Investigation of microstructural changes in impacted polyurea coatings using small angle X-ray scattering (SAXS)

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Three polyureas with decreasing soft segment molecular weights of 1000, 650, and a 250/1000 blend were molded onto circular steel plates and then impacted with a high speed (275 m/s) conical-shaped steel cylinder. The polyurea layer of the post mortem bilayers was characterized on a molecular level by small angle synchrotron X-ray scattering (SAXS) at the Advanced Photon Source at the Argonne National Laboratory. Analysis revealed that the hard domains of the polyureas with lower molecular weight soft segments reformed and oriented over a greater area of the coating, thus increasing the polymer strain hardening and resulting in visibly less out of plane bilayer deformation. This agrees with the hypothesis that polymer strain hardening is a mechanism that retards necking failure of the metal plate. © *2011 International Centre for Diffraction Data.* [DOI: 10.1154/1.3590738]

Key words: polyureas, soft segment molecular weight, high speed impact, SAXS, morphology

I. INTRODUCTION

Polyurea copolymers have been recently shown to be effective coatings for protecting metal structures against penetration by high speed impacts (Mock *et al.*, 2005; Balizer and Mock, 2006). Without the polyurea coating, the metal is penetrated by the impactor. It has been proposed that the mechanism of metal failure is necking. The mechanism of protection is the strain hardening of the polyurea layer that increases the effective modulus of the metal/polymer bilayer and dissipates more energy, resulting in reduction of necking failure (Xue and Hutchinson, 2007). The strain hardening of the polyurea is controlled by the processing and molecular weights (MWs) of the hard and soft segment precursors resulting in their phase separated morphology. Segmental chemical differences cause the hard segment isocyanates to phase separate from the soft segments to form hard domains that act as physical cross-links in the elastic soft segment matrix. The morphology of the phase separated hard segment domains ranges from lamellae type stacks, platelets of isolated domains, to long threadlike regions that overlap or intersect, depending on the quantity of precursors and polymerization conditions (Garrett *et al.*, 2001; Sheth *et al.*, 2004; Das *et al.*, 2007). The elastic and plastic deformation response at high strains involves the orientation of the soft and hard segments and leads to yielding and the breakup of the hard domains and their reformation to an oriented fibrillar form. These morphological domains are on the order of several nanometers and are effectively characterized by SAXS.

We hypothesize that lower soft segment molecular weights would yield and reform to oriented fibrillar hard domains at lower strains and thus increase strain hardening and impact protection. To investigate this hypothesis, three polyurea materials with decreasing soft segment MW of 1000, 650, and a blend of 250/1000 were cast onto steel plates that were subsequently impacted on the steel side with a conical-shaped steel cylinder using a gas gun. The recovered bilayer plates were sectioned and the polyurea was scanned by SAXS yielding the molecular morphology over the plate from the edge to the projectile impact center. The resulting 2D SAXS images, their intensity profiles, and interpreted morphology changes as a function of position about the impact center are described in this publication.

II. EXPERIMENT

A. Materials

Starting amine and isocyanate materials for the polyureas were obtained from Air Products and Chemicals and Dow Chemical, respectively. The diamines are Versalink P-1000, P-650, and P-250 diamines (Air Products). The 1000, 650, and 250 values refer to the nominal molecular weights of the polytetramethyleneoxideglycol starting materials for the diamines. The diamines consist of tetramethyleneoxide repeat units with terminated primary aromatic amine esters. The isocyanate is Isonate 143L (Dow Chemical). Isonate 143L is a eutectic mixture of pure linear, symmetric p,p′-diphenylmethane diisocyantate (MDI) and a carbodiimide modified MDI triisocyanate. The triisocyanate component adds asymmetry to the structure to prevent hard domain crystallinity and provides higher functionality for modest cross-linking. The tetramethyleneoxide component serves as the soft segment for the polyurea while the terminal aromatic amine and isocyanate components serve as the hard segment. The weight percents of hard segments for the polyureas PU1000, PU650, and PU250/1000 blend (2.25:1) are 36%, 47%, and 55%, respectively. These polyureas were cast as 11.1 mm thick layers on circular steel plates with 154.2 mm diameters.

B. High strain rate impact experiments

A 40-mm-bore gas gun (Mock and Holt, 1976) was used to perform the impact experiments for the three polyurea

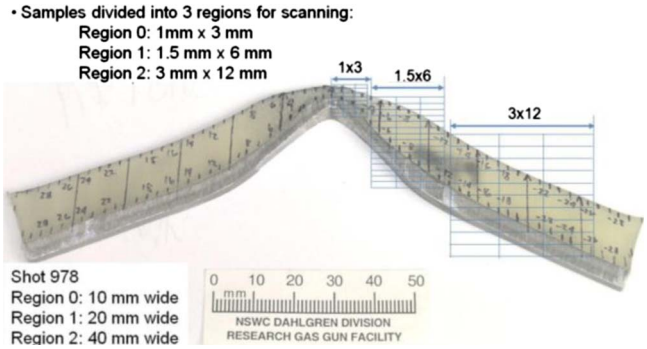

Figure 1. (Color online) The cross section of the polymer/metal bilayer plate with virtual grid illustrating three regions R0, R1, and R2 of the polymer layer. The sample was held vertically during the X-ray scans thus the horizontal and vertical axes are noted in the figure.

mixtures. The average impact velocity was 275 m/s. For each experiment, a conical-shaped steel cylinder impacted a steel plate that had a polyurea layer cast on the back of the plate. The 4340 solid steel impactor (hardness RC 36, 35.6 mm diameter, 45° cone angle) weighing 140 g was epoxied into the recess in the front of a 6061-T6 aluminum sabot and launched at the steel/polyurea composite target plate. The DH36 steel target plate (15.3 cm diameter, 4.8 mm thick) was epoxied to one end of a clear plastic tube that was held onto the gas gun muzzle flange by evacuating the target and gun barrel together before the shot. The sabot velocity was measured just before impact with three charged pins in the side of the barrel. A 68 frame DSR Hadland framing camera (DRS Imaging, 2002) was used to observe the time sequence of events during impact. The PU650 and PU250/1000 layers were bolted to the mild steel target plate since they would detach on impact due to their poor adherence properties. The recovered bilayer plates were cut into an approximate 2 mm wide strip through the center and the polyurea layers were characterized at points between the polymer/air interface and the metal/polymer interface by SAXS. As shown in Figure 1, there is a contiguous region of metal and polymer necking at the plate center due to impact with the ogival nose of the impactor.

C. Small angle X-ray procedure

X-ray scattering measurements were carried out in the 5ID-D enclosure of DND-CAT at the Advanced Photon Source at Argonne National Laboratory (Argonne, IL). The X-ray beam (0.10332 nm wavelength) from a Si-(111) double crystal monochromator was collimated with three sets about 0.2×0.2 mm^2. Wide angle X-ray scattering (WAXS) data were collected on a 100×200 mm^2 dual chip Roper® CCD camera with a sample to detector distance of 136.5 mm. Dark frame, distortion, and flat-field corrections were done with FIT2D. SAXS data were simultaneously collected on a 100×100 mm^2 Roper camera of 158 μm pixel size with a sample to detector distance of 2437.5 mm. X-ray scattering data were obtained with 0.1 s exposures. Calibration samples were silver behenate for SAXS and lanthanum hexaboride for WAXS.

The SAXS scans shown were taken over a grid on the upper half of the polyurea that consisted of three regions of

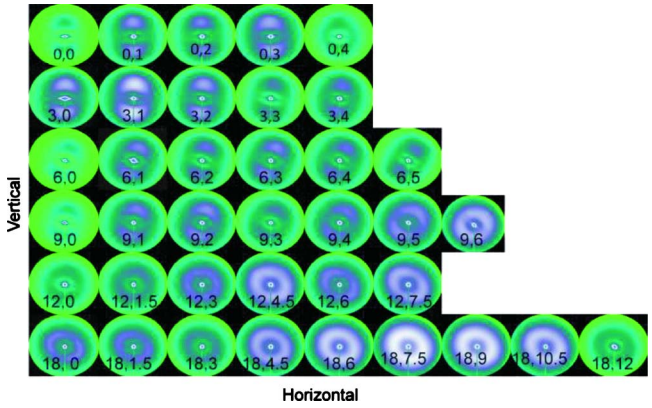

Figure 2. (Color online) The 2D SAXS patterns for the 1000 MW soft segment polyurea as a function of position coordinates (vertical, horizontal). The coordinates are given in mm relative to the impact center at (0,0). The first row shows the grid points 1 mm apart in the horizontal direction (width). The vertical distance scans were made to 66 mm and the horizontal distance varied with width of necking. Note the rotation of pattern due to bending of metal layer.

the polymer layer, as shown in Figure 1: R0 with high curvature at the impact center, R1 with gradual bending of the polymer, and R2 a region where the polymer was unperturbed. The fiducial points irradiated on the sample were as follows: in R0, the fiducial points were taken every 3 mm vertically and 1 mm horizontally; in R1, every 6 mm vertically and 1.5 mm horizontally; and in R2, every 12 mm vertically and 3 mm horizontally.

III. RESULTS

A. 1000 MW 2D SAXS intensity patterns

The PU1000 2D SAXS intensity patterns are shown in Figures 2 and 3. Descriptions of the intensity patterns in each region are as described below.

R2: The resulting SAXS scans in region R2 from 66 to 42 mm show an isotropic ring shaped halo that is uniform in intensity and occurs uniformly at points across the width. *R1:* At the boundary of this region (30 mm), the SAXS pattern shows evolution from the metal boundary where there is an isotropic ring to an ellipse whose major axis is tilted at the free surface. As this region is progressed vertically (18 mm), the ellipse also appears at the metal boundary and across the

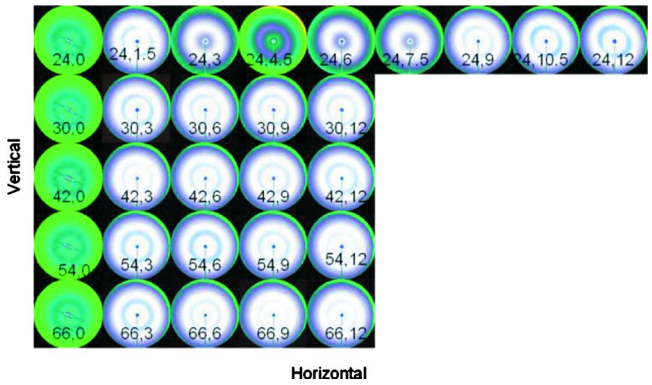

Figure 3. (Color online) The 2D SAXS patterns for the 1000 MW soft segment polyurea as a function of position.

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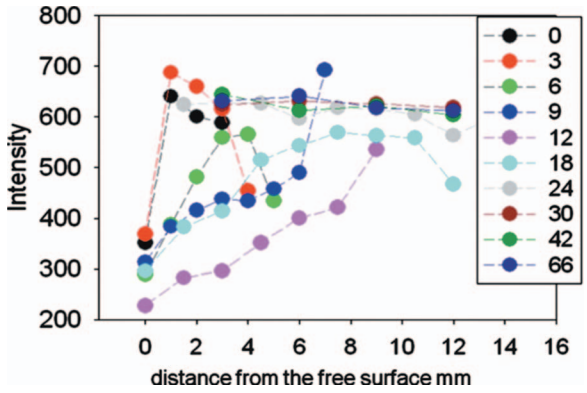

Figure 4. The meridional peak intensity values for the 1000 MW soft segment polyurea. Note the increase in intensity closer to the impact center indicating order of the reformed hard domains. The lowest intensity values occur at 12 mm where a large part of the breakdown/reformation occurs.

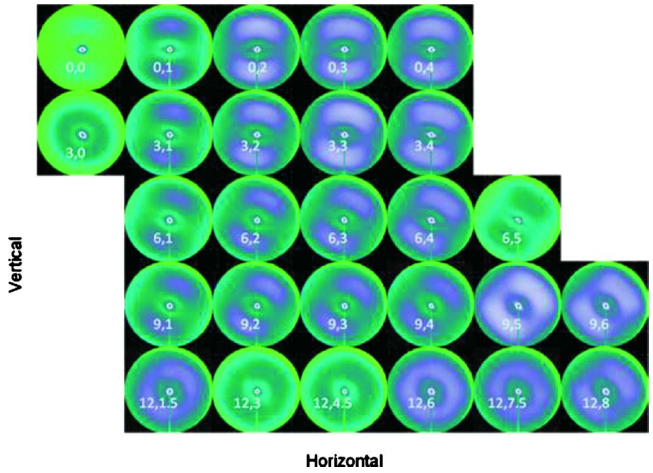

Figure 5. (Color online) The 2D SAXS patterns for the 650 MW soft segment polyurea as a function of position. Polymer coordinates of SAXS images labeled by (vertical, horizontal) pairs.

polymer thickness. Here the intensity decreases along the meridian of the ellipse but remains strong along the equator. The next line (12 mm) shows the transition of the ellipse to a near vertical pattern of overlapping thick arcs. The meridional intensity now is stronger and the equatorial intensity is weaker.

R0: For the SAXS patterns at points beyond this transition (9–3 mm), the meridional arcs become narrower and more oriented toward the vertical, particularly at the free boundary surface. The equatorial intensity meanwhile progressively decreases. The halo for these patterns becomes more elliptical as compared to circular in the preceding region. The impact point region (0–3 mm) shows SAXS patterns of a pair of vertically oriented meridional arcs across the thickness. This high orientation at the impact center (0 mm) occurs over the thinnest region of the polymer where greatest necking of the metal layer occurs.

B. 1000 MW meridional intensities

The range of coherent order to disorder upon destruction of the hard domains is given by the values of the intensity gradient across the polyurea. The meridional intensities as a function of position are shown in Figure 4. In the unperturbed region R2 (30, 42, and 66 mm) the intensities are highest and uniform across the width. At the upper part of R1 (18 mm), there begins at the midline (6 mm) a sharp decrease in both the meridional and equatorial intensities to the free surface boundary. On the transition line (12 mm), the meridional intensities drop to their lowest values at all points through the width. This is interpreted as the region of greatest disorder of the hard domains that are broken down and then reformed. The intensity then sequentially increases closer to the impact center but always with a gradient that is lower at the free surface. At the impact center R0 (0 and 3 mm), the trend reverses and the intensity increases towards the free surface and is on the order of or greater than values in the unperturbed region. Thus, the hard domains at the impact center show a high order and orientation. The meridional intensity values at 0 mm at the free surface decrease, we believe, due to the finite beam width scattering at the air polymer interface. Similarly at the polymer metal interface, part of the beam may hit the metal and part hit the polymer to change the intensity pattern. In the upper region of R0 (9–6 mm), both the d-spacing and intensity decrease within a few mm of the free surface. This indicates reformation of hard domains but decrease in order. At the impact center (0–3 mm), the reformed domains have an increasing intensity gradient towards the free surface indicating a greater order of the reformed domains. This phenomenon will be discussed in the next sections.

The ordering of the hard domains beyond the yield point is the precursor to strain hardening that is needed to delay the necking of the metal plate. We shall find that hard domain ordering occurs over larger regions of the 650 MW and 250/1000 blend polymers than just at the impact center for the 1000 MW soft segment polyurea. We will show in Secs. III C–III G that more protection is provided by these polyureas.

C. 650 MW 2D SAXS intensity patterns

The SAXS 2D intensity patterns for the 650 soft segment molecular weight polyurea are shown by position in Figures 5 and 6. The regions are described as follows: *R2:* There is a circular ring pattern of uniform intensity in the region far from impact at 30 mm. This represents an isotropic distribution of hard domains. *R1:* The incipience of an elliptical pattern occurs at 18 mm. The major axis is not as rotated toward the vertical as the 1000 MW polyurea and the minor axis appears to be more intense than that of the 1000.

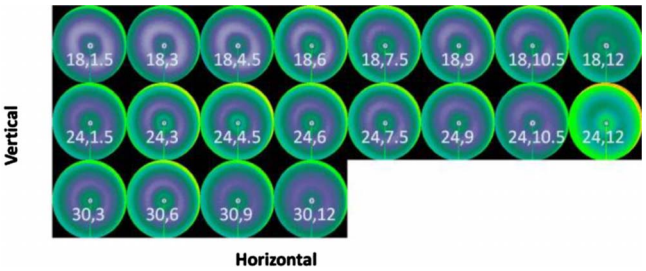

Figure 6. (Color online) The 2D SAXS patterns for the 650 MW soft segment polyurea as a function of position.

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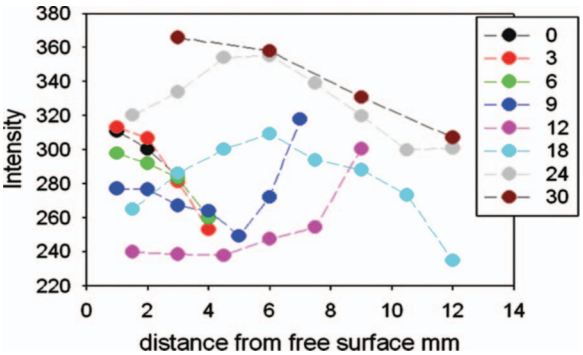

Figure 7. The SAXS meridional peak intensity values for the 650 MW soft segment polyurea. Note that the intensity at the free surface at 12 mm vertical distance begins to increase in value indicating order. This occurs sooner for the 650 MW than that of the 1000 MW soft segment polyurea upon comparison (see Figure 4).

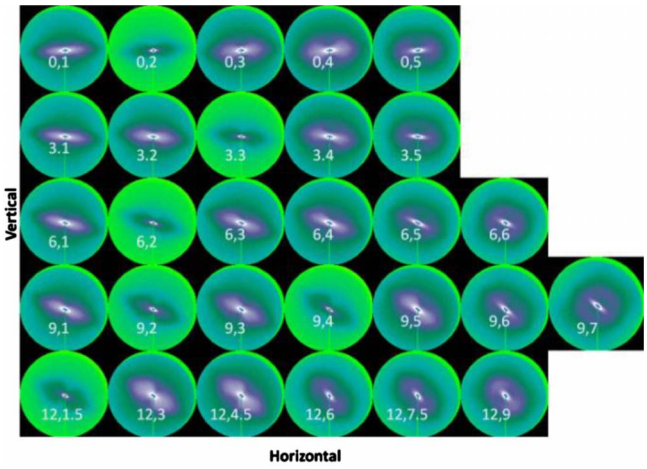

Figure 8. (Color online) The 2D SAXS patterns for the 250/1000 MW blend soft segment polyurea as a function of position.

A transformation from an elliptical pattern to a pair of meridional arcs occurs at 12 mm similar to that for the 1000 MW material. The ellipse is less eccentric than that of the 1000 MW and shows a thicker meridional pattern. In the equatorial region approaching the free surface (12 mm), the two meridional arcs overlap and the intensity is slightly lower. For all remaining SAXS intensity patterns vertically closer than 12 mm to the impact center, the patterns are meridional arcs with decreasing equatorial intensities. The arcs show less curvature than those of the 1000 MW and are distinctly broader.

R0: In the region of the impact (0–3 mm), the intensity of a pair of broadened meridional arcs is maintained with less curvature as compared to that of the 1000 MW soft segment. Superimposed is a broad vertical elliptical halo. Both are vertical in this region through the horizontal thickness (0 mm).

D. 650 MW meridional intensities

The meridional peak intensities from the profiles are shown in Figure 7. The intensity profiles appear to show a trend about the midpoint thickness of 6 mm. For our discussion, we consider the half space between the midpoint at 6 mm and the free surface. In the top of region R1 (24 and 18 mm) in the half space to the free surface, there is a decrease in intensity indicating lack of coherence—a breaking of the hard domains. At the transition line of 12 mm, there is a drop to a lower asymptotic intensity value. This is also found for the 1000 MW material except the leveling of the intensity asymptote, which we believe to be the onset of order of the reformed hard domains that occur earlier for the 650 MW material. In fact, we find that as the impact center is approached (9 and 6 mm) that the increase in intensity implies continuing improved order of the reformed hard segments. In this same area, the equatorial intensity drops fairly linearly also implying meridional orientation order. At the impact center R0 (3 and 0 mm), the highest values of the intensity occur. This is in agreement with the 1000 MW trend in R0. However the increase of intensity to the free surface from the 12 mm through all of R0 (9, 6, 3, and 0 mm) is not found for the 1000 MW polymer; for the 1000, the intensity decreases indicating order is delayed until the distance of 3 mm. We have found that this orientation of the shorter soft segment not only starts earlier but occurs over a larger area in R1 providing strain hardening and improved protection over that of the 1000 MW polymer.

E. 250/1000 MW blend 2D SAXS intensity patterns

The blend of 250 and 1000 soft segment molecular weights forms a weak phase separated system that we have shown in previous work (Balizer *et al.*, 2008). We believe for this system that the neat 250 MW polyurea is phase mixed and does not form hard domains that can be detected by SAXS. When blended it dissolves in the 1000 MW soft segments and increases the soft domains between the hard domains of the 1000 soft segments and results in a larger long period than that of just the 1000 MW polymer. Small tensile strains contribute greatly to the phase mixing of the hard domains of this blend. In our previous work the SAXS patterns (taken at Brookhaven National Laboratory) were that of a mixed system with featureless intensity patterns resulting from uniaxial strains greater than 0.5. The patterns that we report here for the bilayer with the 250/1000 blend were taken at the Argonne Advanced Photon Source that is almost three orders of magnitude more intense than that at Brookhaven and reveals patterns for the 250/1000 polyurea layer as we now describe by region. These appear in Figures 8 and 9.

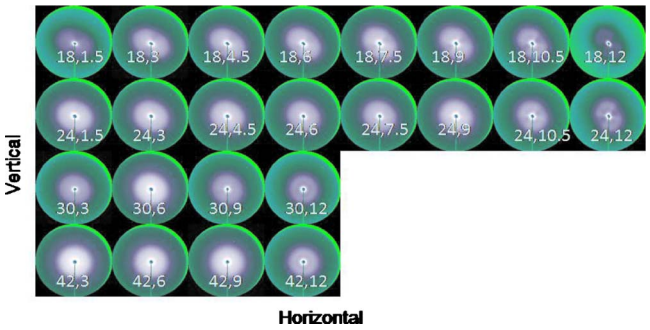

Figure 9. (Color online) The 2D SAXS patterns for the 250/1000 MW blend soft segment polyurea as a function of position.

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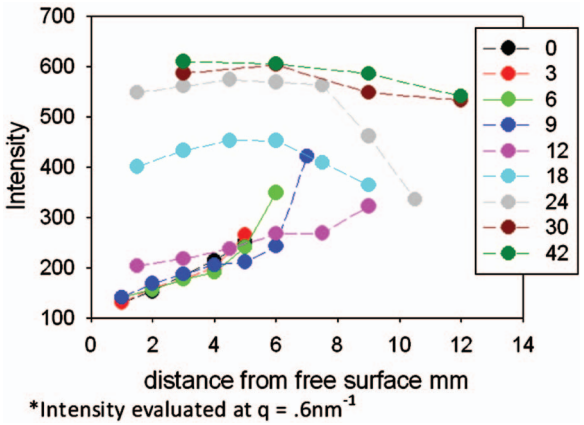

Figure 10. The SAXS meridional peak intensity values for the 250/1000 MW blend soft segment polyurea. The lower intensity in the region of the impact center is, we believe, due to increased phase mixing.

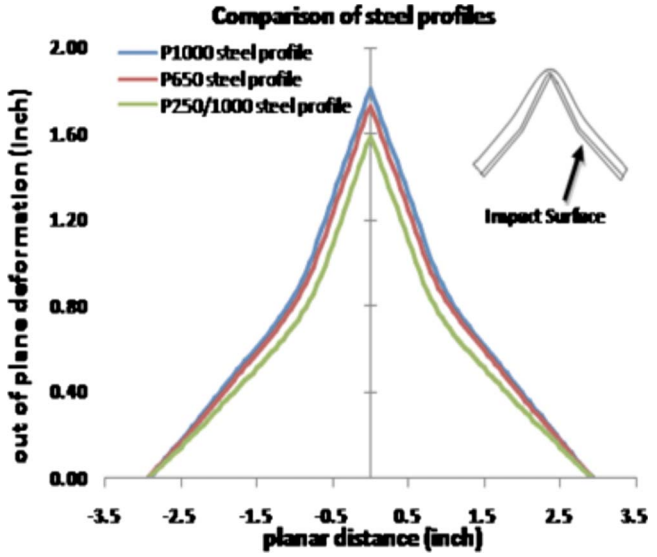

Figure 11. (Color online) The out of plane deformation of the metal and polymer layers corresponding to the 1000 MW, 650 MW, and 250/1000 MW blend conclusively showing the least damage for the lower molecular weights of the soft segment.

R2: In the pre-transformed region (42 and 30 mm), there results an isotropic circle of uniform intensity; an isolated ring does not appear. This intensity pattern occurs for all irradiated points across the width. *R1:* At the upper part of this region (24 and 18 mm), there is the formation of an ellipse that is sequentially rotated counterclockwise toward the horizontal as the free surface is approached. The uniform intensity of the ellipse develops a decrease in meridional intensity at the free surface. At the 12 mm line, the elliptical pattern is approximated by a hexagon and the intensity along the meridional decreases. The intensity pattern appears as a bowtie shape. For the 650 and 1000 MW polymers, this critical transition line (12 mm) is where there is a change from an ellipse to a pair of meridional curved arcs indicating the breaking of hard domains. These patterns, as the impact center is approached, decrease in meridional intensity and become narrower toward the free surface, indicating orientation. Here the spherical halo develops protrusions along the equatorial as the pattern narrows.

R0: These trends continue at the impact center (0 and 3 mm) where the patterns are horizontally aligned and show gradual broadening in the neighborhood of the metal interface (implying lower orientation).

F. 250/1000 MW blend meridional intensities

The shoulder that occurs at a q value of 0.6 nm^{-1} is relatively constant through the regions and we use this intensity value as a reference to substitute for the intensity peak. Using the Bragg equation, the corresponding d-spacing is 10.47 nm, which is larger than that of either the 650 (7.0 nm) or 1000 MW (7.48 nm) polyureas. This is the phase mixed 250 MW soft segment dissolved in the 1000 MW soft segment in the 250/1000 blend and separating the hard domains. The meridional intensities for the 250/1000 blend evaluated at q of 0.6 nm^{-1} are plotted as a function of distance from the free surface in Figure 10. Their trend with region is now given as follows. *R2:* The meridional intensities (42 and 30 mm) are similar through the thickness and represent the unperturbed region. *R1:* There appears to be an asymmetry of intensity about the midpoint at 6 mm that we believe is due to thickness effects. For our discussion we consider the intensity values between the free surface and the midpoint where the polymer thickness is uniform. There is a sharp drop in meridional intensity (24, 18, and 12 mm) in this region and the lowest values occur at 12 mm, the distance for which reformation is found for the other polymers. R0: The intensity continues to drop in this region (9, 6, 3, and 0 mm) and almost linearly decreases to the free surface indicating greater orientation and phase mixing as the hard domains in the meridional direction are being pulled apart due to the greater strain at the free surface.

It is interesting that the equatorial intensity increases close to the free surface in this region. It appears that as the mixing is homogeneous in the meridional direction that the equatorial direction develops density fluctuations that give a higher intensity value. The equatorial intensity profiles within 3 mm of the free surface do not show a shoulder but an intensity continuously rising towards the q value of 0.6 nm^{-1}. We do not have a model that explains the equatorial density fluctuations but it appears to be related to the meridional mixing and orientation.

G. Impacted plate geometry and correlation to polymer orientation

Figure 11 shows the measurements for the cross section of the plates impacted at 275 m/s and protected by the three polyureas. The out-of-plane deformation of the steel plate is greatest for the 1000 MW polyurea and decreases for the 650 MW material and is the least for the 250/1000 blend. For the lower molecular weight soft segments, strain hardening develops at smaller strains and therefore covers a greater area of the polyurea/steel plate for protection. These results are nicely correlated with the earlier incipience of polymer hard domain reformation for the lower molecular weight soft segment polymers. Thus the strain hardening covers a greater area of the steel/polyurea plate for protection.

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IV. CONCLUSIONS

The changes of morphology of a series of polyureas of decreasing soft segment molecular weights of 1000, 650, and 250/1000 blend used as impact resistant coatings for steel plates have been investigated by small angle X-ray scattering. The steel/polymer bilayers were taken from postmortem samples previously impacted by an ogival nose impactor (275 m/s) imparting a triaxial strain. Each of the polyureas had scattering patterns that indicated phase separated morphologies of hard and soft domains, and thus their plastic deformation on the molecular level as a function of position on the coating could be examined by SAXS. There are three regions of morphological response according to their distance from the impact center: R0 at the impact center shows oriented reformed hard domains, R1 shows the transformation from elastic stretching to the breakdown and reformation of the hard domains, and R2 the unperturbed region furthest from the impact center. At the top of R1, stretching of the soft domains begins at the free surface where the strain is not confined and is diminished by the constraint of the metal interface. There is a transition line (12 mm) that begins with stretching of the soft domains at the metal interface and evolves to the breakdown/reformation of the hard domains at the free surface. For distances closer to the impact center, increasing amounts of hard domains breakdown and reformations occur. In the neighborhood of the impact center (0–3 mm) the size or number and orientation of reformed hard domains reaches an asymptotic limit for the particular speed of the impactor used (275 m/s).

The morphology changes with decreasing soft segment molecular weights of 1000, 650, and 250/1000 blend show that the incipience of reformation and order of the hard domains occurs at a distance further from the impact center as interpreted from greater values of the SAXS intensity. As the soft segments become shorter, the yielding and reformation of the polymer begins at lower strains. Thus, a greater area of the polymer coating strain hardens and retards the necking of the metal plate. This is what is observed in the decrease in out-of-plane deformation of the metal layer with decreasing soft segment molecular weight.

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