Supporting Information

Molecular-Weight-Dependent Interplay of Brittle-to-Ductile Transition in High-Strain-Rate Cold Spray Deposition of Glassy polymers

Anuraag Gangineri Padmanaban\textsuperscript{1}, Tristan W. Bacha\textsuperscript{2}, Jeeva Muthulingam\textsuperscript{3}, Francis M. Haas\textsuperscript{3}, Joseph F. Stanzione III\textsuperscript{2}, Behrad Koohbor\textsuperscript{3}, and Jae-Hwang Lee\textsuperscript{1}*  

1. Department of Mechanical and Industrial Engineering, University of Massachusetts, Amherst, Massachusetts 01003, United States  
2. Department of Chemical Engineering, Rowan University, Glassboro, New Jersey 08028, United States  
3. Department of Mechanical Engineering, Rowan University, Glassboro, New Jersey 08028, United States

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*leejh@umass.edu

Aging characteristics of polystyrene microparticles (µPs) and substrate  
Using differential scanning calorimetry (DSC), aging characteristics of polystyrene (PS) were measured (Fig. S1). The µPs showed a slightly depressed $T_g$ when compared to the as received powder, which was expected considering the µPs were processed with ethyl acetate solvent. All samples showed some degree of aging according to the relaxation peak. After the 70 °C oven step, the samples showed slight aging from their original drying step, and an elevated $T_g$ attributed to solvent removal. The melt cast substrate showed a higher degree of aging compared to the other samples. Differences in aging were apparent between the final processed particle state (70 °C oven), and the melt cast sample. Ensuring identical thermal history and aging would require heating the particles above $T_g$ and cooling them the same as the melt cast substrate. This operation was not possible with our equipment and would result in welded agglomerations of µPs. Even without the drying steps, the processing method of the PS µPs incorporates ethyl acetate solvent (a plasticizer) that slowly diffuses from the µPs resulting in an even more complex thermal history relative to $T_g$. Even in it’s neat form, the ageing of PS was expected to be strong within the entire temperature range of 20 °C to 80 °C.\textsuperscript{11} Overall, although the aging effects were unavoidable, they
were not expected to influence the main findings in this study since each set of μPs and substrates with varying molecular weight were treated equally.

**Figure S1** First ramp DSC curves of various degrees of processing for (a) the 10 kDa powder, and b) 100 kDa powder. As received powder was analyzed in its neat form. The “initial warm bath” powder was the initial drying step. The “70 °C oven” step was after 2 weeks of drying in a 70 °C vacuum oven. The “Melt cast substrate” was melt cast as described in the manuscript.

**Characteristics of target substrates**

For polystyrene (PS) target substrate, PS powder in a mold made of glass microscope slides and Kapton tape. The mold in a vacuum oven and purged/pulled vacuum three times, using argon as a purge gas. The mold is heated to approximately 240 °C while purging the oven with argon gas. When the PS powder starts to flow readily around 200 °C, degassing is proceeded to remove air bubbles. The argon purge prevents the polystyrene from oxidizing at the high temperatures. The prepared PS substrates after cooling are used as target substrates in the microscopic collision experiments. Silicon (Si) substrates were cut to 5mm × 5mm and attached to glass substrates using transparent double-sided tape. The surface of the silicon wafer was blown with compressed air to remove any specks of dust or fragments that may have been deposited while cutting the silicon wafer. The Si wafer surface was then gently wiped with a non-abrasive wiper soaked in reagent-grade isopropanol for final cleaning.

**Surface roughness:** The surface roughness of the target substrates is quantified using a laser profilometer (Nexview™, Zygo) with 0.06 nm topographical resolution (Fig. S2). Rms values of the two substrates were 0.55 nm and 1.65 nm, respectively, across the 1 mm scan distance.
Surface roughness measurements

(Fig. S2) A surface profile of a silicon substrate. (b) A surface profile of a polystyrene substrate.

Surface chemistry: The surface chemistry of the prepared Si and PS substrates was assessed by contact angle measurements using distilled water (Fig. S3). The contact angle of the cleaned Si wafer was 55.8±1.5° which is significantly deviated from that of silicon (~81°) and is close to that of fused silica (53°). Due to a native oxide layer on a silicon wafer, the surface chemistry of the silicon wafer substrate is fused silica. The water contact angle of PS substrates was 88.7±3.3° which is also close to the known value (~87°) of PS.

(Fig. S3) Water contact angle measurements of (a) a silicon wafer substrate and (b) a polystyrene (100 kDa) substrate.

Finite Element Analysis

FE model and boundary conditions: A 3D finite element model was created to replicate the impact response of PS µPs during laser-induced projectile impact testing (LIPIT) while allowing for the extraction of local temperature fields. The model was created in ANSYS®.
Autodyn/Explicit Dynamics in a Lagrangian framework. As shown in Fig. S4, the model includes a single particle impacting a cubic substrate. The particle was modeled as a perfect sphere with a diameter of \( D_p = 40 \) µm. To be consistent with experiments and eliminate the possible effects of substrate boundaries on the deformation response of the particle, the dimensions of the cubic substrate were chosen to be 10 times the particle diameter. Based on a mesh sensitivity analysis performed in previous studies,\(^5\) the element size for both particle and substrate was considered to be 1/50\(^{\text{th}}\) of the particle diameter. Meshing system used herein included 8-node brick elements for the substrate and multizone hexahedral elements for the particle. The frictional state between the particle and the substrate was modeled using a constant coefficient of friction equal to 0.2.\(^5\) Except the top surface, all other sides of the substrate were constrained. An initial downward velocity, \( v_i \), was assigned to the particle. The rebound velocity, \( v_r \), was determined by probing the average velocity of the entire element set in the particle after the impact.

![Figure S4](image)

**Figure S4** Finite element model geometry. \( v_i \) and \( D_p \) denote particle impact velocity and diameter, respectively.

**Material constitutive model:** The Johnson-Cook plasticity model (Eq. 1) was used to describe the deformation response of PS µPs and the PS substrate\(^5\):

\[
\sigma_p = \left[ A + B \left( \varepsilon_p \right)^n \right] \left[ 1 + C \ln \left( \frac{\varepsilon_p}{\varepsilon_{p0}} \right) \right] \left[ 1 - \left( \frac{T - T_r}{T_m - T_r} \right)^m \right]
\]  

(1)

In this equation, \( \sigma_p \) is the flow stress, \( \varepsilon_p \) is the equivalent plastic strain, \( \varepsilon_p \) is the equivalent plastic strain rate, and \( \varepsilon_{p0} \) is the reference equivalent plastic strain rate. \( T_m \) and \( T_r \) are melting and reference temperature, respectively. The coefficients \( A, B, n, C, \) and \( m \) are material-dependent constants, defining the strain hardening, strain rate sensitivity, and thermal softening behavior of the material. Due to the unavailability of these parameters for PS in ultra-high rate deformation.
conditions, the model parameters were identified by a statistical data mining approach applied to a wide collection of PS stress-strain data extracted from multiple sources.\cite{6,7,8,9,10} For example, the strain rate sensitivity parameter, \( C \), was identified as the slope of the best linear fit to the yield stress-strain rate data shown in Fig. S5. Similarly, all other parameters of interest were identified and then used as input to the FE model. While not experimentally validated, the Johnson-Cook model proposed based on the identified parameters was proven practical for the analysis of temperature rise in the PS µPs.

To predict the temperature variations due to plastic deformation, the Taylor-Quinney equation (Eq. 2) was implemented.\cite{5}

\[
\Delta T = \frac{\beta}{\rho C_p} \int_0^{\varepsilon_p} \sigma (\varepsilon_p, \dot{\varepsilon}_p, T) d\varepsilon_p
\]

In this equation, \( \rho \) and \( C_p \) are the mass density and heat capacity of PS, respectively, and \( \beta \) is the Taylor-Quinney coefficient, taken to be 0.9. Numerical values for the Johnson-Cook model parameters and other properties used in FE analyses are listed in Table S1. Note that Si substrates in this work were modeled as a linear elastic material with a Young’s modulus and density of 140 GPa and 2300 kg/m\(^3\), respectively.

![Figure S5](image_url) (a) Strain rate parameter identification based on scattered data points extracted from multiple sources.\cite{6,7,8} (b) A visual representation of the PS (\( M_n = 100 \) kDa) yield stress as a function of temperature and strain rate, used as input to the FE analyses.

**Table S1** Numerical values for the Johnson-Cook model parameters and other thermophysical properties of PS used in FE simulations

| \( A \) (MPa) | \( B \) (MPa) | \( n \) | \( C \) | \( m \) | \( \varepsilon_{p0} \) (s\(^{-1}\)) | \( T_m \) (°C) | \( \rho \) (kg/m\(^3\)) | \( C_p \) (J/kg °C) |
|-------------|-------------|-------|------|-----|----------------|--------|--------|--------|
| 116.59      | 68.88       | 1     | 0.027| 0.67| 1              | 270    | 1050   | 1260   |
**FE model validation:** Results of the FE analyses were validated by comparing the coefficients of restitution (CoR = \( v_r/v_i \)) calculated from the model with those determined from LIPIT. Fig. S6 shows the variation of CoR with respect to impact velocity, \( v_i \), obtained from experiments and FE models. The agreement between the curves extracted for two different conditions, *i.e.*, PS-on-PS and PS-on-Si, validates the FE modeling results utilized herein.

![Fig. S6](image)

**Figure S6** Variation of the coefficient of restitution (CoR) with impact velocity for PS-on-PS and PS-on-Si impact, comparing LIPIT and FEA results. Data presented for PS-\( \mu \)Ps with \( M_n = 100 \) kDa.

**Plastic strain fields:** The evolution of equivalent plastic strain in PS-\( \mu \)Ps and the PS substrate for three different impact velocities is shown in Fig. S7. Contour maps in this figure clearly show larger strain values developed in the \( \mu \)P compared with the substrate. The larger strain fields in \( \mu \)Ps are due to the dominant effect of shear strain. The smaller inelastic strains in the PS substrate are attributed to a larger recoiling response compared with that of the particle, as discussed in the main text.

![Fig. S7](image)

**Figure S7** Distribution of equivalent plastic strain in the \( \mu \)Ps and PS substrates for impact velocities of (a) 200, (b) 400, and (c) 600 m/s. Contour maps are extracted at the time instant when the velocities of center-of-mass of \( \mu \)Ps is zero. The \( \mu \)P/substrate interface is marked by dashed white lines.
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