Last Advancements on Molecular Confinement of Polymeric Nanomaterials

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Abstract. Understanding how polymer chains are altered by confinement or physical constraints not only is a fundamental question in polymer physics but also holds significant relevance across various fields, as it can elucidate diverse properties of the macroscopic materials. This phenomenon takes places in a wide variety of nanomaterials with different geometries. In the last decade, fabricating and researching polymeric nanomaterials has raised interest as their properties can overcome those of the starting polymer. It is thought that molecular confinement could help tailor mechanical, thermal, rheological, or chemical properties. Therefore, this review aims to present an overview of the recent advancements in the study of the dynamics of polymeric chains within different polymeric nanomaterials, putting emphasis on nanoporous ones. The review includes (i) a description of diverse polymeric nanomaterials and the origin of molecular confinement and its influence on their properties, (ii) an overview of the advancements on molecular confinement and its effects on polymeric nanoporous materials, and (iii) a summary of well-stablished facts and knowledge gaps.

1   Introduction

Polymeric chains are molecules consisting of many repeated subunits called monomers [1,2]. The resulting properties of the macroscopic polymeric material can be customized taking advantage of a wide range of geometries that make polymeric chains behave differently [3]. In particular, the field of nanotechnology has revolutionized the landscape of material science and engineering, as it offers unparalleled prospects for the design, manipulation, and utilization of materials at the nanoscale.

Currently, there exists a wide range of polymer nanocomposites and nanostructures in which molecules behave very differently [4–7]. One of the phenomena that is well-known for affecting polymeric chains mobility is molecular confinement [8]. This can be referred to as the spatial restriction of molecular motion and reorganization within a limited volume or space, often on a nanometer scale. This is typically observed in materials where the dimensions of the interstitial spaces are comparable to the size of the molecules or polymers contained within them. In such constrained environments, the physical and chemical properties of the confined substances can differ significantly from those in a bulk state.

Confinement can influence a range of molecular behaviors, including dynamics, phase transitions, and transport properties [9–11]. It is believed that it spatially limits the free space over which the polymer chains can move or orient themselves [31–33]. Consequently, the energy requirements for increasing the degrees of freedom of these confined chains should increase significantly from those in bulk materials, which is something that T_g measurements account for [12].

The study of molecular confinement has gained interest in materials science over the past decades, as understanding how confinement affects material properties could be essential for the design and development of new materials with tailored characteristics for specific applications. The landscape of materials science is rich with a great deal of different nanocomposites, nanostructures, nanoporous materials, etc., each of them exhibiting molecular confinement in distinct manners. The disparities of these materials, arising from their unique compositions, morphologies, and structural dimensions, requires individualized analysis in order to understand thoroughly the subtleties of the confinement effects. In this review, the last advancements on this topic will be showcased, focusing the analysis on polymeric nanoporous materials.

2   Confinement in polymer nanostructures and nanocomposites

Polymer nanostructured materials are those polymer-based materials with at least one dimension on the nanometer scale, which include nanoparticles, nanorods, nanowires, thin films, and others [13].

The phenomenon of geometrical confinement is exhibited in many different ways, some of them resulting in opposite outcomes. Because of this, there is still some confusion regarding the exact causes of some of the new properties that arise in some materials when taking their geometries to the nanoscale.

For instance, one would suppose that every geometrical constraint would result in a decrease in chain mobility and an increase in T_g. However, in free-standing thin films with thicknesses within the nanometer scale, the opposite has been found. Among the many examples in the literature, the work from Mattsson et al. [14] is a remarkable one.

They quantified the T_g in numerous free-standing thin films prepared from dilute solutions of monodispersed polystyrene in toluene. The films were spin-cast onto clean glass slides, annealed above the bulk glass transition temperature for $14\ h$, and then slowly cooled at $0.5\ °C/min$ to room temperature, achieving a wide range of thicknesses, some of them below $100\ nm$. Once cooled, they were transferred onto a specially designed film holder using a standard water transfer technique. In a parallel way, Roth el al. [15] studied atactic-PMMA (Poly(methyl methacrylate)) free-standing thin films fabricated by deposition onto various substrates including freshly-cleaved mica, silicon wafers with a native silicon oxide (SiO) layer, and gold-coated silicon oxide surfaces to achieve a thickness of approximately $200\ nm$. For the preparation of the freely-standing PMMA films, the same water transfer technique was utilized to relocate the films to sample holders. The work from Roth el al. will gain interest afterwards, given that the porous materials in which focus will be put are also made out of PMMA.

Both works, alike many others studying free-standing thin films, demonstrate a decrease in the T_g (see **Fig. 1**)). However, opposite to these, in the case of thin films under the interaction of a substrate, the outcome depends on the strength of the interaction of the polymeric side chains with that substrate. Authors in the literature have consistently found that the T_g increases as does the strength of the attractive forces between them. [14–16]. All these results were summarized in a review in 2001 by Forrest et al. [17].
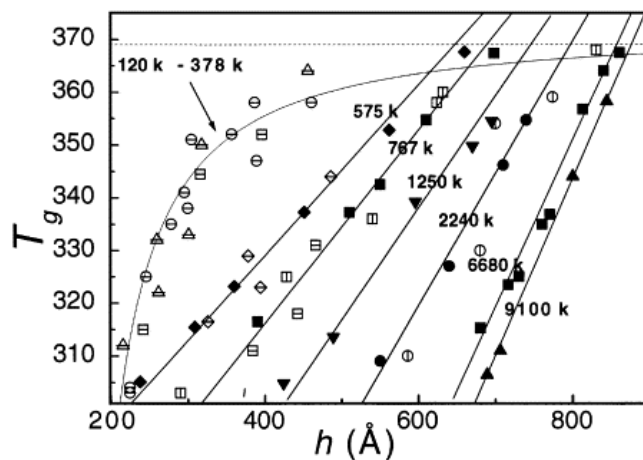

Fig. 1. Measured T_g values for free-standing polymer films in terms of the film thickness (h). Reprinted from Forrest, J.A.; Dalnoki-Veress, K. *The Glass Transition in Thin Polymer Films*, Adv. Colloid Interface Sci. 2001, 94, 167–195, doi:10.1016/S0001-8686(01)00060-4., Copyright (2001), with permission from Elsevier.

The mechanism explaining all these phenomena comes down essentially to the chains' interphase interaction. For free-standing films, the interaction of the polymeric chains with air is negligible, meaning that the chain ends are segregated from the polymer matrix and its intermolecular interactions, finding therefore an increase in mobility

(or decrease in T_g) [14,15,17]. In substrate-supported films, however, a strong interaction tightens and constrains the chains movement, leading to generally higher T_g values [12,14–16,18]. The deviations of the T_g from the bulk where demonstrated to be correlated with the cooling rate at which the films were prepared, diminishing the differences when increasing it [19]. In this case, the rapid cooling hinders polymeric chains in reaching the equilibrium state while interacting with the substrate [20].

An interesting separate case is the work by Wang et al. [21], in which they found that the T_g increased in nanocomposites of polystyrene with 63% of the total volume occupied by nanoparticles of SiO_2 with different diameters (11, 25, and 100 nm). In that case, it was proved that the geometric confinement or mobility constraint of the polymeric chains caused by the nanoparticles had a larger effect than the one of the segregated chains ends of the surface or the weak interaction with the nanoparticles, acting the opposite way. Hence, an increase of 57 °C in the T_g was eventually found.

Another example of polymeric nanostructured materials is one-dimensional ones. These are a versatile kind of nanomaterials that exhibits a wide variety of unique features that help toward the development of miniature devices [22]. Mijangos et al. [23], focused on the study of molecular confinement in polymeric nanostructures produced by infiltration of polymers in anodized aluminum oxide (AAO) nanocavities.

They found, consistently with the previous literature on confinement, that the impediment of molecular motion due to limited space, is often obscured by the effects of surface interactions. These interactions, although related to the material's reduced dimensions, do not stem directly from molecular confinement. Alike in substrate-supported thin films, polymer chains can be situated near surfaces that effectively confine them, leading to notable attractive interactions and mobility reductions. While distinguishing between the effects of surface interactions and pure confinement is of academic interest, this effect was found to be less critical when considering the overall properties of the nanomaterial and was sometimes overlooked [23].

In their studies they demonstrated that the polymeric chain dynamics get altered mainly by the decrease in the lateral dimensions of the nanopores of the AAO template causing changes in the chain conformation, or interactions either mutually or with the confining cavity. These effects were found to take place in diverse scales such as chain dynamics, segmental dynamics [23], and group motions [24]. Moreover, they found that this molecular confinement can affect both thermal and mechanical properties of the material, as well as rheological ones.

3   Confinement in polymer porous materials

Polymeric nanoporous materials are biphasic materials characterized by a porous structure with pore sizes below 500 nm [25–28]. The pore network (gas phase) is dispersed within the polymer (solid phase) by means of either interconnected pores

(continuous), or fully closed ones (discontinuous). These materials can combine the versatility of the solid polymers with the characteristics imparted by their nanoscale porous architecture. The relevance of these materials is underscored by their ability to customize their properties towards various applications, primarily due to their tunable surface-to-volume ratio and adjustable porosity and pore size [29,30]. The utility of these nanoporous structures spans a diverse range of applications, from gas separation [31,32], catalysis [33], environmental remediation [34,35], to drug delivery [36–38] and advanced insulation materials [39].

In the case of polymeric nanoporous materials, the dimensions of the geometries of the solid phase can reach orders of magnitude comparable to those of the polymer chains. This is known to cause a polymeric chain confinement [40]. Here, what is thought to be causing some modified properties polymeric nanoporous materials have with respect to the microporous ones (higher mechanical resistance and thermal insulation among others) is the phenomenon of molecular confinement, occurring within the pore walls [9–11]. This, refers to the restricted movement and altered conformation of polymeric chains confined within the solid walls between the pores of the material. This is a direct consequence of the drastically reduced dimensions of the pore wall thickness, which becomes comparable to the ones of the polymeric chains (radius of gyration between 3-7 nm [9,23,41,42]).

The affected dynamics range from local segmental motions to the level of entanglements and global chain motions [8,9]. Similarly to what Mijangos et al. found [23], the confinement effect is thought to alter the physical and chemical behavior of the macroscopic material, something that is particularly noticeable in the increase in the T_g (see

Fig. 2). It is thought that this effect could offer additional control over the material's properties through the manipulation of nanoscale dimensions [43].
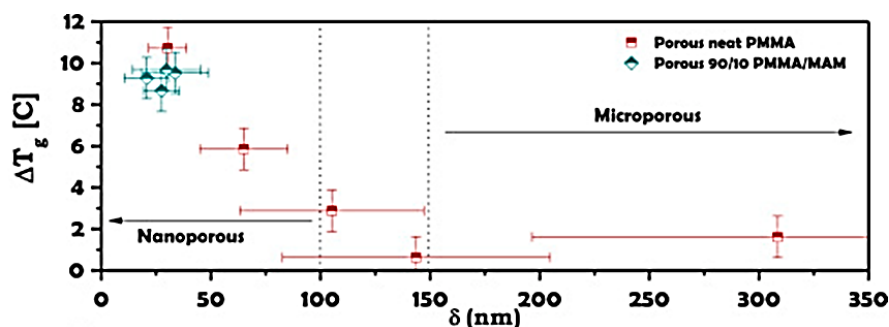

Fig. 2. Increment of the T_g of porous neat PMMA and 90/10 PMMA/MAM samples due to the reduction of the pore wall thickness (δ). Reprinted from Pinto, J.; Notario, B.; Verdejo, R.; Dumon, M.; Costeux, S.; Rodriguez-Perez, M.A. *Molecular Confinement of Solid and Gaseous Phases of Self-Standing Bulk Nanoporous Polymers*

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The phenomenon occurring in free-standing films and polymeric nanoporous materials presents some similarities with each other. In free-standing films, the negligible interaction of polymeric chains with air leads to the segregation of chain ends from the polymer matrix. This segregation results in an increased mobility of the polymer chains, manifesting as a decrease in T_g. In contrast, polymeric nanoporous materials, despite also being surrounded by air and thus sharing some similarities with free-standing films, exhibit a different behavior as proved by T_g measurements. The confinement within the three-dimensional network of pore walls of these materials, with thicknesses of the order of tens of chain-lengths, imposes significant geometrical restrictions that could oppose the segregation of chains, which are also added to the possible fabrication stresses. Additionally, such structures are produced out of thermodynamic equilibrium, while free-standing films are usually produced in equilibrium or quasi-equilibrium procedures. Consequently, despite the potential for some chain ends to segregate in the porous walls, the overall mobility of the polymer chains in nanoporous materials is decreased.

In a recent work [8,9], the presence of molecular confinement in nanoporous polymers was also demonstrated through a series of spectroscopic techniques such as Raman and broadband dielectric spectroscopy. However, some doubts remain unanswered, given that these investigations were carried out on samples that were not proven to be fully relaxed or aged, which could have interfered the results to some extent. Therefore, that research line can be further continued by addressing whether some of the nanoporous properties, come down to confinement effects or to a mix of those and the aforementioned fabrication-related stresses.

Summing up, future work must seek to cover the aforementioned gap by providing insights on the ageing of polymeric nanoporous materials under confinement condition, as well as an additional demonstration of the molecular confinement with a specific focus on completely relaxed/aged samples.

4   Conclusions

This review has shed light on the recent advancements on molecular confinement in diverse polymeric nanomaterial geometries such as nanostructures, nanocomposites and nanoporous materials. The previous literature shows agreement on the existence of polymeric chains confinement and its impact on the physical properties of the macroscopic material. The phenomenon has also been acknowledged to be interfered by polymer-surface interactions. Indeed, in the case of substrate-supported thin films, the

studies show how the glass transition temperature can notably either increase or decrease, depending on the strength of polymer-substrate interactions.

Furthermore, recent studies on nanoporous polymeric materials show that geometrical confinement might be appearing within the walls between pores, which have thicknesses often comparable in to the length of polymeric chains. Such confinement is believed to impact the thermal behavior, as well as mechanical and chemical properties of the porous structure. While this case has similarities with free-standing films, the reduced dimensions of the three-dimensional network of the pore walls of nanoporous materials, obtained by an out-of-equilibrium procedure, lead to a significant geometrical confinement, perhaps opposing the chain segregation effect, and eventually decreasing the mobility of polymer chains.

Despite the advancements made on polymeric nanoporous materials, a critical gap remains in the demonstration of confinement effects in completely relaxed or aged samples. This is crucial to conclusively ascertain whether the observed enhancements in material properties are solely attributable to confinement effects or are influenced by other factors related to the material's fabrication and aging processes. Addressing this gap is essential for the use of these materials in potential long-term use applications.

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