Experimental report

11/02/2022

Proposal:	**6-04-286**	**Council:**	10/2020
Title:	MICROSCOPIC INSIGHT ON COMPONENT DYNAMICS IN POLYMERIC MIXTURES OF INDUSTRIAL INTEREST		
Research area:	Soft condensed matter		

This proposal is a resubmission of 6-04-283

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Samples: SBR/PS

Instrument	Requested days	Allocated days	From	To
IN13	8	8	18/02/2021	26/02/2021

Abstract:

Blends of SBR and PS are of interest for the tire industry. Here we want to use them also as model systems to investigate basic properties of dynamically asymmetric mixtures. In particular, we want to exploit neutron scattering on labelled samples to follow the mean squared displacements of each of the blend components, and see their evolution across the broad range of temperatures over which the calorimetric glass transition in the blend spans. This information will allow us to determine the 'microscopic' individual glass-transition temperatures of the components in the blend. In addition, this could help us to look for a microscopic interpretation for the relevant region of the dielectric response Rc, which seems to be universal, practically independent of temperature and composition, always of about 1nm. THIS PROPOSAL WAS ACCEPTED IN THE PREVIOUS ROUND BUT IS ON HOLD DUE TO 'NATIONAL BALANCE' (SPAIN). WE RESUBMIT IT WITH THE MICHELIN COLABORATORS (NOT EXPLICITELY INCLUDED IN THE PREVIOUS PROPOSALS) AS CO-PROPOSERS.

MICROSCOPIC INSIGHT ON COMPONENT DYNAMICS IN POLYMERIC MIXTURES OF INDUSTRIAL INTEREST

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Being the main component of tire formulation, Styrene-Butadiene Rubber (SBR) is the synthetic polymer with highest production worldwide. A possible route to optimize the dynamical behavior of a system in relationship with the traction versus rolling resistance compromise is by mixing an elastomer with a compound with higher glass-transition temperature (T_g). Such material is categorized as a binary mixture with dynamic asymmetry. In this work, we tried to shed light on the microscopic dynamics of blends of SBR and polystyrene (PS) oligomers (molecular weight = 500 g/mol) as simplified systems of interest in the tire industry. Using isotopically (h/d) labeled samples, we selectively followed the temperature dependence of the intensity elastically scattered on IN13, that is supposed to be dominated by the incoherent contribution of the protonated component. In a complementary D7 experiment, we had determined the ratio between coherent and incoherent contributions in the different samples, to check that such an assumption is valid. The results of this IN13 experiment were combined with those previously obtained through a CRG proposal, to extend the study to three different blend compositions (80%, 50% and 20% of SBR), and the protonated homopolymers as reference.

The thicknesses of the samples were chosen such that a transmission of about 90% was expected. They were filling flat aluminum sample holders and placed at 135° with respect to the incident beam. The experiments consisted of recording the elastically scattered intensity in isothermal conditions for the different scattering angles, covering an effective Q-range $0.52 \leq Q \leq 4.5 Å^{-1}$. At every temperature considered, the measuring time was of about 2h. The samples were first cooled down to 20K, where the reference measurement was performed. Thereafter, measurements were carried out in the temperature interval $50 \leq T \leq 300$ K, with steps of 50 or 20 K (glassy state) and 10 K (around and above the calorimetric T_gs). The perpendicular transmission of the samples was determined to properly subtract the background signal measured on an empty cell at 285 K. The results at each temperature were normalized to the reference measurement at 20 K. The results obtained on the different samples investigated were fitted to the expansion

$$\frac{I_{el}(Q,T)}{I_{el}(Q,T\approx 0)} = I_o exp\left(-\frac{\langle r^2(t_R,T)\rangle}{6}Q^2 + \frac{\alpha_2(t_R,T)\langle r^2(t_R,T)\rangle^2}{72}Q^4 + \cdots\right) \quad (1)$$

where $\langle r^2(t_R,T)\rangle$ is the mean squared displacement (msd) and $\alpha_2(t_R,T)$ is the non-Gaussian parameter at the IN13 resolution time (t_R≈80ps). The results on these two magnitudes are plotted in Figure 1. As can be seen, the dynamic asymmetry of the two homopolymers manifests in their clearly different T_gs –microscopically detected as the abrupt change in the slope of the msd. The components within the blends display an 'effective' T_g that depends on composition. This microscopic and component-selective information will be exploited to interpret the features of the calorimetry results in these mixtures of industrial interest.

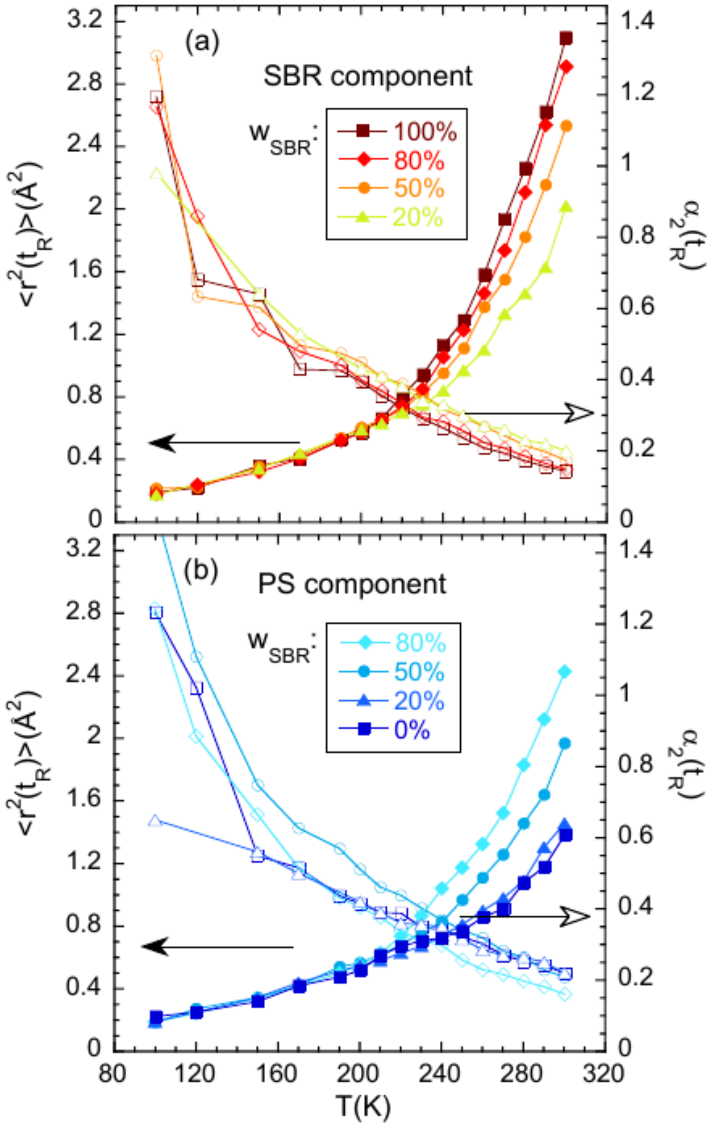

Figure 1: Mean squared proton displacement (filled symbols, scale on the left) and non-Gaussian parameter (empty symbols, scale on the right) at the IN13 instrumental resolution time deduced from the fits of Eq. 1 to the IN13 results on the hSBR/dPS samples (a) and on the dSBR/hPS samples (b). Different symbols correspond to the different SBR compositions indicated; lines connecting points are guides for the eye.