Review Article

Indentation Depth Dependent Mechanical Behavior in Polymers

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Received 20 April 2015; Accepted 9 July 2015

1. Introduction

Nanoindentation is one of the most commonly applied methods for determining of material properties and characterization of deformation behavior at nano- to micrometer length scales. Performing nanoindentation experiments, the mechanical behavior of various materials has been found to be dependent on the indentation depth indicating changing deformation mechanisms with the length scale. Length scale dependent deformation has been experimentally observed in different materials including metals and polymers. In metals, size dependent deformation has been reported in micro- and nanoindentation tests of bulk materials [1–7], micromized beam bending experiments [8], microtorsion of thin wires [9], tension of perforated plates [10, 11], nanoindentation of thin films [12], particle-reinforced metal matrix composites [13, 14], and so forth. Similar to metals, length scale dependent deformation has been also experimentally observed in polymers at micro to submicron length scales by nanoindentation [15, 16], micromized beam bending experiment [17, 18], and bending test of nanofibers [19, 20], as well as in particulate reinforced composites (a relatively recent review can be found in [21]). The length scale dependent deformation has been experimentally observed in various polymers such as epoxy [16, 17, 22–27], polycarbonate (PC) [15, 16, 28], polystyrene (PS) [15, 28], polymethyl methacrylate (PMMA) [15, 28, 29], polydimethylsiloxane (PDMS) [30–35], silicon rubber/elastomer [36–38], nylon (PA66) [39], polypropylene (PP) [18], polyimide (PI) [40], polyvinyl chloride (PVC) [28], polyamide 6 (PA6) [41], and polystyrene acrylonitrile (SAN) [28].

In metals, length scale dependent deformation is usually associated with geometrically necessary dislocations [42, 43] resulting in an increase of strain gradients with decreasing length scale [44–48]. In polymers, however, such a notion is not applicable and different explanations have been suggested in the literature as a rationale for such size effects including higher order displacement gradient models [16, 17, 22–25, 29, 33, 49–51], surface effects [36, 52], changes in the material properties through thickness (heterogeneity of the material) [15, 31], and friction [34]. Due to the complex and varied molecular structures of polymers, the mechanisms of the abovementioned length scale dependent deformations in polymers are arguably more complicated than in metals. Furthermore, as polymers are known to be rate and temperature sensitive, such length scale dependent deformations in polymers should be more affected by rate/temperature changes than in metals.

While length scale dependent deformation in polymers has been observed in different experiments including bending of microbeams, nanoindentation, bending of nanofiber and particulate-reinforced composites, in this paper, the
length scale dependent deformation in polymers observed with indentation experiments is reviewed along with the notions on its physical origin as well as theoretical models that predict such length scale dependent deformations in polymers. In Section 2, the length scale dependent deformation of polymers observed in nanoindentation testing is critically reviewed followed by discussions on the possible explanations for the origin of length scale dependent deformation in polymers in Section 3.

2. Size Dependent Deformation of Polymers Observed in Nanoindentation Experiments

To set the stage and clarify the notation, Figure 1(a) shows a schematic load-displacement curve of nanoindentation consisting of loading (section A-B), holding (section B-C), and unloading (section C-D) sequences [25]. A corresponding schematic cross section of such an indentation is depicted in Figure 1(b) identifying parameters used in the analysis [53, 54] which will be discussed later.

2.1. Hardness and Elastic Modulus Determination. Similar to metals [2], the hardness parameter (indentation hardness [53] and universal hardness [54]) is usually used to investigate the indentation size effect (ISE) in polymers [15, 22]. Indentation hardness $H_I$ can be obtained as

$$H_I = \frac{F_{\text{max}}}{A_c},$$

where $F_{\text{max}}$ is the maximum applied force (shown in Figure 1(a)) and $A_c$ is the projected contact area at the maximum applied force $F_{\text{max}}$. The projected contact area $A_c$ as a function of contact depth $h_c$ (see Figure 1(b)) for some common indenter geometries is given in Table 1 [55]. As can be seen in Figure 1(b), the contact depth $h_c$ is determined by

$$h_c = h_{\text{max}} - h_s, \quad (2)$$

Table 1: Projected contact area, surface area, angles, geometric constants, and geometry correction factors for common indenter geometries [55] where $h_s$ is the contact depth (shown in Figure 1(b)), $h$ is the indentation depth under applied force $F$ (see Figure 1(a)), $R$ is the radius of spherical tip, $\theta$ is the semiangle of indenter tip (for pyramidal tips $\theta$ is the face angle with the central axis of the tip [55]), $\alpha$ is the half angle defining an equivalent cone, $\epsilon$ is the geometric constant (for the pyramidal tips $\epsilon$ is theoretically 0.72; however, a value of 0.75 has been experimentally found to better represent experimental data [55]), and $\beta$ is the geometry correction factor used for the determination of elastic modulus [53]. Note that $A_s$ and $A_c$ given in Table 1 for Berkovich, Vicker, Knoop, cube corner, and cone indenters are, respectively, the projected and surface areas of a perfectly sharp indenter without imperfection/bluntness (see, e.g., [53, 55], for the projected contact area of a blunt indenter).

| Indenter tip     | Projected contact area $A_c$ | Surface area $A_s$ | Semiangle $\theta$ (deg) | Effective cone angle $\alpha$ (deg) | Geometric constant $\epsilon$ | Geometry correction factor $\beta$ |
|------------------|-------------------------------|-------------------|--------------------------|-----------------------------------|-------------------------------|-------------------------------|
| Sphere           | $\pi(2h_s R - h_s^2)$        | N/A               | N/A                      | N/A                               | 0.75                          | 1                             |
| Berkovich (perfect) | $3\sqrt{3}h_s^2 \tan^2 \theta$ | $3\sqrt{3}h_s^2 \tan \theta / \cos \theta$ | 65.03°                    | 70.3°                             | 0.75                          | 1.034                         |
| Berkovich (modified) | $3\sqrt{3}h_s^2 \tan^2 \theta$ | N/A               | 65.27°                   | 70.3°                             | 0.75                          | 1.034                         |
| Vicker           | $4h_s^2 \tan^2 \theta$      | N/A               | 68°                      | 70.3°                             | 0.75                          | 1.012                         |
| Knoop            | $2h_1^2 \tan \theta_1 \tan \theta_2$ | N/A               | $\theta_1 = 86.25°$       | $\theta_2 = 65°$                  | 0.75                          | 1.012                         |
| Cube corner      | $3\sqrt{3}h_s^2 \tan^2 \theta$ | N/A               | 35.26°                   | 42.28°                            | 0.75                          | 1.034                         |
| Cone             | $\pi R^2 \tan^2 \alpha$     | N/A               | $\alpha$                 | $\alpha$                          | 0.727                         | 1                             |

Figure 1: (a) Schematic representation of load-displacement curve in nanoindentation testing. (b) Schematic representation of cross section through indentation of a material sample.
where $h_{\text{max}}$ is the indentation depth $h$ at the maximum applied force $F_{\text{max}}$ before the unloading section (see Figure 1) and $h_t$ is determined by

$$h_t = \frac{F_{\text{max}}}{S}$$

(3)

in which $S$ is the initial slope of unloading curve (see Figure 1(a)) and $e$ is a geometric constant given in Table 1 for different tip geometries. To determine the stiffness $S$ by the Oliver and Pharr approach [53], the unloading curve of Figure 1(a) is described as

$$F = B (h - h_t)^m,$$

(4)

where the parameters $B$, $m$, and $h_t$ are obtained by fitting the upper portion of unloading curve. Thus, $S$ is determined by taking the derivative of $F$ with respect to $h$ in (4) at the maximum applied force $F_{\text{max}}$ shown in Figure 1(a).

In addition to the indentation hardness $H_I$, the universal hardness $H_U$ (also known as Martens hardness) can be also determined from nanoindentation tests. The universal hardness for a perfect Berkovich (unmodified Berkovich) and Vicker tips is defined as follows:

$$H_U = \frac{F}{A_s},$$

(5)

where $A_s$ is the surface area under the initial surface (see Figure 1(b)) given in Table 1 as a function of indentation depth $h$. As mentioned above, the indentation size effect of materials is usually described by measuring the hardness ($H_I$ and/or $H_U$) at different indentation depths ranging from microns to few nanometers. However, in contrast to metals [56, 57], in polymers length scale dependent deformation has been also experimentally observed by monitoring the elastic modulus determined from indentation experiments by various approaches with sharp indenter tips which will be denoted as indentation elastic modulus in the following. The indentation elastic modulus of materials is often obtained following Oliver and Pharr (O&P) [53] as

$$E_{\text{r O&P}} = \frac{\sqrt{2\beta S}}{2\beta \sqrt{A_s}},$$

(6)

where $\beta$ is the tip geometry correction factor (see Table 1) and $E_{\text{r O&P}}$ is the reduced elastic modulus [53] which is related to the elastic modulus of polymer, $E_{\text{r O&P}}$, via

$$\frac{1}{E_{\text{r O&P}}} = 1 - v_1^2 E_{\text{r O&P}} + 1 - v_1^2 E_1,$$

(7)

in which $E_i$ and $v_i$ are, respectively, the elastic modulus and Poisson’s ratio of indenter tip with $v$ being the Poisson’s ratio of the polymer.

2.2. Indentation Size Effect in Polymers. The indentation size effects of various polymers are depicted in Figure 2 where the indentation hardness $H_I$ increases with decreasing $h_{\text{max}}$ [15, 16, 26, 36, 39]. Therein, it can be seen that there is a significant rise in the indentation hardness of epoxy [16, 26], polycarbonate (PC) [15, 16], polystyrene (PS) [15], polymethyl methacrylate (PMMA) [15], silicon elastomer [36], and nylon (PA66) [39] as $h_{\text{max}}$ decreases. However, $H_I$ of ultra-high molecular weight polyethylene (UHMWPE) [15] remains almost constant for $h_{\text{max}} > 100$ nm where there is only a slight increase in the indentation hardness of UHMWPE at very shallow indentation depths $h_{\text{max}} < 100$ nm which will be discussed later. Similar to the trend observed for the indentation hardness of polymers in Figure 2, length scale dependent deformation of polymers can be also observed in Figure 3 where the universal hardness, $H_U$, increases with decreasing $h_{\text{max}}$ [15, 25, 28]. Comparing $H_I$ of Figure 2 with $H_U$ of Figure 3, the indentation hardness is found to be slightly higher than the universal hardness as the projected contact area $A_s$ (see (1)) is usually smaller than the surface area $A_s$ used in (5) [25].

Generally, due to the complex structures of polymers and their rate, temperature, and pressure dependence behavior, in addition to the higher order displacement gradient effects, indentation size effects can be caused by various sources. These sources include but are not restricted to surface effect [36, 52], change in the glass transition temperature [41], adhesion [59, 60], tip bluntness [61], material inhomogeneity [15], and confined molecular motion interfacial region (formation of an interfacial region of confined molecular motion between the surface and probe by contact loading) [62].

It can be seen in Figures 2 and 3 that the characteristics of length scale dependent deformation in polymers significantly differ from polymer to polymer. As shown in Figures 2 and 3, the depth $h_{\text{max}}$ at which the hardness starts to noticeably
Increase can be remarkably different for different polymers [67]. For instance, the hardness of epoxy starts to increase below about $h_{\text{max}} = 3 \mu\text{m}$ [16, 25, 26], while for PC, PS, and PMMA hardness starts to rise below about $1 \mu\text{m}$ [15, 16]. Such an increase of hardness in PA66/nylon is only observed for $h_{\text{max}} < 200 \text{ nm}$ [39] where there is no increase in the hardness of UHMWPE for $h_{\text{max}} > 100 \text{ nm}$ [15] indicating that the characteristics of length scale dependent deformation can strongly vary in different polymers [68]. Furthermore, the increase in the hardness is significantly different in different polymers. In epoxy [16], PC [15, 16], PS [15], and PMMA [15] $H_{\text{I}}$ increases by a factor of about 1.3 and in silicon elastomer [36] by a factor of about 6.7 for the indentation depth range of around 2 to 0.2 $\mu\text{m}$, while no size effect is observed in UHMWPE [15] and polytetrafluoroethylene (PTFE) [69] for the same indentation depth range of about 2 to 0.2 $\mu\text{m}$. In the following, the indentation size effect of polymers in the literature is reviewed in three polymer categories of thermosets, thermoplastics, and elastomers.

2.2.1. Thermoset Polymers. In addition to the microsized beam bending experiment [17], length scale dependent deformation of epoxy has been experimentally observed by nanoindentation testing in various studies [16, 22–27]. Length scale dependent deformation of thermoset epoxy was first observed in [16, 22] where the indentation hardness, $H_{\text{I}}$, of epoxy with 10 parts per hundred resin (phr) was found to increase with decreasing $h_{\text{max}}$ as shown in Figure 2. Nanoindentation tests of [16] were performed by a sharp Berkovich tip in load-controlled mode with a constant loading and unloading rate of $0.01 F_{\text{max}}$. The indentation hardness of epoxy (see (1)) was determined according to Oliver and Pharr [53] where a 10 s holding time (sections B-C in Figure 1(a)) was applied to minimize viscous effects. To ensure the accuracy of the hardness data $H_{\text{I}}$, the projected contact area $A_{\text{c}}$ at each test was measured by atomic force microscopy (AFM) and compared with the one determined by the unloading curve (see (2)) where good agreement was achieved between the measured (AFM method) and determined (O&P method) contact areas.

Such length scale dependent deformation of epoxy was also experimentally observed in [26] with a Berkovich indenter tip at an indentation depth range between 4500 and 500 nm. Nanoindentation tests in [26] were performed in load-controlled mode with the following sequences: loading segment with a constant strain rate of 0.05 s$^{-1}$ until the maximum applied force $F_{\text{max}}$ followed by a holding time of 10 s at the maximum applied force; unloading segment with a constant unloading rate equal to 70% of the loading rate until 80% of the maximum applied force $F_{\text{max}}$ is removed; a second holding period of 2 s followed by a final unloading segment until $F_{\text{max}}$ is completely removed. Indentation hardness of epoxy determined according to [53] as a function of $h_{\text{max}}$ is plotted in Figure 2 where each point represents an average value of ten indents.

Performing nanoindentation tests with a sharp Berkovich indenter tip, the indentation size effect in epoxy has been also experimentally observed in [25] where $H_{\text{I}}$ increases with decreasing $h_{\text{max}}$ as shown in Figure 4. Taking the effects of tip bluntness/imperfection into account, it was shown that, for a sharp Berkovich tip with a tip roundness of about 40 nm, tip bluntness becomes significant only at $h_{\text{max}} < 250 \text{ nm}$ as illustrated in Figure 5 (see [25] for tip roundness determination). As the indentation size effect is observed at large depths far above $h_{\text{max}} \approx 250 \text{ nm}$, it was concluded in

Figure 3: Universal hardness $H_{\text{I}}$ versus $h_{\text{max}}$ for various polymers redrawn from [15] (PC, PS (a), PMMA (a)), [28] (PS (b), PMMA (b)), and [25] (epoxy with 5 s loading time).

Figure 4: Indentation hardness of epoxy with 20 phr from [25] (with 20 s loading, holding, and unloading times) and [23] (with a constant loading and unloading rate of 1% of the maximum applied force with a 10 s holding time) obtained by the Oliver and Pharr approach [53].
Figure 5: Effect of tip bluntness on the indentation size effect in epoxy with 20 phr ($H_{U\text{corrected}}$ and $H_{U\text{uncorrected}}$ represent the universal hardness with and without considering the effect of tip bluntness, resp.) [25].

Figure 6: Cross-link density of epoxy as a function of hardener percentage [23].

Figure 7: Indentation hardness of epoxy at large indentation depth $h_{\text{max}}$ as a function of hardener percentage [23].

Figure 8: Indentation hardness of epoxy with different hardener contents as a function of indentation depth $h_{\text{max}}$ [23].

[25] that the tip bluntness cannot explain such size effect in epoxy.

The effect of cross-link density on the length scale dependent deformation of epoxy was investigated in [23] by varying the hardener content. To this end, the cross-link density $\rho_x$ of epoxy resin cured with varying amount of hardener content was first determined by dynamic mechanical tests. In Figure 6, the cross-link density of epoxy determined from the dynamic mechanical tests is plotted for the hardener contents (phr) of 7.5, 9, 11, 15, and 20. The highest cross-link density was observed at 11 phr where $\rho_x$ reaches its maximum value [23]. As $H_o$ (indentation hardness at large depths where size effect is negligible) is directly proportional to the yield stress, Figure 7 implies that the yield stress of epoxy decreases with $\rho_x$. Using a sharp three-sided Berkovich tip, the indentation hardness $H_I$ as a function of $h_{\text{max}}$ is depicted in Figure 8 for the hardener contents (phr) of 8.7, 10, 11, 15, and 20. Length scale dependent deformation of epoxy is observed in Figure 8 where indentation hardness of epoxy increases with decreasing $h_{\text{max}}$ for all phr hardener values. Analyzing the hardness data of Figure 8, it was observed that the length scale dependent deformation of epoxy becomes
more significant with increasing cross-link density. The effect of cross-link density on the size effect of epoxy observed in [23] is consistent with results presented in [34] which will be later discussed. It should be mentioned that epoxy samples of [23] were prepared in the same way as in [16] where both liquid resin (bisphenol A epichlorohydrin) and curing agent (diethylene triamine) were mixed and cast into a rectangular Teflon crucible. As the curing agent of epoxy is hydrophilic while Teflon is hydrophobic, such opposing tendencies may potentially cause depletion of curing agent from the surface of epoxy samples and segregation of resin and curing agent [23]. If curing agent is segregated from resin, then the surface region should contain less curing agent than the interior region of the sample. Subsequently, the hardness should be lower at small indentation depths close to the surface of the sample. However, an opposite trend is observed in Figure 8 where indentation hardness of epoxy increases with decreasing indentation depth \( h_{\text{max}} \) indicating that the length scale dependent deformation of epoxy is not associated with the segregation of curing agent during sample preparation [23].

The effect of plastic strain/deformation on the length scale dependent deformation of epoxy was studied by Lam and Chong [24]. Prismatic epoxy specimens with 20 phr were first loaded between two parallel glass plates (uniaxial compression) to induce plastic strain. Figure 9 shows the compressive stress-strain behavior of unprestrained epoxy where material hardening is observed with increasing compression. After compressive prestraining, nanoindentation testing was performed on the optically smooth side of epoxy specimen orthogonal to the loading direction [24]. All nanoindentation tests were conducted in a displacement controlled mode with a Berkovich tip at an indentation range of 3.2 to 0.1 μm. A 10 s holding time was employed at the maximum applied load \( F_{\text{max}} \) to minimize time dependent effects. Results obtained from the nanoindentation tests are depicted in Figure 10 where indentation hardness \( H_I \) (obtained by the Oliver and Pharr approach [33]) is plotted as a function of indentation depth \( h_{\text{max}} \) for plastically prestrained epoxy samples. In contrast to Figure 9, the hardness of epoxy (depicted in Figure 10) decreases as prestraining increases. The decrease in the hardness of prestrained epoxy samples was attributed to the Bauschinger effect [24]. The Bauschinger effect has been experimentally observed in polymers when a prismatic specimen compressively prestrained in the uniaxial direction exhibits softening when it is compressed in the orthogonal direction [70]. Similarly, indentation hardness \( H_I \) in the orthogonal direction decreases with inducing prestrain as a result of Bauschinger effect [24]. Taking the Bauschinger effect into account, an energy based methodology was presented in [24] to separate the size effect from the prestrain softening effect (Bauschinger effect). As shown in Figure 11, after correcting for the Bauschinger effect, the indentation hardness \( H_I \) increases with increasing plastic strain which is in agreement with the hardening behavior observed in Figure 9. It is seen in Figure 11 that size effect in epoxy diminishes with increasing plastic deformation.

In addition to epoxy, indentation size effect of thermoset PMR-15 polyimide has been also studied in the literature. Redrawn from [40], the indentation hardness of PMR-15 polyimide as a function of indentation depth is depicted in Figure 12. A sharp Berkovich tip with a nominal tip radius of less than 20 nm was used to determine the indentation hardness of Figure 12 where a 2 s loading time was applied for all indentation tests. Creep effects were also taken into account in [40] for the determination of \( H_I \) of Figure 12 where \( h_{\text{max}} \) in (2) was replaced by \( h_{\text{max}} - h_{\text{creep}} \) with \( h_{\text{creep}} \) being the change in the indentation depth during the holding time and \( S \) in (3) was replaced by \( S_c \) which is the elastic contact stiffness with considering the creep effect

\[
\frac{1}{S_c} = \frac{1}{S} - \frac{h_{\text{creep}}}{P},
\]
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Figure 11: Indentation hardness of 20 phr epoxy after correction for the Bauschinger effect where $\varepsilon$ and $\varepsilon_o$ are, respectively, prestrain level and initial uniaxial yield strain [24].

Figure 12: Indentation hardness of PMR-15 polyimide with a Berkovich indenter tip [40].

where $h_c$ is the creep rate at the end of the holding time and $P$ is the unloading time. Thus, the contact depth $h_c$ of (2) is determined as

$$h_c = \left( h_{\text{max}} - h_{\text{creep}} \right) - e F_{\text{max}} \left( \frac{1}{S} - \frac{h_s}{P} \right). \quad (9)$$

It is seen in Figure 12 that indentation size effect in PMR-15 polyimide is less pronounced than in epoxy and becomes noticeable only at shallow indentation depths of $h_{\text{max}} < 500$ nm [40].

2.2.2. Thermoplastic Polymers. Performing nanoindentation tests with a Berkovich indenter tip, indentation size effect of four thermoplastic polymers PC, PS, PMMA, and UHMWPE was investigated by Briscoe et al. [15]. The effect of tip bluntness/imperfection on the size effect of PMMA is depicted in Figure 13 where $H_I^{\text{corrected}}$ (indentation hardness $H_I$ obtained by a calibrated area function) starts to deviate from $H_I^{\text{uncorrected}}$ (indentation hardness $H_I$ assuming a perfectly sharp Berkovich tip) at $h_{\text{max}}$ of below about 400 nm. It is seen in Figure 13 that tip bluntness becomes important at shallow indentation depths; however, length scale dependent deformation in PMMA is still significant even after tip bluntness correction. Taking the effect of tip bluntness into account, indentation hardness of amorphous polymers PC, PS, and PMMA (including $H_I^{\text{corrected}}$ of Figure 13) is shown in Figure 14 where 10 s loading, holding, and unloading times together with strain rate of 0.1 s$^{-1}$ were imposed in all indentation tests. Size effects are observed for all three polymers as indentation hardness (after correction for the tip bluntness) increases with decreasing indentation depth. High scatter in the experimental data is observed for all three polymers at shallow indentation depths below 100 nm indicating the presence of potential inaccuracies in the hardness determination at these small depths. Ignoring hardness data below 100 nm due to possible inaccuracies such as surface roughness, remarkable length scale dependent deformations are still observed at $h_{\text{max}} > 100$ nm in all three polymers. Similarly, size effects in PC, PS, and PMMA can be observed in Figure 15 where the universal hardness (after correction for the tip bluntness) of these polymers, determined from the same experiments of Figure 13, is plotted over the indentation depth. Higher scatter in the data is again observed at small indentation depths $h_{\text{max}} > 100$ nm. It should be noted that while size effects are clearly observed in PC, PS, and PMMA at depths of above 100 nm the indentation hardness of UHMWPE obtained from the same experiments of Figures 14
Figure 14: Indentation hardness of thermoplastic polymers obtained with 10 s loading, holding, and unloading times together with 0.1 s$^{-1}$ strain rate [15].

Figure 15: Universal hardness of thermoplastic polymers [15] obtained from the same experiments of Figure 14 (10 s loading, holding, and unloading times together with 0.1 s$^{-1}$ strain rate).

and 15 does not show size effect for the same depth range (see Figure 2 where indentation hardness of UHMWPE remains almost constant).

Length scale dependent deformation of thermoplastic polymers is also observed in [28] where nanoindentation tests were performed by a Vicker tip at constant tip velocity during loading and unloading together with a 6 s holding time. The maximum applied force $F_{\text{max}}$ varies from 0.2 to 300 mN where loading rate also increases from 0.14 to 70.61 mN/s with increasing $F_{\text{max}}$. Figure 16 shows indentation size effect in PS and PMMA where universal hardness increases with decreasing $h_{\text{max}}$ [28]. In addition to PS and PMMA, size effects were also observed in other amorphous thermoplastic polymers such as PC, PVC, and SAN where the hardness at shallow indentation depth (universal hardness at $F_{\text{max}} = 0.2$ mN) was found to be significantly higher than the bulk hardness (universal hardness at large indentation depths) [28]. The ratio of the universal hardness at $F_{\text{max}} = 0.2$ mN ($H_{U}^{0.2 \text{mN}}$) to the bulk microhardness ($H_{U}^{\text{bulk}}$) is shown in Table 2 for different amorphous thermoplastic polymers of PS, PMMA, PC, PVC, and SAN. This ratio is around 1.8 for all glassy polymers of Table 2; however, for the more ductile polymer of PVC this ratio is slightly lower (about 1.6) [28]. The effect of material inhomogeneity (change in the material properties through thickness) and surface roughness on the size effect of polymers was also experimentally shown in [28]. In Figure 17, the universal hardness of PS is depicted as a function of indentation depth after 0.5, 1, and 5 $\mu$m of the top surface are removed. A significant decrease is observed in the hardness of PS after removing the top layers of the surface indicating a softening after surface removal. The softening was speculated in [28] to be attributed to a rough surface.

Table 2: $H_{U}^{0.2 \text{mN}}/H_{U}^{\text{bulk}}$ ratio where $H_{U}^{0.2 \text{mN}}$ and $H_{U}^{\text{bulk}}$ are, respectively, the universal hardness at $F_{\text{max}} = 0.2$ mN and large indentation depths [28].

| Sample | $H_{U}^{0.2 \text{mN}}/H_{U}^{\text{bulk}}$ |
|--------|------------------------------------------|
| PS     | 1.84                                     |
| SAN 1  | 1.79                                     |
| SAN 2  | 1.73                                     |
| PMMA 1 | 1.78                                     |
| PMMA 2 | 1.77                                     |
| PVC 1  | 1.60                                     |
| PVC 2  | 1.57                                     |
| PC     | 1.71                                     |
profile (compared to the smooth original surface) due to the cutting process.

Size effects were also observed in nylon 66 (PA66) by nanoindentation experiments with a Berkovich tip [39, 71, 72]. Nanoindentation tests were performed with a continuous stiffness measurement (CSM) approach as follows: loading segment with a constant strain rate of 0.05 s\(^{-1}\) to a depth of 5000 nm, a holding time of 60 s at the maximum applied force followed by unloading segment with the same rate of loading until 10% of the maximum applied force \(F_{\text{max}}\) is reached. The indentation size effect of PA66 is illustrated in Figure 2 where \(H_I\) increases with decreasing \(h_{\text{max}}\) at shallow indentation depths. As observed in [39], polishing does not significantly affect the hardness of PA66 depicted in Figure 2. The indentation size effect of PA66 was found to be unaffected by polishing as almost similar trends in the hardness were obtained for both polished and unpolished samples [39]. Performing nanoindentation tests with the same experimental details of PA66 [39, 71, 72], size effects were also experimentally observed in nylon 6 (PA6) [73–75] which exhibited a similar characteristic as observed in Figure 2 for PA66.

In addition to nylon 66 (PA66) [39, 71, 72] and nylon 6 (PA6) [73–75], length scale dependent deformation was also experimentally observed in nylon 11 (PA11) by nanoindentation testing with a Berkovich indenter tip [63]. As shown in Figure 18, indentation hardness of PA11 remarkably increases with decreasing indentation depth. The same experimental details of PA66 [39, 71, 72], size effects were also experimentally observed in nylon 6 [64]. Indentation hardness \(H_I\) and universal hardness \(H_U\) of PA11 for an indentation depth range of about 30 to 1 \(\mu\)m were depicted in Figure 19 where 20 s loading and unloading times (without holding) were imposed in all tests [64].

Load-controlled indentations on polyamide-imide (PAI) with a Berkovich tip showed that size effect becomes significant at \(h_{\text{max}}\) below 10 \(\mu\)m [64]. Indentation hardness \(H_I\) and universal hardness \(H_U\) of PAI for an indentation depth range of about 30 to 1 \(\mu\)m are depicted in Figure 19 where 20 s loading and unloading times (without holding) were imposed in all tests [64].

Indentation hardness of glassy poly(ethylene terephthalate) (PET) obtained with a Vicker tip is shown in Figure 20 where a 6 s holding time was applied in all nanoindentation tests [61]. It is seen in Figure 20 that indentation hardness \(H_I\) is independent of indentation depth \(h_{\text{max}}\) at \(h_{\text{max}} > 2000\) nm. However, \(H_I\) of PET significantly increases with decreasing \(h_{\text{max}}\) at small indentation depths (see \(H_{I, \text{uncorrected}}\).
in Figure 20). This increase in the hardness of PET with decreasing indentation depth was attributed to indenter tip defects in [61] which will be later discussed in Section 3. Replacing the contact depth $h_{c}$ of (2) with the corrected contact depth $h^{c}$, which includes tip bluntness, indentation hardness of PET is depicted in Figure 20 where hardness remains almost constant with indentation depth (see $H^{c}_{I}$ in Figure 20).

As mentioned above, indentation size effects become more pronounced in thermoset epoxy with increasing crosslink density [23]. Nanoindentation tests on thermoplastic PS with a Berkovich tip (with a tip curvature radius $r = 50$ nm) revealed that the indentation size effects increase with increasing molecular weight [58]. Six different polystyrene standards with molecular weights $(M_{p})$ of 4920, 10050, 19880, 52220, 96000, and 189300 g/mol were studied by nanoindentation testing [58] where 1.2 $\mu$m/min loading and unloading rates were imposed without holding time at peak load. Figure 21 demonstrates the indentation size effect of PS with $M_{p}$ of 52220 g/mol as indentation hardness $H_{I}$ determined by O&P method [53] increases with decreasing depth. The experimental hardness data of Figure 21 has been fitted with the theoretical hardness model of Nix and Gao [1]

$$H = H^{*} \sqrt{\frac{h^{*}}{h} + 1}$$

(10)

where $H^{*}$ is the hardness at infinite/macroscopic depth and $h^{*}$ is a length scale parameter. As shown in Figure 22 and Table 3, the length scale parameter $h^{*}$ increases with increasing molecular weights [58]. Such an increase in the length scale parameter $h^{*}$ indicates that size effect in PS becomes more pronounced by increasing molecular weight. This change in the length scale parameter $h^{*}$ with molecular weight is depicted in Figure 22 for $M_{p}$ of 4920, 10050, 19880, and 52220 g/mol. As molecular weight $L$ increases with increasing molecular weights (see Table 3), it was concluded that $h^{*}$ and subsequently the size effect in PS increase with increasing molecular length [58]. Note that in Figure 22 there is a sudden change in the slope of $h^{*} = M_{p}$ curve between 19880 and 52220 g/mol. A possible explanation for such a sudden change in Figure 22 might be associated with the degree of entanglement [58]. As shown in Figure 22, a critical molecular weight $M_{c} = 36000$ g/mol is reported for PS which can be associated with the minimum length of chains needed for generating chain entanglements. Polystyrene samples with molecular weights lower than $M_{c}$ are characterized by few or no chain entanglement (PS samples with $M_{p}$ of 4920, 10050, and 19880 g/mol), while polystyrene samples with molecular weights higher than $M_{c}$ are characterized by considerable number of chain entanglement (PS sample with $M_{p}$ of 52220 g/mol) which may influence the length scale dependent deformation of PS [58]. It should be mentioned that indentation tests on PS samples with high molecular weights (PS samples with $M_{p}$ of 19880 and 52220 g/mol) provided highly scattered hardness data for which no length scale parameter $(h^{*})$ could be deduced [58]. As shown in Table 3, analogous to size effect in metals where $h^{*}/b$ is constant $(b$ is the Burgers vector) [58], the ratio $h^{*}/R$ is almost constant in PS where $R$ is the end-to-end distance (see [58] and references therein for further information about $R$). In addition to the Oliver and Pharr’s method [53], a direct measurement method was also used to determine the indentation hardness of PS samples where the contact area of the sample at the maximum applied force was calculated by an atomic force microscope (AFM). The hardness data obtained from the direct measurement method, $H^{d}_{I}$, was found to be lower than the ones determined by Oliver and Pharr [53]. However, similar to the trend of $H_{I}$ in Figure 21, a significant increase was observed in $H^{d}_{I}$ (hardness of PS determined by the direct measurement method) with decreasing $h_{\text{max}}$ illustrating the existence of length scale dependent deformation in PS [58].

**Table 3**: Molecular length $L$, end-to-end distance $R$, length scale parameter $h^{*}$, and $h^{*}/R$ ratio of PS with different molecular weights $M_{p}$ [58].

| $M_{p}$ (g/mol) | $L$ (µm) | $R$ (µm) | $h^{*}$ (µm) | $h^{*}/R$ |
|-----------------|----------|----------|--------------|-----------|
| 4920            | 0.015    | 0.0047   | 0.082        | 17        |
| 10050           | 0.030    | 0.0068   | 0.100        | 15        |
| 19880           | 0.059    | 0.0095   | 0.150        | 16        |
| 52220           | 0.150    | 0.0150   | 0.170        | 11        |

2.2.3. Elastomer/Rubber. Redrawn from [36], the indentation hardness of a silicon elastomer as a function of indentation depth is depicted in Figure 2. Comparing with the size effects observed in glassy polymers (both thermoset and thermoplastic) presented above, the size effects in the silicon elastomer [36] are more pronounced as the hardness increases.
by a factor of about seven with decreasing indentation depth from about 1500 to 200 nm. Such an amazing increase in the indentation hardness of silicon elastomer with decreasing depth is also reported in [37] which is redrawn in Figure 23. Nanoindentation tests were carried out by a Berkovich tip with constant loading and unloading rates of 150 $\mu$N/s where Oliver and Pharr’s method [53] was adopted to determine the indentation hardness of Figure 23 [37].

Other nanoindentation studies reported in the literature on filled silicon rubber [38]; natural rubber [76] and PDMS [30–35] also show significant indentation size effects which are also considerably more pronounced than in thermostet and thermoplastic polymers. The size effects in PDMS can be observed in Figure 24 where $H_I$ of two different samples of PDMS (prepared in the same way with 1:1 weight ratio of base agent to curing agent) is plotted with respect to $h_{\text{max}}$ [32]. Each point in Figure 24 represents ten indentations carried out by a Berkovich tip with a curvature radius of about 100 nm [32]. Nanoindentation tests were performed with the same loading and unloading times of 40 s and a holding time of 3 s (each point represents ten indentations) [32].

Similarly, indentation size effect in PDMS was observed in [33] where universal hardness $H_U$ obtained by a sharp Berkovich tip was found to significantly increase with decreasing indentation depth from 5000 to 100 nm. Figure 25 illustrates the length scale dependent deformation of PDMS with 10% cross-link density by volume where $H_U$ is determined with three loading times of 5, 20, and 80 s [33]. It is seen that size effect in PDMS is time independent for $h_{\text{max}} > 1000$ nm. However, $H_U$ increases with decreasing loading time at shallow indentation depths $h_{\text{max}} < 1000$ nm.
indicating time dependence of size effect in PDMS at small indentation depths [33]. In a recent study, indentation size effect of PDMS (with 10% cross-link density by volume) was investigated for an indentation depth of about 5 to 30 μm [59]. Universal hardness of PDMS determined with a Berkovich tip is shown in Figure 26 for two different loading times of 20 and 80 s [59]. It should be here mentioned that, similar to thermoset epoxy [23], size effect in PDMS was observed to increase with increasing cross-link density [34]. Performing indentation tests with a Vicker indenter tip on PDMS samples (with three different cross-link densities of 2.5%, 5%, and 10% by volume) showed that size effect in PDMS becomes more pronounced with increasing cross-link density [34]. As shown in [30, 33, 34, 59] and depicted in Figures 24–26, in addition to being significant, size effect in PDMS can be observed at very high indentation depths (indentation depth in which size effect in PDMS becomes significant was found to be dependent on the cross-link density of PDMS [34]). However, in contrast to [30, 33, 34, 59, 77], size effect in PDMS was only observed at small indentation depths $h_{\text{max}} < 200 \text{ nm}$ [78, 79] indicating that size effect in soft polymers is more complicated as it can be caused by various sources (such as surface detection or adhesion) which will be discussed later.

### 3. Origins of Indentation Size Effect in Polymers

In metals, size effect is usually considered to be associated with geometrically necessary dislocations arising from an increase in strain gradients related to nonuniform plastic deformation [1]. However, size effect characteristics in polymers are more complicated than metals as size effect in polymers has been also observed in elastic deformation [17, 18, 30, 33]. Also, in some polymers as in UHMWPE [15], size effects are essentially absent. Various explanations suggested as the origin of size effect in polymers will be reviewed in the following.

#### 3.1. Higher Order Displacement Gradients

Similar to metals, where indentation size effect is considered to be associated with an increase in strain gradients with decreasing indentation depth [1, 4], size effects in polymers are also attributed to higher order gradients in the displacement [16, 17, 22–25, 29, 33, 49–51, 68]. The effects of higher order displacement gradients on the length scale dependent deformation of polymers were experimentally studied in [25] where the elastic modulus of epoxy was obtained by two indenter tips with different geometries: a Berkovich tip with a curvature radius $r < 40 \text{ nm}$ and a spherical tip with a radius of $R = 250 \mu m$. Figure 27 depicts the elastic modulus of epoxy determined by the Berkovich tip, $E_{\text{Berkovich}}$ (using Oliver and Pharr method [53], see (7)), and the spherical tip, $E_{\text{Hertz}}$ (using Hertz theory [80]), where the elastic modulus $E_{\text{Hertz}}$ is obtained by the Hertz contact theory

$$F = \frac{4}{3} \left( \frac{h}{R} \right)^{3/2} R^2 E_{\text{Hertz}}$$

in which $F$ is the applied force, $h$ the probing depth, $R$ the radius of the sphere, and $E_{\text{Hertz}}$ the reduced elastic modulus obtained from Hertz theory which is related to the elastic modulus of polymer, $E_{\text{Hertz}}$, via

$$\frac{1}{E_{\text{Hertz}}} = \frac{1 - v^2}{E_i} + \frac{1 - v_i^2}{E_i}$$

where, similar to (7), $E_i$ and $v_i$ are, respectively, the elastic modulus and Poisson’s ratio of indenter tip with $v$ being the Poisson’s ratio of the polymer. As it is seen in Figure 27, the
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Figure 27: Elastic modulus of epoxy [25] determined with a Berkovich tip, $E^{\text{Oliver and Pharr}}$, (using Oliver and Pharr method [53] with 20 s loading, holding, and unloading times) and with a spherical tip, $E^{\text{Hertz}}$, (using Hertz theory with 20 s loading time).

The elastic modulus of epoxy obtained with the Berkovich tip, $E^{\text{Oliver and Pharr}}$, increases with decreasing $h_{\text{max}}$ while $E^{\text{Hertz}}$ obtained by the spherical tip remains constant with $h_{\text{max}}$ [25]. Such a different trend in the elastic modulus of epoxy determined by the Berkovich and spherical tips over the probing depths is attributed to the effect of higher order displacement gradients [25]. As shown in Figure 28, applying a sharp indenter tip, the higher order displacement gradients (strain gradients $\chi$ in Figure 28) increase in magnitude with decreasing indentation depth, while these gradients remain essentially constant with $h_{\text{max}}$ when a spherical tip is used [65, 66]. Note that, for a spherical tip, the strain gradient $\chi$ is only dependent on the radius of tip, $R$, and is essentially independent of indentation depth as shown in Figure 28. Similar trends have been also observed in PDMS [59] where elastic modulus of PDMS determined by a Berkovich tip increases with $h_{\text{max}}$, while $E^{\text{Hertz}}$ obtained from spherical tests remains almost constant with indentation depth. As illustrated in Figure 29, the elastic modulus of PDMS determined with a Berkovich tip ($E^{\text{Oliver and Pharr}}$ and $E^{\text{Sneddon}}$ using O&P method and Sneddon’s theory, resp.) increases with decreasing depth, while $E^{\text{Hertz}}$ (applying Hertz theory) obtained with a spherical tip (with a radius of 250 μm) does not change with indentation depth. For elastic materials and a conical tip, $E^{\text{Sneddon}}$ [81] for frictionless indentation can be obtained by Sneddon’s theory via the following load-displacement relation:

$$F = \frac{2\tan(\alpha)E^{\text{Sneddon}}}{\pi(1 - \nu^2)}h^2,$$  \hspace{1cm} (13)

where $\alpha = 70.3^\circ$ is the half angle defining a cone equivalent to a Berkovich tip. It should be here mentioned that, similar to Figures 27 and 29, Swadener et al. [2] observed different trends for the hardness of metals determined by Berkovich and spherical tips. Similar to the present finding in epoxy and PDMS, it was shown that, for metals, hardness determined with a Berkovich tip increases with decreasing $h_{\text{max}}$ whereas hardness is independent of indentation depth when a spherical tip is used [2].

As classical elastoplastic theories do not take the effects of higher order displacement gradients into account, length scale dependent deformation of polymers presented above cannot be predicted by these local classical theories. To capture the abovementioned size effect in polymers, few theoretical models have been developed where size effect of polymers is attributed to the effect of higher order displacement gradients at micro to submicro scales.

Based on a molecular kinking mechanism and the molecular theory of yielding of glassy polymers, a strain gradient plasticity law was developed in [16, 22] where a molecular and temperature dependent strain gradient plasticity parameter was proposed and related to indentation hardness. A theoretical indentation hardness model

$$H = H_\ast \left(1 + \frac{h_\ast}{h}\right)$$  \hspace{1cm} (14)

was proposed in [16, 22] which shows good agreement with the experimental hardness data of the thermoset epoxy and the thermoplastic PC [16] depicted in Figure 2 where $H_\ast$ is the hardness at infinite depth and $h_\ast$ is a constant dependent on material behavior and temperature [16, 22]. A strain gradient plasticity was suggested in [16, 22] which was incorporated into a viscoelastic-plastic constitutive model of [82] to predict size effect of glassy polymers observed in nanoindentation experiments [51]. Finite element simulation results demonstrated that higher order gradients of displacement should be incorporated into constitutive model to capture the length scale dependent deformation of glassy polymers in micro/nanoindentations [51].

Another higher order displacement gradients based model was developed in [49] where size effect in elastic deformation of polymers was attributed to rotation gradients effects arising from finite bending stiffness of polymer chains and their interactions. To account for the effect of higher order gradients of displacement on the deformation mechanism of polymers, the local elastic deformation energy density $W^s$ is augmented by a nonlocal rotation gradients term $W^s_\chi$ yielding the total elastic deformation energy density $W$ [49]

$$W = W^s + W^s_\chi = \frac{1}{2}\epsilon_{ij}C_{ijkl}\epsilon_{kl} + \frac{\vec{K}}{3}X^s_{ij}X^s_{ji}$$  \hspace{1cm} (15)

where $\epsilon_{ij}$ is the infinitesimal strain tensor, $C_{ijkl}$ is the elasticity tensor, and $\vec{K}$ is a material constant (see [49] where $\vec{K}$ is micromechanically motivated). Following couple stress elasticity theory of [83], it is seen in (15) that only the symmetric part of the rotation gradient

$$X^s_{ij} = \frac{1}{2}\left(X_{ij} + X_{ji}\right) = \frac{1}{2}\left(\omega_{ij} + \omega_{ji}\right)$$  \hspace{1cm} (16)
is assumed to contribute to the total elastic deformation energy density $W$ (more specifically to $W_\chi$ in (15)), where the symmetric part of the rotation gradient tensor $\chi_{ij}^S$ in (16) can be either defined by the rotation gradient tensor

$$\chi_{ij} = \frac{1}{2} e^r_{ijm} u^m_{i,jn}$$

or the infinitesimal rotation vector

$$\omega_i = \frac{1}{2} e^r_{ijm} u^m_{n,ji}$$

where $u_i$, $u^r_{i,j}$, and $e^r_{ijm}$ are the displacement vector, displacement gradients, and permutation symbol, respectively [49]. The abovementioned rotation gradient based elastic formulation was extended in [50] to include inelastic deformation and a theoretical hardness model was developed

$$H = H_0 \left( 1 + \frac{c_\ell}{h} \right),$$

where, similar to $H_*$ in (14), $H_0$ is the hardness at infinite/macroscopic depth and $c_\ell$ is the material length scale parameter which has been micromechanically motivated in [50]. The theoretical hardness model (19) showed good agreement with the experimental hardness data of PC [68], epoxy [25,68], PS [68], PAI [68], PA66 [68], PMMA [68], and PDMS [33]. Based on the hardness model (19), a theoretical stiffness model

$$K = H_0 C (c_\ell + 2h)$$

was proposed by Alisafaei et al. [25] where the parameters $H_0$ and $c_\ell$ are obtained by fitting the hardness model (19) to the experimental hardness data and $C$ is a constant equal to 26.43 for Berkovich tip. The theoretical stiffness model (20) was compared with the experimental stiffness, $K_m$, of epoxy [25] and PDMS [33] obtained from nanoindentation tests. $K_m$ is obtained by calculating the derivative of force $F$ with respect to indentation depth $h$ at the last data point of loading curve (point B in Figure I(a)) [25,33]. In Figures 30 and 31, the theoretical stiffness model (20) is compared with the experimental data of $K_m$ obtained for PDMS [33] and epoxy [25], respectively. As demonstrated in Figures 30 and 31, good agreement is found between the experimental stiffness data of PDMS and epoxy with the theoretical stiffness model (20) corroborating the validity of the hardness model (19) to predict the size effects in elastomer PDMS and thermoset epoxy. It is seen in Figures 30 and 31 that, unlike materials which do not exhibit size effect, $K_m$ experimentally determined for PDMS and epoxy do not approach zero when $h_{\text{max}} \to 0$. This trend observed in the experimental stiffness $K_m$ is consistent with the theoretical stiffness model (20) which predicts a nonzero value of the stiffness ($K = c_\ell H_0 C$) when $h_{\text{max}} \to 0$. For materials which do not show size effect ($c_\ell = 0$), the theoretical stiffness model (20) predicts a linear relation between the stiffness $K$ and indentation depth $h$ ($K = 2H_0 C h$) which is consistent with experimental stiffness data of fused silica in [25,33] (size effect in fused silica is known to be not pronounced [84]).

In addition to the two higher order displacement gradient based theories [22, 49] mentioned above, extending the mechanism based theories of crystalline metals, Voyiadjis...
et al. [29] recently developed a strain gradient plasticity formulation for semicrystalline polymers in which size effects in semicrystalline polymers were attributed to crystalline subphase embedded within an amorphous matrix. Two kink mechanisms of grounded kink and active kink were considered to, respectively, capture nonlocalized effects (e.g., uniform plastic deformation) and localized effects (viscoplastic deformation effects induced by nonuniform slippage mechanisms, e.g., localized plastic deformation which is found in indentation tests around a sharp indenter tip). Utilizing a Cosserat continuum formulation and adopting considerations in [49], size effects in amorphous polymers were also elaborately modeled in [29] where a flow rule was proposed for amorphous polymers. Furthermore, a theoretical hardness model was developed

$$\left( \frac{H}{H'} \right)^{\beta} = 1 + \left( \frac{h'}{h} \right)^{\beta/2}, \quad (21)$$

where, similar to (10), (14), and (19), $H'$ is the hardness at infinite depth (microhardness of material which is determined in the absence of size effect), $\beta$ is the tip geometry correction factor represented in (6) and defined in Table 1, and $H'$ is a material constant which is related to the material length scale [29].

It may be worth noting that for the material model of (15) to (18), a finite element procedure has been developed in [85, 86] with which two-dimensional numerical simulations have been performed in [87] to study stiffening effects in reinforced polymer composites with decreasing reinforcement sizes [21]. Similar to the experimental results [21], numerical simulations of [87] showed stiffening of reinforced polymer composites with decreasing reinforcement size at high fiber volume fractions.

3.1.1. Influence of Molecular Structure on ISE. As discussed in Section 2, size effects in elastomers are considerably more pronounced than in plastic polymers (thermoset and thermoplastic polymers). However, as shown in Figure 2, the characteristics of size effects even in thermoset and thermoplastic polymers were found to differ for different polymers. The characteristics of size effect in thermoset and thermoplastic polymers were attributed to molecular structures of these polymers [68] which are discussed here.

**Depth Dependent Hardness of Polymers with Aromatic Components.** Indentation size effect of PC [16] shown in Figure 2 is redrawn in Figure 32 together with a sequence of its molecular structure [68] and the theoretical hardness model (19) where $H_0 = 0.165 \text{ GPa}$ and $c_0 = 0.0442 \mu\text{m}$. It is seen that there is excellent agreement between the experimental hardness data of PC and the theoretical hardness model (19). Such a strong indentation size effect observed at large indentation depths is also observed in epoxy, PS, and PAI where all these polymers contain aromatic components (see [68] for their molecular structures) and their experimental hardness data show excellent agreement with the hardness model (19).

**Depth Dependent Hardness of Polymers without Aromatic Components.** Indentation hardness of UHMWPE as a function of $h_{\text{max}}$ depicted in Figure 2 is redrawn in Figure 33 as well as a sequence of its molecular structure [68]. As mentioned in Section 2 and shown in Figure 33, UHMWPE does not exhibit any significant indentation size effect even at shallow indentation depths $h_{\text{max}} < 50 \text{ nm}$. As demonstrated in Figure 33, unlike the abovementioned polymers with aromatic components, UHMWPE has a homogenous
and highly flexible molecular structure. Similar trend can be observed in PTFE [69] where indentation hardness $H_i$ remains constant with indentation depth indicating that PTFE does not show any indentation size effects at an indentation depth range of about 2000 to 20 nm. Note that, similar to UHMWPE shown in Figure 33, PTFE has a homogenous and highly flexible molecular structure without any aromatic components (see [68]). Indentation size effect of PA66 [39] presented in Figure 2 is also depicted in Figure 34 along with the hardness model (19) with $H_0 = 0.0905$ GPa and $c_i = 0.0276$ μm. Compared to UHMWPE and PTFE, PA66 has a more complex molecular structure (see Figures 33 and 34) and shows indentation size effect at smaller indentation depths (compared to those polymers which contain aromatic components) [68].

3.2. Surface Effect, Friction, Tip Imperfection, and Material Inhomogeneity. In addition to the abovementioned higher order displacement gradient based models, there are also other explanations suggested as the origin of size effect in polymers including change in the material properties through thickness [15], friction [34], surface effects [36, 52], tip imperfection [61], adhesion, and others. Unlike in indentation size effects in metals, where the elastic modulus remains constant with depth, elastic moduli of polymers were found to increase with decreasing indentation depth. As illustrated in Figure 27, elastic modulus $E_{O&P}$ of thermoset epoxy determined by a Berkovich tip increases with decreasing indentation depth. Corresponding to Figures 14 and 15, elastic modulus $E_{O&P}$ of thermoplastic polymers PC, PS, and PMMA, obtained from the same experiments of Figures 14 and 15, increases with decreasing indentation depth (see Figure 35). In addition to thermoplastic polymers PC, PS, and PMMA mentioned above, elastic moduli of other thermoplastic polymers PA66 [39], PMR-15 [40], and PA6 [41] were also found to increase with decreasing $h_{\text{max}}$ (however, opposite to the abovementioned trend for $E_{O&P}$ of thermoplastic polymers, elastic modulus $E_{O&P}$ of PS in [58] was reported to be independent of indentation depth). In addition to thermoset and thermoplastic polymers, elastic modulus of PDMS elastomer was also shown to increase with decreasing indentation depth [30, 59]. As demonstrated in Figure 29, elastic modulus of PDMS obtained by a Berkovich tip ($E_{O&P}$ and $E_{\text{Sneddon}}$ using O&P method and Sneddon’s theory, resp.) increases as $h_{\text{max}}$ decreases [59]. Similarly, in a careful elaborated nanoindentation experiments with a Berkovich tip [30], elastic modulus of PDMS shown in Figure 36 was found to significantly increase with decreasing indentation depth indicating the existence of size effect in elastomers. A straightforward possible explanation for such a change in the elastic modulus can be changes in the material properties through the depth of the polymer [15].
However, in [25, 59, 76] it has been argued that such material inhomogeneities (changes in the material properties through the depth) cannot be the only source of indentation size effect in polymers as the measured elastic moduli of epoxy and PDMS obtained by a spherical tip \((E_{\text{Hertz}},\text{resp.})\) presented in Figures 27 and 29) stay constant with \(h_{\text{max}}\) while the elastic moduli determined by a sharp Berkovich tip increase with decreasing indentation depth. The influences of material inhomogeneity and surface roughness on the size effect of polymers have been investigated in [28] where a significant decrease in the hardness of PS was observed by removing the top surface as shown in Figure 17. However, the hardness of PS still increases with decreasing \(h_{\text{max}}\), even after removing the top layers of the surface, indicating that material inhomogeneity and surface roughness cannot be the only source of length scale dependent deformation in polymers. Furthermore, studying the effects of material inhomogeneity on the size effect of epoxy [17] revealed that the significant increase in the bending rigidity of epoxy microbeams is not associated with the presence of stiff surface layers. Considering material inhomogeneity, it should be mentioned that certain sample fabrication/processing methods may induce structural inhomogeneity that may even result in anisotropic behavior of the polymer sample [88].

In addition to the material inhomogeneity, surface effect/stress and surface roughness are also known to be among the factors that cause indentation size effect at shallow indentation depths [36, 52]. There exists a critical indentation depth below which surface effect plays an important role on the length scale dependent deformation of polymers [36]. Adhesion [89–94] is also another factor that can cause indentation size effect particularly at small indentation depths of soft polymers [59, 60].

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Acknowledgment**

The material of this paper is based on work supported by the U.S. National Science Foundation under Grants no. 1102764 and no. 1126860.

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