

EFFECT OF SIZE ON PROPERTIES OF NANO-STRUCTURED POLYMERS –TRANSITION FROM MACROSCALING TO NANOSCALING

K. W. Lem^{*(1a)}, J. R. Haw⁽¹⁾, D. S. Lee⁽²⁾, C. Brumlik⁽³⁾, S. Sund⁽⁴⁾, S. Curran⁽⁵⁾,
P. Smith⁽⁶⁾, S. Brauer⁽³⁾, D. Schmidt⁽⁷⁾, and Z. Iqbal⁽⁸⁾

- (1) Department of Materials Chemistry & Engineering, Konkuk University, Seoul, Korea. jrhaw@konkuk.ac.kr
(a) Corresponding author :(O) 822-20496247 ;(FAX) 822-4443490; kwlem@konkuk.ac.kr; kwlem2001@yahoo.com
(2) Department of Chemical Engineering, Chonbuk National University, Jeonju, Korea. dslee@jbnu.ac.kr
(3) Nanobiz, LLC, NJ, USA. brumlik@nanobizllc.com; sambrauer@nanotechplus.net
(4) Nygard Consulting, LLC, NJ, USA. seas_nj@yahoo.com
(5) Boston Scientific, MA, USA. sean.curran2@bsci.com
(6) Knowles Electronics, IL, USA. apetesmith@aol.com
(7) Materials to Market, LLC, NJ, USA. j.david.schmidt@embarqmail.com
(8) Department of Chem. and Environmental Sci., New Jersey Institute of Technology, NJ, USA. iqbal@adm.njit.edu

ABSTRACT

The growth in investment on the effect of size in nanoscience and nanotechnology has been astounding. Of the \$12.4B spent in 2006 worldwide Nanotechnology research funding [1], at least 50 % was spent on the effect of size for the development of nanomaterials and devices. The focus of nanoscience is to understand the influence of size on the material properties, while nanotechnology focuses on using size effects to create structures, devices and systems with novel properties and functions.

Based on literature data, we have demonstrated that a modified Hall-Petch relation is useful to relate the observed “effective” nanosize to physical properties. Several viscoelastic models have been developed to explain the role surface molecular dynamics plays in thermal mechanical behavior. The polymers examined including polystyrene, polymethyl methacrylate, and MetafuseTM.

Keywords: nanoscaling, tunable properties, hall-petch relation, transitions, interfacial dynamic

1. INTRODUCTION

Materials such as metals, ceramics, and polymers exhibit characteristic bulk properties, as well as characteristic response to sizes on the nanoscale. Metals are strong and ductile, but optically opaque and reflective. They exhibit high thermal and electrical conductivity. Ceramics are compounds of metallic & non-metallic elements such as oxides, carbides, nitrides, sulfides. They are brittle, glassy, elastic, and non-conducting. Polymers are of long chain organic molecules with many repeated units. They are soft, ductile, low strength, low density; and can be optically translucent or transparent. They are typically thermal and electrical insulators.

Fundamental structure changes with size have led to the size dependent material properties which are substantially different from their counterparts in bulk[2]. The extent of delocalization of valence electrons can vary with the size of the system, and quantum effects become relevant for sizes less than 10 nm. Material properties become tunable by size; notably, coordination number imperfection, surface relaxation behavior and surface, nanosolidification in physical properties, superplasticity in mechanical properties, melting and thermal diffusivity in thermal properties, acoustic phonon hardening and optical phonon softening behavior, quantum confinement effects in optical properties, work function and dielectric suppression in electrical properties, and magnetic modulation in magnetic properties. For example, the bandgap of semiconductors such as ZnO, CdS, and Si, changes with size, and magnetic materials such as Fe, Co, Ni, Fe₃O₄, etc., exhibit size dependent magnetic memory properties.

2. EFFECT OF SIZE ON PROPERTIES

The Hall-Petch relation in Eq. 1 where $b = -0.5$ has been used to describe the effect of grain size on the yield or flow stress for metal systems empirically[3]

$$\sigma_y = \sigma_o + K_y * d^b \quad (1)$$

Where σ_y is the yield stress for a polycrystal, σ_o is the yield stress for a single crystal or a polycrystal with an infinitely large grain size, d is the average grain size, and K_y is a Hall-Petch material specific constant. Grain boundaries in metal systems play a critical role obstructing the movement of dislocations, thereby influencing the yield or flow stress. When the grain size is very large or extremely small, Hall-Petch relation at $b = -0.5$ fails to describe the effect of grain size on yield or flow stress, and toughness for metal systems. Consequently, a new

relationship must be developed to predict grain size effects at the nanoscale.

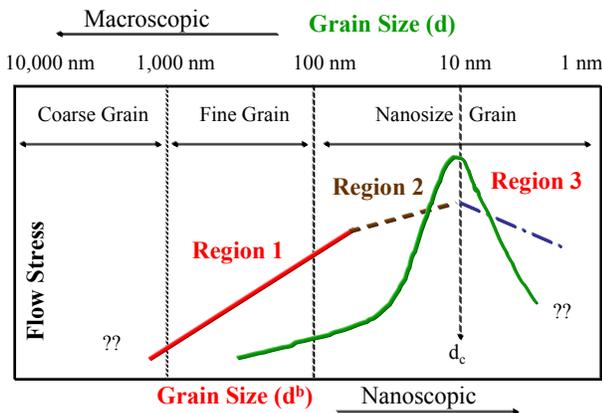
3. SIZE EFFECT ON NANOSCALING

Nanoscale, material properties vary as a function of the size compared with the same materials on a macroscale. Sun in 2007[2] has given an extensive review on evaluation of the bond-order-length-strength (BOLS) mechanism on the effect of size on the usual behavior of material properties. An inverse Hall–Petch relation was reported by Nieh and Wadsworth[4] for grain sizes below a certain threshold, d_c as seen in Figure 1. Conrad and Jung[5] have identified the following three discernible regions in relationship of the effect of grain size from mm to nm on the flow stress and plastic deformation kinetics of Au particles at 300 °K:

1. Region I ($d > \sim 0.5 \mu\text{m}$), Grain size hardening in accord with the Hall–Petch Relation;
2. Region II ($d \approx 10\text{--}500 \text{ nm}$) Grain size hardening in accord with the Hall–Petch Relation;
3. Regime III ($d < \sim 10 \text{ nm}$). Grain size softening with the flow stress proportional to $b = 1$ in Relation (Inverse Hall–Petch Relation).

They reported that the general behavior of Au nanoparticles is similar to that reported previously for Cu and Ag nanoparticles. Sülleiová et al.[6] have confirmed findings of these three regions in their work on nanocrystalline copper. They reported that the Hall-Petch equation is applicable to the range from mono-crystal to the grain size of $1 \mu\text{m}$, where the exponent, b , has values from -0.5 to 1 . However, at grain size ranging from 10 to 100 nm b is less than -0.5 . Finally for the grain sizes $< 10 \text{ nm}$, b can change its value. At this level of grain size, the material has extremely high volume fraction of grain boundaries, exceeding 50% [6].

Figure 1 - Macroscopic to Nanoscopic Transition
Adopted from Nieh and Wadsworth[4]; Sülleiová et al.[6]



TUNABLE PROPERTIES BY SIZE

In most of nanotechnology studies, the size range of greatest interest is typically from 100 nm down to approximately 0.2 nm , because in this size range properties of the materials become tunable. Three primary reasons for this tunable behavior are believed to be:

- (1) Increases in relative surface area vs. bulk volume,
- (2) Increases in % of atoms/molecules on the surface,
- (3) The dominance of quantum effects.

The increased surface area per unit mass and % of atoms on the surface result in a corresponding increase in chemical reactivity. Thus, some nanomaterials become useful as catalysts to improve the efficiency of fuel cells and batteries, or in “soft” nanotechnology for cosmetics and pharmaceuticals[7].

The effect of size on other properties such as surface tension or ‘stickiness’ and thermal transition temperatures are also important, because these characteristics directly affect physical and chemical properties.

4. EQUATIONS FOR NANOSCALING

Based on the data reported in the literature to date, an equation similar to Hall and Petch relation (Eq. 1) has been reported to predict size dependent nanomaterial properties as shown in Eq. 2.

$$A = A_0 + K * d^b \quad (2)$$

Where A is the size-dependent material properties, A_0 and K are material specific constants independent of size. They may be affected by temperature, time, pressure, and other service parameters. The exponent, b , is a constant for a given size range.

We must point out at this juncture that equations obtained empirically may oversimplify underlying scientific principles. Such equations should be used with caution. However this empirical approach may find its usefulness when the data is difficult to obtain. It may provide at least an order of magnitude estimate to predict trends of tunable material properties.

Some examples of such predictions are given in the literature. Nanda[8] highlighted that Pawlow in 1909 had predicted a melting point depression of nano metal particles. Melting point is inversely proportional to the particle size (d) using a thermodynamic model. Similar results were reported by Kang et al.[9] in their phonon spectrum study. In a simulation based on a statistical melting criterion, they found that a lowering in nano metal particles’ melting point is inversely proportional to the particle size (d). Kelsall et al.[10] reported that the linear strain of a nanomaterial is inversely proportional to particle

size (d) as the nearest-neighbor distance decreases with decreasing size. Surface cohesion energy can be actually more stable than the volume cohesion energy in nanoparticles due to the fact that cohesion energy decreases as diameter of nanoparticles decrease. Yaghmaee and Shokri[11] have proposed Eq. (3) illustrating that the cohesive energy of nanoparticle is inverse proportional to the nanoparticle' diameter.

$$E_p = E_b \left(1 - \frac{1}{f_v} \frac{d_a}{d_p} \right) \quad (3)$$

Where E_p is the cohesive energy for particle, and E_b is the cohesive energy in bulk, f_v is the package factor, d_a is the diameter of the atom in neutral state, and d_p is the diameter of the particle.

5. POLYMER HYBRIDS - METAFUSE™

DuPont's MetaFuse™ product line is based on nanocrystalline metal/polymer hybrid materials that have lightweight engineering plastics components in complex shapes with the stiffness of soft metals such as magnesium or aluminum. The technology is based on deposition of nanocrystalline metal (such as nickel with average grain size of 20 nm) on the surface of molded engineering plastics. According to Ray[12], at this range of the grain size, the nanocrystalline metal particles increase the mechanical properties including yield strength, hardness, and wear resistance because it follows a Hall-Petch relation (see Eq. (1)). Interestingly, Sun [2] reported that the onset of modulus increase in nickel nanoparticles is ~ 2 – 3 nm, at which the inverse Hall-Petch relation may prevail.

Polymers are viscoelastic which means they exhibit both viscous and elastic responses when undergoing deformation. Viscoelastic behaviors are dynamic in nature, characterized by their time dependence, loading history dependence, and lack of a one-to-one correspondence between stress and strain. All polymers exhibit a glass transition temperature (T_g) and this can be considered to be one of the most important polymeric material properties. Below the glass transition temperature, the materials act as hard, rigid glasses. Above T_g , they are soft and flexible. In general, any factor that affects segmental mobility will affect T_g . This includes factors that influence the nature of the moving segment, chain stiffness or steric hindrance, and those that influence the free volume available for segmental motion. All of these factors come into play for nanoscaled polymer structures.

6. NANOSCALING IN POLYMERS

In the last two decades, literature studies have reported that the dynamic properties of polymer materials at a nanosize thickness (typically <100nm thick) are found to be

very different to those found in the bulk materials. Fu et al.[13] reported recently that the Young's modulus of poly(vinyl alcohol) (PVA) nanofibers increased dramatically when their diameter became very small. The onset of the change is at approximately 140 nm. They report that the Young's modulus increases from 35 GPa at 160 nm diameter to about 530 GPa at 20 nm diameter. In their recent dielectric dynamic study of isotactic PMMA, polyvinylacetate, poly(2-vinylpyridine), and hyperbranched aromatic polyesters, Sergei et al.[14] observed that branched polymers (hyperbranched aromatic polyesters) appear to experience a more pronounced change in measured mean relaxation time for the dynamic glass transition compared with linear polymers (isotactic PMMA). In addition, the onset of the change for the branched polymers was observed to take place at much larger film thicknesses than that of the linear polymers. They reported onset temperatures of isotactic PMMA at 6 nm, polyvinylacetate at 16 nm, poly(2-vinylpyridine) at 36 nm, and hyperbranched aromatic polyesters at 200 nm film thickness.

The root cause of these anomalies is believed to be interfacial properties. This hypothesis has been substantiated by both experiments and computer simulation. Most researchers have found that these anomalies become profound with decreasing film thickness. Thus, the dependence of dynamic properties of nanothin polymer films qualitatively follows the relation described by Eq. (2). Yet quantitative understanding of the role of the interface still remains an elusive and controversial topic[15].

7. NANOTHIN POLYMER FILMS - T_g

Kim et al.[16] reported that the T_g increases with decreasing film thickness for the nanothin films of polymers that have attractive interaction such as PMMA and P2VP. The T_g of nanothin polystyrene (PS) films was reported to be lower than the T_g of bulk films when the thickness of the film was reduced. At approximately 10 nm film thickness, the T_g of PS films can be decreased by as much as 25 °K compared to the T_g in the bulk [17]. Singh et al. [18] have observed that the decrease in T_g depends on both film thickness and polystyrene molecular weight.

Table 1 gives a summary of the equations reported in the literature for T_g of as a function of film thickness in form of Eq. (2).

Table 1 – PS Films Thickness on T_g in Eq. (2)

| A_0 | K | b | Source |
|--|--|-------------|---------------------------------|
| $A_0 = T_{g, \text{bulk}}$ | $K = - (T_{g, \text{bulk}}) \times (a)^{1.8}$, where $a = 32$ angstroms | $b = -1.80$ | Forrest and Dalnoki-Veress [17] |
| $A_0 = T_{g, \text{bulk}} = (366 - 113000/Mw)$ | $K = - (T_{g, \text{bulk}}) \times (g)$, where $g = (1/14.4) \times (Rg)^{1.78}$ and $Rg = \{s^2\}^{1/2} = \text{RMS radius of gyration}$ | $b = -1.78$ | Singh et al. [18] |

Table 2 gives a summary of regression results based on the data and equation (by keeping $b = -1.78$) as reported by Singh et al.[18]. As seen on Table 2, The value A_0 is very close to the bulk T_g of polystyrene ($\sim 92^\circ\text{C}$ or 365°K), whereas the material constant, K , is related to the radius of gyration of polystyrene. K shows a molecular weight and molecular weight distribution dependence as expected.

Table 2: Regression Results for T_g as a Function of PS Films Thickness in Eq. (2)

| Polymer | A_0 | K | b | Source |
|-------------------------------|--|---|-------------|-------------------|
| Polystyrene | $A_0 = T_{g, \text{bulk}} = (366 - 113000/Mw)$ | $K = -(T_{g, \text{bulk}}) \times (g)$, where $g = (1/14.4) \times (Rg)^{1.78}$ and $Rg = \{s^2\}^{1/2}$ = RMS radius of gyration | $b = -1.78$ | Singh et al. [18] |
| Mw/Mn = 2.00; Mw = 239,700 | $A=367.5$ | $K = -3203.5$ | $b = -1.78$ | $R^2 = 0.98$ |
| Mw/Mn = 1.05; Mw = 212,400 | $A=365.7$ | $K = -2029.1$ | $b = -1.78$ | $R^2 = 0.98$ |
| Mw = 157,100 | $A=365.0$ | $K = -5087.7$ | $b = -1.78$ | $R^2 = 0.89$ |
| Mw = 212,400 | $A=365.9$ | $K = -1970.0$ | $b = -1.78$ | $R^2 = 0.95$ |
| Mw = 560,900 | $A=365.9$ | $K = -3677.2$ | $b = -1.78$ | $R^2 = 0.97$ |

8. FUTURE STUDIES

In this paper, we showed how a modified Hall-Petch relation was found to be useful to predict the effect of size on the change of nanomaterial properties. It provides a “quick and dirty” means to qualitatively evaluate nanoscaling trends and forecast material properties. Nonetheless, we need to be cautious because these types of relations are empirical and often oversimplify the underlying science. Ideally, size effect on dynamic interface properties and the role molecular dynamics at the surface interface should be quantified from the scientific first principles. As the size of matter is reduced to <100 nm, and material properties become tunable, specific quantum effects need to be identified that play a critical role in significantly changing a material’s optical, magnetic, electrical, thermal and mechanical properties.

The studies from Serghei et al.[14], Qi[15] and Sun[2] should be continued with a focus to determine the role of molecular dynamic at the surfaces. The techniques developed by Han[19] (especially the plots of \log (storage modulus) vs. \log (loss modulus)), and Nagai et al. [20] (nanorheological measurement by AFM) should be employed to study the effect of size on dynamic flow behavior and molecular mobility. This will provide an understanding of the role of molecular characteristics and chemical nature in transitions from the bulk to the interface. The focus on the molecular characteristics include molecular weight, molecular weight distribution, degree of long chain branching, influence of ionic, hydrogen and other secondary bonding. Chemical nature is emphasized on flexible homopolymers, miscible and immiscible blends, composites, block and graft copolymers, liquid crystalline polymers, laminates, nanocellular plastics, and polymer

hybrids. Our current research focus is on pursuing this elucidation of the relationships of polymer properties to chemistry, molecular weight, branching at the nanoscale.

REFERENCES

- [1] V. Mamikunian, “Investor Enthusiasm for Nanotech Opportunities in Electronics,” Lux Research Inc. 3-15, 2007
- [2] C. Q. Sun, Progress in Solid State Chemistry, 35, 1-159, 2007.
- [3] W.D. Callister, Jr. and D. G. Rethwisch, “Materials Science and Engineering – An Introduction,” 8th Edition, Wiley & Sons, 2010.
- [4] T.G. Nieh and J. Wadsworth, *Scripta Metall. Mater.* **25**, 955, 1991.
- [5] H. Conrad, K. Jung, Materials Science and Engineering A 406, 78–85, 2005
- [6] K. Sülleiová, M.Besterici, and T.Kvackaj, METAL 2009, 5, 19–21, 2009
- [7] S. Brauer, K.W. Lem, and J.R. Haw, Presented in Nano and Green Technology Conference 2009, New York City, November 17-19, 2009.
- [8] K.K. Nanda, PRAMANA - Journal of Physics, 72 (4), 617-628, 2009.
- [9] K. Kang, S. J Qin, C. Wang, Physica E41, 817–821, 2009.
- [10] R.W. Kelsall, I.W. Hamley and M Geoghegan; “Nanoscale Science and Technology,” Wiley & Sons, 2005.
- [11] M. S. Yaghmaee and B. Shokri, Smart Mater. Struct. 16, 349–354, 2007.
- [12] M. R. Day, “Nanometal Polymer Hybrid,” Advanced Materials & Processes, 25-27, April 2008.
- [13] Q. Fu, Y. Jin, X. F. Song, J. Y. Gao, X. B. Han, X.G. Jiang, Q. Zhao, and D.P. Yu, Nanotech. 21, 095703, 2010.
- [14] A. Serghei, M. Tress, and F. Kremer, J. Chem. Physics 131, 154904, 2009.
- [15] D. P. Qi, “On near-free-surface dynamics of thin polymer films,” Ph.D. Dissertation, University of Waterloo, Waterloo, Ontario, Canada, 2009.
- [16] C. J. Kim, A. Facchetti, and T. J. Marks, JACS, 131, 9122-9132, 2009.
- [17] J. A. Forrest and K. Dalnoki-Veress, Advances in Colloid and Interface Science, 94, 167-196, 2001.
- [18] L. Singh, P. J. Ludovice, C.L. Henderson, Thin Solid Films 449, 231–241, 2004.
- [19] C. D. Han, “Rheology and Processing of Polymeric Materials (Vol. 1 & 2)”, Oxford University Press, 2007.
- [20] S. Nagai, S. Fujinami, K. Nakajima, and T. Nishi, Composite Interfaces, 16, 13–25, 2009.

¹ [2010 NSTI – Paper# 301] Nanotech 2010, 696 San Ramon Valley Boulevard, Suite 423, Danville, CA 94526-4022, Ph: (925) 353-5004, Fax: (925) 886-8461, swenning@nsti.org.