

Rheology of Solvent-Cast Polymer Films

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Synopsis

This paper describes and analyzes the results of an experiment where various thin polymeric films are continuously sheared between smooth glass substrates. The shear force per unit area has been measured as a function of mean uniaxial stress and temperature using representative "good" and "poor" casting solvents followed by a range of heat treatments. The polymers studied include high density polyethylene, polybisphenol-A-carbonate, poly(ethylene terephthalate), atactic polystyrene, isotactic polystyrene, atactic poly(methyl methacrylate), isotactic poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl pyrrolidone), poly(vinyl chloride), and polytetrafluoroethylene. The results indicate that the casting solvent has a very pronounced influence upon the rheology of the film. The casting solvents may apparently confer either ductile or brittle failure in the film and also influence the nature of the temperature and pressure dependence of the shear stress. The data have been analyzed using Eyring theory and also by reference to relevant published literature on the influence of solvent and thermal treatments on the morphology and deformation behavior of polymers. "Good" solvents generally tend to promote a brittle mode of failure with little temperature dependence. The same type of solvents also produced films which have higher shear strengths and show greater increases in shear strength with pressure. These data are adequately rationalized using free volume and entanglement notions.

INTRODUCTION

This paper describes the results of an experimental study of the interfacial shear properties of thin polymeric films. Thin films (ca. 100 nm thick) were formed on optically smooth silica glass substrates. These films were deformed in shear by loading a smooth glass hemisphere against the flat substrate and setting the latter in reciprocating motion.¹⁻⁴ The size of the contact region may be calculated using elastic contact mechanics⁵ and is identified with the area of film undergoing deformation. The interfacial shear strength may be calculated from the quotient of the shear force and the contact area whereas the quotient of the normal load and the contact area indicates the mean contact stress. The variation of the interfacial shear strength with both the mean contact stress and the temperature is described for a number of the film morphologies of different polymers.

The interfacial shear strength is a deformation property corresponding to high strains and strain rates ($\sim 10^6 \text{ s}^{-1}$). The films are subject to contact stresses of order 10^8 Pa which are applied in times of the order 0.05 s. The shear of thin polymeric films reveals deformation data under very different conditions to conventional yield studies on monolithic polymer samples. The interfacial shear process does, however, have much in common with the conventional shear of large specimens.^{4,6} There is a strong body of experimental evidence which suggests

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that thin films dissipate frictional work by processes similar to those occurring in bulk yield or rupture. The shear of a film has been proposed as involving either plastic flow in the film or a fracture-type mechanism at the film-substrate interface.³ Further insight into the nature of the interfacial shear is provided by the experiments described below.

Previous studies have established the general form of the relationships between the shear strength and a number of variables such as the contact stress, the temperature, the strain rate, and the time of application of the contact stress for a variety of organic polymers.^{1-4,6-8} In the present study the effect of the film preparation and history on the shear strength is reported. The results indicate that the type of casting solvent and temperature and subsequent heat treatment have a profound effect on the shear strength dependence on both the contact stress and the temperature. The corresponding volume and morphological changes have been speculated upon, drawing on the extensive studies of polymer-solvent interactions using infrared, electron microscopy, and differential scanning calorimetry techniques. A rationale has been developed to relate the morphological properties of the films to their shear strength characteristics. These experiments further afford the application of a stress-aided thermally activated flow model and thereby a comparison with bulk polymer deformation.

EXPERIMENTAL PROCEDURE

The polymers used in this study are listed in Table I with the abbreviations used in this text. Thin films were prepared on flame-cleaned optically smooth float glass plates which had been degreased in a methanolic potassium hydroxide solution and thoroughly washed in deionised distilled water. Films of HDPE were prepared by directly rubbing the bulk polymer onto a warmed substrate.⁴ The other polymer films were cast from a dilute ($\sim 0.5\%$ w/w) solution of the polymer in a purified solvent. For each polymer at least two solvents of different theta temperature were used. The films were in most cases cast at room temperature although some PS, IPS, and PMMA films were cast at temperatures below ambient. To cast films at a low temperature, the substrate was immersed in the solution and transferred to the cold stage of a cryostat and a few mL of the solvent placed in the cryostat housing. The temperature was reduced using a liquid nitrogen input to the cryostat. In a relatively crude manner, the solvent

TABLE I

High density polyethylene	HDPE
Polybisphenol-A-carbonate	PC
Poly(ethylene terephthalate)	PET
Atactic polystyrene	PS
Isotactic polystyrene	IPS
Atactic poly(methyl methacrylate)	PMMA
Isotactic poly(methyl methacrylate)	IPMMA
Poly(vinyl acetate)	PVAC
Poly(vinyl alcohol)	PVAL
Poly(vinyl pyrrolidone)	PVP
Poly(vinyl chloride)	PVC
Polytetrafluoroethylene	PTFE

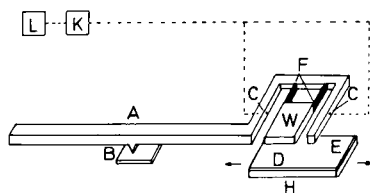


Fig. 1. Schematic diagram of the friction apparatus used to measure the shear strength properties of thin organic films: (A) beam of chemical balance; (B) agate fulcrum; (C) displacement transducers; (D) glass hemisphere; (E) float glass substrate; (F) leaf springs; (H) heating block; (K) carrier wave frequency bridge; (L) ultraviolet recorder; (W) applied dead load.

may then be removed at low temperature by the pumping system of the cryostat.

Following fabrication, the films were given a thermal treatment in either nitrogen or air atmospheres in a circulating air oven for a fixed period of time prior to testing. A nitrogen environment was achieved by filling a glass cell to a pressure below atmospheric at ambient temperature.

Certain films of PVAL were exposed to constant humidity atmospheres at room temperature. This was effected by placing the substrate in a small dessicator over a saturated salt solution using the data of Young.⁹

The prepared film thickness was found to lie in the range 100–500 nm as observed using multiple beam interferometry. Negligible variations in the shear strength were detected within these extremes of film thickness in agreement with previous work.^{2,4} The actual film thickness during sliding is inaccessible in the present technique and may be very different to the initial value.

A schematic illustration of the experimental apparatus is shown in Figure 1. A flame cleaned pyrex hemisphere of radius ca. 2 mm was loaded against a substrate on which the film had been deposited. The float glass substrate was driven in a reciprocating motion over a track of 2 mm length at a speed of 2.4×10^{-4} ms^{-1} , the use of a low sliding speed minimizing frictional heating. The frictional force at equilibrium was detected using a transducer arrangement shown in Figure 1.

The sheared area of film may not be directly observed, but an estimate may be made using Hertz elasticity theory.⁵ It is assumed that the area of contact of the two glass substrates is a fair approximation of the sheared area of the film. This assumption is justified to some extent by a comparison of the results with those in which the generation of stress occurs in a contact with a plastically deforming indenter.¹⁰ Further, the very small thickness of the film vindicates the use of a dry elastically deforming contact approximation. Another assumption of the technique is that no direct contact of the substrates occurs. The hemisphere was examined before and after an experiment, and the results were discarded if damage was found. The occurrence of glass–glass contact is also revealed through erratically high friction data. The sheared area A is used to calculate the interfacial shear strength τ and the mean contact stress P in the film:

$$\tau = F/A, \quad P = W/A$$

where F is the equilibrium frictional force and W is the applied normal load on the contact.

The shear strength τ was obtained as a function of the mean contact stress P in the range 10^7 – 10^9 Pa at ambient temperature. The shear strength was also investigated as a function of temperature T in the range 20–160°C at a contact stress of 9.9×10^7 Pa by means of a heated brass block in contact with the lower substrate (Fig. 1).

EXPERIMENTAL RESULTS

The dependence of the shear strength τ on the contact stress P has been shown in previous work on a wide variety of inorganic and organic polymer films to be well described by^{2,4,7,10}

$$\tau = \tau_0 + \alpha P \quad (1)$$

where τ_0 and α are constants for a given temperature and strain rate. The data of the current study are generally well described by eq. (1). The values of the constants α and τ_0 for each polymer film are listed in Table II for the casting solvent, casting temperature, thermal history, and treatment medium conditions used. Films of HDPE were also given different heat treatments in nitrogen and air environments and the values of τ_0 and α also given in Table II. Films of the water-soluble polymers PVAL and PVP were exposed to different constant humidity media for periods of time followed by determination of their shear strength properties. The variation of the values of α and τ_0 is listed in Table III for each experimental treatment.

The application of eq. (1) to some of the data reveals negative values of τ_0 (Tables II and III), which are physically unrealistic. A more general empirical equation which describes *all* the data of this study may be written

$$\tau = \tau' \exp \bar{\alpha} P \quad (2)$$

where τ' and $\bar{\alpha}$ are constants for a given temperature and strain rate. The values of τ' and $\bar{\alpha}$ for representative films and fabrication histories are given separately in Table IV.

The use of the contact stress variable to probe the interfacial shear properties of a polymer film shows a large diversity of results. The casting solvent and the ensuing thermal treatment and medium have a pronounced effect on the values of τ_0 and α [of eq. (1)]. Initially a film shows deviation from the linearity of eq. (1), but, after further heat treatment, the value of α falls and τ_0 becomes positive. When a film is heated at a temperature in the region of the glass transition T_g , the shear strength depends on the casting solvent. The films cast from a high theta point or poor solvent tend to possess lower values of α . Heat treatment of films in a nitrogen cell at 160°C generally leads to lower values of α and τ_0 than are achieved in air near T_g . Furthermore, heat treatment under these conditions removes the solvent quality effect encountered at the lower temperature. The use of air as the heating medium in place of nitrogen at 160°C leads to different shear strength properties. Exceptions to these trends are evident, particularly with high boiling point casting solvents which confer high shear strengths to films even after prolonged high temperature heating. The casting of films at low temperature followed by solvent removal by evacuation leads to low values of the shear strength. The above results embody the combined effects of solvent and thermal history on the shear strength. Their separate contributions have

TABLE II
Dependence of Shear Strength on Contact Stress^a

Time (h)	Heat treatment		τ_0 ($\times 10^7$ Pa)	α
	Temp ($^{\circ}$ C)	Medium		
(i) Isotactic polystyrene (IPS) $T_g \approx 100^{\circ}$ C				
Toluene (good solvent)—cast at room temperature				
2	80	Air	-1.4	0.90
6	100	Air	+0.4	0.38
24	100	Air	+0.4	0.20
25	160	Air	+0.7	0.24
12	160	Nitrogen	+0.3	0.27
36	160	Nitrogen	+0.4	0.42
Carbon tetrachloride (poor solvent)—cast at room temperature				
2	80	Air	-0.9	0.80
24	100	Air	+0.4	0.11
8	160	Nitrogen	+0.4	0.27
16	160	Nitrogen	+0.1	0.12
35	160	Nitrogen	+0.1	0.08
Carbon disulphide (poor solvent)—cast at room temperature				
4	80	Air	+0.4	0.15
6	100	Air	+0.4	0.09
24	160	Nitrogen	+0.1	0.09
Decalin (poor solvent)—cast at room temperature				
8	160	Nitrogen	+0.4	0.21
12	160	Nitrogen	+0.6	0.54
Carbon Disulphide—cast at -78° C				
Decalin—cast at 0° C				
—	As made		+0.2	0.09
24	100	Air	+0.2	0.09
(ii) Atactic polystyrene (PS) $T_g \approx 100^{\circ}$ C				
Carbon tetrachloride (good solvent)—cast at room temperature				
2	80	Air	-1.0	0.75
24	80	Air	+0.4	0.56
6	100	Air	+0.4	0.70
16	100	Air	+0.4	0.42
30	100	Air	+0.4	0.22
24	160	Nitrogen	+0.2	0.09
Propan-2-ol (poor solvent)—cast at room temperature				
2	80	Air	-0.2	0.75
6	80	Air	+0.4	0.70
24	80	Air	+0.5	0.08
24	100	Air	+0.7	0.17
8	160	Air	+0.4	0.66
24	160	Nitrogen	+0.2	0.09
Carbon disulphide—cast at -78° C				
Decalin—cast at 0° C				
	As made		+0.2	0.12
24	100	Air	+0.2	0.12

TABLE II (Continued from the previous page.)

Time (h)	Heat treatment		τ_0 ($\times 10^7$ Pa)	α
	Temp ($^{\circ}$ C)	Medium		
(iii) Atactic poly(methyl methacrylate) (PMMA) $T_g \approx 120^{\circ}$ C				
Chloroform (good solvent)—cast at room temperature				
2	80	Air	-0.7	0.54
4	120	Air	+0.7	0.40
8	120	Air	<u>+1.0</u>	<u>0.40</u>
18	160	Air	+1.0	0.67
12	160	Nitrogen	+0.4	0.22
24	160	Nitrogen	<u>+0.1</u>	<u>0.12</u>
Toluene (good solvent)—cast at room temperature				
2	80	Air	-1.0	0.75
4	120	Air	+0.1	0.55
8	120	Air	<u>+1.0</u>	<u>0.26</u>
22	160	Air	+1.3	0.73
10	160	Nitrogen	+0.5	0.25
24	160	Nitrogen	<u>+0.1</u>	<u>0.09</u>
Paraxylene (poor solvent)—cast at room temperature				
2	120	Air	0	0.26
8	120	Air	<u>+1.0</u>	<u>0.11</u>
8	160	Nitrogen	<u>+0.1</u>	<u>0.09</u>
Carbon tetrachloride (poor solvent)—cast at room temperature				
2	80	Air	-0.3	0.31
4	120	Air	+0.4	0.27
10	120	Air	<u>+0.6</u>	<u>0.19</u>
8	160	Air	+0.8	0.50
8	160	Nitrogen	<u>+0.1</u>	<u>0.08</u>
Decalin—cast at 0° C				
—	As made		+0.4	0.10
24	120	Air	<u>+0.4</u>	<u>0.10</u>
(iv) Isotactic poly(methyl methacrylate) (IPMMA) $T_g \approx 50^{\circ}$ C				
Chloroform—cast at room temperature				
2	80	Air	-1.1	0.71
8	80	Air	+1.0	0.35
8	160	Air	+1.0	0.75
8	160	Nitrogen	+1.8	0.32
16	160	Nitrogen	<u>+2.4</u>	<u>0.35</u>
Carbon tetrachloride—cast at room temperature				
2	80	Air	-1.5	0.87
4	80	Air	<u>+0.8</u>	<u>0.44</u>
12	160	Air	+1.2	0.67
Decalin—cast at room temperature				
4	80	Air	-1.0	0.46
24	80	Air	<u>+0.4</u>	<u>0.09</u>
4	160	Air	+0.4	0.25
19	160	Air	<u>+0.7</u>	<u>0.36</u>
24	160	Nitrogen	+0.5	0.22
48	160	Nitrogen	<u>+0.8</u>	<u>0.36</u>

TABLE II (Continued from the previous page.)

Heat treatment		Medium	τ_0 ($\times 10^7$ Pa)	α
Time (h)	Temp ($^{\circ}$ C)			
(v) Poly(bisphenol-A-carbonate) (PC) $T_g \approx 160^{\circ}$ C				
Chloroform (good solvent)—cast at room temperature				
4	80	Air	-1.0	0.80
4	130	Air	0	0.47
16	130	Air	+1.0	<u>0.24</u>
24	160	Air	+0.9	<u>0.23</u>
24	160	Nitrogen	+0.8	0.21
44	160	Nitrogen	+0.7	<u>0.08</u>
Ethanol (poor solvent)—cast at room temperature				
4	80	Air	-2.5	0.77
4	130	Air	+0.4	0.13
6	130	Air	+0.5	0.08
14	130	Air	+0.5	0.11
9	160	Air	+0.2	<u>0.60</u>
24	160	Nitrogen	+0.5	0.17
44	160	Nitrogen	+0.5	<u>0.06</u>
(vi) Poly(ethylene terephthalate) (PET) $T_g \approx 70^{\circ}$ C				
Nitrobenzene (good solvent)—cast at room temperature				
24	100	Air	-0.6	0.80
48	100	Air	+0.6	0.23
72	100	Air	+0.5	<u>0.19</u>
40	160	Air	+0.9	<u>0.27</u>
25	160	Nitrogen	+0.2	0.45
48	160	Nitrogen	+1.0	0.12
72	160	Nitrogen	+1.0	<u>0.08</u>
Methanol (poor solvent)—cast at room temperature				
4	80	Air	-0.9	0.92
24	100	Air	+0.7	0.08
72	100	Air	+0.4	<u>0.10</u>
40	160	Air	+0.5	<u>0.27</u>
24	160	Nitrogen	+0.1	0.33
48	160	Nitrogen	+1.1	0.15
72	160	Nitrogen	+1.1	<u>0.09</u>
(vii) Poly(vinyl alcohol) (PVAL) $T_g \approx 70^{\circ}$ C				
Water (good solvent)—cast at room temperature				
2	80	Air	0	0.26
25	100	Air	+1.0	<u>0.28</u>
4	160	Air	+0.9	0.29
40	160	Air	+0.8	<u>0.56</u>
20	160	Nitrogen	-2.4	0.80
44	160	Nitrogen	-1.1	0.69
84	160	Nitrogen	+1.8	<u>0.23</u>
Chloroform (poor solvent)—cast at room temperature				
2	80	Air	-0.2	0.73
24	100	Air	+0.7	0.11
39	100	Air	+0.5	<u>0.09</u>

TABLE II (Continued from the previous page.)

Time (h)	Heat treatment		Medium	τ_0 ($\times 10^7$ Pa)	α
	Temp ($^{\circ}$ C)				
24	160		Air	<u>-0.5</u>	<u>0.64</u>
24	160		Nitrogen	-2.1	0.81
48	160		Nitrogen	+0.6	0.42
87	160		Nitrogen	<u>+1.1</u>	<u>0.22</u>
(viii) Poly(vinyl acetate) (PVAC) $T_g \simeq 28^{\circ}$ C					
Chloroform (good solvent)—cast at room temperature					
20	40		Air	+0.9	0.40
4	80		Air	-1.0	0.62
13	80		Air	<u>-0.9</u>	<u>0.87</u>
8	160		Air	<u>-1.8</u>	<u>0.90</u>
20	160		Nitrogen	+0.6	0.23
44	160		Nitrogen	<u>+1.2</u>	<u>0.13</u>
(ix) Poly(vinyl pyrrolidone) (PVP) $T_g \simeq 70^{\circ}$ C					
Water—cast at room temperature					
4	100		Air	+0.9	0.20
24	100		Air	<u>+1.2</u>	<u>0.23</u>
20	160		Nitrogen	0	0.51
37	160		Nitrogen	+1.8	0.32
72	160		Nitrogen	+1.9	0.28
87	160		Nitrogen	<u>+1.8</u>	<u>0.23</u>
(x) High density polyethylene (HDPE)					
Deposited from a bulk sample					
As made					
				+0.2	0.09
8	100		Air	<u>+0.1</u>	<u>0.09</u>
16	160		Air	<u>+0.1</u>	<u>0.32</u>
48	160		Air	0	0.46
14	160		Nitrogen	<u>+0.1</u>	<u>0.06</u>

^a The values of the constants α and τ_0 of eq. (1). Equilibrium conditions are underlined.

been studied in the case of rubbed-on HDPE films and the humidity experiments with PVP and PVAL. The latter show that the presence of an appreciable quantity of solvent is responsible for deviation from shear strength-contact stress linearity [eq. (1)].

TABLE III
Treatment of Water Cast Films in Different Humidity Environments

Treatment	τ_0 ($\times 10^7$ Pa)	α
(i) PVAL		
Heated in air at 100 $^{\circ}$ C	+0.6	0.35
Equilibrium at 53% relative humidity (RH)	-0.9	0.75
Equilibrium in air	+0.8	0.14
Equilibrium in 11% RH	+0.7	0.14
(ii) PVP		
Heated in air at 100 $^{\circ}$ C	+1.0	0.23
Equilibrium in 53% RH	-0.6	0.55

TABLE IV
Dependence of Shear Strength on Contact Stress^a

Thin film	α	τ_0 ($\times 10^7$ Pa)	$\bar{\alpha}$ ($\times 10^{-8}$ Pa ⁻¹)	τ' ($\times 10^7$ Pa)
PMMA Cast from toluene, heat-treated in air at 80°C for 2 h	0.75	-1.0	1.5	+1.4
PC Cast from chloroform, heat-treated in air at 80°C for 4 h	0.80	-1.0	2.1	+0.7
PVAL Cast from water, heat-treated in nitrogen at 160°C for 20 h	0.80	-2.4	1.4	+1.1
PET Cast from methanol, heat-treated in air at 100°C for 72 h	0.10	+0.4	0.7	+0.7
PS Cast from carbon tetrachloride, heat-treated in air at 80°C for 24 h	0.56	+0.4	2.0	+0.7
PVAC Cast from chloroform, heat-treated in nitrogen at 160°C for 24 h	0.17	+1.2	0.7	+1.4
HDPE				
(i) Heat-treated in air at 160°C for 16 h	0.32	+0.1	1.5	+0.7
(ii) Heat-treated in nitrogen at 160°C for 14 h	0.06	+0.1	1.0	+0.2

^a The values of the constants $\bar{\alpha}$ and τ' of eq. (2) are recorded together with those of α and τ_0 [of eq. (1)] for selected polymers, casting solvents, and thermal histories.

The dependence of the shear strength on temperature T is shown in Figures 2 and 3 for some typical polymer films. The form of the functionality varies until at equilibrium reversible data are obtained. The thermal history accorded by temperature cycling of a film is unique and the values of the shear strength may not be deduced from those obtained in constant temperature heating. The form of the data recorded in Figures 2 and 3 is, however, reproducible for a given polymer and casting solvent.

Two types of temperature dependence of the shear strength have been noted in the present work: type I, the shear strength decreases uniformly with increasing temperature; type II, the shear strength is approximately constant up to a temperature corresponding to the T_g of the polymer followed by a monotonic decrease as the temperature is further increased. In previous work on polymer films the temperature functionality was found to be of these two types.¹⁻⁴ The present data are summarized in Table V.

DISCUSSION

The Temperature Dependence of the Shear Strength

The temperature dependence of the interfacial shear strength provides some insight into the nature and location of the dissipation process involved in thin

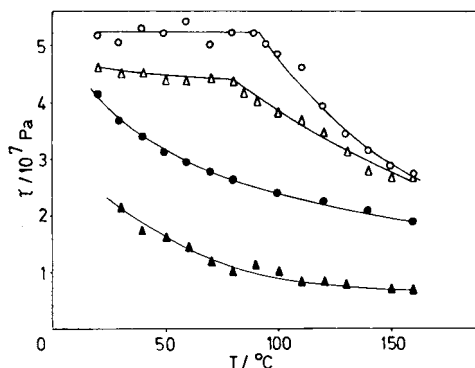


Fig. 2. The shear strength τ of films cast at room temperature as a function of temperature T at equilibrium. Contact pressure $P = 9.9 \times 10^7$ Pa. Sliding speed $= 2.4 \times 10^{-4}$ ms $^{-1}$. (Δ) PVAL film cast from water (good solvent); (\blacktriangle) PVAL film cast from chloroform (poor solvent), (\circ) PET film cast from nitrobenzene (good solvent); (\bullet) PET film cast from methanol (poor solvent).

film shear. Two types seem to exist and they correspond to the two categories of temperature dependence observed experimentally. (The behavior of certain HDPE films does not fit into either of these categories.) Type I behavior comprises a monotonic decrease in the shear strength with increasing temperature; type II involves a constant or slightly decreasing shear strength followed by a rapid decrease with increasing temperature, the transition being associated with the glass transition (T_g) of the polymer. Earlier experiments on thin films using temperature as a variable revealed these two functions. Type I behavior was observed in semicrystalline polymers such as HDPE and PTFE whereas type II was demonstrated by PS, PMMA, and PVC which are amorphous and possess a T_g within the experimental temperature range.⁴ The deduction from these studies was that the degree of crystallinity affected the temperature dependence of the shear strength. A parallel correlation of the temperature functionality with the transfer behavior of the polymer during sliding has also been proposed.³ Below their T_g 's, the interfacial adhesion of the amorphous polymers PMMA, PS, and PVC does not appear to be as strong as the polymer itself. Consequently, there is no transfer of the polymer to the sliding counterface. Above T_g , the

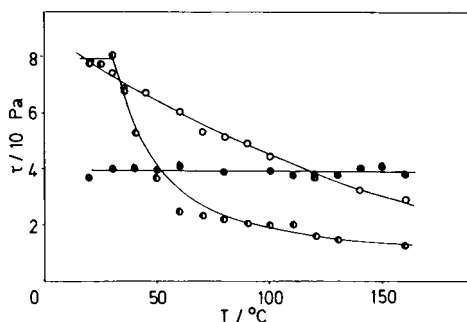


Fig. 3. The shear strength τ of films cast at room temperature as a function of temperature T at equilibrium. Contact pressure $P = 9.9 \times 10^7$ Pa. Sliding speed $= 2.4 \times 10^{-4}$ ms $^{-1}$. (\circ) PC film cast from ethanol (poor solvent); (\bullet) PC film cast from chloroform (good solvent); (\bullet) PVAC film cast from chloroform (good solvent).

TABLE V
Temperature Dependence of Interface Shear Strength in the Range 20–160°C. Response Type
Using "Good" and "Poor" Casting Solvents^a

	Good	Poor
PET	II	I
PVAL	II	I
PC	II	I
PVAC	II	II
IPMMA	II	I
IPS	II	I
IPMMA	II	I
PMMA	II	II
IPS	II	I
PS	II	II
PVC ^b	II	II
HDPE ^b		I
PTFE ^b		I

^a Type I: monotonic decrease of shear strength with increasing temperature (e.g., PVAL cast using poor solvent—Fig. 2). Type II: shear strength constant for $T < T_g$, type I behavior for $T > T_g$.

^b Solvent quality variable not examined. Data taken from Ref. 2.

interfacial adhesion is greater than the cohesive rupture strength of the polymer resulting in transfer. The latter case also applies to the semicrystalline polymers. The dissipation of energy occurs within the film itself when transfer occurs and at the substrate–polymer interface in the absence of transfer.

True interfacial sliding is thought to occur by a mechanism which has been likened to the continuous propagation of a brittle fracture.³ PMMA and PS are generally classed as brittle polymers at ambient temperature, which is consistent with this type of sliding. The sliding of a sphere over a flat surface is conducive to fracture phenomena. The maximum tensile stress occurs at the edge of the circle of contact, and a ring crack will be produced at a critical normal load.¹¹ The sliding process increases the tensile stress at the rear of the sliding sphere which reduces the critical load for tensile cracking. A series of parallel curved cracks may be formed in the wake of the indenter. Bethune¹² has observed the formation of such surface cracks when ball-bearing indentors were made to slide over bulk specimens of PS. The normal load necessary to cause cracking was reduced further by the presence of an active environment. Cracking phenomena were also observed with PMMA, PVC, and PC when immersed in liquid media. Although no direct evidence for surface cracks has been found in thin film shear, the work of Bethune suggests that fracture phenomena are possible in a sliding experiment particularly in the presence of solvents. A further comment on the temperature functionality of the shear strength may be made with reference to the bulk polymer literature. The yield stress of a bulk polymer falls monotonically with increasing temperature, approaching zero at the T_g . In contrast, the fracture stress of a polymer is less temperature-dependent, particularly at low temperatures.^{13,14} The shear strength dependence on temperature may not be directly identified with the yield or fracture stresses, which has been attributed to the very different conditions in thin film shear and bulk deformation experiments.¹⁵ It is, however, interesting that the fracture process is less temperature sensitive than the yield mechanism. This is consistent with the behavior of the

shear strength in true interfacial sliding and in shear within the film, respectively.

In the present study type II behavior was shown by PVAC, PMMA, and PS whereas both types were exhibited by the other polymers. The latter observation sets a precedent in that hitherto one temperature function was associated with each polymer. In particular, type I has now been observed for polymers whose T_g 's are within the temperature range of study. It is known that solvents tend to reduce the T_g of a polymer.¹⁶ The T_g of a polymer may be reduced below ambient temperature by suitable solvents. This would explain the observance of type I behavior in the polymers which possess a T_g at a temperature above ambient. Two arguments counter this possibility. First, the available evidence suggests that good solvents lower the T_g by a greater extent than poor solvents which is contrary to the observation of type I with poor solvent-cast films and of type II with good solvent-cast films. (Table V). Secondly, the transition in the type II behavior is close to that of the bulk polymer and is not lowered.

Initially the behavior of the IPS films appears to accord with the notion that the amorphicity of the polymer governs the temperature dependence of the shear strength. In studies of the crystallization of IPS from solution, it has been observed that the growth rate is 3 or more orders of magnitude greater in poor solvents.¹⁷ On the assumption that a casting solvent crystallizes a thin film by similar kinetics to the crystallization in dilute solution, the poor solvent-cast film would be more crystalline and would exhibit the type I temperature function whereas the good solvent cast film would be sufficiently amorphous to display the type II function (Table V). However, other evidence from the effects of solvents on bulk polymers¹⁶ suggests that good solvents produce a higher level of crystallinity than poor solvents. The observation of type I behavior in poor solvent-cast crystallizable polymer films is contrary to this form of crystallinity induction. It may be, however, that other factors are important, such as the ductility of the film. Kambour et al.¹⁸ studied the crazing and fracture properties of polymers in the presence of solvents. They observed the decrease of the T_g of PC by various solvents and the crazing propensity of the polymer. The crazing resistance decreased in proportion to the reduction of the T_g . A good solvent reduces the strain to craze of a polymer and independently induces a greater level of crystallinity than a poor solvent. More recently, Yaffe and Kramer¹⁹ have observed the growth of crazes at a much lower stress in certain environments than in air. They also remarked on the large difference in the microstructure and craze mechanical properties of PS films in poor and in good solvents. Although the craze morphology differs in thin films and in bulk specimens of a polymer,²⁰ the following discussion assumes that solvent-cast films may be understood by analogy with bulk polymers in liquid media. The influence of the *crazing propensity* rather than the *degree of crystallinity* on the temperature functionality is now considered.

Wellinghoff and Baer²¹ defined two types of amorphous polymer glass on the basis of their crazing behavior. Vinyl polymers such as PMMA and PS were observed to craze over all the temperatures from -195°C to their T_g 's. PET and PC, having flexible main chain links, exhibited considerable ductility and only crazed in a narrow temperature range just below their T_g 's. Bethune¹² similarly ranked PMMA and PS as brittle and PET as a tough polymer which suffers from plastic instability but is susceptible to environmental stress cracking.

The polymers PS and PMMA would be expected to show a brittle response independent of solvent. The current data reveal that these polymers show a type II function independent of the casting solvent quality, which is associated with a fracturelike dissipation of energy (Table V). PVAC also falls into this category, although it is not normally considered a brittle polymer. The proximity of the T_g to ambient temperature prevented the detailed exploration of the constant shear strength region of the type II function for this polymer. The high strain rates in the thin film shear experiment would, however, tend to favor a brittle response despite the low strain rate classification of this polymer as ductile. PET and PC are assumed to retain sufficient ductility when cast from a poor solvent so that yield occurs within the film itself. The casting of these films from a poor solvent would cause only a slight lowering of the T_g and a subsequent insignificant reduction of the strain to craze. The type I temperature function would then be characteristic. The casting of these films from a good solvent would lower the T_g and the strain to craze considerably. A fracture-type mechanism would be favored instead of plastic yield flow, resulting in a type II temperature dependence. It is envisaged that, by the time a reversible shear strength dependence on temperature is obtained, very little solvent would be retained. This is consistent with the location of the type II discontinuity close to the T_g of the "dry" bulk polymer. It is, nonetheless, probable that the good casting solvent confers a craze susceptible morphology prior to its evaporation. The other polymers of this study, PVAL, IPS, and IPMMA, are hypothesized to respond in a similar manner to PET and PC.

Finally, the form of the temperature dependence of the shear strength suggests that thin film shear is a stress-aided thermally activated process. The treatment of the data in terms of the logarithm of the shear strength and the reciprocal of the temperature leads to an estimate of the activation energy Q .⁴ The value of Q is of the order $10 \text{ kJ}\cdot\text{mol}^{-1}$ for type I behavior of a large range of organic polymers. Two values of Q are, however, typical of type II behavior. Below the T_g , Q is approximately zero and, above T_g , it takes on values in the range $10\text{--}30 \text{ kJ}\cdot\text{mol}^{-1}$.

Eyring Theory Applied to Thin Film Shear

The previous section indicates the thermally activated nature of the interfacial shear process. The Eyring approach may be developed further to generate an insight into the molecular nature of the deformation process. This model has been applied to plastic flow in polymers in terms of the movement of molecular segments over each other. The shear stress is given by

$$\tau = \frac{KT}{\nu} \sinh^{-1} \left[\frac{\lambda_1 h \dot{s}}{2\lambda KT} \exp \left(\frac{E + P\Omega}{KT} \right) \right] \quad (3)$$

for a single process where K is the Boltzmann constant, E is the activation energy, ν is the shear activation volume, Ω is the pressure activation volume, \dot{s} is the shear rate, h is Planck's constant, λ_1 is the separation of the molecular layers, and λ is the mean separation of equilibrium positions in the direction of motion.

A detailed description of the model and the definition of the parameters is given in Ref. 22. The model has been modified to account for the influence of the contact stress by the enlargement of the activation barrier through the term

$P\Omega$. This follows the treatment of Ward,²³ who allowed for the influence of hydrostatic pressure in the Eyring model. Equation (3) may be approximated in the extremes of $\tau\nu \gg KT$ and $\tau\nu \ll KT$. The correct approximation is not obvious since the value of ν is not known for polymer thin film shear. The two approximations of eq. (3) are given as follows:

$\tau\nu \gg KT$:

$$\tau = \frac{1}{\nu} \left[KT \ln \left(\frac{\lambda_1 h \dot{s}}{\lambda KT} \right) + E \right] + \frac{\Omega}{\nu} P \quad (4)$$

$\tau\nu \ll KT$:

$$\tau = \frac{\lambda_1 h \dot{s}}{2\lambda\nu} \exp \frac{E}{KT} \exp \frac{P\Omega}{KT} \quad (5)$$

It is evident that Eyring theory is able to predict the form of the empirical equations (1) and (2). At this stage eqs. (1), (2), (4), and (5) are used to permit a consideration of the volume changes occurring during the thermal treatment of a solvent-cast film. From eqs. (1) and (4) it is seen that

$$\alpha = \Omega/\nu$$

Alternatively, eqs. (1) and (5) provide as an approximation $\alpha \propto \Omega/\nu$. Following the arguments of Amuzu et al.²⁴ for the time-averaged conservation of volume, the volume of the mobile segment ν is equated to the sum of the instantaneous volume relaxation Ω and the available free volume Ω' . The physical identity of Ω and ν follows the interpretations given by Davis and Pampillo²⁵ and Haward and Thackray²⁶:

$$\alpha = 1 - \Omega'/\nu \quad \text{or} \quad \alpha \propto 1 - \Omega'/\nu \quad (6)$$

Equation (6) allows a crude interpretation of α in terms of the two volume parameters. It follows that the value of α is less than unity and attains a maximum value in a system which comprises large moving segments with little available free volume for their motion.

The parameter τ_0 may not be conveniently described in quantitative terms. It is a somewhat nebulous parameter which is determined by the nature of the intermolecular forces and the presence of orientation and order which in turn may be traced back to the magnitude of the internal energy and the entropy of the polymer matrix.

The Effect of the Casting Solvent and Thermal History on the Shear Strength Parameters

The effect of the thermal history above is considered in the case of HDPE (Table II). The heat treatment of HDPE films would not be expected to increase the degree of order since it is a semicrystalline polymer. The molecular freedom facilitated by a rise in temperature would only serve to weaken the HDPE matrix which may well be retained on cooling to room temperature, at least over the time period of experimental measurement. This is consistent with a decrease in τ_0 on heat treatment. The free volume of a polymer is constant below its T_g but increases linearly with a temperature increase above T_g .²⁷ The T_g of HDPE is controversial, but it would certainly be situated below the temperature range

of this study. The heat treatment of HDPE films will cause an increase in their free volume. On cooling, this increased volume will not be frozen in, but it may be partially retained over the period of experiment. The decrease in the value of α is then rationalized through an increase in Ω' .

The casting of a polymer film from a solution invokes a complication through the effect of the residual solvent in the polymer matrix. The exposure of films of the water-soluble polymers PVAL and PVP to different humidity atmospheres permits an exploration of solvent effects independently of heat treatment (although the films were initially heat-treated after casting). The exposure of these films to a high humidity environment results in an increase in the value of α and a negative value of τ_0 , indicating deviation from shear strength-contact stress linearity. On attaining equilibrium in air, the value of α was lower than at the commencement of exposure and τ_0 had become positive. A further period of treatment in a dry environment resulted in very little change in the shear properties of the PVAL film. These observations tend to indicate that films possessing a high proportion of solvent show a deviation from the linearity of eq. (1). It is interesting to note with reference to Tables II and III that the value of α for a PVAL film exposed to water and then dried in air is much lower than that obtained when such a film is heated in air. Indeed, the α value is more comparable with a chloroform cast film heated at 100°C for at least 24 h. A molecular explanation centers on the reswelling of the PVAL film by the water. The second evacuation of the water molecules without thermal treatment enables the retention of the swollen solvent volume without any volume contraction due to thermal ordering (see later). The free volume typical of the polymer matrix would thus be higher and as a result the α term is characteristically lower.

In a similar experiment a carbon-disulphide-cast PS film was exposed to carbon tetrachloride vapor in a dessicator and given the same heat treatment as followed its initial casting. The value of α increased to that typical of casting from carbon tetrachloride. These experiments indicate that the shear strength properties may be changed after casting and imply that a film may be effectively recast after exposure to another solvent or the same solvent. In the conventional fabrication of a thin polymer film, solvent casting followed by heat treatment is employed. The shear properties change through interacting solvent and thermal history effects. In the following paragraphs the salient features of the shear properties of this study are discussed drawing on the data in Table II.

Heat Treatment in Air

The heat treatment of films in air at a temperature close to the T_g of the polymer leads to a fall in the value of α . The intrinsic shear strength τ_0 is initially negative after little heat treatment and becomes more positive up to its equilibrium value (Table II). It is relevant to recall that morphology studies on a variety of solvent-cast thin films²⁸⁻³⁰ have shown an increase in the ordered regions following annealing treatments. The free volume and the number of entanglements and intergranular crosslinks would correspondingly fall.³⁰ The deviation from eq. (1) indicates the retention of the solvent, which is consistent with independent comments³¹ that solvent molecules have been detected in cast films many days after casting. The heat treatment of the films results in progressive removal of the solvent molecules as shown by restoration of eq. (1) lin-

earity. The vacation of the solvent molecules will provide additional free volume. The decrease in α may be explained in terms of an overall increase in Ω' [eq. (6)] caused by the vacated solvent volume exceeding the volume shrinkage due to thermal ordering. The decrease in the number of entanglements and crosslinks with annealing would be expected to weaken the polymer structure and hence τ_0 . The annealing of bulk and thin sheet polymers has been shown to cause an increase of the yield stress.^{30,32} A greater force is required to cause the relative motion of ordered regions which become better packed on annealing.³⁰ By analogy with deformation studies on bulk polymers an overall increase in the intrinsic shear strength τ_0 would be expected (Table II).

The exception to this trend is shown by PVAC which obeys eq. (1) after mild heat treatment and deviation after further heating. It is possible that the solvents used to cast PVAC films are easily removed and that prolonged heat treatment merely causes degradation. Further, the proximity of the T_g to ambient temperature suggests that the shear strength dependence on contact stress may be affected by a tendency towards liquidlike behavior at low contact stress. A deviation from yield stress–hydrostatic pressure linearity was observed in bulk specimens of PVAC which was attributed to the influence of the glass transition.³³

Solvent Quality

Films cast from poor solvents (high theta temperature) have lower values of α and τ_0 than films cast from good solvents (low theta temperature) when heat-treated in air at temperatures close to the T_g of most of the polymers. Good solvents are known to swell polymers to a greater extent than poor solvents.³⁴ The polymer/good solvent system comprises expanded entangled polymer molecules which entrap the solvent molecules more efficiently than the polymer in the presence of a poor solvent. In this way a greater volume of a good solvent cast film is occupied by solvent molecules which decreases the available volume and results in a higher value of α . The more entangled structure of a good solvent cast film conceivably influences its higher intrinsic shear strength.

Low Values of the Contact Stress Coefficient α

Heat treatment of films in a nitrogen environment at an elevated temperature (160°C) confers the lowest values of α . These films have comparable shear strength values independent of the quality of the casting solvent. The heating temperature is above the T_g of all polymers of this study and permits an increased molecular mobility. The free volume of the polymer increases above T_g ,²⁷ and this may be frozen in on cooling, particularly over the time scale of the experiments. Additionally, this elevated temperature would allow the removal of the majority of the solvent molecules which would further increase the available volume and lower α . The removal of the solvent and the corresponding molecular mobility at this temperature are consistent with a shear strength, which is independent of the casting solvent.

For the decalin-cast IPMMA films the lowest values of α are obtained by heating the films in air at 100°C. Similarly, IPS films cast from toluene possess higher values of α when they are heated at 160°C in nitrogen than when they are

heated at 100°C in air. It is likely that large amounts of these high boiling point solvents are trapped on casting and the closed nitrogen cell maintains a high vapor pressure at the film. The available free volume would therefore be less than in those cases where the solvent is completely removed. The higher values of α would then be anticipated.

Low Values of the Intrinsic Shear Strength

The lowest values of the intrinsic shear strength τ_0 are fabricated by a 160°C heat treatment in the case of PC, PS, IPS, and PMMA films. The lowest τ_0 values are obtained by heating a solvent cast film at 100°C in air for IPMMA, PET, and PVAL. The attainment of low values of τ_0 in some films after high temperature (160°C) heat treatment may be rationalized in terms of the retention of the weaker structure, which is typical of a polymer at temperatures above its T_g . The four polymers which attain their lowest τ_0 values after heating at 160°C all possess a T_g in the range 100–150°C. Thus the 160°C treatment temperature will permit the rearrangement of the molecular structure unlike the air treatment temperatures of 100–130°C which are at or below the T_g 's. The polymer films which attain low values of τ_0 after 100°C heat treatment possess low T_g values (50–70°C). A temperature of 100°C is therefore high enough to allow mobility in the films in the low T_g polymers. In fact their treatment at 160°C gives higher values of τ_0 , which may result from the greater temperature drop before vitrification occurs. A correspondingly longer time interval is available for reordering of the polymer structure prior to its being frozen in at the T_g .

Degradation Effects

Heat treatment of films in air at 160°C results in different values of the shear strength compared to those of films heated in a nitrogen environment. This evidence tends to suggest the occurrence of degradation at high temperatures. The shear strength dependence on the contact stress of PVAC films becomes increasingly nonlinear with progressive heat treatment in air, although linearity is observed when a nitrogen medium is used. A nonlinear contact stress dependence of the shear strength is typical of both solvent-containing and degraded films. Similar conclusions are afforded by the behavior of chloroform-cast PVAL films.

Low Temperature Casting of Films

The casting of films at a low temperature results in low shear strength parameters, although the experiments were restricted to PMMA and the polystyrenes. The casting of films at a low temperature directs the polymer-solvent systems nearer to their theta points. This would be expected to confer properties typical of poorer quality solvents. These films do, however, achieve their low shear strength properties without thermal treatment. This suggests that the vacuum system largely removes the solvent molecules in the same way as heating and cooling.

The low values of α are explained by the large free volume vacated by the weakly entrapped solvent molecules. The low values of τ_0 result from a paucity

of entanglements at a low temperature near the theta point. The value of τ_0 does not approach the low value facilitated by mobility above the T_g , but it is lower than the ordered molecular structure of films heated at 100°C. This statement is illustrated by the case of IPS films cast from carbon disulphide (Table II). It is also apparent that low shear strength films are possible using decalin as a casting solvent at low temperature whereas ambient casting and thermal treatment in a nitrogen environment is ineffective.

The above considerations of the available free volume in a film and its relationship to the constant α have assumed that the shear activation volume ν is constant [eq. (6)]. The available evidence suggests that the value of ν depends on the degree of cooperative motion in the flow process.³⁵ It would be expected that the polymer molecules are widely spaced in a heavily solvated network and that the deformation process is localized, resulting in a low value of ν . The removal of the solvent would increase the degree of cooperative motion with a consequent rise in ν . This is consistent with a decrease in α on the removal of the solvent.

The trends in the thin film shear properties may be due to some extent to the influence of the casting process and the presence of a substrate. It would be misleading to rigidly compare the data of Table II with the yield and morphology of bulk polymers and their solvent interaction. Films cast on rigid substrates suffer from internal stress which develops during solvent removal and thermal treatment. Cooling films from above their T_g also introduces tensile stresses due to a contraction of the polymer.³⁶ The latter effect would tend to lower the intrinsic shear strength of the nitrogen environment heat-treated films, in keeping with the experiment. Subsurface discontinuities have been observed in cast PS films particularly when rapid evaporation of the solvent occurs,³⁷ which would tend to weaken the films. The use of high boiling point solvents, particularly when their evaporation is hindered in a nitrogen cell, tends to produce high intrinsic strength films, which indicates that some stress-relaxation may be operating to improve the strength of these films.

A Molecular Topography Approach to the Adhesion Component of Friction

Earlier experiments on the frictional properties of polymers have indicated that molecular topography is instrumental in determining the shear strength and hence the adhesion component of sliding friction. [Sliding friction may be considered to a good approximation as being of two kinds: interface shear and gross bulk deformation. The distinction is not precise, but the former corresponds to local deformation at the interface (adhesion component) and the latter to large subsurface deformation (deformation component).] The substitution of the hydrogen atoms in polytetrafluoroethylene with bulky chlorine groups was observed to cause an increase in the polymer friction.³⁸ A comparison of the shear properties of the poly(*n*-alkyl methacrylates) revealed that the shear strength increased with the size of the pendant alkyl group.²⁴ The different tactic forms of polystyrene and poly(methyl methacrylate) provide a further means of evaluating molecular "roughness" as an influence in polymer friction.³⁹ The IPS and IPMMA molecules comprise a helical conformation of the carbon backbone which form a smooth profile leading to easy shear of the polymer. The

PS and PMMA molecular structure is irregular, and a molecular interaction approach to shear would predict high shear strength properties. The data of Table II indicate that high and low shear strength properties are possible with both the atactic and isotactic isomers. Under similar fabrication conditions the IPS films do not have significantly lower shear strengths. A similar conclusion is afforded by a comparison of the films fabricated at low temperature. The IPS films were cast under conditions which are known to cause gelation.³⁹ The IPS gel structure is fibrillar in profile and a low shear strength would be anticipated. In practice, these films have similar shear strength properties to PS and PMMA films cast under similar conditions and to some ambient cast films.

The evidence suggests that the molecular topography has at most a second-order effect on the shear strength in solvent-formed films. The fabrication procedure plays a dominant role in determining the frictional properties of a thin film.

The Deviation from Shear Strength-Contact Stress Linearity

The shear strength dependence on the contact stress has been found to obey eq. (1) in the majority of thin film experiments. In almost all cases, deviation from this linear equation was observed with as-made or lightly heated films and also with those which had been subjected to a high temperature treatment in air. These data are better described by eq. (2). The derivation of eqs. (1) and (2) according to Eyring theory has been described earlier. A comparison of eqs. (2) and (5) yields

$$\bar{\alpha} = \Omega/KT$$

In this way the pressure activation volume Ω may be estimated (Table VI). The values of Ω are given in Table VI together with some estimates of the quantity from rather different experiments described in the literature. It must be emphasized that Ω takes on a different meaning in thin film shear and bulk yield. In bulk systems Ω is the hydrostatic pressure activation volume whereas in thin film shear it is a uniaxial contact stress activation volume. In a simplistic approach the pressure activation volume is approximately three times greater in the bulk than in thin film shear. With this factor the values of Ω in Table VI are in close agreement for a given polymer for thin film and monolithic shear.

In the Eyring description of thin film shear a change of applicability from eq. (4) to eq. (5) would be caused by a decrease in the value of $\tau\nu$ relative to KT . In the room temperature experiments KT takes on the constant value of 3.8×10^{-21} J. The value of ν varies from the order 4700 \AA^3 in isotropic bulk yield experiments^{29,40} to 17 \AA^3 for the yield of highly drawn specimens of HDPE.³⁵ The product $\tau\nu$ thus varies from 10 to 0.1 of the product KT for $\tau = 10^7$ Pa. Since thin films tend to be highly oriented, a low value of ν would be expected for thin film shear. The presence of a large proportion of solvent would be expected to lower ν , as described earlier. This is consistent with the better fit to the data of the $\tau\nu \ll KT$ approximation [eq. (2)] in these circumstances.

The inadequacy of a "single Eyring process" description of yield has long been indicated. Some analyses have used a two-process Ree-Eyring model⁴¹ to describe the yield of bulk polymers. Typically, one process is dominant at low strain rates and another is superimposed at high strain rates.⁴² It is noteworthy

TABLE VI
Pressure Activation Volume of Eyring Theory [Eq. (5)] for Thin Film Shear and Bulk Polymer Deformation, Respectively^a

Polymer	Activation volume (Å ³)	
PMMA	59 (177)	Thin film shear
	100	Bulk polymer extrusion (Ref. 44)
PC	85 (255)	Thin film shear
	150	Bulk yield (Ref. 40)
PVAL	57 (171)	Thin film shear
PET	29 (78)	Thin film shear
PS	79 (237)	Thin film shear
PVAC	27 (81)	Thin film shear
HDPE	{ 55 (165)	Thin film shear
	{ 38 (114)	
	225 I	Bulk yield (Ref. 42)
	105 II	Two-process Eyring theory; Contribution (II) applies at high strain rates
	344	Bulk yield (Ref. 40)

^a The equivalent hydrostatic pressure activation volume for thin film shear is given in parentheses.

that the high strain rate contribution is characterized by a lower value of ν . A similar trend is revealed in the application of single process Eyring theory to the yield of PMMA films at different strain rates.²⁹ This evidence tends to suggest that eq. (5) should be the better approximation in describing thin film shear. The more general validity of eq. (2) in describing the data of this study would support this argument. The use of eq. (5) to describe data which is adequately described by both eqs. (1) and (2) allows further calculations of Ω , which are listed in Table VI.

The physical meaning of the parameter Ω has recently been discussed by Tabor.⁴³ For a wide range of hydrocarbon materials it has a value between 50 and 100 Å³. It was speculated to correspond to a trans-gauche rotation of a C—C bond or to a crankshaft motion. The values of Ω accumulated in Table VI from the application of eq. (5) show that similar values are obtained in thin film shear.

CONCLUSIONS

The experimental determination of the shear strength properties of thin polymeric films reveals that the magnitude of the energy dissipated or of the frictional force may be varied over a wide range by the judicious choice of the casting solvent and the thermal treatment of the film. The molecular architecture has at most a second-order effect on the shear properties. The shear strength properties do, however, only apply in the absence of further heat treatment and exposure to active environments. In particular, the effect of long term aging of the films on their properties has not been studied.

The linear dependence of the shear strength on the contact stress has been found to apply to virtually all of the films. The retention of solvent and degradation do, however, lead to a deviation from linearity. A dependence of the shear

strength on the exponent of the contact stress has been found to describe all the data of this study. The description of polymer thin film shear as a stress-aided thermally activated process allows the application of Eyring theory. This approach predicts the dependence of the shear strength on the contact stress as a linear or an exponential relationship depending on the magnitude of the shear activation volume. The contact stress coefficient of shear strength has been related to the free volume in the film for a number of fabrication conditions. The pressure activation volume has also been calculated and compared with the experimental predictions, in the Eyring approximation of very small shear activation volumes. The validity of the exponential contact stress dependence of shear strength implies that at ambient temperature the shear activation volume is very much less than 400 \AA^3 .

The effect of the temperature variable is complicated by the effect of this particular thermal history on the shear strength. A reversible shear strength dependence is attainable over a fixed temperature range. The present data fall into two categories, as observed in previous studies. The functionality was formerly associated with the degree of crystallinity, and this is in fact consistent with the response of thin films of isotactic polystyrene with reference to the solution properties of this polymer. A more widely applicable explanation involves the location of the shear zone in the polymer film. True interfacial sliding is thought to occur in a fracture type process and involves a shear strength, which is virtually temperature-independent below the T_g . This behavior is observed in films of brittle and embrittled ductile polymers. The casting of films of ductile polymers is proposed to lead to embrittlement when good solvents are used since they reduce the strain to craze of the polymer. Films of ductile polymers are not embrittled by poor casting solvents, and therefore shear occurs by plastic yield and flow within the polymer film. In these cases the shear strength falls monotonically with increasing temperature. Above the glass transition the shear strength of all polymers falls with increasing temperature corresponding to shear within the film. For brittle and embrittled polymers, the shear zone moves from the interface to within the film at the glass transition, resulting in a transition in the shear strength dependence on temperature.

The thin film shear experiment permits the evaluation of the deformation character of the polymer under vastly different conditions than are available in conventional mechanical property tests on bulk specimens. The effects of solvents and thermal history on the polymer response have been individually and jointly examined. In many cases the thin film response may be predicted by extrapolating the behavior of bulk polymers to extremes of orientation and high strain rate. Mechanical properties have been associated with the many morphologies described in independent studies of the structure of solvent-cast thin films which have been given various heat treatments. The available data on the response of bulk polymers to temperature, solvent, and thermal history variations have been used to indicate the energy dissipation mechanisms in the adhesion component of polymer friction. The present data and these comparisons indicate the film morphology as conferred by the casting solvent and modified by heat treatment and exposure to solvents has a pronounced effect on the rheology of the film. The resulting ductility of the film has a major influence on the variation of the shear strength with temperature. The pressure dependence of the shear strength indicates the importance of the magnitude of the free volume and affine character of the film.

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