Entanglement Density-Dependent Energy Absorption of Polycarbonate Films via Supersonic Fracture

Edwin P. Chan,†,‡,§, turtles.159K PC with Aroclor 1260 at 5 mass %, 10 mass %, and 15 mass % Aroclor. As a reference, we prepared PS thin films. We control the entanglement density of PC in two ways.7 The first is via changes to the molecular mass of the PC and the second is via the addition of Aroclor, a chlorinated biphenyl plasticizer for PC. Details of the sample preparation procedure are provided in the Supporting Information. Table 1 summarizes the thickness (h), the number (M̅), and weight (M)n average molecular mass of the PC films studied using LIPIT. The plasticized PC series were prepared by combining the 15.9K PC with Aroclor 1260 at 5 mass %, 10 mass %, and 15 mass % Aroclor. As a reference, we prepared PS films for LIPIT testing using a similar sample preparation procedure. All the films were targeted to be ≈200 nm thick. We also conducted LIPIT measurements on the same materials at other thicknesses and did not see noticeable changes in the results.

Figure 1a is a schematic of the LIPIT instrument, which utilizes laser ablation of gold to propel a microparticle to the target and to measure the puncture energy from LIPIT.

Supporting Information

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The LIPIT experiments were conducted in vacuum to minimize the effects of air drag. In the absence of air drag, $\Delta E_k = E_p$, with $E_p$ encompassing the various dissipation mechanisms including elastic stretching, fracture, and adiabatic heating of the film. Since $E_p$ also includes the kinetic energy transfer to the film and the removal of a plug of material, it is expressed as

$$E_p = \frac{\rho_p A h}{2} v_i^2 + E_d$$

(2)

The first term is the minimum inelastic energy transfer to the material for a given $h$ and puncture area, which is estimated by $A = \pi a^2$. The second term ($E_d$) represents all other energy dissipation mechanisms. To compare materials with different mass densities ($\rho_p$), the specific puncture energy is used instead as it is insensitive to the mass of the material ($\rho_p A h$) in contributing to energy dissipation.

$$E_p^\# = \frac{E_p}{\rho_p A h} = \frac{v_i^2}{2} + E_d^\#$$

(3)

Therefore, $E_p^\# = E_d/\rho_p A h$ is a metric for quantifying the extent of energy dissipation of a given material as the first term represents the lower limit of energy dissipation.

The strain rate ($\dot{\varepsilon}$) is a function of the radial rate of expansion of the deformed region of the polymer film, which is approximated as a cone-shaped expanding membrane of radius $R_c$.

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Table 1. Summary of Polycarbonate (PC) Film Properties Studied in This Work$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_n$ (kg/mol)</th>
<th>$T_g$ (°C)</th>
<th>$\rho_f$ (g/cm$^3$)</th>
<th>$h$ (nm)</th>
<th>$v_i$ (m/s)</th>
<th>$A_{lm}$ (µm$^2$)</th>
<th>$v_r$ (m/s)</th>
<th>$t_p$ (10$^{-9}$ s)</th>
<th>$\Delta \varepsilon/\Delta t$ (10$^{-7}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Mass Series</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.3K</td>
<td>8.3 ± 0.3</td>
<td>25.2 ± 1.0</td>
<td>149</td>
<td>1.19</td>
<td>200 ± 8</td>
<td>508 ± 22</td>
<td>114 ± 13</td>
<td>≈743</td>
<td>≈8.1</td>
<td>≈2.9</td>
</tr>
<tr>
<td>11.4K</td>
<td>11.4 ± 0.2</td>
<td>38.0 ± 0.4</td>
<td>↓</td>
<td>↓</td>
<td>140 ± 9</td>
<td>483 ± 16</td>
<td>167 ± 12</td>
<td>≈719</td>
<td>≈10.1</td>
<td>≈2.2</td>
</tr>
<tr>
<td>14.8K</td>
<td>14.8 ± 0.5</td>
<td>48.2 ± 3.1</td>
<td></td>
<td></td>
<td>165 ± 6</td>
<td>514 ± 29</td>
<td>185 ± 19</td>
<td>≈749</td>
<td>≈10.2</td>
<td>≈2.3</td>
</tr>
<tr>
<td>15.9K</td>
<td>15.9 ± 2.1</td>
<td>59.3 ± 3.7</td>
<td></td>
<td></td>
<td>271 ± 2</td>
<td>513 ± 24</td>
<td>215 ± 14</td>
<td>≈748</td>
<td>≈11.1</td>
<td>≈2.1</td>
</tr>
<tr>
<td>26.0K</td>
<td>26.0 ± 0.4</td>
<td>59.3 ± 0.5</td>
<td></td>
<td></td>
<td>200 ± 6</td>
<td>504 ± 19</td>
<td>246 ± 36</td>
<td>≈740</td>
<td>≈12.0</td>
<td>≈1.9</td>
</tr>
<tr>
<td>Plasticized Series</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% aro.</td>
<td>15.9 ± 2.1</td>
<td>59.3 ± 3.7</td>
<td>132</td>
<td>1.22</td>
<td>166 ± 8</td>
<td>513 ± 21</td>
<td>159 ± 26</td>
<td>≈748</td>
<td>≈9.5</td>
<td>≈2.5</td>
</tr>
<tr>
<td>10% aro.</td>
<td>15.9 ± 2.1</td>
<td>59.3 ± 3.7</td>
<td>116</td>
<td>1.24</td>
<td>143 ± 14</td>
<td>510 ± 23</td>
<td>108 ± 15</td>
<td>≈741</td>
<td>≈7.9</td>
<td>≈3.0</td>
</tr>
<tr>
<td>15% aro.</td>
<td>15.9 ± 2.1</td>
<td>59.3 ± 3.7</td>
<td>103</td>
<td>1.26</td>
<td>163 ± 11</td>
<td>503 ± 29</td>
<td>126 ± 18</td>
<td>≈732</td>
<td>≈8.6</td>
<td>≈2.7</td>
</tr>
</tbody>
</table>

“$^a$The glass transition temperatures ($T_g$) were obtained from Psurek et al.$^8$ The error represents standard deviation of at least three measurements.

Figure 1. LIPIT experiment. (a) Schematic of the LIPIT instrument. The instrument utilizes laser-induced forward transfer to launch a 7.6 µm SiO$_2$ microparticle at supersonic velocity from the surface of a rapidly expanding polydimethylsiloxane (PDMS) membrane to puncture a free-standing thin polycarbonate (PC) film that is adhered to a TEM grid. (b) Stroboscopic image of the puncture event used to quantify the velocity profile of the microparticle. (c) Velocity profile of the microparticle illustrating the difference in the impact velocity ($v_i$) prior to puncture of the PC film and the residual velocity ($v_r$) following puncture.
where $e_{\text{max}} \cong (v_t/2R_c)^2$ is a 1-D approximation of the maximum tensile strain for an isotropic membrane experiencing biaxial deformation. The parameter, $t_p \cong R_c/v_\nu$, is the puncture time of the microparticle and is related to the cone velocity ($v_\nu \cong 1.23c_\pi\sqrt{E/\rho}$), where $c_\pi = \sqrt{E/\rho}$ is the in-plane speed of sound in the material that is a function of the plane-strain elastic modulus ($E^* = E/(1 - \nu^2)$) and mass density of the polymer.\(^{10}\)

The strain is maximum near the center of impact, it decreases radially and reduces to zero at $\approx v_x/t_p$. This 1-D model underestimates $e_{\text{max}}$, because it assumes the mass of the local volume element responding to the propagating mechanical wave is held constant whereas the mass increases radially from the center of impact in a 2-D membrane. Thus, the actual radial strain profile is strongly localized around the puncture center and decreases faster than the prediction by this 1-D model.\(^2\) We use scanning electron microscopy (SEM) to quantify the postpuncture plastically deformed area ($A_{\text{def}}$) of each polymer film and estimate $R_c \approx \sqrt{A_{\text{def}}/\pi}$. Assuming the elastic modulus for bulk PC ($E^b \approx 3.5 \times 10^4$ N/m$^2$), $c_\nu \approx 1700$ m/s and $v_\nu \cong 734$ m/s for $v_\nu \cong 500$ m/s. Thus, $\Delta e/\Delta t$ ranges from $\approx 2 \times 10^4$ s$^{-1}$ to $\approx 3 \times 10^4$ s$^{-1}$.

The work of fracture of a material, closely approximated by the area beneath a stress vs strain curve, is enhanced with increasing volume of plastic deformation. This trend is observed in Figure 2 when we compare $E_p^*$ with $A_{\text{def}}$ Top-down SEM micrographs of the punctured PC samples show that the molecular mass PC series all undergo shear yielding.

![Figure 2](image-url)  
**Figure 2.** Specific puncture energy ($E_p^*$) vs plastically deformed area ($A_{\text{def}}$) for the molecular mass and the Aroclor plasticized PC series. The cartoon illustrates the deformation of the film during the puncture event and highlights the conically deformed area of the film. The top down SEM micrographs illustrate the deformation mechanism for all the PC samples post puncture. The error bars represent standard deviation of at least three measurements. Scale bar = 10 µm.
induces a ductile-to-brittle transition. The shape of the stress–strain curve for the plasticized PC is more consistent with a classic brittle fracture with little plastic deformation. As demonstrated in Figure 2, it is challenging to correlate $A_{d,c}$ which is a projected area averaged around the punctured region, with $E_{p}^e$ due to the difficulty in identifying the true interfacial regions of the film that has plastically deformed. Based on the simulations results of Hoy and Robbins that showed that strain hardening is a result of an increased plasticity with ε and $\nu_e$ at high rates,14 we instead use $\nu_e$ as a metric for quantifying plastic deformation. Specifically, we use Bersted’s entanglement model15 to estimate $\nu_e$ for our materials

$$\nu_e = \frac{2\rho_p N_A}{3M_e} \left(1 - \frac{M_e}{M_n}\right)$$

where $M_e \approx 2M_n$, with $M_e \equiv 1.8\text{ kg/mol}$ corresponding to the entanglement molecular mass for PC with $M_e/M_n \approx 8.8$.16

Since $\rho_p$ and $M_e$ for the plasticized PC series are not known, we approximate them by assuming that the increase in Aroclor content leads to proportional changes to these quantities, $\rho_p(x) \equiv x\rho_p(0) + (1 - x)p_{aro}$ and $M_e(x) \equiv M_{e,PC}/\phi_p$ where $x_p$ is the mass fraction of PC, $\rho_p(0)$ is the density of the neat PC, as listed in Table 1, $\rho_{aro} = 1.57\text{ g/cm}^3$ is the density of Aroclor,17 and $\phi_p \equiv (x_p/\rho_p)/(x_p/\rho_p + (1 - x_p)/\rho_{aro})$ is the volume fraction of PC. Figure 4 shows that $E_{p}^e$ is strongly correlated with $\nu_e$ for the materials investigated, suggesting that $E_{p}^e \propto \nu_e$.
density of these flaws/voids, thereby increasing the propensity for craze formation since $\sigma_c \ll \sigma_f$.

In summary, our results demonstrate the role of entanglement density in polymer glasses on the energy dissipation in extremely high rate puncture events based on LIPIT. This mechanism of energy dissipation is unique to polymers due to their viscoelastic nature. This control is shown by the proportional change in the specific penetration energy with entanglement density via (1) increasing the molecular mass of the polymer or (2) reducing the plasticizer content that changes the size of the deformation region as well as dictate the specific failure mechanism. One important point we would like to make is that adiabatic heating can be substantial in LIPIT due to extensive shear deformation that leads to thermal softening and increased plasticity. It was suggested that the temperature rise for PS can reach as high as 400 °C.\textsuperscript{5,20} However, simulation results for PC show that it is unique compared to other polymer glasses in that adiabatic heating does not appear to contribute significantly to the high rate mechanical behavior.\textsuperscript{21} This may also help to explain the significantly higher $E_p$ values seen in PC compared with PS since $\nu_e$ would be greatly reduced with adiabatic heating. Additionally, secondary relaxations such as $\beta$ relaxations contribute significantly to the fracture toughness of PC at high testing rates as this molecular relaxation becomes establishing this relationship for PC using LIPIT. Besides $\nu_e$ and failure modes discussed here were established from quasi-static testing conditions. We expect that this relationship to change with deformation rate and we are currently working on the best available for the purpose.

Materials, experimental details, and derivations (PDF)

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00264.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(7) Certain instruments and materials are identified in this paper to adequately specify the experimental details. Such identification does not imply a recommendation by the National Institute of Standards and Technology, nor does it imply that the materials are necessarily the best available for the purpose.


(17) https://pubchem.ncbi.nlm.nih.gov/compound/2_2__3_3__4_4_4_4_hexachlorobiphenyl#section=Top

