in intensity.

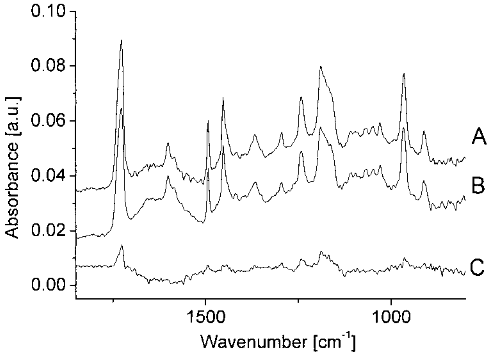

Figure 1: Infrared spectra of PS-PB-PCL triblock copolymer quenched in water and liquid nitrogen, recorded with a) radiation polarized parallel, b) radiation polarized perpendicular and c) difference spectrum. Elongation is 0%.

Despite of the difficulties in accurately evaluating the angle α, an attempt is made to investigate the orientation of the SBC triblock copolymers and the orientation factor quantitatively. The absorption bands at 966 cm^{-1} (trans C-H wag out-of plane) were used to determine the molecular orientation of the polybutadiene, while for PS the in-plane phenyl stretching ring vibration at 1493 cm^{-1} was taken. It was estimated from X-ray data that the plane of the phenyl ring to the PS polymer chain has an angle of 70° [6]. Since the 1493 cm^{-1} vibration is an in-plane ring vibration, the angle α of the transition moment of this vibration is also assumed to be 70°. The angle of the transition moment of the C-H out-of-plane vibration at 966 cm^{-1} in polybutadiene is not exactly known, but it is found to be perpendicular to the main axis of the polymer chain. To compare the orientation functions of the PCL, PB and the PS fraction the orientation function of the 966 cm^{-1} vibration of PB was calculated with an angle of 85°. To determine the orientation of the PCL phase, a distinction is made between the crystalline phase and the amorphous phase. The carbonyl band is deconvoluted into 2 bands by means of a curve fitting program. For the amorphous carbonyl (C=O) the vibration band at 1733 cm^{-1} is used, while for the crystalline carbonyl stretching the band at 1725 cm^{-1} is used. The angle α of the transition moment used in this study is 89° for the carbonyl vibration.

The IR absorption spectrum with radiation polarized parallel and perpendicular to the tensile direction together with the dichroic difference spectrum of an undrawn sample are depicted in Figure 1 for wavenumbers from 1850 to 800 cm^{-1}. As can be expected for undrawn material, the dichroic difference spectrum does not show any peaks. Upon deformation a strong difference in absorption with the polarization direction can be observed. An example is given in Figure 2 for an elongation of 25%. The orientation function f

$$f = \left(\frac{D_0 + 2}{D_0 - 1}\right)\left(\frac{D-1}{D+2}\right)$$

is calculated from the dichroic ratio D and displayed in Figure 3. It can be clearly seen that after a macroscopic strain of 10% the crystalline PCL phase shows a strong orientation. This sudden increase is most probably caused by surpassing the yield stress and the onset of necking. Subsequently, the PS phase starts to orient and at a draw ratio of 1.6 the total fraction of oriented PS is almost as large as the oriented fraction of crystalline PCL. It is remarkable that the PB phase does not show any orientation during the total tensile tests. This is also partly observed in the amorphous rubbery PCL phase for which the fraction oriented materials remain considerably low during the complete stretching experiment. The only explanation for this phenomenon is stress relaxation, caused by cavitation. The crystalline PCL chains are the first to orient strongly after a draw ratio of 1.1 (or after the build up of a certain amount of stress). Therefore, it may be concluded that upon deformation initially the cavitation initiation stress in PCL is reached and, consequently, cavities are formed within the PCL cylinders. This results in a relieve of the high internal stresses which were created during the quenching process. Cavitation of the PCL cylindrical domains causes a strong orientation of the crystalline PCL domains in the stretching direction, accompanied with stress relaxation of the amorphous PCL and the rubber PB cylindrical shell. The glassy PS matrix subsequently deforms and orients in the tensile direction. The sharp decrease in the total fraction PS which is maximal oriented, decreases rapidly after a draw ratio of 1.6. Somewhere between a draw ratio of 1.6 to 1.8 cracks develop in the samples, which gives rise to stress relaxation.

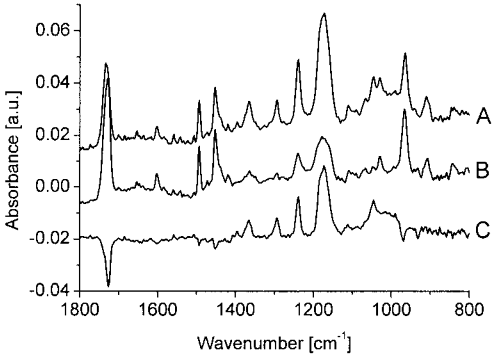

Figure 2: Infrared spectra of PS-PB-PCL triblock copolymer quenched in water and liquid nitrogen, recorded with a) radiation polarized parallel, b) radiation polarized perpendicular and c) difference spectrum. Elongation is 20%.

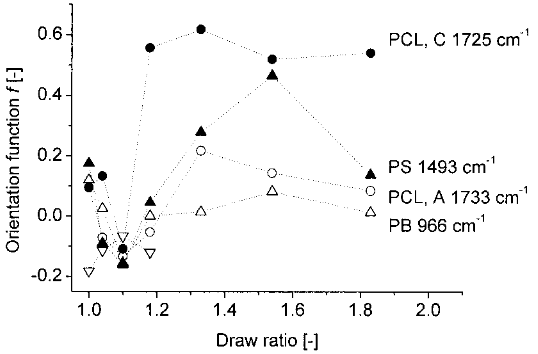

Figure 3: Orientation factor of 966 cm^{-1} (PB) oriented parallel (Δ), 1493 cm^{-1} (PS) oriented parallel (▲), 1733 cm^{-1} (amorphous PCL, C=O) (○) and 1725 cm^{-1} (crystalline PCL, C=O) (●).

It has to be noted that the angle of the trans microstructure of the polybutadiene chain to the deformation direction is arbitrary chosen to be 85°. When this angle is decreased to 70° the effective orientation factor will be larger, although in this specific sample, the influence will be minor since the PB phase hardly shows any orientation.

SBS triblock copolymer

In Figure 4 the infrared spectra recorded with radiation parallel and perpendicular to the tensile direction and the dichroic difference spectrum of the stretched SBS polymer, which is solvent cast from toluene are shown at an elongation of 96 %. Figure 5 represents the dichroic difference curve for SBS cast from MEK at an elongation of 8 %, prior to failure.

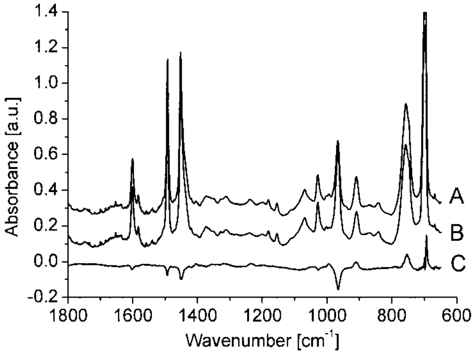

Figure 4: Infrared spectra of toluene-cast SBS; a) radiation polarized parallel, b) radiation polarized perpendicular and c) dichroic difference spectrum. Elongation = 96 %.

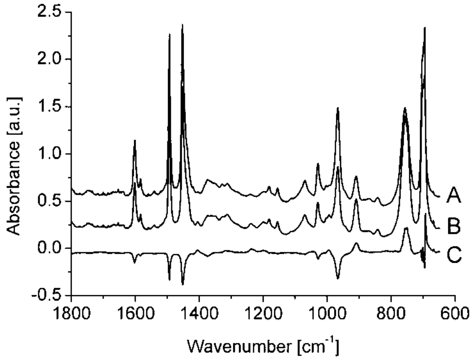

Figure 5: Infrared spectra of MEK-cast SBS; a) radiation polarized parallel, b) radiation polarized perpendicular and c) dichroic difference spectrum. Elongation = 8 %, spectra recorded from local neck.

For the unstretched sample the dichroic difference spectrum does not show any peaks, indicating that these samples possess almost no orientation. When the toluene cast polymer is elongated to a draw ratio of 2, the dichroic difference spectrum clearly shows orientation in especially the PB bands at 966 cm^{-1} (trans C-H wag out-of plane) and 909 cm^{-1} (1,2 vinyl C-H wag out-of plane). The dichroic difference band at 966 cm^{-1} is negative, while the difference band at 909 cm^{-1} is positive. Since the transition moment of the vibration at 966 cm^{-1} is perpendicular to the polymer chain and that at 909 cm^{-1} parallel, it can be concluded that the PB chain is oriented parallel to the stretching direction. Also the PS absorption bands at 1493 cm^{-1} and 1028 cm^{-1} (in-plane ring vibrations) show some orientation, although far less than the PB bands.

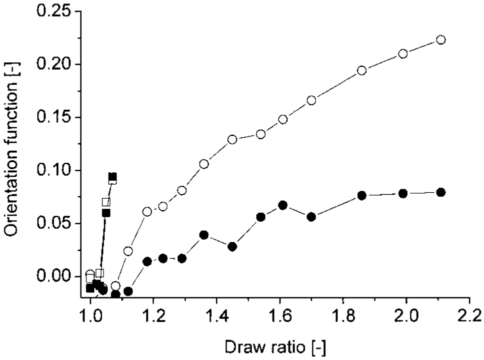

Figure 6: Orientation factor of 966 cm^{-1} (PB) cast from toluene (○), 1493 cm^{-1} (PS) cast from toluene (●), 966 cm^{-1} (PB) cast from MEK (□) and 1493 cm^{-1} (PS) cast from MEK (■).

The calculated orientation functions of SBS triblock copolymer cast from respectively toluene and MEK are given in Figure 6 as a function of draw ratio. Clear differences in the orientation behavior of both samples can be observed. In the MEK cast films, a neck is formed at small macroscopic strains. Within this neck (high local strain), the fraction of orientation of the PS and PB phase is almost equal and both phases orient almost directly after loading. The sample fractures after a macroscopic strain of only 8%. The orientation of the PS phase may be ascribed to the formation of fibrillar structures in between the oriented PB domains. The orientation of the PB phase in the toluene cast films monotonically increases with the strain and starts at a lower draw ratio compared to the PS fraction. This shows that, initially, the deformation predominantly proceeds in the PB phases, which explains the elastomeric character during tensile testing. With increasing strain, also the PS vibration bands gradually show some dichroism, although the fraction oriented PB phase remains three times larger compared to the PS phase.

Conclusions

The deformation behavior of a SBC triblock copolymer was explored to study the influence of thermal history and long range order on the occurrence of cavitation and crazing. It was shown that the high ductility can be attributed to the crystallinity of the core in the irregularly packed polygonal cylinders. The FTIR spectroscopic investigations showed significant differences in the orientation behavior of the individual components. The crystalline PCL showed a strong and sudden increase in the orientation. This may be explained by cavitation and orientation of the PCL cylindrical domains in the tensile direction under a strong relieve of the initially present high triaxial stress state.

For SBS copolymers, the molecular orientation upon deformation turned out to depend on the morphology of the undrawn film and to have a strong correlation with the stress-strain behavior. For the toluene as-cast films, a rubber-like behavior was observed. Stretching of PB chains parallel to the stretching direction was accompanied by orientation, cavitation and fracture of the PS lamellae. The material deforms homogeneously. For the MEK as-cast film, a strong continuous orientation of both PS and PB was detected as a function of strain. Since the matrix is mainly composed of the glassy PS phase, plastic deformation was observed without rubber-like characteristics. For an isotropic sample, most of the grains are initially oriented with their lamellar normal at an angle to the deformation axis, with a minority of grains having the lamellae either parallel or perpendicular to it. The prevalent mechanism is expected to be formation of new internal boundaries, parallel to the deformation axis. Cavitation, yielding and eventually fracture of the layers at the interface is followed by rotation of the tilted lamellar stacks towards the deformation axis.

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