Microstructural Characterization of Shear Transformation Zones and Modeling Indentation Size Effect in Amorphous Polymers

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MICROSTRUCTURAL CHARACTERIZATION OF SHEAR TRANSFORMATION ZONES AND MODELING INDENTATION SIZE EFFECT IN AMORPHOUS POLYMERS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in The Department of Civil and Environmental Engineering

by

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B.S., Sharif University of Technology, 2009
M.S., Sharif University of Technology, 2012
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TO
MY BELOVED PARENTS ALI AND PARVANEH,
MY HUSBAND AREF,
MY DAUGHTER LEAH,
AND MY SISTERS FATEMEH AND ZAHRA
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ABSTRACT

The first aim of this work is developing a procedure for experimental and analytical characterization of nano-scale microstructures which mediate large scale deformation in amorphous polymers. Glassy polymers are extensively used as high impact resistant, low density, and clear materials in industries. Nevertheless, their response under severe loading conditions is yet to be appropriately unraveled. Due to the lack of long-range order in the microstructures of glassy solids, their plastic deformation is different from that in crystalline solids. Shear Transformation Zones (STZs) are believed to be the main plasticity carriers in amorphous solids and defined as the localized atomic or molecular deformation patches induced by shear. Employing Nanoindentation and Atomic Force Microscopy (AFM), the micromechanical and microgeometrical properties of STZs are obtained for different polymers. Moreover, since the nucleation of STZs strongly depends on the initial microstructural state of the material, the possible relationship between the microstructural state variables, such as free volume as inherent defects in amorphous solids, and plasticity sites is investigated using Positron Annihilation Lifetime Spectroscopy (PALS) for a better understanding of the response of polymers during deformation. The second objective of this dissertation is proposing a model for observation of the physico-mechanical properties of amorphous polymers at small scales, i.e., indentation size effect (ISE) based on the STZ mediated theory which is one of the challenging concepts in physics and deformation of non-crystalline solids. Employing the shear transformation mediated flow theory and considering the statistical nature of formation and distribution of the flow sites, a rate dependent ISE model for glassy polymers is developed. This model is based on the possibility of occurrence of discrete shear transformation sites within the deformed volume under the indenter which is controlled by the indentation depth and geometry.
CHAPTER 1
INTRODUCTION

1.1. Literature Review

In general, polymers are divided into two different categories: semicrystalline and amorphous (glassy) polymers. Amorphous polymers have recently become one of the most important and ubiquitous materials which have been used for manufacturing variety of elements, from simple kitchenware to composite panels used in aircrafts and space structures, in a wide range of scale sizes. The impact resistance, low density, low cost, processability, and durability of polymeric glasses (PGs) have given these materials the advantage to be utilized as reliable structural members for different loading conditions. Glassy polymers are composed of entangled and disordered long molecular chains, and there is no significant chain alignment in their intra- and inter-molecular structures. Since the molecular structure of the PGs is totally different from that of the crystalline solids, the plastic deformation process does not obey the crystal plasticity rules.

In the context of crystal plasticity, crystal dislocations are the principal carriers of plasticity, and their slips result in plastic deformation (Argon, 2008). But, due to lack of coherence in structure of glassy solids, they possess no analogous mobile defects. Consequently, the flow and the mechanism of plastic response in the microstructural level are different from crystalline solids.

During the past decades, numerus models have been proposed to physically or phenomenologically describe the distinct behavior of glassy polymers. Among the earliest hypothesis for the plastic deformation of amorphous polymers is the one proposed by Eyring (1936) who postulated that the molecular rearrangement during the deformation mediates the flow. Based on Eyring’s theory (and its modified version, the Ree-Eyring model (Ree and Eyring, 1955) the restriction of the polymer chains degree of freedom with increasing the strain rate or decreasing
the temperature is responsible for the elevated resistance to deformation observed in the experiments on PGs. Later, Robertson (1966) considered the chain straightening as the key factor for the plastic deformation of glassy polymers which was distinguished from rubber-like deformation. While his model successfully predicts the PGs’ deformation behavior at temperatures close to the glass transition ($T_g$), it fails to describe the deformation at $T<T_g$. The double kink model, which was inspired by the disclination like localized twist in macromolecular chains, was introduced by Argon (1973). This model was extremely successful in capturing the pressure, strain rate, and temperature sensitivity of the amorphous polymers flow, and used by many researchers to interpret the post-yield behavior (Arruda et al., 1995; Boyce et al., 1988) and the strain gradient plasticity (Lam and Chong, 1999; Voyiadjis et al., 2014) of PGs.

1.2. Problem Statement

Rather than concentrating on the microstructural defects as carriers of plasticity (like dislocation in crystalline solids (Argon, 2008)), the early studies of the plastic deformation in PGs mainly focused on the molecular rearrangements. This approach seems reasonable since amorphous materials lack long-range order in their atomic/molecular structures. However, the experimental analysis of the variation of the deformation energy with the strain for some glassy polymers by Oleinik and coworkers (Oleinik, 1991; Oleinik et al., 2007) revealed significant amount of stored energy for plastically deformed samples. While this amount of stored energy can never be carried through conformational chain rearrangement, Oleinik (1991) suggested that there should be localized plastic deformation sites which possess considerable elastic fields around them, like Eshelby’s inclusion model (Eshelby, 1957; Mura, 1982). These sites represent lumped localized deformations each encompasses glide, slip, or shear rotation of the chains inside them. Since they are only sensitive to the shear component of the applied stress (Oleinik, 1991), these
sites are called the shear transformation zones (STZs). Shear transformations (STs) are believed to mediate the plastic deformation in all types of disordered solids (Argon, 2013), although they were originally proposed for metallic glasses (MGs) plasticity (Argon, 1979; Spaepen, 1977). Since they are localized transition events rather than actual defects, STZs have never been observed (Wang et al., 2013), but strong evidence exists to prove the nucleation of these localized disturbances during the plastic deformation in glasses (Falk, 2007; Oleinik, 1991; Pauly et al., 2010).

1.2.1. Microstructural Characterization of Plasticity Sites Using Nanoindentation

The STZs are isolated irreversible stress relaxation events which form around free volume sites with the thermal fluctuations assistance under the action of an applied shear stress (Argon, 1979; Argon, 2013; Falk et al., 2005). The absence of long-range coherence in glassy materials results in the sessile transformations which, once formed, do not expand by translational movements of their interfaces. Therefore, the plasticity mediated by the shear transformations is nucleation controlled (Argon, 1993; Spathis and Kontou, 2001). Since PGs are considered as homogeneous and isotropic materials, a localized disturbance in their bulk can be considered as an Eshelby inclusion problem (Eshelby, 1957). The Eshelby leading-edge homogenization method, which has been extensively applied for solving a broad area of problems in inhomogeneous media, is based on the strain compatibility of a medium containing non-elastic strains (Mura, 1982). Using this method for amorphous solids, the STZ’s nucleation energy, which is essentially required for formulating the kinetics of STZ mediated plasticity, can be obtained (Argon, 2013). Based on the Eshelby solution, the microgeometrical and micromechanical properties of the embedded STZ, i.e., size, shape, and transformation shear strain, are determining parameters for evaluating the STZ’s nucleation energy in glassy solids. These characteristics have been extensively studied,
especially for metallic glasses (Ju et al., 2011; Pan et al., 2008; Yang et al., 2007). In contrast, the number of studies devoted to evaluate the STZs quantitatively in glassy polymers are limited. Therefore, the geometrical and micromechanical properties of plasticity sites (STZs) are highly needed to be experimentally and theoretically obtained through precise and reliable procedures. Moreover, the obtained results provide reliable and precise values required as inputs for solving boundary value problems in theoretical and numerical simulation studies of yielding and plasticity of PGs at macroscopic level; and the nanoindentation experimental procedure outlined here could be used for characterizing other glassy materials.

1.2.2. Effect of Microstructural State of Material on Plasticity Sites

It should be noted that the very nature of being disordered in amorphous materials necessitates the presence of considerable amount of “voids” or “free volumes” in their microstructure (Hofmann et al., 2002; Jean et al., 2013). In the shear transformation mediated plasticity, the STZs tend to form around these localized cavities; and accordingly, the localized nature of the flow process might require the local distribution of free volumes to play a role in thermo-mechanically activated processes of shear transformation events as the plasticity carriers in amorphous materials. The free volume content in glassy polymers is one of the key quantities which determines the microstructural state of the material. Since the nucleation of STZs strongly depends on the initial microstructural state of the material, there should be a correlation between the microstructural state variable, i.e., free volume, and plasticity sites. Moreover, the free volume evolution upon thermal pre-treatment can induce a remarkable effect on the characteristic microstructural and micromechanical parameters of these sites, e.g., shear activation volume. Therefore, the investigation of the possible relationship is required for a better understanding of the response of these class of materials during deformation.
1.2.3. Modeling of Indentation Size Effect

The size dependent behavior of materials including metals and polymers have been observed in micron to submicron length scales using micro and nanoindentation (Abu Al-Rub et al., 2009; Briscoe et al., 1998; Han, 2010; Samadi-Dooki et al., 2016; Voyiadjis and Al-Rub, 2005; Voyiadjis et al., 2014), microbeam bending test (Deng et al., 2017; Lam et al., 2003; McFarland and Colton, 2005), and bending test of nanofibers (Arinstein et al., 2007; Sun et al., 2008). When measured at small scales the mechanical characteristics of material usually improve over the corresponding bulk properties. Characterization, rationale, and prediction of these size dependent phenomena in polymers are of great importance not only for technological advancement but also for the fundamental advancement of polymer physics and chemistry. Technological applications of polymers with small dimensions include for example coatings for corrosion protection, micro-/nano-electromechanical systems, composites, and medical applications. Alongside the technological importance, the size dependent deformation is also of importance for fundamental issues in polymer physics/materials science, e.g., fracture and delamination, adhesion, contact, effect of surface roughness on friction, and deformation mechanisms at material interface.

Indentation testing is probably the most convenient material testing method to study the size dependent deformation at various length scales. A representative example of such size effects is the so-called indentation size effect (ISE), which is manifested as an increase in hardness \( H \) with decreasing the indentation depth \( h \), impression size \( A \) or peak load \( P_{\text{max}} \). In the case of crystalline materials including metals, it is known that the observed ISE is mainly attributed to the geometrically necessary dislocations and their interactions with the statistically stored dislocations (Abu Al-Rub et al., 2009; Voyiadjis and Al-Rub, 2005; Gao and Huang, 2003; Nix and Gao, 1998). Since the flow and plasticity response mechanism is different for non-crystalline solids and the
main carriers of plasticity are shear transformations instead of dislocations, their size dependent behaviors cannot be explained by dislocation-mediated plasticity. Moreover, the observed size effects in all aforementioned experiments have usually been attributed to the displacement gradients existing in these measurements. The length scale dependent behavior of polymers has also been reported in uniaxial tensile experiments of polymeric nanofibers which is intrinsically a displacement gradient-free situation (Pai et al., 2011; Papkov et al., 2013; Wong et al., 2008). Accordingly, the existence of size dependent behavior in both displacement gradient-free and -dominant situations in addition to considering the stochastic nature of the formation and distribution of the flow sites imply that the ISE phenomenon in glassy polymers cannot be interpreted using the existing models. As a result, an investigation is required to discover the physically and mechanistically appropriate mechanisms at microstructural level to model the indentation size effect in glassy polymers.

1.3. Objectives and Outline

This research is focused on application of the new mechanical testing methods at small scales and advanced microstructural characterization techniques for examining the deformation microstructures in non-crystalline solids. Accordingly, the main objective is experimental and analytical characterization of nano-scale microstructures which are responsible for the observed mechanical behavior of amorphous polymers at different scales. Employing the findings and observations, the ultimate purpose is to explore the origin of size effect behavior in nanoindentation experiments and develop a strain rate dependent ISE model for glassy polymers. The details of this research are presented in the following 6 chapters.

Chapter 2 is devoted to characterize the geometrical and micromechanical properties of the shear transformation zones in glassy polymers. The characteristic properties of shear
transformations in amorphous polymers are different from those in metallic glasses. Moreover, the reported values in the literature are not the same for different metallic glasses. To investigate the universality or uniqueness of STZ’s properties in glassy polymers, two different polymers, i.e., polymericpoly(methyl methacrylate) (PMMA) and polycarbonate (PC), are selected as widely used amorphous polymers. The accurate and reliable nanoindentation technique is employed to investigate the strain rate and temperature sensitivity of the flow in amorphous polymers. Employing continuous stiffness measurement (CSM) technique at room temperature indentations, and basic loading rate control method for nanoindentations at elevated temperatures, the mechanical properties of the samples are measured. Furthermore, to explore the effect of thermal history of the samples on the STZ’s characteristics, the experiments and analyses are presented for both as-cast and thermally treated samples. Atomic Force Microscope (AFM) and Optical Profiler for measuring the surface roughness and Differential Scanning Calorimetry (DSC) for annealing of the samples are employed for this research.

An Arrhenius relation is then used as a flow theory to analyze the experimental observations. Modeling the plasticity sites as Eshelby inclusions, their geometrical and micromechanical characteristics including shape, size, number of containing monomers, transformation shear strain, shear activation volume, and activation energy are obtained.

Chapter 3 addresses investigating the possible relationship between the microstructural state variables and plastic deformation since the mechanical loading induced flow of glassy polymers, which is triggered by the nucleation of shear transformation sites, strongly depends on the initial microstructural state of the material. In this chapter, free volume content is considered as a state variable and thermal treatment is selected as a process through which the accelerated and forced evolution of the free volume can be imposed. The free volume content alteration upon
annealing is then monitored via positron annihilation lifetime spectroscopy (PALS), and the changes of the micro- and macro-mechanical properties are also obtained by utilizing nanoindentation technique and employing the homogeneous amorphous flow theory. The correlation between the microstructural state variable, i.e., free volume, and the micromechanical state variable, i.e., shear activation volume, is then investigated. Accordingly, the possibility of the existence of an interrelation between these two state variables is critically discussed.

The obtained information from chapters 2 and 3 provides valuable data for modeling and simulation of plastic deformation in polymers; however, it has been missing in the literature. The studies carried out hitherto count as building block for amorphous plasticity of polymers and are vital steps towards understanding the nature of the localization effect such as indentation size effect in this class of materials. Chapters 4 to 6 are devoted to investigation of ISE in polymers, including both amorphous and semicrystalline samples, the possible influencing parameters on ISE, and exploring the ISE mechanism.

In chapter 4, the nanomechanics of poly(ether-ether-ketone) (PEEK) as a tough high performance polymer (HPP) is scrutinized using the nanoindentation technique. Semicrystalline high performance polymers exhibit desirable thermomechanical properties which make them suitable materials in several industries. However, when their mechanical characteristics are investigated at nano-scale, the inhomogeneous nature of semicrystalline HPPs results in measurement of localized properties which might not represent the overall material response. It is demonstrated how surface properties of this polymer can affect the nanoindentation measurements and reveal significant anomalies compared to the nanoindentation of fully crystalline or amorphous solids. In addition, polishing and annealing procedures are introduced as simple techniques that can be used for eliminating the inhomogeneity of the mechanical response of PEEK. Lastly, the
capability of depth sensing indentation for determining the distribution of crystalline and amorphous sub-regions within semicrystalline solids is scrutinized and critically discussed.

One of the key factors in studying the mechanical behavior of viscoelastic-viscoplastic materials, like polymers, is the rate at which they are loaded. In fact, these materials show a strong rate dependent behavior under different loading conditions. Since time related parameters such as loading rate and strain rates can be easily adjusted in the nanoindentation experiments, the effect of loading/strain rates on the mechanical response of polymers can be investigated using the nanoindentation experiment. Moreover, for the case of the nanoindentation, where these behaviors are evaluated at nano-scales, there are different techniques in which the loading rate can be controlled in a way that the strain rate remains constant or varies during the experiment.

Since polymers show highly rate dependent behavior in nanoindentation tests in a way that a higher hardness is obtained for a higher value of strain rate, the observed ISE might be related to the higher value of strain rate at shallow indentation depths. In chapter 5 this possibility is studied in detail. In fact, by studying the actual variation of strain rate during nanoindentation and considering the relationship between the hardness and strain rate, its contribution on the observed indentation size effect is thoroughly investigated. Furthermore, other contributing factors for this phenomenon are discussed for their possible effects.

In chapter 6, employing the shear transformation mediated flow theory and considering the statistical nature of the formation and distribution of the flow sites, a rate dependent ISE model for glassy polymers is developed. This model is based on the possibility of the occurrence of discrete shear transformation regions within the deformed volume under the indenter which is controlled by the indentation depth and geometry. The details considered in the model development in terms
of the variations of indentation strain rate and elastic modulus with depth as well as validity and limitations of the model are discussed. Finally in chapter 7 the summary, conclusion and future perspectives are presented.
CHAPTER 2
GEOMETRICAL AND MICROMECHANICAL CHARACTERIZATION OF SHEAR TRANSFORMATION ZONES USING NANOINDENTATION*

2.1. Introduction

As mentioned in chapter 1, STZ’s characteristics have been extensively studied, especially for metallic glasses (MGs). It has been found that a single STZ in MGs possesses an average volume of less than 10 nm$^3$ including $\leq$ 500 atoms (Pan et al., 2008), with the average nucleation energy of about 1.5 eV (Yu et al., 2010) and transformation shear strain of 0.07 (Argon, 2013). In contrast, the number of studies devoted to evaluate the STZs quantitatively in glassy polymers are limited. The plastic deformation units pertaining parameters of some glassy polymers have been obtained by Argon and Bessonov (1977) based on double kink theory. Later, in a molecular dynamics simulations Mott et al. (1993) scrutinized the plastic deformation kinematics in amorphous atactic polypropylene, and found the transformation shear strain of about 0.015 in the spherical plastic flow units with the average 10 nm diameter. Moreover, Ho et al. (2003) also inquired the correlation between the STZ size scale and entanglement density by performing different compressive tests on mixable polystyrene-poly (2,6-dimethyl-1,4-phenylene oxide) (PS-PPO) blends at different mix ratios.

In this chapter, the nanoindentation technique is used to probe the flow nature of PMMA and PC as glassy polymers, and, consequently, their STZs’ micromechanical and geometrical characteristics are obtained. This chapter is organized as follows: in the first section, the experimental procedure is explained in two parts: sample preparation and the nanoindentation

technique. In the second section, it is first shown that at tested temperatures and strain rates the flow is homogeneous in these polymers. The homogeneous flow theory is then elaborated based on the Eshelby’s solution for non-elastic strain in an embedded inclusion in the representative volume element (RVE) and the Arrhenius function relating the shear flow stress to the shear flow strain rate. In the third section, the obtained results from the nanoindentation experiments on samples with two different thermal histories: as-cast and annealed are presented. The characteristic properties of STZs including the nucleation energy barrier, size and shape of an STZ, and the shear activation volume are then obtained by utilizing the flow theory. Furthermore, the observed jump in the activation energy of the STZ is ascribed to the $\beta$-transition, and the energy barrier for this transition is found to be about 10% of the STZ nucleation energy. At the end, the concluding remarks are summarized in the last section.

2.2. Experimental Procedure

2.2.1. Sample Preparation

Commercially available 2.0 and 5.0 mm thick sheets of amorphous PMMA and PC, Goodfellow® catalogue # ME303020 and #L5433027, Cambridge, UK, are selected for this study, respectively. There is no preexisting molecular chain orientation in the sheets, since they have been produced through the traditional method of cell cast. All the sheets are cut into 20×20 mm square samples small enough for handling the nanoindentation experiments. The residues of the protective film covering the sheets are then removed by washing them with 30% Isopropyl Alcohol (IPA), and thoroughly rinsing by distilled water. To eliminate any moisture caused by the washing process, all the specimens are stored in a desiccator for at least 10 days before any experiments are conducted. The glass transition temperature of the samples are measured by means of a TA Instrument 2920 DSC device, which is operating under the nitrogen flow and by using standard
aluminum pans. The DSC cycles are conducted at 10 °C min⁻¹ from ambient temperature to 200 and 250 °C for PMMA and PC, respectively. The calorimetric measurements reveal that the glass transition temperature of the PMMA and PC specimens are about 110 and 148 °C, respectively.

Half of the samples, prepared as described above, are subjected to the following thermal treatment to study the effect of thermal history on their STZs’ micromechanical and microstructural characteristics. Initially, they are annealed at 120 °C for 4 hours in a vacuum oven. They are then cooled down at 10 °C hr⁻¹ to room temperature. This thermal process is done in a vacuum oven to prevent the specimens’ surfaces oxidation (Hirata et al., 1985). An Agilent 5500 atomic force microscope (AFM) and a Wyko Optical Profiler are used to measure the surface roughness of the samples, which markedly has effects on the nanoindentation experiment results (Kim et al., 2007; Nagy et al., 2013). The average surface roughness (Rₐ) of the PMMA and PC samples are measured to be 0.372 ± 0.013 and 0.305±0.021 nm, respectively. Accordingly, since the samples’ surfaces can be assumed as almost flat (Kim et al., 2007), no modification is needed for the obtained experimental results. Figure 2.1 represents a sample AFM scanning of the specimen surface. To indent the samples, they are mounted on aluminum stubs applying thermoreistant epoxy putty (Drummond™ Nu-Doh Epoxy Repair Compound Titanium Reinforced) for indentations at high temperature on hot stage apparatus and super glue for indentations at ambient temperature.
2.2.2. Nanoindentation Technique

The nanoindentation technique has been utilized to measure the mechanical properties of the materials including the elastic modulus, $E$, and the hardness, $H$. The indentation load-hold-unload cycles have been performed using an MTS Nanoindenter® XP equipped with a three-sided pyramidal Berkovich diamond tip. The analysis of the applied load-indentation depth curves is mainly based on the original formalism developed by Oliver and Pharr (1992, 2004) as described in the following.

The hardness is described as the mean contact pressure under the indenter as follows

$$H = \frac{P_{\text{max}}}{A_c}$$

in which $P_{\text{max}}$ is the peak indentation load and $A_c$ is the projected area of the tip-sample contact at the maximum load. According to Eq. (2.1), one needs an accurate measurement of the projected contact area under the load to evaluate the hardness from indentation load-displacement data. For a perfectly sharp Berkovich indenter, the contact area which is a function of the contact depth, $h_c$, can be calculated as

Figure 2.1. Sample of AFM scanning of the PMMA sample surface.
\[ A_c = 24.56h_c^2 \] \hspace{2cm} (2.2)

For a practical indenter, which is not ideally sharp, the contact area function is required to be obtained by tip calibration with introducing additional terms to the aforementioned second order relation as follows

\[ A_c = 24.56h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + \ldots + C_8 h_c^{1/128} \] \hspace{2cm} (2.3)

where \( C_1 \) through \( C_8 \) are constant coefficients which account for deviations from ideal geometry due to the blunting of the tip, and determined by using the indentation results on a standard fused silica sample and curve fitting performed on the Analyst\textsuperscript{®} software. To obtain the exact contact area, an accurate determination of the depth over which the test material makes contact with the indenter, \( h_c \), is required. The contact depth is generally different from the total penetration depth, and is estimated using

\[ h_c = h - \varepsilon P \] \hspace{2cm} (2.4)

in which \( S \) is the measured elastic contact stiffness and \( \varepsilon \) is a constant which depends on the indenter geometry (for a Berkovich indenter \( \varepsilon = 0.75 \)) (Oliver and Pharr, 1992).

As already stated, the CSM technique makes the continuous measurement of the contact stiffness as a function of depth possible during the loading segment of the indentation. Considering the imposed driving force as \( P = P_0 e^{i\omega t} \) and the indenter displacement response as \( h(\omega) = h_0 e^{(i\omega t + \varphi)} \), the elastic contact stiffness is calculated as follows

\[ S = \left[ \frac{1}{P_0} \frac{1}{h(\omega) \cos(\varphi) - (K_s - m\omega^2)} - \frac{1}{K_f} \right]^{-1} \] \hspace{2cm} (2.5)
in which \( P_0 \) is the force oscillation magnitude, \( \omega \) is the oscillation frequency, \( h_0 \) is the resulting displacement oscillation magnitude, and \( \varphi \) is the phase angle between the displacement and force signals. The other contributing parameters are the leaf spring constant, \( K_s \), that supports the indenter, the indenter mass, \( m \), and the indenter frame stiffness, \( K_f \) (Li and Bhushan, 2002).

The elastic modulus of the sample, \( E \), is calculated from Eq. (2.6) as follows

\[
\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}
\]

(2.6)

In this equation, \( E_i \) and \( \nu_i \) are the indenter elastic modulus and Poisson’s ratio, respectively, \( \nu \) is the sample Poisson’s ratio, and \( E_r \) is the reduced elastic modulus. The reduced modulus which accounts for elastic deformation in both the indenter and the sample can be obtained from the following relation developed by Sneddon (1965)

\[
E_r = \frac{S}{2 \rho} \sqrt{\frac{\pi}{A_c}}
\]

(2.7)

where \( \rho \) is a constant that depends on the indenter geometry equal to 1.034 for the Berkovich tip.

2.2.2.1. Room-Temperature CSM Nanoindentation

The room temperature nanoindentation experiments are conducted by employing the continuous stiffness measurement (CSM) technique. The CSM method makes the continuous measurement of the mechanical properties of materials possible during the indentation loading segment from zero to the maximum indentation depth during a single test; this includes the measurement of the elastic contact stiffness at any point along the loading curve, and not just at the point of initial unload as in the basic mode (Hay et al., 2010; Li and Bhushan, 2002; Lucas et al., 1998; Pethica and Oliver, 1988). In this technique, a small sinusoidally varying load is
superimposed on top of the primary loading signal that drives the motion of the indenter, and the resulting response of the system is analyzed by means of a frequency-specific amplifier. The displacement amplitude and the frequency of the superimposed oscillating force are set as 2 nm and 45 Hz, respectively, which are optimum values for the MTS nanoindentation® XP.

Utilizing the so-called CSM technique, the indentation load-hold-unload cycles are performed by keeping the loading rate divided by the load ratio ($\dot{P}/P$) constant during the loading segment over the course of a single indentation test. In a deep indentation test, where the indentation size effect is negligible (i.e., the hardness value is almost constant), the loading path follows a Hertzian contact relation as $P = ah^b$, where $P$ represents the indentation load, $h$ is the indentation depth, $a$ is a material dependent parameter, and $b$ is a curve fitting parameter close to 2 for the Berkovich tip (Johnson, 1987; Zhang et al., 2005). Accordingly, for pyramidal indenters, the indentation strain rate $\dot{\varepsilon}_i$, which is defined as the descent rate of the indenter divided by its instantaneous depth, can be obtained by

$$\dot{\varepsilon}_i = \frac{\dot{h}}{h} = \frac{1}{b} \frac{\dot{P}}{P}$$

(2.8)

Therefore, since the $\dot{P}/P$ ratio is remained constant during the CSM test, at deep enough indentations, the indentation strain rate approaches a constant value equal to $\frac{\dot{P}}{2P}$ (Lucas and Oliver, 1999). Moreover, the effective shear strain rate induced by the indentation is then related to the indentation strain rate as follows

$$\dot{\gamma} = \sqrt{3}C\dot{\varepsilon}_i = \frac{\sqrt{3}C}{b} \frac{\dot{P}}{P}$$

(2.9)

where $C$ is a constant equal to 0.09 (Poisl et al., 1995; Schuh and Nieh, 2003; Schuh et al., 2004).
After samples preparation and calibration of the indenter tip function, the tests are carried out by loading-hold-unloading sequences as follows: prior to any measurement the tip is held on the top of the sample surface until its drift rate is stabilized at a rate below 0.05 \( \text{nm/s} \). The tip then starts downward travel until it reaches the surface. Once the indenter tip comes into the contact with the sample surface, the loading segment begins with the constant value of \( \dot{P}/P \) until a pre-defined maximum depth of about 10 \( \mu \text{m} \); the load is then held at the maximum value for 10 s to account for the material creep behavior of the polymer surface; and finally, the unloading stage is carried out with the constant unloading rate until 10\% of the maximum load is attained. Since one of the main purposes of this study is investigation of the strain rate dependency of the flow in PMMA and PC, a series of experiments are conducted at room temperature with the values of \( \dot{P}/P \) varying from 0.001 to 0.2 and 0.002 to 0.4 \( \text{s}^{-1} \) on annealed and as-cast PMMA and PC samples, respectively. A total of 25 indents are performed for each \( \dot{P}/P \) value with a minimum distance of 150 \( \mu \text{m} \) between neighboring indents to prevent any interaction.

### 2.2.2.2. High-Temperature Nanoindentation Procedure

The MTS Nanoindenter® XP is equipped with temperature control system for elevated temperature nanoindentation tests. The system includes a hot-stage, a coolant apparatus to transfer the extra heat to the outside of the instrument, and a heat shield to keep the indenter transducer apart from the heat source. The load control experiments are performed by using the basic method which is employed for high-temperature indentations. To make sure that there is no indentation size effect, and making the obtained date comparable to those of the CSM tests as well, the experiments are carried out with a maximum load of 300 \( mN \). Loading rates of 4, 10, 50, 100, and 300 \( mNs^{-1} \) for PMMA and 10, 100, and 300 \( mNs^{-1} \) for PC, which are constant during the tests, are
applied for temperatures varying from room temperature to 100 and 140 °C (slightly lower than the samples glass transition temperature) for PMMA and PC, respectively.

While the loading rate $\dot{P}$ is kept constant during the loading and unloading segments of the basic mode, evaluating the $\dot{P}/P$ ratio shows that it changes with $1/h^b$ during the test since the load-depth ($P-h$) curve follows a Hertzian relation according to the statements in the preceding section. Therefore, the indentation strain rate $\dot{\varepsilon}_i$ varies as $1/h^b$ during the test as well. Using Eqs. (2.8) and (2.9) to calculate the effective shear strain rate, an average value of $\dot{P}/P$ over the deep part of the indentation (5 $\mu$m in this study) is considered in each test. Accordingly, the corresponding effective shear strain rates for the load rates given above are 0.0014, 0.0035, 0.0175, 0.035, and 0.105 s$^{-1}$ for PMMA and 0.0035, 0.035, and 0.105 s$^{-1}$ for PC, respectively.

Applying a thermoresistant epoxy putty, the samples are mounted on the hot stage. Since polymer samples and the adhering thermoresistant have low thermal conductivity, the temperature of the sample surface can be considerably different from the set temperature. For precise evaluation, at the end of the tests, an Omega® SA1-K-SRTC thermocouple is attached to a sample surface to measure its temperature. The temperature is recorded by means of an Omega® HH74K handheld monitoring device coupled with the thermocouple. The discrepancy between the measured and set temperatures are significant for high temperatures. The number of indentation points for each set temperature and loading rates is reduced to 12 for the elevated temperature tests to minimize the risk of the contamination of the tip by the softened polymer at high temperatures; the minimum distance of the adjacent indents is also increased to 200 $\mu$m. Prior to performing the loading cycle, each sample is heated to the set temperature inside the indenter; and then it is left to equilibrate for 2-3 hours. On the onset of the test cycle, the tip is held at the distance of about 1
µm from the sample surface for about 10 minutes to adjust allowable thermal drift. This delayed contact is believed to help the tip to reach a thermal equilibrium with the sample.

2.3. Theory of Homogeneous Flow for Glassy Polymers

The inhomogeneous flow in amorphous solids is mediated by the formation of shear bands, whereas their homogeneous flow is triggered by the nucleation of STZs (Spaepen, 1977). There are some important differences between inhomogeneous and homogenous flows of glassy solids. While the inhomogeneous flow is strain rate independent in a way that the flow stress does not change significantly with the strain rate, in a homogenous flow, the higher strain rate applied to the sample results in a considerable higher flow stress (Schuh and Nieh, 2003; Schuh et al., 2007; Yang et al., 2007). Another significant distinction is the generation of multiple pop-ins in the load-displacement curves during the inhomogeneous flow which appears only in the nanoindentation experiments (Golovin et al., 2001; Yang et al., 2007; Zhang et al., 2005).

It has been shown that the flow behavior of metallic glasses is temperature dependent in a sense that there exists a transition from inhomogeneous to homogeneous flow at a certain temperature. The temperature at which the transition happens is also strain rate sensitive: the higher the applied strain rate, the higher the transition temperature (Yang et al., 2007). To investigate the flow nature in PMMA and PC as glassy polymers, the nanoindentation tests are performed on both as-cast and annealed samples. Figures 2.2 and 2.3 represent the variation of the hardness with temperature for as-cast and annealed PMMA and PC samples at different loading rates, respectively. Considering the direct relation between the hardness \( H \) and the flow stress \( \sigma_y \) as \( H = \lambda \sigma_y \) with \( \lambda \) is Tabor’s factor, these figures show that the hardness (or flow stress) is greatly strain rate sensitive in a way that a higher hardness is obtained at a higher strain rate (loading rate) at a given temperature. This observed rate dependent softening, which is attributed to the thermally
activated nature of the flow, indicates that the flow of PMMA and PC at tested temperatures, which are below their glass transition temperatures $T_g$, is homogeneous. In addition, Figures 2.4 and 2.5 show the load-displacement curves of the samples at the loading rates of 10 and 300 $mN s^{-1}$ and different temperatures. All the curves are represented with the origin offset of 2 $\mu m$ except the first one at room temperature. The curves are smooth with no pop-in events which further confirm the homogenous nature of the flow in PMMA and PC.

![Figure 2.2](image1.png)

Figure 2.2. Variation of the PMMA hardness with temperature at different loading rates for (a) as-cast and (b) annealed samples.

![Figure 2.3](image2.png)

Figure 2.3. Variation of the PC hardness with temperature at different loading rates for (a) as-cast and (b) annealed samples.
Figure 2.4. Load-indentation depth curves for as-cast and annealed PMMA samples at different temperatures and the load rates of (a) 10 mNs$^{-1}$, and (b) 300 mNs$^{-1}$. 
Figure 2.5. The load-indentation depth curves for as-cast (solid line) and annealed (dashed line) PC samples at different temperatures and loading rates of (a) 10 mNs$^{-1}$, and (b) 300 mNs$^{-1}$.

The flow in glassy solids is mediated by the irreversible local disturbances which form rearranged atomic (in MGs) or molecular (in PGs) clusters. These cooperative rearrangements result in isolated unit increments of shear, and are known as STZs. While in the homogeneous flow regime each volume element has contribution to the total plastic strain, the strain is localized in distinct shear bands in the inhomogeneous flow regime (Spaepen, 1977). The thermally activated
homogeneous flow in glassy polymers can be described based on the flow mechanism developed by Argon (1979) and Spaepen (1977).

For the STZs mediated homogeneous flow in glassy solids, the kinetic relation for the shear strain rate $\dot{\gamma}$ due to the applied shear stress $\tau$ is well expressed by an Arrhenius relation as follows

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta F_0}{k_B T}\right) \sinh\left(\frac{\gamma^T \Omega}{2 k_B T}\right)$$

(2.10)

where $\dot{\gamma}_0$ is the pre-exponential factor proportional to the attempt frequency, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\Delta F_0$ is the nucleation energy of an STZ with the shear strain $\gamma^T$ occurring in a region of volume $\Omega$. The factor 2 in the denominator of the argument of the hyperbolic function is due to the reverse transformation probability. To evaluate the nucleation energy of an STZ, this locally transformed region has been treated as an embedded volume with non-elastic strain the micromechanical field of which can be obtained by using Eshelby’s inclusion model (Eshelby, 1957). For the RVE shown in Figure 2.6, the free energy of the nucleation of a single STZ is given as follows

$$\Delta F_0 = [\Xi(\nu) + \Psi(\nu)\beta^2] \mu (\gamma^T)^2 \Omega$$

(2.11)

in which $\mu$ is the shear modulus, $\Xi(\nu)$ and $\Psi(\nu)$ are functions of the Poisson’s ratio $\nu$, and pertain to the shear and dilatational components of the transformation strain tensor, respectively. The coefficient $\beta$ is the dilatancy parameter and can be obtained from the pressure sensitivity of the flow. While $\Psi(\nu) = \frac{2(1+\nu)}{9(1-\nu)}$ is independent of the aspect ratio of the ellipsoid, $\Xi(\nu)$ is shape dependent (Mura, 1982). The STZ’s characteristics in Eq. (2.10), such as shear strain, size, and activation energy have been experimentally obtained for different metallic glasses, but their numerical evaluation for PGs have been limited to some theoretical modeling and simulations.
Figure 2.6. Representative volume element (RVE) of polymer matrix containing a single STZ.

Since $\gamma^T \Omega \tau \gg 2k_B T$ for conventional PGs at temperatures below their glass transition, Eq. (2.10) can be rearranged as

$$ln \dot{\gamma} = \frac{\gamma^T \Omega}{2k_B T} \tau + A_1$$

where $A_1 = ln \frac{\gamma_0}{2} - \frac{\Delta F_0}{k_B T}$ represents a temperature-dependent parameter. In Eq. (2.12), the material constant $\gamma^T \Omega$, which is proportional to the important characteristic parameter of glassy polymers known as shear activation volume $V^*$ (Ward, 1971), can be determined from the derivative of the natural logarithm of the strain rate ($ln \dot{\gamma}$) with respect to the shear flow stress ($\tau$). Accordingly, considering the effect of hydrostatic pressure on the shear yield stress of polymers, the modified shear activation volume is obtained from Eq. (2.13) as follows (Ho et al., 2003)

$$V^* = (1 - \alpha \beta) \gamma^T \Omega = 2k_B T (1 - \alpha \beta) \frac{\partial ln \dot{\gamma}}{\partial \tau}$$

where $\beta$ is the yield stress sensitivity to the pressure as defined before, and $\alpha$ is the loading condition constant which is between 0.6 and 0.7 for different compressive loading conditions (Tervoort, 1996; Ward, 1971). In fact, one can conclude from Eq. (2.13) that the shear activation volume is a modified STZ volume with considering the dilatation effect. Furthermore, since $\gamma^T$ is...
assumed to be a universal constant for all glassy polymers and equals about 0.02 (Ho and Vu-Khanh, 2003; Mott et al., 1993), the size of the single shear transformation zone $\Omega$ can be obtained. Rearranging Eq. (2.10) for a constant strain rate, the shear flow stress can be expressed as a linear function of temperature as follows

$$\tau = TA_2 + \frac{2\Delta F_0}{\gamma^T \Omega}$$  \hspace{1cm} (2.14)

where $A_2 = \frac{2k_B}{\gamma^T \Omega} (\ln \dot{\gamma} - \ln \frac{\dot{\gamma}_0}{2})$ representing a strain rate-dependent constant. As a result, the activation energy of an individual STZ, $\Delta F_0$, can be calculated from the linear interpolation of the variation of the flow shear stress with temperature by incorporating the obtained $\gamma^T \Omega$ values. Knowing all the STZ’s parameters in Eq. (2.11), one can obtain the numerical value of $\Xi(\nu)$, and, consequently, an approximation of the STZ’s shape in glassy polymers.

### 2.4. Calibrating the Nanoindentation Results

The instrumented-indentation testing (IIT) can be employed for the purpose of probing the mechanical properties including hardness and elastic modulus of very small volumes of materials including polymers, which both of them depend on the applied load on the sample surface and the contact area. In the nanoindentation experiments the load is recorded with a $nN$ scale precision while the contact area is calculated as a function of the tip geometry and contact depth. Since the tip in a common indenter is not ideally sharp, the contact area function is required to be obtained by calibrating the tip with introducing a polynomial approximation (Oliver and Pharr, 1992; Voyiadjis and Zhang, 2015). Using the results of the indentation on standard fused silica sample, the tip areal function is calibrated to obtain reliable results.
It is also worth noting that the material pile-up around the penetrating tip can significantly alter the contact area and affect the measured mechanical properties of the material especially at shallow depths of the indentation. Using the optical profiler, the pile-up values are precisely measured for the indentation on PMMA and PC samples. As can be seen in Figure 2.7 which shows a sample of pile-up measurement on PC specimen, the pile-up is highly unsymmetrical with the maximum values around the pyramidal tip faces. The maximum pile-up is measured to be about 400 nm, which in comparison with the maximum indentation depth of 10 μm is very small. For that reason, the pile-up effect is neglected in the nanoindentation measurements.

![Figure 2.7. A sample of the indentation pile-up measurement on PC specimen using Wyko Optical Profiler.](image)

To prevent the ISE in the current study, the CSM indentation results are first evaluated to find the indentation depth beyond which the obtained hardness reaches the stable value. The variation of hardness versus the indentation depth for both annealed and as-cast PMMA and PC samples are presented in Figures 2.8 and 2.9, respectively. As these figures show, the profound ISE is completely eliminated for the indentation depth beyond 2 and 4 μm for PMMA and PC samples, respectively. Accordingly, the hardness values are averaged over the indentation depth beyond 5 μm where the ISE is absent. The elevated temperature tests are performed by using the
basic mode in which the hardness value is only reported at the maximum indentation depth. While the maximum indentation depth is the input for the CSM technique, the maximum load is the input in the basic mode. As mentioned before, to avoid the indentation size effect, and also make the obtained date comparable to those of the CSM tests, the high temperature experiments are carried out with a maximum load of 300 mN, which corresponds to the maximum indentation depth of about 10 μm. Furthermore, since the ISE reduces at elevated temperatures (Voyiadjis et al., 2011), it is assured that the obtained hardness results are within the stable region.

Figure 2.8. Variation of the hardness versus the indentation depth for three different $P/\dot{P}$ values for (a) as-cast, (b) annealed PMMA samples. The legend numbers represent the $P/\dot{P}$ values.
2.5. Shear Activation Volume

In addition to the hardness, the elastic modulus is another mechanical property of the material which is continuously recorded during the loading segment of the CSM nanoindentation as a function of displacement. Figures 2.10 and 2.11 represent the variation of the material elastic modulus versus the indentation depth for some selected $\dot{P}/P$ values for PMMA and PC samples, respectively. In comparison to the hardness, the elastic modulus is almost constant for the indentation depth beyond about 100 and 150 nm for both as-cast and annealed PMMA and PC samples, respectively. More importantly, while the hardness values significantly change with the strain rate (see Figures 2.8 and 2.9), the elastic modulus does not show any significant strain rate sensitivity.
Figure 2.10. Variation of the elastic modulus versus the indentation depth for three different $\dot{P}/P$ values for (a) as-cast and (b) annealed PMMA samples. The legend numbers represent the $\dot{P}/P$ values.

Figure 2.11. Variation of the elastic modulus versus the indentation depth for three different $\dot{P}/P$ values for (a) as-cast and (b) annealed PC samples. The legend numbers represent the $\dot{P}/P$ values.

Using the Tabor’s factor, the hardness values $H$ obtained from the nanoindentation experiments can be converted to the yield stress $\sigma_y$ of the material as follows

$$H = \lambda \sigma_y$$  \hspace{1cm} (2.15)
in which $\lambda$ is Tabor’s factor which is approximately 3.3 for amorphous polymers at high indentation strains (Prasad et al., 2009). Additionally, since the shear flow stress is about half of the yield stress in plane stress condition for monotonic loading (Yang et al., 2007), the ratio of the hardness to the shear flow stress is about 6.6. Figures 2.12 and 2.13 illustrate the shear flow stress-shear strain rate data points for the as-cast and annealed PMMA and PC samples measured by CSM method at room temperature, respectively. The obtained results for PC is in good agreement with the ones obtained by Bauwens-Crowet et al. (1969) at 21.5 °C. As it is expected, the annealed samples have slightly bigger shear flow stresses compared to the as-cast ones at the same shear strain rate (Jancar et al., 2013). The outstanding feature of Figure 2.12 is the existence of a significant transition at a certain value of the strain rate beyond which the strain rate sensitivity of the shear flow stress increases. This phenomenon is believed to be a result of strain rate shift of the $\beta$-relaxation process in the storage modulus of the PMMA, which is related to the restriction of the ester side group rotations at high strain rates, besides the intermolecular and local back bone motion restrictions (Argon, 2013; Calleja et al., 1994; Mulliken and Boyce, 2006). As obviously shown in Figure 2.12, the transition shear strain rate is approximately 0.005 s$^{-1}$ for both as-cast and annealed PMMA samples. Following the descriptions presented in Mulliken and Boyce (2006), the flow stress regimes below and above the transition shear strain rate might be referred to as $\alpha$ and $\beta$ regimes, respectively. However, it is noteworthy to mention that since the room temperature $\beta$-transition strain rate of PC has been previously detected to be about $10^2$ s$^{-1}$, which is beyond the strain rates that can be applied in nanoindentation experiments, no considerable jump is observed in Figure 2.13 for the range of strain rates in this study.
Figure 2.12. Variation of the shear flow stress with the shear strain rate for both as-cast and annealed PMMA samples.

Figure 2.13. Variation of the shear flow stress with the shear strain rate for both as-cast and annealed PC samples.

Based on Eqs. (2.12) and (2.13), the shear activation volume $V^*$ for an amorphous polymer can be obtained by linear interpolation of $\tau - \ln \dot{\gamma}$ curve. In these figures, the slopes of the semi-logarithmic stress-strain rate plots are almost the same for samples with different thermal history, which suggest that the shear activation volume and, therefore, the size of a single STZ are almost independent of the thermal history of the samples. Incorporating Eq. (2.12) and the data represented on Figures 2.12 and 2.13, the factor $\gamma^T \Omega$ for as-cast and annealed samples is obtained about 3.66 and 3.69 nm$^3$ for PMMA, and 8.94 and 9.14 nm$^3$ for PC, respectively. Accordingly, by
assuming $\alpha=0.65$, $\beta=0.204$ for PMMA (Ward, 1971) and 0.27 for PC (Rittel and Dorogoy, 2008), $V^*$ is found to be 3.17 and 3.20 $nm^3$ in $\alpha$ regime for PMMA, and 7.37 and 7.54 $nm^3$ for PC, for as-cast and annealed samples, respectively. The obtained values of shear activation volume are in consonance with the molecular dynamics simulation results (Argon, 2013). As results show, the shear activation volume for samples with different thermal histories is almost the same, and this small discrepancy might be due to the short time of annealing in this study (4 hours). Since it has been shown that the flow stress of glassy polymers increases logarithmically with the annealing time at temperatures below their glass transitions (Hutchinson et al., 1999), a more profound difference might be expected between the shear flow stress results of the as-cast and annealed samples in Figures 2.12 and 2.13 for longer annealing time. However, the increased difference may or may not result in a considerable difference in the shear activation volume since it depends on the slope of the $\tau - ln \dot{\gamma}$ plots and not the shear flow stress solely.

2.6. STZ’s Activation Energy

In light of Eq. (2.14), a linear interpolation of the flow stress as a function of the temperature $\tau - T$ can be used to obtain the STZ’s activation energy. Figures 2.14 and 2.15 represent the variance of the shear flow stress of PMMA and PC with temperature, respectively, for different strain rates which is well interpolated with linear functions at each loading rate. Assuming the parameter $\gamma^T \Omega$ does not vary with temperature, the STZ’s activation energy for both as-cast and annealed samples can be calculated at different shear strain rates as shown in Figure 2.16 for PMMA. One of the most important features of this figure is the existence of jump in the activation energy at the strain rate range of 0.0035 to 0.0175 $s^{-1}$ which is consistent with the $\beta$-transition strain rate obtained from room-temperature CSM nanoindentation. Therefore, this jump might be referred to as the $\beta$-transition activation energy. Although the discrepancy in the
activation energy for the annealed and as-cast samples is small for strain rates above the $\beta$-transition strain rate, the difference is profound for strain rates below this transition. Since the annealed PMMA sample is expected to have more ordered chains in comparison to the as-cast one, the slip and rotation of these chains are more restricted in this sample; consequently, the STZ’s activation energy increases. In contrast, beyond the $\beta$-transition strain rate the rapid loading does not allow the chains to rotate or slip smoothly which puts the annealed and as-cast samples in the same deformation condition, and as a result, the activation energy of STZs for high strain rates is approximately identical for samples with different thermal histories.

Another important feature of Figure 2.16 is that the $\beta$-transition activation energy is much bigger for the as-cast PMMA than the annealed one (almost 3 times). Furthermore, the $\beta$-transition energy is about one order of magnitude smaller than the thermal activation energy of an STZ for PMMA, which is in agreement with the findings of Barral et al. (1994) who found almost the same ratio for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC). In comparison, the $\beta$-transition activation energy has been obtained to be almost equal to the STZ’s activation energy in the metallic glasses (Yu et al., 2010).
Figure 2.14. Variation of the shear flow stress with temperature at different loading rates for (a) as-cast and (b) annealed PMMA samples.

Figure 2.15. Variation of the shear flow stress with temperature at different loading rates for (a) as-cast and (b) annealed PC samples.
Figure 2.16. STZ’s activation energy for both as-cast and annealed PMMA samples at different shear strain rates.

As defined in Eq. (2.11), the Helmholtz free energy also depends on the shear modulus $\mu$ of the material which itself is temperature dependent. Since the shear modulus of the PMMA does not change considerably for temperatures below about 100 $K$ (Gall and McCrum, 1961), Eq. (2.14) is still valid, and $\Delta F_0$ might be referred to as activation energy at 0-100 $K$. Using the elastic modulus data for different temperatures, obtained by the basic method nanoindentation, and the relation between the elastic modulus and shear modulus as: $\mu = \frac{E}{2(1+\nu)}$, the variation of the shear modulus with temperature for both as-cast and annealed PMMA samples at two different strain rates are represented in Figure 2.17. Assuming the variation to remain linear for temperatures down to 100 $K$, and constant for temperatures below 100 $K$ (which is a valid assumption based on the experiments of (Gall and McCrum, 1961), the variation of the STZ’s activation energy with temperature can be obtained as shown in Figure 2.18. It is also noticeable that the STZ’s activation energy is around 0.6 $eV$ at room temperature which is about one third of that for metallic glasses.
Doing the same calculations on the obtained results for PC samples, the activation energy of a single STZ is presented in Table 1. As expected, the activation energy is slightly bigger for the annealed samples, and is almost strain rate insensitive which is in agreement with the continuum mechanics principal. Since the obtained activation energies are calculated using the extrapolation of the $\tau - T$ values to the 0 K, they should be referred to as the zero Kelvin STZ’s activation energies, and are shown by $\Delta F_0$ hereafter. It should be mentioned that since the room
temperature β-transition strain rate of PC is beyond the strain rates in this study, the β-transition activation energy barrier cannot be captured for PC samples.

2.7. STZ’s Geometry

Incorporating Eqs. (2.11) and (2.14), the intercept of τ – T linear interpolation with τ axis is equal to \( \frac{2\Delta F_0}{\gamma T \Omega} = 2[\varepsilon(\nu) + \Psi(\nu)\beta^2] \mu \gamma T \). As it is mentioned before, \( \Psi(\nu) = \frac{2(1+\nu)}{9(1-\nu)} \) does not vary with the STZ shape, and is about 0.5 and 0.48 for PMMA and PC, respectively (considering the Poisson’s ratio of 0.38 for PMMA and 0.37 for PC). However, \( \varepsilon(\nu) \) is determined by the shape of the STZ which varies between \( \frac{7-5\nu}{30(1-\nu)} = 0.27 \) and 0.5 pertaining to the spherical and flat ellipsoidal shape of STZ, respectively (Mura, 1982). Taking \( \mu_0 = 3.1 \, GPa \) from Figure 2.17 and \( \beta = 0.204 \), the value of \( \gamma T \) varies between 0.03 and 0.05 for PMMA, with the lower and upper bounds pertaining to the flat ellipsoidal and spherical transformation zones, respectively. Based on the molecular dynamics simulation (Mott et al., 1993), the shear strain \( \gamma T \) of 0.05 is a large value for polymeric glasses, therefore, the shape of the transformation zone is more likely to be a flat ellipsoid for PMMA instead of a sphere. Using the previously obtained factor \( \gamma T \Omega \) and assuming \( \gamma T = 0.03 \), the volume of an individual plastic deformation unit \( \Omega \), which is almost the same for as-cast and annealed PMMA samples, is obtained to be about 123 nm\(^3\) which is at least one order of magnitude bigger than that of the metallic glasses (Pan et al., 2008; Yu et al., 2010). Assuming the PMMA monomers as cylinders with the length of 1.55 Å and radius of 2.85 Å (Argon and Bessonov, 1977), the single STZ is found to contain about 3000 monomers.

In a same way, using \( \mu_0 = 2.4 \, GPa \) (Argon 2013) and \( \beta = 0.27 \) (Rittel and Dorogoy, 2008), \( \gamma T \) is obtained equal to 0.035 for the spherical and about 0.02 for the flat ellipsoidal shapes of the STZ for both as-cast and annealed PC samples. Due to the aforementioned reason, it can be
inferred that the STZs in PC are regions with the shapes close to flat ellipsoids rather than spheres. In addition, the volume of an STZ, $\Omega$, is calculated to be about 470 and 488 nm$^3$ which has in average 5600 and 5800 idealized cylindrical shape monomers with 2.8 Å length and 3.09 Å radius (Argon and Bessonov, 1977) for the as-cast and annealed PC samples, respectively. All the obtained characteristic properties of a single STZ in PC samples are presented in Table 2.1.

Table 2.1. Characteristic properties of the STZs in PC for samples with different thermal histories.

<table>
<thead>
<tr>
<th>Thermal history</th>
<th>$\gamma T\Omega$ (nm$^3$)</th>
<th>$V^*$ (nm$^3$)</th>
<th>Activation energy ($eV$) at the shear strain rate of</th>
<th>$\gamma T$</th>
<th>$\Omega$ (nm$^3$)</th>
<th>Number of monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>8.94</td>
<td>7.37</td>
<td>1.32 1.35 1.37</td>
<td>0.019</td>
<td>470</td>
<td>5596</td>
</tr>
<tr>
<td>annealed</td>
<td>9.14</td>
<td>7.54</td>
<td>1.33 1.36 1.38</td>
<td>0.0187</td>
<td>488</td>
<td>5810</td>
</tr>
</tbody>
</table>

2.8. Concluding Remarks

In summary, a series of nanoindentation experiments have been conducted on as-cast and annealed specimens to explore the temperature and strain rate sensitivity of the flow in PMMA and PC as amorphous polymers. Showing that the flow is homogeneous in these polymers at temperatures below their glass transitions and incorporating a homogeneous flow theory, geometrical and micromechanical characteristics of the STZs, as main carriers of plasticity in amorphous polymers, have been investigated in the molecular level. Since the experimental studies on the STZs in glassy polymers is less addressed in the literature in comparison to the metallic glasses, the nanoindentation technique is employed as an accurate, repeatable, and nondestructive method to answer some of the current open questions in this area. The findings suggest that the STZs are flat ellipsoidal regions with the volume of about 123 and 480 nm$^3$ and the transformation shear strain of about 0.03 and 0.02 in PMMA and PC samples, respectively. In addition, the nucleation energy of the shear transportation zones for both samples as well as the $\beta$-transition
energy barrier for PMMA samples have been obtained. The procedure used for obtaining the β-
transition energy based on the nanoindentation technique is an innovative approach which can be
used for other glassy solids. The experimentally evaluated parameters produce unequivocal values
as inputs for further theoretical and numerical investigations of yielding and plasticity in polymeric
glasses.

In light of the obtained results for PMMA and PC, the following remarks are made:

1) The STZ’s nucleation energy in amorphous polymers is about 1 eV which is not considerably smaller than that of the metallic glasses. Since the nucleation energy of an STZ directly depends on the material shear modulus, this energy is expected to be much higher for MGs due to their considerably bigger shear modulus. However, the nucleation energy also depends on the STZ size. Consequently, the bigger size of the STZs in PGs compared to MGs compensates for their shear modulus discrepancy, and levels the activation energy in the two materials.

2) The transformation shear strain $\gamma^T$ is slightly bigger than what is believed to be the universal value for PGs. The transformation shear strain has been considered to be about 0.015 in all types of glassy polymers (Argon, 2013), however, the current study suggests that this parameter is unique to a particular polymer, and is about 0.02 in PC and 0.03 in PMMA.

3) While the current study suggests that the shear transformation zones are formed in the regions with the shape close to the flat ellipsoid in PMMA and PC, the STZ shape is assumed to be spherical in all types of glassy solids (Ho et al., 2003; Li et al., 2013).

4) Since all experiments are performed at temperatures beyond 0.6 $T_g$, the observed homogeneous flow is in accordance with the amorphous flow theory at elevated temperatures (Argon, 1979; Argon, 2013). With the current nanoindentation technology, it seems impossible to
perform experiments at temperatures below 0.6 $T_g$ for available PGs (-43 and -20 °C for PMMA and PC, respectively). Undoubtedly, experiments at temperatures below 0.6 $T_g$ would result in a better understanding of the flow nature in glassy polymers at a wider temperature range.

5) The obtained results for the STZs shape are based on the acceptable values of transformation shear strain in polymers which is considerably smaller than that in metallic glasses. A precise evaluation, requires the STZs direct observation, which is not possible to do conveniently since STZs are local transition events rather than being actual defects like dislocations, or their indirect observation via localized stress field monitoring which has not been reported yet. The only indirect experimental measurement of the STZ’s size scale is one by Liu et al. (2011) in which the 2.5 nm size of the viscoelastic heterogeneities observed by Transmission Electron Microscopy (TEM) has been related to the size of the STZ in a metallic glass.
CHAPTER 3
INTERRELATION BETWEEN MICROSTRUCTURAL EVOLUTION AND PLASTICITY SITES

3.1. Introduction

Casting, molding, and in general forming of glassy polymers are mainly performed at elevated temperatures where these materials are molten or possess a semi-fluid like flow behavior. They are then cooled down to room temperature to solidify. Supercooling of the amorphous polymers from the fluid-like to the glassy state during molding forces the macromolecular chains to freeze randomly at fixed positions. In fact, rapid cooling of the molten amorphous polymers to temperatures below their \( T_g \) inhibits a proper and effective molecular relaxation and generates an unstable non-equilibrium state. At this state, glassy polymers have a higher volume, configurational entropy, etc., than they would have in the thermodynamic equilibrium state (Cangialosi et al., 2016; Hutchinson et al., 1999; Struik, 1977); these increments are due to the formation of excessive frozen-in free volume during quenching. During post-solidification time, the material starts to approach a metastable equilibrium through a slow and gradually continued structural relaxation phenomenon which is called physical aging. The physical aging term was first described in detail by Struik (1977) which was distinguished from chemical and other aging phenomena. For amorphous polymers at temperatures below their \( T_g \), physical aging leads to the reduced molecular segmental mobility and free volume, and a more ordered state (Martinez-Vega et al., 2002). In addition, if the temperature at which the polymer is aged is in the range of temperatures from the secondary transition to the glass transition, \( T_\beta - T_g \), the transition from unstable to stable structure is accelerated and accomplished within shorter amount of time (Greiner

and Schwarzl, 1984; Struik, 1977); this is called the annealing process. It’s widely held that the structural relaxation due to aging/annealing is accompanied by changes in almost all of the polymers’ physico-mechanical properties. Therefore, the process of aging and its effects on the material behavior manifests important consequences on design, manufacture, and use of the components and structures fabricated from polymers.

The changes in quantities characterizing the microstructure, and consequently the macro-scale properties of the material are strongly dependent on the time and temperature of aging process during the annealing or thermal pre-treatment (Soloukhin et al., 2003; Tanio and Nakanishi, 2006; Wypych et al., 2005). Therefore, the investigation of the mechanisms and direction of the microstructural changes, e.g., free volume evolution, mediated by these two parameters are of interest. Free volume content in glassy polymers is one of the key quantities which determines the microstructural state of the material; hence, the physical aging phenomenon might be explained from the concept of free volume variation point of view. Accordingly, many studies have been performed during the past decades to investigate the free volume evolution upon annealing (Cangialosi et al., 2003; Sandreczki et al., 1996; Tanio and Nakanishi, 2006), and consequently, to justify the remarkable changes of the material properties, including the enhancement of the mechanical behavior (Hasan et al., 1993; Voyiadjis and Samadi-Dooki, 2016). In the literature, there exists a large number of studies on the variation of free volume with annealing time and temperature and also its contribution to the relaxation processes, as well as the alteration of the macroscopic mechanical, thermal, or dielectric properties of amorphous polymers (Cangialosi et al., 2003; Hasan et al., 1993; Hill et al., 1990; Sandreczki et al., 1996). In particular, considerable interests have been attracted to the variation of the deformation response of materials, including their elastic and plastic responses under loading, with annealing and free volume
changes. For instance, remarkable increment of the elastic modulus and yield stress have been found for the polymeric samples which were annealed at certain temperatures or for a longer duration (Boersma et al., 2004; Martinez-Vega et al., 2002; Soloukhin et al., 2003).

Since exploring the large deformation mechanism in glassy polymers, which includes the primary strain softening and secondary hardening regions, have become an attractive topic for material scientists (Nasraoui et al., 2012), the effect of the thermal treatment on the macroscopic plastic response of these materials, including their yield and post yield behaviors, has been investigated in a number of studies. In particular, finding the relationship between the mechanical behavior at large deformation and the structural state of the material through experimental works and atomistic simulations have offered insights into the main features of the material state which are responsible for the observed intense effect of annealing (Argon, 2013; Hasan and Boyce, 1995; Voyiadjis and Samadi-Dooki, 2016). Based on these finding, the redistribution of free volume size and intensity at large deformation might partly affect the response of the material (Hasan et al., 1993).

The localized nature of flow process in glassy polymers might require the local distribution of free volume to play a role in thermo-mechanically activated processes of shear transformation events as the plasticity carriers in amorphous materials (Argon, 2013). In this way, since it has been proposed that the free volume content in glassy solids plays an important role as fertile site for the nucleation of localized discrete relaxation events (Deng et al., 1989; Spaepen, 1977), the free volume changes upon thermal pre-treatment can induce a remarkable effect on the characteristic microstructural and micromechanical parameters of these sites, e.g., shear activation volume and STZ’s nucleation energy, respectively (Brady and Yeh, 1971). In particular, as shown in chapter 2, studies on the yield behavior of glassy polymers with different thermal histories have
shown that for annealed samples, both the shear activation volume and STZ nucleation energy are larger in comparison with the quenched or as-cast ones. These observations at microstructure scale might be used to justify the remarkable alterations of plasticity behavior at macro-scale, as what was expressed in Voyiadjis and Samadi-Dooki (2016).

Though the effect of physical aging, in general, and annealing, in particular, on free volume and macroscopic mechanical properties have been broadly studied and discussed in the previous investigations, a proper inter-connection between micro- and macro-scale evolutions upon thermal treatment of the amorphous polymers is seldom presented. This chapter is aimed at scrutinizing the effect of annealing temperature on the microstructure of glassy polymers as well as their macroscopic mechanical properties. Accordingly, PMMA and PC are annealed at a range of temperatures from below to above their respective glassy temperatures. Their free volume contents are then measured using positron annihilation lifetime spectroscopy; and the macroscopic mechanical properties, namely the hardness and Young’s modulus, are obtained by utilizing nanoindentation technique at a range of strain rates. By employing the homogeneous deformation theorem for STZ mediated plasticity, the microgeometrical and micromechanical properties of the localized deformation units are also extracted from the nanoindentation results as described in detail in chapter 2. The effect of annealing temperature on free volume, yield stress, Young’s modulus, and shear activation volume are then presented and the interrelation between these parameters and their evolutions are discussed.

3.2. Thermal Treatment

The amorphous polymers used in this chapter are 3.2 and 3.0 mm thick sheets of PMMA and PC, respectively. Using DSC, the glass transition temperature is obtained to be about 107 °C for PMMA and 146 °C for PC samples. To study the effect of thermal treatment on micro- and
macro-mechanical characteristics of these glassy polymers, they have been annealed at a range of temperatures from below to just above their respective glassy temperatures. While annealing at sub-glass-transition-temperature is considered as a physical aging process, the implication of the super-glass-transition-temperature annealing is not straightforward, and depending on the cooling rate, it might function as a rejuvenation process which is in contrast to the aging; this will be further discussed later in this chapter. Since the nanoindentation testing method generally presents the mechanical response of the material at its surface, it is important to ensure that the surface properties of the material (with applying appropriate conversions) are representative of the bulk properties. Accordingly, to avoid the surface oxidation of the polymers at elevated temperatures, the annealing process is performed in a vacuum oven. The samples are first heated from the room temperature to the target annealing temperature \( (T_a) \) with the rate of 20 °C/hr; they are then maintained at \( T_a \) for 4 hours, and finally, cooled down to the room temperature with the rate of 10 °C/hr. The slow cooling rate ensures the homogenous relaxation of the samples such that the surface mechanical properties can be assumed to be a representative for the bulk of the material. The annealing temperatures for the PMMA samples are 80, 90, 100, 110, 120, and 130 °C and those for the PC samples are 110, 120, 130, 140, and 150 °C. It should be mentioned that the maximum annealing temperature of 150 °C for PC samples is selected due to the onset of flow behavior of this material at temperatures slightly above its \( T_g \). This phenomenon can cause local and superficial phase transition which changes the surface texture and roughness of the sample dramatically. Since the sample surface roughness significantly affects the nanoindentation experiments results (Kim et al., 2007; Nagy et al., 2013), the surface undulations caused by excessive heat on PC can compromise the nanoindentation results. Hence, the super-glass-transition-temperature annealing of PC is limited to the temperature just above its \( T_g \).
3.3. Positron Annihilation Lifetime Spectroscopy

Positron annihilation lifetime spectroscopy, as a unique and powerful method, is used to characterize the free volume properties, including the average hole size and concentration, as microstructural state variables of the glassy polymer (Dlubek et al., 2002; Dlubek et al., 2003; Wang et al., 1990). In this technique, the anti-particle of electrons, the positron, is employed as a nuclear probe. The positron source used in this study is $^{22}\text{Na}$ which emits positrons through a nuclear decay to $^{22}\text{Ne}$ (Jean, 1990). This decay is accompanied by the emission of a $\gamma$-ray of energy 1.28 $\text{MeV}$ which is used as a starting signal for the birth of positron in the lifetime measurements. Upon injection of the high-energy positrons (with an energy of the order of hundreds $\text{keV}$) into the sample, they slow down within a few $\text{ps}$ and then annihilate with electrons into $\gamma$ quanta. The detection of positron-electron annihilation relies on the emission of $\gamma$ at energy of 0.511 $\text{MeV}$.

Prior to annihilation, a fraction of the positrons can form positronium (Ps), the light electron-positron hydrogen-like exotic atom. Therefore, a positron might have the following possible states at the time of annihilation: free positron state, and free Ps state. Since the free volume holes are more favorable trapping sites than the bulk for positron and Ps, the delayed annihilation signals are found to be mainly associated with the positron and Ps annihilation in free volume holes. The Ps possesses one of the two states regarding its spin: an anti-parallel spin state called para-positronium (p-Ps), and a parallel spin state called ortho-positronium (o-Ps). In positron annihilation lifetime spectroscopy of condensed matters, the o-Ps lifetime and its intensity depend on the free volume hole size and concentration, respectively (Jean et al., 2013). The characteristic positron lifetime spectrum from a polymer is usually analyzed by its three components. The longest lifetime ($\tau_3$) is due to the o-Ps annihilation which is most sensitive to the thermal state of the sample. The shorter lifetime components ($\tau_1$ and $\tau_2$) correspond to p-Ps and
other positron annihilation, respectively, and depend less on the structural state of the polymer (Sandreczki et al., 1996).

In this research, the lifetime spectroscopy is performed on an Ortec® system and analyzed using the PALSfit software. For each annealing temperature, the measurements are acquired from tests on two identical samples to obtain the best $\chi^2 (<1.1)$ and reasonable standard deviations. Describing the o-Ps lifetime rate ($\lambda_3$), the mean free volume hole radius, $R$, can be obtained by the following semi-empirical relation (Jean, 1990)

$$\lambda_3 = \frac{1}{\tau_3} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]$$

(3.1)

where $\tau_3$ and $R$ are expressed in ns and Å, respectively. In Eq. (3.1), $R_0 = R + \Delta R$ where $\Delta R$ is a fitted empirical electron layer thickness (= 1.656 Å for polymers). The fractional free volume $f$ (%) is described as

$$f = V_f (A I_3 + B)$$

(3.2)

in which $V_f = \frac{4}{3} \pi R^3$ (in Å³) is the volume of free volume hole calculated using the spherical radius ($R$) of Eq. (3.1), $I_3$ (in %) is the o-Ps intensity associated with $\tau_3$, and $A$ and $B$ are constants empirically determined to be about 0.018 and 0.39, respectively (Wang et al., 1990).

### 3.4. Free Volume Content

Figure 3.1 demonstrates the variation of the positrons lifetime ($\tau_3$) and intensity ($I_3$), which are respectively correlated with the average size and concentration of free volume holes in condensed matter, for PMMA and PC annealed at a range of temperatures. While the free volume concentration seems to be almost independent of the annealing temperature, its average size shows different directions of variations for sub- and super-glass-transition-temperature annealing.
Figure 3.1. Variation of the positrons lifetime ($\tau_3$) and intensity ($I_3$) with annealing temperature for (a) PMMA, and (b) PC.

For both PMMA and PC, the Ps particles lifetime, or equivalently the free volume hole average size, decreases with the increment of annealing temperature up to the temperatures close to $T_g$, and then slightly increases for the annealing temperatures of beyond $T_g$ for both PMMA and
PC. Nevertheless, the observed increment after $T_g$ is more intense for PC compared to PMMA. This observation suggests that the mechanism of free volume evolution for annealing of polymers at temperatures above their glass transition temperatures is different from that for samples annealed at below glass transition temperatures which is further explored in the Analysis and Discussion section. It should be mentioned that since a different evolution of the free volume has been observed for above-$T_g$ annealing, all the processes from annealing to the mechanical properties measurements have been repeated which resulted to the same findings.

3.5. Macroscopic Mechanical Properties

The macroscopic mechanical properties, namely, Young’s modulus and hardness, are evaluated using instrumented indentation. The average results for deep part of the indentation ($5<h<10$ $\mu m$), which satisfactorily represent the macroscopic behavior of the material, are extracted from each test. Figure 3.2 shows the hardness values of PMMA and PC, annealed at different temperatures, within a range of indentation strain rates of $0.0005$ to $0.1$ $s^{-1}$. While the variation of $H$ with the logarithm of the indentation strain rate for PC is acceptably linear in the rage of tested rates, that for PMMA is divided into two linear sub-regions. The double linear behavior of PMMA might be attributed to activation of the so-called $\beta$-transition mechanism based on the work by Mulliken and Boyce (Mulliken and Boyce, 2006). The onset of this transition is at the strain rate of order $10^{-2}$ $s^{-1}$ for PMMA and $10^{2}$ $s^{-1}$ for PC at room temperature (Malekmotiei et al., 2015). Apparently, the $\beta$-transition activation rate is beyond the tested rates for PC, however, that for PMMA is well distinguished in the experiments and revealed to be almost independent of the thermal history of the sample.

In Figure 3.3, the Young’s modulus values vs the indentation strain rate for PMMA and PC with different annealing histories are represented. The recorded elasticity modulus values do
not show significant variation with the strain rate, as expected due to the fact that the elastic modulus of glassy polymers is controlled by the intermolecular van der Waals interactions which are rate independent (Argon, 2013; Perez, 1998). Therefore, the average value over the tested strain rates might be presented as the Young’s modulus, $E$, for each annealing temperature as shown in Figure 3.4. It first increases with increasing the annealing temperature and then in the glass transition temperature region decreases; this trend of anomalies occurs at temperatures well below the glassy temperature of PC, while that for the PMMA is just below its $T_g$. Since the operative $T_g$ for an annealing time of about 4 hours should be substantially lower than the initially recorded values for the as-cast samples, the onset of softening behavior for PC at the temperature of about 130 °C makes sense. However, the behavior of PMMA, apparently, does not follow this hypothetical rule. For super-glass-transition-temperature annealing, the Young’s modulus retrieves its increasing trend.
Figure 3.2. Variation of the macroscopic hardness with indentation strain rate for (a) PMMA and (b) PC samples annealed at different temperatures. Error bars are not shown to avoid data point interference, but the maximum standard deviation for each data point is less than 2.25% and 2.32% for PMMA and PC, respectively.
Figure 3.3. Variation of the Young’s modulus with indentation strain rate for (a) PMMA and (b) PC samples annealed at different temperatures. Error bars are not shown to avoid data point interference, but the maximum standard deviation for each data point is less than 1.58% and 1.28% for PMMA and PC, respectively.
Figure 3.4. Variation of the average Young’s modulus with annealing temperature for (a) PMMA and (b) PC.
3.6. Analysis and Discussion

The parameter which indicates a size scale of the localized plasticity events is the shear activation volume $V^*$ and as presented in Eq. (2.13), can be obtained from the slope of the shear yield stress vs logarithm of the shear strain rate curves. Such curves can be readily obtained from hardness vs indentation strain rate values presented in Figure 3.2 through utilizing Eqs. (2.9) and (2.15). Figure 3.5 demonstrates these curves for PMMA and PC with appropriate logarithmic fits. The values for PMMA are only shown and interpolated for pre-$\beta$-transition rate, which has relevant implications for finding the activation volume. Substituting the results obtained in Figure 3.5 into Eq. (2.13), the variation of the shear activation volume of PMMA and PC vs the annealing temperature can be obtained, as shown in Figure 3.6. Increasing the annealing temperature seems to primarily increase the shear activation volume, and a maximum value is reached at temperatures around the glass transition temperature for both materials. From the overall observation point of view, the increment of the shear activation volume upon annealing observed in this study is in agreement with findings in chapter 2 and other studies on amorphous polymers (Brady and Yeh, 1971) and metals (Choi et al., 2012). In particular, however, the current study shows that while annealing temperature has a considerable impact on the shear activation volume, the maximum shear activation volume is reached around $T_g$, and beyond that no additional variation is taking place (even a slight reduction for PMMA is beheld).
Figure 3.5. Variation of the shear flow stress with shear strain rate for (a) PMMA and (b) PC samples annealed at different temperatures. $R^2$ values are >0.99 for all curve fittings.
Figure 3.6. Variation of the shear activation volume and free volume content with annealing temperature for (a) PMMA and (b) PC.
In Figure 3.6 it is also shown the variation of the free volume content, which is calculated using the results presented in Figure 3.1 and utilizing Eqs. (3.1) and (3.2), with the annealing temperature. Having Eq. (3.2) in mind and noticing that the free volume concentration \( I_3 \) remains almost unvaried after thermal treatment, the variation of the free volume content, expectedly, follows the pattern of that for the average hole size (associated with \( \tau_3 \)). The free volume content decreases for both PMMA and PC for sub-glass-transition-temperature annealing, and reaches its minimum value at the glass transition region where the glassy state approaches an equilibrium. Interestingly, the free volume content slightly increases due to annealing at temperatures beyond \( T_g \). Apparently at temperatures below \( T_g \), the heat treatment acts as an aging process, and it induces a relaxation through ordering mechanism which is followed by reduction of the free volume content (Struik, 1977). The observed increment of free volume fraction might be the result of the fact that at high temperatures the chains start to freely rotate, and the resulting disordered phenomenon overcomes the ordering process (Golden et al., 1967); Hence, the free volume content increases; this increment is more noticeable for PC. Although glass transition is not a first order phase transition, at temperatures beyond this critical point, the increased thermally activated rotations of the chains cause a rapid increment of the specific volume which is equivalent to the rise of the free volume content; this might be referred to as the so-called rejuvenation process. While PC starts to transform into a material with fluid-like flow behavior when heated slightly above its glass transition, its rejuvenation is more pronounced compared to PMMA which maintains its solid and glassy state at temperatures well above its \( T_g \) and less than its flow point (160 °C). It is worth noting that the variation of the free volume content for super-glass-transition-temperature annealing might also depends on other parameters. For example, the rate of cooling the samples from annealing temperature to the room temperature has considerable effect on the
amount and structure of the free volume remained in the sample. The cooling rate is 10 °C/hr in this study; if the annealed samples are cooled down with much lower rate, it is possible that no considerable change of free volume fraction to be observed for annealing temperatures beyond $T_g$ and, therefore, it remains at the level of equilibrium state. The increase of free volume content might also occur due to chemical side reactions which possibly proceed in the polymers at high temperature treatment. If that is the reason, it should be investigated that the chemical reactions do not change the polymer’s structure during treatment. In fact, a number of competitive physicochemical phenomena take place during annealing of polymers having an inhomogeneous free volume distribution, and therefore presumably different predominance of these events leads to changes in the free volume content upon annealing (Soloukhin et al., 2003). However, studying the other possible factors is not within the scope of this research.

As it is demonstrated in Figure 3.6, the variation of the free volume content and shear activation volume with annealing temperature are in opposite directions. Since the shear transformations are thought to form around the free volume cavities, the dissimilar variations of these two parameters versus a third variable (annealing temperature in here), at the first glance, might seem an inconsistent observation. However, a precise investigation justifies this observation: the average size of the free volume holes is about an order of magnitude smaller than that of the shear activation volume (a couple of hundred cubic angstroms compared to a couple of cubic nanometer, respectively (Argon, 2013; Sandreczki et al., 1996)). Hence, the free volume holes serve only as active sites for shear transformations rather than accommodating them. Therefore, the bigger free volume cavities can cause more localized shear events with smaller sizes. On the other hand, when the free volume holes are smaller, or when there is a more uniform structure, the localization effect is less dominant; so, a broader region of material is engaged in adjusting the
applied stress and the extent to which strains are accommodated increases. Although this behavior has been observed in other studies on glassy solids (Brady and Yeh, 1971; Choi et al., 2012), this hypothesis requires further investigation via direct visualization of the STZs, a task which has not been practiced yet due to the transitional nature of the STZs rather than being actual defects (Kanungo et al., 2004).

From the nanoindentation results, it is also possible to demonstrate the variation of the shear yield stress with annealing temperature for each tested strain rate, as shown in Figure 3.7. For both PMMA and PC, the trend of variation is independent of the rate, and the increase of the applied strain rate only causes a jump in the yield stress. This trend of variation observed in the experiments is well predicted in Eqs. (2.10) and (2.12) in which the shear stress varies only with the logarithm of the shear strain rate, while the STZ activation free energy remains constant with the rate as a requirement for consistency of the model with the principles of continuum mechanics and thermodynamics. In addition, for both PMMA and PC, and at different strain rates, the variation of shear yield stress with the annealing temperature almost follows the same fashion as that of the Young’s modulus, as presented in Figure 3.4. Both elastic modulus and yield stress initially increase with the increment of the annealing temperature, and then undergo a reduction for annealing at temperatures around $T_g$ (which is more considerable for PC). The reduction in yield stress upon annealing in the $T_g$ region (rejuvenation) is a known effect related to the material reaching the equilibrium at such high annealing temperatures (Golden et al., 1967; Wang et al., 2013). During the super-glass-transition-temperature annealing, the increasing trend of the yield stress is retrieved. The stepwise increase in the elastic modulus and hardness was also observed by Soloukhin et al. (2003) for PC as a function of aging time and linked to the densification of the material due to the changes in orientations of the polymeric chains. Soloukhin et al. have
performed many analyses to provide evidence of conformational interchange and alterations in molecular weight distribution during annealing which lead to changes in free volume of the polymer. The variations found, however, could not elucidate the reason why the stepwise changes in mechanical properties occurred at different annealing times. Therefore, in the case of the present study in which the trend of variations of the free volume fraction with annealing temperature is different in sub- and above-$T_g$ regions, finding a reasonable relationship between the observed changes in mechanical properties and microstructural state variable, i.e., free volume content, alterations with thermal treatment temperature is even more complicated.

It has been previously hypothesized that the activation energy of shear events in glassy solids is significantly affected by the free volume content (Argon, 2013; Bauwens-Crowet and Bauwens, 1982; Voyiadjis and Samadi-Dooki, 2016). These hypotheses consider the effect of post-yield adjustment of the free volume (Hasan et al., 1993), and result in with acceptable interpretation of the experimental observations through thermodynamically consistent models. Nevertheless, they assume that other parameters which contribute to the activation energy, e.g., shear modulus, remain unvaried. This assumption is valid during the plastic deformation at a constant temperature. In this study, however, it is observed that the thermal history of the polymeric sample not only determines the free volume content of the sample, it also controls its elastic modulus, and the effect of the alteration of the latter is more pronounced on the yield behavior of the sample. This observation also confirms the validity of the assumption of the Eshelby’s inclusion problem (Li et al., 2013; Mura, 1982), whose energy is directly proportional to the elastic constants of the isotropic solid, for STZ mediated plasticity of amorphous solids.
Figure 3.7. Variation of the shear flow stress with annealing temperature for (a) PMMA and (b) PC samples at different strain rates.
3.7. Conclusion

Synthesized polymers are becoming ubiquitous structural materials which are used as substitutes for traditional metallic elements. Although the superior properties of thermoplastics such as low density, high formability, etc., are promising, their use is limited by the fact that the strength and ductility of this type of materials are lower than conventional metals. Several upgrading methods are available to overcome these drawbacks and let polymers be used in the structures where severe loading condition is expected. Reinforcing of polymers with stronger materials, such as carbon fibers, is an efficient method, and the resulting composite is qualified to even be used as parts of space-structures or in automotive industries. This process, however, is expensive, and is not considered as an in-house strengthening method. A simple process of altering the mechanical properties of amorphous polymers is the heat treatment. Since the commercially casted polymers are usually supercooled from fluid-like to solid state, they possess huge amounts of frozen-in free volume content. While the content of free volume considerably affects the mechanical response of the polymer, it can be adjusted by the thermal process.

In this chapter, the effect of annealing process on the free volume content of glassy polymers is investigated. PMMA and PC, as two widely used amorphous polymers which their thermomechanical properties in blends, composites or as individual materials are the topic of many recent studies (Gunlock and Basaran, 2011; Gunel and Basaran, 2013; Nie and Basaran, 2005; Zhao and Schiraldi, 2005), are critically investigated with versatile positron lifetime spectroscopy. In addition, the characteristics of their flow unites have also been scrutinized through utilizing the homogenous shear transformation mediated plasticity theory which has been proven to be the most physically based model that can justify the thermomechanical experimental observations. Accordingly, the changes of the micromechanical characteristics of the plastic flow units of
amorphous polymers with annealing are also studied, and the correlation between the micro- and macro-scale mechanical properties is discussed. It is observed that, while sub-glass-transition-temperature annealing induces a reduction of free volume content, it generally enhances the macroscopic mechanical properties. For annealing in the $T_g$ region, the free volume content maintains its decreasing trend; but the macroscopic mechanical properties, namely the yield stress and Young’s modulus, remain unvaried or even reduce. The super-glass-transition-temperature annealing induces a rapid increase of Young’s modulus, yield stress, and free volume. These observations imply that, annealing at temperatures close to $T_g$ is, in general, not beneficial for strengthening the polymer. In addition, although super-glass-transition-temperature annealing considerably enhances the macromechanical properties, the increased free volume content at these temperatures can increase the brittleness of these materials. Hence, annealing of polymeric glass at temperatures well below their $T_g$ could be the most efficient strengthening process via thermal treatment. In this way, the time of annealing would be an important role-playing parameter that can affect the final result.
CHAPTER 4
NANOINDENTATION OF SEMICRYSTALLINE POLYMERS*

4.1. Introduction

During recent decades, use of polymers as a replacement for conventional materials like metals and ceramics has been rapidly growing. However, the fact that most polymers exhibit low thermal resistance and mechanical strength limits their application in mechanical parts at severe loading conditions. A class of thermoplastics that meets the expectations for such intense conditions are generally termed as high performance polymers. These thermoplastics may exist in amorphous or semicrystalline states, nevertheless, semicrystalline HPPs exhibit more desirable thermomechanical characteristics since they can remain functional even at temperatures well beyond their glass transition (Hiemenz and Lodge, 2007; Mittal, 2011).

Poly(ether-ether-ketone) is a semicrystalline HPP with excellent thermal, mechanical, chemical and radiation resistance which make it a desirable solid in medical implant, automotive, aerospace and chemical process industries (Cogswell, 2013). In addition, it has been broadly used as the polymer matrix in high performance and hybrid composites (Díez-Pascual et al., 2010; LiuJie et al., 2007; Molazemhosseini et al., 2013; Nisa et al., 2008). For mechanical characterization of PEEK and its nanocomposites, the nanoindentation technique has been extensively used recently (Díez-Pascual et al., 2015; Godara et al., 2007; Iqbal et al., 2011; Iqbal et al., 2013; Powles et al., 2007). Nevertheless, the semicrystalline and tough nature of this polymer necessitates considering the factors that compromise the validity of the generalization of the mechanical properties obtained from depth sensing indentation to the bulk of the material.

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This chapter is aimed at critically exploring the effect of PEEK surface and thermal history properties on its nanoindentation characterization. As such, as-received, mechanically polished, and thermally annealed samples are tested in a set of systematic CSM nanoindentation at different rates. It is shown how surface roughness and microstructural heterogeneity due to nonproportional cooling during casting can affect the nanoindentation hardness and modulus measurements. The rate dependence of PEEK mechanical behavior is also demonstrated, and capability of nanoindentation as a tool for measuring the crystallinity of PEEK reported in the literature (Iqbal et al., 2013) is examined and critically discussed.

4.2. Material

Semicrystalline PEEK 6.5 mm thick sheets were purchased from a commercial supplier (Goodfellow, PA, USA; catalogue number EK303460). PEEK Sheets were received in 150x150 mm² plates, and were cut into 20x20 mm² squares that could be conveniently mounted on the indentation sample stage. For evaluating the degree of crystallinity and glassy temperature of PEEK specimens examined in this research, DSC is utilized. Test cycles are performed from room temperature up to 400 °C under nitrogen flow. In addition, in order to alter the thermal history of the specimens, annealing at different temperatures is implemented on a fraction of samples. All such heat treatments are conducted in a vacuum oven to avoid possible PEEK surface oxidation at high temperatures. Moreover, to reveal the surface features of PEEK samples, an AFM and a Quanta™ 3D DualBeam™ high resolution Field Emission Gun Scanning Electron Microscope (FEG-SEM) are used.

4.3. Nanoindentation of As-Received PEEK

Depth sensing indentation offers a fast, repeatable and nondestructive technique for evaluating the mechanical properties of solid state materials while requiring minimal sample size
and preparation. Although it was originally used for mechanical characterization of metallic materials, its use for characterization of polymers has recently increased rapidly (Chandrashekar and Han, 2016; Shen et al., 2006; Yang, 2016). To be a representative of the bulk mechanical behavior of the material, the homogeneity of the microstructure from surface to inner layers of the solid is a requirement in nanoindentation characterization of materials. This criterion is usually satisfied for nanoindentation of fully crystalline or amorphous solids (Chen et al., 2017; Fujisawa et al., 2017; Humood et al., 2017), however, semicrystalline solids are essentially inhomogeneous and their local mechanical properties might not represent the overall material behavior. In the following sections, it is demonstrated how the nanostructural inhomogeneity of semicrystalline solids can affect the generalization of the nanoindentation results by revealing irregular patterns in nanoindentation of as-received semicrystalline PEEK; and convenient procedures which can suppress the effect of such inhomogeneities are presented and discussed. To this end, at least 10 indentations to a depth of 1000 nm are performed for obtaining each data set. To avoid the interaction of the plastic regions around the impressions, a spacing of 50 μm was set between the adjacent indents.

As-received PEEK samples without any modification are tested at the indentation strain rate of 0.01 s⁻¹ using the CSM mode, and the hardness and modulus are obtained, as depicted in Figure 4.1. There are two distinguishable features in this figure that significantly differ from common nanoindentation of polymers (Briscoe et al., 1998). The first major discrepancy is the softening-hardening variation trend of both hardness and modulus with increasing indentation depth. The hardness variation of most solids in nanoindentation experiments exhibits a hardening fashion with decreasing the indentation depth; a phenomenon which is known as the indentation size effect. In fact, the hardness decreases monotonically with increasing indentation depth and
approaches the macro-scale hardness at deep enough penetrations. Such a trend of variation might also be observed for the modulus during nanoindentation, however, it is of less physical significance compared to the ISE of hardness. Nevertheless, the hardness (and modulus) variation of as-received PEEK with depth demonstrates an initial softening followed by a considerable hardening with depth increment. While the initial softening can still be attributed to the ISE phenomenon, the secondary hardening deviates from the normal material behavior as expected in nanoindentation. While Iqbal et al. (2013) have attributed this abnormal PEEK behavior to the morphological aging and localized oxidation effects, Shen et al. (2004), who observed the same trend in nanoindentation of semicrystalline Nylon 66, have referenced this phenomenon to the variation of crystallinity degree of the polymer with depth. They stated that, during the manufacturing process, molded polymers are usually cooled to room temperature from the liquid (melted) phase, hence, different layers might experience different cooling rates during solidification. The outer layers solidify faster than the inner parts, so the macromolecular chains in the core of the sample have more time to “organize” and “crystallize”. Due to the fact that crystalline polymers usually exhibit higher stiffness and strength compared to their amorphous counterpart, the transition from less crystalline regions in the surface to more crystalline regions in the core of the semicrystalline polymer during nanoindentation might be responsible for the observed secondary hardening (Figure 4.2). To examine this hypothesis, the degree of crystallinity of the tested as-received PEEK is measured using DSC (Naffakh et al., 2006). While the crystallinity degree of PEEK at its surface is measured at about 30.5%, that in the innermost part was about 35.4%. This discrepancy suggests an inhomogeneous microstructural composition that can bring about the anomalies in the mechanical characteristics of PEEK in nanoindentation. To further investigate the effect of microstructural uniformity on the nanoindentation results, a heat
treatment is utilized as a layer wise experimental homogenization technique in this research, as presented in the forthcoming sections.

Figure 4.1. Variation of the hardness and modulus of an as-received PEEK sample. The indentation strain rate is set at 0.01 $s^{-1}$ ($\frac{dp}{Pdt} = 0.02 s^{-1}$).

Figure 4.2. Schematic representation of the penetration of the indenter tip into the semicrystalline polymer with traveling from less crystalline regions in the surface to more crystalline ones in deeper parts.

Another irregular observation in Figure 4.1 is the high standard deviation values associated with both hardness and modulus curves, even at deep indentations. Iqbal et al (2013) also observed the same scattering in nanoindentation of PEEK, and associated it with the so-called “bimodal”
behavior of this semicrystalline material in nanoindentation. Nevertheless, the study by Shen et al. (2005) on semicrystalline Nylon 66 demonstrates that this dispersity could be an artifact of the surface roughness of the polymer, and polishing can remarkably eliminate that. Accordingly, the surface topography of the tested as-received PEEK sample is evaluated using SEM and AFM. Figure 4.3-a illustrates typical SEM surface image of the as-received PEEK. As can be seen in this figure, the specimen surface is not only uneven, but also contains some asperities that can possibly move during loading and negatively affect the recorded data during indentation at nano-scale. In addition, the typical surface topography of the same sample was measured by tapping mode AFM, as shown in Figure 4.3-b. The average surface roughness based on the AFM measurement is about 13.4±1.06 nm with a maximum hill-to-valley height difference of about 230 nm. Such values of surface roughness can significantly affect the results of nanoindentation experiments, hence, a polishing scheme was used for smoothing the surface of PEEK samples, as presented and discussed in the next section.

Figure 4.3. Typical (a) SEM and (b) AFM measurements of surface topography of an as-received PEEK sample. For SEM imaging, the surface of the sample is sputter coated with an ultra-thin layer (<10 nm thick) of gold to prevent charging of the specimen.
4.4. Effect of Polishing

The as-received semicrystalline PEEK samples are polished using silicon carbide grinding papers up to 1200/P4000 grit size (median particle diameter of 2.5 μm), followed by polycrystalline diamond in high viscosity liquid suspension with particle size down to 1 μm. Their surface topography is then examined by SEM and AFM. As the SEM result of Figure 4.4-a demonstrates, polishing significantly smoothen the surface of PEEK (compared to Figure 4.3-a) and surface asperities are eliminated after this process. In addition, the AFM surface scanning in Figure 4.4-b further proves the surface uniformity after polishing; the maximum hill-to-valley height difference and average roughness were reduced to 5.0 and 0.92±0.10 nm, respectively.

![SEM and AFM measurements of surface topography of mechanically polished PEEK samples.](image)

The CSM hardness and modulus measurements of polished samples are depicted in Figure 4.5-a and b, respectively, and compared with the results from indentation of as-received samples. Interestingly, the standard deviation of both hardness and modulus curves (as shown with half-length error bars in Figure 4.5) decreases with polishing. In addition, the softening-hardening behavior of hardness is lowered by polishing, and that for the modulus curve has almost eliminated.
Since a layer of material is indeed removed from the surface of the sample by polishing, more crystalline polymeric chains in the inner layers are being exposed to this process, hence, the transition from less crystalline to more crystalline regions during nanoindentation is abated. Polishing itself can leave some residual stress or strain on the sample surface that can affect the indentation results. Nevertheless, the fact that the recorded modulus does not show a significant alteration after stabilizing at very shallow depths suggests a minimal effect of residual fields.

![Graph](image)

**Figure 4.5.** Variation of (a) hardness and (b) modulus of a polished and unpolished PEEK sample with indentation depth. The indentation strain rate is set at 0.01 s$^{-1}$ ($\frac{dP}{Pdt} = 0.02$ s$^{-1}$).
4.5. Effect of Annealing

To further investigate the effect of microstructural inhomogeneity on the nanoindentation of PEEK, an annealing process is performed on this semicrystalline polymer to promote the homogeneity of the samples. Using a vacuum oven, well-polished PEEK samples are heated at a rate of 20 °C/hr to different super-glass-transition annealing temperatures at which they are kept for 4 hrs. They are then cooled down to room temperature at a rate of 10 °C/hr. The glassy and crystalline melting temperatures of the tested PEEK samples are determined to be about 145 and 340 °C, respectively, using the DSC device, hence, annealing temperatures of 150, 200, and 250 °C are selected for heat treatment process.

Figure 4.6 depicts the hardness variation of polished PEEK samples with different thermal histories at indentation strain rate of 0.04 s⁻¹. There are a number of interesting features of PEEK hardness alteration with annealing that could be noted in this figure. Firstly, the heat treatment process seems to increase the macroscopic hardness (the plateau value of each curve) of PEEK up to the annealing temperature of 200 °C, beyond which no further strengthening is observed. The increment of the macroscopic hardness with annealing seems to be a result of crystallization in the samples which is facilitated at higher temperatures. In addition, even the amorphous regions can undergo a degree of reordering during annealing with a reduction in the free volume content (Hasan et al., 1993; Voyiadjis and Samadi-Dooki, 2016). However, annealing beyond a certain temperature (200 °C here) does not induce further macroscopic strengthening of PEEK, which implies that no additional macromolecular ordering takes place at these temperatures. This observation is consistent with the fact that the maximum achievable degree of crystallinity is less than 50% for PEEK (Iqbal et al., 2013).
Figure 4.6. Effect of annealing on hardness of PEEK measured via CSM nanoindentation. The indentation strain rate is set at 0.04 s\(^{-1}\) \(\frac{dp}{Pdt} = 0.08 s^{-1}\).

The second notable feature of Figure 4.6 is the elimination of the softening-hardening behavior with annealing of the PEEK samples. While the hardness of polished as-received PEEK undergoes a softening-hardening trend with increasing the indentation depth, it consistently reduces for annealed samples as the indentation depth increases. The latter behavior is closer to the characteristic response of homogeneous solids during nanoindentation experiments which show an apparent ISE. However, the observed ISE behavior also varies significantly with annealing temperature, exhibiting a more intense size effect for higher annealing temperatures, which is another important highlight of Figure 4.6. To justify this observation, two different scenarios might be considered as explained here. One might firstly contemplate the effect of vacuum environment during annealing on the microstructural organization in amorphous sub-regions. As such, as the temperature is elevated well beyond the glass transition, the polymer can “soften” at the surface, especially in amorphous sub-regions. Alongside the continuously applied vacuum environment, this localized “thermal softening” can further reduce the free volume in amorphous regions. As the free volume acts as a “defect” in amorphous materials which can
facilitate plastic deformation, its reduction at higher annealing temperatures (assisted by vacuum action) can induce the observed ISE variation trend in Figure 4.6. This hypothesis, however, cannot be proved easily at this stage since it requires the measurement of the free volume content within the “skin” of the samples. Current free volume measurement techniques such as PALS are only capable of indicating an average free volume size and distribution within the bulk of the material.

Another possible factor which may be responsible for the observed ISE variation trend is the surface roughness. In general, the annealing process increases the surface roughness of polymers as observed in chapter 2. In addition, samples with higher surface roughness have been shown to exhibit a more severe ISE (Liu and Ngan, 2001). Hence, the more significant ISE for samples annealed at higher temperatures can reasonably be (partly) attributed to their higher surface roughness. To scrutinize this hypothesis, the surface roughness of polished PEEK samples annealed at different temperatures is measured using AFM. Recalling that the surface roughness of the polished (not annealed) sample is $0.92 \pm 0.10 \text{ nm}$, it increased to $1.31 \pm 0.17$, $1.58 \pm 0.24$, and $1.66 \pm 0.19 \text{ mm}$ for samples annealed at 150, 200, and 250 °C, respectively. Hence, the more pronounced indentation size effect for samples annealed at higher temperatures is consistent with the trend of increase in surface roughness of these samples.

There might be some other factors that can also partially contribute to the ISE variation in Figure 4.6. For example, possible polymorphism of PEEK at higher annealing temperatures (Chen and Woo, 1995), which can alter the mechanical properties of the crystalline sub-regions. However, since the macroscopic hardness does not vary with annealing beyond 200 °C, the possible polymorphism is concluded to be unlikely to play a role in ISE alteration.
4.6. Effect of Strain Rate

Polymers are generally considered as viscoelastic-viscoplastic materials since their mechanical response to external loading is noticeably rate dependent. Studying the rate dependence of yielding behavior of polymers is not only of essential importance in improving structural design criteria, but also gives some information about microstructural deformation that mediates plasticity in these solids. The hardness of a material is known to be proportional to its yielding stress. Hence, obtaining the variation of the hardness with the indentation strain rate during nanoindentation can reveal the rate dependency of the material resistance to failure and flow. Figure 4.7 shows the variation of the hardness with indentation depth at 3 different indentation strain rates for a well-polished PEEK sample annealed at 200 °C. The hardness curves at each rate exhibit a noticeable ISE and stabilize at indentation depth beyond 700 nm. As the inset in this figure shows, the macroscopic hardness (plateau of each curve) of PEEK reveals a considerable rate dependence, exhibiting higher hardness at higher rates.

Figure 4.7. Effect of indentation strain rate on the hardness of annealed PEEK in CSM nanoindentation. Curves are associated with indentation strain rates of 0.01, 0.025, and 0.04 s⁻¹ (\(\frac{dP}{dt} = 0.02, 0.05, \text{and } 0.08 \text{ s}^{-1}\), respectively).
In studying the plastic deformation of solids, shear activation volume is an important parameter from thermodynamics point of view. As mentioned in chapter 2, the shear activation volume $V^*$, which is a size scale for localized plastic deformation units (Argon, 2013), is proportional to the slope of the shear yield stress $\tau$ vs shear strain rate $\dot{\gamma}$ as

$$V^* = 2k_B T (1 - \alpha \beta) \left( \frac{\partial \tau}{\partial \ln(\dot{\gamma})} \right)^{-1} \quad (4.1)$$

The shear yield stress vs shear strain rate can be obtained, as presented in Figure 4.8. The shear yield stress in this figure is obtained from the average hardness in deep indentation (700-1000 nm). In addition, by using Eq. (4.1), the shear activation volume for PEEK is obtained to be about $3.44 \text{ nm}^3$ at room temperature.

![Figure 4.8](image.png)

Figure 4.8. Variation of the shear yielding stress of PEEK with the shear strain rate. The solid line represents the logarithmic interpolation with the equation and $R^2$ value as shown in the figure.

### 4.7. Bimodal Behavior of PEEK in Nanoindentation?

There exist a number of different methods for calculating the crystallinity degree of semicrystalline polymers such as diffractometry analysis via X-ray diffraction (XRD) or calorimetric analysis using DSC. Recently, Iqbal et al. (2013) have suggested that the hardness
response of semicrystalline PEEK can be used for detecting the distribution of the crystalline and amorphous regions within the material surface. Their research shows that the PEEK nanoindentation exhibits a bimodal hardness behavior such that the lower hardness values can be assumed to represent penetration of the tip into the soft amorphous regions while higher hardness values are associated with indentation of the stiffer crystalline regions. Accordingly, they have found the crystallinity degree of PEEK from the nanoindentation hardness distribution and compared it with the DSC measurements.

To further examine the appropriateness of nanoindentation technique for indirect measurement of polymers crystallinity degree, 96 indentations to the depth of 1000 nm and at an indentation strain rate of 0.025 s⁻¹ are performed on a polished PEEK sample annealed at 200 °C. The average hardness and modulus for the indentation depth of 700-1000 nm are then calculated for each curve (similar to what is shown in Figure 4.7), and the distribution of these average values for 96 indents are obtained, as shown in Figure 4.9. The distribution of both hardness and modulus are analogous to a normal distribution which implies homogeneous overall behavior of the material at its surface. In addition, the hardness and modulus are distributed in a narrow range with standard deviations of 2.61% and 1.25%, respectively.
Figure 4.9. Distribution of the average macroscopic PEEK (a) hardness and (b) modulus for a sample annealed at 200 °C and tested at the indentation strain rate of 0.025 s⁻¹ \( \left( \frac{dP}{Pdt} = 0.05 \text{ s}^{-1} \right) \).

The frequency of hardness which shows a bimodal distribution in the study by Iqbal et al. (see Figure 11 of (Iqbal et al., 2013)) is based on the hardness values at an indentation depth of 4 \( \mu m \). At this depth the projected area of the Berkovich tip is about 400 \( \mu m^2 \) which corresponds to an equilateral triangle with sides of about 30 \( \mu m \). However, the spherulite size of PEEK is about 10 \( \mu m \) (Wang et al., 1991), hence, indentation of PEEK at a depth of 4 \( \mu m \) with a Berkovich tip should result in a statistically homogeneous response of the material rather than an inhomogeneous
and deterministic one. In addition, the PEEK crystals possess a 3D structure and distribution in surrounding amorphous matrix, hence, a 2D surface analysis is unlikely to be able to reveal their spatial distribution. Moreover, even the indentation analysis performed in the current study, which scrutinizes PEEK mechanical response at shallower depths (700-1000 nm), indicates homogeneous response of the material. While the PEEK samples tested in the current study are provided by the same supplier as those tested in Iqbal and coworkers’ experiments (Iqbal et al., 2013), their observation of the bimodal response could be an artifact resulted by surface roughness of the material (which was reported to be as high as 0.5 μm) as it was mentioned before. It is agreed that the difference in mechanical response of the crystalline and amorphous sub-regions can be used for microstructural characterization of semicrystalline polymers, nevertheless, the indentation size scale should be small enough to demonstrate the heterogeneity of the material rather than its overall response. Such analyses require impression sizes in the scale of tens of nanometers, whereas, the Berkovich probes that are currently used in nanoindentation usually have a blunt, spherical tip with a radius of 20-50 nm, which results in elastic deformation at very shallow depth. In addition, the ISE at very shallow depths would be mixed with the strength analysis which is aimed at microstructural analyses. Accordingly, it is believed that the current nanoindentation testing procedure is not capable of directly determining the microstructural distributions such as crystallinity degree of semicrystalline solids. However, other techniques such as the AFM surface scanning can be used to obtain a rough estimation of the map of the surface mechanical properties at very small scales.

4.8. Concluding Remarks

In this chapter, the mechanical response of the PEEK as a widely used semicrystalline HPP is investigated at the nano-scale using the nanoindentation technique. It is shown that, since the
as-received PEEK possesses a high surface roughness and uneven crystallinity within its thickness, its mechanical response (hardness and modulus) exhibit an abnormal trend of softening-hardening behavior. To eliminate the surface roughness, mechanical polishing is utilized, which shows satisfying surface smoothing results with no considerable residual stress field. Use of mechanical polishing for soft polymers is usually a questionable process due to the fact that the hard polishing micro particles can detach from the polishing paper and get stuck in polymer surface. However, the current research shows that tough polymers such as PEEK undergo an acceptable surface modification using this technique.

The different cooling rate during casting of semicrystalline polymers is likely to induce varying degree of crystallinity from the “skin” to the “core” of the sample. Due to the difference in mechanical strength of crystalline and amorphous structures, the more amorphous polymer at shallow depths exhibits a softer response compared to the more crystalline regions in deeper parts. The annealing process employed for homogenizing the crystallographic properties of PEEK in this research reveals acceptable results in the sense that the nanoindentation response of such thermally treated samples is more similar to other homogeneous crystalline or amorphous materials.

Finally, the capability of nanoindentation for determining the crystallinity degree of semicrystalline polymers is scrutinized in this chapter. The aforementioned difference in mechanical response of crystalline and amorphous regions of a material has been used by some researchers in order to determine the spatial distribution percentage of each of these microstructural formats. Nevertheless, the current study casts doubts on such analyses by revealing a statistically normal distribution of the mechanical properties rather than a deterministic one. This observation is supported by the fact that the impression size in nanoindentation with meaningful results is usually bigger than the spherulites size of PEEK. In addition, limiting the indentation
depth to small values also might not be a reasonable strategy to enhance the resolution of such analyses due to the blunt head of the tip, and also considerable indentation size effect, which can affect the strength response of both amorphous and crystalline regions in an unknown manner. Hence, the use of nanoindentation with the Berkovich tip is not suggested for characterizing the crystallinity degree of polymers at this stage.
CHAPTER 5
STRAIN RATE EFFECT ON INDENTATION SIZE EFFECT*

5.1. Introduction

Although a large series of constitutive models and experimental methods by which the properties of polymers can be thoroughly captured in millimeter or larger size scales has been presented (Anand and Gurtin, 2003; Hasan et al., 1993; Hoy and Robbins, 2006; Mulliken and Boyce, 2006; Van Breemen et al., 2012; Voyiadjis and Samadi-Dooki, 2016), there are still many questions about the behavior and deformation mechanism in sub-micron size scales. To acquire the precise and reliable results for mechanical properties, including elastic modulus and hardness, of very small volumes of materials, instrumented-indentation testing can be employed. In this technique, an indenter induces a localized deformation by applying a specified load on the material surface. As mentioned in chapter 2, basically there are two different indentation methods: (1) basic mode in which, with monotonic loading and unloading, the mechanical properties are only measured at the predefined maximum load from the unloading curve, and (2) CSM mode in which a small oscillation force is superimposed on the primary loading signal, and the resulting response of the system is analyzed through a frequency-specific amplifier. Employing the second procedure, the material mechanical properties can be continuously measured from zero to the maximum indentation depth during the loading segment. In addition, while in the former, the contact stiffness is measured just at the initial point of the unloading, the measurement of the contact stiffness at any point along the loading segment is possible in the latter with a smaller time constant (Hay et al., 2010; Li and Bhushan, 2002; Pethica and Oliver, 1988). Therefore, the small time constant of

the CSM method makes it more useful for measuring the properties of materials especially those which are strongly time dependent. The loading (or strain) rate is controlled in a different way in these two modes; during the basic mode, the load is applied with a constant rate \( \dot{P} \) on the sample surface by the indenter until it reaches a determined maximum value, however, in the CSM mode, the indenter travels up to a predefined maximum depth and the load is controlled so that the loading rate divided by the load \( \dot{P}/P \) remains constant over the course of a single indentation.

The loading and strain rates are adjustable parameters in nanoindentation experiments, and their variations have shown profound effects on the mechanical response of time dependent materials like polymers (KRAFT et al., 2001; Mazeran et al., 2012; Odegard et al., 2005; White et al., 2005; Zhang et al., 2009). That being the case, a closer look at the strain (loading) rate variation during the indentation is required since the generated strain and stress fields in the material due to the loading by a self-similar tip is inhomogeneous. In the basic mode nanoindentation, although the test is conducted with a constant loading rate \( \dot{P} \), the strain rate is considerably decreasing at shallow depths, and it eventually approaches almost stable value after a long distance travel of the tip into the material. For this reason, an average value of the strain rate over the deep part of the indentation can be considered as the representative strain rate of the test (Schuh and Nieh, 2003) On the other hand, in the CSM nanoindentation experiments, the \( \dot{P}/P \) ratio is set as a constant value at the beginning of the test. It has been shown that the indentation strain rate can also be assumed to remain constant during the constant \( \dot{P}/P \) experiment where the material hardness has the steady-state value, i.e., \( \dot{H} = 0 \) (Lucas and Oliver, 1999). However, the ISE has been observed during the nanoindentation experiments on many materials including crystalline and amorphous solids (Briscoe et al., 1998; Voyiadjis and Zhang, 2015). In a study on Al-based foams, it has been observed that the strain rate varies about 3 orders of magnitude during the first 200 nm of the
indentation before reaching a steady-state value (KRAFT et al., 2001). Therefore, in the case of the CSM mode, the indentation strain rate can be considered constant in that part of the test where the ISE is negligible.

Conducting the CSM nanoindentation experiments on PMMA and PC as polymeric glasses, the variation of the strain rate during the course of a single test is investigated as a main goal in this chapter. Examining the variation of the $\dot{P}/P$ ratio during the test shows that although the $\dot{P}/P$ ratio is set to remain invariant during the loading segment, it takes a considerable tip travel distance until it stabilizes and reaches the set value. Furthermore, the indentation strain rate, which has been incorrectly considered as the $\dot{P}/P$ ratio in some studies (Shen et al., 2004; Shen et al., 2006; Vachhani et al., 2013), is also found to change at shallow depths of indentation. The obtained results show a good correlation between the instantaneous indentation strain rate, which is evaluated directly from the indentation depth-time data recorded during the loading segment, and the strain rate relation proposed by Lucas and Oliver (1999) based on the variation of the load and hardness. As another purpose, the possible relation between the variation of the strain rate during the nanoindentation and the observed ISE in polymers is also scrutinized in this chapter. While the high values of strain rate in shallow depths can cause the increment of material hardness, it is discussed here that it cannot be the reason for the observed ISE since the obtained high values of hardness could be the result of the indentation strain rates which are orders of magnitude higher than the actual recorded strain rate values.

5.2. The Indentation Strain Rate

As mentioned before in chapter 2, in the nanoindentation experiments, the strain rate affects the material in a direction perpendicular to the sample surface and is correlated with the displacement/loading rate of the indentation. For a pyramidal indenter, the indentation strain rate
is defined as the penetration rate of the indenter into the material divided by its instantaneous depth as follows (Mayo and Nix, 1988)

\[
\dot{\varepsilon}_i = \left( \frac{1}{h} \right) \left( \frac{dh}{dt} \right)
\]

(5.1)

where \( t \) is time. In a study, (Lucas and Oliver, 1999) investigated that by keeping the loading rate divided by the load \((\dot{P}/P)\) constant during the CSM nanoindentation, the indentation strain rate can also remain constant. It has been shown that incorporating the loading and hardness data, the indentation strain rate can be obtained as

\[
\dot{\varepsilon}_i = \frac{\dot{h}}{h} = \frac{1}{2} \left( \frac{\dot{P}}{P} - \frac{\dot{H}}{H} \right)
\]

(5.2)

in which \( \dot{H} \) is the hardness variation rate and other parameters are defined before. According to Eq. (5.2), the indentation strain rate reaches a constant value \((\frac{1}{2} \frac{\dot{P}}{P})\) at large indentation depths where the material hardness is almost unvaried, i.e., \( \dot{H} = 0 \).

It is noteworthy to mention that two main simplifying assumptions have made to get this relation: (a) the projected contact area relation is considered as \( A = 24.56h^2 \) which is used for an ideal Berkovich indenter tip, and (b) instead of the contact or plastic depth, the total depth is used in the contact area function.

5.3. Variation of the \( \dot{P}/P \) in the course of an Indentation

The applied load on the sample and the tip travel distance are recorded as unbroken curves in the CSM nanoindentation experiments with \( nN \) and sub-\( nm \) exactness, respectively. Since the loading rate divided by the load is constant during the loading stage, i.e., \( \dot{P}/P = \eta \), the load is expected to be an exponential function of time as follows
\[ P = \xi e^{\eta t} \]  \hspace{1cm} (5.3)

where \( \xi \) is the constant obtained by solving the ordinary differential equation (ODE). The load variation with time during the loading section of the nanoindentation on PC sample is presented in Figure 5.1; the figure shows the results for three different set \( \dot{P}/P \) ratios and their exponential interpolations (lines) for comparison. The result curves depart from the exponential behavior at shallow indentation depths while they behave in accordance with the exponential variation within the long tip travel distance, especially for higher \( \dot{P}/P \) values. This discrepancy at the early stages of loading is due to the fact that based on Eq. (5.3) the initial loading condition is \( P(0) = \xi \), however, the set initial condition for the experiment process is \( P(0) = 0 \). Thus, the indenter \( \dot{P}/P \) ratio can be adjusted to the set \( \dot{P}/P \) value after several nanometers of indentation displacement (or several seconds).

![Figure 5.1](image-url)

**Figure 5.1.** Variation of load vs time response of the indenter for PC sample measured on the loading segment of the nanoindentation experiment at 3 different set \( \dot{P}/P \) values. The lines represent the exponential interpolations.

The actual variation of \( \dot{P}/P \) ratio as a function of the indentation depth is presented in Figure 5.2 for PC and PMMA at three different set values of this ratio which are shown as...
As mentioned before, the actual $\dot{P}/P$ values do not approach their set values right after the indenter tip comes into the contact with the sample surface. Furthermore, the depth at which the $\dot{P}/P$ ratio stabilizes does not depend on the material, however, it is extremely dependent on the set $\dot{P}/P$ value. As depicted in Figure 5.2, the depth beyond which the actual $\dot{P}/P$ approaches the set value and stabilizes is smaller for the bigger set value of $\dot{P}/P$: it is almost 1000 nm for the set $\dot{P}/P$ value of 0.005 s$^{-1}$, and reduces to 200 and 100 nm for the set $\dot{P}/P$ values of 0.05 and 0.11 s$^{-1}$, respectively. Interestingly, the starting point of actual value of $\dot{P}/P$ is not dependent on the material and set $\dot{P}/P$ ratio, and it approximately equals 0.3 s$^{-1}$ for all experiments.

* Note that data points below 10 nm are not shown since they are representing the fully elastic contact due to the blunt tip which has spherical head with a miniscule radius.
Figure 5.2. Variation of the actual $\dot{P}/P$ values with indentation depth at 3 different set $\dot{P}/P$ values for (a) PC, and (b) PMMA.

5.4. Variation of the Strain Rate in the Course of an Indentation

In the CSM nanoindentation method, since the tip displacement is recorded continuously with time, the indentation strain rate can be directly calculated by using Eq. (5.1) and simple numerical differentiation as a continuous function of the indentation depth. In addition, indirect evaluation of the indentation strain rate during the loading segment of the test is possible by
incorporating Eq. (5.2) and using the recorded load on the sample and the measured material hardness as functions of the depth. Since to employ Eq. (5.2) the variation of the instantaneous hardness rate divided by hardness ($\dot{H}/H$) is required, this parameter is represented in Figure 5.3 at three different set $\dot{P}/P$ ratios for PC and PMMA. As depicted in Figure 5.5, the material hardness is higher at shallower indentation depths (ISE), and then reaches a plateau at the certain depth which is the representative of the macroscopic hardness. Therefore, this trend results in the negative values of the $\dot{H}/H$ ratio at the initial stages of the loading section and finally zero values of $\dot{H}/H$ at deep part of the indentation (see Figure 5.3). As another result obtained from Figure 5.3, the depth beyond which $\dot{H}$ can be assumed zero depends on the material and the set $\dot{P}/P$ value.

Figure 5.4 displays the variation of the indentation strain rate with the indentation depth calculated based on the two different approaches. Since both methods show almost the same results, it reveals the validity of the assumptions made by Lucas and Oliver (1999) to obtain Eq. (5.2) not only for deep, but also shallow indentations of polymeric glasses. The most important result is that the indentation strain rate is not constant during the loading segment of the CSM nanoindentation of glassy polymers; and its variation is material and rate dependent. However, it can be assumed to be constant and equal to $\frac{1}{2} \frac{\dot{P}}{P}$ for deep enough indentation experiments.
Figure 5.3. Variation of the instantaneous hardness rate divided by hardness ($\frac{dH}{dt}$) with indentation depth for PC and PMMA at set $\dot{P}/P$ equal to (a) 0.005, (b) 0.05, and (c) 0.11 s$^{-1}$. 
Figure 5.4. Variation of the indentation strain rate based on Eq. (5.1) (Δ), and Eq. (5.2) (○) vs indentation depth for experiments on PC (a-c) and PMMA (d-f) at 3 different set $\dot{P}/P$ values.

The dashed lines represent the expected values of strain rate $\frac{\dot{P}}{2P}$. 
5.5. Indentation Size Effect

In rate dependent materials including polymers the flow stress extremely depends on the applied loading (strain) rate: the higher the experiment strain rate, the higher the yield stress (Richeton et al., 2006; Rottler and Robbins, 2003; Voyiadjis and Samadi-Dooki, 2016). Therefore, since there is a relation between the flow stress and hardness of the material through Tabor’s relation (Prasad et al., 2009), the higher value of hardness is expected from nanoindentation with the higher strain rate. The variation of hardness vs the tip displacement is presented in Figure 5.5 for experiments on PC and PMMA samples at three different set $\dot{P}/P$ values. It is observed that the obtained hardness values are higher as the strain rate increases; especially, the macroscopic hardness which is the hardness at the deep part of the nanoindentation and is the plateau for each curve depends on both material and strain rate. It is clear in these figures that the strain rate dependency of PMMA is more considerable which is, physically, demonstrated as smaller shear activation volumes in this material. Another observation in Figure 5.5 is the profound increment of the hardness as the depth decreases during each indentation which is known as the ISE at nano-scales (Lam and Chong, 1999; Shen et al., 2006; Zhang and Xu, 2002). Due to the above mentioned reason, the increased values of the material hardness at shallow indentation depths might be correlated with the higher values of the strain rate at these depths. However, an exact quantitative analysis is needed to understand and evaluate this possible relationship.
Figure 5.5. Variation of the hardness vs indentation depth during the loading segment of the experiments on (a) PC, and (b) PMMA at 3 different $\dot{P}/P$ values.

Many studies show that there is a linear relationship between the flow stress (or hardness) of the polymeric glasses and the logarithm of the strain rate. The explicit relationships have been previously obtained for PC and PMMA by nanoindentation evaluations in chapter 2. Using the obtained formulations and the strain rate variation during indentation, the fictitious hardness can be calculated for each test. It should be mentioned that to calculate the fictitious hardness, it is
assumed that the hardness variation is just the result of the strain rate variation during the loading stage. Figure 5.6 shows the actual measured hardness as well as the calculated hardness vs the indentation depth for PC and PMMA at 3 different set $\dot{P}/P$ values for comparison. The curves of PC sample show that the calculated hardness is almost constant and there is no considerable changes during a test, however, its variation during each indentation on PMMA sample is notably large in amount and follows almost the same hardening pattern at shallow depths as the actual hardness variation trend. In addition, for PMMA, the calculated hardness is the same (about 336 MPa) for all $\dot{P}/P$ values when the loading stage is triggered, which is acceptable for the reason that the strain rate at the beginning of the indentation is also the same for different $\dot{P}/P$ ratios (Figure 5.4), while the actual hardness at this point (maximum hardness in each curve) is different for different $\dot{P}/P$ values in both PC and PMMA. More importantly, as Figure 5.4 represents the strain rate variation in the course of an indentation is approximately material independent, however, PMMA reveals a more intense strain rate dependency of hardness response than PC (Figure 5.5); therefore, a more profound indentation size effect is expected to be observed in the nanoindentation of PMMA. Nevertheless, the real situation is different since the hardness variation at shallow depths is more noticeable for PC in comparison with PMMA (see Figures 5.5 and 5.6). The main result from these observations is that although the strain rate variation during the loading segment of the CSM nanoindentation on PC and PMMA is notable, it cannot be the major cause of the observed ISE in amorphous polymers. As a matter of fact, the indentation strain rate variation during the loading has no contribution to the observed ISE of PC, and its contribution to the ISE phenomenon in PMMA is negligible. Additionally, assuming the constant strain rate during the CSM nanoindentation of polymeric glasses for the size effect studies seems to be
reasonable and there should exist other mechanisms behind this phenomenon which are correlated to the localization and or free surface effects (Alisafaei and Han, 2015; Han et al., 2016).

It is noteworthy to mention that another important factor which can affect the contact area and, subsequently, the measured hardness, especially at shallow depths of the indentation, is the material pile-up around the indenter tip. In Figure 5.6, since the calculated hardness is obtained from the direct measurement of the indentation strain rate ($\dot{h}/h$), it is not affected by the material pile-up, while the actual measured hardness in this figure could be affected by the pile-up. For this reason, the material pile-up around the tip could be another factor that causes the difference between the calculated hardness of material and the actual one.

Another important phenomenon which is usually observed during the CSM nanoindentation experiments is a small size effect on the recorded elastic modulus of the material. As shown in Figure 5.7, it is an increased Young’s modulus at shallower indentation depths. This phenomenon is in contrast to the earlier observations from particle embedment experiments (Hutcheson and McKenna, 2007; Karim and McKenna, 2011, 2012, 2013; Teichroeb and Forrest, 2003). As discussed comprehensively in the literature (Parry and Tabor, 1973, 1974) the applied hydrostatic pressure on the polymer samples can hamper the chain movements which are required for relaxation processes; and can subsequently result in a considerable increment of the glass transition temperatures of the material. Based on that, it has been proposed that, in nanoindentation experiments, the contact loading at the indenter tip-polymer interface induces hydrostatic pressure under the tip which increases the glass transition temperature of the sample near the surface; and correspondingly, the increased stiffness of the material at low indentation depths has been related to the increment of $T_g$ (Gacoin et al., 2006; Tweedie et al., 2007). Therefore, the observed considerable material stiffening at shallow indentation depths (for depths of <50 nm in Figure 5.7)
could also attribute to the elevated values of $T_g$ at the surface layer within this tip travel distance compared to the bulk. Moreover, incorporating the shear transformation theory, Voyiadjis and Samadi-Dooki (2016) have proposed a model for yielding and plasticity of amorphous polymers which shows the relationship between the yield stress (which is proportional to hardness through Tabor’s relation), and an activation energy which itself is a function of the elastic modulus of the material. Thus, as another confirmation, there exists a possibility that the increased hardness observed at the shallow indentation depths to be inter-related to the increased elastic modulus at these depths. This hypothesis, however, should be viewed as a qualitative observation and treated cautiously since there is a noticeable difference between the length scales during which the elastic modulus and hardness increments are observed (see Figures 5.5 and 5.7).
Figure 5.6. Variation of the calculated (△) and actual (○) hardness vs indentation depth during the loading segment of the experiments on PC (a-c) and PMMA (d-f) at 3 different set $\dot{P}/P$ values.
Figure 5.7. Variation of the elastic modulus vs indentation depth during the loading segment of the experiments on (a) PC, and (b) PMMA at 3 different set $\dot{P}/P$ values.

5.6. Conclusion

The mechanical behavior of viscoelastic-viscoplastic materials, including polymers, strongly depends on the rate at which they are loaded. In the case of the nanoindentation, where these behaviors are evaluated at nano-scales, there are different methods in which the loading rate can be controlled in a way that the strain rate changes or remains constant during the experiment.
For many reasons, for example, to study the effect of the temperature, thermal history, composition of alloys, etc., it is desirable to conduct a test during which the strain rate remains constant. The CSM nanoindentation is a technique which offers testing at constant loading rate to load ratio ($\dot{P}/P$) ratios; this has been manifested as constant strain rates during the test. In this chapter, the assumption of the constant strain rate during this nanoindentation technique is studied for glassy polymers. Investigating the instantaneous variations of $\dot{P}/P$ and strain rate during the CSM nanoindentation on PMMA and PC samples showed that this assumption is not valid during the whole test and the strain rate changes in the early stages of the indentation before acceptable stabilization; the depth beyond that this parameter stabilizes depends on the material and the set $\dot{P}/P$ value. It has been shown that although by assuming the constant value of $\dot{P}/P$, an exponential load-time response of the indenter is expected, the load-time curves do not obey the exponential variation in early stages of the loading. The reason is the incompatibility of the actual initial load with the initial condition of the exponential loading which is required to assure a constant $\dot{P}/P$. To overcome this problem, one can apply a very small load prior to the main loading segment of the experiment; this adjusts the aforementioned incompatibility of the initial condition. By this adjustment, it is expected that the $\dot{P}/P$ value during the whole test remains constant and equals the initial set value. However, it may not lead to a constant strain rate since the hardness variation rate also contributes to the strain rate variation as proposed by Lucas and Oliver (1999). The strain rate can be assumed constant only at deep enough indentations where the load-displacement curve obeys the Hertzian relation. In this chapter, the possible effect of the variation of the strain rate during the indentation on the observed ISE in amorphous polymers has also been discussed. While it is concluded that the increased strain rate within the shallow indentation depths cannot be the sole reason for the observed profound ISE, contribution of the other factors, such as material pile-
up around the tip and stiffening due to the glass transition temperature \((T_g)\) shift induced by the hydrostatic component of the stress, have been qualitatively discussed.
6.1. Introduction

The so-called ISE is manifested as an increment of hardness, $H$, with decreasing indentation depth for Berkovich and conical indenters and decreasing indenter radius for spherical indenters (Pharr et al., 2010). For crystalline materials including metals, this phenomenon has been extensively investigated and mostly attributed to the geometrically necessary dislocations required to accommodate the induced plastic strain gradients (Gao and Huang, 2003; Nix and Gao, 1998). Although the ISE phenomenon has also been observed in non-crystalline (amorphous) materials such as glassy polymers, its origin is not well understood. A limited number of attempts to mechanistically model this phenomenon and discover the appropriate mechanisms at the microstructural level have been undertaken (Lam and Chong, 1999; Van Breemen et al., 2012; Yang et al., 2007). Lam and Chong (1999) developed a strain gradient plasticity law for indentation in glassy polymers based on the Argon’s molecular kink pair theory (Argon, 1973). They suggested the formation of statistically stored kink pairs along with the geometrically necessary kink pairs when the material is under yield condition and strain gradient. Later, Swaddiwudhipong et al. (2005) employed Lam and Chong strain gradient plasticity theory to model the ISE in glassy polymers using finite element method. However, since the kink pair model was physically and mechanistically unsound, it was abandoned in the 80s in favor of much more realistic and very general model of plasticity based on shear transformations with ready applicability in amorphous metals and glassy polymers† (Argon, 2013). Among the other suggested models, some were

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† Private communication with Prof. Ali S. Argon
constructed in a way very similar to that developed by Nix and Gao for metals based on the strain gradient plasticity (Nix and Gao, 1998); the main difference is the use of non-crystalline flow defects instead of dislocations. In particular, the same approach of “geometrically necessary” and “statistical stored” defects (either STs (Lam and Chong, 2001) or excess free volumes (Yang et al., 2007)) has been assumed to verify the size dependent behavior in metallic glasses. In these models a direct relationship between the hardness and density of defects has been considered. Therefore, the increased density of the defects at shallow indentation depth is mainly responsible for the ISE. However, this mechanism may not be reasonable since it has been shown that the increment of flow defects brings about softening instead of hardening (Bei et al., 2006; Yoo et al., 2009). In another suggestion made by Van Steenberge et al. (2007), it was proposed that the mechanical softening during indentation is due to the increment of the flow defect concentration associated with free volume. They have also provided a relationship that predicts the increment of free volume concentration with the strain rate during nanoindentation. However, as shown in chapter 5, the indentation strain rate decreases with depth (KRAFT et al., 2001) which, according to the provided relationship, should result in the reduction rather than enhancement of free volume concentration that is not in agreement with the suggested mechanism for the ISE. Furthermore, Han and Nikolov (2007) related the size effects in polymers to Frank elasticity arising from bending distortions of the polymer chains and their interactions. On the basis of this theory, a model for ISE in polymers due to rotational gradients has been developed.

As explained in chapter 1, since the size dependent behavior of polymers is observed in both displacement gradient-free and -dominant situations, it might be concluded that the ISE phenomenon cannot be interpreted using any of the existing models and might be explained in a different way (Jang et al., 2011). The new approach to interpret the size effect in glassy polymers
presented in this chapter is based on the assumption that this phenomenon, especially in nanoindentation, might derive from the size of the unit shear transformation events and how they relate to the volume of material required to elastically/plastically deform under the indenter. This means that the formation probability of shear transformations varies with the indentation depth in a way that at shallow indentations the highly stressed region beneath the indenter is too small to accommodate sufficient numbers of STs of average size, hence, material behaves ideally and the whole highly stressed region undergoes permanent deformation. On the other hand, at deep indentations the large volume of deformation zone is more probable to possess high activities of STs which results in the flow of material under a smaller amount of stress (reduction of hardness). Accordingly, in a quantitative model of strain rate and temperature dependent plastic resistance, some statistical considerations of the probability of finding the unit plastic relaxations in the deformed region is needed to justify the indentation size effect. For this purpose, the model described herein relates the total probability of finding a fertile region that can undergo shear transformation to the size of a single ST and the deformation zone under the indenter. The probability relation is an extension of the well-known Cohen and Turnbull model (Cohen and Turnbull, 1959) which was recently modified for treatment of shear transformation mediated homogeneous plasticity of polymers (Voyiadjis and Samadi-Dooki, 2016). Results obtained using the current model compare well with those obtained experimentally in chapter 2 for PMMA. Thus, it may predict the ISE in the measured hardness at a range of indentation strain rates pertinent to the commonly used nanoindentation procedures.
6.2. Shear Transformation Mediated Plasticity Theory

It is needed to recall the ST mediated homogeneous flow in terms of an Arrhenius function that describes the relation between the shear strain rate $\dot{\gamma}$ and shear yield stress $\tau$ as (Argon, 1979; Spaepen, 1977)

$$\dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta F_0}{k_B T}\right) \sinh\left(\frac{\gamma^T \Omega \tau}{2k_B T}\right)$$  \hspace{1cm} (6.1)

where $\dot{\gamma}_0$ is the pre-exponential factor described as

$$\dot{\gamma}_0 = \varnothing_{ss} \gamma^T \nu_G$$  \hspace{1cm} (6.2)

in which the coefficient $\varnothing_{ss}$ is proportional to the volume fraction of fertile sites capable of undergoing shear transformations and $\nu_G$ is the attempt frequency in the range of $10^{10}$ s$^{-1}$ (Argon, 2013). The coefficient $\varnothing_{ss}$ varies with the plastic strain (Hasan et al., 1993; Voyiadjis and Samadi-Dooki, 2016), however, for the indentation experiments which represent the yielding state, it has a constant value of about 0.5. In Eq. (6.1), the parameter $\gamma^T \Omega \tau$ is considerably larger than the unit thermal activation energy $k_B T$ for polymers at temperatures below their glass transition, hence, considering $\Delta F_0 = f(\nu, \beta)\mu(\gamma^T)^2 \Omega$, Eq. (6.1) can be rearranged as

$$\tau = \frac{2k_B T}{\gamma^T \Omega} \left[ \ln\left(\frac{2\dot{\gamma}}{\dot{\gamma}_0}\right) + \frac{\mu(\gamma^T)^2 \Omega f(\nu, \beta)}{k_B T} \right]$$  \hspace{1cm} (6.3)

which expresses the generalized rate and temperature dependent shear yield stress of an amorphous polymer.

6.3. Size Dependent Yielding in Nanoindentation

As it was previously mentioned, the yield behavior of glassy polymers exhibits size dependency observed in uniaxial tension, micro bending, and indentation experiments. Since ST formation and distribution are statistical phenomena, at small scales one needs to consider
probabilistic description for their spatial distribution rather than considering deterministic formalism based on a representative volume element. The size of a unit shear transformation event is typically about 200-500 nm$^3$ in linear chain glassy polymers (Argon, 2013), which could be manifested as a spherical region with a diameter of about 10 nm. Hence, at small deformation lengths, the size effect in plasticity must derive from the probability of formation of these discrete sites within the volume of material required to plastically deform. As it is schematically depicted in Figure 6.1-a, at very small indentation depths the size of the deformation zone is not adequate to accommodate discrete shear transformations, hence, the whole volume undergoes plastic deformation that grows in size with increasing the indentation depth (Figure 6.1-a and b). As the size of the deformation zone increases, the probability of formation of discrete shear transformations increases and at “deep indentation” ST formation is the main plasticity process that controls the kinetics of deformation (Figure 6.1-b and c). Accordingly, the total shear yield stress might be expressed as

$$\tau_{tot} = \chi \tau_{ST} + (1 - \chi)\tau_{local} \quad (6.4)$$

in which $\tau_{ST}$ is the shear stress associated with formation of a single ST, $\tau_{local}$ is the shear stress associated with the plastic deformation of the highly stressed region, and $\chi$ is the total probability of finding a fertile zone that can undergo discrete shear transformation within the deformation zone which is a function of indentation depth. While $\tau_{ST}$ can be calculated directly using Eq. (6.3) with setting $\Omega$ equal to the volume of an ST, $\tau_{local}$ may be obtained by setting $\Omega$ in the same equation equal to the size of the deformation zone which is a function of the indentation depth as

$$\Omega_{local} = \frac{2\pi}{3} r^3 - \frac{1}{3} A_c h \quad (6.5)$$
which expresses the volume of the hemisphere under the indenter with subtracting the volume of the pyramidal indenter itself. In this equation, \( r \) is the equivalent radius of the contact region as shown in Figure 6.2 which is equal to 4.35 \( h \) for a Berkovich tip with the half angle of about \( \theta = 65.3 \) degrees, and \( A_c \) is the projected contact area of the tip equal to 24.56 \( h^2 \) assuming a perfect tip. Hence, \( \Omega_{local} \) is about 164 \( h^3 \) for a 3 sided pyramidal Berkovich tip of 65.3° half angle.

![Figure 6.1. Schematic representation of the proposed variation of the plastic deformation mechanism in nanoindentation of glassy polymers with a triangular tip: (a) at small depth, the whole highly stressed region undergoes plastic deformation; (b) with increasing the indentation depth, the distinct shear transformations start to form within the deformation zone; (c) at deep indentations, the formation of the district shear transformation zones controls the kinetics of deformation and the local plastic zone under the tip head does not grow.](image)

![Figure 6.2. Schematic representation of the dimensions associated with the Berkovich tip.](image)

In order to find the total probability function, \( \chi \), an extension of Cohen and Turnbull diffusive rearrangement model (Cohen and Turnbull, 1959) is utilized herein. According to this model, the total probability of finding a fertile site that can undergo shear transformation is expressed as

\[
\chi = \exp \left( \frac{-\delta \nu^*}{\nu_f} \right) \tag{6.6}
\]
in which $\delta$ is a correction factor for overlap of the fertile volumes which is between 0.5 and 1, $v^*$ is a minimum size of a fertile site that can accommodate an ST, and $v_f$ is the average free volume content per ST. The average free volume per ST can be expressed as

$$v_f = \frac{V^f}{N} \quad (6.7)$$

where $V^f$ is the total free volume and $N$ is the number of STs. The total free volume is a function of the total volume that undergoes plastic deformation, i.e., deformation zone, and may be expresses as

$$V^f = \kappa V_p \quad (6.8)$$

in which $V_p$ is the size of the deformation zone (equal to $164 h^3$ for a Berkovich tip with a half angle of $65.3^\circ$) and $\kappa$ is a constant to describe the fraction of the free volume which is close to 0.05 for PMMA (Hristov et al., 1996; Voyiadjis and Samadi-Dooki, 2016). Considering Eqs. (6.7) and (6.8) and the fact that the minimum size of a fertile site which can accommodate at ST can be assumed to be proportional to the average volume size of an ST, $\Omega_{ST}$, the total probability of formation of a single ST in the deformation zone can be expressed as

$$\chi = \exp \left( \frac{-k_0 \Omega_{ST}}{h^3} \right) \quad (6.9)$$

in which $k$ is a fitting parameter, accounting for proportionality and free volume fraction constants.

Considering Eqs. (6.3-6.5) and (6.9), the shear yield stress as a function of depth is

$$\tau_{tot} = \frac{2k_B T}{\gamma T} \left[ \frac{\chi}{\Omega_{ST}} \left( \ln \left( \frac{2\dot{\gamma}}{\dot{\gamma}_0} \right) + \frac{\mu(\gamma T)^2 \Omega_{ST} f(\nu, \beta)}{k_B T} \right) \right.$$  
$$\left. + \frac{(1 - \chi)}{164 h^3} \left( \ln \left( \frac{2\dot{\gamma}}{\dot{\gamma}_0} \right) + \frac{\mu(\gamma T)^2 164 h^3 f(\nu, \beta)}{k_B T} \right) \right] \quad (6.10)$$
6.4. Hardness and Modulus

The average CSM load-hold-unload curves as a function of depth for experiments on PMMA are depicted in Figure 6.3 for the maximum indentation depth of 2 microns and indentation strain rates \( \frac{h}{h} \) ranging from 0.005 to 0.05 \( s^{-1} \). These indentation strain rates correspond to the \( \frac{\rho}{\rho} \) values of 0.01-0.1 \( s^{-1} \). Accordingly, the nanoindentation hardness and modulus results can be obtained for each strain rate as a function of depth as shown in Figures 6.4 and 6.5. Overall, both hardness and Young’s modulus exhibit size effect with increasing values for decreasing the indentation depth. However, the size effect is more pronounced for the hardness with values at small depth up to 3 times of those for deep indentation region (macroscopic hardness), while that ratio for the modulus is less than 1.6. In addition, the hardness shows a rate dependent behavior which is perceived as the increment of the macroscopic hardness with increasing the indentation strain rate, whereas, the modulus seems to be rate independent. Since the hardness is proportional to the yield stress of the material, its rate dependency is reasonable for visco-elasto-plastic solids like polymers. On the other hand, the elastic modulus is mainly correlated with the intermolecular van der Waals interactions in polymeric materials and is independent of the applied loading or strain rate (Argon, 2013; Perez, 1998). It is also worth noting that the Young’s modulus values obtained in nanoindentation are somewhat larger than the values obtained during uniaxial experiments (see also reference (Jin et al., 2015)). This observation is mainly due to the 3D state of stress under the indenter, and also the dynamic nature of the nanoindentation which induces a stiffer response of the viscoelastic materials, such as polymers. In addition, the PMMA samples used in this study were annealed at super-glass-transition temperature. The annealing process causes a reduction in the free volume content and chain mobility, which in turn can cause increased
hardness and modulus values. Nevertheless, since all the samples possess the same thermal history, the inter-specimen comparison of the results remains valid.

Figure 6.3. The average CSM load-hold-unload curves as a function of depth for experiments on PMMA at different indentation strain rates.

Figure 6.4. Variation of the hardness with indentation depth for PMMA at different indentation strain rates.
6.5. Variation of Strain Rate during each Indentation

As it was previously mentioned in chapter 5, despite the initial setting of the instrument to keep the $\frac{\dot{p}}{p}$ ratio at a constant value in order to maintain the indentation strain rate constant, the indentation strain rate at very shallow depths might not necessarily equal the set value according to the incompatibility of the actual initial load with the initial condition of the exponential loading which is required to assure a constant $\frac{\dot{p}}{p}$. Since the indentation depth is recorded as a function of time in CSM nanoindentation, one is able to calculate the $\frac{\dot{h}}{h}$ values numerically as shown in Figure 6.6. Apparently, the indentation strain rate is not a constant value for each test and increases as the indentation depth decreases. While for polymers with viscous nature the variation of the strain rate is important, the values shown in Figure 6.6 are directly used in calibrating the model based on Eq. (6.10) and Figure 6.4 with incorporating Eq. (2.15) for converting the indentation strain rate to the shear strain rate.
Figure 6.6. Variation of the indentation strain rate with indentation depth for PMMA for different set indentation strain rate values.

6.6. Size of a Single ST

The size of a single ST was measured at about 120 $nm^3$ for PMMA with analyzing the rate dependency of the hardness in chapter 2. In this chapter, the macroscopic hardness values are directly used for evaluating the ST volume. This method enables one to calculate the ST volume at each rate, instead of a single ST size for the whole tested rates. To this end, Eq. (6.10) is used with setting the proportionality value $\chi$ equal to one for deep indentations. The temperature is set at 295 $K$ for room temperature experiments, and $\gamma^T$ is considered to be equal to 0.04 according to the range of 0.03-0.05. Other parameters in this equation are set at the previously expressed values. To obtain the $\Omega_{ST}$ value at each rate, the macroscopic hardness of the representative rate is converted to the shear yield stress using Tabor’s relation. Accordingly, $\Omega_{ST}$ at each rate is obtained as demonstrated in Figure 6.7. As this figure implies, the ST volume size slightly increases with increasing the indentation strain rate which is in contrast to the findings obtained by Choi et al. (2012) for metallic glasses. The results of Figure 6.7 are in the range of the ST size of about 120 $nm^3$ found in chapter 2.
6.7. Size Effect in Hardness

Considering Eqs. (6.9) and (6.10), the hardness can be expressed as a function of the indentation depth. Accordingly, the required shear modulus and strain rate can be directly incorporated from Figures 6.5 and 6.6, respectively, while the size of the ST, $\Omega_{ST}$, is derived from Figure 6.7 at each indentation strain rate. As such, Eq. (6.10) can be fitted with the hardness curves of Figure 6.4 as depicted in Figure 6.8. Interestingly, the $\kappa$ parameter in Eq. (6.9) is evaluated to be similar for all indentation strain rates and is about $10^4$. It is also observed in Figure 6.8 that the model presented herein excellently predicts the indentation size effect of PMMA at different rates. In addition, the total probability function, $\chi$, of finding an ST in the deformation zone is readily obtained as shown in Figure 6.9. Based on this figure, the probability of finding an ST increases rapidly with increment of the indentation depth and reaches 90% at the $h=45 \text{ nm}$ and 99% at $h=100$ nm.

* The shear modulus can be obtained from the Young’s modulus values using the relation $\mu = \frac{E}{2(1+\nu)}$ with setting the Poisson’s ratio $\nu$ equal to 0.38 for PMMA.
nm. This rapid variation seems reasonable according to the average diameter of about 10 nm for a single ST.

Figure 6.8. Comparison of the hardness-indentation depth obtained from the experiments (hollow squares) with those based on the proposed model (solid lines) for the indentation strain rates of (a) 0.005, (b) 0.0125, (c) 0.025, (d) 0.0375, and (e) 0.05 s⁻¹.
Figure 6.9. Variation of the total probability of finding a fertile zone that can undergo shear transformation in the deformation zone with indentation depth for nanoindentation of PMMA at the indentation rate of 0.005 s⁻¹. The curves associated with other rates do not exhibit noticeable variation from the one shown above, hence, they are not depicted here.

6.8. Concluding Remarks

Shear transformation mediated plasticity of amorphous solids provides a physically basis for understanding the mechanisms that control the large deformation of these materials. An important parameter that can actively control the kinetics of the yielding and plasticity is the size of the shear transformation. At large scales, the STs’ size has been shown to exhibit a statistical distribution (Zhong et al., 2016). Nevertheless, the homogeneous plastic deformation of such materials can be satisfactorily modeled via assuming a single value to represent the average size of an ST (Argon, 2013; Voyiadjis and Samadi-Dooki, 2016). On the other hand, when the total size of the material that is subjected to the plastic deformation is small, one needs to incorporate the probability of finding a region that can undergo the shear transformation with an average size. Such circumstances might occur for one or two dimensional materials with ultra-small size in other dimensions, and mechanical loadings that impose deformation at very small scales such as nanoindentation experiments. The mechanical behavior of glassy polymers have been investigated for both cases with exhibiting markedly increasing resistance to plastic deformation at small size.
scales. Accordingly, in this work the probability function of finding STs within the deformation zone is considered for justifying the profound size effect in nanoindentation of PMMA. Considering the average diameter of about 10 nm for STs in PMMA, the total volume of the indented material with the stress level that can trigger the formation of discrete STs is not big enough to practically accommodate such inclusions at shallow indentation depths. Accordingly, it is proposed that at such shallow depths, instead of formation of discrete shear transformations, the whole highly stressed volume beneath the indenter undergoes plastic deformation which is not free volume assisted. With increasing the indentation depth, the probability of finding a fertile zone that can discretely undergo plastic deformation increases, and at deep enough indentation, the deformation kinetics is mainly controlled by the STs formation. To come up with an appropriate description for the probability function, use is made of Cohen and Turnbull’s theory with adjustments for the case of glassy polymers (Cohen and Turnbull, 1959; Voyiadjis and Samadi-Dooki, 2016).

Another important feature of the current model is considering other factors that can contribute to the indentation size effect. For example, it is shown that despite the assumption of constant indentation strain rate for CSM nanoindentation, this quantity varies significantly at small indentation depths. On the other hand, the yielding and plasticity of visco-elasto-plastic materials such as glassy polymers are extremely rate dependent. Hence, in implementing the model, the variation of the strain rate with depth is also considered. Although in chapter 5 it has been shown that this effect cannot solely justify the indentation size effect of polymers, its contribution to this phenomenon cannot be neglected.

In addition, instead of considering the elastic modulus of material to be a constant during indentation, the recorded modulus values versus the indentation depth are incorporated in the
model. Although the variation of the modulus is less significant compared to that of the hardness, it can affect the kinetics of yielding according to Eq. (6.1). According to these statements, the indentation size effect in polymers is a combination of the effect of the variation of the indentation strain rate, modulus, and probability of finding a single ST in the deformation zone under the indenter.

An important criterion for validity of any size effect model for indentation is its dependency on the geometry of the indenter. In this respect, the indentation size effect should be affected by the half angle of the indenter, and for a sharper tip more pronounced increase of hardness at shallow depths is expected to be observed. The theorem developed in this formalism considers the geometry of the indenter with introducing the relationship between the volume of the deformation zone and the tip angle as expressed in Eq. (6.5). Although the formalisms presented here are developed for a Berkovich tip with a 65.3° half angle, one can easily extend them for any other angle. In this way, the hardness values for the indentation strain rate of 0.005 s⁻¹ obtained for a tip with 45° half angle are compared with those for a 65.3° one as shown in Figure 6.10. The total probability function for finding a fertile zone that can undergo shear transformation associated with these tips with different half angles are also shown in Figure 6.11. The results of Figures 6.10 and 6.11 for a 45° half angle Berkovich tip might not exactly predict the experimental values since the input parameters for the Young’s modulus and indentation strain rate variations with depth are incorporated from the 65.3° tip and the volume of the deformation zone is only modified in Eq. (6.10) for the tip angle variation. Nevertheless, these figures show a significant increase in size effect for sharper tip. It should be mentioned that since there was no access to tips with different geometries, this aspect of the proposed model is not experimentally investigated.
The ST size dependency of the proposed model can also be readily investigated. The ST size has been shown to increase with increasing the strain rate. This increment, nevertheless, has no effect on the hardness at small deformation depth at which the size of the local highly stressed region under the indenter tip determines the material resistance to the plastic deformation. Since
the size of this local highly stressed region is determined by the tip shape, it is expected that at shallow depths, all the curves approach the same hardens values. This expectation is compatible with the observation in Figure 6.8 where all the curves approach a hardness value of about 0.7 GPa. On the other hand, when the size of the ST increases, the probability of finding a fertile zone that can undergo shear transformation is expected to be postponed to deeper indentations. This is also compatible with Eq. (6.9) which implies that at the same indentation depth, the value of the total probability function for a material with bigger ST size is smaller than that for a material with smaller ST size. Accordingly, the model predicts that the hardness curves for a material with a bigger ST size should approach its bulk value at deeper indentation depths. Comparing the hardness curves for PC with average ST size of 480 nm$^3$ with that of the PMMA with the average ST size of 120 nm$^3$ supports this hypothesis as shown in Figure 6.12.

Although the current approach demonstrates a more physically based method to investigate the observed ISE in nanoinetration of polymers compared to the previously proposed methods, it has its own limitations. The first limitation is associated with the temperature dependence of size effect which is not considered here. Although the model can consider the effect of temperature, performing CSM indentation at elevated temperatures is not feasible on the device used for running the experiments. In fact, it was not possible to minimize the thermal drifts of the tip in order to perform CSM experiments with meaningful data. Another limitation associated with this study is the assumption of a rate dependent universal size for STs at deep indentations for PMMA, whereas, even for ST mediated plasticity of large samples, ST sizes show a statistical distribution. Nevertheless, this assumption does not negatively affects the generality of the proposed method

* It should be noted that for all the curves in Figure 6. the indentation strain rate at shallow depths approaches the same value according to Figure 6., hence, observation of the same hardness value at shallow depths is compatible with rate and size dependency criteria.
according to the homogeneous behavior of PMMA whose yield behavior does not depend on individual STs. Despite the aforementioned limitations, the current model shows a promising performance in justifying the size dependent behavior during indentation of glassy polymers.

Figure 6.12. Variation of the hardness vs indentation depth during the loading segment of the nanoindentation experiments on (a) PC, and (b) PMMA at indentation strain rate of 0.055 s⁻¹. The results for PC exhibit deeper indentations for reaching the stabilized macroscopic hardness values according to its bigger ST size.
CHAPTER 7
SUMMARY, CONCLUSION, AND FUTURE PERSPECTIVES

In this chapter, the summary of the performed research along with the deduced conclusions in this dissertation are presented. In addition, the suggestions and future perspectives based on this research are also presented.

7.1. Summary

Due to the absence of the long-range structural order in glassy (amorphous) solids, their flow and plastic response mechanisms in the microstructural level are different from crystal plasticity where dislocations are the main carriers of plasticity as line defects. Many efforts have been made to characterize the mechanism of plasticity in disordered solids, which have resulted in different phenomenological models. The current widely accepted mechanism for the plastic deformation in glassy solids is the cooperative localized rearrangement of atomic or molecular clusters in small distinct regions which are called shear transformation zones (STZs). Therefore, the STZs are recognized as the main carriers of plasticity in all types of non-crystalline solids.

This dissertation deals with the challenging and under-researched topic of the shear transformation mediated flow theory in amorphous solids which, as a first step, requires a comprehensive characterization of microstructural defects responsible for the mechanical behavior of material at different length scales. Therefore, employing the reliable and precise nanoindentation technique along with Atomic Force Microscopy (AFM), the plasticity sites have been experimentally and analytically characterized to obtain their geometrical and micromechanical characteristics (chapter 2). To investigate the uniqueness of these characteristics for glassy polymers, the study has been performed on two samples (PC and PMMA) and the
mechanical properties are studied at different temperatures and strain rates and for samples with different thermal histories.

The free volume content, inherent in unordered structure of glassy polymers, is a key factor in the formation of STZs since they need the free voids for their molecular rearrangements. Hence, the size and fraction of free volume in the material might considerably affect the characterizing parameters of shear transformations as well as the mechanical response of the material. To investigate this effect, thermal treatment (annealing) is selected as a process by which the free volume content can be altered and its evolution is monitored by Positron Annihilation Lifetime Microscopy (PALS) (chapter 3). The results reveal opposite directions of alterations of free volume and shear activation volume with annealing temperature. Accordingly, the beheld changes of macro-mechanical properties of selected amorphous polymers through the sub- and above-glass-transition-temperature annealing processes are discussed and justified according to these microstructural alterations.

The main objective of this work is exploring the proper physical mechanism behind the size dependent behavior of glassy polymers which has been observed in many experiments at micron to submicron length scales. Indentation Size Effect (ISE) is one of these size dependent behaviors which is manifested as the increment of hardness, $H$, with decreasing the indentation depth for Berkovich indenters. In the case of crystalline materials, this phenomenon has been studied in detail and mostly attributed to the dislocation interactions and evolutions; but in non-crystalline materials such as glassy polymers, its origin is not well understood. The main part of this dissertation focuses on investigating the effect of possible parameters on the ISE in polymers and, consequently, developing a rate and temperature dependent model based on the shear transformation mediated plasticity. Accordingly, since the strain rate is an adjustable parameter in
nanoindentation experiments and its variation has shown profound effects on the mechanical response of time dependent materials like polymers, its contribution on the observed ISE is studied in detail (chapter 5). Evaluating the alteration of strain rate value during an indentation test and considering the relationship between the hardness and strain rate (obtained in chapter 2) reveal that the strain rate contribution is not able to justify the observed indentation size effect. As the final result, making use of all the information obtained from characterization of STZs and observations during this research, an ISE model which shows excellent agreement with the experimental values is developed.

7.2. Conclusion

The following conclusions are drawn from the work in this dissertation:

1. The nucleation energy of a single shear transformation at zero Kelvin in both PC and PMMA is almost the same and equal to 1 eV. Furthermore, since the parameter is in the same order for the metallic glasses, it can be conclude that the STZ’s activation energy is in the same order for all amorphous polymers and metals.

2. The transformation shear strain $\gamma^T$ is not a universal value for the glassy polymers and depends on the material. This parameter is also smaller in the glassy polymers than that in the metallic glasses.

3. Although the shape of the STZs has been assumed to be spherical in all types of amorphous solids, this work reveals that they are flat ellipsoids in glassy polymers.

4. The size of a single STZ in glassy polymers depends on both the material and thermal history of the sample.
5. The results reveal opposite direction of alterations of free volume and shear activation volume with annealing temperature. Therefore, the bigger free volume cavities, the smaller shear activation volume. In particular, the maximum shear activation volume is reached around $T_g$, and beyond that no additional variation is taking place.

6. Annealing of polymeric glasses at temperatures well below their $T_g$ could be the most efficient strengthening process via thermal treatment.

7. The nano-structural inhomogeneity of semicrystalline polymers can cause irregular patterns in mechanical properties measured by nanoindentation. It is found that surface polishing and thermal treatment as convenient procedures can suppress the effect of such inhomogeneities.

8. The strain rate can be assumed unvaried only at deep enough indentations where the load-displacement curve obeys the Hertzian relation and there is no size effect.

9. Although the increased strain rate within the shallow indentation depths enhances the hardness, its contribution is not able to justify the observed indentation size effect in glassy polymers and there should be other mechanisms for this behavior.

10. It is shown that the physically and mechanistically appropriate mechanism at microstructural level to model the indentation size effect in glassy polymers is originated from the activity of discrete shear transformation units in the deformation zone under the nanoindentation. The proposed model which is in excellent agreement with the experimental results can predict the dependency of ISE on temperature, strain rate, and indentation geometry.
7.3. Future Perspectives

The followings are suggestions for future research based on the work presented in this dissertation:

1. The observation of homogeneous flow and characterization of STZs have been performed at temperatures beyond 0.6Tg of selected glassy polymers and also at limited range of strain rates which are possible with the accessible nanoindentation instrument. Investigations at wider ranges of temperatures (below 0.6Tg) and strain rates are required for a complete understanding of the behavior of glassy polymers since their flow nature strongly depends on temperature and strain rate at which the load is applied.

2. Variations of chemical composition of tested polymers with annealing at high temperatures might also occur besides physical alterations. Such chemical changes might include side chain reactions and alteration of molecular weight. Investigation of the effect of any chemical variations on the physical phenomena pertinent to the plastic deformation of thermoplastics might unravel novel aspects of STZ mediated large deformation of these solids.

3. Modeling of large deformation of polymers entails a realistic formalism in 3D that can be implemented in commercial finite element software. Although the presented work defines the fundamental aspects of a physically based model for plasticity of polymers, its generalization to 3D simulation in future developments would add a valuable reference to the current state of knowledge.

4. Size dependency is investigated in this research for the case of nanoindentation only. For future analyses, it is suggested that the mechanical behavior of solid state polymers to be studied for other small scale structures such as micro and nano pillars and beams. Since the model
presented herein is capable of describing the size effect for different loading modes, the investigation of the physics of size dependency for other small scale structures via the developed formalism herein would be of interest.


Karim, T.B., McKenna, G.B., 2013. Comparison of surface mechanical properties among linear and star polystyrenes: Surface softening and stiffening at different temperatures. Polymer 54, 5928-5935.


Pai, C.-L., Boyce, M.C., Rutledge, G.C., 2011. Mechanical properties of individual electrospun PA 6 (3) T fibers and their variation with fiber diameter. Polymer 52, 2295-2301.


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VITA

Leila Malekmotiei was born in 1986 in the city of Tehran, Iran. Leila received her primary and secondary education in public and private schools in Tehran, and subsequently joined Sharif University of Technology (SUT) in to pursue a bachelor degree in Civil Engineering in 2004. In 2009, she was admitted to the Master’s program in Structural Engineering at SUT with focus on Theoretical and Applied Mechanics. She graduated from this program in 2012 and jointed the doctoral program in Civil Engineering at the Computational Solid Mechanics Laboratory of the Louisiana State University (LSU) under the supervision of Boyd Professor George Z. Voyiadjis in 2013. The completed research work in the field of nanomechanics of polymers is presented in this dissertation. In addition, during her PhD program Leila has been involved in research in several other areas, such as Nanoindentation, Microtension, and AFM experiments, sample preparations and thermomechanical analysis of solids. She also served as instructor and teaching assistant for several undergraduate level course at LSU. Her future plans involve continued research on materials characterization with the aid of submicron scale testing, microscopy techniques and multi-scale modeling.