Competing Fracture in Kinetically Controlled Transfer Printing

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Transfer printing by kinetically switchable adhesion to an elastomeric stamp shows promise as a powerful micromanufacturing method to pickup microstructures and microdevices from the donor substrate and to print them to the receiving substrate. This can be viewed as the competing fracture of two interfaces. This paper examines the mechanics of competing fracture in a model transfer printing system composed of three laminates: an elastic substrate, an elastic thin film, and a viscoelastic member (stamp). As the system is peeled apart, either the interface between the substrate and thin film fails or the interface between the thin film and the stamp fails. The speed-dependent nature of the film/stamp interface leads to the prediction of a critical separation velocity above which separation occurs between the film and the substrate (i.e., pickup) and below which separation occurs between the film and the stamp (i.e., printing). Experiments verify this prediction using films of gold adhered to glass, and the theoretical treatment extends to consider the competing fracture as it applies to discrete micro-objects. Temperature plays an important role in kinetically controlled transfer printing with its influences, making it advantageous to pickup printable objects at the reduced temperatures and to print them at the elevated ones.

1. Introduction

Large-scale integration of discrete micro/nanoscale components with well-controlled organization onto arbitrary substrates represents a general challenge for the development of useful, unconventional systems. Certain processing routes to macroelectronic systems, for example, rely on the fabrication of transistors and other devices on semiconductor wafers, removal of the devices from the wafers, and assembly of the devices on large-area, low-cost, and/or flexible substrates.¹⁻⁷ These routes require the ability to direct the placement of devices or components that are too small, too fragile, and too numerous to economically handle by conventional pick-and-place technologies. Possible solutions therefore include self-assembly⁸ and new approaches based on adhesion to elastomeric stamps.^{2,4,9} In these so-called "stick-and-place" approaches, loosely bound devices are retrieved from a donor substrate onto a stamp, and the devices are transfer printed onto another substrate (receiving substrate). The transfer

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- Northwestern University.
- (1) Ahn, J. H.; Kim, H. S.; Lee, K. J.; Jeon, S.; Kang, S. J.; Sun, Y. G.; Nuzzo, R. G.; Rogers, J. A. Science 2006, 314, 1754-1757.
- (2) Mack, S.; Meitl, M. A.; Baca, A. J.; Zhu, Z. T.; Rogers, J. A. Appl. Phys. Lett. 2006, 88 (21), 213101
- (3) Menard, E.; Lee, K. J.; Khang, D. Y.; Nuzzo, R. G.; Rogers, J. A. Appl. Phys. Lett. 2004, 84 (26), 5398-5400.
- (4) Menard, E.; Nuzzo, R. G.; Rogers, J. A. Appl. Phys. Lett. 2005, 86 (9), 093507.
- (5) Sun, Y. G.; Menard, E.; Rogers, J. A.; Kim, H. S.; Kim, S.; Chen, G.; Adesida, I.; Dettmer, R.; Cortez, R.; Tewksbury, A. Appl. Phys. Lett. 2006, 88 (18), 183509.
- (6) Zhu, Z. T.; Menard, E.; Hurley, K.; Nuzzo, R. G.; Rogers, J. A. Appl. Phys. *Lett.* **2005**, *86* (13), 133507. (7) Yuan, H. C.; Ma, Z. Q.; Roberts, M. M.; Savage, D. E.; Lagally, M. G.
- J. Appl. Phys. 2006, 100 (1), 013708.
- (8) Stauth, S. A.; Parviz, B. A. Proc. Natl. Acad. Sci. U.S.A. 2006, 103 (38), 13922 - 13927
 - (9) Sun, Y. G.; Rogers, J. A. Nano Lett. 2004, 4 (10), 1953-1959.

of devices from the stamp onto the receiving substrate may be governed by the use of glues^{4,7} or adhesion cascades.¹⁰ Recent work¹¹ showed that the strongly rate-dependent strength of adhesion to elastomers may form the basis of a kinetically controlled transfer printing approach. Figure 1 outlines the transfer printing process. A soft poly(dimethylsiloxane) (PDMS) elastomeric stamp is applied to small solid objects/microdevices on a donor substrate, leading to conformal contact, driven by van der Waals interactions.¹²⁻¹⁴ The adhesion between the solid objects and the stamp is sensitive to the rate at which the stamp separates from the donor. If the stamp is peeled away from the donor substrate with sufficiently high peel velocity, the adhesion is strong enough to lift the solid objects from the donor onto the surface of the stamp. The stamp is then brought into contact with a receiving substrate and removed with a lower peel velocity, producing a relatively weak adhesion to the stamps. This allows the objects to adhere preferentially to the device substrate and separate from the stamp, that is, "printing" the solid objects.

The pickup at the high peel velocity and printing at the low peel velocity suggest that there must be a critical peel velocity for each stamp/ink/substrate system that separates the pickup and printing regimes and determines the direction of transfer. This paper focuses on the fundamental understanding of kinetically controlled printing and the determination of the critical velocity for transfer printing. It also presents the important rateand temperature-dependent peel data for the most widely used elastomer material (i.e., PDMS from Dow Corning) for printing and soft lithography in the research communities. The paper is

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⁽¹⁰⁾ Kraus, T.; Malaquin, L.; Delamarche, E.; Schmid, H.; Spencer, N. D.; Wolf, H. Adv. Mater. 2005, 17 (20), 2438-2442.

 ⁽¹¹⁾ Meitl, M. A.; Zhu, Z. T.; Kumar, V.; Lee, K. J.; Feng, X.; Huang, Y. Y.;
 Adesida, I.; Nuzzo, R. G.; Rogers, J. A. Nat. Mater. 2006, 5 (1), 33–38.
 (12) Huang, Y.; Zhou, W. X.; Hsia, K. J.; Menard, E.; Park, J. U.; Rogers, J. A.; Alleyne, A. G. Langmuir 2005, 21 (17), 8058–8068.

 ⁽¹³⁾ Hsia, K. J.; Huang, Y.; Menard, E.; Park, J. U.; Zhou, W.; Rogers, J.;
 Fulton, J. M. Appl. Phys. Lett. 2005, 86 (15), 154106.
 (14) Zhou, W.; Huang, Y.; Menard, E.; Aluru, N. R.; Rogers, J. A.; Alleyne,
 A. G. Appl. Phys. Lett. 2005, 87 (25), 251925.



Figure 1. Schematic illustration of the generic process flow for transfer printing solid objects.



Figure 2. Schematic diagram of the peel test.

outlined as follows. Section 2 establishes the basic theory that gives the critical velocity in terms of material properties of transfer-printed systems. Experimental measurements of the critical velocity are described in section 3. Section 4 focuses on the application of the present theory to the kinetically controlled transfer printing of discrete microdevices. Section 5 discusses the temperature dependence of the critical velocity.

2. Basic Theory for Kinetically Controlled Transfer Printing

Figure 2 shows a schematic diagram of a stamp on a substrate subjected to a peel force *F* normal to the stamp/substrate interface. The stamp is peeled away from the substrate at a steady-state speed v, which is similar to the steady-state propagation of a crack at the same velocity. The energy release rate *G* for steady-state crack propagation is related to the peel force by^{15–20}

$$G = \frac{F}{w} \tag{2.1}$$

where *w* is the width (in the out-of-plane direction). The parameter *G*, here, accounts for both the energy of interfacial bond breaking and viscoelastic dissipation around the crack tip. The crack propagates steadily once *G* reaches the critical energy release rate based on the Griffith criterion in fracture mechanics.²¹

The pickup and printing shown in Figure 1 can be modeled as two competing fracture paths that may have different critical energy release rates. Figure 3shows schematic diagrams of the pickup and printing of a thin film from and to the substrate, respectively. The pickup is represented by the peeling away of the thin film from the substrate (Figure 3a), while the printing is modeled by the peeling away of the stamp only,that is, leaving the thin film on the substrate (Figure 3b). For simplicity, we consider a continuous thin film in this section and account for the pickup and printing of discrete objects (e.g., Figure 1) in section 4.

The thin film and substrate are both elastic, while the stamp is viscoelastic. The critical energy release rate for the film/substrate interface is denoted by $G_{\text{crit}}^{\text{film/substrate}}$, which is considered as a material property of the interface and is independent of the peeling velocity v since the film and substrate are elastic. (For a bimaterial interface, the critical energy release rate may also depend on the crack tip mode mixity. The mode mixity, however, remains unchanged during steady-state propagation.) The critical energy release rate $G_{\text{crit}}^{\text{stamp/film}}$ for the stamp/film interface, however, depends on the peeling velocity

$$G_{\rm crit}^{\rm stamp/film} = G_{\rm crit}^{\rm stamp/film}(v)$$
 (2.2)

This is a monotonically increasing function because the energy dissipation in the viscoelastic stamp increases with the peeling velocity. An example of this function is the power law^{22-26}

$$G_{\rm crit}^{\rm stamp/film}(v) = G_0 \left[1 + \left(\frac{v}{v_0}\right)^n \right]$$
(2.2a)

where G_0 is the critical energy release rate as indicated by a peeling velocity v approaching zero, v_0 is the reference peeling velocity at which the critical energy release rate doubles to G_0 , and the exponent n is a scaling parameter that can be determined from the experiments. The power law relation (eq 2.2a) has been shown to hold for either low or high peel velocity,^{15,16,23,24} for a wide range of temperatures,^{15,23} and for both metal/polymer and polymer/polymer interfaces.^{23–26} The peel velocity in the experiments to be described in the next section is less than 50 cm/s, which falls into the low peel velocity range. It is important to point out that the present theory is applicable for the general velocity-dependent critical energy release rate in eq 2.2 and is not limited to the power law in eq 2.2a.

The pickup of a thin film (Figure 3a) occurs when the energy release rate in eq 2.1 reaches $G_{\rm crit}^{\rm film/substrate}$ for the film/substrate interface first, which gives the critical peel force for pickup as

$$F_{\rm pickup} = wG_{\rm crit}^{\rm film/substrate}$$
(2.3)

- (19) Kim, K. S.; Kim, J. J. Eng. Mater. Technol. 1988, 110 (3), 266–273.
 (20) Kim, K. S.; Aravas, N. Int. J. Solids Struct. 1988, 24 (4), 417–435.
- (21) Anderson, T. L. Fracture Mechanics: Fundamentals and Applications.
- 2nd ed.; CRC Press: Boca Raton, FL, 1995.
 - (22) Tsai, K. H.; Kim, K. S. Int. J. Solids Struct. 1993, 30 (13), 1789–1806.
 (23) Gent, A.; Schultz, J. J. Adhes. 1972, 3, 281–294.
- (24) Maugis, D.; Barquins, M. J. Phys. D.: Appl. Phys. 1978, 11, 1989-2023.

⁽¹⁵⁾ Gent, A. N. Langmuir 1996, 12 (19), 4492-4496.

⁽¹⁶⁾ Gent, A. N.; Lai, S. M.; Gent, A. N.; Lai, S.-M. J. Polym. Sci., Part B: Polym. Phys. 1994, 32 (8), 1543-1555.

⁽¹⁷⁾ Kendall, K. Science 1994, 263 (5154), 1720-1725.

⁽¹⁸⁾ Brown, H. R. Annu. Rev. Mater. Sci. 1991, 21, 463-489.



Figure 3. Schematic diagrams of the pickup (a) and printing (b) of a thin film.



Figure 4. Schematic diagram of critical energy release rates for the film/substrate interface and for the stamp/film interface. The intersection of the horizontal line in the middle with the curve represents the critical peel velocity for the kinetically controlled transfer printing. The horizontal lines at the bottom and top represent very weak and very strong film/substrate interfaces, respectively, corresponding to pickup only and printing only.

Similarly, the printing of the thin film (Figure 3b) occurs when the energy release rate reaches $G_{\rm crit}^{\rm stamp/film}(v)$ for the stamp/film interface first, defining the critical peel force for printing as

$$F_{\rm printing} = w G_{\rm crit}^{\rm stamp/film}(v) \tag{2.4}$$

a parameter that depends explicitly on the peel velocity v.

The criterion for pickup and printing is obtained by comparing their corresponding critical peel forces, that is, $F_{\text{pickup}} < F_{\text{printing}}$ or equivalently

$$G_{\text{crit}}^{\text{film/substrate}} \le G_{\text{crit}}^{\text{stamp/film}}(v) \quad \text{for pickup}$$
 (2.5)

of the thin film and $F_{\text{pickup}} > F_{\text{printing}}$ or equivalently

$$G_{\rm crit}^{\rm film/substrate} > G_{\rm crit}^{\rm stamp/film}(v)$$
 for printing (2.6)

Figure 4 shows a schematic diagram of critical energy release rates $G_{\rm crit}^{\rm film/substrate}$ and $G_{\rm crit}^{\rm stamp/film}(v)$ versus the peel velocity v, where $G_{\rm crit}^{\rm film/substrate}$ corresponds to a horizontal line (the hori-

zontal line around the middle of Figure 4) since it is independent of v, while $G_{\text{crit}}^{\text{stamp/film}}(v)$ is a monotonically increasing function of v. There exists a critical velocity v_c at which the two critical energy release rates are equal,

$$G_{\rm crit}^{\rm film/substrate} = G_{\rm crit}^{\rm stamp/film}(v_{\rm c})$$
 (2.7)

For a peel velocity $v > v_c$, $G_{crit}^{film/substrate}$ is less than $G_{crit}^{stamp/film}(v)$ such that the film is peeled away from the substrate (i.e., pickup). For $v < v_c$, $G_{crit}^{film/substrate}$ is larger than $G_{crit}^{stamp/film}(v)$ such that the film remains on the substrate (i.e., printing). It follows from the above that the critical velocity, v_c , which governs the pickup and printing in the kinetically controlled transfer printing, is completely determined by the energy release rates for the film/substrate and stamp/film interfaces. For the example of the power law relation of $G_{crit}^{stamp/film}(v)$ in eq 2.2a, the critical velocity is

$$v_c = v_0 \left(\frac{G_{\text{crit}}^{\text{film/substrate}} - G_0}{G_0} \right)^{1/n}$$
(2.7a)

For the limit of a very weak film/substrate interface (the horizontal line at the bottom of Figure 4) such that $G_{\rm crit}^{\rm film/substrate}$ $< G_0$, the film is always peeled off regardless of the peel velocity and therefore cannot be printed on the substrate (Figure 4). For the other limit of a very strong film/substrate interface (the horizontal line at the top of Figure 4) such that $G_{\text{crit}}^{\text{film/substrate}} >$ $G_{\rm crit}^{\rm stamp/film}(v_{\rm max})$ (where $v_{\rm max}$ is the maximum peeling velocity that can be achieved in the experiment), the film is never peeled off and therefore cannot be "picked up" (Figure 4). For these limits, transfer printing cannot be kinetically controlled. The kinetically controlled transfer printing method used in this configuration thus requires a film/substrate combination with a critical energy release rate, $G_{\text{crit}}^{\text{film/substate}}$, that lies within the experimentally realizable range of $G_{\text{crit}}^{\text{stamp/film}}(v)$. In this (planar) configuration in which the nature of the interfaces is uniform throughout, such intermediate values of $G_{\rm crit}^{\rm film/substrate}$ may arise from carefully controlled interfacial chemistries. Interfacial chemistries that are very strong (e.g., uniformly covalently bound interfaces) or very weak relative to the range of $G_{\text{crit}}^{\text{stamp/film}}(v)$ will not exhibit an experimentally realizable v_c . In practice, ^{2,4,9,11} the use of different, nonplanar configurations and different substrates for pickup and printing expands the range of materials systems to which the kinetically controlled transfer printing strategy applies. In some implementations, for example, carefully designed geometries aid the pickup process by controlling fracture,²⁷ and adhesive layers on the receiving substrate aid the printing process.^{4,9} In each of these cases, the reliability of the printing approach depends on control of the rates. Materials systems having the stacked-planar configuration studied in this paper give valuable insights into the rate-dependent nature of the printing process.

3. Experimental Section

We performed peel tests of a poly(dimethylsiloxane) (PDMS) elastomer stamp on a Au film deposited on a glass substrate subjected to several modifications. Each is described below.

Stamps. PDMS elastomer (Sylgard 184, Dow Corning) was cast between two flat polycarbonate plates (1 mm apart) and cured for 24 h at 60 °C. Stamps (1×7.62 cm²) were cut from the sheet, rinsed with IPA for 30 s, and dried under a stream of nitrogen for 1 min.

Sample Preparation/Surface Treatment. Glass slides (Fisher Scientific) were cleaned in a Pirahna solution (1:1 H₂SO₄/H₂O₂ 30%) for 5 min, rinsed thoroughly with deionized (Milli-Q) water, and

⁽²⁵⁾ Barthel, E.; Roux, S. Langmuir 2000, 16, 8134-8138.

⁽²⁶⁾ Barquins, M.; Ciccotti, M. Int. J. Adhes. Adhes. 1997, 17, 65-68.

⁽²⁷⁾ Meitl, M. A.; Feng, X.; Dong, J. Y.; Menard, E.; Ferreria, P.; Huang, Y.; Rogers, J. A. *Appl. Phys. Lett.* **2007**, *90* (8), 083110-1



Figure 5. Critical energy release rate versus peel velocity for the PDMS stamp/Au film/glass substrate. Three different surface treatments (Ti, HMDS, and FOCTS) are selected for the thin film/ substrate interface.

dried under a stream of nitrogen before surface treatment and the deposition of Au thin films. Three different surface treatments were selected to examine variable strengths of adhesion between the glass slides and the Au thin films. The first treatment produced a perfluorinated self-assembled monolayer on the glass surface via exposure to (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (FOTCS) vapor.^{11,28} To effect this treatment, the glass slides and a vial of FOTCS liquid were placed together in an evacuated vacuum desiccator for 1 h, removed, and loaded into a Temescal electron beam evaporator for the deposition of 100 nm of Au. Other cleaned glass slides were treated with hexamethyldisilazane (HMDS) by exposing the slides to HMDS vapor in a bell jar for 5 min before deposition of 100 nm of Au (as described above). The third set of slides were coated with 1 nm of Ti prior to the 100 nm Au deposition, both by electron beam evaporation. The three surface treatments (FOTCS, HMDS, and Ti) gave different levels of adhesion between the Au films and the glass slides.

Peel Test and Separation Velocity Measurement. Clean PDMS stamps were laminated onto the gold coated side of a substrate and left in conformal contact with the surface for 3 min. Inverting the stamp/slide (stamp side down) and attaching weights to one end of the stamp initiated peeling of the PDMS stamp from the slide. Video recordings of each peel event were used to measure the separation speed.

Figure 5 shows our measured critical energy release rate versus the steady-state peel velocity, v, for a PDMS stamp on a Au film supported on a glass substrate. In these experiments, the stamps were laminated against the Au films on glass, peeled by the application of a series of constant loads, the speed of separation was measured, and the separation interface (stamp/film versus film/substrate) was noted. The thicknesses of the PDMS stamp, Au film and, glass substrate were 1 mm, 100 nm and 1 mm, respectively. Three different surface treatments were selected, and they are denoted as Ti, HMDS, and FOTCS, corresponding to the strong, intermediate, and weak film/substrate interfaces, respectively. All of the experimental data presented in Figure 5 (with the exception of the last two on the right) correspond to the printing regime (i.e., peeling the stamp away from the film) and therefore give $G_{crit}^{stamp/film}(v)$. This relation can be fitted by the equation

$$G_{\rm crit}^{\rm stamp/film}(\nu) = 2.16 \left[1 + \left(\frac{\nu}{1.55 \text{ cm} \cdot \text{s}^{-1}} \right)^{0.65} \right] \text{J} \cdot \text{m}^{-2} \qquad (3.1)$$

as shown by the solid curve in Figure 5. The two data points on the right correspond to the pickup (i.e., high-speed peeling of the film away from the substrate) for the intermediate (HDMS) and very weak (FOCTS) interfaces. For the intermediate (HMDS) interface, the critical velocity is about 15 cm/s, and the corresponding value

of $G_{\rm crit}^{\rm film/substrate}$ is about 12 J/m² (corresponding to the horizontal line around the middle of Figure 4). For the very weak (FOTCS) interface, the film is always peeled away, and $G_{\rm crit}^{\rm film/substrate}$ is less than 4 J/m² (corresponding to the horizontal line at the bottom of Figure 4). For the very strong (Ti) interface, the film is never peeled away, and $G_{\rm crit}^{\rm film/substrate}$ is greater than 18 J/m² (corresponding to the horizontal line at the top of Figure 4).

4. Kinetically Controlled Transfer Printing of Discrete Microstructures

We turn from the consideration of the mechanics involving a continuous thin film to the adhesion-based transfer of microstructures as discrete solid objects, as shown schematically in Figure 1. The kinetic control of this form of transfer printing of discrete solid objects is discussed in this section. We begin with the adaptation of the general model along lines specific to this case.

For discrete microstructures, the local energy release rate between the stamp and the microstructures, $G^{\text{stamp/microstructure}}$, and that between the microstructures and the substrate, $G^{\text{microstructure/substrate}}$, depend on the microstructure size, shape, spacing, and distribution. For the pickup of microstructures, the energy release during pickup is composed of two parts:

(i) the local energy release between microstructures and the substrate, and during the pickup the local energy release rate reaches its critical value,

$$G^{\text{microstructure/substrate}} = G^{\text{microstructure/substrate}}_{\text{crit}}$$
(4.1)

(ii) the local energy release between the stamp and substrate, and during the pickup the local energy release rate reaches its critical value,

$$G^{\text{stamp/substrate}} = G^{\text{stamp/substrate}}_{\text{crit}}(v) \tag{4.2}$$

(Strictly speaking, the critical energy release rate may depend on the crack tip mode mixity for a bimaterial interface, and the mode mixity may not be a constant for discrete microstructures even for the steady-state propagation. This dependence, however, is not accounted for in the present study.) Let f(0 < f < 1) denote the area fraction of microstructures on the substrate, with f = 1being the limit of a continuous thin film. For the pickup of microstructures from the substrate over the area ΔA that is much larger than the area of each microstructure, ΔA contains $f\Delta A$ microstructure/substrate interface area and $(1 - f)\Delta A$ stamp/ substrate interface area. The energy release is $\int_{f\Delta A} G^{\text{microstructure/substrate}}$ and $G^{\text{stamp/substrate}}$ depend on the microstructure size, shape, spacing, and distribution.

For steady-state pickup, the average energy release rate G^{average} is the energy release over the pickup area ΔA , that is, $G^{\text{average}}\Delta A = \int_{f\Delta A} G^{\text{microstruture/substrate}} dA + \int_{(1-f)\Delta A} G^{\text{stamp/substrate}}(v) dA$. From the energy balance, it also equals the external work done by the peel force, which is approximately $(F/w)\Delta A$. (For a thin film with constant thickness, the external work done by the peel force is $(F/w)\Delta A$. For non-constant thickness (e.g., discrete microstructures), the external work done is approximately $(F/w)\Delta A$.) This gives $G^{\text{average}} = F/w$, which is the same as eq 2.1. On the other hand, the energy release during pickup $G^{\text{average}}\Delta A$ must also equal the energy dissipation, which is $[fG_{\text{crit}}^{\text{microstruture/substrate}}(v)]\Delta A$ from eqs 4.1 and 4.2. This gives the steady-state peel force for pickup as

$$F_{\text{pickup}} = w[fG_{\text{crit}}^{\text{microstruture/substrate}} + (1 - f)G_{\text{crit}}^{\text{stamp/substrate}}(v)] \quad (4.3)$$

⁽²⁸⁾ Xia, Y.; Whitesides, G. M. Angew. Chem., Int. Ed. 1998, 37 (5), 550–575.

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For the printing of microstructures (to the substrate), the printing area ΔA contains $f\Delta A$ stamp/microstructure and $(1 - f)\Delta A$ stamp/ substrate interface areas. The steady-state peel force for printing can be similarly found as

$$F_{\text{printing}} = w[fG_{\text{crit}}^{\text{stamp/microstructure}}(v) + (1 - f)G_{\text{crit}}^{\text{stamp/substrate}}(v)] \quad (4.4)$$

For $F_{\text{pickup}} \le F_{\text{printing}}$, pickup of the microstructures occurs, and the opposite holds for the printing of microstructures. This gives the following criteria for the pickup and printing of microstructures:

 $G_{\rm crit}^{\rm microstructure/substrate} < G_{\rm crit}^{\rm stamp/microstructure}(v)$ for pickup (4.5)

and

$$G_{\rm crit}^{\rm microstructure/substrate} > G_{\rm crit}^{\rm stamp/microstructure}(v)$$
 for printing (4.6)

The above criteria result from the comparison of the average energy release between the pickup and printing of microstructures, and it is therefore independent of the microstructure size, shape, spacing, and distribution. It is also independent of the microstructure area fraction f, and is identical to that for the continuous thin film in section 2 except that the critical energy release rate for the film/substrate interface is replaced by $G_{\rm crit}^{\rm microstructure/substrate}$ for the microstructure/substrate interface. It should be pointed out, however, that the conclusions in this section for the pickup and printing of discrete microstructures are based on the average energy release rate. For other criteria such as the local energy release rate, the pickup and printing may depend on the microstructure size, shape, spacing, distribution, and area fraction.

The steady-state critical velocity v_c , which separates the pickup and printing of microstructures, is obtained from

$$G_{\rm crit}^{\rm microstructure/substrate} = G_{\rm crit}^{\rm stamp/microstructure}(v_{\rm c}) \qquad (4.7)$$

This critical velocity depends only on the critical release rates (interface properties). The peel forces for pickup or printing in eqs 4.3 and 4.4, however, still depend on the microstructure area fraction.

5. Temperature Effect in Kinetically Controlled Transfer Printing

Temperature may play an important role in the kinetically controlled transfer printing. The well-known rate-temperature equivalence for viscoelastic processes^{15,16,29-33} gives the temperature dependence of the critical energy release rate as

$$G_{\rm crit}^{\rm stamp/film} = G_{\rm crit}^{\rm stamp/film}(va_T)$$
(5.1)

where a_T is the so-called temperature shift factor that is a universal function of temperature *T*. It has been found that this parameter is well approximated as³⁴

$$\log_{10} a_T = -17.6 \frac{T - T_g}{52 + T - T_g}$$
(5.2)

(30) Mueller, H. K.; Knauss, W. G. J. Appl. Mech. 1971, 38 (E), 483-488
(31) Mueller, H. K.; Knauss, W. G. Trans. Soc. Rheol. 1971, 15 (2), 217-233.
(32) Knauss, W. G. Advances in Fracture Research, Proceedings of the 7th International Conference on Fracture (ICF-7); Pergamon Press: New York, 1989; pp 2683-2711

(33) Schapery, R. A. Polym. Eng. Sci. 1969, 9 (4), 295-310.



Figure 6. Rate-temperature equivalence of the critical energy release rate for the stamp/film interfaces at different temperatures.



Figure 7. Critical velocity separating pickup from printing versus temperature.

for most polymers within 50 K of the glass transition temperature $T_{\rm g}$. For PDMS, $T_{\rm g}$ is around -125 °C (148 K), and thus, eq 5.2 might not be expected to hold for temperature-dependent printing processes carried out near room temperature. We therefore explicitly tested this critical process parameter, measuring the critical energy release rate between the stamp and the Au film over a variable range close to room temperature. (For this experiment, the glass substrate is coated with 5 nm of Ti and 50 nm of gold film such that the film never delaminates in this system.) Figure 6 shows measured values of $G_{\rm crit}^{\rm stamp/film}$ versus the peeling velocity v for three temperatures, T: 4 °C (277 K); 24 °C (297 K); and 37 °C (310 K). The critical energy release rate in eq 3.1 takes the form

$$G_{\text{crit}}^{\text{stamp/film}}(v) = 2.16 \left[1 + \left(\frac{a_T v}{1.81 \times 10^{-13} \text{ cm/s}} \right)^{0.65} \right] \text{J/m}^2$$
 (5.3)

which degenerates to the critical energy release rate in eq 3.1 at temperature T = 20 °C (293 K). The predicted critical energy release rate given by eq 5.3 is also shown in Figure 6, which agrees very well with the experimental data without any parameter fitting. It therefore follows that the universal function of the temperature shift factor a_T in eq 5.2 still holds at temperatures far from T_g , up to 37 °C (310 K), for PDMS.

In the following, we use eqs 5.2 and 5.3 to estimate the temperature effect. The critical velocity v_c separating the pickup and printing of thin films or microstructures can be determined from eq 2.7 by equating the above $G_{\rm crit}^{\rm stamp/film}(a_T v)$ to the critical

⁽²⁹⁾ Knauss, W. G. Int. J. Fract. Mech. 1970, 6 (1), 7-20.

⁽³⁴⁾ Williams, M. L.; Landel, R. F.; Ferry, J. D. J. Am. Chem. Soc. 1955, 77, 3701–3707.

energy release rate $G_{\text{crit}}^{\text{film/substrate}}$ (=12 J/m²) for the film/substrate interface. This gives the critical velocity

$$v_{\rm c} = \frac{1.90 \times 10^{-12} \,{\rm cm/s}}{a_T} \tag{5.4}$$

which clearly increases with the temperature as shown by the data given in Figure 7. For T = 4 °C (277 K) and 37 °C (310 K), the critical velocity v_c is 6.64 and 40.0 cm/s, respectively. This demonstrates that, for kinetically controlled transfer printing, it is advantageous to pickup a microstructure at a lower temperature and to print it at an elevated one.

6. Concluding Remarks

The mechanics that govern kinetically controlled transfer printing are described by competing fracture between two interfaces: the interface between the stamp and the ink (i.e., microstructure) and the interface between the ink and the substrate. In the work presented, the stamp/ink interface is modeled with a speed-dependent critical energy release rate, or interface toughness, which increases with speed due to the viscoelastic nature of PDMS. Conversely, the ink/substrate interface (elastic) is given a speed-independent critical energy release rate. This treatment predicts a critical speed above which the stamp/ink interface is stronger than the ink/substrate interface and below which the opposite is true. Experimental results confirm that for Au films adhered to glass slides there exists such a critical speed. The treatment predicts similar governing mechanics for both uniform thin films of ink as well as inks composed of discrete micro-objects.

Temperature plays an important role in the dynamics of kinetically controlled transfer printing. In practical terms, it is advantageous to pickup objects at a lower temperature and print them at an elevated one.

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