THE STUDY OF MECHANICAL RESPONSES IN BOTH UNIAXIAL EXTENSION AND COMPRESSION OF POLYMER GLASSES

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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May, 2016
THE STUDY OF MECHANICAL RESPONSES IN BOTH UNIAXIAL EXTENSION
AND COMPRESSION OF POLYMER GLASSES

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ii
ABSTRACT

The study of polymer glasses is an important subject in research on polymeric materials. Although a lot of efforts have been made in the past several decades, there is still no satisfactory understanding at a molecular level to explain many nonlinear mechanical responses. For example, what determines the mechanical strength in polymer glasses? Why some polymers can be ductile but the others behave in a brittle manner?

In this work, we carried out a series of experiments to study the mechanical responses in both uniaxial extension and compression in an effort to collect more phenomenology. By combining the mechanical measurements with in situ temperature reading, significant buildup of internal energy was observed to take place during large deformation. Elastic yielding experiments were then carried out to elucidate the intra-segmental nature of such internal energy. Inter-segmental interactions were also found to contribute to the stored internal energy. Upon exposure to gamma irradiation, chain network is demonstrated to be essential to preserve chain tension and produce elastic yielding. In addition, we also studied the crazing behavior of polymer glasses. Specifically, it is shown that mechanical rejuvenation through either milling or twisting, suppresses crazing in extension of PC. Crazing re-surfaces upon annealing of the mechanically-rejuvenated PC. A tentative proposal is made to offer an explanation.
ACKNOWLEDGEMENTS

First of all, I would like to express my sincere thanks to my advisor, Dr. Shi-Qing Wang, for his guidance and help throughout my doctoral research. I have learned a lot from him, not only on the knowledge of polymer rheology and glasses and critical thinking to solve problems, but also on the attitude to be a good person. I feel really lucky to have this opportunity to work with him and his passion for true science will always encourage me for my whole life.

Also, I would like to thank my dissertation committee: Dr. Mesfin Tsige, Dr. Stephen Z.D. Cheng, Dr. Toshikazu Miyoshi and Dr. David Simmons for their valuable comments and suggestions. I appreciate all their help and instructions on my research projects.

I am grateful for all the help from my previous and current group members: Dr. Xiangyang Zhu, Dr. Greg Zartman, Dr. Shiwang Cheng, Dr. Hao Sun, Dr. Gengxin Liu, Mr. Jianning Liu, Ms. Xiaoxiao Li, Mr. Mengchen Wang, Mr. Yexin Zheng, Ms. Yue Zhao, Mr. Sirui Ge, and Mr. Zhichen Zhao. I really enjoy working with them and benefit a lot from their suggestions and encouragement.

I would like to thank Mr. Ed Laughlin from the machine shop for his help on experimental devices. I would like to thank Ms. Karen Jackson for her help on the design of the homemade oven. I would like to thank Mr. Jack Gillespie for his help on the sample cutting.
I would like to thank all my friends for their support, especially my friends from “poly 龙 er”. Without them, I cannot imagine my life at Akron.

Last but not least, I would like to thank my family for their love.
TABLE OF CONTENTS

LIST OF TABLES ............................................................................................................. ix
LIST OF FIGURES ............................................................................................................. x

CHAPTER
I. INTRODUCTION ............................................................................................................1
II. CHARACTERISTICS OF POLYMER GLASSES ..........................................................4
  2.1 Glass Transition ....................................................................................................... 5
  2.2 External deformation of polymer glasses ............................................................... 7
  2.3 Nonlinear behavior of polymer glasses upon deformation ....................................... 8
    2.3.1 Yielding, necking and strain hardening ............................................................ 8
    2.3.2 Brittle failure ................................................................................................... 10
    2.3.3 Rejuvenation effect vs. aging effect ................................................................ 11
  2.4 The molecular picture of the hybrid structure ....................................................... 16
    2.4.1 Melt stretching ............................................................................................... 19
    2.4.2 Physical aging vs. mechanical rejuvenation ................................................... 21
III. ORIGIN OF STRESS IN EXTENSION AND COMPRESSION OF POLYMER GLASSES ................................................................................................................. 23
  3.1 Background ............................................................................................................. 23
    3.1.1 Experimental studies on the origin of stress ................................................... 24
    3.1.2 Simulations on the origin of stress ................................................................. 27
    3.1.3 Theories on the origin of stress ...................................................................... 28
3.2 Experiments ........................................................................................................... 30
  3.2.1 Materials and sample preparation ................................................................. 30
  3.2.2 Apparatus and methods ................................................................................. 32
3.3 Theoretical analysis ............................................................................................. 32
  3.3.1 Neck front propagation in isotropic PC during uniaxial extension .......... 33
  3.3.2 Uniform extension ....................................................................................... 39
  3.3.3 Uniform compression ................................................................................. 40
3.4 Results .................................................................................................................... 41
  3.4.1 Isotropic PC during uniaxial extension ......................................................... 42
  3.4.2 Milled PC during uniaxial extension ............................................................. 49
  3.4.3 Melt-stretched PC during uniaxial extension ................................................. 55
  3.4.4 Isotropic PC during uniaxial compression .................................................... 57
3.5 Discussions ............................................................................................................ 63
  3.5.1 Nature of internal potential energy $u_2$ ...................................................... 64
  3.5.2 Difference between milled and melt-stretched PC: dissipative vs. elastic .... 67
  3.5.3 Difference between uniaxial extension and compression ........................... 68
3.6 Summary ................................................................................................................. 68
IV. ELASTIC YIELDING BEHAVIOR ........................................................................... 70
  4.1 Background ......................................................................................................... 70
  4.2 Experiments ....................................................................................................... 74
    4.2.1 Materials and sample preparation ............................................................... 74
    4.2.2 Apparatus and methods .............................................................................. 75
  4.3 Results ............................................................................................................... 77
    4.3.1 Pre-draw rate effect .................................................................................... 77
4.3.2 Pre-draw ratio effect ....................................................................................... 79
4.3.3 Annealing temperature effect ........................................................................ 83
4.3.4 Gamma irradiation effect ................................................................................ 84
4.4 Discussions ............................................................................................................ 93
  4.4.1 Mechanism of elastic yielding ........................................................................ 93
  4.4.2 Gamma irradiation effect ................................................................................ 95
4.5 Summary ................................................................................................................ 96

V. CRAZING BEHAVIOR IN CREEP MODE ................................................................. 98
  5.1 Background ............................................................................................................ 98
  5.2 Experiments ......................................................................................................... 103
    5.2.1 Materials and sample preparation ................................................................. 103
    5.2.2 Apparatus and methods ................................................................................. 104
  5.3 Results .................................................................................................................. 104
    5.3.1 Rejuvenation effect ....................................................................................... 104
    5.3.2 Aging effect .................................................................................................. 114
  5.4 Discussions ........................................................................................................... 120
    5.4.1 Mechanism for crazing ................................................................................ 120
    5.4.2 Mechanical rejuvenation vs. physical aging ................................................. 121
    5.4.3 Parallel direction vs. perpendicular direction for milled samples ............... 122
  5.5 Summary .............................................................................................................. 122

VI. SUMMARY ............................................................................................................... 124

BIBLIOGRAPHY ............................................................................................................ 126
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Sample characteristics of polymer glasses</td>
<td>74</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>2.1 Illustration of glass transition: specific volume change as a function of temperature. Upon rapid cooling, the liquid could first form supercooled liquid and then glass.</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Modulus change of polymer as a function of temperature during glass transition.</td>
<td>6</td>
</tr>
<tr>
<td>2.3 Illustration of the uniaxial extension. A rectangular sample is extended along the length direction at either a constant force $F$ or a constant rate $V$. The dimensions change from $A_0 \times L_0$ to $A \times L$.</td>
<td>7</td>
</tr>
<tr>
<td>2.4 Illustration of uniaxial compression. A cylindrical sample with initial diameter of $2R_0$ and height of $H_0$ is squeezed to dimensions of $2R \times H$ at either a constant force $F$ or a constant rate $V$.</td>
<td>8</td>
</tr>
<tr>
<td>2.5 Typical illustration of stress vs. strain curves of ductile polymer glasses during both uniaxial extension (black) and compression (red).</td>
<td>9</td>
</tr>
<tr>
<td>2.6 Typical stress vs. strain curve of brittle polymer glasses.</td>
<td>10</td>
</tr>
<tr>
<td>2.7 Craze formation of PS (replot of Figure 13.11 from Ward, I. M.; Sweeney, J., <em>Mechanical Properties of Solid Polymers</em>. Wiley: 2012).</td>
<td>11</td>
</tr>
<tr>
<td>2.8 Stress vs. draw ratio curves of milled PC with different thickness reduction at a constant crosshead speed of $V_0=3$ mm/min. All open symbols represent the deformation of milled PC in the direction parallel to the milling direction. The black line shows the sample with a thickness reduction of 38.3% stretched in the perpendicular direction.</td>
<td>13</td>
</tr>
<tr>
<td>2.9 Stress vs. draw ratio curves for isotropic (red circles) and milled (blue squares) PMMA. Both uniaxial extension tests involves a crosshead speed of $V_0=3$ mm/min at room temperature. The milled PMMA has a thickness reduction of 34% through milling at 60 °C.</td>
<td>14</td>
</tr>
<tr>
<td>2.10 Stress vs. draw ratio during uniaxial extension at a crosshead speed of $V_0=3$ mm/min for: (a) isotropic PC (red circles); (b) twisted PC (blue squares); (c) twisted PC after aging at 105 °C for 1 d (green diamonds). These samples are dog-bone cylinders involve middle dimensions of $\phi 2$ mm × 10 mm.</td>
<td>15</td>
</tr>
</tbody>
</table>
2.11 Stress vs. draw ratio of both isotropic (red circles) and aged PC (blue squares) at a crosshead speed of $V_0=3$ mm/min at room temperature. Isotropic PC was annealed at 135 °C for a month to get aged sample.

2.12 Hybrid structure for polymer glasses: chain network due to intra-segmental connectivity and primary network due to non-bonded interaction. A load-bearing strand is depicted by two pairs of hairpins.

2.13 Illustration of structure of a polymer glass under deformation: (a) polymer chains are frozen at room temperature; (b) surrounding segments start to be activated; (c) most segments are activated and macroscopic plastic flow takes place. Dark dots represent the frozen segments and light dots are activated ones.

2.14 Engineering stress vs. strain curve of melt-stretched PS during uniaxial extension at a crosshead speed of 1 mm/min at room temperature. The photos show the sample at initial, at the onset of necking, during necking propagation and after failure, respectively. The sample was melt stretched at a Hencky strain rate of 0.2 s$^{-1}$ at 140 °C (Replotted from Zartman, G. D.; Cheng, S.; Li, X.; Lin, F.; Becker, M. L.; Wang, S.-Q. Macromolecules 2012, 45, (16), 6719-6732).

2.15 Description of an entangled polymer melt state. The chain network, consisting of Gaussian entanglement strands, is represented by straight lines. The big red circles are the cross-section in XY or YZ plane and the filled blue circles inside represent entanglements. Within affine deformation, the entanglement strands are preserved. As a result, geometric condensation occurs in the XY plane and dilution takes place in the YZ plane (Replotted from Zartman, G. D.; Cheng, S.; Li, X.; Lin, F.; Becker, M. L.; Wang, S.-Q. Macromolecules 2012, 45, (16), 6719-6732).


2.17 Illustration of structure of a polymer glass under different conditions: (1) isotropic; (2) physical aging; (3) mechanical rejuvenation. The filled circles represent the degree of vitrification, increasing from light grey to dark. Corresponding energy landscape is shown on top right.

3.1 Illustration of stress vs strain curve of ductile polymer glasses during uniaxial extension. The hardening modulus $G_H$ is defined as the slope of the curve in the strain hardening regime.

3.2 Heat ($Q$), work ($W$), internal energy change ($\Delta U$), and stress ($\sigma$) as a function of extension ratio of PC during uniaxial extension at an elongation rate of 0.542 cm/min (0.18 min$^{-1}$) at 20 °C (replotted from Adams, G. W.; Farris, R. J. J. Polym. Sci., Part B: Polym. Phys. 1988, 26, (2), 433-445).
3.3 DSC scans for annealed PS deformed to different applied strains at a scan rate of 10 K/min (Replotted from Hasan, O. A.; Boyce, M. C. Polymer 1993, 34, (24), 5085-5092).5

3.4 Total stress, heat contribution, potential energy and fitting curves $\sigma$ and $\sigma_0$ under compression for a system with $T=0.2u_0/k_B$, $N=350$, and $N_c=22$ (Replotted from Hoy, R. S.; Robbins, M. O. Phys. Rev. Lett. 2007, 99, (11), 117801).6

3.5 Deformation mechanism of shear transformations theory (Replotted from Rudnev, S. N.; Salamatina, O. B.; Voenniy, V. V.; Oleynik, E. F. Colloid & Polymer Sci 1991, 269, (5), 460-468).7

3.6 Illustration of milling procedure. A sheet of specimen is placed into the gap between two rolls with a diameter of 150 mm at a constant spin rate of 10 rpm. Each passing causes a thickness reduction of 0.1 mm.

3.7 Illustration of the neck front propagation at a crosshead speed of $V_0$ for a specimen of initial dimensions of $A_0=D_0H_0$ in cross section and $L_0$ in length. During the neck front propagation, over $\Delta t$, a fresh amount $A_0\Delta L_{iso}$ is converted from the un-necked part to increase the neck by a length of $\Delta L_{nk}$.

3.8 IR camera measurement of the surface temperature of a heated PC that drops due to air cooling according to eq 3.13 and 3.14.

3.9 Temperature profiles for isotropic PC during uniaxial extension at $V_0=3$ mm/min at 23 oC. (a) Shear yielding occurs at the yield point in 45o to the stretching direction. (b) Temperature mapping at a subsequent moment, showing the propagation of the neck front at the top whereas the bottom neck front slows down. Color bar listed on right refers to temperatures in the unit of Celsius (°C).

3.10 The engineering stress (red circles) of isotropic PC at a crosshead speed of $V_0=3$ mm/min during uniaxial extension and corresponding temperature rise (blue squares) measured from a fixed spatial point on the extending specimen, as a function of either draw ratio (top X axis) or time (bottom X axis).

3.11 Temperature profiles of shear bandings for isotropic PC during uniaxial extension at $V_0=300$ mm/min at 23 °C. A cross is formed by two shear bandings at the initial strain localization with significant temperature increase. Color bar listed on right refers to temperatures in the unit of Celsius (°C).

3.12 Draw ratio $\lambda_{nk}$, characterizing the shape change associated with necking, as a function of the crosshead speed $V_0$ for isotropic PC during uniaxial extension.

3.13 The "plateau" stress level $\sigma_{engr(nk)}$ (red circles and left Y axis) during the neck front propagation at different crosshead speeds of $V_0$ for isotropic PC with $L_0=39$ mm and the corresponding maximum temperature rise ($T_{nk}-T_o$) (open squares and right Y axis), as
measured by IR camera. Filled diamonds are the modified temperature readings that contain corrections from the air cooling and the lateral heat conduction according to eq 3.30………………………………………………………………………………47

3.14 (a) Mechanical work density \( w \) (red circles), internal (kinetic) energy change \( u_1 \) (blue squares) and internal (potential) energy \( u_2 \) (green diamonds) as a function of the crosshead speed \( V_0 \) for isotropic PC with \( L_0=39 \) mm. (b) the ratio of \( u_2/w \) as a function of \( V_0 \) on logarithmic scale (bottom X axis) and draw ratio \( \lambda_{nk} \) on linear scale (top X axis)...........49

3.15 Stress vs. draw ratio curve (red circles) of milled PC during uniaxial extension with \( V_0/L_0 = 1.2 \) min\(^{-1}\) at 23 °C, and simultaneous temperature measurement (blue squares) with \( L_0=39 \) mm. Also plotted is the elastic component of stress decomposition \( \sigma_{engr(E)} \) (green diamonds) according to eq 3.26…………………………………………………………………………………………50

3.16 Temperature profiles of milled PC during uniaxial extension at \( V_0/L_0=1.2 \) min\(^{-1}\) ……51

3.17 Mechanical work density \( w \) (red circles) and excess energy \( u_2 \) (green diamonds) as a function of extensional ratio \( \lambda \) with \( V_0/L_0=1.2 \) min\(^{-1}\) of milled PC with \( L_0=39 \) mm during uniaxial extension………………………………………………………………………………52

3.18 (a) Temperature increase \( \Delta T \); (b) fraction of internal energy storage \( u_2/w \); (c) internal energy \( u_2 \) as a function of the extensional ratio \( \lambda \) at different values of \( V_0/L_0 \) for milled PC (open) with \( L_0=39 \) mm and melt-stretched PC (half-filled) with \( L_0=13.7 \) mm……………54

3.19 Stress vs. draw ratio curves of three different PC during uniaxial extension at a constant crosshead speed of \( V_0=48 \) mm/min at 23 °C: (i) isotropic (circles); (ii) milled (diamonds); and (iii) melt-stretched (triangles)……………………………………………………………………………………………………56

3.20 Stress vs. draw ratio curve (circles) of melt-stretched PC during uniaxial extension at \( V_0/L_0=3.5 \) min\(^{-1}\) at 23 °C, and simultaneous temperature measurement from two spots on the specimen (two types of triangles). Also plotted is the elastic component of stress decomposition \( \sigma_{engr(E)} \) (diamonds). This melt-stretched PC involves a melt-stretching ratio of \( \lambda_{ms}=2.5 \)……………………………………………………………………………………………………56

3.21 Four images of the temperature profile during compression of an isotropic PC specimen with initial cylindrical dimensions of 5.7 mm in diameter and 5.9 mm in height at an initial rate of \( V_0/H_0=1.0 \) min\(^{-1}\), captured with an IR camera………………..58

3.22 Temperature profiles across the specimen at different stages during the compression at \( V_0/H_0=1.0 \) min\(^{-1}\) for isotropic PC at room temperature…………………………………………………………58

3.23 Stress vs. strain curves (squares) and the corresponding temperature-strain curves (circles) for isotropic PC during uniaxial compression, with initial rates of \( V_0/H_0=1.0 \) min\(^{-1}\) (filled symbols) and \( V_0/H_0=0.1 \) min\(^{-1}\) (open symbols) respectively, where \( \Delta T=(T_{max}-T_a) \) with \( T_a \) being the ambient temperature equal to 23 °C and \( T_{max}=T(z=0, t) \) the temperature reading at the middle of the specimen. The initial dimensions of these cylindrical
specimens are 5.7 mm in diameter with a height of \( H_0 = 5.9 \) mm, and 5.3 mm in diameter with a height of \( H_0 = 5.4 \) mm, respectively.

3.24 Internal kinetic energy component \( \sigma' \) associated with the heat release for isotropic PC during uniaxial compression at \( V_0/H_0 = 0.1 \) min\(^{-1} \) (circles) and 1 min\(^{-1} \) (squares) respectively. Also presented is the total true stress \( \sigma \) given by the two continuous curves.

3.25 External work in the continuous curve as well as the measured heat release in solid symbols per unit volume as a function of the compressive strain for isotropic PC at \( V_0/H_0 = 0.1 \) (circles) and 1.0 (squares) min\(^{-1} \), respectively.

3.26 DSC measurements of two PC samples compressed to two different Hencky strains of (a) \( \varepsilon = 0.69 \) and (b) \( \varepsilon = 0.99 \) at \( V_0/H_0 = 1 \) min\(^{-1} \).

3.27 Microscopic structure pictures of isotropic PC during extension as a function of crosshead speed \( V_0 \). We use two different scales: one is using dots to represent chain segments ((a) to (c)) and the other is applying patches to show different domains ((d) to (f)). It should be noted that (a) and (d), (b) and (e), and (c) and (f) express the same information, respectively. Here, different colors to represent different mobility of chains, which increases from dark to light. Specifically, dark dots in (a) to (c) and dark areas in (d) to (f) represent immobilized segments or domains stuck in high potential energy, while light dots or areas are mobilized ones that have the ability to hop over the potential barrier. With increasing speeds from (a) to (c) or from (d) to (f), the immobilized regions decreases, resulting in a decrease of the internal potential energy \( u_2 \). Note we omit any structural and dynamical heterogeneities in this picture.

3.28 Length shrinkage of pre-necked PC as a function of time, prepared with two different crosshead speeds of \( V_0 = 3 \) (circles) and 300 mm/min (squares) at 23 °C with \( L_0 = 39 \) mm to extend to \( L/L_0 = 1.6 < \lambda_{nk} \) before the necking is completed. Here we artificially set \( t \) starts at \( t_0 = 0.03 \) s to have the initial points in the logarithmic scale.

4.1 (a) Length retraction of a pre-necked PC as a function of annealing temperature. The sample was pre-drawn at a crosshead speed of 10 mm/min to a draw ratio of 1.73 and then annealed at different temperatures for 24 h (Replotted from Cheng, S.; Wang, S.-Q. Phys. Rev. Lett. 2013, 110, (6), 065506). (b) Retractive stress as a function of annealing time at various temperatures for a cold-drawn PC. The PC samples were pre-necked at a crosshead speed of 6 mm/min at 20 °C and stored at the same temperature for 24 h (Replotted from Cheng, S.; Wang, S.-Q. Macromolecules 2014, 47, (11), 3661-3671).

4.2 Normalized molecular weight by the original molecular weight before gamma irradiation as a function of absorbed dose through two measurements: intrinsic viscosity (squares) and melt flow index (circles) (Replotted from Acierno, D.; La Mantia, F. P.; Titomanlio, G.; Calderaro, E.; Castiglia, F. Radiation Physics and Chemistry (1977) 1980, 16, (2), 95-99).
4.3 Side view of the heating setup for elastic yielding experiments. A pre-necked sample is fixed onto the clamps of Instron before the homemade heater is applied to warm up the sample. During annealing, the clamps remain fixed and the stress is measured by the machine. A typical dimension for pre-necked PC is also indicated, with a length of 66 mm and a thickness of 0.38 mm (Replotted from Cheng, S.; Wang, S.-Q. Macromolecules 2014, 47, (11), 3661-3671).9

4.4 Elastic yielding stress $\sigma_{EY}$ as a function of annealing time for pre-necked untreated PC at 80 °C. These prenecked specimens were obtained by cold-drawing samples with an initial length of $L_0=39$ mm at room temperature at various crosshead speed $V_0$, ranging from 3 to 600 mm/min, to a final length of $L = \lambda L_0 = 1.7 \times 39 = 66$ mm. A middle portion (ca. 30 mm) of such specimens were heated to 80 °C to observe the elastic yielding behavior. Such retractive stress is normalized by the original cross sectional area before pre-deformation to exclude the effect of $\lambda_{nk}$ varying with rates.

4.5 (a) Retractive stress as a function of annealing time at $T_{el-yield}=86$ °C for pre-drawn milled PC. All the specimens were first milled with a thickness reduction of 30% and then stretched at a constant crosshead speed $V_0=3$ mm/min to different draw ratio, ranging from $\lambda=1$ to 1.40. The inset shows a typical stress vs. draw ratio curve for the pre-deformation of the milled PC at $V_0=3$ mm/min. (b) The corresponding retractive stress plateau as a function of pre-draw ratio.

4.6 (a) Engineering stress vs. draw ratio of milled PMMA at a crosshead speed of $V_0=6$ mm/min at room temperature. (b) Retractive stress as a function of annealing time at $T_{el-yield}=70$ °C for pre-drawn milled PMMA. All the specimens were first milled to a thickness reduction of 30% at 60 °C and then stretched at a constant crosshead speed $V_0=6$ mm/min to different draw ratio, ranging from $\lambda=1$ to 1.16. The inset shows the linear relationship between the final retractive stress plateau and the pre-draw ratio.

4.7 Retractive stress as a function of annealing time at various annealing temperatures for milled PC with a thickness reduction of 30%. All pre-deformation tests are carried out at 23 °C involving a crosshead speed of $V_0=3$ mm/min and a draw ratio of $\lambda=1.20$.

4.8 Engineering stress vs. draw ratio curves of isotropic PC after gamma irradiation with different doses at a crosshead speed of $V_0=6$ mm/min at 23 °C.

4.9 The weight average molecular weight of PC at different applied doses of gamma irradiation obtained from GPC.

4.10 Retractive stress as a function of annealing time at $T_{el-yield}=75$ °C of pre-necked PC at different doses of gamma irradiation. The PC specimen was first pre-deformed at a constant crosshead speed of $V_0=6$ mm/min to a draw ratio of $\lambda=1.7$ at room temperature and then treated with gamma irradiation.

4.11 Engineering stress $\sigma_{engr}$ as a function of draw ratio $\lambda$ for four types of polymer glasses: (1) melt-stretched PS; (2) PPE; (3) PC; (4) extruded PMMA. The brackets show the
experimental temperatures. All cold drawn experiments involve a crosshead speed of \( V_0 = 6 \) mm/min. The melt-stretched PS is firstly stretched at \( V_{ms} = 600 \) mm/min at 135 °C to a stretching ratio of \( \lambda_{ms} = 5 \) before cooled down by icy water and then the cold drawn experiment is carried out.

4.12 Retractive stress as a function of annealing time at \( T_{el-yield} = 70 \) °C of pre-necked melt-stretched PS at different doses of gamma irradiation. Isotropic PS specimens were first melt-stretched at 135 °C at a crosshead speed of \( V_{ms} = 600 \) mm/min to a draw ratio of \( \lambda_{ms} = 5 \) and quenched by icy water. Those melt-stretched samples were then cold drawn at a crosshead speed of \( V_0 = 6 \) mm/min at room temperature and absorbed at different doses of gamma irradiation.

4.13 (a) Retractive stress as a function of annealing time at \( T_{el-yield} = 75 \) °C of pre-necked PMMA at different dose of gamma irradiation. The pre-necked PMMA was pre-deformed at a constant crosshead speed of \( V_0 = 6 \) mm/min at 80 °C to a draw ratio of \( \lambda = 2.2 \). (b) Engineering stress vs. draw ratio of isotropic PMMA after gamma irradiation at a crosshead speed of \( V_0 = 6 \) mm/min at 80 °C during uniaxial extension. The inset shows the magnification of the initial regime.

4.14 Retractive stress as a function of annealing time at temperature of (a) \( T_{el-yield} = 75 \) °C and (b) \( T_{el-yield} = 120 \) °C of pre-necked PPE at different dose of gamma irradiation. The pre-necked PPE was pre-deformed at a constant crosshead speed of 6 mm/min at 23 °C to a draw ratio of \( \lambda = 1.6 \).

4.15 Microscopic structure pictures of a load-bearing strand (LBS) after necking at room temperature and annealing at a higher temperature. Dark dots denote immobilized or more frozen segments, while light dots represent mobilized or more activated segments. The two short arrows show the direction of chain shrinkage.

4.16 Microscopic structures of chemical bonds in response of deformation: (a) covalent bond stretch; (b) covalent bond angle distortion; (c) intramolecular rotation. The dash circles represent the initial positions of atoms before deformation (Replotted from Crist, B., The Physics of Glassy Polymers. Haward, R. N., Ed. Springer Netherlands: 2012, page 158).

4.17 Structure changes of LBSs after gamma irradiation: (a) degradation; (b) crosslink. Red crosses represent positions where chain scissions take place.

5.1 The mechanism of craze tip advance by meniscus-instability: (a) outline of craze tip; (b) top view of craze front; (c)-(d) advance if the craze front by a completed period of interface convolution (Replotted from Argon, A. S.; Salama, M. M. *Philosophical Magazine* 1977, 36, (5), 1217-1234).

5.3 (a) Engineering stress as a function of stretch ratio for isotropic PC during uniaxial extension; (b) draw ratio as a function of time for isotropic PC during creep. Three regimes are characterized as: I. elastic deformation; II. crazing; III. shear yielding and necking (Replotted from Cheng, S.; Johnson, L.; Wang, S.-Q. Polymer 2013, 54, (13), 3363-3369).\textsuperscript{13} .................................................................102

5.4 Illustration of twisting. A cylindrical sample is fixed on the bottom, and twisted to an angle $\phi$, typically 900°, from the top. It is then twisted back to the original position……104

5.5 (a) Draw ratio $\lambda$ as a function of time under a constant engineering stress of 30 MPa for isotropic and milled PC with different milling thickness reduction. The inset figure shows the engineering stress as a function of draw ratio of milled PC at a crosshead speed of 3 mm/min. All these specimens are stretched along the milling direction. (b) Corresponding photos of milled specimens under $\sigma_{engr}=30$ MPa for 1 h at room temperature.................................................................106

5.6 Illustration of change of sample dimensions from $L_0 \times W_0 \times H_0$ to $L_{\text{mill}} \times W_0 \times H_{\text{mill}}$ for PC during milling. Straight lines represent polymer chains, and lines between two crossing points are load-bearing strands (LBSs). During milling, the width of the sample keeps nearly constant…………107

5.7 (a) The draw ratio $\lambda$ as a function of time under different constant engineering stress for milled PC with a thickness reduction of 41.1%. The specimens are stretched along the milling direction. (b) Corresponding photos of the specimens under three different engineering stresses (10 MPa, 40 MPa, and 80 MPa) at room temperature for 1 h.……108

5.8 Engineering stress vs. draw ratio curves at a crosshead speed of 3 mm/min at room temperature for: (1) isotropic PC (black diamonds); (2) milled PC cut in the direction parallel to the milling direction (red circles); (3) milled PC cut in the direction perpendicular to the milling direction (red squares); (4) milled PC cut in the direction parallel to the milling direction after aging at 105 °C for 1 d (blue circles); (5) milled PC cut in the direction perpendicular to the milling direction after aging at 105 °C for 1 d (blue squares). The milled samples in the parallel direction involve a thickness reduction of 41.1%, while the milled samples in the perpendicular direction have a comparable thickness reduction of 38.3%............................................................................................109

5.9 (a) The draw ratio $\lambda$ as a function of time under different constant engineering stress for milled PC. The specimens having a milling thickness reduction of 38.3% are stretched perpendicularly to the milling direction. (b) Corresponding photos of the specimens under two different engineering stresses: 20 MPa and 40 MPa at room temperature for 1 h.……110

5.10 (a) Engineering stress vs. draw ratio curves of isotropic PC, twisted PC and twisted PC after aging at 105 °C for 1d at a crosshead speed of $V_0=3$ mm/min. (b) The draw ratio $\lambda$ as a function of time under different constant engineering stress for twisted PC. (c) Corresponding photos of the specimens under different engineering stress, ranging from 0 MPa to 40 MPa at room temperature for 1 h. All these samples have a dimension of $\phi2$ mm $\times$ 10 mm........................................................................................................113
5.11 Creep tests for milled PC in the perpendicular direction after aging at 105 °C for 1 d. (a) Stress vs. draw ratio curve at a constant crosshead speed of 3 mm/min. The black lines show the initial linear elastic regime, from which the stress deviates at around 20 MPa. (b) Comparison of draw ratio as a function of time at 30 MPa for (1) milled PC, (2) milled PC after aging, and (3) isotropic PC. (c) Stretch ratio $\lambda$ as a function of time at various applied stress ranging from 10 MPa to 40 MPa for milled PC after aging. (d) Corresponding photos of samples under creep for 1 h. .................................................................117

5.12 Creep tests for milled PC in the parallel direction after aging at 105 °C for 1 d. (a) Stress vs. draw ratio curve at a constant crosshead speed of 3 mm/min. The black lines show the initial linear elastic regime, from which the stress deviates at around 40 MPa. (b) Stretch ratio $\lambda$ as a function of time at various applied stress ranging from 10 MPa to 60 MPa. (c) Corresponding photos of samples under creep for 1 h. ...........................................119

5.13 Draw ratio $\lambda$ as a function of time for milled PMMA at a constant engineering stress of 30 MPa and milled PMMA after aging at 105 °C for 1 d at a constant engineering stress of 20 MPa along the milling direction. The inset show the corresponding pictures of samples under creep for 1 h. .................................................................120

5.14 Microscopic structures of polymer glasses after mechanical rejuvenation and physical aging processes. Colors from dark to light represent the glassy state from more vitreous to less vitreous. .................................................................122
CHAPTER I
INTRODUCTION

Polymers are macromolecules formed by a group of repeated units.\textsuperscript{14,15} Due to their chain connectivity and uncrossability, polymers show unique mechanical properties in above and below the glass transition temperature $T_g$ or below the melting temperature $T_m$.\textsuperscript{1,11,16-19} Polymeric materials have become an indispensable part of our daily life and the study of mechanical responses of polymers is of interest in both academic and industrial settings.

To delineate the origin of macroscopic stress in either liquid or solid state, both phenomenological and molecular-level viewpoints have been adopted. When $T>T_g$ or $T_m$, the chain dynamics needs to be considered in polymer rheology. In the past decades a large number of studies has focused on nonlinear polymer melt rheology.\textsuperscript{16-18,20} Although the explicit molecular picture concerning how chain disentanglement takes place in large deformation is still under active development,\textsuperscript{21-28} a satisfactory level of phenomenological understanding has been proposed by Wang and coworkers\textsuperscript{29-31} to recognize the entanglement to disentanglement transition.

Taking advantage of the recent understanding in nonlinear rheology of entangled polymers, we start to explore the responses of polymers at temperature well below $T_g$ for polymer glasses. Due to the extremely slow dynamics in the vitreous state, many issues
remain elusive. In this dissertation, non-linear mechanical behavior of polymer glasses well below $T_g$ will be discussed based on a phenomenological microscopic description for polymer glasses.

In the following CHAPTER II, some basic characteristics of polymer glasses and related deformation modes are introduced. A recently proposed molecular picture\textsuperscript{3} which regards polymer glasses as hybrid structure is reviewed. It also discusses how melt-stretching could turn brittle polymer glasses into ductile materials, why mechanical rejuvenation remove strain softening whereas physical aging reverses the effect.

CHAPTER III describes the application of an IR camera to enable \textit{in situ} measurement of the sample temperature in both uniaxial extension and compression. Through comparing how much the mechanical work results partially in heat, we identify the "missing" energy as the internal potential energy. This kind of internal energy decreases logarithmically with the crosshead speed in uniaxial extension while it shows the opposite trend in uniaxial compression. The viscous stress component is found larger than the mechanical stress during uniaxial compression, implying the release of internal stored energy in form of heat. Moreover, compared with the milled samples, melt-stretched ones store more internal energy during homogeneous extension due to the geometric condensation.

CHAPTER IV further explores the origin of internal energy by carrying out a series of elastic yielding experiments. The contradictory results between retractive stress and the internal energy as functions of deformation rates indicate that the internal energy is of both inter- and intra-segmental origin. Elastic yielding of milled sample reveals the primary network is deformed in the pre-yield regime while in the post-yield regime there is a linear
relationship between retractive stress and the pre-draw ratio. Upon gamma irradiation, chain scissions take place to cause reduced elastic yielding stress.

In CHAPTER V, crazing behavior is studied under constant stress. Specifically, mechanical rejuvenation is applied to suppress the formation of crazes, while physical aging could recover the strain softening and crazes occur again under creep. The molecular picture of hybrid structure is applied to explore the cause for crazes.

In CHAPTER VI, a summary of all the work done in this dissertation will be presented.
CHAPTER II

CHARACTERISTICS OF POLYMER GLASSES

Polymers have been one class of the most important and widely used materials. Every year several hundred billion pounds of polymers are produced and consumed. Many of these polymers, used at ambient temperature, remain in their glassy state. For example, plastic cups are made from polystyrene (PS), greenhouses are made from polycarbonate (PC), and glass windows in aquariums are mostly made from poly(methyl methacrylate) (PMMA).

To better use polymers in our daily life, the study of their mechanical properties becomes critical from the standpoints of both fundamentally scientific research and practical processing. Long polymer chains could form an entanglement network above the glass transition temperature \( T_g \). Upon cooling to the temperature below \( T_g \), chain segments become “frozen” to form a rigid primary network. In order to explore the nature of nonlinear mechanical responses of polymer glasses, not only the intra-segmental interaction from the chain network, but also the inter-segmental interaction caused by van de Waals force have to be taken into account. In the past several decades, many theories have been proposed in this area to study the glassy state, e.g., the random first-order phase transition theory,\(^{32}\) energy landscape paradigm,\(^{33}\) and shear transformation zone theory.\(^{19}\) However, numerous questions remain elusive. Why does mechanical stress increase with
strain in the post-yield regime? Why is PC ductile while PS brittle? How does a polymer
glass turn from ductile to brittle across a narrow temperature window? In order to answer
these questions, it is necessary to further explore the causality relationship and derive more
coherent phenomenology concerning large deformation of polymer glasses.

2.1 Glass Transition

Glass is defined as a non-crystalline amorphous solid which exhibits a glass
transition when heated towards the liquid state.\(^3\) So one unique characteristic of polymer
glasses is that they have a glass transition temperature \(T_g\), which is the transition
temperature from a glassy state to a rubber state. As shown in Figure 2.1, the glassy state
is formed by rapid cooling from the liquid state. Since the chain segments are frozen in the
glassy state, the system is relatively hard and rigid. When heating above \(T_g\), the system
becomes soft and flexible. Figure 2.2 shows the modulus change of polymer as a function
of temperature. Usually, the modulus significantly increases during the transition from
rubbery state to glassy state.

Until today, there is no satisfactory theory to fully understand the glass transition.
One of the widely accepted theories is the *free volume theory*.\(^3\) It assumes that the free
volume does not change below \(T_g\) but increases above \(T_g\). Another one is *kinetic theory*,\(^3\)
which regards glass transition as an kinetic process, as the value of \(T_g\) changes at different
cooling or heating rates. Usually a faster cooling rate would result in a higher value of \(T_g\).
Figure 2.1 Illustration of glass transition: specific volume change as a function of temperature. Upon rapid cooling, the liquid could first form supercooled liquid and then glass.

Figure 2.2 Modulus change of polymer as a function of temperature during glass transition.
2.2 External deformation of polymer glasses

In order to study the mechanical properties of polymer glasses, two types of deformation will be applied in this work: (a) uniaxial extension; (b) uniaxial compression.

As shown in Figure 2.3, during uniaxial extension, a sheet-like sample with initial dimensions of $A_0 \times L_0$ is stretched along the length direction at either a constant force $F$ or a constant rate $V$. The sample is fixed at one end and stretched from the other end. Here, the engineering stress is defined as $\sigma_{engr} = F / A_0$, the true stress is $\sigma = F / A$, and the draw ratio is $\lambda = L / L_0$, where $A$ and $L$ are real time cross-sectional area and sample length, respectively.

![Figure 2.3](image)

Figure 2.3 Illustration of the uniaxial extension. A rectangular sample is extended along the length direction at either a constant force $F$ or a constant rate $V$. The dimensions change from $A_0 \times L_0$ to $A \times L$. 
Figure 2.4 Illustration of uniaxial compression. A cylindrical sample with initial diameter of $2R_0$ and height of $H_0$ is squeezed to dimensions of $2R \times H$ at either a constant force $F$ or a constant rate $V$.

Figure 2.4 shows the schematic of the uniaxial compression. A cylindrical sample with initial diameter of $2R_0$ and height of $H_0$ is placed between two plates and compressed at either a constant force $F$ or a constant rate $V$. The compression ratio is defined as $\lambda = H_0/H$ and true strain is $\varepsilon = ln\lambda$.

2.3 Nonlinear behavior of polymer glasses upon deformation

The study of nonlinear behavior upon deformation is an important aspect in the research of polymer glasses. The following would focus on three types of nonlinear responses for polymer glasses.

2.3.1 Yielding, necking and strain hardening

Upon uniaxial extension, many ductile polymer glasses, like PC, can be stretched with a very large deformation. Figure 2.5 shows a typical stress vs. strain curve (black) of ductile polymer glasses during stretching. There is an initial elastic deformation regime,
which obeys the linear relationship. In this pre-yield regime, the sample can totally recover to its original dimension. After deviating from this linear regime, the stress reaches a maximum, which is identified as a yield point. Subsequently shear yielding takes place. The strain localization, often named “necking”, is then initialized and propagates at a speed proportional to the crosshead speed. After the entire specimen is converted into the necked state, it starts to undergo uniform extension and the stress monotonically rise. Such stress growth in the post-yield regime is known as “strain hardening”.

During uniaxial compression, homogeneous deformation happens, which is different from strain localization during extension. After strain softening, the stress grows monotonically in absence of necking, as can be seen from the red curve in Figure 2.5. The yield stress in compression is also much higher than that in extension. To have a better sense of uniaxial compression, it can be treated as a process combining biaxial extension and hydrostatic compression.

![Stress vs. Strain Curves](image)

Figure 2.5 Typical illustration of stress vs. strain curves of ductile polymer glasses during both uniaxial extension (black) and compression (red).
2.3.2 Brittle failure

Unlike PC, some polymer glasses, like PS, would quickly break at room temperature in a few percentage of strain, usually 3%-8%. As shown in Figure 2.6, mechanical stress increases monotonically to the breaking point during the stretching process. Strain localization, in the form of crazing, always shows up for PS before breaking, as indicated in Figure 2.7.

![Figure 2.6 Typical stress vs. strain curve of brittle polymer glasses.](image-url)
2.3.3 Rejuvenation effect vs. aging effect

Intrinsic strain softening, where the stress decreases with the increasing strain, turns out to be very important in the initiation of strain localization like necking and crazing. Mechanical rejuvenation is regarded as an efficient method to remove strain softening, so that homogeneous deformation and ductile failure can be achieved.\textsuperscript{1, 38-40} Broutman and Patil\textsuperscript{41} reported a method of mechanical rejuvenation by passing the sample through a rolling mill to avoid strain localization. Govaert \textit{et al.}\textsuperscript{42} found that brittle PS could be temporarily ductile through mechanical precondition.
Figure 2.8 studies the effect of milling on PC during uniaxial extension at a constant crosshead speed of $V_0 = 3 \text{ mm/min}$. The engineering stress is plotted as a function of draw ratio at different thickness reduction from two rolls milling. The isotropic sample shows typical yielding, strain softening, necking and strain hardening behavior before breaking. After a thickness reduction of 13.5% (blue) during milling, the engineering stress becomes flat beyond the yield point and rises gradually later when the sample was stretched along the milling direction. Necking is not observed during this process. With the increase of thickness reduction (open symbols from 13.5% to 41.1%), the yield stress increases when stretched along the milling direction, as well as the hardening modulus $G_R$. The stress curve of the milled sample with a thickness reduction of 38.3% (black) in the perpendicular direction to the milling direction is also plotted in Figure 2.8. It can be seen that the yield stress of this sample is much lower than that of isotropic sample. Also, uniform deformation takes place in the post-yield regime, which is different from the necking phenomenon observed in isotropic sample.

Efforts was devoted to make brittle PMMA ductile at room temperature. As indicated in Figure 2.9, isotropic PMMA always breaks at a draw ratio around 1.08. By milling the PMMA specimens through two rolls to a thickness reduction of 34% at 60 °C, it becomes more stretchable at room temperature. The draw ratio increases to 1.17, compared with a value of 1.08 for isotropic samples. And the stress in the post-yield regime keeps almost constant before breaking.
Figure 2.8 Stress vs. draw ratio curves of milled PC with different thickness reduction at a constant crosshead speed of $V_0=3$ mm/min. All open symbols represent the deformation of milled PC in the direction parallel to the milling direction. The black line shows the sample with a thickness reduction of 38.3% stretched in the perpendicular direction.
Figure 2.9 Stress vs. draw ratio curves for isotropic (red circles) and milled (blue squares) PMMA. Both uniaxial extension tests involves a crosshead speed of $V_0=3 \text{ mm/min}$ at room temperature. The milled PMMA has a thickness reduction of 34% through milling at 60 °C.

Another method of mechanical rejuvenation is twisting a cylindrical sample to a sufficient angle and then forcing it to return to its original position, suggested by Govaert et al.$^{43}$ and Senden et al.$^{44}$. Figure 2.10 show the stress as a function of draw ratio of twisted PC (blue squares) during uniaxial extension at a crosshead speed of $V_0 = 3 \text{ mm/min}$. Though the stress is obviously decreased, the sample undergoes homogeneous deformation. Also the data of the isotropic cylindrical sample at the same condition is plotted with red circles for comparison.
Figure 2.10 Stress vs. draw ratio during uniaxial extension at a crosshead speed of $V_0=3$ mm/min for: (a) isotropic PC (red circles); (b) twisted PC (blue squares); (c) twisted PC after aging at 105 °C for 1 d (green diamonds). These samples are dog-bone cylinders involve middle dimensions of $\phi 2$ mm × 10 mm.

While rejuvenation turns brittle polymers into ductile, aging could cause the opposite effect. As shown in Figure 2.11, after annealing at 135 °C for a month, the aged PC loses its ductility and breaks at a draw ratio around 1.05. Moreover, due to aging effect, the yield stress increases by 10 MPa. Similar effect from can be found in our previous observations.\textsuperscript{2, 13} Since mechanical rejuvenation can only cause temporary effect, it will recover after aging for a certain time. As shown in green diamonds in Figure 2.10, stress overshoot shows up again for twisted PC after aging at 105 °C for 1 d, where necking propagates beyond the yield point and was followed by strain hardening.
Figure 2.11 Stress vs. draw ratio of both isotropic (red circles) and aged PC (blue squares) at a crosshead speed of $V_0=3$ mm/min at room temperature. Isotropic PC was annealed at 135 °C for a month to get aged sample.

2.4 The molecular picture of the hybrid structure

In the past decades, a large number of studies explored the origin of stress during nonlinear fast deformation of entangled polymers above $T_g$. Through lots of efforts, Wang and coworkers has established satisfactory understanding of rheological behavior of entangled polymer melts and solutions. In their view, it is crucial to recognize the importance of the entanglement network and to explore the condition for chain disentanglement leading to macroscopic yielding.
Inspired by the knowledge of polymer melt rheology, a phenomenological molecular model was recently proposed to better understand the nonlinear responses of entangled polymer below $T_g$.

Specifically, it treats polymer glass as a hybrid structure consisted of primary network and chain network. Load-bearing strands (LBSs) in the chain network, could be formed by pairing hairpins, as shown in blue and red open circles in Figure 2.12. The surrounding non-load-bearing segments constitute the primary structure due to short-ranged van de Waals inter-segmental interaction, represented by filled circles.

Under external deformation, as shown in Figure 2.13, all the segments are frozen in the elastic deformation regime. Beyond the linear response regime, displacement of the LBSs could activate surrounding segments, e.g., getting them out of the potential barrier. Brittle failure occurs when chain tension builds up to allow chain pullout in absence of sufficient mobilization of the glassy segments, as shown in Figure 2.13 (b). On the other
hand, when most segments are no longer vitreous at the yield point, plastic flow can take place and the sample would undergo ductile deformation.

Why the surrounding segments can be activated sufficiently to produce yielding in some polymers but not others? To answer this question, the factors affecting the activation of segments will be introduced in the following part.

Figure 2.13 Illustration of structure of a polymer glass under deformation: (a) polymer chains are frozen at room temperature; (b) surrounding segments start to be activated; (c) most segments are activated and macroscopic plastic flow takes place. Dark dots represent the frozen segments and light dots are activated ones.
2.4.1 Melt stretching

Zartman et al.\textsuperscript{2} have demonstrated that by melt stretching at a temperature $T > T_g$, PS can be ductile during uniaxial extension at room temperature. Figure 2.14 shows the stress vs. strain curve of melt-stretched PS with strain softening and necking propagation at room temperature. They explained this phenomenon by the geometric condensation during melt stretching, as shown in Figure 2.15. Assume the entanglement strands density is $\psi$ before stretching in the Z direction. Within the affine deformation limit, we have the density change of $\psi_\parallel = \lambda \psi$ in the XY plane and $\psi_\perp = \psi / \sqrt{\lambda}$ in the YZ plane upon stretching. As a result, with geometric condensation in the XY plane, the LBSs become much closer. Consequently, the activation zones do not need to grow as much as isotropic sample to reach the point of global plasticity.

![Stress-strain curve of melt-stretched PS](image)

Figure 2.14 Engineering stress vs. strain curve of melt-stretched PS during uniaxial extension at a crosshead speed of 1 mm/min at room temperature. The photos show the
sample at initial, at the onset of necking, during necking propagation and after failure, respectively. The sample was melt stretched at a Hencky strain rate of 0.2 s\(^{-1}\) at 140 °C (Replotted from Zartman, G. D.; Cheng, S.; Li, X.; Lin, F.; Becker, M. L.; Wang, S.-Q. *Macromolecules* 2012, 45, (16), 6719-6732).\(^2\)

Figure 2.15 Description of an entangled polymer melt state. The chain network, consisting of Gaussian entanglement strands, is represented by straight lines. The big red circles are the cross-section in XY or YZ plane and the filled blue circles inside represent entanglements. Within affine deformation, the entanglement strands are preserved. As a result, geometric condensation occurs in the XY plane and dilution takes place in the YZ plane (Replotted from Zartman, G. D.; Cheng, S.; Li, X.; Lin, F.; Becker, M. L.; Wang, S.-Q. *Macromolecules* 2012, 45, (16), 6719-6732).\(^2\)
2.4.2 Physical aging vs. mechanical rejuvenation

Upon physical aging, the primary network becomes more vitreous, as shown by dark filled circles surrounding the LBSs in Figure 2.17. The system relocates itself to a deeper minima on the energy landscape,\(^3\, 46\) making the surrounding segments more difficult to be activated. Conversely, mechanical rejuvenation allows the glass to stay in a shallower energy minima, represented by light grey filled circles. The activation is more extensive and complete with less vitreous primary network. So it is much easier for the sample to gain macroscopic ductility.
Figure 2.17 Illustration of structure of a polymer glass under different conditions: (1) isotropic; (2) physical aging; (3) mechanical rejuvenation. The filled circles represent the degree of vitrification, increasing from light grey to dark. Corresponding energy landscape is shown on top right.
CHAPTER III
ORIGIN OF STRESS IN EXTENSION AND COMPRESSION OF POLYMER GLASSES

3.1 Background

Why the stress could rise in the strain hardening regime? What is the origin of mechanical stress in the post-yield regime? The physics governing large deformation has been elusive because both plastic and anelastic deformation take place. In this chapter, the nature of mechanical stress for polymer glasses will be first investigated.

Figure 3.1 is a typical tensile curve showing stress as a function of deformation \( (\lambda^2 - 1/\lambda) \) for ductile polymer glasses. It is found that in the strain hardening regime, stress could be well fitted by the classic rubber elasticity formula: \( \sigma = G_R (\lambda^2 - 1/\lambda) \), where \( G_R \) is known as hardening modulus. Therefore, earlier investigations proposed that the strain hardening was caused by the entropic elasticity.\textsuperscript{40, 47-52} Haward and Thackray\textsuperscript{47} suggested a one-dimension model by using an Eyring dashpot to represent the intermolecular resistance and a Langevin spring to represent the entropic interaction. Boyce \textit{et al.}\textsuperscript{48} later developed this model into a three-dimensional “BPA model”. Such three-chain model was then extended to eight-chain\textsuperscript{49} and full-chain model.\textsuperscript{50}

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However, Kramer\textsuperscript{53} pointed out that the explanation of rubber elasticity during large deformation may be not right. First, the hardening modulus $G_R$ is much larger than the elasticity plateau modulus. Also, the elasticity plateau modulus increases with temperature while $G_R$ shows the opposite trend. More recent studies proposed a dissipative mechanism to explain strain hardening as a process predominantly arising from plastic flow, which will be reviewed in the following in three aspects: (1) experiments; (2) simulations; (3) theories.

![Figure 3.1 Illustration of stress vs strain curve of ductile polymer glasses during uniaxial extension. The hardening modulus $G_R$ is defined as the slope of the curve in the strain hardening regime.](image)

$$\sigma = G_R \left( \lambda^2 - \frac{1}{\lambda} \right)$$

$$\lambda^2 - 1 / \lambda$$

3.1.1 Experimental studies on the origin of stress

Since Farren and Taylor\textsuperscript{54} first explored the heat generation during plastic extension of metals, it has been well accepted that plastic deformation would generate heat. In the past several years, a large number of thermodynamic studies have been carried out to investigate the plasticity of polymer glasses upon deformation. According to the first law of thermodynamics, $\Delta U = \Delta W + \Delta Q$. Through calculating the mechanical work applied to
the sample and the heat produced under external deformation, the value of internal stored energy could be figured out.\textsuperscript{4,7,55-57}

By using isothermal deformation calorimetric measurements for PC during extension, Adams and Farris\textsuperscript{4} obtained $\Delta U$ by subtracting $-Q$ from $W$ and demonstrated that around 50-80\% of the mechanical work was dissipated as heat, as shown in Figure 3.2. Later, Rudnev et al.\textsuperscript{7} observed similar phenomenon for several polymer glasses during uniaxial compression.

![Figure 3.2](image)

Figure 3.2 Heat ($Q$), work ($W$), internal energy change ($\Delta U$), and stress ($\sigma$) as a function of extension ratio of PC during uniaxial extension at an elongation rate of 0.542 cm/min (0.18 min$^{-1}$) at 20 °C (replotted from Adams, G. W.; Farris, R. J. \textit{J. Polym. Sci., Part B: Polym. Phys.} 1988, 26, (2), 433-445).\textsuperscript{4}

Another way to measure the heat is to detect the temperature rise using infrared techniques.\textsuperscript{56-59} At sufficient high strain rate, Rittel\textsuperscript{56} found a strain and strain rate dependence on the rate ratio of heat to work under adiabatic condition. Such ratio could be
even larger than 1, because the energy stored at small strains could convert into heat in large deformation, which was consistent with recent results at much lower rates during uniaxial compression.\textsuperscript{58} By applying an infrared detector system, Garg et al.\textsuperscript{57} observed that a large fraction of work was dissipative, especially at higher rates. They suggested that there was an additional barrier to activate the secondary $\beta$ motions at high rates deformation.

Both methods mentioned above have concluded that internal energy is stored during plastic deformation. Such internal energy, associated with enthalpy change, can also be determined by the differential scanning calorimetry (DSC).\textsuperscript{5,60} Two exothermal processes: one in the pre-$T_g$ regime and the other in the post-$T_g$ regime, as shown in Figure 3.3, were regarded as the release of internal stored energy, which may relate to two different deformation mechanism.

Figure 3.3 DSC scans for annealed PS deformed to different applied strains at a scan rate of 10 K/min (Replotted from Hasan, O. A.; Boyce, M. C. \textit{Polymer} 1993, 34, (24), 5085-5092).\textsuperscript{5}
3.1.2 Simulations on the origin of stress

Besides the experimental efforts, simulations also found a small portion of energetic stress in large deformation while the majority of the mechanical stress was associated with plastic arrangements. Hoy and coworkers proposed that the mechanical stress was consisted of two components: heat contribution and potential energy, as indicated in Figure 3.4. It implied that although the heat contribution was still dominant, the potential energy showed up in the final stage. The origin of potential energy was due to the chains between entanglements pulled taut rather than the entropic change. To figure out where the internal energy was stored, Vorselaars et al. calculated both the inter-chain energy and the intra-chain energy. It was found that the nature of yield peak was inter-chain interaction and the nature of strain hardening was intra-chain interaction.

![Figure 3.4](image)

Figure 3.4 Total stress, heat contribution, potential energy and fitting curves $\sigma$ and $\sigma_Q$ of under compression for a system with $T=0.2u_0/k_B$, $N=350$, and $N_e=22$ (Replotted from Hoy, R. S.; Robbins, M. O. Phys. Rev. Lett. 2007, 99, (11), 117801).
3.1.3 Theories on the origin of stress

Based on experimental and simulation results, several theories have been proposed to elucidate the origin of strain hardening. In shear transformations theory first formally introduced by Argon, shear transformations zones are suggested to be the carriers of plasticity. The total stress during uniaxial extension $\sigma_T$ and compression $\sigma_C$ can be expressed in the following equations:

\[
\sigma_T = \frac{(\sqrt{3}\pi/2)\mu[Ay^T(1+1.58\beta^2(\varphi))-mkT/(\Delta\nu^*_\varphi\mu)]}{1+\frac{\sqrt{3}\pi}{12}\beta(\varphi)} + \frac{\rho RT}{M_c} g(\lambda), \tag{3.1a}
\]

and

\[
\sigma_C = \frac{(\sqrt{3}\pi/2)\mu[Ay^T(1+1.58\beta^2(\varphi))-mkT/(\Delta\nu^*_\varphi\mu)]}{1-\frac{\sqrt{3}\pi}{12}\beta(\varphi)} + \frac{\rho RT}{M_c} g(\lambda), \tag{3.1b}
\]

where the first term on right represents the plastic resistance component and the second term is the rubber-like hardening component. The mechanism under deformation can be described in Figure 3.5. The plastic defects (PDs), which is local shear transformations in nature of inter-segmental interaction, are formed after deviation from the elastic deformation. With the increase of strain, PDs could overcome the energy barrier and rearrange to a lower internal energy state.

Moreover, Chen and Schweizer developed a nanometer scale dynamical theory based on the alpha relaxation for strain hardening of polymer glasses. According to their theory, the mechanical stress is mainly in origin of inter-segmental force rather than the entropic rubber elasticity.
In this chapter, an infrared camera will be applied to *in situ* measure the temperature rise of PC during both uniaxial extension and compression. Four types of PC will be studied: isotropic sheeted PC, isotropic cylindrical PC, milled PC and melt-stretched PC. By combining of mechanical responses and thermodynamic behaviors, it is found that significant internal energy is stored upon deformation.

![Deformation mechanism of shear transformations theory](colloid-polymer-sci-1991-269-5-460-468.png)

Figure 3.5 Deformation mechanism of shear transformations theory (Replotted from Rudnev, S. N.; Salamatina, O. B.; Voenniy, V. V.; Oleynik, E. F. *Colloid & Polymer Sci* 1991, 269, (5), 460-468).
3.2 Experiments

In this section, two parts: (a) materials and sample preparation; and (b) apparatus and methods would be introduced.

3.2.1 Materials and sample preparation

Bisphenol A-polycarbonate (PC) in this study is Lexan TM 141 111, provided by SABIC (GE Plastic). The weight average molecular weight is 50 kg/mol, with a polydispersity of 2.01. Its glass transition temperature $T_g$ is 145 °C, measured by a TA Q2000 DSC at a ramping rate of 10 °C/min. In this chapter, four types of PC will be studied: isotropic cylindrical PC, isotropic sheeted PC, mechanical rejuvenated PC by milling, and melt-stretched PC.

The specimens used in compression were prepared by extrusion at around 215 °C through a capillary die which produced an extrudate with a diameter of 5.5 mm. Such an extrudate was cut to a cylinder with a height of 5.5 mm and then placed between two compression plates with lubricant oil on the surface.

To prepare isotropic PC sheets, PC pellets were placed into a 100 mm × 100 mm × 0.8 mm compression mold with two sheets of Kapton HN polyimide film on the surface of both sides in a 50-ton Dake hydraulic press. The pressing temperature was set at 200 °C. PC was first pre-heated between two plates for 30 min, and then pressed with 25 tons of force for another 30 min. The sample was then removed from the press and cooled down to room temperature. Dog-bone shaped samples were obtained by a punch press at room temperature with a dog-bone mold (ASTM D-412) involving an effective length of 39 mm.
The milled samples were prepared by placing an isotropic PC sheet with a dimension of $100 \, mm \times 100 \, mm \times 2 \, mm$ into a gap between two identical counter-rotating (at 10 rpm) rolls of 150 mm in diameter, as shown in Figure 3.6. Such a milling procedure involves a thickness reduction of 0.1 mm in each passing. After many passes, an accumulated thickness decrease of 30% can be achieved. Such milled sheets were then cut into dog-bone (ASTM D-412) shaped specimens with a thickness of 1.4 mm and a length of 39 mm.

To obtain melt-stretched samples, dog-bone shaped PC sheet with middle dimensions of $80 \, mm \times 35 \, mm \times 0.5 \, mm$ was first pressed using the same procedure as untreated PC. The sample were then fixed on Instron 5567 and it was relaxed at 160 °C for 15 min to reach the thermal equilibrium. Uniaxial extension of PC was then carried out at a crosshead speed of $V_0 = 6 \, mm/s$ to a draw ratio of $\lambda_{ms} = 2.5$. At the end of melt stretching, icy water was sprayed onto the sample. Melt-stretched samples were obtained by cutting such samples along the stretching direction by a dog-bone mold (ASTM D-638) with an effective length of 13.7 mm and a thickness of 0.3 mm.

Figure 3.6 Illustration of milling procedure. A sheet of specimen is placed into the gap between two rolls with a diameter of 150 mm at a constant spin rate of 10 rpm. Each passing causes a thickness reduction of 0.1 mm.
3.2.2 Apparatus and methods

Uniaxial compression was performed on Instron 5567, while uniaxial extension tests were carried out on Instron 5543. All experiments were conducted at room temperature around 23 °C. *In situ* measurements of the specimen's temperature were performed by an infrared camera (FLIR SC325) operating at 60 Hz to record the whole time-dependent temperature profile on a video clip. DSC measurements were carried out with a TA Q2000 DSC at a heating rate of 10 °C/min.

3.3 Theoretical analysis

Elementary yet necessary theoretical analysis needs to be carried out to draw conclusions from the experimental data. The experiments involve simultaneous stress measurements and temperature profiles as a function of time at various deformation rates for four different types of specimens. For the isotropic PC upon uniaxial extension, the post-yield regime is characterized by stable neck front propagation, and there is considerable temperature rise in the neck front region. For isotropic PC during uniaxial compression and milled or melt-stretched PC during uniaxial extension, uniform deformation beyond the yield point is accompanied by a spatially homogeneous temperature increase. The analysis to evaluate the concurrent irreversible plastic and reversible elastic processes is different depending on whether the deformation involves: (a) the strain localization or not; (b) extension or compression. Thus, the following three subsections deal with each case separately.
3.3.1 Neck front propagation in isotropic PC during uniaxial extension

To determine the internal kinetic energy increase $dU_1$ which is related with heat release, temperature measurements using an IR camera for thermal imaging were carried out. The tensile extension of ductile PC is performed at room temperature, where one end of the specimen is fixed and the other is moving at a crosshead speed $V_0$. For thermally quenched (isotropic) PC, after shear yielding to initiate necking, the neck front propagates at the expense of the un-necked parts of the specimen. Although there are a few percent elastic extension away from the neck, we treat the un-necked parts as un-deformed to simplify the description. The conversion from the un-necked to the necked can be depicted in terms of the speed at which the neck grows in length. Assuming the neck length increases at a speed of $V_{nk}$ at one front as shown in Figure 3.7, then it is related to $V_0$ as

$$V_0 = V_{nk} - V_{iso},$$  \hspace{1cm} (3.2)

where $V_{iso}$ is the speed at which the un-necked portion shrinks because of its conversion to the necked region. With the assumption that the volume does not change, we have

$$A_0 V_{iso} = A V_{nk},$$  \hspace{1cm} (3.3)

where $A_0$ and $A$ is the cross sectional area of un-necked and necked regions respectively, as shown in Figure 3.7. From eq 3.2 and 3.3 we have

$$V_{nk} = V_0 / (1 - 1/\lambda_{nk}),$$  \hspace{1cm} (3.4)

where $\lambda_{nk}$ is a ratio depicting the shape change due to necking, given by

$$\lambda_{nk} = A_0 / A.$$  \hspace{1cm} (3.5)
Figure 3.7 Illustration of the neck front propagation at a crosshead speed of $V_0$ for a specimen of initial dimensions of $A_0=D_0H_0$ in cross section and $L_0$ in length. During the neck front propagation, over $\Delta t$, a fresh amount $A_0\Delta L_{iso}$ is converted from the un-necked part to increase the neck by a length of $\Delta L_{nk}$.

When $V_0$ is relatively high, the mechanical power can be considerably greater than the rate of heat loss due to the air convection. In other words, the tensile extension test can be essentially adiabatic at sufficient high rate, as there is no enough time to let the sample cool down by air blowing. In this limit during the steady neck front propagation, the temperature increase at the neck front can be used to estimate the portion of the internal kinetic energy change rate,

$$\frac{dU_1}{dt} = \rho c_p A V_{nk} (T_{nk} - T_a) = \rho c_p A_0 V_0 (T_{nk} - T_a)/(\lambda_{nk} - 1), \quad (3.6a)$$

where $\rho$ is the density, $c_p$ is the specific heat capacity, and $(T_{nk} - T_a)$ represents the temperature rise across the specimen during necking with $T_a$ denoting the ambient temperature. We can arrive at the same expression as eq 3.6a by acknowledging that after
extension the entire sample would have undergone a temperature rise of \((T_{nk} - T_a)\) within a period of \(t_{nk}\), which is the time it takes for the neck front propagation to complete at an overall draw ratio of \(\lambda_{nk}\), given by \(t_{nk} = (L_0/V_0)\lambda_{nk} - 1\). In other words, \(dU_1/dt = \rho c_p A_0 L_0 (T_{nk} - T_a)/t_{nk}\), which is eq 3.6a. Over the course of the extension until the completion of the necking, the internal kinetic energy increase density \(u_1\) is simply:

\[
u_1 = U_1/A_0 L_0 = \rho c_p (T_{nk} - T_a).
\] (3.6b)

The increase of \(U_1\) over time is to be compared with the mechanical power approximately given by

\[
dW/dt = \sigma_{engr(nk)} A_0 V_0,
\] (3.7a)

so that the work density at the end of necking completion is approximately

\[
w = \sigma_{engr(nk)} (\lambda_{nk} - 1).
\] (3.7b)

During neck front propagation, the engineering stress \(\sigma_{engr(nk)}\) is nearly constant, which means that the two rates: \(dU_1/dt\) in eq 3.6a and \(dW/dt\) in eq 3.7a are essentially constant. Thus, taking the ratio of eq 3.6a to eq 3.7a or eq 3.6b to eq 3.7b, we have

\[
U_1/W = u_1/w = \rho c_p (T_{nk} - T_a)/[\sigma_{engr(nk)}(\lambda_{nk} - 1)].
\] (3.8a)

This expression gives a rough estimate of the ratio. A more accurate one is given by the integration as

\[
u_1/w = \rho c_p (T_{nk} - T_a)/\int_1^{\lambda_{nk}} \sigma_{engr}(\lambda) d\lambda,
\] (3.8b)

where the mechanical work density \(w\) is evaluated from the stress vs. strain data.

Under adiabatic condition, the first law of thermodynamics states, in terms of the total internal energy,

\[
u = u_1 + u_2 = w.
\] (3.9)
Therefore, the internal potential energy density $u_2$ resulting from tensile extension can be evaluated from a combination of eq 3.8b and 3.9 as

$$u_2/w = 1 - u_1/w = 1 - \rho c_p (T_{nk} - T_a) / \int_1^{\lambda_nk} \sigma_{engr}(\lambda) d\lambda. \quad (3.10)$$

In principle, $u_2/w$ is finite because ductile extension of polymer glasses may not be entirely plastic, which is suggested by previous observations.\(^4, 5, 7, 56, 57, 60\) Elastic yielding reported in the literature\(^8, 9\) is also an evidence that there is elastic stress in cold-drawn polymer glasses.

In our experimental environment, we can hardly reach adiabatic or isothermal conditions. It is necessary to compare the mechanical power with the heat loss due to air cooling that can be significant at low crosshead speeds. The heat loss at the neck front involves a surface area of $2S_{nf}$, as illustrated in Figure 3.7. Air cooling becomes important when

$$2S_{nf} h(T_{nk} - T_a) \sim dU_1/dt = \rho c_p A_0 V_0 (T_{nk} - T_a)/(\lambda_{nk} - 1), \quad (3.11)$$

where $h$ represents the convective heat transfer coefficient. Eq 3.11 can be rewritten to determine the threshold crosshead speed $V_{0(ac)}$ as

$$V_{0(ac)} \approx 2(h/\rho c_p)(S_{nf}/A_0)(\lambda_{nk} - 1). \quad (3.12)$$

To determine the convective heat transfer coefficient $h$, a comparable dog-bone shaped sample with a thickness of 1.2 mm is preheated and an IR camera is applied to record the temperature decrease as a function of time due to the air cooling. Figure 3.8 shows the temperature drop $\Delta T = (T - T_a)$ as a function of time $t$. From the energy balance equation, we have

$$\rho c_p \frac{dT}{dt} = -\frac{2h}{H} \Delta T, \quad (3.13)$$
where $H$ represents the thickness of sample. Approximating the specimen as a thin sheet, we have

$$
\Delta T = (T_i - T_a) \exp \left( -\frac{2h}{\rho c_p} t \right),
$$

(3.14)

where $T_i$ is the initial temperature. For PC, the density is $\rho = 1200 \text{ kg/m}^3$, and the specific heat capacity is $c_p = 1200 \text{ J/(kg} \cdot \text{K)}$. By fitting the temperature data to the exponential function of eq 3.14, we obtain the decay time constant to be 33 s, from which $h$ is estimated to be $h = 25 \text{ W/(m}^2 \cdot \text{K)}$.

![Figure 3.8 IR camera measurement of the surface temperature of a heated PC that drops due to air cooling according to eq 3.13 and 3.14.](image)

Given $\lambda_{nk} = 1.7$, from eq 3.12, we have

$$
V_{0(ac)} \approx \left( S_{nf} / A_0 \right) \text{ mm/min},
$$

(3.15)

Taking $S_{nf} \sim D_0^2$ and $A_0 = D_0 H_0$, where $D_0$ and $H_0$ is the width and thickness of the undeformed region, we have

$$
V_{0(ac)} \approx (D_0 / H_0) \text{ mm/min}.
$$

(3.16)
Given typical values of our specimens, i.e., $D_0 = 3.0$ mm, and $H_0 = 0.8$ mm, we have $V_{0(ac)} = 3.8$ mm/min. Thus, for air cooling to have little effect, i.e., for the extension test to be adiabatic, we need $V_0 \gg 4$ mm/min.

Similarly, we can estimate the effect of lateral heat conduction across the neck front, which is important when

$$kA_0 \frac{T_{nk} - T_a}{D_0} \sim \rho c_p A_0 V_0 \frac{T_{nk} - T_a}{\lambda_{nk-1}}.$$  \hfill (3.17)

Given the thermal conductivity $k = 0.20$ W/(m · K), $D_0 = 3.0$ mm, and $\lambda_{nk} = 1.7$, we have $V_0 = 2.0$ mm/min. Thus, this heat conduction along the stretching direction can be negligible when $V_0 \gg 2.0$ mm/min.

Incorporating the contribution of air cooling and heat conduction along stretching direction, the first law of thermodynamics is given by, in the rate form,

$$\frac{dU_1}{dt} + \frac{dU_2}{dt} = \frac{dW}{dt} - 2S_{nf} h(T_{nk} - T_a) - kA_0 \frac{T_{nk} - T_a}{D_0},$$  \hfill (3.18)

where the first term on either side of eq 3.18 has been expressed in eq 3.6 and eq 3.7, respectively. We can integrate eq 3.18 to estimate the fraction of the mechanical work $W$ that is converted into $U_2$. Specifically, from the combination of eq 3.6, 3.7, and 3.18, we have

$$\frac{U_2}{W} = \frac{u_2}{w} = 1 - \frac{\rho c_p (T_{nk} - T_a)}{\int_1^{\lambda_{nk}} d_{eng} \, d\lambda} \left[ 1 + \frac{2S_{nf} h(\lambda_{nk-1})}{\rho c_p A_0 V_0} + \frac{k(\lambda_{nk-1})}{\rho c_p D_0 V_0} \right].$$  \hfill (3.19)

At high rates where the air cooling and lateral heat conduction corrections are negligible in eq 3.19 so that it reduces to eq 3.10, the maximum temperature rise is experimentally observed to occur away from the neck front. In applying eq 3.19, we will take $T_{nk}$ to represent the observed maximum temperature on the extending specimen.
Here, we should also note there is a temperature gradient across the specimen thickness $H$, on the order of $(T - T_{nk})/H$ due to the air cooling. In other words, the IR thermal imaging only reveals the surface temperature $T_{nk}$ that is lower than the interior temperature $T$. Since the heat exchange can only occur via air cooling at the surfaces, the heat flux due to the thermal conduction cannot exceed the convective heat flux. In other words, the surface temperature $T_s$ can only be lowered by an amount that depends on the convective cooling flux. Thus, the relation of $0 < k(T - T_s)/H \leq 2h(T_s - T_a)$ holds true at all times. This expression can be rewritten as $(T_s - T_a) < (T - T_a) \leq (1 + \alpha)(T_s - T_a)$ where $\alpha = 2hH/k$. A typical value for $k$ of a polymer glass is ca. $0.2 \text{ W/(m} \cdot \text{K})$. Throughout this work we will treat $\alpha \ll 1$, which is realistic for $H < 1 \text{ mm}$. In other words, the surface temperature detected by our IR camera is taken to be the interior temperature. $U_1$ might be slightly underestimated while $U_2$ is overestimated.

3.3.2 Uniform extension

Both sufficiently mechanically rejuvenated and melt-stretched PC specimens undergo homogeneous extension. For a uniformly extended sample, we can describe the mechanical work per unit volume per unit time as

$$dw/dt = \sigma_{engr}\dot{\lambda},$$

(3.20)

where $\dot{\lambda} = V_0/L_0$ is time independent for a fixed $V_0$. When $V_0$ is relatively low, we also need to consider the air cooling effect. In terms of the rate of internal kinetic energy change per unit volume, $du_1/dt$, given by

$$du_1/dt = \rho c_p dT/dt,$$

(3.21)

the first law of thermodynamics is in the following form,
\[ \rho c_p \frac{dT}{dt} + d\mu_2/dt = \sigma_{engr} \dot{\lambda} - (2h/H)(T - T_a). \]  

(3.22)

Defining the work density \( w(\lambda) \) as a function of the draw ratio \( \lambda = L/L_0 \),

\[ w(\lambda) = \int_1^\lambda \sigma_{engr}(\lambda') d\lambda', \]  

(3.23)

we can once again estimate the ratio of the excess energy increase \( u_2 \) to the mechanical work \( w \) as

\[ u_2/w = 1 - \left\{ \rho c_p[T(t) - T_a] + 2h \int_0^t dt'[T(t') - T_a] / H(t') \right\}/w(\lambda). \]  

(3.24)

Finally, it is insightful to divide the mechanical stress into two components, one plastic in nature, associated with change of the internal kinetic energy \( u_1 \) characterized by the rising sample temperature and the other elastic in origin, corresponding to change of \( u_2 \) that can be either inter-segmental or intra-segmental in origin. In either isotropic PC that undergoes necking or milled and melt-stretched PC that experiences homogeneous extension, we are interested in the ratio of the elastic component \( \sigma_{engr(E)} \) to the total stress \( \sigma_{engr} \). For milled PC, we can rewrite eq 3.22 following the practice of Hoy and Robbins\(^6\) as

\[ \sigma_{engr} = \sigma_{engr(E)} + \sigma_{engr(V)}. \]  

(3.25)

The first term on right is given by

\[ \sigma_{engr(E)} = d\mu_2/d\dot{\lambda} = \sigma_{engr} - \rho c_p \frac{dT}{d\dot{\lambda}} - 2h(T - T_a) / (H \dot{\lambda}), \]  

(3.26)

which can be estimated by measuring \( \sigma_{engr} \) and monitoring the temperature rise.

### 3.3.3 Uniform compression

During uniform compression, by rewriting eq 3.25 and 3.26, in the form of true stress, we have

\[ \sigma = \sigma_E + \sigma_V, \]  

(3.27)
where $\sigma_E$ is the elastic component of the mechanical stress and $\sigma_V$ is associated with the measurable heat generation. During uniaxial compression, the majority of heat loss is due to thermal conductivity. Therefore,

$$\sigma_V = \left( \rho c_p \frac{\partial T(z,t)}{\partial t} - k \frac{\partial^2 T(z,t)}{\partial z^2} \right) (H/V_0), \quad (3.28)$$

where $z$ represents compression direction, $H$ is the sample height, and the second item on right is the heat loss through thermal conductivity. For uniform compression, the stress is homogeneous, and the heat generation is the same everywhere in the specimen. In other words, $\sigma_V$ is constant independent of $z$. Thus, we can estimate $\sigma_V$ based on the information at $z = 0$.

Another way is to measure the overall energy conservation. We evaluate the total specific mechanical work and internal kinetic energy change by integrating the data of $\sigma$ and $\sigma_V$ to get

$$w = \int_0^\varepsilon \sigma(\varepsilon) d\varepsilon, \quad (3.29)$$

and

$$u_1 = \int_0^\varepsilon \sigma_V(\varepsilon) d\varepsilon, \quad (3.30)$$

where $\varepsilon$ is the true strain, given by

$$\varepsilon = \ln(\lambda) = \ln(L_0/L). \quad (3.31)$$

3.4 Results

Following will focus on the IR results during both uniaxial extension and compression for PC.
3.4.1 Isotropic PC during uniaxial extension

By applying the IR camera to *in situ* measure the temperature increase during uniform extension, the ratio of $u_2/w$ can be determined according to either eq 3.19 or eq 3.10. Figure 3.9 (a) shows the IR thermal image of shear yielding for isotropic PC, where a band is formed in 45° to the stretching direction upon startup extension at a low speed of $V_0 = 3 \text{ mm/min}$. Figure 3.9 (b) displays the temperature profile at the neck front during its steady propagation. The neck propagates at the top with significant temperature increase while at the bottom neck propagation slows down with much less temperature change. The corresponding stress curve is given in Figure 3.10, along with the temperature measurement of one fixed spot on the specimen. The temperature at this arbitrarily chosen point rises to the maximum when the neck front passes through. It should be also noticed that all the un-necked part could reach similar temperature maximum during propagation. As estimated in eqs 3.11-16, at this low speed there is considerable air cooling and lateral heat conduction that affect the measurement of the temperature. The true temperature rise should be higher than 5 °C as shown in blue squares in Figure 3.10. As the neck front passes away, temperature cools down to room temperature because of air cooling and lateral heat conduction. Figure 3.11 shows another thermal image of isotropic PC during uniaxial extension at a crosshead speed of $V_0 = 300 \text{ mm/min}$, where heat loss is negligible. At such a high speed, two shear bands occur simultaneously to form a “cross” and the temperature rises higher than the low rate one.
Figure 3.9 Temperature profiles for isotropic PC during uniaxial extension at V0=3 mm/min at 23 oC. (a) Shear yielding occurs at the yield point in 45° to the stretching direction. (b) Temperature mapping at a subsequent moment, showing the propagation of the neck front at the top whereas the bottom neck front slows down. Color bar listed on right refers to temperatures in the unit of Celsius (°C).
Figure 3.10 The engineering stress (red circles) of isotropic PC at a crosshead speed of $V_0 = 3$ mm/min during uniaxial extension and corresponding temperature rise (blue squares) measured from a fixed spatial point on the extending specimen, as a function of either draw ratio (top X axis) or time (bottom X axis).
Figure 3.11 Temperature profiles of shear bandings for isotropic PC during uniaxial extension at $V_0=300$ mm/min at 23 °C. A cross is formed by two shear bandings at the initial strain localization with significant temperature increase. Color bar listed on right refers to temperatures in the unit of Celsius (°C).

A series of similar experiments at various $V_0$ ranging from 3 mm/min to 900 mm/min for isotropic PC during uniaxial extension have been carried out to explore the deformation rate effect. With increasing $V_0$ there is more shape change, i.e., $\lambda_{nk} = A_0/A$ increases logarithmically as shown in Figure 3.12. Over this range of crosshead speeds, there is a significant increase in $T_{nk}$, as shown in Figure 3.13. Although the stress level $\sigma_{engr(nk)}$ stays nearly constant at low speeds, it increases logarithmically with $V_0$ at high speeds. Moreover, it is perhaps unsurprising that $\sigma_{engr(nk)}$ does not continue to decrease with lowering $V_0$ because a substantial stress is required to overcome the energy barrier to propagate the neck front regardless of the speeds. At the two low speeds of 3 and 24 mm/min, air cooling and lateral heat conduction are non-negligible. In other words,
according to eq 3.19, with consideration of air cooling and lateral heat conduction, the modified temperature reading at the neck front could be expressed by

\[ T_{nk} - T_a = (T_{nk} - T_a)_{IR} \left[ 1 + \frac{2Snt h(\lambda_{nk}^{-1})}{\rho c_p A_0 V_0} + \frac{k(\lambda_{nk}^{-1})}{\rho c_p D_0 V_0} \right], \]  

(3.30)
i.e., higher than the actual IR measurement by a factor indicated in the squared bracket. In Figure 3.13, the open squares represent \((T_{nk} - T_a)_{IR}\). After the correction, all data points (filled diamonds) fall onto a straight line, revealing \((T_{nk} - T_a) \sim V_0^{1/5}\). It should also be noticed that the temperature readings in Figure 3.13 are maximum values, which involve around 2.5% of experimental error.

Figure 3.12 Draw ratio \(\lambda_{nk}\), characterizing the shape change associated with necking, as a function of the crosshead speed \(V_0\) for isotropic PC during uniaxial extension.
Figure 3.13 The "plateau" stress level $\sigma_{\text{engr(nk)}}$ (red circles and left Y axis) during the neck front propagation at different crosshead speeds of $V_0$ for isotropic PC with $L_0=39$ mm and the corresponding maximum temperature rise $(T_{nk}-T_a)$ (open squares and right Y axis), as measured by IR camera. Filled diamonds are the modified temperature readings that contain corrections from the air cooling and the lateral heat conduction according to eq 3.30.

Given the information in Figure 3.12 and 3.13, $u_1$, $u_2$ and $w$ can be estimated according to eq 3.6b, 3.7b and 3.9 as a function of $V_0$, taking $(T_{nk}-T_a)_{\text{max}}$ as $(T_{nk}-T_a)$ that appears in eq 3.8, 3.10 and 3.19. Figure 3.14a shows how the work density $w$, internal kinetic energy change associated with the temperature rise $u_1$ and internal energy storage $u_2$ respectively change with $V_0$. The process of neck formation becomes increasingly plastic with increasing $V_0$, in agreement with the finding of an earlier similar study. It is
more insightful to evaluate the normalized changes. Figure 3.14b shows that $u_2/w$ actually decreases with $V_0$ logarithmically in the explored range of speeds. Since $\lambda_{nk}$ also has logarithmic dependence on $V_0$, $u_2/w$ is a linear decreasing function of $\lambda_{nk}$ as shown at top X axis in Figure 3.14b. This correlation implies that $u_2/w$ depends on the severity of the spatial rearrangement associated with necking, depicted by $\lambda_{nk}$. 

![Graph showing normalized changes with speed](image-url)
Figure 3.14 (a) Mechanical work density $w$ (red circles), internal (kinetic) energy change $u_1$ (blue squares) and internal (potential) energy $u_2$ (green diamonds) as a function of the crosshead speed $V_0$ for isotropic PC with $L_0=39$ mm. (b) the ratio of $u_2/w$ as a function of $V_0$ on logarithmic scale (bottom X axis) and draw ratio $\lambda_{nk}$ on linear scale (top X axis).

3.4.2 Milled PC during uniaxial extension

Necking can be avoided in extension of PC if PC is pre-treated with mechanical rejuvenation. After two-rolling milling, Figure 3.15 uses double Y axis to display both the engineering stress $\sigma_{engr}$ and the temperature rise $\Delta T$ as a function of the draw ratio $\lambda$ for PC at an initial Hencky rate of $V_0/L_0 = 1.2 \text{ min}^{-1}$. The engineering stress (red circles) grows and shows yielding around 50 MPa at 5 % of extension. The monotonic increase of $\sigma_{engr}$ with $\lambda$ in the post-yield regime can be regarded as "strain hardening". The specimen uniformly cools down during the elastic deformation and then heats up after deviation from
the linear regime as indicated by the *in situ* IR thermal imaging shown in Figure 3.16. The initial temperature decreasing is suggested to relate to the excess enthalpy associated with the free volume increase. Based on the stress vs. strain curve and eq 3.26, the elastic component of the tensile stress $\sigma_{\text{engr}(E)}$ is shown in Figure 3.15. It is suggested to be responsible for the observed stress increase.

Figure 3.15 Stress vs. draw ratio curve (red circles) of milled PC during uniaxial extension with $V_0/L_0 = 1.2 \text{ min}^{-1}$ at 23 °C, and simultaneous temperature measurement (blue squares) with $L_0=39 \text{ mm}$. Also plotted is the elastic component of stress decomposition $\sigma_{\text{engr}(E)}$ (green diamonds) according to eq 3.26.
A second way to depict the nature of the mechanical response is to evaluate how the excess internal energy $u_2$ stores up relative to the mechanical work $w$. Figure 3.17 shows that during extension $u_2$, estimated using eq 3.24, is larger than $w$ at the early stage because of the initial temperature drop. At this rate of $1.2 \text{ min}^{-1}$, $u_2$ keeps smaller than $w$ and monotonically grows for the rest of extension, suggesting that the subsequent extension is not entirely irreversible deformation, i.e., a combination of plastic flow and internal potential energy storage.
Figure 3.17 Mechanical work density \( w \) (red circles) and excess energy \( u_2 \) (green diamonds) as a function of extensional ratio \( \lambda \) with \( V_0/L_0=1.2 \text{ min}^{-1} \) of milled PC with \( L_0=39 \text{ mm} \) during uniaxial extension.

Tensile extension experiments of milled PC at other rates have also been carried out. To summarize, the temperature rise \( \Delta T \) and the ratio \( u_2/w \) as a function of the draw ratio \( \lambda \) are shown in Figure 3.18a and 3.18b, respectively. Several remarks are in order. First, \( u_2/w \) can indeed be greater than unity initially because the extending polymer glass cools down to build internal energy in the first stage of startup extension.\(^{78, 79} \) Second, the trend of \( u_2/w \) indicates the extension becomes increasingly plastic. Third, since \( w \) increases monotonically with strain, the leveling-off of \( u_2/w \) does not mean \( u_2 \) decreases. Actually \( u_2 \) still grows with strain, as shown in Figure 3.18c. Fourth, unlike the rate dependence of \( u_2 \) for isotropic PC involving necking, milled PC shows the opposite trend. At any given draw ratio, \( u_2 \) is lower at a lower rate. Finally, the work \( w_{re} \) required to
affinely stretch the entanglement network in PC is given by the small dots in Figure 3.18c. It shows \( w_{re} \ll u_z \), which means the internal potential energy buildup has little to do with the conformational entropy change\(^{19}\) that produces rubber elasticity above \( T_g \).
Figure 3.18 (a) Temperature increase $\Delta T$; (b) fraction of internal energy storage $u_2/w$; (c) internal energy $u_2$ as a function of the extensional ratio $\lambda$ at different values of $V_0/L_0$ for milled PC (open) with $L_0=39$ mm and melt-stretched PC (half-filled) with $L_0=13.7$ mm.
3.4.3 Melt-stretched PC during uniaxial extension

Another way to have near-homogeneous extension of PC is by a treatment of melt stretching that produces a geometric condensation of load-bearing strands (LBSs) in the chain network. The strengthened chain network is much more effective in activating the primary structure during extension. Figure 3.19 shows a comparison of stress vs. draw ratio curves for three different PC samples: (i) isotropic; (ii) milled; and (iii) melt-stretched at the same crosshead speed of $V_0 = 48 \text{ mm/min}$. Because the extension of melt-stretched PC is essentially uniform, it provides an interesting comparison with the preceding case of milled PC. Figure 3.20 is plotted in the same way as Figure 3.15, involving an initial Hencky rate of $V_0/L_0 = 3.5 \text{ min}^{-1}$. Here "strain hardening" is also evident. But a difference is immediately clear: the temperature increase in the melt stretched PC is lower than the milled PC although the stress level is actually higher, as shown in Figure 3.19. Consequently, there is a much higher component of the elastic stress $\sigma_{engr(E)}$. Without mechanical rejuvenation, the melt stretched PC is less dissipative, leading to a higher ratio of $u_2/w$ in Figure 3.18b. Admittedly, this contrast may be enhanced by the fact that milled PC is of a higher energy state. Because of a slight spatial variation in the temperature, measurements in triangles from two spots on the specimen are presented in Figure 3.20. The diamonds are based on the curve of up-pointed triangles, thus an under-estimate of the elastic component. Because of the lower temperature rise, there is more excess internal potential energy storage $u_2$, as represented by the half-filled squares in Figure 3.18b-c.
Figure 3.19 Stress vs. draw ratio curves of three different PC during uniaxial extension at a constant crosshead speed of $V_0=48$ mm/min at 23 °C: (i) isotropic (circles); (ii) milled (diamonds); and (iii) melt-stretched (triangles).

Figure 3.20 Stress vs. draw ratio curve (circles) of melt-stretched PC during uniaxial extension at $V_0/L_0=3.5$ min$^{-1}$ at 23 °C, and simultaneous temperature measurement from two spots on the specimen (two types of triangles). Also plotted is the elastic component
of stress decomposition $\sigma_{engr(E)}$ (diamonds). This melt-stretched PC involves a melt-stretching ratio of $\lambda_{ms}=2.5$.

3.4.4 Isotropic PC during uniaxial compression

Figure 3.21 shows four thermal images of the temperature rise during compression with an initial Hencky rate of $V_0/H_0 = 1.0 \, \text{min}^{-1}$ for cylindrical isotropic PC, where $V_0$ is the crosshead speed and remains constant during compression, $H_0$ is the initial sample height. The middle colorful part represents the cylindrical PC specimen. Various colors indicate different temperatures, as shown in the color scheme. The thermal imaging of Figure 3.21 allows us to map out a one-dimensional temperature variation along the sample height direction $z$. As an example, Figure 3.22 shows a set of nearly symmetric temperature profiles during ten different stages of the uniaxial compression with an initial strain rate of $V_0/H_0 = 1.0 \, \text{min}^{-1}$. Fitting them by parabolic functions, how much heat loses during compression due to thermal conductivity could be obtained according to eq 3.28. The simultaneous mechanical measurements show the tensile stress vs. strain curves as indicated in Figure 3.23 at initial strain rates of 1.0 and 0.1 $\, \text{min}^{-1}$ respectively, where also plotted is the specimen's maximum temperature change at $z = 0$ as a function of time.
Figure 3.21 Four images of the temperature profile during compression of an isotropic PC specimen with initial cylindrical dimensions of 5.7 mm in diameter and 5.9 mm in height at an initial rate of $V_0/H_0=1.0 \text{ min}^{-1}$, captured with an IR camera.

![Figure 3.21](image.png)

Figure 3.22 Temperature profiles across the specimen at different stages during the compression at $V_0/H_0=1.0 \text{ min}^{-1}$ for isotropic PC at room temperature.

![Figure 3.22](image.png)
Figure 3.23 Stress vs. strain curves (squares) and the corresponding temperature-strain curves (circles) for isotropic PC during uniaxial compression, with initial rates of $V_0/H_0 = 1.0 \text{ min}^{-1}$ (filled symbols) and $V_0/H_0 = 0.1 \text{ min}^{-1}$ (open symbols) respectively, where $\Delta T = (T_{\text{max}} - T_0)$ with $T_0$ being the ambient temperature equal to 23 °C and $T_{\text{max}} = T(z=0, t)$ the temperature reading at the middle of the specimen. The initial dimensions of these cylindrical specimens are 5.7 mm in diameter with a height of $H_0 = 5.9 \text{ mm}$, and 5.3 mm in diameter with a height of $H_0 = 5.4 \text{ mm}$, respectively.

The nature of the mechanical responses can be delineated by determining how the external work is partially stored as internal potential energy. According to eq 3.28, we can evaluate $\sigma_V$. Figure 3.24 shows $\sigma_V$ in open symbols for two speeds of $V_0/H_0 = 0.1$ and $1.0 \text{ min}^{-1}$, along with the total true stress $\sigma$ given by the two smooth curves. The data for $V_0/H_0 = 1.0 \text{ min}^{-1}$ look ordinary in the sense that $\sigma_V < \sigma$, as expected. On the other
hand, the circles in Figure 3.24 show surprising behavior relative to the red curve. In other words, the heat release rate in the post-yield regime is higher than the rate of external work. For $\sigma_\nu > \sigma$, we must have $\sigma_E < 0$ in eq 3.27. Thus, there must have been an excess internal energy build-up prior to the point of $\sigma_\nu > \sigma$ because the overall internal energy of the PC glass cannot decrease from its value of the undeformed state.\textsuperscript{56} Such internal potential energy storage due to external deformation is consistent with the idea that distortion of chain configuration may have occurred at the bond level.\textsuperscript{8, 80} Therefore, the difference between the circles and curve means that beyond the yield point relaxation of some intra-segmental deformation has taken place in the form of released heat as the glassy state returns to a lower energy state.

Figure 3.25 plot $w$ and $u_1$ respectively according to eq 3.29 and 3.30 as a function of strain $\varepsilon$ for both rates. Here the continuous curves represent the work density $w$, which are essentially the same at these two rates, and the solid symbols are the internal kinetic energy density at each stage of the compression at $V_0/H_0 = 0.1$ (circles) and 1.0 $min^{-1}$ (squares) respectively. Since the circles fall on the continuous curve, it confirms that there is not more heat generated than the input mechanical energy. The data above the curve are indicative of the level of experimental error. More interestingly and importantly, the squares stay appreciably below the curve. It indicates a portion of internal energy is built up during uniaxial compression at this rate.
Figure 3.24 Internal kinetic energy component $\sigma V$ associated with the heat release for isotropic PC during uniaxial compression at $V_0/H_0=0.1$ min$^{-1}$ (circles) and 1 min$^{-1}$ (squares) respectively. Also presented is the total true stress $\sigma$ given by the two continuous curves.

Figure 3.25 External work in the continuous curve as well as the measured heat release in solid symbols per unit volume as a function of the compressive strain for isotropic PC at $V_0/H_0=0.1$ (circles) and 1.0 (squares) min$^{-1}$, respectively.
Data in both Figures 3.24 and 3.25 indicate that $\sigma_E > 0$ at all times during the compression with rate $V_0/H_0 = 1.0 \text{ min}^{-1}$, which implies that the internal potential energy keeps building up. To further verify, an independent evaluation of the compressed PC has been carried out at $V_0/H_0 = 1.0 \text{ min}^{-1}$ to two Hencky strains of $\varepsilon = 0.69$ and 0.99 respectively. The internal potential energy buildup during the compression can be detected when subjecting the sample to the DSC measurements.\(^{81-83}\) Specifically, upon heating the excess internal energy will be released, so that the heat flow required to warm up the specimen will be lower. Figures 3.26a and 3.26b indicate that there is indeed internal potential energy release as shown by the difference in the area under the heat flow curves between the first and second cycles. Equating the difference to the internal potential energy per unit volume $u_2$, we find $u_2 = 13.2 \text{ MPa}$ at $\varepsilon = 0.69$ and $24.9 \text{ MPa}$ at $\varepsilon = 0.99$ respectively. These values match the difference observed in Figure 3.25 between $w$ and $u_1$. 

![Heat Flow Curve](image.png)
3.5 Discussions

Our experiments of combined mechanical and thermal measurements enabled \textit{in situ} time-resolved temperature determination and indicated that external deformation builds up internal energy\cite{58,84}. One form of the energy storage may be through covalent bond distortions\cite{85}, leading to chain tension in the chain network\cite{3,8,9}. Important supporting evidence emerges when an elastic retractive stress shows upon warming up a pre-necked sample above the storage temperature. The phenomena of elastic yielding will be discussed in detail in Chapter IV.
3.5.1 Nature of internal potential energy $u^2$

Taking the advantage of the hybrid structure model, a mesoscopic picture is proposed to have a better sense of the deformation mechanism at various crosshead speeds. As shown in Figure 3.27, the dark dots represent segments stuck in a high potential energy state and light dots denote more mobile ones which can overcome the potential barrier. During the uniaxial deformation at the necking front, some segments become jammed again (dark dots) and stored the internal energy with a high potential energy landscape. Others (light dots) could slide past one another after hopping over the potential barrier and converting their potential energy into kinetic energy in the form of heat. The ratio of these two population varies with the applied deformation rate. The data in Figure 3.14 suggest that at low rate, many segments remain in a high energy state, as shown in Figure 3.27 (a). With increasing rate, more segments overcome the energy barrier and anticipate in chain sliding, as shown in Figure 3.27 (b) and (c). We should note that these domains of high energy state may be of a much greater scale. The depiction in Figure 3.27 (d)-(f) represents them on some unspecified scales. Actually the (a) and (d), (b) and (e), (c) and (f) express the same physics, respectively.

Figure 3.27 also implies that during extension there is less structural and dynamical heterogeneity at higher values of $V_0$. The more plastic state depicted by either (c) or (f) of Figure 3.27 should indeed show less heterogeneity. This is consistent with the report based on optical photobleaching measurements that $\beta$ in the stretched exponential of the KWW characterization for relaxation dynamics increases with increasing rate. Moreover, a glass is inherently heterogeneous, perceived by Long and Lequeux to be made of a percolating set of glassy domains. Other studies have also suggested glasses to contain
soft and hard spots.\textsuperscript{89-91} In such a context, our picture of Figure 3.27 for plasticity depicts
the patches on a different length scale from those envisioned by these previous studies.

To further explore the implication of Figure 3.27, we carry out one more experiment
to learn about the glassy state after necking. Figure 3.28 shows relaxation behavior of
isotropic PC at two speeds in terms of stress vs. strain curves. Because of higher mobility
produced by the higher rate, the initial stress relaxation is faster.\textsuperscript{92} We can also unload to
capture how the necked portion of the PC specimen retracts as a function of time. Figure
3.28 reveals measurable shrinkage taking place at different rates. Clearly, the sample is
hardly glassy in the initial moments after clamp release. We note the necked part of the
sample can retract 9 % within a second for 300 mm/min and 8 % in over 100 s for 3
mm/min. This figure indicates that the sample shrinkage clearly takes place on a much
longer time scale when released from the extension at a lower rate. It is entirely plausible
that the state of (a) may undergo significantly slower retraction than the state of (c) in
Figure 3.27 in presence of so many immobilized segments. In other words, the data in
Figure 3.28 are consistent with the picture depicted in Figure 3.27.
Figure 3.27 Microscopic structure pictures of isotropic PC during extension as a function of crosshead speed $V_0$. We use two different scales: one is using dots to represent chain segments ((a) to (c)) and the other is applying patches to show different domains ((d) to (f)). It should be noted that (a) and (d), (b) and (e), and (c) and (f) express the same information, respectively. Here, different colors to represent different mobility of chains, which increases from dark to light. Specifically, dark dots in (a) to (c) and dark areas in (d) to (f) represent immobilized segments or domains stuck in high potential energy, while light dots or areas are mobilized ones that have the ability to hop over the potential barrier. With increasing speeds from (a) to (c) or from (d) to (f), the immobilized regions decreases, resulting in a decrease of the internal potential energy $u_2$. Note we omit any structural and dynamical heterogeneities in this picture.
Figure 3.28 Length shrinkage of pre-necked PC as a function of time, prepared with two different crosshead speeds of $V_0=3$ (circles) and 300 mm/min (squares) at 23 °C with $L_0=39$ mm to extend to $L/L_0=1.6<\lambda_{nk}$ before the necking is completed. Here we artificially set $t$ starts at $t_0=0.03$ s to have the initial points in the logarithmic scale.

3.5.2 Difference between milled and melt-stretched PC: dissipative vs. elastic

As shown in Figure 3.18 between open and half-filled squares, the difference is rather remarkable. The rejuvenation by milling decreases the confining energy barrier and thus has significant effects, e.g., making it much easier to activate the glassy state. Therefore, the yield stress of milled PC (green diamonds) shown in Figure 3.19 is notably lower than the melt-stretched one (blue triangles). Moreover, it also makes the system harder to build chain tension. $u_2$ is expected to be smaller than that of melt-stretched PC because of the additional enhancement rising from the geometric condensation during melt stretching process. Assuming beyond the yield point, e.g., after $\lambda = 1.1$, the glassy state
of milled and melt-stretched PC are comparable, then at any given draw ratio the ability for the post-yield state to build chain tension in LBSs should be the same. As a result, the difference of $u_2$ between the melt-stretched PC (half-filled squares) and milled PC (open symbols) is due to the increasing density of LBSs in presence of geometric condensation.

3.5.3 Difference between uniaxial extension and compression

For isotropic PC, the internal energy storage density $u_2$ shows different trend with the deformation rate between uniaxial extension and compression. $u_2$ decreases with the deformation rate under uniaxial extension as shown in Figure 3.14 while upon uniaxial compression it shows reverse results in Figure 3.25. There might be two reasons. One is that isotropic PC cannot undergo homogeneous deformation in extension and the neck propagation may cause difference in the storage of $u_2$. The other one is that pressure may lead to chain tension in LBSs varies with deformation rates, as compression can be regarded as a combination of biaxial extension and hydrostatic pressure.

3.6 Summary

The origin of mechanical stress in large deformation of polymer glasses has been elusive because they appear to be both plastic and anelastic in the post-yield regime. In this chapter, we explored how much internal energy stored upon external deformation and how the decomposition of dissipative and energetic components changed with the applied deformation rate. For isotropic PC that undergoes shear yielding and neck propagation, the ratio of $u_2/w$ decreases logarithmically with increasing crosshead speed $V_0$. When comparing isotropic PC with milled one at the same lowest rate of $V_0/L_0 = 0.077 \text{ min}^{-1}$,
$u_2$ is about a factor of five to that of the milled PC. Moreover, uniform extension produces much higher $u_2/w$ and $u_2$ for melt-stretched PC than for milled PC. This difference explicitly indicates that chain network drives the buildup of the internal energy storage. In other words, the observed difference between milled and melt-stretched PC supports the recently proposed picture of a structural hybrid for polymer glasses under large deformation. In this model, it is postulated that chain networking is necessary to permit post-yield plastic deformation in polymer glasses.

For our results during uniaxial compression, it is important to note that the excessive heat release as shown in red circles in Figure 3.24 is consistent with the idea that internal energy is stored during deformation. When such energy is released in the form of heat, the glassy state reaches a lower energy state. It may be associated with the recovery of chain tension in LBSs.
4.1 Background

In the past decades, the nature of mechanical stress under large deformation has been widely studied. In Chapter III, we demonstrated that internal potential energy $u_2$ can be stored during both uniaxial extension and compression. Thus the large post-yield deformation is not entirely dissipative or plastic. How is the internal energy stored? Is it due to the inter-segmental interaction related with the van de Waals interaction or the intra-segmental force associated with the chain connectivity? Perhaps there is distortion of covalent bonds, amounting to chain tension in the chain network.\textsuperscript{8, 9} To explore the origin of the stored internal energy, Cheng \textit{et al.}\textsuperscript{8, 9} first draw PC samples to a draw ratio of 1.73 at room temperature. They then found the pre-necked samples shrank after annealing at various temperatures for 24 h as shown in Figure 4.1 (a). Also, they stored the pre-necked samples at room temperature for 24 h and observed a retractive stress upon heating these strained samples up, as indicated in Figure 4.1 (b), which is called “elastic yielding”. They speculated that the chain tension built during the pre-deformation could be preserved by the vitrification and drive polymer chains to shrink at a high temperature. Upon devitrification, the chain tension could transmit across the chain network to show up a macroscopic retractive stress.
Figure 4.1 (a) Length retraction of a pre-necked PC as a function of annealing temperature. The sample was pre-drawn at a crosshead speed of 10 mm/min to a draw ratio of 1.73 and then annealed at different temperatures for 24 h (Replotted from Cheng, S.; Wang, S.-Q. Phys. Rev. Lett. 2013, 110, (6), 065506). (b) Retractive stress as a function of annealing time at various temperatures for a cold-drawn PC. The PC samples were pre-necked at a

On the other hand, in absence of the chain network, chain tension should not be able to transmit through the sample and the retractive stress could be greatly reduced. Therefore, to further reveal the chain network effect for polymer glasses, gamma irradiation is applied to pre-drawn samples to cause chain scissions. This type of high energy irradiation could penetrate the sample in the glassy state and induce either crosslinking or degradation of polymer chains. The total energy absorbed by the specimens is expressed in the unit of Gy, which is energy per unit mass, i.e., 1 Gy=1 J/kg. Given the conversion that 1 J = 6.25x10^{18} eV and the molar mass of a repeated unit being \( m_1 \), the intensity of irradiation in the unit of 1 kGy can be expressed as 1 kGy =\( m_1 \times 6.25 \times 10^{18} / 6.02 \times 10^{23} \) = 1.04 \times 10^{-5} m_1 \) eV per repeated unit. Given that the energy to break a bond is around 300 kJ/mol=3 \times 10^5 \times 6.25 \times 10^{18} / 6.02 \times 10^{23} = 3 \) eV and the energy absorption efficiency is 30\%, then 100 kGy would amount to have \( 10^{-4} m_1 \) of chain scissions per repeated unit. Assuming \( m_1 = 100 \), then 100 kGy would have one bond-bond break per hundred repeated unit.

When subjected to high energy radiation, both chain scission and crosslinking take place, as catalogued by Lawton *et al.* by electron irradiation. Either one may dominate depending on the chemical structure and conditions, e.g., temperature, environment and dose. Charlesby reported crosslinking for polythene by pile irradiation while it was found entirely degradative for PMMA by ionizing irradiation. Acierno *et al.* studied the gamma irradiation effect on PC at various doses. As shown in Figure 4.2, they

72
observed crosslinking predominates at small doses while chain scission is more effective at higher doses.

![Normalized molecular weight](image)

Figure 4.2 Normalized molecular weight by the original molecular weight before gamma irradiation as a function of absorbed dose through two measurements: intrinsic viscosity (squares) and melt flow index (circles) (Replotted from Acierno, D.; La Mantia, F. P.; Titomanlio, G.; Calderaro, E.; Castiglia, F. *Radiation Physics and Chemistry (1977)* **1980**, 16, (2), 95-99).¹⁰

In this chapter, the origin of $u_2$ measured in Chapter III will be further explored by examining the elastic yielding behavior at different pre-draw rates. Both the annealing temperature effect and the pre-draw ratio effect of the milling samples will also be studied to better understand the elastic yielding phenomenon. Gamma irradiation will be applied to break the carbon-carbon bond to explore the role of the chain network. Moreover, four types of polymer glasses: PC, PS, PMMA and PPE will be used to demonstrate the universality of the elastic yielding phenomenon.
4.2 Experiments

In this section, two parts: (a) materials and sample preparation; and (b) apparatus and methods would be introduced.

4.2.1 Materials and sample preparation

Four types of polymer glasses, bisphenol A-polycarbonate (PC), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(2,6-dimethyl-1,4-phenylene oxide) (PPE) are studied in this work. The PC is Lexan TM 14111, received from Sabic (GE Plastic). The PS is Dow Styron 663. The PMMA is from Plaskolite West, Inc. with an item number of CA-86. The PPE is obtained from SABIC Innovative, with a tradename PPO630. Relevant sample properties are listed in Table 4.1.

Table 4.1 Sample characteristics of polymer glasses

<table>
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<th>Sample</th>
<th>$M_w$ (kg/mol)</th>
<th>$M_c$ (kg/mol)</th>
<th>$PDI$</th>
<th>$T_g$ (°C)</th>
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<td>2.01</td>
<td>149</td>
</tr>
<tr>
<td>PS</td>
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<td>13</td>
<td>1.44</td>
<td>103</td>
</tr>
<tr>
<td>PMMA</td>
<td>125</td>
<td>13</td>
<td>1.13</td>
<td>113</td>
</tr>
<tr>
<td>PPE</td>
<td>47.6</td>
<td>5.3</td>
<td>2.75</td>
<td>214</td>
</tr>
</tbody>
</table>

The sample preparation procedures of isotropic PC and milled PC can be found in Section 3.2.1. PS pellets were compression molded into a 100 mm × 100 mm × 1.0 mm sheet at 180 °C in TMP Vacuum Compression Press for 1 h and then cooled down to room temperature. Dog-bone shaped samples were obtained by a punch press at room temperature with a dog-bone mold (ASTM D-638) involving an effective length of 13.7 mm. Such samples were then stretched to a draw ratio of 5.0 at 135 °C with a crosshead.
speed of 600 mm/min. At the end of melt stretching icy water was sprayed onto the sample. PPE powders were compression molded into a 100 mm × 100 mm × 0.5 mm sheet at 280 °C in TMP Vacuum Compression Press for 1 h and then cooled down to room temperature. Dog-bone shaped samples were obtained by a punch press at room temperature with a dog-bone mold (ASTM D-412) involving an effective length of 39 mm. An isotropic PMMA sheet with dimensions of 100 mm × 100 mm × 2.0 mm was prepared under the same condition of PS. Such sheet was then milled to a thickness reduction of 30% at 60 °C. Cylindrical PMMA in this study were extruded by Monsanto Capillary Rheometer. The pellets of PMMA were first heated to 210 °C in the rheometer. A pressure of 123 bar was then applied to compress the resin in the barrel to remove the air. After relaxation for 30 min, the sample was extruded at a wall stress of 0.078 MPa, using a capillary die with a length of 15 mm and a diameter of 1 mm.

4.2.2 Apparatus and methods

The melt stretching preparation of PS was carried out on Instron 5543 with a homemade oven ranging from -100 °C to 200 °C. All cold drawn measurements were carried out by Instron 5543 at either 80 °C for extruded PMMA or at 23 °C for other samples. To run the elastic yielding tests, all the pre-drawn samples were taken off from the clamps and relaxed at 23 °C for 24 h. The elastic yielding experiments were then carried out with a homemade temperature heater to warm up the necked part in the middle while the two ends of the sample were fixed by Instron 5543, as shown in Figure 4.3.9 During annealing at temperatures above the storage temperature, the clamps remained fixed and the stress was captured by Instron 5543. The typical length of necked part to be heated was around 30 mm. Note that gamma irradiation was done in China, it took around 2 months
to finish the tests. Therefore, those samples in the gamma irradiation part, no matter with or without gamma irradiation treatment, experienced aging at room temperature for around 2 months before undergoing elastic yielding measurements.

The molecular weight of PC was determined on a TOSOH® EcoSec HLC-8320 GPC equipped with one TSK-GEL super H 4000 column and two TSK-GEL® super H 3000 columns with chloroform as solvent.

Both isotropic and pre-necked samples were exposed to gamma irradiation at room temperature in Beijing Radiation center with the source of radioactive cobalt (Co$^{60}$). It includes two types of irradiation. One is 1.17 MeV and the other is 1.33 MeV. The dose of gamma irradiation ranged from 0 to 1000 kGy.

Figure 4.3 Side view of the heating setup for elastic yielding experiments. A pre-necked sample is fixed onto the clamps of Instron before the homemade heater is applied to warm up the sample. During annealing, the clamps remain fixed and the stress is measured by the machine. A typical dimension for pre-necked PC is also indicated, with a length of 66
mm and a thickness of 0.38 mm (Replotted from Cheng, S.; Wang, S.-Q. *Macromolecules* 2014, 47, (11), 3661-3671).

4.3 Results

Following will focus on four effects for the elastic yielding: (a) pre-draw rate effect; (b) pre-draw ratio effect; (c) annealing temperature effect; (d) gamma irradiation effect.

4.3.1 Pre-draw rate effect

The results in Chapter III shows that $u_2$ varies with draw rates, which may lead to different chain tension in the chain network. So a series of elastic yielding experiments based on pre-necked isotropic PC produced at various speeds have been carried out, as shown in Figure 4.4. The elastic yielding stress firstly decreases with the sample getting bended, which is related to thermal expansion. In a short induction time, the stress starts to grow up, where the sample quickly straightens. The emergent retractive stress at 65 °C below $T_g$ is a clear indication of the residual elastic stress of an intra-segmental origin trapped at room temperature, plausibly associated with covalent-bond level distortions. Specifically, chain tension is built up through load-bearing strands (LBSs) upon deformation and trapped by the surrounding frozen primary network. When annealing at higher temperatures, the LBSs are able to shrink because of the much weaker interactions with surrounding primary network, resulting in an observable retractive stress $\sigma_{EY}$. Moreover, Figure 3.14 reveals that the overall $u_2$ decreases with increasing stretching rates. However, the retractive stress $\sigma_{EY}$ shows the opposite trend. It increases with the rate of pre-deformation, indicating that there is little correlation between $\sigma_{EY}$ and $u_2$. This
is possible only if $u_2$ has both inter-segmental and intra-segmental components. Figure 4.4 suggests that the intra-segmental component of $u_2$ is less rate sensitive and more internal energy of inter-segmental origin is stored at lower rates. In fact, the combination of Figure 3.14 and Figure 4.4 indicates that $u_2$ is dominantly inter-segmental at low rate since $u_2$ drops to a rather low common level at the highest rates.

Figure 4.4 Elastic yielding stress $\sigma_{EY}$ as a function of annealing time for pre-necked untreated PC at 80 °C. These prenecked specimens were obtained by cold-drawing samples with an initial length of $L_0=39$ mm at room temperature at various crosshead speed $V_0$, ranging from 3 to 600 mm/min, to a final length of $L = \lambda L_0 = 1.7 \times 39 = 66$ mm. A middle portion (ca. 30 mm) of such specimens were heated to 80 °C to observe the elastic yielding behavior. Such retractive stress is normalized by the original cross sectional area before pre-deformation to exclude the effect of $\lambda_{nk}$ varying with rates.
Figure 3.14a shows that the level of $u_2$ is rather high at low rates. On the other hand, the elastic yielding stress in Figure 4.4 is not consistent with the trend of $u_2$, i.e., $\sigma_{EV}$ is smaller at a lower speed. It implies that there should be a substantial inter-segmental part in $u_2$ in addition to the intra-segmental component. In the work done by Garg et al.,\textsuperscript{57} it was suggested that high rates of deformation involved an additional mechanism of $\beta$ motions, which resulted in larger plasticity. With growing rate, the necking process becomes more dissipative, involving segments overcoming the energy barrier and hopping past one another. In contrast, the large $u_2$ at low speeds corresponds to insufficient plastic events of segmental hopping.

4.3.2 Pre-draw ratio effect

During the necking propagation of untreated PC at a constant crosshead speed, the shape of the sample does not change. Therefore, milled PC, which could undergo homogeneous deformation, was used to study the draw ratio effect, as shown in Figure 4.5. The milling samples used here have a thickness reduction of 30%. From Figure 4.5 (a), it is noticed that for the sample without any pre-deformation, i.e., $\lambda = 1.0$, the retractive stress shows up and finally reaches a saturation level of around 9 MPa at 86 °C. It suggests that during the milling procedure, chains already have been stretched. Therefore, the stretched chains shrink when annealing at temperatures above the storage temperature. Moreover, before the yield point at $\lambda \sim 1.05$, the retractive stresses are all comparable, indicating there is no chain tension buildup in the elastic deformation regime. In other words, in the pre-yield regime, $u_2$ is in the origin of inter-segmental interaction. Beyond the yield point, the elastic yielding stress increases with the pre-draw ratio. This result
indicates that with further deformation, more segments participate in chain tension and more internal potential energy is stored. When plotting the final elastic yielding stress plateau as a function of the pre-draw ratio, a linear relationship can be observed in the post-yield regime in Figure 4.5 (b).

To demonstrate the universality of this finding, elastic yielding experiments of milled PMMA are also carried out. The isotropic PMMA is milled to a final thickness reduction of 30 % at a milling temperature of 60 °C. Figure 4.6 (a) is a stress vs. draw ratio curve of milled PMMA at a crosshead speed of $V_0 = 6 \text{ mm/min}$ at room temperature. The engineering stress of milled PMMA is more flat than milled PC beyond the yield point. A similar elastic yielding phenomenon of milled PMMA at $T_{el-yield} = 70 \degree C$ at different draw ratios is observed in Figure 4.6 (b). A retractive stress of 4 MPa occurs for the non-deformed milled PMMA, which is even less than a half of that for PC. Given the same thickness reduction during milling, i.e., the equivalent chain stretching effect during milling, the difference in retractive stress may be caused by the difference of the milling temperature. At a higher milling temperature environment, the surrounding primary network is more mobilized, leading to less chain tension preserved in PMMA. The inset shows the same linear relationship between retractive stress plateau and the draw ratio in the post-yield regime for milled PMMA.
Figure 4.5 (a) Retractive stress as a function of annealing time at $T_{el\text{-}yield}=86$ °C for pre-drawn milled PC. All the specimens were first milled with a thickness reduction of 30% and then stretched at a constant crosshead speed $V_0=3$ mm/min to different draw ratio,
ranging from $\lambda=1$ to 1.40. The inset shows a typical stress vs. draw ratio curve for the pre-deformation of the milled PC at $V_0=3$ mm/min. (b) The corresponding retractive stress plateau as a function of pre-draw ratio.

Figure 4.6 (a) Engineering stress vs. draw ratio of milled PMMA at a crosshead speed of $V_0=6$ mm/min at room temperature. (b) Retractive stress as a function of annealing time at $T_{el-yield}=70$ °C for pre-drawn milled PMMA. All the specimens were first milled to a thickness reduction of 30% at 60 °C and then stretched at a constant crosshead speed $V_0=6$
mm/min to different draw ratio, ranging from $\lambda=1$ to 1.16. The inset shows the linear relationship between the final retractive stress plateau and the pre-draw ratio.

4.3.3 Annealing temperature effect

It is well known that the temperature plays an extremely important role in chain mobility. Though polymer chains remain frozen macroscopically, segments are expected to be more mobilized at higher temperatures. Therefore, a higher temperature should produce more retractive stress than that at a lower temperature. Figure 4.7 shows the result of elastic yield for milled PC at different annealing temperatures ranging from 35 °C to 105 °C. The milled specimens were first drawn at a crosshead speed of $V_0 = 3$ mm/min to a draw ratio of $\lambda = 1.20$. It is noticed that in Figure 4.7 the induction time, characterizing how soon the retractive stress starts to grow, decreases with the annealing temperature. It is about 100 s at 35 °C, and reduces to 10 s at 105 °C. This trend is consistent with the Eyring formula: $\tau \sim \exp(-A\sigma/RT)$.\(^{100}\) The retractive stress increases with an annealing temperature from 35 °C to 65 °C, which was as predicted. However, when the temperature was further increased, the stress saturates on the same level. It is speculated that the residual stress starts to relax at annealing temperatures higher than 65 °C.
Figure 4.7 Retractive stress as a function of annealing time at various annealing temperatures for milled PC with a thickness reduction of 30%. All pre-deformation tests are carried out at 23 °C involving a crosshead speed of $V_0=3$ mm/min and a draw ratio of $\lambda=1.20$.

4.3.4 Gamma irradiation effect

Through exposure to the gamma irradiation at different doses, we could obtain different degrees of change in polymer chain, either chain scission or crosslink. Figure 4.8 shows the engineering stress as a function of draw ratio of isotropic PC at a series of doses, ranging from 0 kGy to 1000 kGy. Up to 200 kGy of gamma irradiation, the engineering stress does not show significant change, though the yield stress has a decreasing trend with increasing doses. At a dose of 500 kGy, the sample can only be stretched to a draw ratio of $\lambda\sim1.17$. In other words, the sample becomes more un-stretchable after gamma irradiation.
By further increasing the dose to 1000 kGy, ductile PC becomes fragile at room temperature. To confirm the chain scission effect, GPC experiments were conducted to characterize the molecular weight change, as shown in Figure 4.9. At gamma irradiation doses lower than 20 kGy, the molecular weight change is very small. But it significantly decreases at doses of 200 kGy and 500 kGy, e.g., the molecular weight decreases by 30% at a dose of 500 kGy.

![Figure 4.8 Engineering stress vs. draw ratio curves of isotropic PC after gamma irradiation](image)

Figure 4.8 Engineering stress vs. draw ratio curves of isotropic PC after gamma irradiation with different doses at a crosshead speed of $V_0=6$ mm/min at 23 °C.
To study the chain network effect upon deformation, we first pre-neck isotropic PC to a draw ratio of $\lambda = 1.7$ at a crosshead speed of $V_0 = 6 \text{ mm/min}$ at room temperature. The pre-necked specimens are subjected to gamma irradiation at various doses at room temperature and then annealed at higher temperature than storage temperature to observe the elastic yielding phenomenon. Figure 4.10 shows the retractive stress as a function of annealing time for pre-necked PC after gamma irradiation at $T_{el-yield} = 75^\circ\text{C}$. With increasing doses of gamma irradiation, the retractive stress significantly decreases. Specifically, at a relatively low dose of gamma irradiation, e.g., 5 kGy, though molecular weight does not change a lot, the retractive stress decreases by a factor of 1/3. By further increasing the dose, for example, the retractive stress reduces to 3 MPa at a dose of 500
With the breakdown of the chain network, we do observe a drop of the retractive stress during elastic yielding.

Figure 4.10 Retractive stress as a function of annealing time at $T_{el\text{-}yield}=75 \, ^\circ\text{C}$ of pre-necked PC at different doses of gamma irradiation. The PC specimen was first pre-deformed at a constant crosshead speed of $V_0=6 \, \text{mm/min}$ to a draw ratio of $\lambda=1.7$ at room temperature and then treated with gamma irradiation.

To demonstrate the universality of the conclusion, other types of polymer glasses are also tested with gamma irradiation: melt-stretched PS, isotropic PPE, and extruded PMMA. Isotropic PPE undergoes ductile deformation at room temperature. After melt stretching, which includes a geometric condensation of the chain network, brittle PS becomes ductile at room temperature. Extruded PMMA could also be ductile when heating above brittle-ductile transition temperature $T_{BD}$. Figure 4.11 shows the typical engineering stress vs. the draw ratio curves of these three types of polymer glasses as well.
as isotropic PC at a crosshead speed of $V_0 = 6 \text{ mm/min}$ during pre-deformation. The extruded PMMA is stretched at 80 °C while the other three are all carried out at room temperature around 23 °C. After deviating from initial linear deformation, all of them quickly reaches the yield point, where shear yielding takes place and necking starts to propagate. The extension is stopped before neck propagation finished and all those pre-necked specimens are taken to absorb gamma irradiation at different doses.

![Figure 4.11](image.png)

Figure 4.11 Engineering stress $\sigma_{\text{engr}}$ as a function of draw ratio $\lambda$ for four types of polymer glasses: (1) melt-stretched PS; (2) PPE; (3) PC; (4) extruded PMMA. The brackets show the experimental temperatures. All cold drawn experiments involve a crosshead speed of $V_0=6 \text{ mm/min}$. The melt-stretched PS is firstly stretched at $V_{ms}=600 \text{ mm/min}$ at 135 °C to a stretching ratio of $\lambda_{ms}=5$ before cooled down by icy water and then the cold drawn experiment is carried out.
The elastic yielding results after gamma irradiation in Figure 4.12 indicate the same decreasing trend for pre-necked melt-stretched PS at an annealing temperature of 75 °C. The non-irradiated sample shows the highest retractive stress while the specimen at 200 kGy shows the lowest value. Meanwhile, the induction time also increases with the dose of subjected gamma irradiation. Another example is extruded PMMA, involving a pre-draw ratio of $\lambda = 2.2$, as shown in Figure 4.13 (a). The retractive stress increases a little at a dose of 5 kGy. It is probably due to the crosslink during gamma irradiation, which is consistent with the yield stress of isotropic sample increases after absorbing a dose of 5 kGy, as shown in Figure 4.13 (b). After severe gamma irradiation treatment of 200 kGy, the specimen breaks in the clamp during elastic yielding with much lower retractive stress. Gamma irradiation is also applied to pre-necked PPE which shows good ductility at room temperature. In Figure 4.14 (a), it is noted that the induction time largely increases with the dose of gamma irradiation at annealing temperature of 75 °C. Within 1 h, the retractive stress even remains negative at a dose of 500 kGy. It may be due to the fact that the annealing temperature for PPE is 145 °C lower than $T_g$, freezing the system too much to retract. Annealing those samples at a higher temperature, e.g., 120 °C in Figure 4.14 (b), the induction time decreases a lot. Moreover, the magnitude of the retractive stress decreases with increasing doses, making the conclusion universal for all types of polymer glasses in this study.
Figure 4.12 Retractive stress as a function of annealing time at $T_{el-yield} = 70 \, ^{\circ}\text{C}$ of pre-necked melt-stretched PS at different doses of gamma irradiation. Isotropic PS specimens were first melt-stretched at 135 $^{\circ}\text{C}$ at a crosshead speed of $V_{ms} = 600$ mm/min to a draw ratio of $\lambda_{ms} = 5$ and quenched by icy water. Those melt-stretched samples were then cold drawn at a crosshead speed of $V_0 = 6$ mm/min at room temperature and absorbed at different doses of gamma irradiation.
Figure 4.13 (a) Retractive stress as a function of annealing time at $T_{el-yield}=75^\circ$C of pre-necked PMMA at different dose of gamma irradiation. The pre-necked PMMA was pre-deformed at a constant crosshead speed of $V_0=6$ mm/min at 80 $^\circ$C to a draw ratio of $\lambda=2.2$. 

Figure 4.13 (b) Extruded PMMA at 80 $^\circ$C

Extruded PMMA $T_{neck}=80$ $^\circ$C, $\lambda_{neck}=2.2$

- ○ 0 kGy
- □ 5 kGy
- ◇ 20 kGy
- ▲ 200 kGy

$T_{el-yield}=75^\circ$C

Extruded PMMA

$b$ $f$

$b$ $f$

$\sigma_{engr}$(MPa)$\lambda$

$\lambda$

$\lambda$

$\lambda$

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(b) Engineering stress vs. draw ratio of isotropic PMMA after gamma irradiation at a crosshead speed of $V_0=6$ mm/min at 80 °C during uniaxial extension. The inset shows the magnification of the initial regime.

Figure 4.14 Retractive stress as a function of annealing time at temperature of (a) $T_{el-yield}=75$ °C and (b) $T_{el-yield}=120$ °C of pre-necked PPE at different dose of gamma irradiation. The pre-necked PPE was pre-deformed at a constant crosshead speed of 6 mm/min at 23 °C to a draw ratio of $\lambda=1.6$. 
4.4 Discussions

Given the results above, we would discuss the mechanism of elastic yielding and the effect of gamma irradiation in this section.

4.4.1 Mechanism of elastic yielding

To elucidate how elastic yielding occurs when annealing above the storage temperature, a microscopic picture was proposed,⁹ as shown in Figure 4.15. It is speculated that the chain tension can be built up during necking in the form of bond distortions, e.g., covalent bond stretching, bond angle distortion and intramolecular rotation, as shown in Figure 4.16. Well below the glass transition temperature, a significant fraction of chain tension can survive the unloading when the uniaxial extension creases and the necked PC is dismounted from the clamps. Over many days at the storage temperature, the residual chain tension develops a balance with the surrounding glassy medium in the sense that the chain tension is no longer able to decline. When annealing above the storage temperature, the balance is broken, titling toward the direction along which the chain tension “pushes” the glassy segments into a state of activation as shown by the lighter dots in Figure 4.15. In other words, the “warmer” environment allows itself to be pushed around by the tension-containing strands so that LBSs re-emerges and a measurable retractive stress shows up.
Figure 4.15 Microscopic structure pictures of a load-bearing strand (LBS) after necking at room temperature and annealing at a higher temperature. Dark dots denote immobilized or more frozen segments, while light dots represent mobilized or more activated segments. The two short arrows show the direction of chain shrinkage.

Figure 4.16 Microscopic structures of chemical bonds in response of deformation: (a) covalent bond stretch; (b) covalent bond angle distortion; (c) intramolecular rotation. The dash circles represent the initial positions of atoms before deformation (Replotted from
4.4.2 Gamma irradiation effect

The purpose to carry out the gamma irradiation tests is to demonstrate that the origin of the elastic yielding is intra-segmental. Figure 4.17 (a) depicts that chain scissions occur along a LBS. Such chain scissions should result in a reduction in the measured retractive stress. Conversely, had gamma irradiation had no effect on the elastic yielding behavior, it would be clear that either the irradiation did not cause enough chain scissions or the elastic yield behavior did not result from chain tension.

On the other hand, some of the newly formed ends with radicals could react with active segments nearby and generate crosslink. Since it is still in the glassy state, the number of crosslink is quite small. It should be noted that this number also depends on the chemical structure. Figure 4.17 (b) shows that branches are formed due to crosslink. Those crosslinks can also serve as junctions to hold LBSs. Therefore, the number of LBSs increases, leading to a rise in retractive force, as shown in Figure 4.13 (a). Note that chain scissions or other more complicated cases may also take place at the same time. Therefore, crosslink or the increase in molecular weight does not guarantee more retractive stress in elastic yielding.
4.5 Summary

In this chapter, elastic yielding experiments have been carried out to explore the role of chain network upon large extension of polymer glasses. By applying various pre-draw rate, it is found that both intra- and inter-segmental interactions contribute to the buildup of internal potential energy. For milled specimens, they also display elastic yielding. Upon extension of milled specimens the retractive stress further increases linearly with the degree of post-yield extension, clearly revealing the relationship between cold drawing ratio and the level of elastic yielding. The gamma irradiated pre-necked samples shows reduced retractive stress. Such experiments confirm that the elastic yielding is driven by chain tension produced during the cold drawing. All these results are consistent with

Figure 4.17 Structure changes of LBSs after gamma irradiation: (a) degradation; (b) crosslink. Red crosses represent positions where chain scissions take place.
the recently proposed molecular picture,\textsuperscript{3} which has recognized the hybrid structure of polymer glasses.
5.1 Background

In this chapter, crazing behavior of polymer glasses will be discussed, since it is crucial to understand mechanical fracture. Usually, the mechanical response is monitored under displacement-controlled mode, where the stress is measured as a function of strain at a constant rate. At the same time, many other investigations applied the constant force mode. Under this mode, polymers creep and molecular motions could be expressed by Eyring model or other related models.

Why some polymers like PS and PMMA always form crazes before breaking, but others like PC prefer to undergo shear yielding rather than crazing? Understanding how crazes are initialized and grow could shed a light on the improvement of toughness for polymer glasses. After first visualization of crazes by Kambour through electron micrographs, plenty of efforts have been made to study the crazing behavior of polymers. As shown in Figure 2.7, white lines occur perpendicular to the extension direction, which is known as stress-whitening or crazes. Since crazes could grow without any macroscopic failure or breaking, they have been recognized as load bearing. Besides the macroscopic investigations, many studies in the microscopic level have been carried out.
Crazing mainly contains two stages of initialization and growth. In the initialization stage, crazes are suggested to be initiated from either surface imperfections or internal dispersed compliant particles. Argon, 12, 19, 52, 111-113 proposed that crazing took place through local dilatant plastic shear event and molecular process of plastic relaxation occurred where nano-scale cavities were initialized. On the contrast, Bucknall 114, 115 suggested that crazing was due to surface imperfections, since crazes could be avoided by polishing the surface. However, neither of them proposed any mechanism regarding localized failure at a molecular level.

Unlike the controversy regarding the crazing initialization, the growth mechanism is clearer. 116-118 It involves both mechanisms of craze tip advance and craze thickening. Figure 5.1 shows the principal mechanism depicted by Argon and Salama 12 on craze-tip advance, where a meniscus-instability type 119 of response occurred at the crack front and a series of parallel furrows were generated and propagated. Meanwhile, besides generating more fibrils by craze tip advance, crazes also increase in thickness. 116 It may increase in two ways. One is that a fibril undergoes creep without new polymer drawn into the fibril. The other is that new polymer could be drawn into the fibrils to maintain the deformation.
Figure 5.1 The mechanism of craze tip advance by meniscus-instability: (a) outline of craze tip; (b) top view of craze front; (c)-(d) advance if the craze front by a completed period of interface convolution (Replotted from Argon, A. S.; Salama, M. M. *Philosophical Magazine* 1977, 36, (5), 1217-1234).\(^{12}\)

Kramer\(^{118}\) also proposed a model on the mechanism of entanglement loss, as indicated in Figure 5.2. The entanglement at C had to be broken to allow crazes to further grow. Kramer suggested two different mechanisms. One was chain scission at temperatures far below \(T_g\), and the other was chain pullout when \(T\) is close to \(T_g\). However, the mechanism of chain scission cannot explain why pressurization could suppress crazes, since pressurization does not change the covalent bond strength.
Figure 5.2 Kramer’s model on the mechanism of entanglement loss. The chains marked with A and B are entangled at C (Replotted from Crist, B., The Physics of Glassy Polymers. Haward, R. N., Ed. Springer Netherlands: 2012).\textsuperscript{11}

A more recent investigation from Cheng \textit{et al.}\textsuperscript{13} focused on the crazing behavior of isotropic PC and concluded with a chain pullout mechanism. They found that melt stretching produced a geometric condensation to the chain network, and crazes were successfully suppressed. Also, they carried out a series of experiments for isotropic PC on creep mode and identified three regimes as shown in Figure 5.3. Within external engineering stress of 25 MPa, where the sample undergoes elastic deformation, no craze occurs within 1 h. After deviation from the linear regime, i.e., the applied stress equals or exceeds 25 MPa, crazes emerge within 1 h. When the stress reaches 48 MPa, which equals to the stress level of necking propagation, shear yielding takes place and necking is subsequently observed.
Figure 5.3 (a) Engineering stress as a function of stretch ratio for isotropic PC during uniaxial extension; (b) draw ratio as a function of time for isotropic PC during creep. Three regimes are characterized as: I. elastic deformation; II. crazing; III. shear yielding and necking (Replotted from Cheng, S.; Johnson, L.; Wang, S.-Q. Polymer 2013, 54, (13), 3363-3369).
In this chapter, tensile tests under creep mode is carried out to further explore the effect of mechanical rejuvenation and physical aging on crazes in polymer glasses. It is found that the mechanical rejuvenation greatly suppresses craze formation while aging shows the opposite effect. The molecular picture which regards polymer glass as a hybrid structure has been applied to better understand the crazing behavior.

5.2 Experiments

In this section, two parts: (a) materials and sample preparation; and (b) apparatus and methods would be introduced.

5.2.1 Materials and sample preparation

In this chapter, both PC and PMMA have been used to study the craze effect. Relative sample characteristics can be found in Table 4.1. The same procedures as described in Section 3.2.1 and 4.2.1 were applied to prepare milled PC and PMMA samples.

To prepare twisted samples, PC pellets were first extruded by Monsanto Capillary Rheometer at 215 °C into a dog-bone mold with middle dimensions of \( \phi 2 \text{ mm} \times 10 \text{ mm} \). Such a cylindrical sample was then twisted over an angle of 900° and subsequently twisted back to original position, as shown in Figure 5.4.

All the milled samples were aged at 105 °C for 1 d to explore the aging effect on crazing.
Figure 5.4 Illustration of twisting. A cylindrical sample is fixed on the bottom, and twisted to an angle $\phi$, typically 90 degrees, from the top. It is then twisted back to the original position.

5.2.2 Apparatus and methods

All the creep measurements were carried out with Instron 5543. The mill machine had two identical rolls with a diameter of 150 mm. Twisting was conducted on a homemade device with a rotational motor. Images of crazes were captured by a Zeiss Standard 25 Transmitted Light Microscope equipped with a Sony DFW-V500 digital color camera at a magnification of 20.

5.3 Results

The following will focus on two effects for crazing: (a) rejuvenation effect; and (b) aging effect.

5.3.1 Rejuvenation effect

To study the rejuvenation effect on crazing behavior, a constant engineering stress is applied to the isotropic PC and milled PC with different thickness reduction (9.5%, 31.9% and 41.1%), as shown in Figure 5.5. The specimens are first stretched to an
engineering stress of $\sigma_{engr} = 30 \text{ MPa}$ at a crosshead speed of $V_0 = 3 \text{ mm/min}$. The stress is then kept constant for certain time to allow crazes to be initialized and grow. Figure 5.5 (a) shows the draw ratio as a function of time under creep mode in a time period of 1 h. The draw ratio $\lambda$ of the milled specimens increases significantly faster than isotropic one. This can be explained by the faster dynamics of chain segments, as mechanical rejuvenation makes the primary network more readily to be activated. For the three milled specimens, $\lambda$ increases faster at lower thickness reduction. This is due to the larger geometric condensation effect for milled samples at higher thickness reduction. As shown in Figure 5.6, the milling procedure is actually a rejuvenation process combined with geometric condensation. Polymer chains are stretched from $L_0$ to $L_{mill}$ in the milling direction with changing the thickness from $H_0$ to $H_{mill}$. The width is kept constant or only tiny changes (1-2%) takes place. With a more condensed chain network for samples with a thickness reduction of 41.1%, the load on each LBS reduces, which leads to slower chain mobility as predicted in Eyring model. The inset in Figure 5.5 (a) shows that the onset of deviation from the linear relationship is around 30 MPa for milled PC. Cheng et al. found that at an applied stress of 30 MPa, crazes could show up within 1 h for isotropic PC. Figure 5.5 (b) shows three images of the milled samples after creep for 1 h. Crazes occur in the form of vertical lines (perpendicular to the stretching direction) in the first photo. However, with a thickness reduction of 31.9%, only a small amount of shallow crazes are observed. And no crazes are generated for milled PC with a thickness reduction of 41.1%. These results indicate that sufficient milling effect can suppress the initialization of crazes.
Figure 5.5 (a) Draw ratio $\lambda$ as a function of time under a constant engineering stress of 30 MPa for isotropic and milled PC with different milling thickness reduction. The inset figure shows the engineering stress as a function of draw ratio of milled PC at a crosshead speed of 3 mm/min. All these specimens are stretched along the milling direction. (b) Corresponding photos of milled specimens under $\sigma_{\text{engr}}=30$ MPa for 1 h at room temperature.
Figure 5.6 Illustration of change of sample dimensions from $L_0 \times W_0 \times H_0$ to $L_{mill} \times W_0 \times H_{mill}$ for PC during milling. Straight lines represent polymer chains, and lines between two crossing points are load-bearing strands (LBSs). During milling, the width of the sample keeps nearly constant.

![Diagram showing dimensions change](image)

Milled PC 41.1%
Figure 5.7 (a) The draw ratio $\lambda$ as a function of time under different constant engineering stress for milled PC with a thickness reduction of 41.1%. The specimens are stretched along the milling direction. (b) Corresponding photos of the specimens under three different engineering stresses (10 MPa, 40 MPa, and 80 MPa) at room temperature for 1 h.

Besides effect of the thickness reduction, the effect of stress is also studied for milled PC with a thickness reduction of 41.1%. The results are shown in Figure 5.7. The draw ratio $\lambda$ as a function of time during continuous uniaxial extension is also plotted in Figure 5.7 (a) in half-filled squares symbols. The sample at 90 MPa breaks in a very short time during creep. For those samples that do not fail within 1 h, the draw ratio $\lambda$ increases with the applied stress, as the mobility induced by stress increases.\textsuperscript{86, 100} Three selective images under applied stress of 10 MPa, 40 MPa, and 80 MPa are displayed in Figure 5.7 (b). No craze is observed up to 80 MPa for milled PC with a thickness reduction of 41.1% in the direction parallel to milling direction.
Figure 5.8 Engineering stress vs. draw ratio curves at a crosshead speed of 3 mm/min at room temperature for: (1) isotropic PC (black diamonds); (2) milled PC cut in the direction parallel to the milling direction (red circles); (3) milled PC cut in the direction perpendicular to the milling direction (red squares); (4) milled PC cut in the direction parallel to the milling direction after aging at 105 °C for 1 d (blue circles); (5) milled PC cut in the direction perpendicular to the milling direction after aging at 105 °C for 1 d (blue squares). The milled samples in the parallel direction involve a thickness reduction of 41.1%, while the milled samples in the perpendicular direction have a comparable thickness reduction of 38.3%.

To remove the geometric condensation effect, the tensile behavior of milled samples cut perpendicular to the milling direction is studied. As shown in Figure 5.8, the engineering stress of two milled samples in both parallel and perpendicular directions
without aging monotonically grows with draw ratio, in absence of any macroscopic strain localization. Compared to milled samples in the parallel direction or isotropic samples, specimens cut in the perpendicular direction can build lower stress during uniaxial extension. Also, the hardening modulus in the perpendicular direction without additional geometric condensation is smaller than that in the parallel direction. Creep measurements of milled PC in the perpendicular direction are then carried out at various applied stress, as indicated in Figure 5.9. Sample quickly breaks at an applied stress of 45 MPa. Note that the straight lines in Figure 5.9 (b) is produced not by stretching but by milling. No craze is observed within 1 h up to a stress of 40 MPa, which is already in the post-yield regime.
Figure 5.9 (a) The draw ratio $\lambda$ as a function of time under different constant engineering stress for milled PC. The specimens having a milling thickness reduction of 38.3% are stretched perpendicularly to the milling direction. (b) Corresponding photos of the specimens under two different engineering stresses: 20 MPa and 40 MPa at room temperature for 1 h.

As another method of mechanical rejuvenation, twisting could also suppress the initialization of crazes. Since the samples is forced to twist back to its initial position, no geometric condensation should be involved and only mechanical rejuvenation could affect the crazing behavior. The comparison of stress vs. draw ratio curves at a crosshead speed of 3 mm/min are shown in Figure 5.10 (a) for isotropic PC, twisted PC and twisted PC after aging at 105 °C for 1 d. All samples are cylinders with dimensions of $\phi 2$ mm $\times$ 10 mm. After twisting, necking is removed and the yield stress greatly decreases from 68 MPa to 35 MPa. By annealing the twisted sample at 105 °C for 1 d, yield point is comparable to the isotropic one and strain softening recovers, followed by necking propagation.

A series of constant engineering stress up to 40 MPa, which is already beyond the yield point, have been applied, as shown in Figure 5.10 (b). The value of $\lambda$ greatly increases from 1.22 to 1.56 within 1 h at 40 MPa in the post-yield regime, which is consistent with
the chain mobility studies by photobleaching method. Figure 5.10 (c) implies that crazes are inhibited by twisting up to 1 h even at sufficiently high external load. The vertical lines in these photos represent roughness at surface of the samples, which is distinct from the structure of crazes.
Figure 5.10 (a) Engineering stress vs. draw ratio curves of isotropic PC, twisted PC and twisted PC after aging at 105 °C for 1d at a crosshead speed of $V_0=3$ mm/min. (b) The draw ratio $\lambda$ as a function of time under different constant engineering stress for twisted PC. (c)
Corresponding photos of the specimens under different engineering stress, ranging from 0 MPa to 40 MPa at room temperature for 1 h. All these samples have a dimension of $\phi 2 \text{ mm} \times 10 \text{ mm}$.

5.3.2 Aging effect

Physical aging is reported to be able to decrease the energy landscape. As a result, the energy required to overcome the barriers increases, making it more difficult to achieve macroscopic yielding. In this section, the aging effect on the formation of crazes is investigate. As shown in Figure 5.8, after aging at 105 °C for 1 d, milled samples in both parallel and perpendicular directions behave in a brittle manner in uniaxial tensile test. Specifically, due to the geometric condensation in the parallel direction, the sample shows a higher yield stress than the one in the perpendicular direction.

To study the crazing behavior of milled samples after physical aging, creep tests in the perpendicular direction are firstly carried out, as shown in Figure 5.11. Figure 5.11 (a) implies that the engineering stress starts to deviate from the linear elastic regime around 20 MPa. Figure 5.11 (b) is a comparison of the draw ratio $\lambda$ between samples with and without aging, which shows that $\lambda$ decreases greatly after aging at the same applied stress. In Figure 5.11 (c), four values of external stress are applied: 10 MPa, 20 MPa, 30 MPa and 40 MPa. At a stress as high as 40 MPa, the specimen undergoes shear yielding and necking after a short induction time. The samples do not break at the other three lower stresses. The corresponding photos in Figure 5.11 (d) show that the surface remains uniform at 10 MPa, while very shallow crazes show up at 20 MPa and deeper and larger crazes take place at 30 MPa. Physical aging recovers the sample from the rejuvenated state and crazes re-emerge. Three different regimes could be observed for milled PC after physical aging, as
shown in Figure 5.11 (c). Regime I is characterized as the linear elastic stage, where no craze is formed. Regime II starts at 20 MPa where the deviation from the linear relationship take place. In this regime, crazes could be initialized and grow while the whole sample retains mechanical integrity. In regime III, sample undergoes shear yielding and necking propagation before failure. These results are consistent with the data previously reported.\textsuperscript{13}
Figure 5.11 Creep tests for milled PC in the perpendicular direction after aging at 105 °C for 1 d. (a) Stress vs. draw ratio curve at a constant crosshead speed of 3 mm/min. The black lines show the initial linear elastic regime, from which the stress deviates at around 20 MPa. (b) Comparison of draw ratio as a function of time at 30 MPa for (1) milled PC, (2) milled PC after aging, and (3) isotropic PC. (c) Stretch ratio $\lambda$ as a function of time at various applied stress ranging from 10 MPa to 40 MPa for milled PC after aging. (d) Corresponding photos of samples under creep for 1 h.

Besides the perpendicular direction, creep measurements of milled samples in parallel direction after aging at 105 °C for 1 d are also conducted in Figure 5.12. Similar conclusion could be drawn. After deviation starting at 40 MPa, crazes show up. Due to the effect of geometric condensation, crazes are significantly shallower even at 60 MPa than those in the perpendicular direction at 40 MPa.
Milled PC after aging (parallel)

(a) $\sigma_{\text{eng}}$ (MPa)

(b) Milled PC after aging (parallel)

$V_0 = 3$ mm/min

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)

$V_0 = 3$ mm/min

Milled PC after aging (parallel)

$\lambda$

$\sigma_{\text{eng}}$ (MPa)
Figure 5.12 Creep tests for milled PC in the parallel direction after aging at 105 °C for 1 d. (a) Stress vs. draw ratio curve at a constant crosshead speed of 3 mm/min. The black lines show the initial linear elastic regime, from which the stress deviates at around 40 MPa. (b) Stretch ratio $\lambda$ as a function of time at various applied stress ranging from 10 MPa to 60 MPa. (c) Corresponding photos of samples under creep for 1 h.

To reveal the universality of the rejuvenation vs. aging effect, creep experiments of milled PMMA with and without physical aging are also studied and the results are shown in Figure 5.13. It can be seen that the draw ratio of milled PMMA increases faster than the aged one. Also, no craze occurs at 30 MPa for milled PMMA, while deep crazes are formed at a stress as low as 20 MPa after physical aging. These results indicate that mechanical rejuvenation and physical aging show converse effects on crazing behavior.
Figure 5.13 Draw ratio $\lambda$ as a function of time for milled PMMA at a constant engineering stress of 30 MPa and milled PMMA after aging at 105 °C for 1 d at a constant engineering stress of 20 MPa along the milling direction. The inset show the corresponding pictures of samples under creep for 1 h.

5.4 Discussions

Given the results above, we would discuss the mechanism for crazing. Also, the mechanical rejuvenation and physical aging would be compared as well as the parallel vs. perpendicular direction effects.

5.4.1 Mechanism for crazing

Neither mechanical rejuvenation nor aging change the strength of covalent bonds, so a chain pullout mechanism instead of chain scission for crazing is proposed in this work. Specifically, such extreme strain localization involves localized yielding of the chain
network, i.e., LBS pull out from junctions. Whether such local yielding could take place or not depends on how much chain tension is built up during deformation. Besides, since polymer glasses are heterogeneous, the strength of junctions may vary and chain pullout might happen at weaker junctions or involve LBS with high chain tension.

5.4.2 Mechanical rejuvenation vs. physical aging

How could mechanical rejuvenation and physical aging affect the crazing behavior? As discussed in Chapter II, aging could cause better local packing with lower energy state, which makes the primary network harder to be activated. On the other hand, after mechanical rejuvenation that alters the energy landscape, vitreous segments can be more readily activated. Consequently chain tension cannot grow to a sufficient high level to cause pullout. In absence of localized failure of the chain network, crazing does not take place. Conversely, physical aging restore the capacity for the glassy state to build up high chain tension during extension. As a consequence, the mechanical rejuvenated, crazing-free PC displays crazes again upon physical aging.

Moreover, as indicated in Chapter III, polymer glasses have thought to be heterogeneous, consisting of soft and hard domains,\textsuperscript{88-91} as shown in Figure 5.14. Here, different colors represent the heterogeneity of polymer glasses. Domains with dark colors are more vitreous than light domains. The effect of the mechanical rejuvenation could be to reduce the inherent structural and dynamic heterogeneity, as shown on the right picture in Figure 5.14. On the other hand, physical aging might have the opposite effect, leading to a more heterogeneous state of the left picture in Figure 5.14. It is possible that the inherent structural heterogeneity is important for the initiation of crazes. But any further speculation is beyond the scope of the present work.
Figure 5.14 Microscopic structures of polymer glasses after mechanical rejuvenation and physical aging processes. Colors from dark to light represent the glassy state from more vitreous to less vitreous.

5.4.3 Parallel direction vs. perpendicular direction for milled samples

In other words, milling along the Z direction produces condensation of LBS strands in the XY plane. Such a treated polymer glass not only is more resistant to tensile stress applied along Z but also faces lower risk of chain tension buildup. Thus, upon physical aging, in absence of geometric condensation, which is the case for the perpendicular extension of milled PC, significant crazing takes place as shown in Fig. 5.11(d). In contrast, the aged PC (parallel) hardly shows any crazing under creep along the original direction of milling as shown in Fig. 5.12(c).

5.5 Summary

In this chapter, the crazing behavior of rejuvenated samples with and without physical aging have been studied under creep mode. It was found that crazes are greatly inhibited through mechanical rejuvenation, either by milling or twisting. Crazes and shear yielding re-emerge after aging. Since mechanical rejuvenation does not remove any
impurities and aging does not introduces any inclusions, the basic cause for crazing should not be the presence of defects as proposed by Bucknall\textsuperscript{114,115} and Argon.\textsuperscript{19,52,111-113}

After the completion of this work, it was discovered that the crazing in PC can be removed if the specimens are kept clean, uncontaminated, i.e, when the specimens are handled using a pair of rubber gloves.
CHAPTER VI
SUMMARY

Polymers as viscoelastic materials, are widely produced and applied in our life. However, no satisfactory microscopic theory of mechanical behavior of polymer glasses is available despite decades of research. This situation formed the motivation for the present doctoral study.

In this dissertation, systematical studies of mechanical responses during both uniaxial extension and compression have been carried out. The focus has been to explore the origin of mechanical stress in large deformation of polymer glasses. It is found that along with plastic deformation internal potential energy $u_2$ also builds up during ductile deformation. The magnitude of internal energy $u_2$ is significantly higher than the energy associated with entropic rubber elasticity, contradictory to earlier suggestions that strain hardening may be due to the entropic forces.\textsuperscript{19, 40, 47, 48, 51, 52} The ratio of $u_2/w$ decreases logarithmically with the deformation rate in room-temperature extension of PC. Homogeneous extension of milled and melt-stretched sample shows that the chain network drives the buildup of internal potential internal energy. When the heat shows up at a rate higher than the instantaneous mechanical power, it is taken to indicate that there is internal energy buildup that can release during plastic deformation.
The effect of chain networking is further explored by studying the elastic yielding phenomenon. The elastic yielding from cold drawing at different draw ratio indicates that there is the stretching of the chain network in the post-yield regime. Gamma irradiation greatly decreases the elastic yielding stress by chain scission whereas crosslinks could result in a slightly increase in retractive stress.

Last but not least, crazing behavior, as a leading form of the material response, has been studied. Upon mechanical rejuvenation, crazing could be largely inhibited or suppressed. On the other hand, sufficient aging could allow crazing to come back and even turn a ductile polymer glass brittle. Moreover, the enhancement of the chain network through melt-stretching could also suppress the formation of crazing.

To understand the mechanical responses of polymer glasses under external deformation, a molecular model\textsuperscript{3} is invoked to provide a rational description. Specifically, the mechanical rejuvenation effect, physical aging effect, and geometric condensation effect are discussed in this work. Mechanical rejuvenation, which lowers the energy barriers, makes polymer glasses more ready to yield. On the other hand, physical aging has the opposite effect, by erecting higher energy barriers and causing polymer glasses more heterogeneous. Melt stretching produces geometric condensation of LBSs, makes it plausible to achieve uniform plastic deformation. Future work should be carried out to examine the validity of this simple-minded model.
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