Temperature Dependence of the Dynamics and Interfacial Width of polymer/Alumina interfaces via atomistic simulations

N. Patsalidis[1], G. Papamokos[2], G. Floudas[2,3], V. Harmandaris [1,4,5]

[11]Computation-based Science and Technology Research Center, The Cyprus Institute, 2121, Cyprus

(n.patsalidis@cyi.ac.cy)

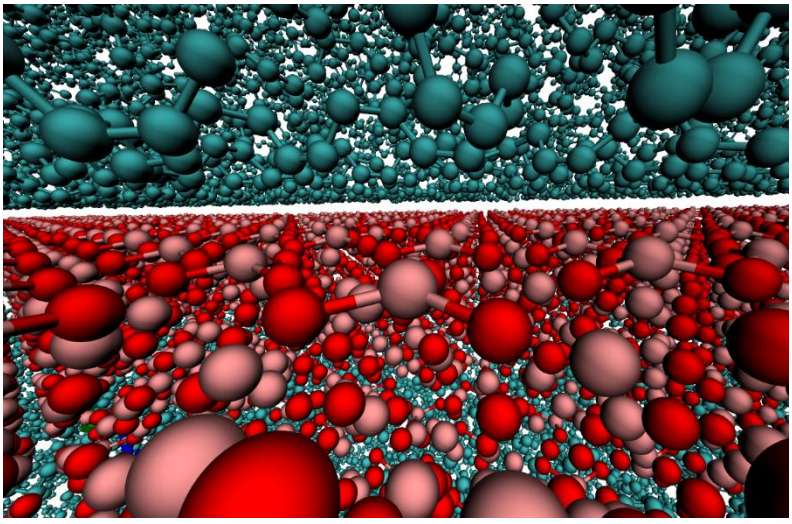
[2]Department of Physics, University of Ioannina, Greece

[3]University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, Ioannina, 45110, Greece

[4]Department of Mathematics and Applied Mathematics, University of Crete, Heraklion, GR-71110, Greece

[5]Institute of Applied and Computational Mathematics, IACM-FORTH, Heraklion, Greece

We present, a detailed computational study on the effect of temperature to the dynamics and the interfacial width of unentangled *cis*-1,4 Polybutadiene (cPB) linear chains confined between strongly attractive alumina layers. We performed long, several μs, atomistic molecular dynamics (MD) simulations for a wide range of temperatures, well above and below glass transition (Tg). The strong polymer/alumina interfacial potential energy is optimized based on Density Functional Theory (DFT) calculations, allowing a chemically accurate description of complex (quantum in origin) interfacial interactions. The interface introduces structural and dynamical heterogeneity in a region of about 2-3 nm, depending on temperature, broadening the relaxation times distribution in accordance with experimental literature.[1,2] The mobility of polymer chains slows down near the interface, exhibiting a higher effective local Tg. Moreover, slow Arrhenius processes (SAP) appear exhibiting an abrupt shift in the activation energy at a critical Temperature of about 80 K above glass transition. This process corresponds to the dynamics of polymer chains in the vicinity of the alumina interface and is also observed experimentally.[3,4] Finally, based on the extend of the structural and dynamical heterogeneity we define the length of the interfacial width. The length peaks around bulk Tg, and decays at lower and higher temperatures.



KEYWORDS: Interface, alumina, polybutadiene, glass transition , SAP, interfacial width, dead layer.

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