AN INTEGRATED CRACK-OPENING METHOD FOR DETERMINING THE WORK OF FRACTURE OF BONDED POLYMER INTERFACES

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This is a simple, non-destructive test of bond toughness that can be used for process development and monitoring. It can be applied to any bonding process that does not introduce major plastic deformation of microstructures at the interface – including plasma- or UV/ozone-activated bonding.

The test method:

Form micro-steps

in one of the layers to be bonded

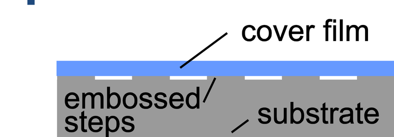
- Steps of the required ~1 µm depth can be formed by micro-casting, hot-embossing injection-molding *etc*
- In this work the steps are hot-embossed.

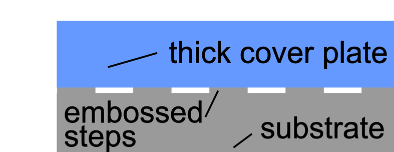
Pre-treat surfaces

- A variety of plasma and chemical treatments have been used to modify polymer surfaces in preparation for bonding [1–3].
- In thermoplastics, the glass-transition temperature of a thin surface layer may be lowered by chain scission during plasma treatment [1].

Bring cover + substrate into contact

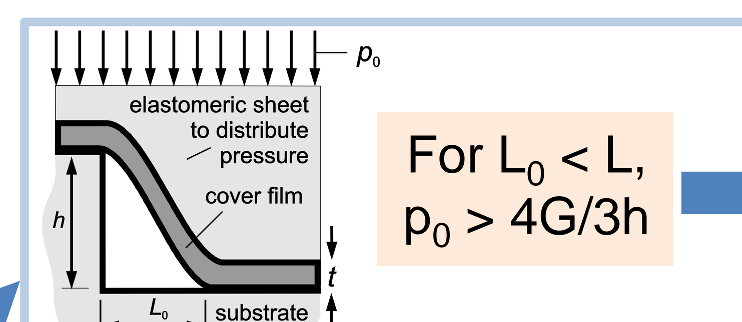
Thin cover; plate-like bending



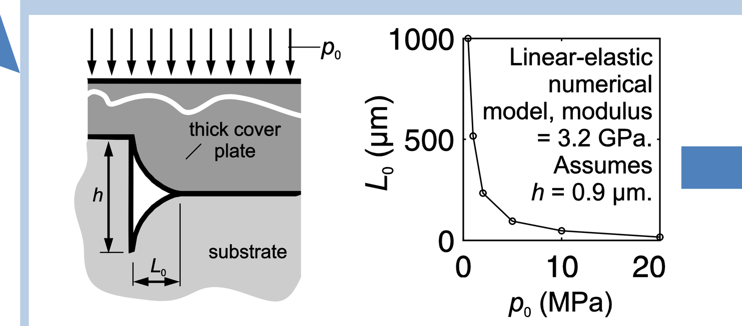


Thick cover; local deformation

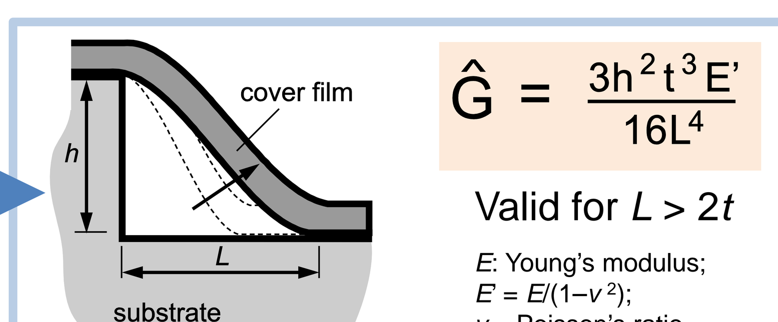
Bond



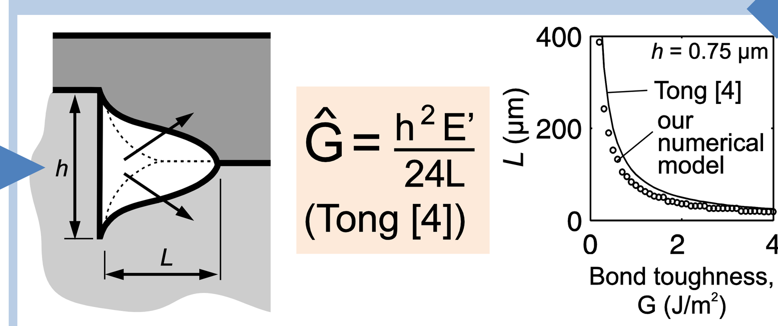
- Apply high enough pressure to close the interfacial gap so that $L_0 < L$.
- Possibly bond at elevated temperature, but below softening temperature of layers



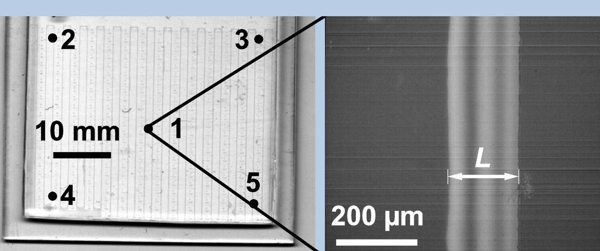
Unload



- Interface peels back from step
- 'Equilibrium' crack length, L, depends on stiffness of material, geometry of step, and interfacial work of fracture

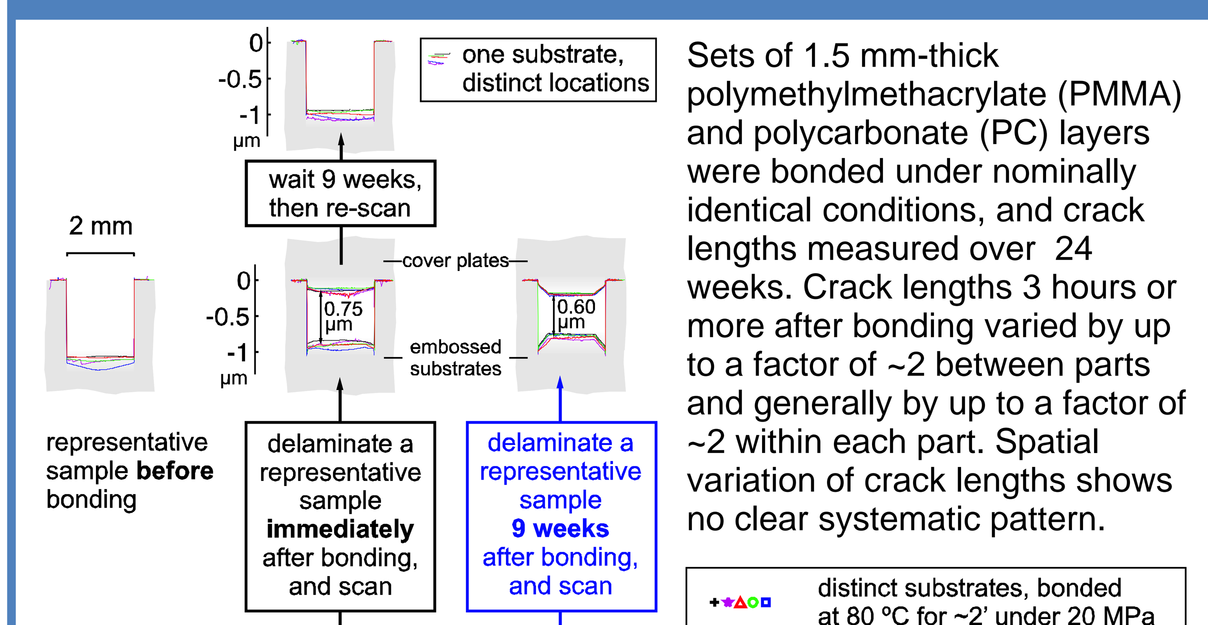


Measure crack lengths

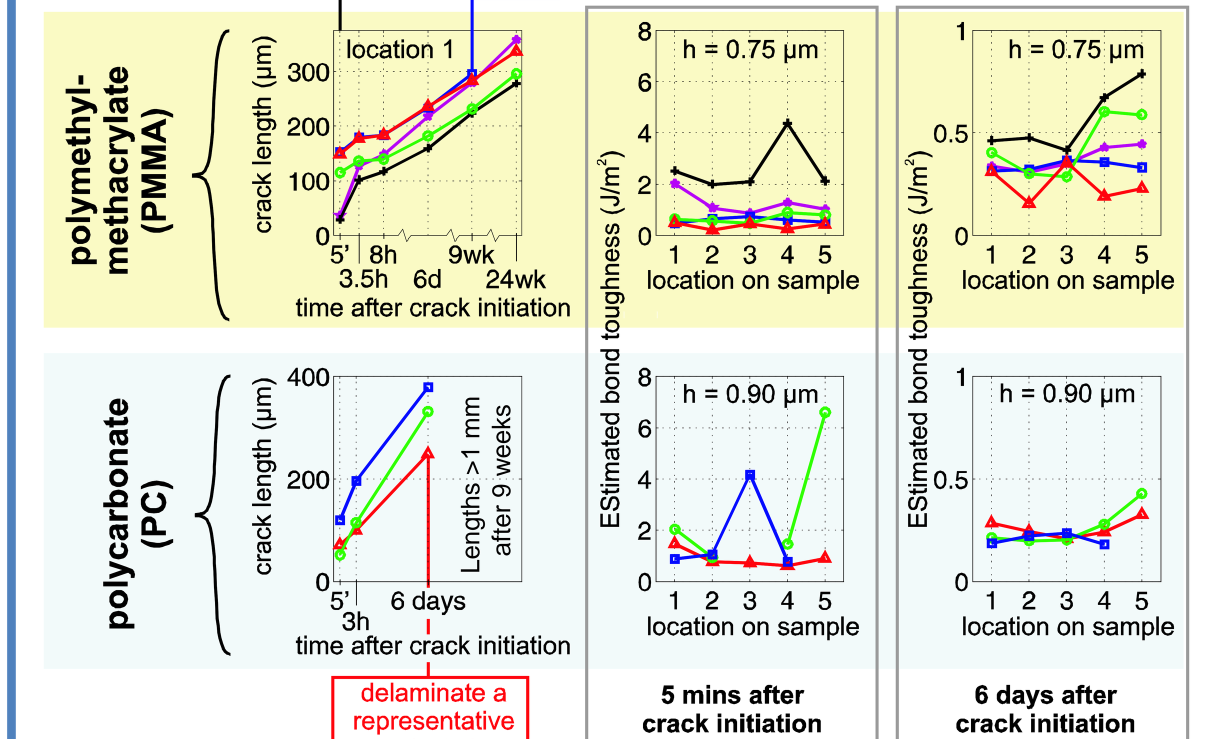


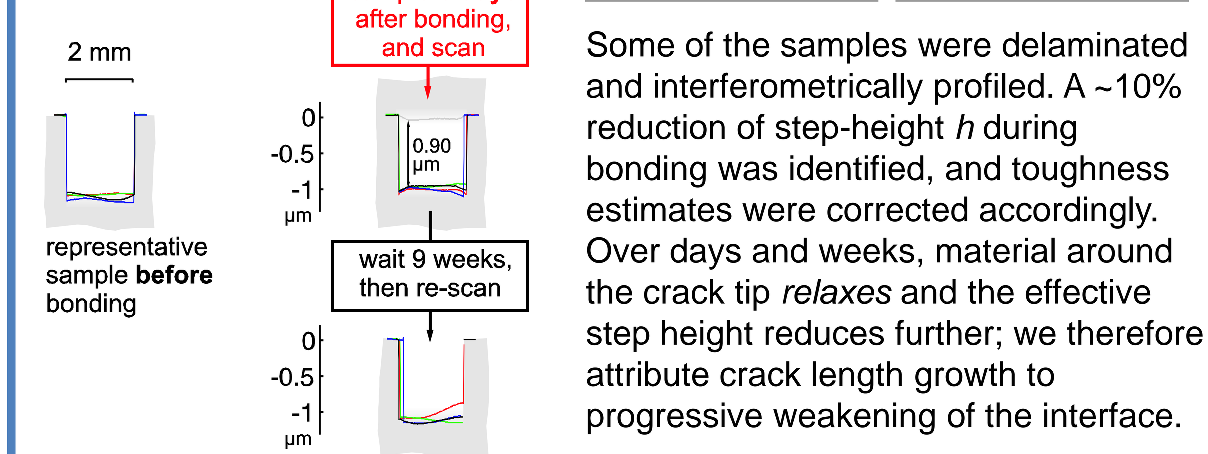
- Can be done with optical microscopy
- Can measure at many locations per sample
- Crack lengths may grow over time

Propagation of micro-cracks; process variability



Sets of 1.5 mm-thick polymethylmethacrylate (PMMA) and polycarbonate (PC) layers were bonded under nominally identical conditions, and crack lengths measured over 24 weeks. Crack lengths 3 hours or more after bonding varied by up to a factor of ~2 between parts and generally by up to a factor of ~2 within each part. Spatial variation of crack lengths shows no systematic pattern.





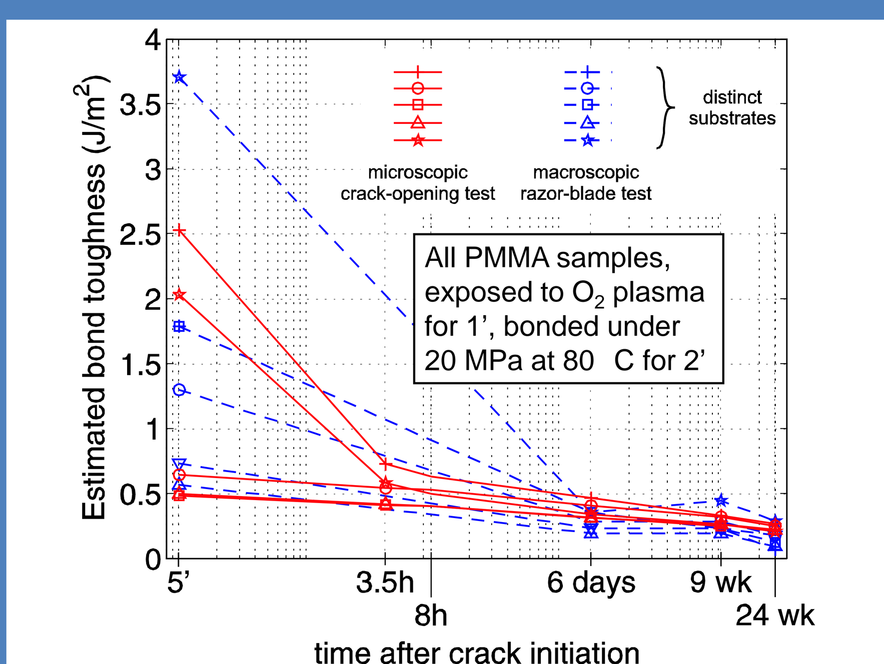
Some of the samples were delaminated and interferometrically profiled. A ~10% reduction of step-height h during bonding was identified, and toughness estimates were corrected accordingly. Over days and weeks, material around the crack tip *relaxes* and the effective step height reduces further; we therefore attribute crack length growth to progressive weakening of the interface.

Detail: polymer mechanical properties

The test method requires an assumption of linear elasticity, which, for a thermoplastic, would break down if bonding and/or unloading was performed too close to the softening temperature of the material. If the time of propagation of the crack were comparable with the relaxation time-constant of the material, our estimate of bond toughness would be an overestimate because a portion of the elastic potential energy released from the material would be unavailable for crack enlargement.

A detailed model of the visco-elastic-plastic behavior of PMMA [8], in combination with analytical results for crack propagation in viscoelastic media [9], lead us to believe that for unloading at 40 C, as in these experiments, an assumption of linear elasticity is valid for at least the first few minutes after unloading. The extent of the subsequent apparent weakening of the bonds may in fact be underestimated because the polymer has relaxed. Analysis of the size of any such error is needed.

Comparison with macroscopic test



The results of integrated micro-crack opening tests were compared with those of macroscopic razor-blade tests. Bond-toughness estimates from the two methods are comparable in magnitude and in their time-evolution.

Six unpatterned samples were bonded and a blade was inserted at the corner of each. The relationship between crack length and estimated bond toughness for triangular plates being prized apart is given by:

$$\hat{G} = \frac{E h^2 t^3}{12 L^4}$$

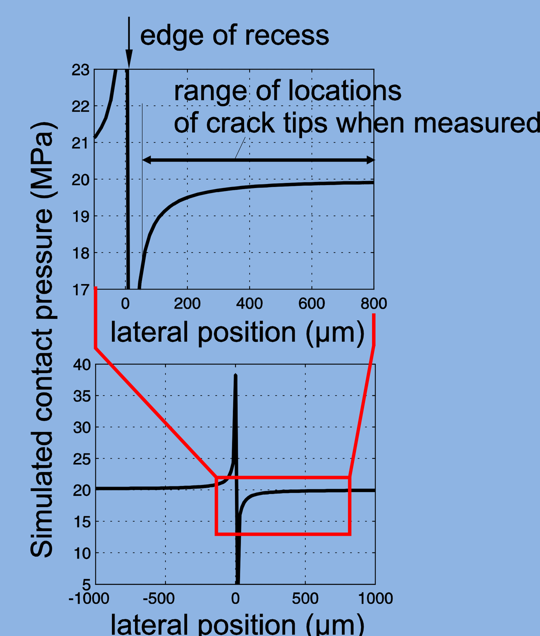
after, e.g., [4, 5]

h: blade thickness, 230 µm
t: plate thickness, 1.5 mm

20 mm

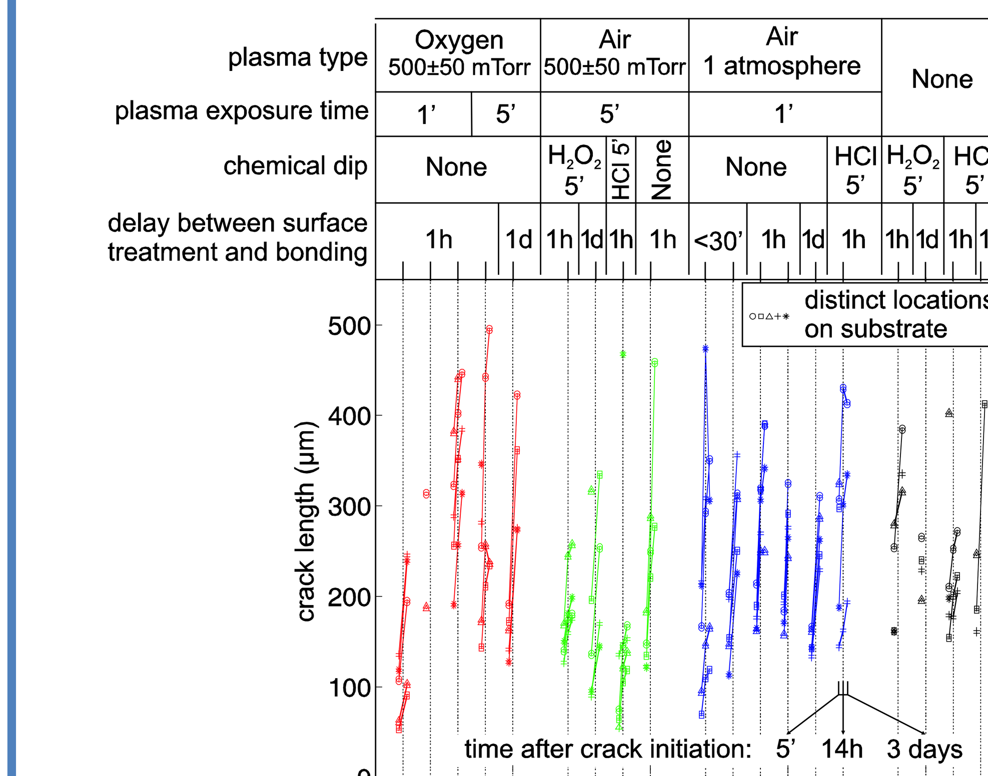
Detail: contact pressure nonuniformity during bonding

It is possible that the toughness of the bond formed depends on the local contact pressure applied during bonding. This is not a variable investigated here but must be controlled. A simulation of the distribution of contact pressure within one of the 2 mm-wide embossed recesses in the present experiments shows that for p_0 = 20 MPa, and assuming E = 1.6 GPa, the contact pressure lies between 17.5 and 19.9 MPa in the region in which crack tips finally reside:



Screening of pre-bonding surface treatments

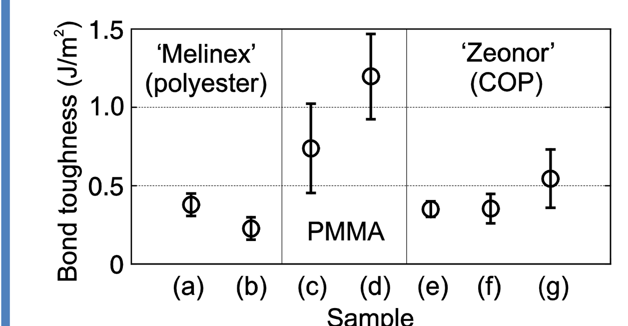
The micro-crack test method was used with a range of possible pre-bonding surface treatments. Bulk PMMA samples were rinsed in methanol and DI water and dried in N_2 before receiving the surface treatments detailed below. Bonding was done under 20 MPa for 2' at 80 C. Crack lengths were measured 5 minutes, 14 hours and 3 days after bonding.



- Attempts to bond with neither plasma pre-treatment nor an H_2O_2 or HCl dip were unsuccessful.
- Part-to-part and within-part crack-length variability for any particular treatment appears to be at least as large in magnitude as any variation relating to the nature of the plasma treatment.
- For oxygen plasma treatment, there is no evidence that a 5' exposure yields a tougher bond than a 1' exposure.
- Samples treated with a plasma generated at atmospheric pressure using a hand-held 'torch' [6] yield similar crack lengths to those treated at 500 mTorr in an air or oxygen plasma.
- A 1-day delay between plasma treatment and bonding does not appreciably diminish the bond toughness obtained in these tests. This result is in strong contrast with results published for plasma-activated *PDMS* bonding [7].
- If a plasma treatment step is *not* performed, a 5' dip in ~35% HCl (aq) can yield comparable crack lengths, but not if bonding is delayed until a day after the dip. Samples treated with only an H_2O_2 dip or bonded 1 day after the HCl dip gave crack lengths that generally reached 1 mm within a few hours.

Bonding of polymer films

Extracted bond toughness estimates for the bonding of three different films to bulk PMMA substrates embossed with 3 µm-relief steps:



(a, b) 130 µm-thick polyester bonded at 70 C and 10 MPa;
(c) 75 µm-thick PMMA bonded at 55–60 C and 2 MPa;
(d) as (c), but bonded at 4 MPa
(e–g) 130 µm-thick COP film bonded at 60–70 C and 2, 5 and 10 MPa

Crack lengths were measured 1 day after bonding. Error bars reflect within-substrate variation of measured crack lengths.

Outlook

The method produces bond toughness estimates approximately consistent with those from the established macroscopic razor-blade method. Observed part-to-part and within-part crack-length variations are larger than can be explained by the measured variation of the pre-bonding step heights; the sources of this variability need further investigation, as does an apparent progressive weakening of the bonds, which are under stress near the crack tips. The test method has been used to compare efficiently a range of surface activation treatments.

Acknowledgements

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