Nano-indentation of Polycarbonate and Diamine Blends

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Abstract

Nanoindentation of complex surfaces is of great interest from academic and industrial point of view. There are unique properties such as indentation effects resulting in strain softening and strain hardening. There is a differentiation in structure with the depth exhibited with variation of Tg. Hertzian and non-linear deformation models including usage of FEM offer opportunity in analyzing nano-indentation. Organic photoreceptors having compounds in Charge Transport Layer for improving charge acceptance and wider spectral sensitivity often results in short operating life from increased wear and scratch rates. Photoreceptor life has been found to be extended by doping polycarbonate with doped with polytetrafluoruethylene (PTFE) and/or silica. Presence of diamine(MTBD) in polycarbonate results in making the surface and bulk brittle and acts as an anti-plasticizer by increasing it modulus and reducing yield stress (hardness) and strain to break. Data on modulus and hardness of polycarbonate and blends of diamine as function of depth (strain) and strain rate are presented and compared with models.

Introduction

In the past decade nanoindentation, using applied load and depth data obtained during the experiment, has been extensively applied to study the surface and near-surface mechanical properties of thin films. At the micro/nanometer scales, the hardness and modulus depend on the indentation depth or load, exhibiting the well-known Indentation Size Effect (ISE). A decrease in the hardness with increasing indentation depth or load has been observed in numerous micro or nano-indentation tests on various materials such as metals, diamond-like carbon, polymers, ceramics, etc. which may be called the normal ISE. The inverse ISE has also been reported, in which the hardness increases with increasing indentation depth or load [1,2]. Surface glass transition temperature (Tg) behavior has been studied for amorphous polystyrene (PS) with implementation of a scanning force microscopy (SFM) force-distance mode. Entanglement of polymer chains, rather than localization of chain-ends at the surface, is responsible for the enhanced polymer chain mobility in a surface layer.

Both linear and non-linear deformation models have been used to describe nano-indentation of surfaces. Most linear deformation models are derived from Hertzian theory of contact between two smooth, ellipsoidal solids. Indentation of a rigid sphere into an elastic half space is analyzed under the assumptions that strains are small, indented solid is a linear elastic, infinite half space and.the surfaces are frictionless. Since indenting tip sample interaction is unavoidable during indentation due to the effect of structure and chemistry of the tip. For large compliant surfaces, Hertz theory was modified to include the existence of attractive forces between both contacting hard and rubber-like solids [3]. Based on classical Hertzian contact theory, the load (P) applied to the indenter tip is related to the total penetration depth into the substrate (h).

$$\frac{dP}{dh} = \frac{2\sqrt{A}E}{\sqrt{\pi}\left(1-\nu^{2}\right)} \tag{1}$$

where P is the load measured by the indenter, E and ν are the Young's modulus and Poisson's ratio of the material that is being indented and h is the displacement of the indenter

For a Berkovich/Vickers indenters, the angle a = 70.3, and the corresponding projected area, A is given by

$$A = \pi \tan^{2}\alpha\, h_{c}^{2} = 245\, h_{c}^{2} \tag{2}$$

where hc refers to the contact depth and is given by

$$h_{c} = h - \frac{2(\pi-2)}{\pi}\frac{P}{dP/dh} \tag{3}$$

Thus, using the load–displacement curve measured during an indentation, one can obtain the elastic constants of the specimen of interest using the following equation:

$$\frac{E}{\left(1-\nu^{2}\right)} = \frac{1}{2\beta}\sqrt{\frac{\pi}{A}}\frac{dP}{dh} \tag{4}$$

where β is a non-dimensional correction factor to account for deviations from the original stiffness equation (β= 1 in (4)). The factor βis used to account for the treatment of a pyramidal indenter as an equivalent conical indenter, β is unity for axisymmetric indenters and close to unity for pyramidal ones, β= 1.012 for square-based indenter, e.g., Vickers, and β= 1.034 for a triangular punch, e.g., Berkovich.

The right-hand side of (4) consists of terms that can be derived using the load–displacement measurements in an indentation experiment. Thus, using this relationship, the term on the left-hand side of the equation consisting of both E and μ, commonly referred to as the reduced modulus, Er, can be evaluated. It is important to note that the elastic constants, E and μ evaluated using this procedure are coupled and thus require a priori knowledge of one of them to calculate the other. When the indenter is not considered as rigid, the reduced modulus, Er is given by

$$\frac{1}{E_{r}} = \frac{\left(1-\nu^{2}_{specimen}\right)}{E_{specimen}} + \frac{\left(1-\nu^{2}_{indenter}\right)}{E_{indenter}} \tag{5}$$

This analysis based on the method of Oliver and Pharr assumes that unloading is elastic, creep influences calculation of S, and thereby E and Ac depends on the initial unloading slope S. (see Figure 1) Additionally, around the indent perimeter, material may pile up, resulting in a larger contact area Ac than inferred from the Oliver and Pharr procedure. Also, A last factor is that for shallow indents (up to 50 nm) the Young's elastic modulus may differ from that of the bulk owing to confinement effects.

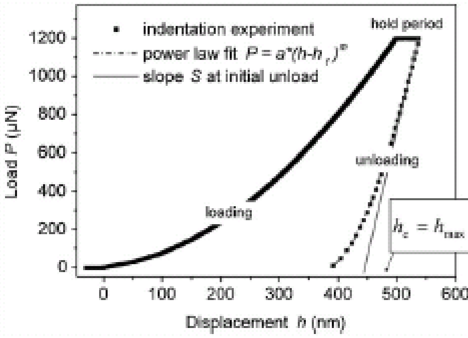

Figure 1. Load–displacement response obtained upon indenting polystyrene with a Berkovich indenter, showing the fit applied in the Oliver and Pharr method to obtain the slope S at the onset of the unloading step as well as the contact depth hc. Pmax and hmax are the load and indentation depth just prior to unloading, respectively. The final displacement hf is the (fitted) identation depth after unloading.

This modified Hertz theory named the JKR (Johnson–Kendall–Roberts) theory considers an apparent Hertz load, or the equivalent load in the absence of adhesion that produces the enlarged contact area. The JKR theory was found to be valid for the indentation of relatively compliant materials with probes of relatively large radii and strong adhesive forces [4]. In contrast, DMT (Derjaguin– Muller–Toporov) theory is applicable under conditions where indenting probe has a small radius and is indenting into a stiff material with weak adhesive forces [5,6]. Consequently, Hertzian deformation profile is expected.

Dimitriadis et al. addressed the failure of Hertzian contact mechanics to estimate elastic modulus from the loading portion of the load indentation response for compliant samples of finite thickness, and offered a modified model including a film thickness correction. The model assumes an appropriate range of sample thickness and indentation depth for a given spherical indenter probe radius. This is based on the assumption that, for a material to behave as a linear elastic solid, the maximum nominal strains should not exceed 10%,[7,8]

A polymer's intrinsic response to deformation is split into two parallel processes: a contribution from the secondary interactions, especially active at small strains, namely the initial modulus and the yield stress σy, determined by the stress-dependent strongly nonlinear viscosity function η, and a contribution from the network in the hardening modulus GR, only active at large strains. The initially linear elastic response up to yield is thus controlled by the secondary intermolecular interactions and, therefore, depends amongst others on the temperature. The higher the interactions between the chains, the more difficult it is for the chains to move (modulus) and start flowing (yielding). Therefore, yield stress is high for strongly interacting polymers. The yield stress level and strain softening can be reversibly decreased by thermal rejuvenation, i.e. heating above Tg followed by quenching. Strain hardening is connected with orienting molecular network and that its magnitude appears to be governed by thermally-induced segmental mobility influenced greatly by transition temperature. Strain hardening is increased by chemical crosslinking of a polymer.

Organic photoreceptor for digital imaging is made up of an imaging member comprising: an electrically conductive substrate or a substrate comprising an electrically conductive layer; a photogenerating layer; and, a charge transport layer deposited on the photogenerating layer. The charge transport layer consists of a polymer binder such as polycarbonate and charge transport molecule such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine Presence of the charge transport molecule in polycarbonate shortens photoreceptor life.

Improvements in photoreceptor life have been patented. For instance, the concentration of the charge transport compound in the charge transport layer decreases from the lower surface to the upper surface. In such a construction, the resulting charge transport layer exhibits enhanced cracking suppression, improved wear resistance, excellent imaging member electrical performance, and improved copy print out quality [9,10]. Similarly in another instance, addition of nano-additives in the composition of transport surface layer enhances photoreceptor life by suppressing crack enhancement [11].

The combination of fillers of large interfacial contact area, high aspect ratio, and low mass density results in interfacial sliding of fillers within a polymer matrix with the potential to cause significant dissipation of energy with minimal weight penalty. Another advantage of nanoparticles is that the nanoscale inclusions could potentially be seamlessly integrated within composite/heterogeneous systems without sacrificing mechanical properties or structural integrity.

Plasticization and antiplasticization

Additives significantly affect relaxation processes in glassy polymers, as evidenced by phenomena such as plasticization and antiplasticization. In the liquid range, the plasticization effect whereby the glass-transition temperature (Tg) of the polymer is reduced when additives are added. It is an acceleration of the cooperative a-relaxation processes of the polymer, and the effect has been satisfactorily explained on the basis of conventional free-volume theories. In the glassy state well below Tg of the polymer mixture, the situation is entirely different [12].

The glassy mixtures are not at all plasticized but rather found to be hardened and more brittle than the neat polymers. This antiplasticization effect is possibly related to the phenomenon that in many polymeric mixtures the secondary mechanical relaxation processes are suppressed. Consequently, either the polymer chains have some small degree of mobility that allows them to align themselves in a more ordered densely packed state or the additives fill the excess volume of the polymer glass. Antiplasticization in polymers is molecular weight dependent and additive concentration dependent. On the basis of these results, they made a hypothesis that the phenomenon can be attributed to a chain-end effect, that is, the additive may initially fill the smaller holes at the chain ends. Mobility of the chain ends is restricted and results in embrittlement of the polymer [13].

Materials and Method:

Materials used in this study were polycarbonate (Makrolon), polyester (bisphenol-A propylene oxide fumarate). Polycarbonate was mixed with silica or a small organic diamine molecule (Alkoxy derivative of tetra phenyl biphenyl diamine). The polymers filled or unfilled were solution coated and dried at 110C for half an hour. The nanoindentation experiments were performed using a Hysitron Triboscope (Hysitron Inc., USA) with a diamond probe. A diamond Berkovich indenter with a tip radius of 50 nm and a maximum load ranging from 100 to 1000 N were used for evaluating the Young's modulus and hardness of the PC material.

Hardness is defined as a measurement of the material resistance to local plastic deformation[14]. Thus, the hardness H can be measured by a probe indentation from the maximum applied load, Pmax; divided by the contact area, A; that is

$$H = \frac{P_{\max}}{A} \qquad (6)$$

$$A(h) = 24.5h^2$$

where the contact area is a function of the penetration depth, h; and is determined according to the following form: The constant of 24.5 was used, since it is assumed that a Berkovich indenter has a perfect tip. Following the molecular theory of yield for glassy polymers, Lam and Chong [15] proposed a size-dependent hardness for polymers.

$$H = H_0\left(1 + \sqrt{\frac{h^*}{h}}\right) \qquad (7)$$

Result and Discussion

The effect of diamine molecule in polycarbonate is to decrease Tg of the polycarbonate composite, decrease percentage of strain to break and increase Young' s modulus (see Table 1 and Figure 2). The Diamine in the PC results Tg. drops and keeps on dropping so much so that at 40% level Tg. drops from 150C to 80C. Correspondingly. Elastic modulus keeps on increasing, while yield stress, strain to break decreases. While PC requires 50% strain before it breaks in compression, addition of 20% and 40% Diamine molecule increases brittleness such that strain to break is reduced to 20% and 5% respectively.

The additive in the polycarbonate acts as an antiplasticizer. The degree of the antiplasticizing effect, in a given polymer, depends on the type and level of the additives used. It is considered that for an additive to act as an antiplasticizer its molecules should be compatible with the polymer, relatively planar and rigid, and contain such atoms as halogen, nitrogen, oxygen, etc. The majority of known antiplasticizers are low molecular weight substances and most studies of anti-plasticization have been devoted to the polymer--diluent interaction

Table 1 Properties of polycarbonate containing various concentrations of diamine

Property	0% Diamine	10% Diamine	20% Diamine	40% Diamine
Tg©	150	120	100	80
%Strain to break	50	30	20	5
E(Mpa)	400	420	450	500
Toughness(MPa/m)	3.5	2.1	1.4	0.35

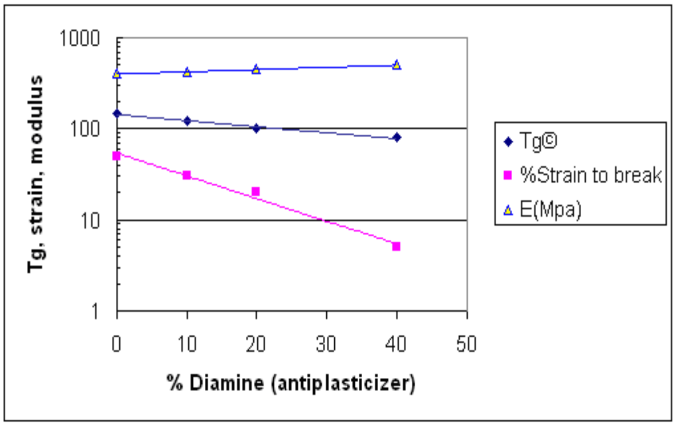

Fig. 2 Effect of % Diamine on polycarbonate composite

Table 2 Effect of surface modulus on depth

Depth (nm)	PC (GPa)	PC+ 10% Diamine) (GPa)	PC+ 20% Diamine) (GPa)	PC+ 40% Diamine) (GPa)
100	300	320	340	370
200	270	300	320	350
400	260	290	310	330
800	250	280	300	320

From the Table 2, it appears modulus of the polycarbonate increases as concentration of Diamine molecule increases. With silicone filler in polycarbonate, composite modulus increases. Hardness of polycarbonate decreases with increase in diamine concentration, an additive (see Table 3).

Table 3 Effect of surface hardness on depth

Depth (nm)	PC (MPa)	PC+ 10% Diamine) (MPa)	PC+ 20% Diamine) (MPa)	PC+ 40% Diamine) (MPa)
100	0.34	0.31	0.27	0.25
200	0.30	0.28	0.25	0.23
400	0.26	0.24	0.21	0.19
800	0.23	0.22	0.18	0.17

Conclusion:

Polycarbonate is a flexible and tough polymer but on addition of Charge Transport Small Molecule to polycarbonate resulted in increase in brittleness and decrease in toughness. Nanocomposites of diamine in polycarbonate results in increase in elastic modulus but decrease in glass transition. This behavior of diamine in polycarbonate is that of an antiplasticizer and is different from that of a filler where both glass transition and modulus are increased as the concentration of filler is increased in polycarbonate.

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Author Biography

Suresh Ahuja received his BS in physics and chemistry from the Punjab University (1959), his MS in Soil Physics from Indian Research Institute (1961) and his PhD in Polymer Physics from Polytechnic Institute of Brooklyn (1967). After working over 37 years at Xerox with several years as Principal Scientist he retired. He has several patents including three this year. He has published over 70 publications and presentations at international conferences. He is a member of APS, ASME, SOR and IST.