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Impression Testing of Self-Healing Polymers

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Impression Testing of Self-Healing Polymers

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Abstract

As part of the BIOSANT program (biologically-inspired smart nanotechnology), scientists at NASA-Langley have identified a “self-healing” plastic that spontaneously closes the hole left by the passage of a bullet. To understand and generalize the phenomenon in question, the mechanical properties responsible for this ability are being explored. Low-rate impression testing was chosen to characterize post-yield material properties, and it turned out that materials that heal following ballistic puncture also show up to 80% healing of the low-rate impression. Preliminary results on the effects of temperature and rate of puncture are presented.

Introduction

After being struck and completely penetrated by a 9 mm bullet, a 6 mm-thick plate of Dupont’s Surlyn® shows only a minor dimple (and sometimes a small projection on the exit side.) The hole is said to spontaneously “self-heal” [1]. A 1996 patent [2] specifies Surlyn® 8940 for use in shooting-range targets. Although the linear viscoelastic behavior [1] and projectile impact [3] of this and some closely-related materials have been studied, healing itself is essentially instantaneous and the detailed mechanism remains in doubt. Simpler, laboratory-based tests would be of use, not only in studying the mechanism, but also in screening new, experimental materials (which might be designed to heal under different environmental conditions or possess other desirable properties such as resistance to space radiation).

The present study explores the use of a moderate-rate impression test [4] as a characterization method. In principle, a single test could give the modulus of elasticity, the strain-hardening exponent, and the strain-rate sensitivity using very small specimens. As will be shown, the results may also be linked more directly to the healing phenomenon.

Experimental

Test panels 6-10 mm thick were compression molded and stored at ambient conditions for at least one week. A small flat-ended cylindrical probe (either 1.6 or 0.8 mm diameter) was mounted to a 445 N load cell in a screw-driven mechanical test frame (Figure 1). Crosshead displacement was monitored via a calibrated displacement transducer. Room temperature was about 23 °C. For a few tests, a small chamber surrounding the probe and specimen was warmed by a regulated heat gun. A preliminary test with an embedded thermocouple showed that a 6-mm thick specimen reached a steady temperature after 10 minutes in the chamber.

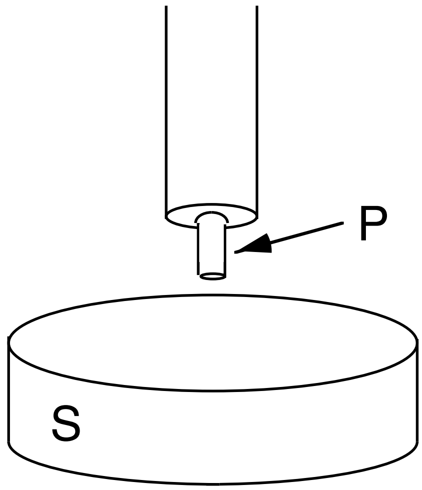


Figure 1. Sketch of impression experiment. S: specimen; P: probe.

Three crosshead speeds were chosen, and the total indentation distance was usually kept constant at 2.5 mm. After the test, the probe was promptly removed (within a few seconds) and the indent was monitored with optical microscopy. (The indentation test is not intended to be directly analogous to ballistic penetration: the probe has a higher aspect ratio than the usual projectiles, and pulling it out in the direction opposite its entry into the material may obscure some features of the original penetration. The tradeoff for these limitations is better control and additional information obtainable from this experiment.) Because the outline of the indentation could be somewhat irregular, the size of the hole was characterized by its area (as viewed from the top surface). ImageJ software (http://rsb.info.nih.gov/ij/) was used for contrast enhancement and area determination of the digital micrographs.

Results and discussion

Indentation forces

Impression tests were performed at three rates. Typical data are shown in Figure 2, which plots normalized load, P, against normalized displacement, h. Qualitatively, the curves resemble that for polypropylene in reference [4].

The stress under a flat-ended indenter, according to an elastic solution, is

$$\sigma = 4E(h/d)/(\pi(1-\nu^2)) \qquad (1)$$

where h is the indentation depth, d is the indenter diameter, E is the compressive modulus and ν is Poisson's ratio [4]. The dashed line in Figure 2 is a least-squares fit in the region of highest slope. Assuming $\nu \approx 0.4$, it would correspond to E= 217 MPa, substantially lower than the manufacturer's value E(flexural) = 350 MPa [5]. The probable reason for the discrepancy is that indentation, as implemented here, is not suited to elastic measurements. The region of very small strains where Eq. (1) would apply is obscured in the "toe" of the curve (which resulted from imperfect alignment and perhaps, to a smaller extent, instrument compliance).

The decreasing slope of the load-displacement curve reflects, in some sense, material plasticity, although at large penetration depths, the frictional force would increase linearly with the portion of the probe in contact with the polymer [6]. In metals, friction typically has a negligible effect [7]. The friction was not measured in these Surlyn tests, but it took substantial force to remove the probe after the test.

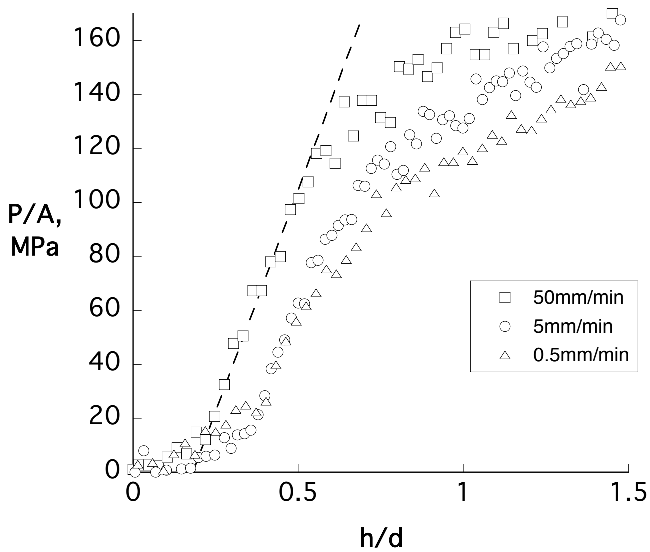


Figure 2. Impression of Surlyn® 8940 with 1.6 mm probe at 23°C. A is the probe area and d is the probe diameter. Dashed line is least-squares fit to region of highest slope.

Experiments on deep indentation of polyethylene [6] suggested that the plastic zone ahead of a cylindrical probe reached a steady state after about one probe diameter of travel. Adopting simple power law plasticity, i.e.

$$\sigma = K\varepsilon_p{}^n \tag{2}$$

the authors in [4] proposed that the strain hardening exponent n could be derived from a plot of indentation stress σ (=load/probe cross sectional area) vs. effective strain ε *(=h/d)*. Figure 3 illustrates such fits to data obtained in the present work and Table 1 summarizes the fitting parameters.

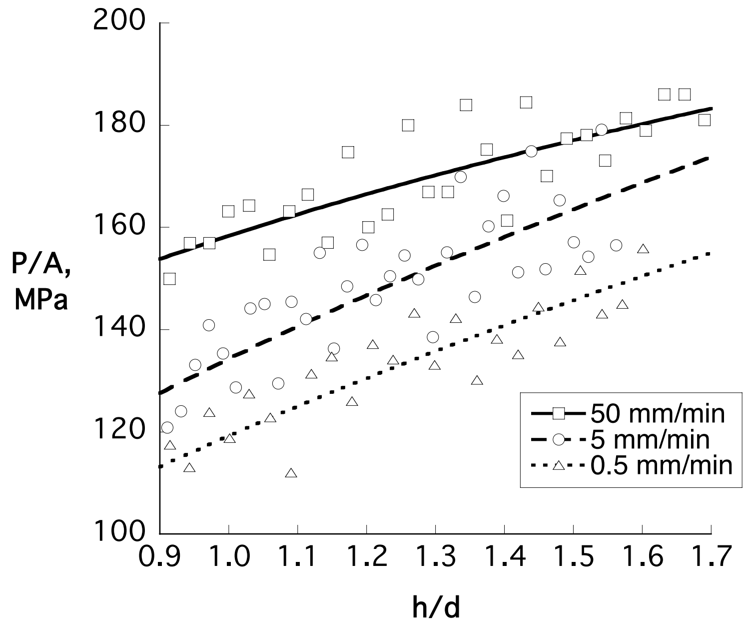


Figure 3. Impression data from Fig. 1 replotted to emphasize deep penetration. Lines: least-square fits to power law (Eq. (2)).

Table 1
Fitting Parameters for Power Law Plasticity

Crosshead speed, mm/min	*K*, MPa	*n*
0.5	119	0.49
5	134	0.49
50	158	0.28

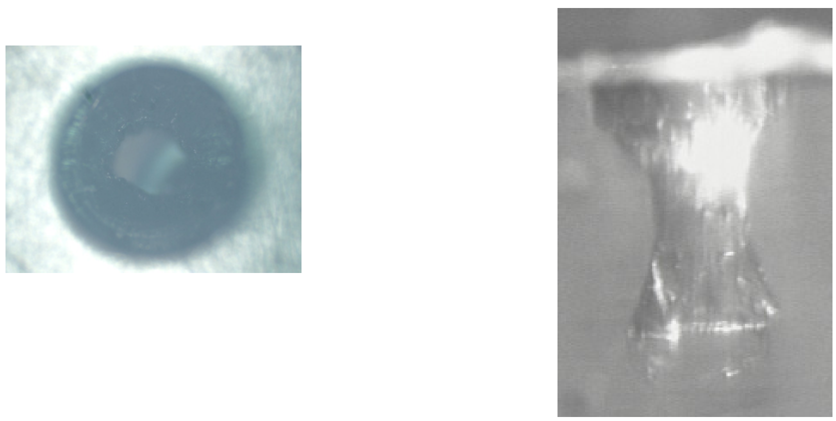
The *K* values in Table 1 (which correspond to the stress at unit strain) follow the expected trend with rate, and Appendix A discusses how these results might be extrapolated to provide information relevant to simulation of ballistic impact.

The exponent *n* derived from fits to Eq. (2) appears to be distinctly different at the highest testing speed. A temperature rise due to more-nearly adiabatic conditions at the higher rate is a possible explanation. A rudimentary heat transfer calculation in Appendix B shows that such an effect is at least plausible.

Fractography

Indentation of high density polyethylene (HDPE) gave a hole with vertical sides and a diameter almost equal to that of the probe. HDPE does not heal on ballistic impact. In contrast, for Surlyn, the hole left on the specimen surface by the impression was in all cases smaller than the probe; the probe could not be re-inserted into the hole it had just been withdrawn from.

Figure 4a is a micrograph of the hole left in Surlyn by a room temperature impression at 50 mm/min. The outer circumference of the indentation is out of focus because the camera was trained on the narrowest section of the indent (seen as the lighter grey area at the center of Figure 4a). This narrow section is located well below the surface, as may be seen more clearly in a side view photographed through the specimen edge (Figure 4b).



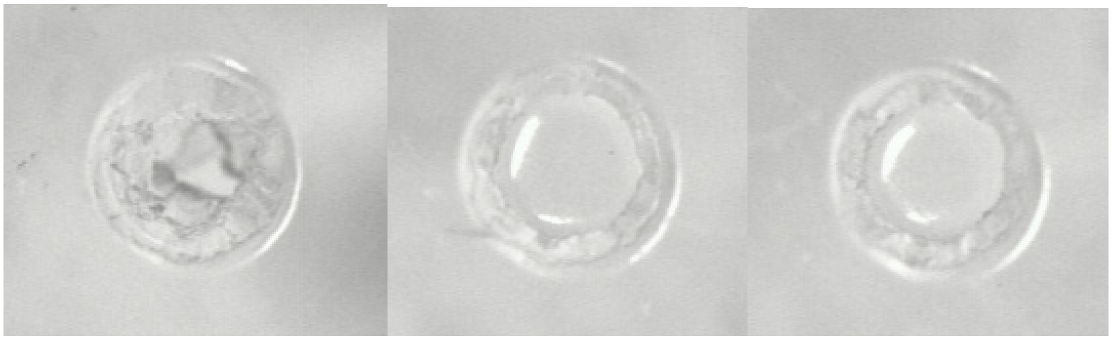
(a) (b)

Figure 4. Optical micrographs of Surlyn indents, room temperature, 50 mm/min. a. top view. b. side view taken through the transparent material.

Although there is some uncertainty about the role of the probe withdrawal in creating the hourglass shape in Figure 4b, the area of the narrow section depends on material, on impression rate, and on healing time and temperature. Consequently, that area was taken as a measure of the degree of healing.

Rate Effects

As an illustration of the rate effect, Figures 5a-c were taken 2 minutes after the indentations were created. The higher the indentation rate, the greater was the degree of healing (the smaller the hole area). Relative to the area of the probe, the holes in Figure 5 were 74, 52, and 56% healed.



(a) (b) (c)

Figure 5. Effect of impression rate on degree of hole closure. Photographed 2 min after room temperature indentation at a: 50 mm/min, b: 5 mm/min, c: 0.5 mm/min crosshead speed.

The hole diameter continued to decrease very slightly with additional recovery time (a few percent over a period of several days). If the probe was left in the material instead of being removed immediately, however, the polymer seemed to relax. Figure 6 shows an impression created by driving the probe into the material, leaving it there overnight and *then* removing it. In this case, the hole is nearly the same size as the probe, so it could be said that virtually no healing occurred.

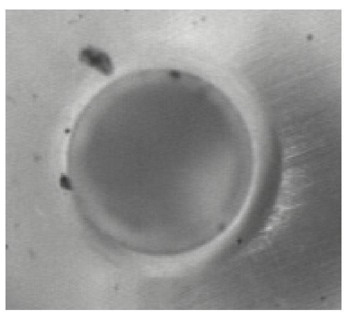


Figure 6: Surlyn indented at room temperature at 50 mm/min, probe left in material. Viewed shortly after removal of probe 16 hours later.

Temperature effect on healing

The amount of recovery (after room temperature indentation) could be increased by warming the specimen. Figure 7 displays the healing over a period of four days.

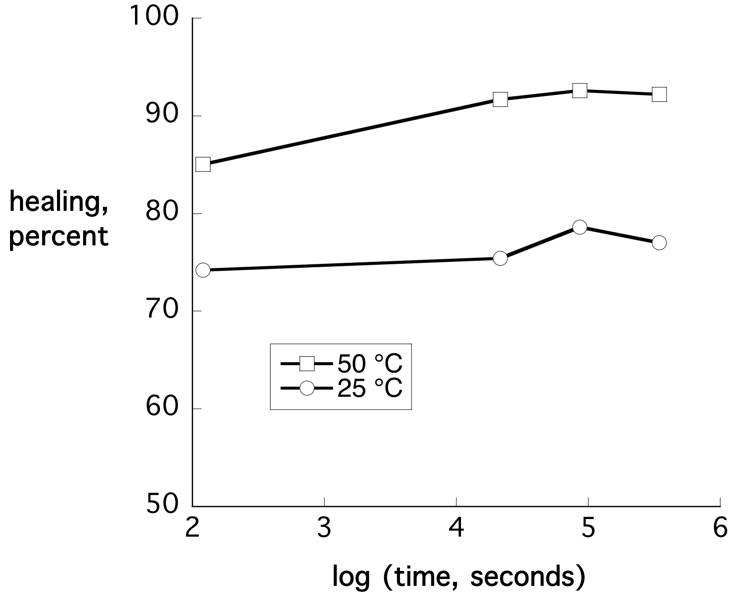
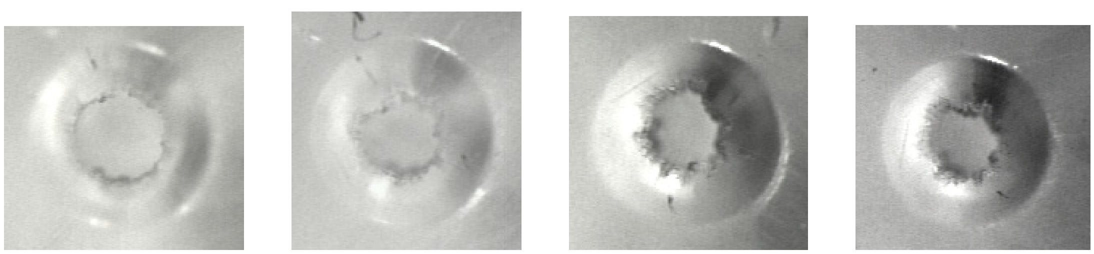


Figure 7. Degree of healing (percent hole closure) during storage at two temperatures. Impression created at 23°C.

When the samples were *indented* at elevated temperature, however, and the probe promptly removed, there was slightly *less* total healing compared to a room-temperature indent (71% vs. 74%). Figure 8 illustrates this.



2 minutes 2 hours 43 hours 91 hours

Figure 8. Specimen indented at 50°C (50mm/min) healing over time at room temperature.

It appears, therefore, that the hole closure seen in Figure 7 is related to anelastic recovery of large-strain deformation with relaxation times at room temperature ranging from less than a second to several days.

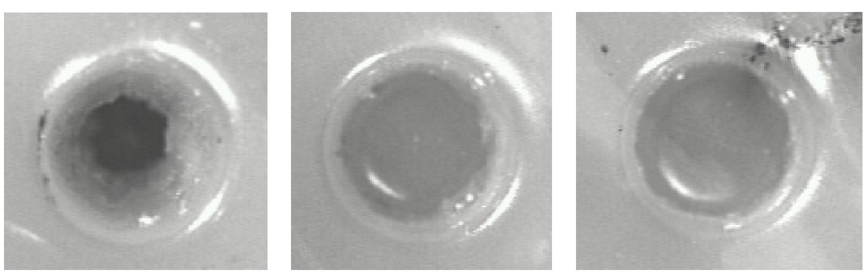
Other Polymers

As mentioned above, polyethylene did not display the hole closure effect; neither did a glassy quaternized styrene copolymer [8], which fractured. Pellethane® 2102-65D (Dow Chemical), was chosen as another thermoplastic elastomer comparable in many respects to Surlyn®. Although it is crosslinked via urethane hard segments (in contrast to Surlyn's crystallites and ion clusters), mechanical properties are similar (Table 2).

Table 2
Mechanical and Thermal Properties of Two Thermoplastic Elastomers

Polymer	Hardness (Shore D)	Vicat softening temperature, °C	Tensile elongation at break, %	reference
Surlyn 8940	65	63	470	5
Pellethane 2102-65D	65	142	390	9

Figure 9 illustrates the results of impression tests on the Pellethane elastomer. Its ability to "heal" the impression is similar to that of Surlyn®, i.e., the hole is much smaller than the probe, especially after impression at the highest rate. Based on this finding, the Pellethane was subjected to ballistic impact with a bullet from a 9mm pistol, and it was found to heal quite well in that test, too.



50 mm/min   5mm/min   0.5 mm/min

Figure 9. Pellethane 2102-65D indents viewed 2 minutes after removal of probe.

Conclusion

It was suggested in Reference 1 that the elastic character of the melt created by the puncture drives self-healing. While complete sealing of a bullet hole must involve melt flow, the picture that emerges from the laboratory testing described here is that a portion of the "self-healing" is due to recovery of anelastic strain. This recovery can be accelerated by heating, but storage of strain energy in the first place is favored by high rates and low ambient temperatures (as long as the material does not fracture).

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Appendix A

The 9mm ballistic tests in [1] occurred at projectile speeds of ~260 m/sec, corresponding to an effective strain rate, *d(h/d)/dt*, of 2.9×10^4. A simplified version of the thermal activation theory of Eyring [10] reduces to

$$d\sigma_y/d(\ln(rate)) = kT/v_s \qquad \text{(A1)}$$

where σ_y is the yield stress, v_s is a shear activation volume, T is temperature, and k is Boltzman's constant. Often this expression does not fit experimental results, in which case additional rate processes are invoked.

The authors of Reference 4 and Matsuoka [11] on the other hand, propose a power-law dependence of σ_y on rate.

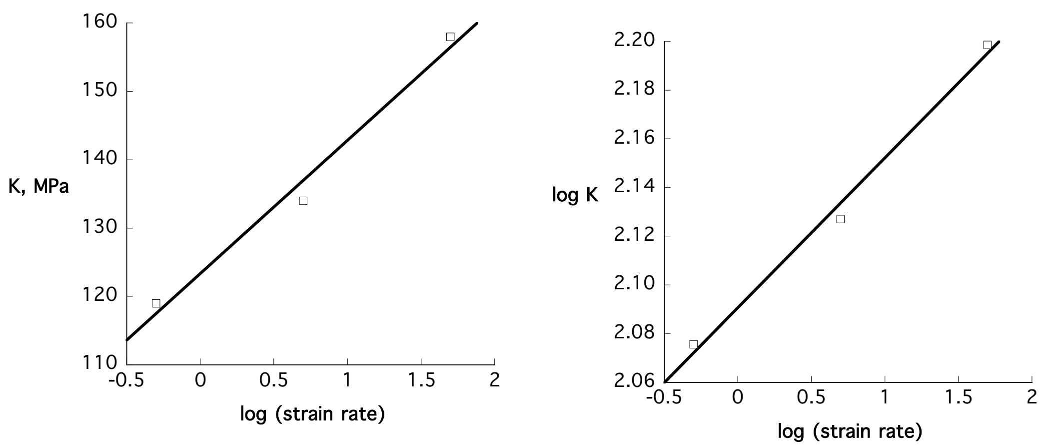

Figure A1. Strain rate effect on yield stress parameter from equation (2) plotted according to two empirical expressions

The strain-rate effect is shown in both forms in Figure A1. An extrapolation of the Eyring expression gives 210 MPa and the power law representation (with a slope of 0.062/decade) gives 232 MPa at the ballistic rate. These values, which correspond to a hypothetical isothermal experiment, could be used as a starting point in a simulation of ballistic impact (for example, using an explicit finite element approach). It is easy to show experimentally, of course, that penetration at ballistic speeds causes considerable heating. A suitable constitutive law would include the temperature dependence as well.

Appendix B

The following simplified calculation illustrates the possible heating during the impression test. Friction is neglected and it is assumed that the heating is due to plastic work. In metals, a good rule of thumb is that 90% of the plastic work is detectable as heat. For polymers, fewer studies exist, but it appears that the number is closer to 50%. When a force of P Newtons moves a probe h meters into the material, the work expended is $P \cdot h$, so the total rate of work input as heat would be roughly

$$dQ/dt=(0.5)P(dh/dt). \qquad \text{(B1)}$$

Next, assume the plastic zone is a region with the same area as the probe, and that heat leaves that zone only through the end of the metal probe. (The polymer is a thermal insulator with a thermal conductivity almost 2 orders of magnitude lower than that of steel). The transient one-dimensional heat transfer solution for conduction into a semi-infinite solid [12] gives a maximum (surface) temperature of

$$T-T_0 = 2q\sqrt{(\alpha t)}/(\kappa\sqrt{\pi}) \qquad \text{(B2)}$$

Where t is time, T is temperature, T_0 is the initial temperature, q is the heat flux, κ is the thermal conductivity, and α is the thermal diffusivity $\kappa/(\rho c)$, where ρ is density and c is the heat capacity).

To model a steady state, the heat flux is equated to the heat produced per area based on Eq. (B1). Setting $h = t(dt/dh)$ and using thermal properties of steel, Eq. (B2) gives $T-T_0 \approx 5$ K when $h = d$. This is probably enough to noticeably affect the polymer properties.

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14. ABSTRACT

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