Using Microprojectiles to Study the Ballistic Limit of Polymer Thin Films

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Supporting Information

Materials

Polycarbonate (Poly(bisphenol-A carbonate), $M_w = 60,000$ g mol⁻¹) was purchased from Scientific Polymer Products, Inc. Cyclohexanone (99 % purity) was purchased from Sigma Aldrich. TEM grids (PELCO, Tabbed 100 mesh, Nickel) were purchased from Ted Pella, Inc. Soda lime glass microspheres were obtained from Cospheric Inc. Polydimethylsiloxane (PDMS, Sylgard 184) was purchased from Dow Chemicals and used in a 10:1 mass ratio of prepolymer to catalyst.

Ablation Target Preparation

Particle targets were prepared by first sputter coating 20 nm of gold on a 20 cm by 40 cm glass cover slip. Next, PDMS was mixed, degassed for 20 min, and subsequently deposited via spin-coating (2500 rpm for 10 minutes) to form a 20 μ m thick elastomeric layer. The deposited film was further degassed for another 10 min and finally thermally cured at 120 °C for 15 min. Microparticles (lime glass) were directly deposited onto the prepared substrate. An air gun was used to evenly disperse the particles on the surface and to remove any excess or large aggregates of particles. Inspection via optical microscopy confirmed that the microparticles were a monolayer thick.

Sample Preparation

Polycarbonate (PC) ($M_w = 60.7 \text{ kg mol}^{-1}$, 3 % by mass to 5 % by mass) was dissolved in cyclohexanone on a stir plate heated at 80 °C until complete dissolution. PC films with thicknesses ranging from 50 nm to 300 nm were prepared by spin coating onto 2 cm by 2 cm silicon substrates cleaned with UV-Ozone irradiation. Thicker films (> 300 nm) were prepared via blade coating using the same solutions. The cast films were dried in a vacuum oven at room temperature for at least 12 h to remove any excess solvents. Film thickness before and after drying was measured at a minimum of 9 spots via optical profilometry (F3-NIR Profilometer, Filmetrics). The thickness variations between the different spots were < 1%. Films were then diced into 2 mm by 2 mm squares with a razor blade and floated off in a water bath. The diced PC films were then transferred directly onto a TEM grid. Each grid was visually inspected with a video camera (PixeLink) prior to testing. The transferred PC films were found to be in good contract with the TEM grid and were used without further processing.

Laser-Induced Projectile Impact Test (LIPIT)

A pulsed diode-pumped solid-state IR laser (Flare NX, $\lambda = 1030$ nm, pulse length = 1.5 ns, Coherent Inc.) was used as the ablation source to accelerate a single particle at the ablation target. A video camera (PixeLink) was used to measure, track, and focus onto individual micro-projectiles through a 20X microscope objective (SLMPLN20x, NA = 0.25, Olympus). Each selected particle ($2a_p = 25 \pm 1 \ \mu m$) is digitally inspected prior to launch, with a small uncertainty from the particles potentially being slightly out-of-focus. The ablation target was set 1 mm away from the sample.

A stroboscopic imaging technique was employed to determine the kinetic energy transfer of this high rate impact event. IR pulses

 $(\lambda = 1030 \text{ nm}, \text{ pulse length} = 300 \text{ fs})$ from a diode-pumped, variable pulse length laser (Monaco Industrial Laser, Coherent Inc.) was converted into green light ($\lambda = 515$ nm) using a doubling crystal. The strobe laser has a tunable repetition rate of 200 kHz to 10 MHz. A sCMOS camera (PCO Edge 4.2, PCO) captures the laser strobes and outputs a single image containing the spatial history of the projectile. The velocity of the microparticle can be determined from the optical image by dividing the distance travelled by the time between each laser pulse, which was determined by the laser repetition rate. The error from the pixel resolution was < 1% of the measured inter-particle distance. Synchronization of the ablation event, laser strobe, and image acquisition was achieved via digital triggers modulated using a digital waveform generator (NI-9402, National Instruments). A schematic of the LIPIT instrument is shown in the Supporting Information. At least 30 ballistic impact tests were conducted for each PC film thickness.

Scanning Electron Microscopy

A scanning electron microscope (Quanta 200 ESEM, FEI) was used to image and evaluate the damaged region and perforation of the PC thin films. For all SEM imaging, the acceleration voltage was set to 3 kV and the working distance was set to 10 mm. Prior to SEM imaging, the PC samples were sputter-coated with 15 nm of gold to enhance electron conductivity.

LIPIT Setup



Figure S1 Schematic of the LIPIT optical setup. L=lens, Obj=objective, M=mirror, F=filter, BS=beam splitter, HWP=half-wave plate, P=polarizer, BE=beam expander, and DC=doubling crystal.

Strain Rate Calculation

Using the analysis detailed by Lee et al.¹, strain rate can be estimated by the maximum cone side and the time it takes for the penetrating event to occur:

$$\dot{\varepsilon} \cong (v_i/L_{max})^2 t_p/2 \tag{S.1}$$

where L_{max} is the maximum radius of the expanding cone-shaped deformation region at the point of impact, and t_p is the penetration time that is estimated by $t_p \cong L_{max}/v_c$. The velocity at which the cone expands, v_c , is approximated by:

$$v_c \cong 1.23 c_{||} [v_i / (2^{1/2} c_{||})]^{2/3}$$
 (S.2)

where $c_{||} = 2270 \text{ m s}^{-1}$ is the in-plane speed of sound for polycarbonate. For $v_i = 55 \text{ m s}^{-1}$ and $L_{max} \approx 20 \mu \text{m}$, the speed

of the expanding cone is calculated to be $v_c \cong 186 \text{ m s}^{-1}$ and $t_p \cong 107.8 \times 10^{-9} \text{ s}$. By plugging these values into **Equation S.1**, the strain rate of the impact is estimated to be $\approx 4 \times 10^5 \text{ s}^{-1}$.

Kinetic Energy Change

Consider a microparticle with mass m_p , density ρ_p , and radius a_p with an impact velocity v_i impacting a film with mass m_f , density ρ_f , and thickness h. If we assume that this impact is an inelastic collision that results in a plug of material, with radius a_f , being removed from the film, then conservation of momentum dictates that:

$$m_p v_i = (m_p + m_f) v_r \tag{S.3}$$

where v_r is the resultant velocity of the combined microparticle and film.

Equation S.3 is derived based on balance of forces between the microparticle and polymer film. For such a collision, the force experienced by either object must be equal and opposite in magnitude, thus $F_p = -F_f$. Since each object interacts with the other one for the same amount of time $(\Delta t_p = \Delta t_f)$, the impulse experienced by each object must satisfy, $F_p \Delta t_p = -F_f \Delta t_f$. Invoking impulse-momentum change theorem ($F\Delta t = m\Delta v$), we obtain: $m_p \Delta v_p = -m_f \Delta v_f$. For $\Delta v_p = v_r - v_i$ and $\Delta v_f = v_r$, this expression simplifies to: $m_p v_i = (m_p + m_f) v_r$. In reference to our LIPIT experiments, the implications of this derivation is that m_f is not a constant defined by the mass of the plug material $(=\rho_f \pi a_p^2 h)$ that is directly in contact with the microparticle, and we may think of m_f as an "effective" mass, which is dependent on the dimensions of the film that interacts with the particle as well as the material properties. This concept of an "added" or "effective" mass has been used for inelastic collisions in hydrodynamics problems and also when determining the coefficient of restitution of compliant objects.²

We can also derive an expression for kinetic energy change:

$$\frac{1}{2}m_p v_i^2 = \frac{1}{2}(m_p + m_f)v_r^2 + E_d$$
(S.4)

with E_d constituting the various energy dissipating processes including work of fracture, adiabatic heating, plastic yielding, and etc. Rearranging **Equation S.4** yields,

$$v_r^2 = \left(\frac{m_p}{m_p + m_f}\right) v_i^2 - \frac{2E_d}{m_p + m_f}$$

$$= \alpha v_i^2 - \gamma$$
(S.5)

where $\alpha = \frac{m_p}{m_p + m_f}$ is the mass fraction of the microparticle relative to the entire system and $\gamma = \frac{2E_d}{m_p + m_f}$ is a energy dissipation term that is normalized by the total mass of the system.

We note that $\beta = 1 - \alpha$ is defined as the fraction of kinetic energy lost due to this inelastic collision event. Specifically, α is the ratio of the kinetic energy after $(E_{k,r})$ and before $(E_{k,i})$ the impact. By substituting $v_r = \frac{m_p}{m_p + m_f} v_i$ from the conservation of momentum (**Equation S.3**),

$$\frac{E_{k,r}}{E_{k,i}} = \frac{\frac{1}{2}(m_p + m_f)v_r^2}{\frac{1}{2}m_p v_i^2} \\
= \frac{\frac{1}{2}(m_p + m_f)\left(\frac{m_p}{m_p + m_f}v_i\right)^2}{\frac{1}{2}m_p v_i^2} \\
= \frac{m_p}{m_p + m_f} = \alpha$$
(S.6)

The fraction of kinetic energy lost is then,

$$\frac{E_{k,i} - E_{k,r}}{E_{k,i}} = 1 - \frac{E_{k,r}}{E_{k,i}}$$
$$= 1 - \frac{m_p}{m_p + m_f} = 1 - \alpha \qquad (S.7)$$
$$= \frac{m_f}{m_p + m_f} = \beta$$

We can determine the relationship between β and E_d by deriving **Equation S.6** and **Equation S.7** differently,

$$\frac{E_{k,r}}{E_{k,i}} = \frac{\frac{1}{2}(m_p + m_f)v_r^2}{\frac{1}{2}m_pv_i^2}
= \frac{\frac{1}{2}(m_p + m_f)\left(\frac{m_p}{m_p + m_f}v_i^2 - \frac{2E_d}{m_p + m_f}\right)}{\frac{1}{2}m_pv_i^2}
= \frac{\frac{1}{2}m_pv_i^2 - E_d}{\frac{1}{2}m_pv_i^2} = 1 - \frac{E_d}{\frac{1}{2}m_pv_i^2}$$
(S.8)

$$\frac{E_{k,i} - E_{k,r}}{E_{k,i}} = 1 - \left[1 - \frac{E_d}{\frac{1}{2}m_p v_i^2}\right] = \frac{E_d}{\frac{1}{2}m_p v_i^2}$$
(S.9)

Equating Equation S.7 with Equation S.9, we obtain,

$$\beta = \frac{E_d}{\frac{1}{2}m_p v_i^2} = \frac{E_d}{\frac{1}{2}m_p V_0^2}$$
(S.10)

where V_0 is the ballistic limit and defined in **Equation S.11**. We set v_i equal to V_0 because $v_i = V_0$ at the ballistic limit, the point at which the maximum amount of energy is dissipated. At the critical film thickness, $\beta = 1$ since $E_d = \frac{1}{2}m_pV_0^2$ but $E_d < \frac{1}{2}m_pV_0^2$ below the critical film thickness.

Extrapolating α

From the above relationships, we see that both α and β scale with v_i and v_r . At a given v_i , we can extrapolate α as a function of h to determine the critical thickness required to prevent perforation 100% of the time. To determine α , we plot v_r^2 vs. v_i^2 for each film thickness and fit the linear function defined in **Equation S.5**. The slope of this function is α .

Ballistic Limit

Equation S.5 shows several trends for a microparticle impact experiment.

- 1. v_r increases as v_i increases thus implying that for a given materials system with fixed m_p , m_f and E_d , the ballistic resistance decreases with increasing v_i of the microparticle.
- 2. v_r increases with increasing m_p due to increased inertia of the microparticle.
- 3. v_r decreases with increasing m_f , which enhances inertial resistance due to the added mass of the film.
- 4. v_r decreases as E_d increases to the point where $v_r = 0$ when $\frac{1}{2}m_p v_i^2 = E_d$ thus defining the ballistic limit of the material.

We define the ballistic limit of the materials system according to comment 4 above. Specifically, the ballistic limit (V_0) is defined as the critical incident velocity at which the residual velocity becomes zero. According to **Equation S.4**, the ballistic limit is related to m_p and E_d ,

$$V_0 = \sqrt{\frac{2E_{d,V_0}}{m_p}}$$
(S.11)



Figure S2 β vs. h.

Energy Dissipation

If we consider the simplest scenario where E_{d,V_0} is attributed entirely to the work of fracture (W_f) of the plug of material (diameter $= 2a_f$) being sheared away from the film,

$$W_f = \int_0^h (2\pi a_f) \sigma_Y z dz$$

= $\pi a_f \sigma_Y h^2$ (S.12)

Assuming $E_{d,V_0} = W_f$ and using **Equation S.11**,

$$\sigma_{Y,V_0} = \frac{E_{d,V_0}}{\pi a_f h_{V_0}^2} = \frac{m_p V_0^2}{2\pi a_f h_{V_0}^2}$$
(S.13)

Assuming $m_p = 28.7$ ng, $V_0 = 55$ m s⁻¹, $h_{V_0} = 200$ nm and $a_f = a_p = 12.5 \ \mu$ m, we obtain $\sigma_{Y,V_0} \cong 27$ GPa according to **Equation S.13**, which is an extremely high and improbable value given that reported values for PC at similar testing velocity is 3 orders of magnitude lower ($\sigma_Y \cong 100$ MPa). This implies that $W_f \ll E_{d,V_0}$ and other mechanisms of energy dissipation contribute to E_d . We can gain some insight by focusing on the films below the critical thickness. Based on the results shown in **Figure S2**, $\beta \sim h^3$.

If we account for the elastic deformation of the film during impact, the elastic energy of this process (ignoring deformation of the microparticle) is,

$$E_{el} \cong \frac{1}{2} k_f \delta^2 \tag{S.14}$$

where $k_f = \frac{E_f^* h^3}{c_\delta l^2}$ with the plane-strain elastic modulus $(E_f^* = 1/(1 - v_f^2))$, *l* is the span of the film and δ is the out-of-plane deformation of the film. c_δ is a geometric parameter that is defined by the deformation profile of the film and is a function of the film's Poisson's ratio (v_f) , δ , and *l*. Specifically, we now assume that $E_d = W_f + E_{el}$. Combining **Equation S.12** and **Equation S.14** into **Equation S.10**,

$$\beta = \frac{\pi a_p \sigma_Y h^2 + \frac{1}{2} \frac{E_f^* (\delta_f / l)^2}{c_\delta} h^3}{\frac{1}{2} m_p V_0^2} = D_2 h^2 + D_3 h^3$$
(S.15)

where $D_2 = \frac{2\pi a_p \sigma_Y}{m_p V_0^2}$ and $D_3 = \frac{E_f^* (\delta_f / l)^2}{c_\delta m_p V_0^2}$.

From the SEM images of the post-perforated samples, there is evidence that the PC films experience film drawing most likely due to adiabatic work (W_T). We assume that E_T depends on the deformation rate (i.e., v_i) since adiabatic work is related to the amount of plastic work that is converted to heat,

$$W_T \cong \rho_p v_i^2 V_f \tag{S.16}$$

where ρ_p is the density of the microparticle and $V_f \cong \pi a_f^2 h$ is the volume of the film. Therefore, we assume that $W_T \sim h$.

Since our LIPIT experiments were conducted in ambient conditions, another energy dissipation mechanism is air drag (E_{drag}) of the microparticle.

$$E_{drag} = \frac{1}{2} C_d \rho_{air} \pi a_p^2 \delta_p {v_i}^2 \tag{S.17}$$

where $C_d = 0.47$ is the coefficient of drag for a spherical microparticle. E_{drag} describes the amount of energy expended when the microparticle traveling at v_i displaces a mass of air over a distance δ_p . This mass of air is defined by $\pi a_p^2 \delta_p \rho_{air}$.

Combining Equation S.16 and Equation S.17 with Equation S.15 and defining $D_0 = E_{drag}/(m_p v_i^2/2)$ and $D_1 h = W_T/(m_p v_i^2/2)$,

$$\beta = D_0 + D_1 h + D_2 h^2 + D_3 h^3 \tag{S.18}$$

For the parameter D_3 , we estimate c_δ using the work of Heap on the deflection of a circular plate (Case I),³

$$c_{\delta} = \frac{3}{2} \left[\frac{a_p^2}{l^2} + ln \left(\frac{l}{a_p} - 1 \right) \left(1 - \frac{2a_p^2}{l^2 - a_p^2} \left(ln \frac{l}{a_p} \right)^2 \right) \right]$$
(S.19)

We quantify c_{δ} by estimating *l* from the microprojectile image (S3) and assuming $a_p = 12.5 \ \mu\text{m}$.



Figure S3 Representative microprojectile image used to estimate *l*.

Materials Properties Extrapolation

The literature values for the yield stress (σ_Y) and elastic modulus (E_f) of PC were obtain from the dynamic impact testing results of PC by Sarva and Boyce.⁴

Figure S4 plots the true yield stress vs. true yield strain results on the Kolsky bar compression testing of PC from Sarva and Boyce up to the highest strain rate measured ($\approx 5000 \text{ s}^{-1}$). We use this result to extrapolate σ_Y , by fitting with the expression shown in the figure, to a strain rate relevant to our LIPIT experiments. At a strain rate of $4 \times 10^5 \text{ s}^{-1}$, we obtain $\sigma_Y \cong 169$ MPa.

Figure S5 plots the true stress vs. true strain results on PC at a compressive strain rate of $\approx 5000 \text{ s}^{-1}$. We extrapolate the results to obtain the elastic modulus of PC, $E_f \cong 3.2$ GPa at this strain rate.

Notes and references

- J.-H. Lee, P. E. Loya, J. Lou and E. L. Thomas, Science, 2014, 346, 1092–1096.
- [2] R. Cross, Sports Engineering, 2014, 17, 3–22.
- [3] J. C. Heap, Journal of Engineering for Industry, 1968, 90, 268– 278.
- [4] S. Sarva and M. Boyce, Journal of Mechanics of Materials and Structures, 2007, 2, 1853–1880.



Figure S4 True yield stress vs. true strain rate data from Sarva and Boyce on dynamic compression of PC. $^{\rm 4}$



Figure S5 True stress vs. true strain data from Sarva and Boyce of PC deformed at a compressive strain rate $\approx 5000~s^{-1}.^4$