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Polymer friction and polymer yield: a comparison

B. J. Briscoe
Imperial College of Science and Technology, London SW7 2AZ, UK

and A. C. Smith
Cranfield Institute of Technology, Bedford, UK
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This report examines the nominal similarity between one mode of energy dissipation which occurs during the sliding of polymers and the process of polymer yield. When an organic polymer is slid over a smooth and clean surface, substrate energy is dissipated within a very narrow interfacial zone. A detailed study of this process is facilitated by isolating this narrow zone as a thin film ~100 nm thick and then deforming it between rigid substrates. In this way it is possible to investigate the energy dissipated per unit area as a function of many variables, in particular the applied uniaxial stress. The sliding process has much in common superficially with polymer yield. The basis for comparison developed here is the way in which the sliding and conventional yield processes are influenced by the application of a hydrostatic stress.

The yield behaviour of bulk isotropic polymers has been extensively studied in a variety of stress states in the past fifteen years[1–6]. In particular the yield stress of a large number of polymers[3–6] has been determined as a function of an applied hydrostatic pressure. The interfacial shear properties of polymer films have received comparatively less attention. They have frequently been obtained by confining a thin film in a loaded contact and shearing the film through the relative motion of the contact substrates. The interfacial shear strength, which is defined as the frictional force per unit area of a material sheared, has been obtained as a function of the mean contact stress in the film for a wide range of organic polymers[7–10]. To a good approximation we may assume that the applied uniaxial stress produces an hydrostatic pressure in the film.

The interfacial shear strength provides an estimate of the level of energy dissipation in the polymer without implying any particular mechanism. It is a deformation property of the polymer determined under very different conditions compared with the yield stress of bulk samples. The strain rate in thin film shear experiments is considerably higher ($\sim 10^4$ s^{-1}) than in bulk yield observations (10^{-3}–10 s^{-1}), Further the thin film is subject to the repeated application of transient contact stresses, typically a contact (quasi hydrostatic) stress cycle from around zero to a mean of 10^8 Pa is applied and reversed in 0.2 s, whereas simple bulk polymer yield is a single or unit process. The other principal difference between thin film shear and isotropic bulk yield concerns the position and direction of the yield plane. During bulk polymer yield this plane is within the polymer but often its direction is only prescribed by yield criteria. The converse situation applies in the thin film experiments. The direction of yield is constrained to within a few degrees of the displacement vector because of the contact geometry. Although the position is closely defined it may be at either the interface between the substrates and the polymer or within the polymer itself. The experimental method does not distinguish the two cases.

Earlier papers have attempted to correlate the yield stress dependence on hydrostatic pressure with that of the shear strength on the contact stress[11]. The funtionality was found to be approximately linear in both cases for polymethyl methacrylate and high density polyethylene at room temperature. The hydrostatic pressure coefficient of the torsional yield stress was found to be comparable with the contact stress coefficient of the shear strength. The shear strength at zero contact stress was found to be one-tenth of the yield stress at atmospheric pressure. The latter discrepancy was rationalized in terms of the very different deformation processes occurring in the bulk and thin film. In this report a common basis for the description of bulk yield and thin film shear is sought and this comparison is examined in more detail.

The shear strength of a polymer film is measured in the plane of the film for a contact stress normal to the film. The empirical relationship between the interfacial shear strength (σ_s) and the mean contact stress (σ_n) may be written to a very good approximation as:

$$\sigma_s = \sigma_c - \mu\sigma_n \qquad (1)$$

in the convention that a compressive stress is negative and where σ_c and μ are constants.

The Mohr–Coulomb criterion states that yield will occur when the shear stress on any plane in the bulk material reaches a critical value which varies linearly with the normal stress on that plane[4]. This criterion may be written in the same form as equation (1). It must be emphasized that the thin film shear data do not obey the Mohr–Coulomb criterion but merely a relationship which is formally identical to it. Since equation (1) may be used to describe thin film shear and the yield of bulk polymers it forms the basis for their comparison through the constants σ_c and μ.

The yield stress of bulk isotropic polymers has been obtained in a variety of stress states and the results have been fitted to a number of yield criteria. Among the simplest and popular are the Mohr–Coulomb, pressure modified Tresca and pressure modified von Mises criteria. The parameters of these criteria may be interrelated and this is demonstrated in the Appendix for some simple stress states. The yield criteria have been individually

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Table 1 Comparison of typical numerical values of σ_c and μ (equation (1)) for thin polymeric films undergoing interface shear and the nominally similar isotropic monolithic specimens during bulk yielding

Polymer	Thin film						Bulk		
			Casting Solvent	Thermal History*					
	σ_c(x10^7 Pa)	μ		Time	Temperature	Medium	σ_c(x10^7 Pa)	μ	Key
Polymethyl methacrylate	1.0	0.40	chloroform	8 h	120°C	air	5.3	0.21	a
PMMA	0.1	0.49	chloroform	8 h	160°C	nitrogen	4.6	0.26	b
Polystyrene	0.4	0.22	carbon tetrachloride	30 h	100°C	air	6.3	0.09	c
PS	0.2	0.09	carbon tetrachloride	24 h	160°C	nitrogen	4.0	0.15	d
Polyethylene terephthalate	0.5	0.19	nitrobenzene	72 h	100°C	air	5.8	0.08	e
PET	1.0	0.08	methanol	72 h	160°C	nitrogen	3.1	0.05	c
Bisphenol A polycarbonate	0.5	0.06	ethanol	44 h	160°C	nitrogen	4.2	0.06	f
PC	1.0	0.24	chloroform	16 h	130°C	air	3.5	0.08	c
Polypropylene† PP	0.5	0.17	directly rubbed from bulk polymer. No thermal treatment				1.6	0.11	g
							2.0	0.20	h
High density Polyethylene	0.2	0.09	directly rubbed from bulk polymer. No thermal treatment				1.4	0.03	e
HDPE	0.1	0.06	directly rubbed	14 h	160°C	nitrogen	1.4	0.04	g
							0.8	0.18	i
Polyvinyl acetate PVAC	1.2	0.13	chloroform	44 h	160°C	nitrogen	3.5	0.20	j

* The specification of thermal history refers to the films; data and experimental method reported in references 8, 11, 21, 22. Data on bulk polymers in Key. The σ_c and μ values for the films and the monolithic specimens are intended to illustrate the range observed. No correlation between values within the same nominal chemistry is intended

† Ref. 21

Key, Table 1 Bulk Deformation Characteristics

T (°C)	$\dot{\gamma}$ (S^{-1})	Reference	Stress state	Criterion used
a ~23		1	Orthogonal uniaxial tension and compression	Mohr–Coulomb
b ~23	4 x10^{-4}	15	Torsion under hydrostatic pressure	Mohr–Coulomb
c ~23		16	Tension under hydrostatic pressure	Von Mises Use of *Tables A2, A3* to give σ_c, μ
d ~23		17	Tension, compression, torsion, biaxial, tension in plane strain, punch indentation in plane strain compression	Mohr–Coulomb
e ~23	4 x10^{-4}	15	Torsion under hydrostatic pressure	Equation (2) Use of *Table A3* to give σ_c, μ
f ~22	4 x10^{-2}	5	Torsion under hydrostatic pressure	Von Mises Use of *Tables A2, A3*, to give σ_c, μ
g ~23		18	Tension under hydrostatic pressure	Equation (2) Use of *Table A3* to give σ_c, μ
h ~23	1.7 x10^{-3}	19	Torsion under hydrostatic pressure	Equation (2) Use of *Table A3*, to give σ_c, μ
i ~22	1.1 x10^{-3}	13	Oriented polymer. Yield and flow in tension	Resolved shear stress criterion. Formally identical to Equation (1)
j ~34	8 x10^{-4}	20	Torsion under hydrostatic pressure	Equation (2) Use of *Table A3*, to give σ_c, μ

T = Temperature; $\dot{\gamma}$ = Strain rate

identified with the empirical yield stress dependence on hydrostatic pressure which has been approximately represented by[4]

$$\sigma=\sigma_0+\alpha P \qquad (2)$$

where P is the hydrostatic pressure, σ is the yield stress, σ_0 and α are constants. The results of several published studies of yield in isotropic bulk polymers have been listed in *Table 1* in terms of the parameters of the Mohr–Coulomb criterion (equation (1)). Where necessary the data have been converted into the constants σ_c and μ using the Appendix *Tables A1, A2* and *A3*.

The value of the constants of equation (1) are listed in *Table 1* for the results of thin film shear experiments carried out at ambient temperature and at an estimated strain rate in excess of 10^4 s^{-1}. It has been shown that the casting solvent and the thermal treatment of the polymer films have a profound effect on their shear strength[10,12]. The extremes of the constants σ_c and μ are given for each polymer together with the accompanying fabrication and thermal history conditions.

The results of *Table 1* indicate that μ in bulk studies varies between 0.3 and 2.9 times μ as obtained for thin films for all the polymers. The value of σ_c is between 3 and 53 times greater in the case of the bulk polymer (*Table 2*). On average the values of μ are comparable whilst σ_c in the bulk data is about ten times that obtained for the thin film.

Table 2 σ_c (Bulk)/σ_c (Thin film) and μ (Bulk)/μ (Thin film) values for various polymers

Polymer	σ_c (Bulk) / σ_c (Thin film)	μ (Bulk) / μ (Thin film)
PMMA	4.6–53.0 (28.8)	0.5–2.9 (1.7)
PS	10.0–31.0 (20.05)	0.4–1.7 (1.05)
PET	3.1–11.6 (7.35)	0.3–1.0 (0.65)
PC	3.5–8.4 (5.95)	0.3–1.3 (0.8)
PP	3.2–4.0 (3.6)	0.7–1.2 (0.95)
HDPE	7.0–14.0 (10.5)	0.3–0.7 (0.5)
PVAC	2.9 (2.9)	1.5

Bracketed quantities are arithmetic means. The overall average values of μ (Bulk)/μ (Thin film) and σ_c (Bulk)/σ_c (Thin film) are respectively 0.9 and 11.3

It is interesting that a resolved shear stress criterion identical in form to equation (1) has been used to describe the yield and flow behaviour of oriented bulk high density polyethylene (HDPE)[13]. The value of σ_c lies in between the thin film and isotropic bulk values. The thin films of HDPE are known to be highly oriented[14] and hence it is possible that σ_c decreases with increasing orientation which is generated during sliding for certain polymers.

In summary we conclude that, with regard to a hydrostatic environment, to a first rather crude approximation a thin polymeric film dissipating frictional work during sliding behaves very much like a monolithic specimen of the same polymer undergoing yield. The functionality of the hydrostatic pressure dependence is the same and the pressure coefficients are comparable. The absolute values of shear strength differ by, on average, a factor of ten with the friction experiment providing the lower strengths. In subsequent publications we will seek to confirm the basic similarity using temperature and time as investigative variables.

REFERENCES

1 Bowden, P. B. and Jukes, J. A. *J. Mat. Sci.* 1968, **3**, 183
2 Raghava, R., Caddell, R. M. and Yeh, G. S. Y. *J. Mat. Sci.* 1973, **8**, 225
3 Pugh, H. L. D., Chandler, E. F., Holliday, L. and Mann, J. *Poly. Eng. Sci.* 1971, **11**, 463
4 Ward, I. M. *J. Mat. Sci.* 1971, **6**, 1397
5 Duckett, R. A., Goswami, B. C., Smith, L. S. A., Ward, I. M. and Zihlif, A. M. *Brit. Poly. J.* 1978, **10**, 11
6 Pae, K. D. and Bhateja, S. K. *J. Macromol. Sci. Macromol. Rev. Chem.* 1975, **C13**, 1
7 Bowers, R. C. *J. Appl. Phys.* 1971, **42**, 4961
8 Briscoe, B. J. and Tabor, D. *J. Adhesion* 1978, **9**, 145
9 Briscoe, B. J., Scruton, B. and Willis, F. R. *Proc. Roy. Soc.* 1973, **A333**, 99
10 Briscoe, B. J. and Smith, A. C. *Rev. Deformat. Behaviour Mat.* 1980, 3, 151
11 Briscoe, B. J. and Tabor, D. *Trans. ASLE* 1974, **17**, 158
12 Smith, A. C. *PhD Thesis* (1979), University of Cambridge
13 Simpson, L. A. and Hinton, T. *J. Mat. Sci.* 1971, **6**, 558
14 Pooley, C. M. and Tabor, D. *Proc. Roy. Soc.* 1972, **A329**, 251
15 Rabinowitz, S., Ward, I. M. and Parry, J. S. C. *J. Mat. Sci.* 1970, **5**, 29
16 Christiansen, A. W., Baer, E. and Radcliffe, S. V. *Phil. Mag.* 1971, **24**, 451
17 Argon, A. S., Andrews, R. D., Godrick, J. A. and Whitney, W. *J. Appl. Phys.* 1968, **39**, 1899
18 Mears, D. R., Pae, K. D. and Sauer, J. A. *J. Appl. Phys.* 1969, **40**, 4229
19 Joseph, S. H. and Duckett, R. A. *Polymer* 1978, **19**, 837
20 Duckett, R. A., Joseph, S. H., Sumner, H. and Stachursky, Z., 4th International Conference: Deformation, Yield and Fracture of Polymers, Churchill College, Cambridge, (1979), p 37
21 Amuzu, J. K. A. *PhD Thesis* (1976), University of Cambridge
22 Briscoe, B. J. and Smith, A. C. *J. Macromol. Sci.-Phys.* (in preparation)

APPENDIX

Table A1 The pressure modified Tresca criterion*

Stress state (with hydrostatic pressure)	σ_0	α
Pure shear	τ_0	μ^1
Uniaxial tension	$\dfrac{6\tau_0}{3+2\mu^1}$	$\dfrac{6\mu^1}{3+2\mu^1}$
Uniaxial compression	$\dfrac{6\tau_0}{2\mu^1-3}$	$\dfrac{6\mu^1}{^2\mu^1-3}$
Plane strain compression	$\dfrac{2\tau_0}{\mu^1-1}$	$\dfrac{2\mu^1}{\mu^1-1}$

* This criterion states that yields occurs when the resolved shear stress on any plane in the material, τ, reaches a critical value given by $\tau_0 + \mu^1\sigma_m$ where τ_0 and μ^1 are constants and σ_m is the hydrostatic component of stress.

$\sigma_m = -1/3(\sigma_1 + \sigma_2 + \sigma_3)$ where $\sigma_{1,2,3}$ are the principal stress components.

The parameters τ_0 and μ^1 are related to α and σ_0 of equation (2) for some simple stress states under hydrostatic pressure

Table A2 The pressure modified Von Mises Criterion*

Stress state (with hydrostatic pressure)	σ_0	α
Pure shear	$\dfrac{3}{\sqrt{6}}\tau^1$	$\dfrac{3K}{\sqrt{6}}$
Uniaxial tension	$\dfrac{3\tau^1}{K+\sqrt{2}}$	$\dfrac{3K}{K+\sqrt{2}}$
Uniaxial compression	$\dfrac{3\tau^1}{K-\sqrt{2}}$	$\dfrac{3K}{K-\sqrt{2}}$
Plane strain compression	$\dfrac{2\sqrt{6}\tau^1}{\sqrt{6}K-2}$	$\dfrac{2\sqrt{6}K}{\sqrt{6}K-2}$

* This criterion states that yield occurs when the octahedral shear stress reaches a critical values given by $\tau^1 + K\sigma_m$ where τ^1 and K are constants and σ_m is the hydrostatic component of stress. The octahedral shear stress, τ_{oct}, is given by

$$9\tau_{\text{oct}}^2 = (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2$$

where $\sigma_{1,2,3}$ are the principal stress components and $\sigma_m = -1/3(\sigma_1 + \sigma_2 + \sigma_3)$.

The parameters τ^1 and K are related to α and σ_0 of equation (2) for the same stress states as in *Table A1*

Table A3 The Mohr–Coulomb criterion

Stress state (with hydrostatic pressure)	σ_0	α
Pure shear	$\dfrac{\sigma_c}{\sqrt{1+\mu^2}}$	$\dfrac{\mu}{\sqrt{1+\mu^2}}$
Uniaxial tension	$\dfrac{2\sigma_c}{\mu+\sqrt{1+\mu^2}}$	$\dfrac{2\mu}{\mu+\sqrt{1+\mu^2}}$
Uniaxial compression Plane strain compression	$\dfrac{2\sigma_c}{\mu-\sqrt{1+\mu^2}}$	$\dfrac{2\mu}{\mu-\sqrt{1+\mu^2}}$

* The parameters σ_c and μ of equation (1) are related to α and σ_0 of equation (2) for the same stress states as in *Table A1*