DEFORMATION AND FAILURE MECHANISM OF NANOSTRUCTURED POLYMER THIN FILMS

A Dissertation Presented

by

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Polymer Science and Engineering
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Polymer Science and Engineering
To my family
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ABSTRACT

DEFORMATION AND FAILURE MECHANISM OF NANOSTRUCTURED POLYMER THIN FILMS

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In this research, we develop models to describe the impact of nanostructures on the elastic deformation and failure of polymer thin films. First, we use polystyrene-b-poly(2-vinyl-pyridine) as a model material to investigate the effect of nanodomains and surface terracing on the crazing process. Here, we find that well-aligned lamellar domains can alter the extension ratio of craze fibrils and delay craze growth rate. Additionally, nanoscaled surface terraces impede the craze initiation and significantly decrease the failure strain of polymer thin films.

To investigate the impact of inorganic nanodomains on the crazing process, we
use a model and well-dispersed nanocomposite of polystyrene blended with surface modified cadmium selenide nanoparticles (diameter ~3.5 nm). With this material design, enthalpic interaction is minimized and entropic interaction dominates the mechanical properties. Due to high surface-to-volume ratio of nanoparticles and nanoparticle-polymer entropic interaction, the elastic modulus of our nanocomposites decreases as a function of volume fraction of nanoparticles (V). During craze formation and growth, nanoparticles undergo three stages of rearrangement: 1) alignment along the precraze, 2) expulsion from craze fibrils, and 3) assembly into clusters entrapped among craze fibrils. This entropically-driven rearrangement leads to the altered craze morphology and an increase in failure strain by 60% at an optimal V. This optimal volume fraction is related to the balance of two mechanisms: 1) the decrease in the volume fraction of cross-tie fibrils, and 2) the decrease in extensibility of the craze.

In the last part of this research project, larger nanoparticles (diameter is ~6.0 nm) are used to increase nanoparticle-polymer entropic interaction. Here, we find that nanoparticles segregate to the film surface during the film casting process on the substrate. This entropically-driven segregated layer of nanoparticles leads to a significant drop in the elastic modulus at very low V (0.2%) and an increase in failure
strain by 100% in an optimal V.
# TABLE OF CONTENTS

ACKNOWLEDGEMENT ...............................................................................................................v

ABSTRACT .............................................................................................................................. viii

LIST OF FIGURES ................................................................................................................ xvi

CHAPTER ONE: INTRODUCTION

1.1 Motivation .....................................................................................................................1

1.2 Organization of thesis .................................................................................................2

CHAPTER TWO: FUNDAMENTALS AND CHARACTERIZATION OF CRAZING

2.1 What is a craze? ...........................................................................................................6

2.2 Crazing Process ..........................................................................................................10

2.2.1 Craze initiation .......................................................................................................10

2.2.2 Craze growth ...........................................................................................................11

2.2.3 Breakdown of craze fibrils ....................................................................................16

2.2.4 Crack propagation .................................................................................................18

2.2.5 Factors affecting crazing .....................................................................................20
2.3 Experimental Characterization of Crazing

2.3.1 Copper grid technique

2.3.2 Definition of specific strains

2.3.3 Craze growth rate

CHAPTER THREE: CRAZING IN GLASSY BLOCK COPOLYMER THIN FILMS

3.1 Introduction

3.2 Experiment

3.2.1 Materials

3.2.2 Combinatorial method

3.2.3 Sample preparation and craze characterization

3.3 Results and Discussions

3.3.1 Craze vs. shear deformation zone

3.3.2 Craze initiation

3.3.3 Craze growth

3.3.4 Craze failure

3.4 Conclusion

3.5 Acknowledgement
CHAPTER FOUR: IMPACT OF SURFACE MODIFIED NANOPARTICLES ON 
GLASS TRANSITION TEMPERATURE AND ELASTIC 
MODULUS OF POLYMER THIN FILMS

4.1 Introduction ...................................................................................................58
4.2 Experiment .....................................................................................................59
  4.2.1 Thin film preparation ..............................................................................59
  4.2.2 Modulus measurement ...........................................................................60
  4.2.3 T_g measurement ...................................................................................62
4.3 Results and Discussions ...............................................................................63
  4.3.1 Modulus decreasing ..............................................................................63
  4.3.2 Ligand vs. plasticizer (T_g) ....................................................................65
  4.3.3 Ligand vs. plasticizer (modulus) ............................................................70
4.4 Conclusion .....................................................................................................72
4.5 Acknowledgement ..........................................................................................72

CHAPTER FIVE: NANOPARTICLE ALIGNMENT AND REPULSION DURING 
FAILURE OF GLASSY POLYMER NANOCOMPOSITES

5.1 Introduction ..................................................................................................73
## CHAPTER 5: EXPERIMENT

5.2 Experiment

5.2.1 Synthesis of surface modified nanoparticles

5.2.2 Sample preparation and test

5.2.3 Characterization of nanoparticles and crazes

5.3 Results

5.4 Discussions

5.6 Conclusion

5.7 Acknowledgement

## CHAPTER 6: FAILURE MECHANISM OF GLASSY POLYMER-NANOPARTICLE COMPOSITES

6.1 Introduction

6.2 Experiment

6.3 Results and Discussions

6.3.1 Low volume fraction nanocomposites

6.3.2 High volume fraction nanocomposites

6.4 Conclusion

6.5 Acknowledgement
CHAPTER SEVEN: IMPACT OF ENTROPICALLY-DRIVEN SEGREGATION OF NaNOPARTICLES ON MECHANICAL PROPERTIES OF GLASSY POLYMER THIN FILMS

7.1 Introduction .................................................................................................113

7.2 Experiment ..................................................................................................114

7.3 Results ........................................................................................................115

7.4 Discussions .................................................................................................120

7.4.1 Distribution of nanoparticles ......................................................120

7.4.2 Impact on T_g and elastic modulus ..............................................121

7.4.3 Impact on crazing and failure .....................................................124

7.4 Conclusion ..................................................................................................128

7.5 Acknowledgement ......................................................................................129

CHAPTER EIGHT: SUMMARY AND FUTURE WORK

8.1 Summary ..................................................................................................130

8.1.1 Effect of Nanodomains on Crazing ............................................130

8.1.2 Effect of Surface Defects on Crazing ........................................131

8.1.3 Effect of Nanoparticles on Elastic Deformation .........................132
8.1.4 Effect of Nanoparticles on Crazing ............................................132

8.1.5 Impact of Segregated Nanoparticles on Mechanical Properties .........................................................................................................................134

8.2 Proposed Future Work .................................................................................................................................134

REFERENCES .............................................................................................................................................137
LIST OF FIGURES

CHAPTER TWO

Figure 2.1a  Crazes in a tensile bar of PS .................................................................7
Figure 2.1b  SEM image of craze fibrils in PS .........................................................7
Figure 2.1c  TEM image of craze fibrils in PS .........................................................7
Figure 2.2   Formation of cross-tie fibrils .................................................................8
Figure 2.3   Schematic profile and TEM image of a craze in PS .............................9
Figure 2.4a  Schematic of craze fibril formation by meniscus instability ..........12
Figure 2.4b  Schematic of a “phantom fibril” .........................................................12
Figure 2.5a  AFM image of the craze .................................................................15
Figure 2.5b  Section analysis of AFM image of the craze .................................15
Figure 2.6a  Optical microscopy image of craze initiation .................................19
Figure 2.6b  Optical microscopy image of craze fibril breakdown ......................19
Figure 2.6c  Optical microscopy image of craze failure ......................................19
Figure 2.7a  Plot of percent increase of the number of crazes and area fraction of crazes vs. tensile strain for PS .........................................................26
Figure 2.7b  Plot of normalized area fraction vs. tensile strain for PS ..............26
CHAPTER THREE

Figure 3.1 Scheme of surface morphologies on BCP thin films.........................31
Figure 3.2a PS-b-P2VP thin film with thickness gradient..................................34
Figure 3.2b Mapping of PS-b-P2VP thin film with thickness gradient.................34
Figure 3.3a TEM image of craze fibrils in PS....................................................37
Figure 3.3b TEM image of craze fibrils in PS-b-P2VP.........................................37
Figure 3.4 Craze initiation strain for PS, BCP_F, BCP_P and BCP_C ...............39
Figure 3.5 Plot of percent increase of the number of crazes and area fraction of crazes of PS, BCP_F, BCP_P vs. tensile strain .........................41
Figure 3.6 Normalized area fraction vs. film thickness.................................42
Figure 3.7 Plot of normalized area fraction vs. tensile strain for PS, BCP_F and BCP_P .................................................................43
Figure 3.8 Chain conformation in lamellar domains of BCP thin film.............45
Figure 3.9a AFM image of craze-in-island .......................................................48
Figure 3.9b AFM image of craze-in-hole .........................................................48
Figure 3.10a AFM image of island domains on PS-b-P2VP thin film ...............49
Figure 3.10b AFM image of hole domains on PS-b-P2VP thin film...............49
Figure 3.11a Optical microscopy image of the craze in polystyrene ...............52
Figure 3.11b Optical microscopy image of the craze in PS-b-P2VP with flat surface
............................................................................................................52

Figure 3.11c Optical microscopy image of the craze in PS-b-P2VP with island
domains ..............................................................................................52

Figure 3.11d Optical microscopy image of the craze in PS-b-P2VP with hole
domains ..............................................................................................52

Figure 3.12 Failure strain for PS, BCP_F, BCP_P and BCP_C.........................54

CHAPTER FOUR

Figure 4.1 Images of buckles of polymer thin films.............................................61

Figure 4.2 Plot of E and T_g vs. weight fraction of nanoparticles.......................64

Figure 4.3 Schematic morphology of chains around a nanoparticle......................66

Figure 4.4 Plot of ΔT_g vs. weight fraction of plasticizer and surface ligand
............................................................................................................68

Figure 4.5 Plot of E vs. weight fraction of plasticizer and surface ligand.........71

CHAPTER FIVE

Figure 5.1a Top-view TEM image of nanoparticles dispersed in PS .................76

Figure 5.1b Fluorescence image of nanocomposite thin film.............................76

Figure 5.1c Cross-section TEM image of nanocomposite thin film....................86
Figure 5.2a  Schematic of craze regions in homopolymer .................................80
Figure 5.2b  Schematic of craze regions in nanocomposite ..............................80
Figure 5.3a  TEM image of precraze in nanocomposite .....................................81
Figure 5.3b  TEM image of premature craze in nanocomposite ...........................81
Figure 5.3c  TEM image of transition region of craze in nanocomposite ..............81
Figure 5.3d  TEM image of mature craze in nanocomposite ..............................81
Figure 5.4  Magnified TEM image of precraze in nanocomposite .......................84
Figure 5.5  Confocal fluorescence image of mature craze .................................88
Figure 5.6  Schematic summary of the interaction between polymer molecules and nanoparticles during crazing process ...........................................90

CHAPTER SIX

Figure 6.1  TEM images of CdSe nanoparticles dispersed in PS matrix with different volume fractions of nanoparticles ...........................................96
Figure 6.2  TEM images of holes on nanocomposite thin films with different volume fraction of nanoparticles ...........................................97
Figure 6.3  Summary of copper grid test of nanocomposites (CdSe35) ..............99
Figure 6.4a TEM image of premature craze in PS .............................................101
Figure 6.4b TEM image of premature craze in nanocomposite .........................101
Figure 6.5a  Plot of percent increase of the number of crazes and area fraction of crazes vs. tensile strain for nanocomposites.................................103

Figure 6.5b  Plot of normalized area fraction vs. tensile strain for nanocomposites ........................................................................................................103

Figure 6.6  TEM images of mature crazes in nanocomposites .........................108

CHAPTER SEVEN

Figure 7.1  TEM images of polymer nanocomposite thin film ..........................116

Figure 7.2  Plot of $T_g$ and elastic modulus vs. weight fraction of nanoparticle ........................................................................................................118

Figure 7.3  Summary of copper grid test of nanocomposites .............................119

Figure 7.4  Plot of $T_g$ and elastic modulus vs. weight fraction of surface ligand and Plasticizer.................................................................122

Figure 7.5  TEM image of mature craze in polymer nanocomposites..............126
CHAPTER ONE

INTRODUCTION

1.1 Motivation

Nanostructured materials have a significant potential to uniquely impact a wide range of applications from enhanced structural supports to optoelectronic devices. For example, the addition of nanofillers into polymer matrix leads to a significant increase in the elastic modulus and toughness. Alternatively, self-assembled periodic nanodomains of block copolymers can be used for photonic crystals and nanotemplates. For all of these applications, the deformation and failure of materials are important in determining materials' success. Here, we use thin films of the glassy diblock copolymer and nanoparticle-polymer composite as model nanostructured materials to investigate the impact of nanodomains and nanoparticles on the deformation and failure of nanostructured polymer materials.

Crazing is a dominant deformation process in most glassy polymers. This process involves the nucleation of a yielded region, which then grows into an array of nanoscale fibrils. Since a craze is a precursor of a crack that propagates through the breakdown of nanofibrils, understanding the crazing process is important to predict...
failure properties of glassy polymers. In our research, we specifically focus on the impact of nanoscale structures on the crazing process in our model materials.

1.2 Organization of Thesis

To provide a full understanding of the impact of nanostructures on crazing, we introduce the fundamentals of crazing in homopolymers and experimental techniques to characterize craze morphologies in chapter 2. We decide the four primarily stages of crazing process: craze initiation and growth, breakdown of craze fibrils, and crack propagation. We also explain the background and details of the copper grid technique for the characterization of craze morphologies.

In chapter 3, we begin to focus on the impact of polymer nanostructures on the crazing process. Specifically, we investigate the impact of block copolymer nanostructures. Compared to homopolymers, there are three additional factors that influence crazing in glassy block copolymer thin films: extended chain conformation within nanodomains, incompatibility among individual blocks and surface island/ hole morphologies. The tensile direction relative to oriented chains within nanodomains can lead to a different extension ratio of craze fibrils, which is significantly related to the breakdown of craze fibrils (crack initiation). In addition, the majority of applied
strain energy is expected to be dissipated by the formation of craze fibrils instead of craze growth, due to incompatible individual blocks staying together in the confined space, craze fibrils. This dissipation process can lead to the slow growth of the craze, decreasing the probability of fibril breakdown. The formation of surface defects (islands or holes) leads to the sudden change of film thickness, consequently altering local stress field and crazing process. All of these mechanisms contribute to the failure properties of crazing in glassy block copolymer thin films.

In chapter 4, we focus on the impact of surface modified nanoparticles (diameter is 3.5 nm) on the elastic modulus and glass transition temperature of polymer nanocomposites. To facilitate the dispersion of nanoparticles, ligands compatible to the polymer matrix are grafted onto nanoparticles, consequently altering particle-matrix interfacial properties. Due to high surface-to-volume ratio of nanoparticles, interfacial properties significantly affect macroscopic properties of polymer nanocomposites. Moreover, the entropic interaction between particles and polymer chains becomes dominant when the size of particles is close to the radius gyration of polymer chains. In our research, we specifically investigate the role of the surface ligand and the nanoparticle-polymer entropic interaction on the glass transition temperature and elastic properties. The results are compared to those
obtained from a control experiment based on a blend of short polymer chains with a polymer matrix.

After elastic deformation, further increase in stress/strain causes localized yielding in glassy polymers, and subsequent crazing. In chapter 5, we investigate the rearrangement process of nanoparticles during crazing based on entropic interaction. The diameter of craze fibrils is on the same order of nanoparticle diameter. Therefore, nanoparticles will interact with not only polymer chains, but nanoscaled craze fibrils entropically during craze formation and growth, leading to the rearrangement of nanoparticles, consequently impacting craze morphologies and crazing process.

In chapter 6, we focus on the impact of the nanoparticle rearrangement process on the failure properties of polymer nanocomposites. We compare samples with different volume fraction of nanoparticles to study the effect of volume fraction on failure properties of polymer nanocomposites.

In chapter 7, we focus on the impact of nanoparticles with stronger entropic interaction on particle dispersion, elastic modulus and failure properties of polymer nanocomposites. Specifically, larger nanoparticles (6.0 nm in diameter) are used to increase entropic interaction between particles and polymer chains. This stronger force results in a larger driving force for nanoparticle rearrangement.
Through the completion of these parts, we build a foundation for understanding the fundamental mechanism of elastic deformation and failure in nanostructured polymer materials. These lessons help guide future design of polymer-based nanostructured materials.
CHAPTER 2
FUNDAMENTALS AND CHARACTERIZATION OF CRAZING

2.1 What is a Craze?

Crazes are long-narrow white bands appearing on most glassy polymers under stress or strain (Figure 2.1a). In general, they are 50 ~ 1000 µm in length, and 0.5 ~ 2 µm in width. A craze consists of arrays of nanofibrils that bridge two surfaces of uncrazed matrix (Figure 2.1b). Thus, unlike a crack, a craze is load-bearing. Diameters of craze fibrils can be directly measured from TEM images of the craze (Figure 2.1c). To avoid serious overlap of fibrils in thickness direction, thinner films (below 250 nm) are preferred for TEM. In general, the diameter of craze fibrils is 5 to 30 nm and spacing is 20 to 30 nm. Polymer chains residing within craze fibrils are oriented in the fibril direction with a extension ratio, $\lambda$ (fibril extension ratio). In addition to the main fibrils, short fibrils, or cross-tie fibrils, run between main fibrils. Cross-tie fibrils result from the pile-up of entangled polymer chains during craze widening and the subsequent passing of the craze-bulk interface (Figure 2.2).

The craze can be divided into three regions (Figure 2.3): precraze, premature and mature. The precraze is a fluid-like region, and polymer chains in this region
Figure 2.1 (a) Crazes (narrow white lines) on the tensile bar of polystyrene. (Ward, I. M.; Sweeney J. “The Mechanical Properties of Solid Polymers”, John Wiley and Sons 2004) (b) SEM and (c) TEM images of a craze with multiple nanofibrils in polystyrene. Scale bar is 50 nm and 100 nm respectively. The arrows indicate the direction of tensile force.
**Figure 2.2** Formation of cross-tie fibrils during craze widening (surface drawing). The shaded region is air. (Miller, P.; Buckley, D. J.; Kramer, E. J. *J. Of Materials Science* 1991, 26, 4445-4454)
Figure 2.3 Top: scheme of the craze. The arrow indicates the direction of tensile force. Middle: profile of the craze width as a function of distance from the origin of the craze. Bottom: TEM images of precraze, premature and mature crazes.
have higher mobility compared to chains outside the crazed region. No fibrils form at this stage. Detailed descriptions about precraze can be found in section 2.2.2. Following precraze, nanofibrils are observed, and the width of the craze increases as a function of the distance from the craze tip (Figure 2.3). Subsequently, the craze width becomes independent of the distance from the craze tip, thus defining the mature craze. The main difference between the premature and mature crazes is the volume fraction ($v_f$) or density of craze fibrils. In the mature craze, $v_f$ is significantly higher than $v_f$ in premature crazes. The TEM image of individual regions are also shown in Figure 2.3.

2.2 Crazing Process

To provide basic understanding for subsequent chapters, we review the fundamental mechanisms for the craze development process in the following sections.

2.2.1 Craze Initiation

Craze initiation is a heterogeneous nucleation process. Crazes are initiated at edges of inclusions within the material or under surface grooves, where a stress concentration exists. Specifically, yielding is initiated at these sites of stress
concentration and further deformation of materials will be localized in this yielded region due to strain-softening of glassy polymers. Subsequently, a triaxial stress state is developed locally. This triaxial state of stress can depress shear yielding and facilitate the formation of microvoids within the locally yielded region. After void initiation, the voids grow in length, and the nucleus of the craze forms. The size of the craze nucleus is estimated to be 75 nm (three spacings of craze fibrils). 

2.2.2 Craze Growth

After a craze nucleus forms, the craze grows in length (advancing) and width (thickening) with the increase in stress or strain. When growing in air, a craze advances and thickens by the mechanisms of meniscus instability and surface drawing respectively. For craze advancing, a wedge-shaped and plastically deformed region (precraze) forms ahead of fibrillated crazed region (premature craze). This plastically-deformed region (yielded region) propagates by separating two interfaces between a fluid-like region (yielded region) and the glassy matrix. During separation process, fibrils form by deforming polymer webs between fingers (Figure 2.4a). This fibrilation process is similar to the process of separating two rigid plates joined by a liquid layer or a Saffman-Taylor instability. For craze thickening, fibrils grow in
Figure 2.4 Top-view of (a) craze fibril formation by meniscus instability (Ward, I. M.; Sweeney J. “The Mechanical Properties of Solid Polymers”, John Wiley and Sons 2004). Tensile stress is in y direction. The yielded region (pre-craze) is shown ahead of craze fibrils. (b) A “phantom fibril” (undeformed cylinder: diameter is $D_0$) is drawn into a fibril of diameter D. Chains within the fibril are in the stretched state.
length by drawing new polymer chains from uncrazed region into fibrils. This process is differentiated from creep by the fact that $v_f$ is a constant along the craze.

Polymer chains staying within craze fibrils are in extended state with certain extension ratio, $\lambda$ (Figure 2.4b). $\lambda$ is a constant along the direction of craze, except for the region near the craze tip. $\lambda$ is related to the volume fraction of fibrils ($v_f$) within the craze and the density of chain entanglements ($v_e$) by equation (2.1) and (2.2) respectively.

$$\lambda = \frac{1}{v_f}$$  \hspace{1cm} (2.1)

$$\frac{1}{\lambda^2} \sim v_e = \frac{\rho N_{av}}{M_e}$$  \hspace{1cm} (2.2)

$\rho$ is the density of polymers; $N_{av}$ is Avogadro’s constant; $M_e$ is entanglement molecular weight, and $l_0$ is the contour length for the whole polymer chain. The volume fraction, $v_f$, can be obtained experimentally from microdensitometry analysis of TEM image of the craze. $\lambda$ is an important parameter to evaluate failure properties of glassy polymers and will be discussed in more detail in section 2.2.3.

To separate two craze-bulk interfaces, a normal tensile stress, called the surface drawing stress or crazing stress ($S_c$), is applied on the craze-bulk interfaces. Theoretically, $S_c$ has been described in the form of:
\[ S_v = \frac{4}{\beta} \left[ \frac{2(n + 2) \nu}{\sqrt{3} \varepsilon_f h} \right]^{\frac{1}{2n}} \sqrt{\frac{\sigma_{fc}}{\varepsilon_f \Gamma}} \] (2.3)

Since the polymer in the active zone is modeled as a strain-softened non-Newtonian fluid, \( n, \sigma_{fc} \) and \( \varepsilon_f \), are material parameters in the flow law.\(^9\) \( h \) is the interfacial thickness (active zone) between the bulk polymer and the craze; \( \nu \) is moving velocity of the interfaces, which is related to strain rate. \( \Gamma \) is the energy required to create surfaces during craze growth (widening and advancing) and can be described by:\(^9\)

\[ \Gamma = \gamma + \frac{1}{4} \nu_c d U \] (2.4)

\( \gamma \) is the Van-der-Waals surface energy; \( U \) is the energy needed to break a primary bond of single chain (geometrically necessary loss of chain entanglements\(^7\)); \( \nu_c \) is the density of entanglements; and \( d \) is the mesh size of the entanglement network.

In addition to growing in width and length, crazes also increase in depth from a surface, called micronecking,\(^10\) eventually attaining an equilibrium value. One parameter to describe this micronecking process is the ratio of the craze depth to film thickness (Figure 2.5). Yang et al found that the depth-to-thickness ratio for PS is 0.35\(^10\) and we found that this ratio is material-dependent (chapter 3). The depth-to-thickness ratio can be related to \( \varepsilon \) by equation (2.5).\(^11\)

\[ \varepsilon = 2 \ln \left[ \frac{t_o}{t} \right] \] (2.5)
Figure 2.5 (a) AFM image of the craze in polystyrene. Arrow indicates the direction of (b) section analysis. Depth of the craze is 76 nm. The rough surface of the crazed region attributes to the existence of craze fibrils.
where $\varepsilon$ is the local strain within the craze, which is proportional to $\lambda$; $t_o$ is the film thickness in the uncrazed region; $t$ is the thickness of the crazed region. Therefore, a large depth-to-thickness ratio implies large local strain, i.e. large fibril extension ratio ($\lambda$).

2.2.3 Breakdown of craze fibrils

The loss of chain entanglements in the active zone (craze-bulk interface) during craze widening leads to the possibility of fibril breakdown (crack initiation). Moreover, Yang and Kramer found that fibril breakdown always occurs at the craze-bulk interface during widening of the craze. Two mechanisms are primarily responsible for the loss of entanglements in the active zone: geometrically necessary loss and “postdisentanglement”. The number of entangled strands surviving geometrically necessary loss ($n_E$) equals:

$$n_E = n_o q \left(1 - \frac{M_e}{qM_n}\right) \quad (2.6)$$

$n_o$ is the total number of entangled strands that cross a given sectional area of the “phantom fibrils”, which is the product of the areal entanglement density ($\frac{\nu_e d}{2}$) and the cross sectional area of the phantom fibril ($\pi D_0^2/4$). The “phantom fibril” is a
cylindrical region of the isotropic, undeformed glass with a diameter \( D_0 \) (fibril spacing) from which fibrils form during the drawing process. (Figure 2.4b).\(^7\), \(^{14}\) 

\( (1 - \frac{M_c}{qM_n}) \) is a correction for chain end segments which can not support a stress;\(^9\) \( q \), a function of \((D_0/d)\), is the probability surviving geometric entanglement loss during fibrillation.\(^{14, 15}\) Following geometrically necessary loss, a further loss of entangled strands by chain disentanglement localized near the craze interface occurs (postdisentanglement). \((1 - \xi)\) is the probability that an entangled strand survives “postdisentanglement”. Fibril breakdown occurs when no entangled strands survive after the processes of geometrically necessary loss and “postdisentanglement”. Consequently, the probability of no entangled strands surviving above two mechanisms equals to:\(^{12}\)

\[
[1 - q(1 - \xi)]^n \approx \exp[- n_0 q(1 - \xi)] = \exp[- n_c (1 - \xi)] \quad (2.7)
\]

The high probability of complete entanglement loss leads to low fibril stability or resistance. After fibril breakdown, microvoids form within the craze and crack propagation subsequently initiates. Therefore, increasing fibril stability can lead to the increase in failure strain of materials.

Since \( n_0 \) is proportional to \( v_c \), polymers with high entanglement density and molecular weight can have large \( n_E \) according to equation (2.6), consequently large
craze fibril stability and failure strains. In addition, Kramer and coworkers have demonstrated that the increase in the entanglement density also resulted in an increase in $q$. Beyond molecular considerations, dust particles within materials can facilitate fibril breakdown. When the craze-bulk interface meets a dust particle during widening, stress concentration occurs, consequently enhancing “postdisentanglement” of chains and decreasing the probability of strands surviving entanglement loss.

### 2.2.4 Crack Propagation

After crack initiation resulting from fibril breakdown, cracks within the craze (Figure 2.6e) advance by breaking fibrils. This process is facilitated by the lateral load transfer provided by cross-tie fibrils, as described by Brown. To describe this process mechanically, Brown considered a craze as an anisotropically elastic strip ($\sigma_t$ is proportional to $(E_1/E_2)^{1/4}$) and determined the critical fracture energy ($G_c$) equal to:

$$G_c = \left(\Sigma f_s^2 2\pi D / S\right) \left(E_2 / E_1\right)^{1/2} \left(1 - 1/\lambda\right)$$  \hspace{1cm} (2.8)

$E_2$ and $E_1$ are the elastic moduli of the crazed region (elastic strip) parallel and normal to the direction of main fibril. $\lambda$ is the fibril extension ratio of the craze. $S$ is the crazing stress. $D$ is the diameter of fibrils. $f_s$ is the force to break polymer chains. $\Sigma$ (equivalent to $n_0$ in equation 2.6) is the density of entangled strands that cross a plane
Figure 2.6 Optical microscopy images of (a) craze initiation, (b) fibril breakdown (indicated by the circle) and (c) failure of polystyrene thin films. Arrow indicates the direction of tensile stress. (d) Zoom-in image of the white circle shown in (b). (e) TEM image of the micro-void resulting from fibril breakdown within the craze (scale bar is 500 nm).
in the “phantom fibril”, which is also proportional to the density of chain entanglement \( (v_e) \). Hui and Kramer et al found that \( (E_2/E_1) \) is proportional to \( (f_m/f_c) \),\(^{17}\) where \( f_c \) and \( f_m \) are the volume fractions of cross-tie fibrils and main fibrils, respectively. According to above arguments, a high volume fraction of cross-tie fibrils (high \( f_c \)) can lead to the decrease in \( G_c \), thus facilitating the propagation of voids or cracks within the craze.

2.2.5 Factors affect crazing process

**Density of chain entanglements \( (v_e) \).** Localized shear yielding is also a dominant deformation process in many glassy polymers. The main difference between crazing and localized shear yielding is that fibrillar structures are only observed within crazed regions. Whether glassy polymers proceed by crazing or localized shear yielding depends on the competition between yielding stress \((\sigma_y)\) and crazing stress \((S_c)\). If \( S_c \) is larger than \( \sigma_y \), polymers proceed by shear yielding instead of crazing. If \( \sigma_y \) is larger than \( S_c \), polymers proceed by crazing instead of shear yielding. Since the yielded volume of shear yielding is larger compared to crazing, polymers that deform by shear yielding are more ductile than these by crazing. Polymers with high \( v_e \) will have large \( \Gamma \), leading to high crazing stress \((S_c)\) (equation
Therefore, glassy polymers with high $\nu_e$ tend to shear yielding instead of crazing.

**Chain orientation.** In addition to be related to the density of entanglements ($\nu_e$), fibril extension ratio ($\lambda$) is related to the angle between applied tensile stress and chain orientation. Nigel and Kramer found that the fibril extension ratio of crazes is smaller ($\lambda=2.2$) compared to isotropic PS ($\lambda=4.3$) when the primary tensile stress is parallel to preoriented PS chains.$^{18}$ Moreover, the extension ratio becomes larger ($\lambda=20$) when the tensile stress is perpendicular to preoriented chains.$^{18}$ Larger $\lambda$ implies low $\nu_e$ (equation 2.2), which is known to result in the low fibril stability (section 2.2.3). Therefore, craze fibrils are more easily broken for chains that are “perpendicular” compared to “isotropic” and “parallel”.

**Strain rate.** The high strain rate leads to high moving velocity of the craze-bulk interface, consequently high $S_c$ (crazing stress, equation 2.3). The high $S_c$ at craze-bulk interface contributes to the higher probability of fibril breakdown. Yang *et al* found that high strain rate results in the early fibril breakdown and material failure.$^{13}$
2.3 Experimental Characterization of Crazing

2.3.1 Copper Grid Technique

To characterize the craze structures and crazing process in polymer thin films, we use the copper grid technique developed by Lauterwasser and Kramer. A polymer thin film is cast on a rigid substrate, then floated on water. The floated film is transferred onto a copper grid and subsequently is strained uniaxially at a strain rate of $2.3 \times 10^{-4} \text{s}^{-1}$ by a custom-built, automated strain stage. For multiple strain experiments, we wait 10 minutes for crazes to reach equilibrium before unloading the copper grid. For tensile strain $\leq 3\%$, the increment of applied tensile strain is 0.5%; for tensile strain $> 3\%$, the increment of applied tensile strain is 2%. Every grid square can be regarded as independent samples of polymer thin films. The copper grid strain is transferred to the polymer film, and due to the low yield strain and plasticity of the annealed copper, the copper grid can maintain the applied strain after the sample is unloaded. Upon unloading at different applied strains, atomic force microscopy (AFM), optical microscopy (OM), and transmission electron microscopy (TEM) are then used to characterize the resultant crazes. Since all independent samples (grid squares) are prepared and tested at the same time, results are very statistical and consistent.
Optical microscopy images are taken for every grid square under bright and dark fields in an automated manner. Dark field enhances the contrast between the craze and the matrix, thus facilitating subsequent image analysis. Image analysis is performed in an automated, objective manner to obtain the number of crazes and area fraction occupied by crazes of each grid in the whole polymer film. To collect and analyze data efficiently, we have developed a high-throughput method to collect optical microscopy images and perform subsequent analysis through a program written in the National Instrument’s LabView environment. This image analysis routine standardizes our measurement process of crazes and minimizes errors introduced by human interpretation.

For AFM, the strained copper grid is fixed to a glass slide by tape. To perform AFM on a film suspended by a copper grid, we scan the crazed regions close to the edge of the grid bars to prevent excess deflection. A similar technique has been previously described. For TEM, we use a razor blade to cut a section from the copper grid. This section is then directly mounted into the TEM sample holder. Images are taken by JEOL 2000FX under 200 keV acceleration voltage.
2.3.2 Definition of Specific Strains

Strains of craze initiation, fibril breakdown and material failure are obtained from copper grid test. Craze initiation (Figure 2.6a) is defined as over 50% of grid squares observed with crazes. A similar 50% definition is applied to strains of fibril breakdown and material failure. Fibril breakdown can be observed as local wrinkles within crazes under optical microscope (Figure 2.6b). The inset of Figure 2.6b shows TEM image of void formation resulting from fibril breakdown within the craze. Craze failure is observed when the polymer film breaks catastrophically (Figure 2.6c).

2.3.3 Craze Growth Rate

Craze growth rate is defined as the increase in the area of one craze per unit strain. If the craze growth rate is small, the probability of fibril breakdown decreases, which leads to an increase in fibril stability and failure strain of materials. To obtain the craze growth rate, we quantify the total area fraction occupied by crazes within the grid as a function of applied strain. The area fraction is proportional to both the number of crazes and craze dimensions (length and width). The former is related to craze nucleation and the latter is related to craze growth. Image analysis is performed
in an automated, objective manner to obtain the number of crazes and the area fraction occupied by crazes of each grid.

Since both craze nucleation and growth contribute to the area fraction, we need to differentiate these two contributions. By plotting the percent increase of the area fraction and the number of crazes as a function of strain (Figure 2.7a), we can find the specific strain (\( \varepsilon_p \)) beyond which the percent increase of the number of crazes attain a plateau (all potential nucleation sites are initiated). However, the percent increase of the area fraction is expected to increase continuously as a function of strain. Therefore, craze growth becomes dominant to the area fraction beyond \( \varepsilon_p \) compared to craze nucleation. The craze growth rate (\( R_c \)) is obtained from the slope of
Figure 2.7 (a) Percent increase of the number of crazes (solid square) and area fraction occupied by crazes (hollow square) as a function of the applied strain in polystyrene. ($\varepsilon_p$ is 1.5%) (b) Plot of normalized area fraction ($A_t$) as a function of the applied strain.
normalized area fraction \((A_f)\) as a function of strain beyond \(\varepsilon_p\) (Figure 2.7b). \(A_f\) is equivalent to the average area fraction of one craze in one grid.

\[
R_c = \frac{\partial A_f}{\partial \varepsilon} \\
A_f = \left( \frac{\text{average area fraction occupied by crazes per grid}}{\text{average number of crazes per grid}} \right) \times 100
\]

\(\varepsilon\) is tensile strain
3.1 Introduction

Crazing in homopolymers and block copolymers has been studied extensively over the past several decades. For block copolymers in particular, much of previous research has focused on rubber-glassy systems (e.g. polystyrene-b-polybutadiene), where enhanced toughness can be achieved. In these materials, crazes grow by cavitation of rubber domains and elongation of voids, which is different from the conventional crazing mechanism and complicates analysis of block copolymer architecture on crazing. In glassy block copolymer materials, several factors can alter the crazing process (initiation, growth, and failure). The first is chain orientation. Block copolymers self-assemble into periodic nano-scale structures (sphere-bcc, cylinder-hexagonal or lamellae). Within these domains, chain conformations are in a perturbed state, not random Gaussian coils, and the orientation of these stretched chains relative to that of applied stress can alter the crazing process. This effect of chain orientation has been observed previously for homopolymers. The second factor is incompatibility. Most block copolymers
(BCPs) consist of incompatible blocks. In crazing, matrix molecules are drawn to form a dense region of microfibrils which are 5-20 nm in diameter. Therefore, the incompatibility of segments in a block copolymer will either impact the morphology of the craze fibril and/or the energy required for craze drawing. The last factor is the difference in mechanical properties among blocks. Will crazing be dictated by composite properties or will it be confined to a single microdomain as in rubber-glass BCPs? In this project, we present experimental results and a qualitative discussion of these factors, including the first evidence for the effect of nano-scale surface defects on the crazing process.

To understand the effect of BCP microstructure on crazing, we use symmetric polystyrene-b-poly-(2-vinylpyridine) (PS-b-P2VP) as a model material. Due to the strong Flory interaction parameter between the two individual blocks and their relative interaction with air/substrate, thin films of this BCP can self-assemble into well-aligned one dimensional lamellar domains parallel to the substrate (silicon oxide) solely by surface energetics. This alignment helps to ensure that all chains have the same orientation relative to applied tensile stress and provides a model geometry for initial data analysis and interpretation. In addition to chain orientation, symmetric BCP thin films are known to form surface terraces (islands or holes) spontaneously.
due to a mismatch between the total film thickness and the molecular-defined lamellar spacing, $L_0$ (Figure 3.1). These nano-scale “surface defects” are expected to alter the local stress field and affect the microscopic crazing process. Finally, PS-b-P2VP is a model choice for this study due to the similar mechanical properties for each block (glass transition temperature, crazing stress, entanglement molecular weight and elastic modulus). These attributes allow us to focus on two primary effects: the effect of ordered microstructure and the effect of surface terraces on crazing (initiation, growth, and failure) in thin glassy polymer films.

In the following sections, we describe our experimental methodology, present our results and relevant discussions, and summarize the main points of this project. The overall flow of the discussion follows the process of crazing: craze initiation, craze growth, and craze failure.

3.2 Experiment

3.2.1 Materials

PS-b-P2VP is obtained from Polymer Source Inc. The $M_n$ of PS block is 57 K; $M_n$ of P2VP block is 57 K; PDI of PS-b-P2VP is 1.02. As a control, we compare crazing in PS-b-P2VP to crazing in homopolymer PS thin films. The PS is obtained
Figure 3.1 Scheme of surface morphologies of flat, island, bicontinuous and hole on annealed symmetric diblock copolymer thin films. ($L_0$: lamellae spacing)
from Polymer Source Inc. with a $M_n = 126K$ and PDI = 1.02. Thin films of polystyrene are cast from 5.5 wt % toluene (Fisher-Scientific) solution, and PS-b-P2VP thin films are cast from 4.5 wt % toluene solution.

### 3.2.2 Combinatorial Method

Total film thickness is expected to play a role in the crazing process of PS-b-P2VP.\textsuperscript{41} Most directly, the total film thickness relative to the lamellar spacing $(h/L_0)$ controls the number of lamellae available to contribute to crazing and dictates the type of the film surface morphology.\textsuperscript{35-37} For example, if $h/L_0$ equals $(n + 0.5)$, where $n$ is a positive integer, then a flat surface (without terracing) can be obtained. If $h/L_0$ does not equal $(n + 0.5)$, then surface terraces will decorate the thin film surface. The height of these terraces is controlled by $L_0$. To efficiently quantify the effect of all surface morphologies on crazing, we use a gradient-based combinatorial sample design. Specifically, our samples will consist of a thin film with a continuous gradient of film thickness in one direction. With this sample design, all surface morphologies are prepared in one library at one time. We divide grids of the whole library of PS-b-P2VP into three categories: flat surface without any terraces (BCP_F), surface partially covered by terraces (BCP_P), and surface completely covered by
terraces (BCP_C). This library ensures that all samples are prepared, processed and tested at the same time, thus providing experimental consistency. One library can have up to 138 samples (grids). Excluding grids with defects, there are 60 grids of BCP_C, 30 grids of BCP_F and 30 grids of BCP_P.

3.2.3 Sample Preparation and Craze Characterization

To quantify the crazing process for polymer thin films, we use a well-established copper grid technique (section 2.3.1). We begin by flow coating a thickness gradient thin film on a silicon substrate with a thick silicon oxide layer (350 nm). The substrate is treated by acetone, toluene and UV-Ozone prior to film casting. For flow coating, a volume of 0.1 ml dilute polymer solution is deposited under the flow coater razor blade, then a moving stage moves at a fixed acceleration to create a thickness gradient thin film. A thickness range of 130 nm ~ 250 nm can be obtained by controlling the acceleration of the moving stage and the height between the razor blade and substrate. For block copolymer thin films, the cast film is annealed at 180 °C under vacuum for 72 hours. After annealing, periodic transitions of the surface morphology (flat to islands to holes) are observed along the thickness gradient direction (Figure 3.2a). To quantify film thickness throughout the library, we make
Figure 3.2 (a) Surface morphology of PS-b-P2VP thin film with thickness gradient. (b) Mapping of PS-b-P2VP thin film.
discrete and equally spaced thickness measurements by interferometry (Filmetrics) and interpolate a thickness map (Figure 3.2b).

After mapping the film thickness, we float the film on water (for PS film) or 5 vol. % aqueous hydrofluoric acid solution (for PS-b-P2VP film). Note that two edges of the film are removed during floating to avoid edge effects where irregular gradients in thin film thickness are observed. After floating block copolymer thin films, we extract hydrofluoric acid solution and replace with 0.2 M sodium hydroxide solution until the pH is larger than 10. This process removes the coordinated hydrofluoric acid ions in the P2VP segments of the BCP thin film. After this removal, we dilute the sodium hydroxide solution with water until the pH is equal to 7, and transfer the film onto a copper grid precoated by P2VP (for PS-b-P2VP film) or PS (for PS film) homopolymer. The film on the copper grid is dried for 12 hours, and then exposed to tetrahydrofuran (for PS-b-P2VP film) or toluene (for PS film) vapor to remove wrinkles and increase adhesion between the copper grid and the film. After exposure, the film is dried again for 24 hours.

Detailed descriptions about sample test and craze characterization by OM, TEM and AFM can be refereed to section 2.3.1.
3.3 Results and Discussions

3.3.1 Craze vs. Shear Deformation Zone

Crazing and shear yielding are both possible local deformation processes for glassy amorphous polymers.\(^{43}\) Polymers with high entanglement molecular weight or low density of entanglements tend to craze, while polymers with low entanglement molecular weight or high density of entanglements tend to shear yield.\(^{9,44}\) Since the entanglement molecular weight for chains in lamellar domains could be different compared to the chains in bulk state of homopolymers, we use TEM to characterize the deformation zones in both PS-b-P2VP and PS films. The deformation bands in all grids of PS and PS-b-P2VP with different film thickness (135 nm ~ 245 nm) consist of dense arrays of fibrils, which are characteristic of traditional crazes. These images show that fibril morphology (diameter and density) does not change over this thickness range, but some differences exist between PS and the BCP. The density of fibrils in the crazed region of PS is higher than that of PS-b-P2VP (Figure 3.3), thus implying that the fibril extension ratio of PS-b-P2VP is larger compared to PS. The details about fibril extension ratio are given below in a section on craze growth and micronecking (section 3.3.3). We also find that the fibril morphology in the flat
Figure 3.3 TEM images of fibril morphology of crazes in (a) PS (b) PS-b-P2VP.
(Film thickness is 244 nm; strain is 1.5 %.)
region is the same as that in the hole and island domains; therefore, surface terracing
does not cause any changes in fibril morphology.

3.3.2 Craze Initiation

For our PS thin films, most crazes are initiated at the edge of the copper grid
where the most significant defects reside. Similarly, most crazes in our PS-b-P2VP
films (terraced or flat surface) also initiate from the edge of the grid, but in a few
cases, surface terraces are found to serve as craze initiation sites. In these cases, the
islands or holes are isolated, large, and serve as a significant defect in the thin film
structure.

For craze initiation strain, we observe an alteration by the presence of surface
terraces. Specifically, we find that the strain at which crazes are initiated is larger for
PS-b-P2VP films that are completely covered with surface terraces (BCP_C in Figure
3.4). This increase in initiation strain is not large, but it is statistically significant. Due
to the combinatorial design of our sample library, we can confidently say that the
initiation strain in flat, non-terraced regions of our structured BCP film is not altered;
therefore, this delayed initiation is not a material difference but one dictated by the
surface geometry. In fact, PS-b-P2VP has the same initiation mechanism as PS based
Figure 3.4 Craze initiation strain for PS, BCP_F, BCP_P and BCP_C. Craze initiation strain for BCP_F, BCP_P, BCP_C is defined as over 50 % grids of the category having at least one craze. Three libraries are prepared and tested to confirm the results. The increment for applied tensile strain is 0.5%.
on a plot - the percent increase of the number of crazes as a function of different strains (Figure 3.5). In this plot, BCP_F, BCP_P, and PS all have similar trends. We also know that this alteration in strain is not a consequence of changing film thickness. For PS thin films with thickness varying from 135 nm ~ 245 nm, no deviation in the initiation strain (1%) is observed as a function of thickness.

3.3.3 Craze Growth

To compare craze growth in PS to our BCP films, we use craze growth rate ($R_c$). Detailed description about craze growth rate is described in section 2.3.3. Since the percent increase of the number of crazes in a given square of PS does not change significantly after 1.5% strain ($\varepsilon_p = 1.5\%$ mentioned in section 2.3.3), compared to percent increase of area fraction occupied by crazes in a given square of PS (Figure 3.5), $A_f$ is dominated by craze growth, not nucleation after 1.5% strain. For our PS libraries, we observe that thickness has little to no effect on $A_f$ within the thickness range of 135 nm ~ 245 nm (Figure 3.6). This observation is expected according to current models on craze growth.$^{41}$

The relationship between $A_f$ and strain is linear for PS, BCP_F and BCP_P (Figure 3.7), and the slope is the craze growth rate, $R_c$. This slope is equivalent to the
Figure 3.5 Percent increase of the number of crazes (solid symbol) and area fraction occupied by crazes (hollow symbol) per grid of PS (square), BCP_F (circle), BCP_P (triangle) as a function of applied tensile strain. Data points for PS are compiled averages of over 120 grids, 30 grids for BCP_F and BCP_P, respectively.
Figure 3.6  Normalized area fraction ($A_f$) as a function of film thickness of polystyrene. Each data point is the average result from six grids with the same thickness.
Figure 3.7 Plot of normalized area fraction ($A_f$) as a function of tensile strain for PS, BCP_F and BCP_P. The numbers are the slopes of linear fitting lines. Data points for PS are compiled averages of over 120 grids, 30 grids for BCP_F and BCP_P, respectively.
average growing extent of one craze in one grid per strain, and we only consider this
growth at applied strain $\geq 1.5$ after most crazes have initiated. Since over 50% of the
grids for BCP_C fail at 2% strain, we do not plot BCP_C in Figure 3.7. Crazing is an
energetic process where the applied strain energy drives the development of crazes.
Therefore, Figure 3.7 compares the use of applied strain energy in different materials.
BCP_F and BCP_P have very similar slopes, and this suggests that a minority
coverage of surface terraces has little to no effect on the rate of craze growth. On the
other hand, PS and BCP_F have very different rates of craze growth. Due to similar
modulus between PS and PS-b-P2VP (PS and P2VP homopolymers have similar
modulus$^{38-40}$), this observation implies that craze growth in PS-b-P2VP lamellar films
is more energetically costly compared to PS. We attribute this energy difference to the
fibril formation in PS-b-P2VP. To form fibrils in an aligned block copolymer film,
chains need to rotate due to the direction of the applied stress field relative to the
orientation of chains in their lamellar domains. Additionally, upon drawing into the
craze fibrils, the two incompatible blocks are confined to fibrils that are 10~20 nm
(Figure 3.8). Both of these two processes require additional energy; therefore, the
growth of a craze per unit strain in PS-b-P2VP requires more energy, and will proceed
at a slower rate. This effect can be summarized in the form of a relationship:
Figure 3.8 Chain conformation in the lamellar domain of symmetric diblock copolymer thin film before and after tensile load.
\[ E_{\text{app}} = E_c + E_{\text{rot}} + E_{\text{int}} \]

\[
\frac{\partial E_{\text{app}}}{\partial \varepsilon} = \frac{\partial E_c}{\partial \varepsilon} + \frac{\partial E_{\text{rot}}}{\partial \varepsilon} + \frac{\partial E_{\text{int}}}{\partial \varepsilon}
\]

where \( E_{\text{app}} \) is the applied strain energy; \( E_c \) is the energy of crazing (craze growth); \( E_{\text{rot}} \) is the energy of chain rotation; \( E_{\text{int}} \) is the interaction energy of polymer chains in fibrils. Based on the result of Farrar and Kramer\(^{18}\), the surface stress for crazing is larger for preoriented chains perpendicular to the applied tensile direction compared with the case of chains parallel to the applied tensile direction. This result implies that fibril formation for the perpendicular case takes more energy compared to the parallel case. For homopolymers where chains are randomly arranged, \( \frac{\partial E_{\text{rot}}}{\partial \varepsilon} \) is much less than that of our BCP thin films with oriented chains perpendicular to tensile direction. Additionally, due to incompatibility between two individual blocks, \( \frac{\partial E_{\text{int}}}{\partial \varepsilon} \) of BCP is much larger than that of PS. Therefore, if \( \frac{\partial E_{\text{rot}}}{\partial \varepsilon} \) and \( \frac{\partial E_{\text{int}}}{\partial \varepsilon} \) are larger for BCP and the \( \frac{\partial E_{\text{app}}}{\partial \varepsilon} \) is the same for both BCP and PS since their moduli are nearly identical, then \( \frac{\partial E_c}{\partial \varepsilon} \) will be less for the BCP as observed in Figure 3.7.

We also found that BCP_F has larger \( A_f \) compared to BCP_P and PS (Figure 3.7), implying that BCP_F has larger area fraction of the craze (larger width and
length of the craze) at early stage (strain $\leq 1\%$). At this stage, craze initiation is dominant to crazing process. Since defects at the edge of grid squares are dominant to craze initiation, further controlled experiment are required to conclusively determine the impact of nanodomains or surface terraces on $A_f$.

In addition to growing in length and width, crazes in thin films also experience a micronecking process in the thickness direction (section 2.2.2). One quantity that describes this micronecking is the ratio of craze depth to total film thickness. Yang et al reported the ratio of depth of craze in PS to total film thickness is a constant, equal to 0.35. Similarly, Crosby et al used a combinatorial method to investigate micronecking phenomenon in PS and measured statistically a ratio of 0.37. In our measurements on PS, we also measured a ratio of 0.37, but for PS-b-P2VP the craze depth ratio equals 0.47. This ratio is maintained not only in flat regions, but also as crazes pass through island and hole domains (Figure 3.9). In these terraced regions, the constant ratio is calculated by using the exact local thickness of $L_0*(n+0.5)$, where $L_0$ is the lamellae spacing and $n$ is the number of lamellae. $L_0$ (54 nm) is measured by the height of islands and depth of holes (Figure 3.10). The depth of the craze is measured directly from AFM section analysis.
Figure 3.9 AFM images (a) craze-in-island and (b) craze-in-hole. The image size is $30 \mu m \times 30 \mu m$. Film thickness is 244 nm in island regions, 136 nm in hole regions, and 190 nm in flat regions. Applied tensile strain is 1.5 %. 
Figure 3.10 AFM images of (a) island domains and (b) hole domains on annealed PS-b-P2VP thin film cast on silicon substrate with thick oxidized layer (350 nm). The height of islands and depth of holes are both 54 nm obtained from section analysis. The image size is 50 μm × 50 μm. Film thickness is 244 nm in island regions, 136 nm in hole regions, and 190 nm in flat regions.
The craze depth ratio of 0.47 for all crazes in PS-b-P2VP compared to 0.37 for PS suggests that this ratio is material dependent. According to equation (2.5) in section 2.2.2, the depth-to-thickness ratio is related to the fibril extension ratio. Larger depth-to-thickness ratio implies a larger fibril extension ratio. Based on our measurements, PS-b-P2VP has a larger depth-to-thickness ratio, so it has a larger fibril extension ratio compared to PS. This result is also consistent with our observations of the less dense fibril morphology compared to PS in TEM micrographs (Figure 3.3). The less fibril density implies low volume fraction of craze fibrils, consequently high fibril extension ratio (equation 2.1). We attribute the higher fibril extension ratio to the chain orientation in lamellar domains, similar to the observations of Creton and Kramer. In their experiments, Creton and Kramer measured craze morphology in a film of poly-(2-vinylpyridine)-b-polystyrene-b-poly-(2-vinylpyridine) with a lamellar morphology. They found that the fibril extension ratio is 5.7 for chains perpendicular to tensile direction and 4.4 for chains parallel to tensile direction. From these results, they calculated the chain extension ratio of 1.2 in lamellar domains before deformation. This increase is consistent with our observations of the increased micronecking ratio.
Although surface terraces do not play a dominant role in altering the craze growth process compared to inherent material properties such as the fibril extension ratio and incompatibility between blocks, surface terraces can alter the local stress distribution. This stress change is observed to alter the path of craze propagation. In the absence of surface terraces, such as films of PS and PS-b-P2VP with flat surfaces, crazes are straight, narrow bands (Figure 3.11a and b). Crazes in PS-b-P2VP with terraced surfaces are slightly sinuous (Figure 3.11c and d). We attribute this altered propagation path to the influence of local stress fields. For example, due to the increased local thickness within an island domain, the local stress is lower compared to surrounding regions. Therefore, as a craze approaches an island domain, the preferred path of propagation is around the island domain where the stress and energy are higher. This diversion of crazes around island domains is also dependent upon the deflection angle. On the contrary, the stress near a surface hole is greater than surrounding regions, so crazes are “attracted” to hole domains. They tend to pass through the holes, not evade them. Regardless of the direct action, these observations point to the impact of nano-scale defects on failure mechanisms in thin polymer films. Even though the island and hole domains only have a height of 54 nm, they create
Figure 3.11 Optical microscopy images of crazes on (a) PS and (b) PS-b-P2VP with (b) flat surface, (c) island domains (the circled area emphasized the evading of the craze) and (d) hole domains.
local stress fields that significantly alter the onset, propagation and failure of local crazes.

3.3.4 Craze Failure

It is known that the failure of crazed materials is caused by fibril breakdown at the interface between the crazed region and matrix during the surface drawing process (section 2.2.3). Fibril breakdown is largely due to the existence of stress concentrating defects, such as dust particles or intrinsic weak spots (ex. chain ends) which can not support stress (section 2.2.3). As surface terraces appear in the PS-b-P2VP films, the failure strain decreases with increasing coverage of these nano-scale surface defects. The reason for the early failure is the increased occurrence, or high probability for crazes to propagate into island or hole domains. Both island and hole domains are sudden changes in the local film thickness. Therefore, at their boundaries, a large stress gradient or stress concentration is generated. Consequently, these domains serve as stress concentration points, similar to dust particles responsible for conventional fibril breakdown. Accordingly, this mechanism is independent of materials, and nano-scale surface defects in other crazing polymers are expected to act in a similar manner. Figure 12 shows the failure strain among PS and PS-b-P2VP
Figure 3.12 Failure strain for PS, BCP_F, BCP_P and BCP_C. Failure strain of crazes is defined as over 50% grids of a given morphology having failed. Three libraries are prepared and tested to confirm the results. The increment of applied tensile strain is 0.5% when tensile strain $\leq 3\%$, and 2% when tensile strain $>3\%$. 
with different surface morphologies. For BCP_C, the effect of surface terraces is quite dramatic since craze initiation is delayed and failure is promoted at early strain.

Overall, this data truly points to the importance of surface defects at the nano-scale on impacting the strength of polymer thin films.

For PS and PS-b-P2VP with flat surface morphology, the failure strain in both cases is measured as 7 % strain. The same failure strains may result from the compromise between craze growth rate and fibril extension ratio. Compared to PS homopolymer, larger fibril extension ratio for PS-b-P2VP facilitates fibril breakdown. However, smaller craze growth rate delays fibril breakdown.

3.4 Conclusion

Surface terraces that self-assemble on the surface of BCP thin films alter the initiation, propagation and failure of crazes in these materials. Specifically, they slightly delay the initiation of crazes, alter the path of crazes, and ultimately decrease the failure strain by more than 70%. While these effects are significant, we also find that surface terraces do not have any influence on fibril morphology, craze growth rate, and the depth-to-thickness ratio in the micronecking process. These results not only show how crazing in thin films can be altered through self-assembled surface
nanostructures, but they also demonstrate the importance of “surface defects” in the overall integrity of polymer thin films and coatings.

Beyond surface terraces, the nanostructure of aligned, lamellar PS-b-P2VP alters the crazing process compared to homopolymer PS films. We find by TEM craze morphology analysis and AFM quantification of micronecking that the lamellar PS-b-P2VP films have a larger fibril extension ratio compared to PS. This change in fibril extension ratio also causes the depth-to-thickness ratio for micronecking to be 0.47 for block copolymer compared to 0.37 for PS. The craze growth rate in PS-b-P2VP is also smaller compared to PS. This difference is associated with the increased energy required to form fibrils in the aligned BCP film due to the rotation of chains and confinement of two incompatible blocks within single fibrils. The larger fibril extension ratio and smaller craze growth rate give rise to the failure strain of 7% for PS-b-P2VP with flat surface, same as PS homopolymer.

Overall, these results demonstrate the importance of nano-scale morphologies on the crazing process and point to new directions for understanding the fundamental mechanisms for crazing in advanced materials.
3.5 Acknowledgement

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CHAPTER FOUR

IMPACT OF SURFACE-MODIFIED NANOPARTICLES ON GLASS TRANSITION TEMPERATURE AND ELASTIC MODULUS OF POLYMER THIN FILMS

4.1 Introduction

To take advantage of unique and enhanced properties for nanoparticle-filled materials, the nanoparticles must be well-dispersed.\textsuperscript{46, 47} Surface modification of the particles is one of the most effective strategies to improve compatibility and ensure dispersion.\textsuperscript{48} Often, ligands that are compatible with the polymer matrix are grafted on or from the surface of the nanoparticles.\textsuperscript{48-50} Due to the large surface area per volume of the nanoparticle, the ligands play a significant role in the overall composite properties. Although the role of the ligand is more defined when it establishes high strength bonds with the surrounding matrix,\textsuperscript{51-53} its role in material properties is less clear when only weak interactions are present (i.e. only entropic interaction exists between ligands and matrix). To provide insight into the physical mechanisms that control material properties in polymer nanocomposites, we have designed a model material system to emphasize entropic interactions. Here, we report the impact of these interactions on the elastic modulus and the glass transition temperature ($T_g$) of
the polymer nanocomposites. We focus on the impact of nanoparticle weight fraction and develop relationships to decouple the roles of inorganic particles and ligand molecules in defining nanocomposite properties.

4.2 Experiment

4.2.1 Thin Film Preparation

A nanocomposite of cadmium selenide nanoparticles with narrow size distribution (diameter is 3.5 nm) blended into polystyrene matrix (MW= 131K g/mol, PDI= 1.02, Polymer Source Inc.) is chosen as our model material. To attain well-dispersed nanoparticles within the polystyrene matrix (PS), short polystyrene chains (ligands, MW= 1000 g/mol) are grafted onto the surface of the cadmium selenide nanoparticles (CdSe) (synthesized by Qingling Zhang in Emrick research group). In addition to aiding dispersion of nanoparticles, the enthalpic interaction and entanglement between nanoparticles and polymer matrix are minimized due to surface-grafted short polystyrene chains. Detailed information about the synthesis of our surface modified CdSe and the dispersion of nanoparticles within PS matrix can be found in chapter 5. Solutions of nanoparticles and PS in toluene are prepared with
different weight ratios to facilitate the casting of polymer films. Subsequently, a polymer thin film is cast on the silicon substrate by flow coating (section 5.2.2).

### 4.2.2 Modulus Measurement

To measure the elastic modulus of polymer thin films, we use a recently-reported technique, SIEBIMM (Strain-Induced Elastic Buckling Instability for Mechanical Measurements). In short, this technique involves the floating of a thin polymer film onto a thick, crosslinked polydimethylsiloxane PDMS substrate. (Dow Corning Sylgard\textsuperscript{TM} 184, weight ratio of prepolymer to crosslinker is 1:20; curing temperature is 70 °C for 2 hours) After drying the film/PDMS bilayer 24 hours, the bilayer is uniaxially strained in a custom-built, automated strain stage. Due to the large difference in modulus between the nanocomposite film and PDMS substrate, a net compressive stress develops orthogonal to the tensile direction and buckles the nanocomposite thin film (Figure 4.1). By measuring the buckling wavelength ($\lambda$), the modulus of polymer film ($E_p$) can be obtained:

$$E_p = \frac{\left(1 - \nu_P^2\right) \cdot 3E_{PDMS} \cdot \left(\frac{\lambda}{2\pi h}\right)^3}{\left(1 - \nu_{PDMS}^2\right)}$$
Figure 4.1 Schematic and optical microscopy images of buckles of polymer thin films on a PDMS substrate. Two opposite arrows indicate the direction of tensile force.
$E_{PDMS}$ is the elastic modulus of PDMS substrate, as measured using a contact mechanical test.\textsuperscript{55} We assume the Poisson’s ratio of the PDMS substrate and polymer film are $\nu_{PDMS} = 0.5$ and $\nu_p = 0.33$, respectively. The thickness of the nanocomposite thin films, $h$, is controlled by flow coating and quantified by interferometry (Filmetrics Inc.).\textsuperscript{56} The thickness of films used in the following experiments ranges from 180~210 nm. $\lambda$ is the periodic wavelength of buckles obtained via Fast Fourier Transform (FFT) of optical images.

### 4.2.3 $T_g$ Measurement

$T_g$ of our polymer thin films is measured by differential scanning calorimetry (DSC). For DSC measurement, instead of transferring film onto PDMS substrate, we float the polymer film on water and transfer the film into a DSC sample holder. The sample is dried under vacuum at room temperature for 24 hours before measurement. Nanoparticles may re-organize due to entropy-driven mobility during heating;\textsuperscript{57-62} therefore, $T_g$ of our nanocomposite is determined from first-run heating for all samples (heating rate is $10^0\text{C/min}$). All samples are made from solution casting and dried at room temperature, to cause the same thermal history. Therefore, $T_g$ obtained
from first-run heating will not be affected by the difference in thermal history amongst samples.

4.3 Results and Discussions

4.3.1 Modulus Decreasing

Frequently, adding rigid particles into polymer matrix will lead to an increase in elastic modulus of materials as a function of volume or weight fraction of particles.\textsuperscript{53, 63} However, the elastic modulus of our nanocomposite films decreases as a function of weight fraction of nanoparticles (W) (Figure 4.2). In a consistent manner, the glass transition temperature ($T_g$) decreases as a function of $W$ (Figure 4.2). These effects can be attributed to two mechanisms. One is a plasticizing effect from surface ligands. The ligands are low molecular weight PS (MW= 1000 g/mol). Therefore, the addition of these short molecules will naturally lead to a decrease in $T_g$ and modulus.\textsuperscript{64} The second mechanism is linked to the entropic interaction between nanoparticles and matrix polymer chains. According to simulation results,\textsuperscript{65, 66} when the enthalpic interaction between particles and matrix is very weak or neutral, a reduction in monomer density at a rigid particle-matrix interface occurs due to entropically-driven repulsion of polymer chains from nanoparticle surface. The schematic plot of
Figure 4.2 Plot of elastic modulus ($E$, hollow squares) and $T_g$ (solid circles) as a function of weight fraction of nanoparticles. Each data point is the average result of three samples.
“monomer vs. distance” is shown on Figure 4.3. This decreased density leads to the increase in chain mobility, consequently $T_g$ depression. The Schadler and Kumar research groups have demonstrated this $T_g$ depression in experiment when a poorly-bound (or non-wetting) interface exists between particles and polymer matrix. This depression in $T_g$ from entropic interaction may also lead to the decrease in elastic modulus.

### 4.3.2 Ligand vs. Plasticizer ($T_g$)

To decouple these two mechanisms, we compare the material properties of the nanocomposite PS system to a simple blend of short PS chains and a PS matrix. The polymer blend consists of low molecular weight PS (MW= 1000 g/mol, same as the molecular weight of surface ligands) and PS matrix (MW= 131K g/mol, same as matrix in the polymer nanocomposites). For clarity, in the following discussion, the low molecular PS added into PS matrix (polymer blend) is referred to as “plasticizer”. To facilitate comparison and isolate the effect of the surface ligands, we quantify the weight fraction of the surface ligands in the nanoparticle-polymer composite. Based on TGA (thermogravimetric analysis) measurement, we determine the weight fraction of surface ligands to nanoparticle be ~ 4%. Consequently, the weight fraction of
Figure 4.3 Top: schematic plot of “monomer density ($\rho$) vs. distance ($r$)”. $R_n$ is the radius of a nanoparticle. $R_l$ is the distance from the center of a nanoparticle to the end of ligands. $R_d$ is the distance from the center of a nanoparticle to the interface of low density area region and bulk PS. Bottom: schematic morphology of polymer chains around a nanoparticle with neutral enthalpic interaction.
surface ligands relative to matrix polymer chains can be determined for different
filler/matrix weight fractions.

Based on the Flory-Fox equation and the assumption that the $T_g$ for the PS
matrix (MW= 130K g/mol) is close to the $T_g$ for an infinitely long PS molecule, the
depression of $T_g$ ($\Delta T_g$) for a miscible blend is:

$$\Delta T_g = T_g - T_{g,\infty} = \left( T_{g,1} - T_{g,\infty} \right) W$$

$T_g$ and $T_{g,\infty}$ are the glassy transition temperature of the polymer blend and
homopolymer with infinite molecular weight respectively. $W$ is the weight fraction of
low molecular weight PS. For both the polymer blend and nanocomposite systems, a
linear relationship between $\Delta T_g$ and weight fraction of ligands/plasticizers is
observed (Figure 4.4). From measured values of $T_g$ for PS matrix ($T_{g,\infty} = 107^\circ$C ) and
best-fit linear slopes in Figure 4.4, $T_{g,1}$ of the plasticizers and surface ligands can be
obtained. Using this method, we determine $T_{g,1}$ of the plasticizer to be 2$^\circ$C and -526
$^\circ$C for the nanoparticle-bound surface ligands. The value for the plasticizer is
comparable to independent DSC measurements on 100% PS (MW= 1000 g/mol) $\sim$7
$^\circ$C, but the value for the surface-bound ligands is unrealistic. DSC measurements on
samples of 100% nanoparticles measured a $T_g$ of 0$^\circ$C. Therefore, this result implies
that another mechanism is contributing to the decrease in $T_g$ in the nanocomposites.
Figure 4.4 Plot of $\Delta T_g$ as a function of weight fraction of the plasticizer (PS, MW=1000) in the polymer blend (hollow diamonds) and surface ligands in polymer nanocomposites (solid triangles). Each data point is the average result of three samples.
As mentioned previously, when the enthalpic interaction is neutral, monomer density near the nanoparticle surface is lower compared to that in the bulk due to the entropic effects (Figure 4.3). Therefore, polymer segments in this low density region have higher mobility and associated lower $T_g$. Accounting for these additional polymer segments with a lower $T_g$ would effectively increase the weight fraction of “surface ligands” for the nanocomposite data in Figure 4. In Figure 4, the slope of the surface ligands is six times larger than the slope of the plasticizers, thus implying that the polymer chains in the low density area ($R_l < r < R_d$ in Figure 4.3) gives an additional five times weight fraction of low molecular weight polymer in matrix. Assuming the density of polymer segments in the low density region ($R_l < r < R_d$ in Figure 4.3) equals the density of surface ligands ($R_n < r < R_l$ in Figure 4.3), we can use the difference in the slopes ($K$) to estimate $R_d$ based on volume arguments:

$$
\frac{R_d}{R_n} = \left[ K \left( \frac{R_l}{R_n} \right)^3 - 1 \right]^{1/3} + 1
$$

$R_n$ (Figure 4.3) is the radius of a nanoparticle, equal to 1.75 nm in our materials. $R_l$ is the distance from the center of a nanoparticle to the end of ligands, which is 2.75 nm if the fully-extended conformation of ligands is assumed (ligand length is 1nm). $R_d$ is the distance from the center of a nanoparticle to the interface of low density area.
region and bulk PS, which is approximately 4.6 nm based on a measured value of \( K = 6 \). Consequently, the affected range of entropic interaction is 1.85 nm \((R_d - R_l)\). This value of 1.85 nm is close to the length scale reported previously\(^{66}\) and supports our hypothesis that the entropic contributions are a plausible mechanism for the rapid decrease in \( T_g \) exhibited by the nanocomposite samples.

### 4.3.3 Ligand vs. Plasticizer (Modulus)

Similar to our measurements for \( T_g \), the elastic moduli for the blend of PS (MW= 131K g/mol) and PS (MW= 1000 g/mol) are compared to the nanocomposite as a function of weight fraction of surface ligands and plasticizers (Figure 4.5). In the nanocomposite system, the elastic modulus decreases significantly at low weight fraction of surface ligands. However, this trend of the decrease in the elastic modulus is not observed for the polymer blend system. The trend of modulus decreasing as a function of weight fraction for the polymer blend system is similar to the results reported previously.\(^{54,64}\) Therefore, similar to the \( T_g \) effect, we attribute the trend exhibited by the nanocomposite to the decreased polymer segment density near the rigid filler surface. More details for this mechanism will be explored in future investigations.
Figure 4.5 Plot of elastic modulus (E) as a function of weight fraction the plasticizer (PS, MW= 1000) in the polymer blend (hollow diamonds) and surface ligands in polymer nanocomposites (solid triangles). Each data point is the average result of three samples.
4.4 Conclusion

We have demonstrated that the addition of rigid nanoparticles with neutral surface interactions leads to a decrease in the elastic modulus. The properties of surface ligands attached to the nanofillers must be properly considered for the design of nanocomposite systems. The effect of the entropic interaction between nanoparticles and matrix polymer chains leads to enhanced depressions in the $T_g$ and elastic modulus. The rate of $T_g$ drop and the trend of the decrease in elastic modulus as a function of weight fraction of nanoparticles is determined by 1) the mobility of surface ligands, 2) the strength of particle-matrix enthalpic interaction and 3) the entropic interaction which is related to the relative length scale between particles, surface ligand chains, and matrix chains.

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CHAPTER 5

NANOPARTICLE ALIGNMENT AND REPULSION DURING FAILURE OF GLASSY POLYMER NANOCOMPOSITES

5.1 Introduction

Simulations and experiments of polymer-nanoparticle composites suggest that the similar length scale of nanoparticles and polymer chains can lead to advantageous control of composite mechanical properties\textsuperscript{47, 70-73}. Perhaps most significantly, these synergistic length scales play a dominant role in the deformation and failure properties of polymer/nanoparticle composite. Most previous work has focused on the reinforcement mechanism of nano-scale fillers\textsuperscript{47, 70-73}, but at these length scales, the mobility of the filler particles, controlled by entropy, can be equally important. In fact, it has been shown that for enthalpically neutral systems, conformational entropy of polymer chains can lead to the preferential migration of nanoparticles to cracks, thus leading to a self-healing mechanism for advanced materials\textsuperscript{58, 59, 62}. Although these results concentrate on the interactions of nanoparticles and polymers in the presence of a crack, many glassy polymer nanocomposites deform first through the onset and propagation of a craze (chapter 2). These deformation zones in homogeneous materials\textsuperscript{8} and micro-composites\textsuperscript{74} have been studied extensively. Here, we present
the first experimental results on the behavior of well-defined nanoparticles during the onset and propagation of a craze. These results provide understanding of failure mechanism (ex. crazing) of glassy polymer nanocomposites, as well as a new way to alter the spatial distribution of nanoparticles dispersed in a glassy polymer matrix by direct stress and/or strain field.

Due to the large surface-to-volume ratio of nanoparticles, incompatibility between nanoparticles and matrix leads to serious aggregation compared to micron-sized particles. Therefore, the nanoparticle-matrix enthalpic contributions dictate the processing of most conventional nano-scale composites and prevents the composite from fully exploiting possible morphologies. In this work, a model material system was chosen such that entropic factors would be primarily responsible for the behavior of the composites. The polymer matrix is polystyrene (MW=126K g/mol), and the nanoparticle fillers are polystyrene-modified (MW=1000 g/mol) cadmium selenide (CdSe). Due to the existence of grafted short polystyrene chains on the surface of nanoparticles, effects of enthalpic interaction and entanglement between grafted chains and matrix are minimized. The CdSe diameter is 3.5 nm, smaller than the 10 nm radius of gyration ($R_g$) of the polystyrene. A toluene solution of the polystyrene-grafted nanoparticles and polystyrene homopolymer is cast using a
flow-coating process to form thin films (h=230 nm) (section 2.3.1). Figure 5.1a and b show transmission electron microscope (TEM) and optical fluorescence micrographs, which confirms uniform dispersion and photoluminescence of the nanoparticles upon film formation by flow casting. Distribution of nanoparticles through the thickness of the thin films is also observed (Figure 5.1c). Subsequently, we use the copper grid technique to characterize craze morphology (section 2.3.1). Based on previous reports, the crazing process and resulting morphology is not thickness dependent for polymer thin films over 150 nm in thickness.

5.2 Experiment

5.2.1 Synthesis of Surface Modified Nanoparticles.

CdSe nanoparticles were synthesized by Qingling Zhang in Emrick research group, according to published procedures to give ~3.5 nm tri-n-octylphosphine oxide (TOPO) covered particles. There TOPO-covered nanoparticles (~10 mg) were dissolved in anhydrous pyridine and refluxed under argon for 24 hours. Most of the remaining pyridine was removed under vacuum, and hexane was added to precipitate the pyridine covered CdSe nanoparticles. Anhydrous toluene (~2 mL), and thiol-terminated polystyrene (~100 mg, MW= 1000, Polymer Source Inc.) was added
Figure 5.1 Nanoparticles dispersed in PS matrix. (a) Top-view TEM image. (scale bar is 100 nm) (b) Fluorescence image. (scale bar is 5 µm) Intensity of fluorescence is uniform. (c) Cross-section TEM image. (scale bar is 100 nm)
to the pyridine covered nanoparticles. This mixture was heated to 60 °C overnight to
give a clear solution. Then, hexane was added dropwise until a cloudy suspension
was seen. The polystyrene-covered nanoparticles were isolated by centrifugation and
purified by repeated dissolution in toluene and precipitation in hexane.

5.2.2 Sample Preparation and Test

Crazing in polymer nanocomposite thin films is studied using the copper grid
technique (section 2.3.1). Polystyrene (Mn=126K, PDI=1.02, Polymer Source Inc.)
and surface modified CdSe nanoparticles are dissolved in toluene; the volume
fraction of CdSe is 0.42 %. The nanocomposite thin film (230 nm, measured by
interferometer, Filmetrics) is cast on silicon substrate by flow coating. For flow
coating, a volume of 0.1 ml dilute CdSe-PS solution was deposited under the razor
blade, then a moving stage translated at a fixed velocity to create a thin film with
uniform thickness (200 nm ± 20 nm). Within this range, thickness have no effect on
craze morphology and crazing process as reported previously.41, 56, 75 Subsequently,
we floated the film on water and transferred the film onto a copper grid precoated by
PS homopolymer. The film on the copper grid was dried for 12 hours and then
exposed to toluene vapor to remove wrinkles and increase adhesion between the copper grid and the film. After exposure, the film was dried again for 24 hours.

A custom-built, automated strain stage was used to apply fixed strains to the copper grid samples at a strain rate of 2.3×10^{-4} (1/sec). One polymer film transferred onto the copper grid sample contains 90 independent grid squares (samples). These samples are all prepared and tested at the same time. Therefore, our results are very consistent and statistical. Polymer nanocomposites with different volume fractions of nanoparticles and PS homopolymer samples were prepared for copper grid testing.

5.2.3 Characterization of Nanoparticles and Crazes

To prepare samples for TEM top-view images, we use a razor blade to cut a grid from the copper grid. This section is then directly mounted into the TEM sample holder. For TEM cross-section image (collected by Jia-Yu Wang in Russell research group), a thin layer of carbon (~ 20 nm) is evaporated onto the surface of nanocomposite thin film before samples are embedded in epoxy and cured at 60 °C for overnight. The film is removed from the substrate by dipping into liquid N₂. All samples are microtomed at room temperature with a diamond knife, and then
transferred to copper grids. TEM measurements are performed on a JEOL TEM200CX at an acceleration voltage of 200 kV.

For scanning confocal microscopy, the copper grid is fixed on a glass slide by tape. The fluorescence image is taken by a Leica TCS-SP2 confocal microscope. The excitation wavelength is 488 nm, and the emission wavelength between 500 and 550 nm is collected by the photon multiplier tube.

5.3 Results

In PS homopolymer, a craze is a whole integral craze (Figure 5.2a and 2.3). However, the spatial distribution of nanoparticles and craze morphology during craze formation and propagation is altered in polymer nanocomposites. TEM micrographs reveal an assembly and alignment of nanoparticles along the path of the precraze (Figure 5.3a). Following the precraze region, the premature craze in the nanocomposite is split into multiple, small “secondary crazes” (Figure 5.2b and Figure 5.3b). This structure is strikingly different from a conventional premature craze (compare Figure 5.2a to 5.2b) and has not been observed previously. The secondary crazes form a well-defined path of an “overall” craze and alternate from side to side within this overall craze path. Close inspection of the TEM image shows
Figure 5.2 Scheme of craze regions in (a) homopolymer and (b) nanoparticle-polymer composite. Dash line denotes the overall path of the craze.
Figure 5.3 TEM images of the craze regions in polymer nanocomposite. (a) precraze. Arrows indicate the alignment of nanoparticles. (b) premature. (c) transition (merging). and (d) mature region. Inset is a magnified image of the black frame. Smaller white frames highlight selected nanoparticle cluster bands located near the center of the mature craze. Scale bars in all figures are 200 nm.
that no nanoparticles are present within the secondary crazes (Figure 5.3b), even though the regions outside the craze are clearly populated with nanoparticles. This observation implies that the nanoparticles are repelled during the formation of the nano-scale craze fibrils. As the secondary crazes grow in width, they merge to form a transition zone (Figure 5.2b and 5.3c). In this zone, the regions between each secondary craze disappear and nanoparticle are observed in the craze region (Figure 5.3c). After this merging of secondary crazes, the mature craze forms with its edges clearly aligned in the “overall” craze zone. Here, large cluster bands of nanoparticles are observed near the center (inset of Figure 5.3d), and smaller clusters are distributed uniformly throughout the mature craze (Figure 5.3d). The distribution of nanoparticle clusters and bands across the craze width provides a natural “timeline” of how the nanoparticles interact with the craze.

It should be noted that all phenomena described above (i.e. alignment and repellence of nanoparticles, formation of secondary crazes, clustering of nanoparticles) are observed reproducibly for nanocomposites with volume fractions of nanoparticles larger than 0.34%. For low volume fractions (e.g. 0.14 %), crazes follow the same growing mechanism as that in polystyrene homopolymer.
5.4 Discussions

For nanocomposites with volume fractions within the critical regime, conformational entropy of the polymer chain drives the observations of these experiments, similar to simulations and experiment on the migration of enthalpically neutral nanoparticles to cracks\textsuperscript{58, 59, 62}. In the PS/CdSe nanocomposites, the rigid, enthalpically neutral interface of the brush-covered nanoparticles limits the conformation of polymer chains in its vicinity. Polymer chains close to nanoparticles are stretched and extended, which results in entropy penalty. This decrease in polymer conformational entropy is greater than the decrease in nanoparticle translational entropy, thus nanoparticle-polymer interactions are minimized by segregation of the nanoparticles. This segregation leads to the alignment of nanoparticles in the precraze region, the repulsion from nanoscale fibrils, and the cluster formation in a mature craze.

In the precraze region, which is fluid-like due to the concentrated stresses that exceed the yield criteria for the matrix, nanoparticles align due to the large gradient of polymer chain mobility in this confined region (Figure 5.4). At the boundary of the precraze region, the polymer chains are constrained due to the fixation of segments in the uncrazed, glassy matrix, while the chains near the center are highly mobile. This
Figure 5.4 Magnified TEM image of precraze (left) in polymer nanocomposite and corresponding scheme (right). White dash lines in TEM image depict precraze-bulk boundary. Polymer chains in the center are more mobile than chains at the boundary due to fixation of segments in the glassy matrix. Regions with solid gray color (right scheme) represent uncrazed bulk polymer.
gradient of constraint directs the alignment of nanoparticles, similar to the effect observed in ordered block copolymer matrices where nanoparticles align in the central region of a miscible domain parallel to the microphase boundaries \cite{57,60,61}. The narrow width of the precraze (~50 nm), similar to the width of block copolymer microphases, contributes to this alignment process.

While nanoparticle assembly and alignment in the precraze region does not stop the onset of fibril formation in the premature craze, it does alter the structure of the craze significantly. The premature craze in the nanocomposite material consists of a series of alternating secondary crazes. Although the exact origin of this structure is not yet understood, this observation is the first evidence that clearly demonstrates that inorganic filler particles on nanometer length scales impact the growth of a polymer craze. Previous research on the crazing of polymer composites suggested that craze growth mechanism are not influenced by fillers of sub-micron dimensions \cite{74}. Our results contradict this conclusion definitively.

In addition to causing the onset of secondary craze structures, nanoparticles are repelled from the craze nano-fibrils within these secondary crazes. This mechanism is directly related to the conformational entropy of the polymer molecules. As the craze fibrils grow, polymer molecules from the surrounding region are drawn into the fibril
and subsequently stretched and aligned. The fibril volume is highly confined (diameter = 5 to 30 nm); therefore, the presence of a 3.5 nm particle within a fibril will significantly decrease the conformational entropy of a polymer chain. This repulsion is similar to the “depletion attraction” phenomenon described by Balazs et al.\textsuperscript{59, 62, 77, 78}.

For mature crazes, the repulsion during fibril growth in length leads to nanoparticle entrapment between craze fibrils. This entrapment begins as the material between the secondary crazes is drawn completely into the craze fibrils (merging of secondary crazes) and one continuous craze structure is formed (mature craze). During this merging process, the repelled nanoparticles from secondary crazes are entrapped between the newly formed fibrils and are observed as large cluster bands close to the center of the mature craze (inset of Figure 5.3d). The newly-formed mature crazes continue to grow in width as polymer chains are drawn into fibrils, and nanoparticles are repelled from the confines of the nano-fibrils. The distribution of nanoparticle clusters throughout the craze width (Figure 5.3d) implies that nanoparticles are initially repelled, assembled at the edge of the craze, and eventually surpassed and entrapped by the growing craze fibril network/array. The polymer chains forming the nano-fibrils follow the path of least resistance and grow around
regions of sequestered nanoparticles. Since nanoparticles do not stay within craze fibrils, they can not strengthen craze fibrils directly. This trapping of nanoparticles would also occur in the premature region if the extent of fibril growth was sufficient prior to the merging of the “secondary crazes”. Details about the impact of altered morphology (ex. “secondary craze” of premature region) and rearranged nanoparticles (entrapment of nanoparticles in mature craze) on the failure of polymers will be discussed in chapter 6.

Although nanoparticles form aggregated clusters within the mature craze, the nanoparticles do not coalesce, and their fluorescent properties are not compromised. This observation is confirmed by the uniformity of nanoparticle fluorescence both within and outside the mature craze region (inset of Figure 5.5). Scanning confocal microscopy is used for these images to avoid geometric effects since a craze is a depressed region on the surface of the material\textsuperscript{10}. By conventional reflected light fluorescence microscopy, very weak or no fluorescence is observed within the mature craze region (Figure 5.5 inset), and this observation alone may cause misinterpretation of nanoparticle distribution within mature craze. Fluorescence both within and outside the craze is in direct agreement with high-resolution TEM of the mature craze region (Figure 5.3d), where nanoparticle clusters are distributed.
**Figure 5.5** Confocal fluorescence image of the mature craze. Intensity of fluorescence within and outside the craze is uniform. (Scale bar is 2 µm) Inset: epi-fluorescence image of the mature craze. (scale bar is 5 µm) Very weak or no fluorescence is observed within the mature craze.
throughout the region. The two narrow dark bands along the edges of the mature
craze in the scanning fluorescence micrograph are not due to the loss of fluorescence,
but rather attributed to optical effects that result from inclination of the craze edge.
Further evidence that these bands are produced optically is provided by scanning
reflection mode microscopy where only excitation not emission light is collected by
the detector. Under this mode, the same dark bands are observed.

5.6 Conclusion

Figure 5.6 qualitatively summarizes the four primary mechanisms of
copolymers-nanoparticle composite behavior with respect to crazing: 1) nanoparticles
align in the precrase; 2) premature crazes advance through “secondary” crazes and
nanoparticles are repelled from craze fibrils; 3) secondary crazes merge to form
mature craze; and 4) nanoparticles are entrapped by the craze fibril array in a mature
craze. In addition to demonstrating the alignment and change in spatial distribution of
nanoparticles in a glassy polymer matrix, these experimental results provide direct
evidence that nano-scale particles do not prevent the formation of nanoscale fibrils,
nor do they provide enhanced strength by the reinforcement of the fibrils. However,
alignment, formation of secondary crazes and repulsion of nanoparticles leads to the
Figure 5.6 Summary of the interaction between polymer molecules and nanoparticles during crazing process. (1) Nanoparticles are aligned and assembled along the precraze. (2) Premature region consists of several secondary crazes (two are shown in the scheme). Nanoparticles are repelled from secondary crazes during the formation of nano-fibrils. (3) Merging of secondary crazes (transition region). Nanoparticles are trapped within the crazed region during merging process. (4) Within mature craze, larger cluster bands of nanoparticles are observed near the center of the craze, and smaller clusters are distributed uniformly within the mature craze.
formation of new craze nanostructures with nanoparticle clusters entrapped within mature craze. This “self-assembled” nanostructure will be the key mechanism for enhancing the deformation and failure properties in these materials (chapter 6) and is clearly linked to the unique size-scale dependent, entropically-driven mobility provided by the interfacially-toned nanoparticles.

5.7 Acknowledgement

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6.1 Introduction

The addition of nanoscale fillers to polymer materials has led to markedly enhanced control of a wide-range of technically-important material properties, from opto-electronic to mechanical.\textsuperscript{47, 79} For mechanical properties, in particular, nanoscale fillers of different shapes and compositions have led to improvements in processing,\textsuperscript{80, 81} modulus,\textsuperscript{51, 82-84} strain-to-failure\textsuperscript{85, 86} and toughness,\textsuperscript{71, 72, 84, 87, 88} relative to microscale fillers. Despite these demonstrated property enhancements, a fundamental rationale describing the origin of such enhanced properties remains elusive for the most basic of nanocomposites. Although it is widely known that the surface-to-volume ratio increases for decreasing nanofiller size, this effect has mostly been considered in the context of enthalpic contributions. As the nanofiller size decreases, entropic contributions to material properties become increasingly important. According to the results from Balazs, Russell and Emrick research group, the entropic interaction between particles and polymer chains can lead to nanoparticle patterning in block copolymers\textsuperscript{60, 61} and material self-healing\textsuperscript{58, 59, 62}, when particle
size is close to the radius gyration of polymer chains. This entropically-driven mobility/rearrangement of nanoparticles dispersed in polymer matrix also impacts the failure mechanism of polymer nanocomposites\textsuperscript{89} and is the focus of this experimental investigation.

In glassy polymers, crazing is a dominant deformation process, subsequently leading to the formation of cracks and complete fracture of materials. Therefore, understanding the crazing process in the presence of nanoscale fillers is important to define the mechanical robustness of these materials. We previously showed\textsuperscript{89} that nanoparticles undergo three stages of rearrangement due to entropic interactions during craze formation and propagation in a polystyrene matrix. These stages are: 1) nanoparticle alignment of nanoparticles along the precraze, 2) nanoparticle expulsion of nanoparticles from craze fibrils of the premature craze, and 3) nanoparticle entrapment among craze fibrils in the mature craze. Here, we demonstrate the impact of these nanoparticle-induced processes on craze initiation and growth, breakdown of craze fibrils, and crack propagation.

Cadmium selenide (CdSe) nanoparticles, or quantum dots, of ~3.5 nm diameter were prepared and functionalized with short polystyrene chains (MW= 1000 g/mol). These PS-functionalized nanoparticles were then blended with polystyrene (MW=
131K g/mol, $R_g \sim 10$ nm) to give a dispersion of the nanoparticles in the PS matrix. Through this “grafting to” and blending approach, aggregates of nanoparticle fillers are largely avoided. Importantly, this nanocomposite design precludes the need for other additives (e.g. dispersants) that can alter the crazing process. In addition to aiding nanoparticle dispersion, the effect of both enthalpic interactions and entanglements between the nanoparticles and matrix are minimized by the polystyrene grafts. In this article, we demonstrate that the entropic interaction between the nanoparticles and the matrix with minimal enthalpic interactions and entanglements can lead to enhanced failure properties.

### 6.2 Experimental

Details about the synthesis of nanoparticles (by Qingling Zhang in Emrick research group) are described in section 5.2.2. The polystyrene-covered CdSe nanoparticles and PS (MW= 131K g/mol, PDI= 1.02, Polymer Source Inc.) were dissolved in toluene at various weight ratios. Using the known densities of CdSe (5.8 g/cm$^3$) and PS (1 g/cm$^3$), the nanoparticle volume fraction is calculated.$^{91}$

To quantify the crazing process for polymer nanocomposites, we used a well-established copper grid technique (section 2.3.1). The details about thin film
fabrication, film transferring on the copper grid and characterization of the craze morphology and crazing process are described in section 5.2.2.

6.3 Results and Discussions

Obtaining a uniform dispersion of nanoparticles in polymer matrix is a critically important precursor to the study of mechanical properties of nanocomposites. Based on the controlled synthesis and functionalization of our nanoparticles, uniform size and spatial distribution of particles in PS matrix are found, and individual particles are observed distinctly without aggregation (Figure 6.1a–d). This uniform dispersion of nanoparticles excludes the effect of aggregation on failure properties of polymer nanocomposites. From the cross-section image of our nanocomposite thin film, the distribution of nanoparticles through the thickness is also observed (Figure 6.1e).

Uniform dispersion is maintained over all volume fractions tested, but for nanocomposites with volume fraction of nanoparticles (V) \( \geq 3.3\% \), we observe surface depressions, or holes, on our nanocomposite thin films (Figure 6.2). These holes form spontaneously after the film is cast on the silicon substrate. Since these “surface defects” also contribute to the failure of polymer thin films, our discussion
Figure 6.1 Top-view TEM images of CdSe nanoparticles dispersed in polystyrene matrix with different volume fractions of nanoparticles: (a) 0.14% (b) 0.34% (c) 0.68% (d) 2.1%; scale bars are 200 nm. (e) cross-section TEM image of polymer nanocomposite thin film. Volume fraction of nanoparticles is 0.68%; scale bar is 100 nm.
Figure 6.2 TEM images of holes on nanocomposite thin films with different volume fraction of nanoparticles: (a) 3.3% and (b) 14.5%. Scale bars are 1 µm.
will be divided into two sections according to nanocomposites with low \((V < 3.3\%)
\) and high \((V \geq 3.3\%\)) volume fraction of nanoparticles.

### 6.3.1 Low Volume Fraction Nanocomposites \((V < 3.3\%\))

According to classic crazing models, the crazing process includes four stages based on the sequence of material failure: craze initiation, craze growth, fibril breakdown and crack propagation. We discuss how nanoparticles impact these four stages.

**Craze initiation.** Crazes are nucleated from surface defects or inclusions. According to accepted theories,\(^7\) these regions lead to stress concentration and the existence of a hydrostatic stress, which causes local yielding, cavitation, growth of voids and subsequent formation of craze nuclei. For samples with \(V < 3.3\%\), craze initiation occurs statistically at 1\% strain, which is the same as PS homopolymer (Figure 6.3). According to this result, the existence of nanoparticles in PS matrix does not lead to a significant change in the local stress field to alter craze initiation strain at low \(V\). Larger defects associated with the edges of the copper grid cause most crazes to initiate from this location (Fig. 2.6a).
Figure 6.3 Summary of copper grid test. Strains of craze initiation (circles), fibril breakdown (triangles) and material failure (squares) as a function of volume fraction of nanoparticles. Dotted grey line indicates critical volume fraction above which hole formation on the surface of nanocomposite films is observed. Two copper grids are prepared and tested to confirm the results. The increment of applied tensile strain is 0.5 % when tensile strain $\leq 3\%$, and 2% when tensile strain $> 3\%$. 
**Craze growth.** Crazes grow in length by a meniscus instability and in thickness by drawing polymer chains from the unyielded matrix into the craze (surface drawing). As strain increases, crazes become wider and longer. To follow the sequence of craze growth, we divide a craze into three regions: precraze, premature craze, and mature craze (Figure 2.3). The precraze is a locally yielded region at the leading tip of the craze. Following the precraze, nano-fibrils form in the premature craze and eventually lead to the formation of the mature craze with nanofibril arrays at a larger volume fraction. In our nanocomposites with $V < 0.68\%$, the premature craze is an integral craze, similar to a craze in PS homopolymer (Figure 6.4a). However, for samples with $V \geq 0.68\%$, the premature craze consists of multiple “secondary crazes” (Figure 6.4b). This morphological change was reported in a previous publication.

Craze growth is an energetic process where the applied strain energy drives the formation of craze fibrils and growth of crazes (advancing and widening). Using a craze growth rate ($R_c$), we can compare the energetics of growing crazes in the different nanoparticle volume fraction materials (section 2.3.3). Although $A_f$ is linked to both craze nucleation (proportional to the number of crazes) and craze growth, the percent increase of the number of crazes plateaus after 1.5% strain ($\varepsilon_p = 1.5\%$), while
Figure 6.4 TEM images of premature crazes in (a) polystyrene homopolymer and (b) nanocomposite (volume fraction of nanoparticles is 2.1%). Scale bars are 400 nm.
$A_f$ continues to increase as a function of applied strain (Fig. 6.5a). Therefore, $A_f$ is dominated by craze growth, not nucleation, after 1.5% strain. By plotting $A_f$ as a function of strain after 1.5% strain (Fig. 6.5b), the relationship between $A_f$ and strain is linear and the slope is the craze growth rate.\textsuperscript{56} For clarity, only three volume fractions are plotted on Figure 6.5. Other samples have similar trend as ones shown in Figure 6.5. The applied strain energy for craze growth is inversely proportional to the slope ($R_c$).\textsuperscript{56} Materials with $V < 3.3\%$ have the same craze growth rate, as indicated in Fig. 6.5b. Thus, the formation of secondary crazes and rearrangement of nanoparticles during crazing do not alter the craze growth rate. Consequently, the energetics of craze growth in our nanocomposites is similar to PS homopolymer.

In addition to growing in length and width, crazes in thin films also experience a micronecking process in the thickness direction (section 2.2.2). One quantity that describes this micronecking is the ratio of craze depth to total film thickness.\textsuperscript{10} Micronecking requires the extension of craze fibrils from the uncrazed surface to the surface depth of craze section. Therefore, the depth-to-thickness ratio is related to fibril extension ratio of crazes,\textsuperscript{11} consequently stability or breakdown of craze fibrils.

In our measurements, all crazes in nanocomposites have the same depth-to-thickness ratios of $0.38 \pm 0.005$, which is close to 0.37 of PS homopolymer.\textsuperscript{19,56} This result
Figure 6.5 (a) Percent increase of the number of crazes (solid line) and area fraction of crazes (dotted line) per grid and (b) plot of normalized area fraction ($A_f$) as a function of tensile strain for nanocomposites with different volume fraction of nanoparticles: 0% (square), 0.68% (circle) and 2.1% (triangle). Grey straight lines in (b) are obtained from linear fitting. Data points are compiled averages of 90 grid squares.
suggests that nanoparticles do not affect the micronecking process and the associated fibril extension ratio

**Breakdown of craze fibrils.** During the craze widening process, the eventual breakdown of craze fibrils occurs at the craze-bulk interface by chain scission or disentanglement.\(^9,^{13}\) Fibril breakdown results in the formation of microvoids within the craze (Figure 2.6b), which eventually grow into a crack (crack initiation) and lead to the failure of materials. One term to describe fibril breakdown is “fibril stability”,\(^{13}\) defined as the difference between fibril breakdown strain and craze initiation strain. According to classic crazing model, fibril stability is related to the fibril extension ratio and craze growth. For fibril extension ratio, large fibril extension ratio facilitates fibril breakdown, resulting in lower fibril stability.\(^9\) For craze growth, the probability of fibril breakdown decreases with craze growth rate \((R_c)\) decreasing, consequently leading to higher fibril stability. As mentioned early, crazes in samples with \(V < 3.3\%\) have the same fibril extension ratio and craze growth rate. Therefore, they have the same fibril stability. The same fibril stability and craze initiation strain among these samples give rise to the independence of fibril breakdown strain of \(V\) (Figure 6.3).

**Crack propagation.** In addition to fibril breakdown (crack initiation), the growth of the void or crack resulting from fibril breakdown plays an important role in
the material’s failure. Since nanoparticles have no effect on fibril breakdown, the impact of nanoparticles on the failure strain of nanocomposites is attributed to the propagation of the crack through the craze. In Figure 6.3, a maximum failure strain at an optimal V is found. This maximum failure strain suggests a balance between two competing mechanisms; one that leads to an increase in failure strain as a function of V, and one that leads to a decrease in failure strain as a function of V.

One possible explanation for increasing the failure strain with increasing V is that the nanoparticles are serving as plasticizers (due to the existence of low MW polystyrene ligands), which decrease the elastic modulus and increase the density of chain entanglements within craze fibrils.\textsuperscript{12} The decrease in elastic modulus alters the strain energy applied to the material as a function of strain; therefore an increased craze initiation strain and strain-to-failure is typically observed for plasticizers that decrease the composite modulus.\textsuperscript{12} Although we measure a decreased modulus as a function of V,\textsuperscript{92} the craze initiation strain is independent of V in our materials. Therefore, the decrease in elastic modulus is not a main mechanism for the enhanced ductility of these nanocomposites. The existence of plasticizers also can lead to the increase in the density of chain entanglement within craze fibrils, consequently leading to an increase in failure strain. This effect causes a change in the fibril
extension ratio. However, the fibril extension ratio of our nanocomposites is independent of V. Consequently, the increase in failure stain of our nanocomposites as a function of V is not consistent with the nanoparticles serving as a plasticizer.

An alternative mechanism, which is consistent with our observations, for the increased failure strain as a function of V is related to the cross-tie fibrils within the craze structure. As reported previously, during craze widening, an entangled strand spanning two fibrils in the craze-bulk interface must be segmented, then drawn into two fibrils. Occasionally, the piling up of several entangled strands at the craze-bulk interface occurs. This pile of strands is difficult to break energetically compared to a single strand. Thus, the craze-bulk interface bypasses these strands. This process leads to the formation of cross-tie fibrils, which connect two main fibrils within the craze. According to the model of Brown and Kramer et al., cross-tie fibrils lead to lateral load transfer between main fibrils. This load transfer causes stress concentration in the center of the main fibril closest to a crack tip within the craze and facilitates breakdown of main fibrils to grow the microvoid or crack. By considering the craze as an anisotropically elastic strip, the fracture toughness \( G_c \) is related to the ratio of tensile modulus parallel to main fibrils \( E_{22} \) to the modulus perpendicular
to main fibrils ($E_{12}$), and the relative volume fraction of main fibrils ($f_m$) to cross-tie fibrils ($f_c$). \(^{16,17}\)

$$G_c \propto \left( \frac{E_{22}}{E_{12}} \right)^{1/2} \propto \left( \frac{f_m}{f_c} \right)^{1/2}$$

As mentioned in our previous paper,\(^9\) nanoparticles are entrapped within the mature craze during craze widening and are surrounded by craze fibrils. These entrapped nanoparticles disrupt the formation of cross-tie fibrils. As $V$ increases, more nanoparticles are entrapped in the craze in our nanocomposites (Figure 6.6), implying more nanoparticles passing through craze-bulk interface with $V$ increasing. Due to the increased mobility of polymer segments at an enthalpically-neutral nanoparticle surface, nanoparticles in the craze-bulk interface can serve as a separator between polymer chains. Therefore, the probability for chains to form pile-up entangled strands at the craze-bulk interface decreases as $V$ increases. Consequently, less cross-tie fibrils form in the craze as $V$ increases. Therefore, $f_c$ decreases and greater strain is required to exceed $G_c$ for crack propagation according to equation (1). This effect contributes to an increase in failure strain as a function of $V$ (Figure 6.3).

In a competing manner, the entrapped nanoparticles within the craze also affect the extension properties of the craze. Similar to treatments by Brown, Hui and
Figure 6.6 TEM images of mature crazes in nanocomposites with different volume fractions of nanoparticles: (a) 0.14% (b) 0.34% (c) 0.68% (d) 2.1%. Scale bars are 300 nm.
Kramer,\textsuperscript{16,17} the crazed region can be considered as an elastic strip with a constant stress on the boundary between the craze and unyielded polymer.\textsuperscript{16,17} Due to the entrapment of nanoparticles within the craze, the crazed region can be considered as a “polymer composite”. According to Nielsen’s model for polymer composites,\textsuperscript{93} the macroscopic failure strain of composites decreases due to the decrease in the volume fraction of compliant material, i.e. polymer matrix, as the volume fraction of rigid particle filler increases. Consequently, according to a simple geometric derivation, the strain-to-failure ($\varepsilon_B$) of a polymer composite with good filler-matrix adhesion can be related to the volume fraction ($\phi$) of fillers by:\textsuperscript{93}

$$\varepsilon_B \sim (1 - \phi^{1/3})$$

If poor filler-matrix adhesion is assumed, $\varepsilon_B$ decreases as a function of $\phi$ with a smaller decaying rate.\textsuperscript{93} In either case, an increased particle volume fraction leads to a decreased $\varepsilon_B$. In our materials, more nanoparticles are entrapped within the crazes as $V$ increases (Figure 6.6), therefore the extensibility of the craze decreases with $V$ increasing.

Combining these two processes, the failure strain of our nanocomposites reaches a maximum at an optimal volume fraction with $V$ increasing (Figure 6.3).
6.3.2 High Volume Fraction Nanocomposites ($V \geq 3.3\%$)

As mentioned above, surface depressions form spontaneously on the nanocomposite thin films when the loading percentage of nanoparticles exceeds 3.3 vol.%. The density of surface depressions increases as $V$ increases (Figure 6.2), but their depth (50 nm from AFM) and lateral dimensions (~ 0.5 µm) is independent of $V$. Although the mechanism for the formation of these depressions is currently unexplained, the existence of these “surface defects” can alter the local stress field and the local crazing process. These holes are sudden changes in the local film thickness. Specifically, a large stress concentration is generated at the boundaries of holes, similar to dust particles that are responsible for early fibril breakdown and material failure.\textsuperscript{13} In the nanoparticle composites discussed here, more “surface defects” are found in the sample with $V = 14.7\%$ compared to $V = 3.3\%$ (Figure 6.2). Accordingly, fibril breakdown and material failure occurs at lower strain for $V = 14.7\%$ compared to the sample with $V = 3.3\%$ (Figure 6.3). This result is similar to findings in previous research,\textsuperscript{56} where hole formation on block copolymer thin films leads to early failure of materials. In both cases, the depth of the depressions is ~ 50 nm, the lateral dimension is on the order of 1 µm and the thickness of the film is 135 ~ 245 nm.
Although the failure strain trend is similar to block copolymer films, the initiation strain decreases at higher $V$ for the nanoparticle composites. These results are not consistent with hole structures on model block copolymer films (i.e. hole structures leads to the increase in craze initiation strain).\textsuperscript{56} This inconsistency suggests an important contribution from the presence of the nanoparticles, but further exploration remains for a future investigation.

### 6.4 Conclusion

For nanocomposites with volume fraction of nanoparticles $< 3.3\%$, nanoparticles have no effect on craze initiation, craze growth, and fibril extension ratio. However, we find that nanoparticles impact crack propagation, leading to an increase in failure strain by 60\% at an optimal volume fraction of $\sim 0.7\%$. This optimal volume fraction represents the balance of two mechanisms: 1) increasing fracture toughness ($G_c$) with decreasing number of cross-tie fibrils, and 2) decreasing extensibility of the craze with increased volume fraction of nanoparticles entrapped within the craze. These results offer insight into the impact of nanoparticles on the crazing process and failure of glassy polymer nanocomposites based on entropic interactions and help to predict the effective design of nanoparticle-based materials.
6.5 Acknowledgement

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7.1 Introduction

In polymer composites, the interactions between particles and matrix play an important role to determine material properties. These interactions are both enthalpic and entropic in nature. Strong enthalpic interaction between particles and matrix leads to a strong interfacial adhesion and often a high density of matrix chain segments at the particle-matrix interface.\textsuperscript{66, 94} These effects lead to a significant increase in the elastic modulus and often a drastic decrease in ductility compared to composites with weak matrix-particle adhesion.\textsuperscript{93} In addition to enthalpic interactions, polymer chains are perturbed significantly when the size of particles is on the same order of the radius of gyration of polymer chains. To maximize conformational entropy of neighboring polymer chains, nanoparticles are repelled by the chains, causing an entropically-driven mobility/rearrangement for the nanoparticles when enthalpic interaction are minimized.\textsuperscript{60, 61, 95, 96} Based on this entropically-driven mobility, several research groups have demonstrated that nanoparticles can migrate into
cracks \cite{58, 59, 62} align in block copolymer domains.\cite{57} Additionally, we have shown that entropic driving forces can cause nanoparticles to align, repel and entrap within a craze structure (chapter 5). This entropically-driven rearrangement of nanoparticles in crazes leads to an increase in strain-to-failure by 60\% compared to homopolymer without nanoparticles (chapter 6). Hence, not only enthalpic interactions, but entropic interactions play an important role in the mechanical properties of polymer nanocomposites.

The entropic interaction is related to the ratio of nanoparticle diameter (d) to the radius gyration of polymer chains ($R_g$). In this project, we compare the effect of nanoparticles of two different diameters (d= 3.5 nm and 6.0 nm) within a matrix of polymer chains ($R_g$= 10 nm). Specifically, we focus on the impact of entropic interactions on the distribution of nanoparticles in the polymer matrix and mechanical properties of these nanocomposites.

7.2 Experiment

Cadmium selenide nanoparticles of ~ 6.0 nm diameter (CdSe60) are prepared and functionalized with short polystyrene chains by Qingling Zhang in the Emrick research group according to previous procedures (section 5.2.1). The
PS-functionalized nanoparticles and polystyrene (PS, MW= 131K, Polymer Source Inc.) are dissolved in toluene with different weight ratios and cast on a silicon substrate by flow coating (section 5.2.2). The film thickness is 200 nm. Through this “graft-to” and blending approach, aggregates of nanoparticles are avoided and the need for dispersants that may alter material properties are also precluded. In addition, the effect of both enthalpic interaction and entanglements between nanoparticles and matrix are minimized by the polystyrene grafts.

The SIEBIMM technique and DSC are used to measure the elastic modulus and \(T_g\) of polymer thin films. Detailed procedures are described in sections 4.2.2 and 4.2.3. We use the copper grid technique to investigate the crazing process and failure properties in polymers. Detailed procedures for sample preparation and characterization can been seen in section 5.2.2 and 5.2.3. The cross-section TEM image of the nanocomposite thin film is collected by Jia-Yu Wang in the Russell research group.

7.3 Results

For nanoparticles of 3.5 nm diameter, distribution through the film thickness is observed (Figure 7.1a). However, for nanoparticles of 6.0 nm diameter, nanoparticles
Figure 7.1 TEM images of polymer nanocomposite thin films with nanoparticle diameter 3.5 nm (a and c, same as Figure 6.1) and 6.0 nm (b and d). Weight fraction of nanoparticles is 3.85%. White arrows indicate the segregation of nanoparticles near film surface (b) and the local clustering of nanoparticles (d).
are segregated to the film/air interface after the film casting (Figure 7.1b). In addition to surface segregation, local clustering of nanoparticles is observed (Figure 7.1d), compared to nanoparticles of 3.5 nm diameter (Figure 7.1 c). Unlike particle aggregates where individual particles can not be differentiated, individual particles within local clusters are still distinct due to PS grafts on the nanoparticle surface.

Although the nanoparticle diameter has a significant impact on the nanocomposite morphology, the impact of this morphology on the thermal properties is not significant. Both segregated (d= 6.0 nm) and well-dispersed (d= 3.5 nm) nanoparticles lead to the decrease in T_g as a function of weight fraction of nanoparticles and have the same depressing rate (Figure 7.2a).

The depression of T_g for the different nanoparticle diameters is consistent with the decrease in the composite elastic modulus. However, the modulus depressing rate of the segregated system is larger than that of the well-dispersed system (Figure 7.2b).

In the copper grid test, the presence of nanoparticles (d= 6.0 nm) impacts the failure strain of the polymer nanocomposites (Figure 7.3a). Specifically, the failure strain increases by nearly 100% at an optimal volume fraction of nanoparticles, then decreases at higher weight fractions. This impact from segregated nanoparticles
Figure 7.2 Plot of (a) $T_g$ and (b) elastic modulus of polymer thin films as a function of weight fraction of nanoparticles (solid symbols: $d = 3.5$ nm; hollow symbols: $d = 6.0$ nm). Each data point is the average result of three samples.
Figure 7.3 Plot of craze initiation (square), fibril breakdown (triangle) and failure (circle) strain of polymer nanocomposites as a function of weight fraction of nanoparticles of (a) 6.0 nm diameter and (b) 3.5 nm diameter (same as Figure 6.3). Two libraries are prepared and tested to confirm the results. The increment of applied tensile strain is 0.5 % when tensile strain $\leq 3\%$, and 2% when tensile strain $> 3\%$. 
(diameter is 6.0 nm) on the failure strain of polymer nanocomposites is similar to that from well-dispersed nanoparticles (d= 3.5 nm) (Figure 7.3b). In addition, same as well-dispersed nanoparticles, segregated nanoparticles have no impact on craze initiation and fibril breakdown strains. However, at high weight fraction of nanoparticles (W ≥ 33.3%), the crazing process is depressed and materials fail at significant low strain of 1%. This is different from well-dispersed nanoparticles (d= 3.5 nm), where crazing still occurs at such a high W.

7.4 Discussions

7.4.1 Distribution of Nanoparticles

When polymer chains are close to rigid nanoparticles, their possible confirmations are limited to packing constraints and chain stretching. Consequently, the polymer conformational entropy decreases. To minimize perturbation and maximize conformational entropy, nanoparticles are repelled by polymer chains, and generally segregate into nanoparticle-rich domains, or clusters (“depletion-attraction” process). The driving force for “depletion-attraction” is related to (d/R_g). Under the circumstance of the same polystyrene matrix (R_g= 10 nm), nanoparticles of 6.0 nm diameter have a larger entropic driving force for segregation compared to
nanoparticles of 3.5 nm diameter. This larger entropic force contributes to the surface segregation of nanoparticles after the film casting.

**7.4.2 Impact on T\text{g} and Elastic Modulus**

As mentioned in chapter 4, for surface modified nanoparticles, both short surface ligands and the nanoparticle-polymer entropic interaction contributes to the decrease in T\text{g} and the elastic modulus of polymer nanocomposites. To decouple these two mechanisms, the material properties of nanocomposite system (particle diameter is 6.0 nm) is compared to a blend of short PS chains and a PS matrix. To facilitate comparison and isolate the effect of the surface ligands, we quantify the weight fraction of the surface ligands (W\text{s}) in the nanoparticle-polymer composite.

\[
W_s = \frac{\text{weight of surface ligands}}{\text{weight of surface ligands} + \text{weight of matrix}}
\]

Based on TGA (thermogravimetric analysis) measurement, we determine the weight fraction of surface ligands to nanoparticle be \(~4\%\). Consequently, the weight fraction of surface ligands relative to matrix polymer chains can be determined for different filler/matrix weight fractions.

By plotting “\(\Delta T_g\) vs. W\text{s}” for nanocomposite systems and the polymer blend, the linear relationship is obtained (Figure 7.4a), which follows Flory-Fox equation.
Figure 7.4 Plot (a) $\Delta T_g$ and (b) elastic modulus as a function of weight fraction of the plasticizers in polymer blend (hollow diamonds) and surface ligands in polymer nanocomposites with nanoparticle diameter 3.5 nm (hollow triangles) and 6.0 nm (solid stars). Each data point is the average result of three samples.
Here, $W_s$ is the weight fraction of surface ligands on nanoparticles ($d=3.5\text{ nm or }6.0\text{ nm}$). The slope of segregated nanocomposite system ($d=6.0\text{ nm}$) is very close to that of the well-dispersed system ($d=3.5\text{ nm}$), which is six times larger than the slope of the polymer blend. Compared to the polymer blend, this significant drop in $T_g$ for the nanocomposite results from the low density area of monomers around nanoparticles due to particle-polymer entropic interaction. Details about the formation of the low density area are described in section 4.3.2. By the same equation and calculation in section 4.3.2, the affected range (low density region of monomers, $R_l<r<R_d$ in Figure 4.3) of the entropic interaction can be obtained. The value of 2.51 nm is close to the value of 1.85 nm for the well-dispersed system. Both nanocomposites ($d=3.5\text{ nm and }6.0\text{ nm}$) have the same slope (same $K$ value), therefore it implies that both segregated and well-dispersed nanoparticles with short PS grafts lead to the same weight fraction of the low density region of polymer segments in the matrix. Therefore, they have the same impact on $T_g$ decreasing.

The elastic modulus of two nanocomposite systems and the polymer blend as a function of the weight fraction of the surface ligands and plasticizers are shown in Figure 7.4b. For the nanocomposite with particle diameter of 6.0 nm, the elastic modulus decays much faster as a function of $W$ compared to the nanocomposite with
particle diameter of 3.5 nm. Both trends of modulus decreasing are different from that of the polymer blend. Although segregated and well-dispersed nanoparticles have the same impact on \( T_g \) decreasing, they have different impacts on modulus decreasing. Therefore, another mechanism contributes to the significant decrease in the modulus for surface segregated system. Details for this mechanism will be investigated in the future.

7.4.3 Impact on Crazing and Failure

According to current crazing models, fibril stability and crack propagation in glassy polymers are two dominant mechanisms to determine the failure of materials. In these models, low fibril stability leads to the high probability of fibril breakdown (crack initiation). One indicator of fibril stability is the fibril extension ratio,\(^7\) which is related to the micronecking ratio of the craze depth to film thickness.\(^{11}\) From AFM measurement on crazes in both nanocomposites (\( d=3.5 \) nm and 6.0 nm), all crazed samples have the same depth-to-thickness ratio of 0.37, which is the same as polystyrene homopolymer. Additionally, fibril stability is defined as the difference between the strains of fibril break down and craze initiation.\(^9,\)\(^13\) For both nanocomposites, this difference in craze initiation and fibril breakdown strains is
independent of W for lower weight fraction of nanoparticles (Figure 7.3). Accordingly, the nanoparticles are not impacting fibril stability significantly.

Failure strain is also related to the mechanism of crack propagation through the craze region. Crack propagation in glassy polymers is related to the number fraction of cross-tie fibrils within the craze and extensibility of the crazed region behind the crack. In previous research on well-dispersed nanocomposite system (chapter 6), an optimal volume fraction of nanoparticles for a maximal failure strain results from the balance of two effects: the decrease in cross-tie fibrils and extensibility of the craze due to entrapped nanoparticles within the craze. With W increasing, more nanoparticles are entrapped within the craze, disrupting cross-tie fibrils, consequently leading to the increase in fracture toughness and ductility. However, considering the craze with entrapped nanoparticles as a “polymer composite”, the ductility or extensibility of the craze decreases as a function of W.93

For segregated nanocomposite system, nanoparticles entrapped within the craze are also observed (Figure 7.5). These entrapped nanoparticles can also have the same effect on crack propagation as the well-dispersed nanocomposite system. However, for segregated nanocomposite system, nanoparticles (diameter is 6.0 nm) are only located near film surface. In addition, crazes are initiated from film surface
Figure 7.5 TEM image of the craze in polymer nanocomposites with nanoparticle diameter 6.0 nm. Weight fraction of nanoparticles is 3.85%.
(micronecking). Therefore, it implies that the interaction between nanoparticles and craze fibrils at the early stage of craze formation can still lead to an increase in failure strain.

The surface segregation of nanoparticles can lead to a local high concentration of nanoparticles near film surface. Based on recent experimental results and theoretical models for polymer thin films, as the interparticle distance decreases, the number of entanglements may also decrease. The local high W near film surface will lead to the decrease in interparticle distance. Consequently, a significant decrease in the number of chain entanglements near film surface is expected. According to classic crazing models, a critical number of entanglements is required for craze formation and stability of craze fibrils. Micronecking, as described in previous investigations on crazing, occurs on the film surface and induces the formation of the craze. Therefore, the high weight fraction of nanoparticles will depress the craze initiation on film surface. Without crazing, materials will fail in a very brittle manner.
7.4 Conclusion

We have demonstrated that diameter plays an important role in the nanocomposite morphology for particle-matrix interfaces with minimal enthalpic contributions. Specifically, larger diameter nanoparticles segregate to the air/film interface during film casting. These larger nanoparticles form larger clusters compared to smaller nanoparticles. These effects are attributed to $d/R_g$, related to the entropic force. Nanoparticle size also plays an important role in determining the elastic modulus and failure properties of the nanocomposite.

Segregated nanoparticles lead to a significant decrease in the elastic modulus at very low weight fraction of nanoparticles (W). An increase in failure stain by nearly 100% at an optimal W is also observed. However, when more nanoparticles are added into polymer matrix ($W \geq 33.3\%$), segregation results in a locally high concentration of nanoparticles at film surface. This high density leads to the loss of chain entanglements and depresses craze formation. Consequently, the nanocomposites at high W fail in a brittle manner.
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CHAPTER EIGHT

SUMMARY AND FUTURE WORK

8.1 Summary

Copper grid and SIEBIMM techniques are used to study elastic deformation and the crazing process in nanostructured polymer thin films. Combinatorial sample design, high throughput methods of data collection and analysis are successfully developed to obtain efficient, statistical and consistent results. Two model materials of PS-b-P2VP and PS blended with surface modified nanoparticles are used. Models are developed to describe the impact of nanodomains, surface nanodefects and nanoparticles with neutral enthalpic interaction on the elastic modulus and crazing process of polymer thin films.

8.1.1 Effect of Nanodomains on Crazing

Tensile direction relative to chain orientation within nanodomains plays a critical role to the extension ratio of craze fibrils in block copolymers, which is significantly related to the breakdown of craze fibrils (crack initiation). For example,
tensile stress perpendicular to chain orientation leads to a large fibril extension ratio, consequently facilitating fibril breakdown.

Craze growth rate obtained from image analysis of each grid square is used to investigate the energetic process of crazing in polymers. Due to incompatibility between individual blocks, applied strain energy is dissipated by fibril formation and does not contribute craze growth. This process leads to the small craze growth rate and low probability of fibril breakdown in block copolymers.

8.1.2 Effect of Surface Nanodefects on Crazing

Surface terraces (islands or holes) which form spontaneously on block copolymer thin films are a sudden change in film thickness, leading to a stress concentration at the edges of terraces. When crazes pass through these terraces, the stress concentration facilitates breakdown of craze fibrils, and leads to an early failure of thin films. This result implies that surface roughness of nanodevices or nanotemplates, which may result from the fabrication process, can cause a catastrophic failure of materials, and limit the application of these devices or templates.
8.1.3 Impact of Nanoparticles on Elastic Deformation

Two mechanisms are found to contribute to the elastic deformation of polymer nanocomposites with enthalpically-neutral interaction between particles and matrix. Due to the high surface-to-volume ratio of nanoparticles, surface ligands, which are grafted on particles to facilitate particle dispersion, play an important role in the elastic deformation of materials. We found that ligands with high mobility (ex. low molecular weight PS) decrease $T_g$ and the elastic modulus of composites, similar to the effect of plasticizers. Additionally, at nanometer scales the entropic interaction between nanoparticle core and polymer chains can result in the decrease of the monomer density around particles. This process leads to an additional decrease in $T_g$ and elastic modulus.

8.1.4 Effect of Nanoparticles on Crazing

Based on our material design, enthalpic interaction and entanglement effect between nanoparticles and PS matrix are minimized. Therefore, the first evidence of the entropic interaction impact on crazing and failure of polymer nanocomposites is demonstrated. Here, we found that nanoparticles can alter the morphology of the craze: the premature craze consists of several “secondary crazes” instead of an
integral craze in homopolymer. In addition, during craze formation, nanoparticles are aligned along the precraze and located in the center of the precraze. During fibril formation, nanoparticles are excluded from the confined space of craze fibrils. During the merging process of secondary crazes and widening of the mature craze, nanoparticles are entrapped among craze fibrils. This entire rearrangement process is driven by the configurational entropy of the polymer matrix chains.

For high volume fraction nanocomposites (V ≥ 3.3%), surface depressions (nanoholes) form spontaneously after film cast on the substrate. The number of nanoholes increases as a function of V and causes early failure of thin films, similar to the effect of surface terraces on the failure of block copolymer thin films. For low volume fraction nanocomposites (V < 3.3%), nanoparticles have no effect on craze initiation, extension ratio of craze fibrils and craze growth rate. However, nanoparticles did impact crack propagation by decreasing number of cross-tie fibrils and extensibility of the craze. Consequently, a maximum increase in failure strain by 60% is found at an optimal volume fraction of nanoparticles (~0.7%) due to the balance of the above two effects.
8.1.5 Impact of Segregated Nanoparticle on Mechanical Properties

Larger nanoparticles are segregated to the film surface after the film is cast on the substrate. The segregation process may result from the larger ratio of particle diameter to radius gyration of polymer chains (larger entropic interaction). These segregated nanoparticles near the film surface also lead to an increase in the failure strain by nearly 100% at an optimal volume fraction of nanoparticles and a decrease in the elastic modulus as a function of volume fraction of nanoparticles.

8.2 Proposed Future Work

- In chapter three, PS-b-P2VP thin films with thickness gradient are fabricated to investigate the effect of surface defects on crazing process. However, due to large thickness gradient, one grid square contains islands or holes with different area densities and sizes. Therefore, effects of the size and area density of surface terraces on crazing process are still unexplored. In the future, PS-b-P2VP thin films with smaller thickness gradient could be fabricated. Therefore, one grid squares can contains islands/holes with well-defined size and area density.
We have shown the impact of nanoparticle-polymer entropic interaction on the elastic and failure properties of polymer nanocomposites. However, the role of surface ligands is still not fully explored. In the future, polystyrene ligands with different molecular weight can be grafted onto nanoparticles to tune entropically-driven mobility of nanoparticles. For example, when molecular weight of ligands is larger than the entanglement molecular weight of the polymer, the entanglement between ligands and matrix may prevent nanoparticles from excluding from craze fibrils. Consequently, nanoparticles may stay within craze fibrils, enhancing the strength of craze fibrils. In addition, ligands with different molecular weight lead to different ability to soften polymer matrix due to high surface-to-volume ratio of nanoparticles. In addition to the entropic interaction, different surface ligands and matrix can be used to tune enthalpic interaction between matrix and nanoparticles. Therefore, the effect of enthalpic interaction on the elastic and failure properties of nanocomposites can be investigated.

We have shown that nanoparticles can segregate to the film surface due to the increase in the particle size. The change of the particle size leads to the change of entropic force between particles and polymer chains, which is related to the ratio
of particle diameter to radius gyration of polymer chains. In the future, polymer matrix with different molecular weight (different radius gyration) can be used to tune nanoparticle dispersion in thickness direction of polymer thin films. The effect of nanoparticle dispersion on mechanical properties can be also investigated.
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