Progress in Polymer Science 54–55 (2016) 128–147

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Effect of nanostructure on the thermal glass transition and physical aging in polymer materials

Daniele Cangialosi[a], Angel Alegría[a,c], Juan Colmenero[a,b,c,*]

[a] Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain
[b] Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain
[c] Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain

ARTICLE INFO

Article history:
Available online 23 November 2015

Keywords:
Glass transition
Segmental mobility
Enthalpy relaxation
Physical aging
Confinement
Diffusion model

ABSTRACT

We review the recent activity aiming to clarify glassy dynamics in nanostructured polymer glasses, in particular thin films, nanocomposites and nanospheres. Special emphasis is devoted to recent results on the out-of-equilibrium dynamics, that is, the way the system leaves equilibrium when cooling, marking the thermal glass transition, or recovers it once in the glassy state – the so-called physical aging. Apart from those systems exhibiting strong interactions at the interface, we show that a huge number of studies probing glassy dynamics in nanostructured glasses finds negative deviations from bulk T_g and accelerated physical aging. Analysis of the dependence of the rate of spontaneous fluctuations – namely the linear dynamics – on nanostructuring indicates that there exists a significant component exhibiting bulk-like dynamics. This is the case even in the most extreme case of nanostructuring, that is, semi-isolated polymer chains and freestanding thin film with thickness ∼10 nm. In the latter case this is found at temperatures around the bulk glass transition temperature (T_g), that is, in the range where deviations of the out-of-equilibrium dynamics are normally observed. All together these results indicate that the linear dynamics alone cannot provide an exhaustive description of the out-of-equilibrium dynamics in nanostructured systems. In this case, purely geometric factors must be included. We discuss recent approaches aiming to capture the phenomenology of glassy dynamics in nanostructured glasses. Special attention is dedicated to the free volume hole diffusion (FVHD) model.

Contents

---

* Corresponding author at: Centro de Física de Materiales (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain.
E-mail address: juan.colmenero@ehu.eus (J. Colmenero).

http://dx.doi.org/10.1016/j.progpolymsci.2015.10.005
0079-6700/

1. Introduction

Recent developments in modern technology have motivated increasing interest in the study of amorphous polymers with typical dimensions in the nanometers range. These nanostructured systems can be employed in a wide range of technologically relevant applications. For instance, submicron thick polymer films are exploited as templates in microelectronics [1], non-biofouling protective coatings [2], membranes in separation technologies [3], active layers in photovoltaic cells [4]. Polymer nanocomposites are extensively employed in tire technologies and in those application where mechanical reinforcement, enhancement of barrier properties, flame resistance, electro-optical, and bactericidal properties, are required [5]. Polymer nanospheres have received increasing interest in the last years in applications such as vehicles in drug delivery [6], components in fluorescent imaging [7], performance reinforcing additives [8], and components in photonic structures [9].

Beside the technological interest of nanostructured polymers, the reduction of the typical size of the material has raised numerous fundamental concerns regarding the physics behind the alteration of properties at the nanoscale. Among the topics currently subject of investigation, the alteration of glassy dynamics in nanostructured glasses has been one of the most intensely debated since the finding in the early 90s of depressed glass transition temperature (T_g) in thin polymer films [10,11]. Since then, a huge number of studies regarding glassy dynamics in nanostructured polymers have been reported.

After a brief introduction to the main aspects of the glass transition, we focus on the recent activity on the glassy dynamics in the non-linear regime of nano-structured polymers, that is, the efficiency of maintaining equilibrium when cooled down from the melt (providing the T_g) or recovering it once in the glassy state. In doing so, we critically review those studies where the effect of nanostructure on the T_g and the recovery of equilibrium in the out-of-equilibrium glass is investigated. We show that, in these systems, the non-linear dynamics may not be exclusively related to the rate of spontaneous fluctuations, that is, to the glassy dynamics in the linear regime. In view of this finding, we emphasize the role of the typical length scale of nanostructuring, an argument based on geometric aspects, in determining the efficiency of equilibration in the glassy state. Finally, we recall the theoretical activity aiming to elucidate the connection of the non-linear to the linear dynamics via geometric arguments.

2. Phenomenology of the glass transition

2.1. Equilibrium dynamics

Liquids differ from crystalline solids not only for the absence of structural order, but also because they exhibit molecular motion beyond atomic vibrations. The time scale at which such motion occurs provides the rate of spontaneous thermal fluctuations in the liquid. The temperature dependence of such fluctuations is Arrhenius-like for standard liquids. However, for those liquids that can be supercooled below their melting temperature, the so-called glass-forming liquids, such temperature dependence drastically becomes more pronounced. This is shown in Fig. 1 (left panel) where the typical time scale of spontaneous fluctuations (τ), represented as the frequency corresponding to the most probable rate in experiments based on oscillatory fields ($\omega_{max} = \tau^{-1}$), is shown for polystyrene (PS) [12]. Within more or less limited temperature intervals, such strong temperature dependence is often described by the Vogel–Fulcher–Tammann (VFT) equation [13–15]:

$$\omega_{\max} = \omega_0 \exp[-B/(T - T_0)] \qquad (1)$$

with ω_0, B and T_0 the pre-exponential factor, the Vogel activation parameter and the Vogel temperature respectively. As can been seen in Fig. 1 (continuous line, left axis), the VFT equation provides a suitable description of experimental data.

In the case of polymers, the process exhibiting VFT behavior is called the segmental or the α relaxation. In the rest of the Review, we will refer indifferently to rate of spontaneous fluctuations, linear dynamics or segmental (or α) relaxation. This behavior is believed to be associated to the cooperative rearrangement of several structural units. Numerous attempts to estimate the length associated to such rearrangement have been presented since this idea was first introduced by Adam and Gibbs (AG) [16]. Their theory relies on the connection of dynamics of glass forming liquids to their thermodynamics via the configurational entropy (S_c). According to the theory the size (z) of the region involved in glassy dynamics increases with decreasing temperature following the relation: $z \sim S^{-1}$. Since the AG theory numerous approaches have