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The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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To cite this Article Vera, Richard , Baer, Eric and Fort Jr., Tomlinson(1974) 'The Effects of High Contact Pressures and Temperatures on the Adhesion of Amorphous Polystyrene to Borosilicate (Pyrex) Glass', *The Journal of Adhesion*, 6: 4, 357 – 375

To link to this Article: DOI: 10.1080/00218467408075038

URL: <http://dx.doi.org/10.1080/00218467408075038>

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The Effects of High Contact Pressures and Temperatures on the Adhesion of Amorphous Polystyrene to Borosilicate (Pyrex) Glass[†]

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(Received August 7, 1972)

The effects on adhesive joint strength of four pressure-temperature histories, each over the range of pressures from 1 to 1500 bars and temperatures from 25 to 200°C, has been investigated with polystyrene-Pyrex glass butt joint specimens. The various pressure-temperature histories were designed to show the separate effects of permanent stresses, transient stresses and interfacial contact on joint strength. This strength increased as the number of stress concentration loci were reduced through application of high contact pressures on the melt. However, isobaric solidification of the polymer led to a maximum in fracture stress as a function of applied molding pressure because of the existence of a critical pressure at which permanent thermal stresses were minimized. A series of isothermal compression-decompression molding operations showed fracture stress to increase with interfacial contact area until maximum contact was achieved. A 100 per cent gain in bond strength was realized when interfacial contact was maximized concurrent with minimizing both the permanent and transient stresses which normally develop when the adhesive joint is formed. Microscopic observations of interfaces in both non-fractured and fractured butt joints established a qualitative relationship between debonding, the mechanism of fracture, and joint strength.

[†] Presented, in part, at the National Meeting of the American Chemical Society, Boston, Massachusetts, Spring 1972.

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I. INTRODUCTION

A conservative estimate of the molecular forces involved in the adhesion of polymers to adherend surfaces leads to bond tensile strengths considerably above those realizable in practice.^{1,2} This difference has long been explained by the occurrence of minute imperfections and the development of stresses at the bonding interfaces.³ The imperfections are caused by poor wetting and/or weak boundary layers. The stresses result from two factors. One is the differential contraction of adhesive and adherend when the adhesive solidifies. The second is the unequal deformation experienced by the two materials when they are subjected to external loading.

Among the principal methods now used to minimize these strength weakening factors are protection and cleaning of the adherend surfaces, promotion of spreadability of the adhesives, use of fillers to reduce shrinkage, optimization of the adhesive film thickness and coupling agents to promote adhesion.^{4,5,6} The first two of these methods work directly against the occurrence of interfacial defects. Methods three and four reduce interfacial stresses caused by adhesive contraction. Method five helps to strengthen imperfect joints. None of these methods is completely effective.

Through study of the dependence of specific volume^{7,8} (V_s) of amorphous polymers on pressure and temperature it was observed that, though this parameter is a function of the history of the sample, the normal thermal expansion of both glassy polymers and their melts can be suppressed by application of high pressures. High pressures should also force more complete contact of a polymer adhesive with an adherend surface.^{9,10} Both factors should improve adhesive bond strength. Application of high molding pressures thus appeared to be a promising new route to improved adhesion.

This idea has been explored by subjecting amorphous polystyrene-Pyrex glass butt joint specimens to four basic pressure and temperature histories (cycles) with the following objectives:

- 1) minimize the interfacial stresses produced by differential contraction of adhesive and adherend through proper application of temperature and pressure;
- 2) minimize the development of flaws by forcing contact of the polymer with the Pyrex glass surface;
- 3) establish the principles involved in order to predict the behavior of other adhesive systems.

The butt joint specimens were tested in uniaxial tension. Type of fracture and extent of interfacial stresses before fracture were characterized with the aid of optical and scanning electron microscopes. Additional tests were

conducted to determine the influence of three pressure-temperature histories on the tensile strength of the pure polymer to better explain the behavior of the butt joint specimens.

A unique feature of this work is the use of different combinations of temperature and high pressures (up to 1,500 bars) to improve adhesive joint strength. Upon maximization of interfacial contact and minimization of changes in specific volume during setting of the adhesive polymer, increases in joint strength of 100 per cent were finally achieved.

II. EXPERIMENTAL

A. Materials

The thermoplastic used as adhesive was anionic polystyrene (PS) (Dow Chemical Company, Midland, Michigan). It was described as free of additives and with $M_w = 256,000$ and $M_w/M_n = 1.2$. The adherend was borosilicate glass, known as Pyrex glass or B-glass, in the form of rod 6.0 mm in nominal diameter (Corning Glass Works, Corning, New York).

B. Sample preparation

The polymer was purified using a fractionation technique,¹¹ vacuum dried at 80°C, ground, and redried at 75°C in vacuum to constant weight. Differential thermal analysis showed no crystallinity and the glass transition temperature (T_g) to be 100°C. Intrinsic viscosity measurements indicated $M_v = 251,000$.

The Pyrex glass rod was carefully selected and circumferentially indented at regular intervals with hydrofluoric acid solution, then fire polished and properly annealed.¹² Each rod was cut between indentions with a 6 mils thick diamond wheel (Elgin National Watch Company, Elgin, Illinois). The end surfaces of the Pyrex glass pieces were both ground 0.5 mm down and polished with silicon carbide powder up to grit number 3000 according to a Buehler procedure.¹³ Edges were protected during these operations by coating and at the same time fixing the side surfaces of the glass pieces to the polishing holder with Crystal Bond Resin 509 (Aremco Products Incorporated, Briarcliff Manor, New York). After dissolving the resin the cylinders were washed in distilled water, soaked briefly in hydrofluoric acid solution and thoroughly washed again in distilled water. Finally, they were vacuum dried at 200°C and put in a desiccator for further use. A micrograph of the bonding surface of a prepared rod is shown in Figure 1.

The butt joint specimens were premolded before exposing them to high pressures and temperature to the configuration shown in Figure 2. A minimum temperature of 160°C was required for a casting force equivalent to one bar

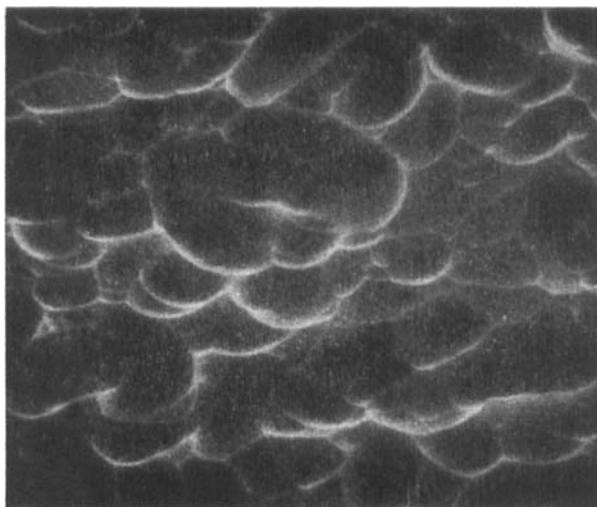


FIGURE 1 Micrograph of a prepared Pyrex glass bonding surface (2000X).

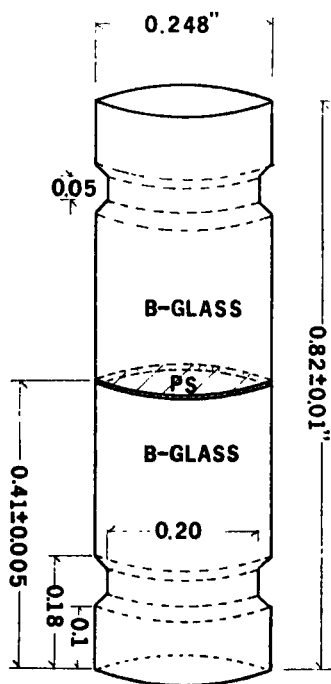


FIGURE 2 Diagram of a Pyrex glass-polystyrene-Pyrex glass butt joint specimen.

under vacuum. The tolerances required by ASTM Procedure D 2094-69 were kept by molding the polystyrene between the end surfaces of the Pyrex glass pieces in a tight cast.

After determining the effect of thickness of the polymer film on joint tensile strength, a constant value of 0.25 ± 0.02 mm was chosen for all specimens to be exposed to pressure-temperature (P-T) experiments.

For conducting the high P-T experiments, a high pressure dilatometer made by Baer and Kardos¹⁴ proved to be practical with the following modification in the technique. To avoid starvation of the polymer at the bonding surfaces all specimens were sealed in 1 mil thick aluminum foil to fit tightly in the bore of the cell. Besides avoiding starvation, the seal permitted smooth extraction of the specimens after the experiments.

Cylinders of pure polystyrene were molded under vacuum at 160°C and exposed to the same P-T histories to which butt joints were subjected. The specimens were then machined on a lathe and polished with 3.0 μ diameter cerium oxide powder.

C. Pressure-temperature cycles

The P-T histories or cycles to which the specimens were subjected are:

Cycle I Figure 3a. The specimen is compressed at room temperature T_r , line AB. Temperature is raised keeping constant pressure to a temperature T_i equal to the corresponding T_g , point E plus 30°C,

$$T_i = (T_g)_p + 30^\circ\text{C}$$

at an average rate of 15°C/hr, line BCD. After 2 hours at point D (holding time) cooling at room temperature takes place at the same rate, line DEF, and the specimen is released from pressure, line FG. The experiment is repeated at different pressures with other specimens.

Cycle II Figure 3b. The specimen is heated at atmospheric pressure to a temperature T_i , line AHL. Compression takes place, line ID, and these conditions are kept for the holding time, point D. The specimen is cooled to T_r , line DEF, and pressure brought to zero, line FG.

Cycle III Figure 4a. The path is similar to that in Cycle II to the point D then pressure is brought to zero at constant temperature T_i , path DI. After 1 hour at point I cooling takes place at atmospheric pressure, path IHA.

Cycle IV Figure 4b. The specimen is heated at atmospheric pressure to a temperature T_i greater than T_g such that upon compression, line ID', the volume of the liquid is equal to that of the solid at atmospheric conditions. Then the specimen is brought to the original point A by decreasing the pressure and temperature in such a way that volume remains unchanged, path D'A.

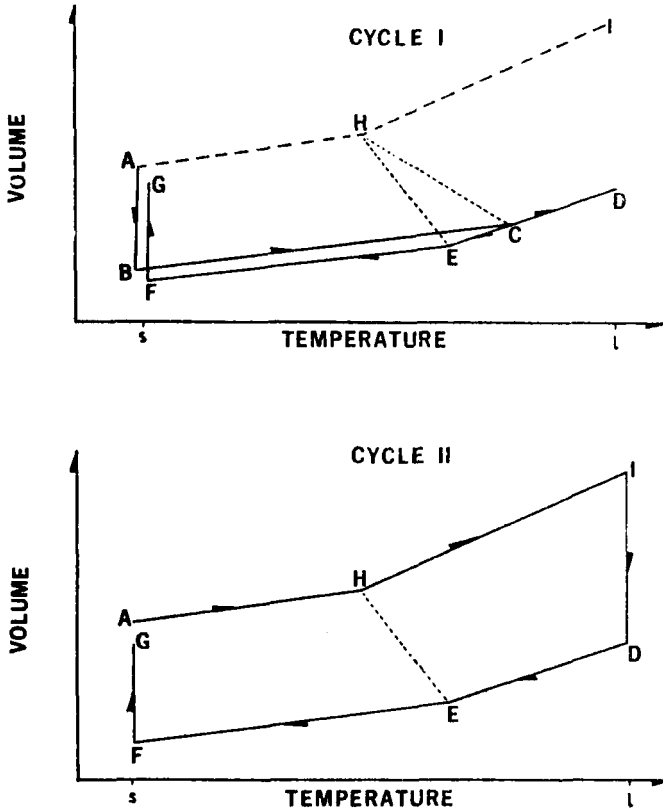


FIGURE 3 Pressure-temperature history diagrams for (a) Cycle I and (b) Cycle II.

D. Mechanical testing

All mechanical tests were made in uniaxial tension with the aid of an Instron Universal Instrument, Model TT-CM-L (Instron Engineering Company, Canton, Massachusetts) following ASTM Procedures D 2095-69 and D 638-68 for butt joints and polystyrene, respectively. Strain rate was always 0.2 inches per minute. Gripping of butt joints for the tensile tests were achieved by fitting carefully machined tapered hollow cylinders of aluminum to each Pyrex glass piece so that specially designed jaws could hold the specimens properly.

Each reported fracture stress is the average of at least four determinations. Precision of the measurements made on the butt joint specimens was better than ± 150 psi and precision of the measurements made on the pure polystyrene samples was better than $\pm 4\%$. The stress-strain curve was always essentially linear up to the fracture point.

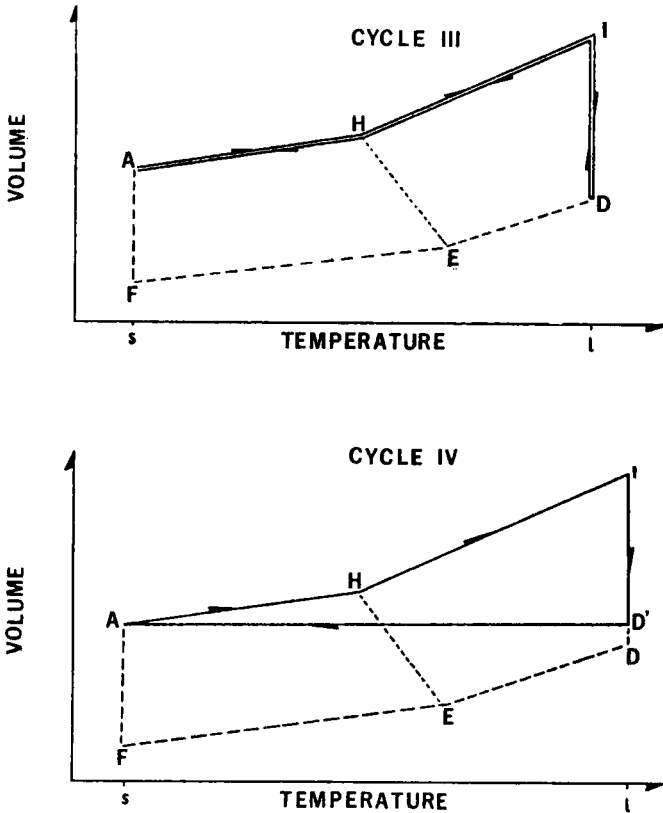


FIGURE 4 Pressure-temperature history diagrams for (a) Cycle III and (b) Cycle IV.

E. Fractography

To estimate the extent of polystyrene-Pyrex glass debonding caused by residual stresses, some butt joint specimens were prepared using non-indented Pyrex glass cylinders. The specimens were subjected to the different P-T histories at selected contact pressures. These specimens were not subjected to mechanical tests. Instead, the bonding interfaces were observed in a Reichert Wien Optical Microscope (Reichert Optical Company, Vienna, Austria) by passing an incident beam of monochromatic light through one of the end surfaces of the specimen and focusing on an interface through the opposite end surface. Debonded regions could be distinguished by their poor light transmittance.

To obtain information about the locus of failure, fracture surfaces of samples which had been subjected to mechanical testing were examined with a M.A.C. Model 700 Scanning Electron Microscope (Materials Analysis Company, Palo Alto, California).

III. RESULTS AND DISCUSSION

A. Preliminary experiments

Preliminary tests were conducted to determine the best methods for preparing the Pyrex glass adherend cylinders, minimizing entrapped air in the polymer adhesive layer, and gripping the butt joint specimens during mechanical testing. Investigation of the dependence of joint strength on the thickness of the adhesive layer was also undertaken.

Previous annealing and edge protection of the Pyrex glass pieces during grinding and polishing were found necessary to obtain crack-free surfaces. Omitting either of these steps led to failure in the Pyrex glass and/or a marked reduction in joint strength. Entrapping of air in the polymer layer also reduced joint strength but this defect could be avoided by premolding under vacuum.

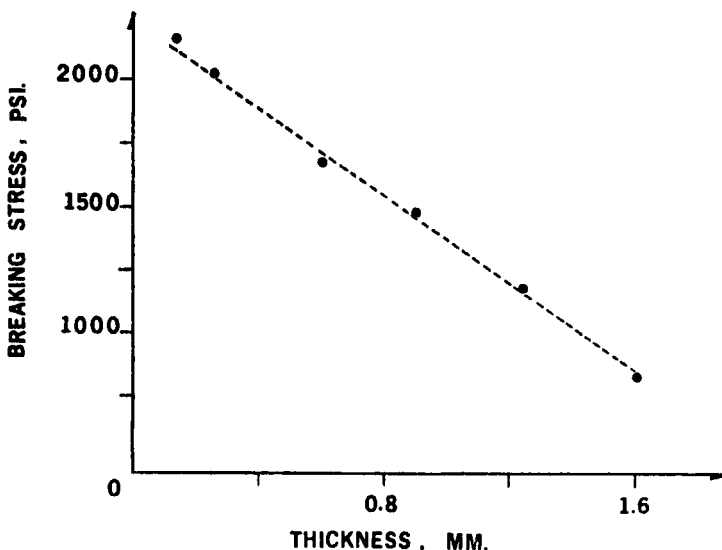


FIGURE 5 Plot of tensile strength of control butt joints as a function of thickness of the adhesive layer.

Butt joint specimens having a polymer layer thickness, t , of 0.01 inches yielded a tensile strength, σ_{ff} , maximum of 1100 psi when molded at 160°C and 1 bar in presence of air while σ_{ff} of those molded under vacuum at the same temperature was 2000 ± 150 psi. This latter value is referred to here as the strength of the control joint.

The decrease of joint strength with thickness of the adhesive layer, t , has been extensively studied.^{2, 15-17} A decay in strength of control joints with thickness equal to 20,000 psi/in. was observed in this work and is shown in Figure 5. This value is of the same order of magnitude as reported by Meissner

and Merrill.¹⁶ Kraus and Manson² reported a minimum variation in the strength of polystyrene-steel butt joints at an adhesive layer thickness of 0.01 inches. Based on these observations and also on the fact that the line in Figure 5 lost its linearity at values of t below 0.0075 inches, a thickness of 0.010 inches was chosen for all further experiments.

B. Effects of molding history on fracture stress

1. *Butt joints subjected to Cycle I and Cycle II* First studies of the effects of molding history were designed to establish that high pressures could, indeed, affect joint strength. A second objective was to establish whether application of pressure before (Cycle I) and after (Cycle II) melting the polymer had equivalent effects. The effect of pressure on σ_{fj} of the butt

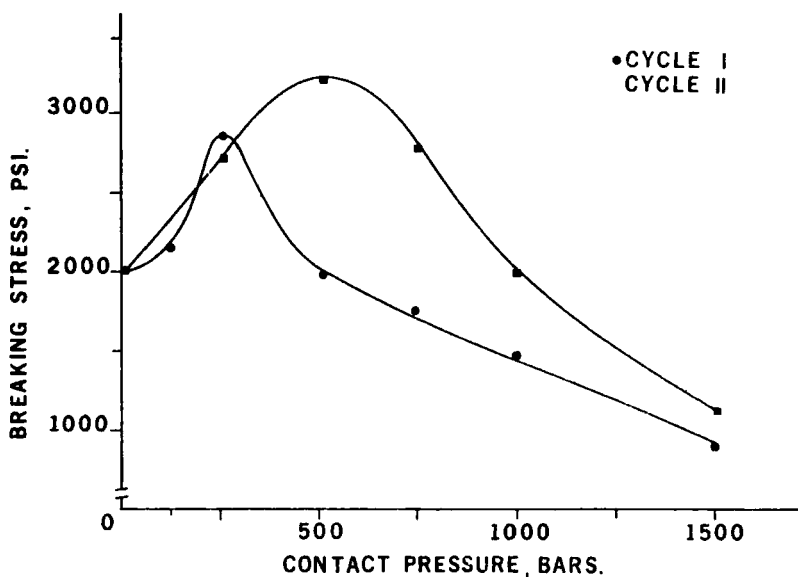


FIGURE 6 Plot of tensile strength as a function of molding pressure for butt joints prepared according to Cycle I and Cycle II.

joint specimens subjected to these cycles is shown in Figure 6. A maximum in σ_{fj} as a function of contact pressure was observed in both cycles. In Cycle I this maximum appears at 250 bars and in Cycle II at 500 bars with respective increments in σ_{fj} of 40% and 60% in comparison to the control. After the maximums σ_{fj} falls below that of the control.

The appearance of a maximum in σ_{fj} as a function of contact pressure cannot be explained simply in terms of changes in contact areas since as pressure increases more contact of the polystyrene with the Pyrex glass surface

should occur. Neither does the effect of pressure on the thermal expansion coefficient, α , of the polymer provide a complete answer because the α 's for both the polymer melt and glass decrease monotonically as pressure increases. An explanation can, however, be made in terms of the total volume change experienced by the polymer as it is cooled from the corresponding T_g to room conditions. This total volume change, ΔV_s , is given by:

$$\Delta V_s = V_E - V_G$$

where V_E is the specific volume of polystyrene at its T_g under pressure and V_G is the specific volume at room conditions. It will be shown that conditions for minimization of this volume change correspond exactly to conditions of maximum joint strength. It is assumed, in establishing this relationship, that no significant stresses develop at temperatures above T_g . Also, the Pyrex glass is assumed to be ideally rigid in comparison with the polystyrene.

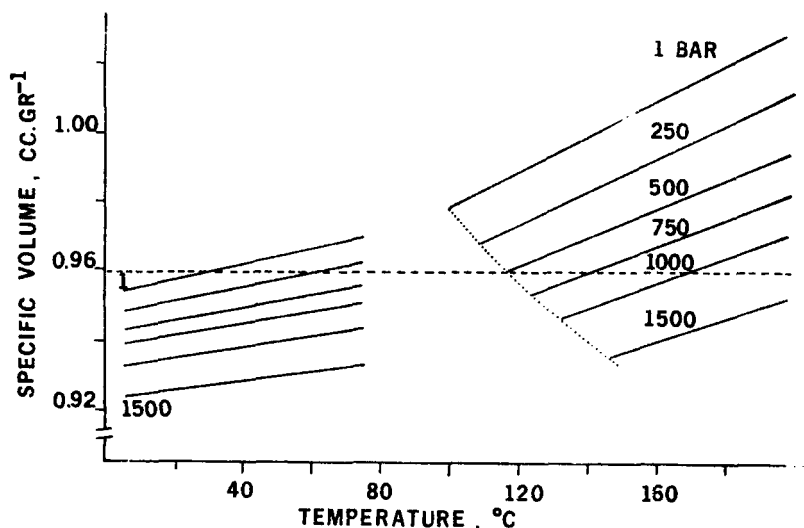


FIGURE 7 Plot showing specific volume of polystyrene as a function of temperature at different constant pressures.

The specific volume of polystyrene at room conditions can also be attained at higher temperatures under pressure. This fact is illustrated in Figure 7 by the intersection of the horizontal dashed line with the high pressure isobars. (The isobars are reproduced from the data in reference 7.) This intersection is very close to T_g for the 500 bars isobar. The dependence of ΔV_s on pressure is illustrated in Figure 8. The solid line in this figure corresponds to the absolute values of ΔV_s . As pressure increases ΔV_s decreases initially until it reaches zero at 550 bars, then it increases in absolute value. The molding pressure where ΔV_s is zero corresponds to the maximum fracture stress of

butt joints subjected to Cycle II. This fact is in accord with previous studies of classical adhesive systems^{6, 16} which have shown that the less the contraction of the adhesive the less the residual stresses and the greater the joint strength.

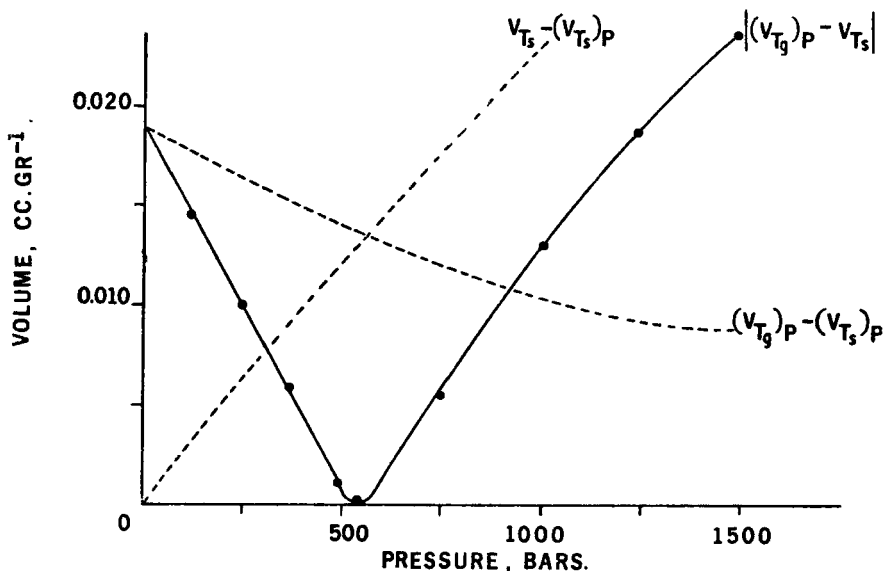


FIGURE 8 Plot showing changes in specific volume of polystyrene occurring from the glass transition temperature to room conditions according to Cycle I and Cycle II.

ΔV_s is the result of two volume changes. One occurs upon cooling at constant pressure, path EF in Figures 3a and 3b, and the other upon decompression at room temperature, path FG.

$$\Delta V_s = (V_E - V_F) + (V_F - V_G) = V_E - V_G$$

where V_E , V_F and V_G are the specific volumes of polystyrene at points E, F and G in Figure 3. The first of these volume changes is illustrated in Figure 8 by the dotted line with negative slope, the second volume change is given by the dotted line with positive slope. The greater of these two volume changes at a given pressure, represented by a line following the upper profile of the two dotted lines, causes the greater stresses. This upper profile also shows a minimum at 550 bars, given by the intersection of the two dotted lines. The volume changes represented by the dotted lines are, of course, only transients and will permanently effect the adhesive joints only if they somehow lead to permanent flaws or stresses in the adhesive layer. Evidence that these transients caused flaws and, therefore, a reduction in joint strength is given below.

The maximum fracture stress of butt joints subjected to Cycle I was lower than that of joints subjected to Cycle II. It is shown below that the difference was caused by cracking of the glass when specimens were subjected to the former molding procedure.

2. *Butt joints subjected to Cycle III and Cycle IV* Two more types of P-T histories were studied. Cycle III was designed to show the pure effect of interfacial contact on joint strength. Under this cycle the thermal contraction of the polymer is not affected because the applied pressure is released before solidification of the polymer takes place. Cycle IV was designed to show the effect on joint strength of maximization of interfacial contact concurrent with suppression of volume changes, including transients, in the polymer adhesive layer. Tensile strength of the butt joints subjected to these cycles is shown in Figure 9. In both cycles σ_{fj} increased initially with contact pressure, then remained constant above 500 bars in Cycle III and above 600 bars in Cycle IV, with respective increments in σ_{fj} of 37 and 100%.

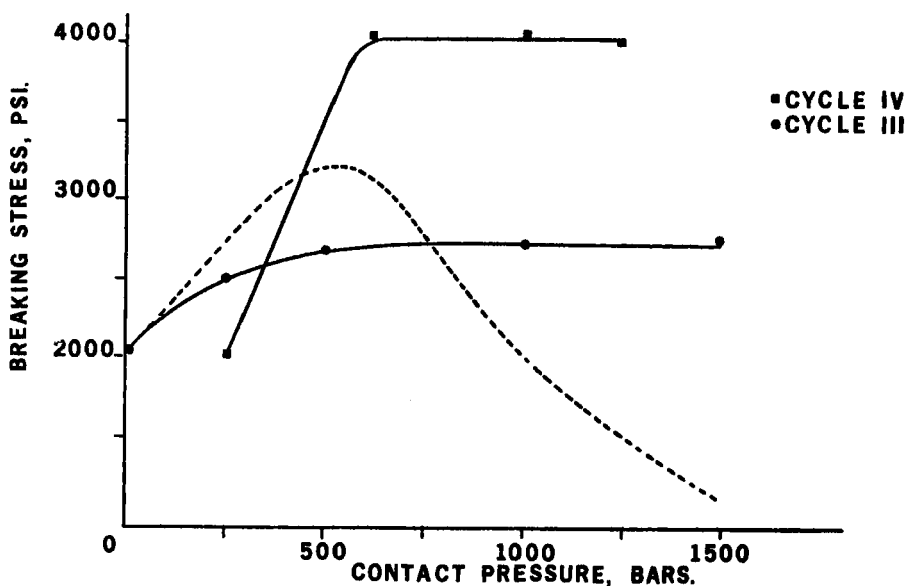


FIGURE 9 Plot showing tensile strength as a function of molding pressure for butt joints prepared according to Cycle III and Cycle IV (solid lines) and Cycle II (dashed line).

The shape of the curve in Cycle III indicates that contact area increases with pressure until it reaches its greatest value at 500 bars. Other investigators^{1, 18, 19} have reported similar curves to that for Cycle III, although their experiments were made under similar conditions to Cycle II. The

pressures they used (up to 50 bars) were low enough to affect only contact area. While Bikerman¹ reports that adhesion to glass still increases at 50 bars, Ponds¹⁸ and Wolock¹⁹ found that above 30 bars adhesion to glass is independent of pressure. The much higher (500 bars) pressure required to achieve the greatest fracture stress in the present work may be due to differences in the glass used or to differences in the methods of preparing the glass surfaces for study.

The graph of σ_{fj} vs. pressure for samples subjected to Cycle IV shows that maximum bond strength for the system studied here is achieved if complete contact of the polymer melt with the Pyrex glass is achieved by application of high pressure and pressure and temperature are then simultaneously decreased in such a way that the specific volumes of the polymer melt and glass are always equal to the specific volume of the polymer at room conditions. Such a process avoids the occurrence of the volume change transients discussed above and is responsible for the higher maximum fracture stress observed for Cycle IV than for Cycle II.

Other features of the data from Cycle IV also need comment. These are the low fracture stress of the samples subjected to contact pressures of 250 bars and the indication in Figure 9 that maximum fracture stress in Cycle IV is not achieved at contact pressures below 570 bars. Both these features result from the fact that the conditions of pressure and temperature necessary to keep constant volume in Cycle IV are such that below 570 bars the polystyrene is below its glass transition temperature as shown in Figure 7. At 250 bars the temperature to keep specific volume constant is 54°C, well below T_g . Good contact of the polymer with the Pyrex glass was not achieved, and no increase in σ_{fj} was observed. But at 600 bars the temperature to keep specific volume constant is 20°C above the T_g at atmospheric pressure and the polymer could easily be made to contact the Pyrex glass. Then, fracture stress increased by 100%.

From the pressure where the line for Cycle IV in Figure 9 intersects that for Cycle II to 570 bars the polymer is in the transition region and adhesion should increase. Meissner and Merril¹⁶ report insignificant adhesion in polystyrene-steel butt joints at 82°C, the T_g of their sample at room conditions, after applying a pressure of 670 bars. However, they gave no consideration to the effect of pressure on T_g (30°C/kbar). Therefore, under their molding conditions their polymer was about 20°C below its glass transition temperature.

3. Pure polystyrene In an effort to correlate the effects of pressure-temperature history on the behavior of the adhesive with those on the polymer itself, polystyrene specimens were exposed to Cycles I, III and IV. The results of these experiments are shown in Figure 10 where σ_f is plotted as a function

of molding pressure. A slight maximum appears between 250 and 500 bars for samples subjected to Cycle I showing a maximum increment in σ_f of 6%. For samples subjected to Cycle III and Cycle IV a slight initial increase in σ_f occurred after which the curve levels off at about 500 bars and 600 bars respectively. This initial increase is more apparent in the latter case.

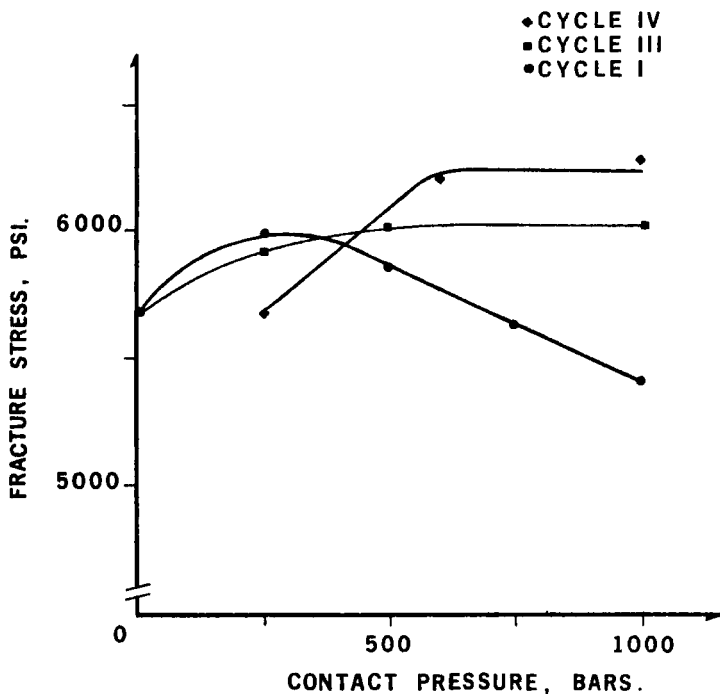


FIGURE 10 Plot showing tensile strength of pure polystyrene as a function of pressure for specimens prepared according to Cycles I, III and IV.

Though the observed effects of pressure on the pure polymer were small, they were reminiscent of those observed in the adhesive joints. The large difference in respective points between σ_f and σ_{fj} reflects the importance of the residual stresses and stress concentration risers in adhesion. Dale and Rogers²⁰ reported the occurrence of a maximum in the compressive yield stress of polystyrene at a molding pressure of 1000 bars in specimens subjected to a cycle similar to Cycle II and showed evidence of internal instability in the polymer after it was subjected to pressures about 1000 bars. They explained the initial increase in the yield stress in terms of a more compact polymer which has less segmental movability and more extensive interchain forces. In the present work the maximum in σ_f occurred at lower pressures. However, it must be recalled that here the specimens were tested in tension

which should be more sensitive test than compression because in the latter case crazes and expanded structures diminish in size as load is applied. In tension the opposite occurs; i.e. crazes tend to open and structural defects act more readily as stress concentration risers. In addition, tensile failure in polystyrene is of the brittle type while in compression, fracture is preceded by plastic flow. Thus, the effect of structural defects would be expected to be more intense and sharp in tension than in compression.

The slight initial increase in σ_f with pressure in Cycle III can be explained in terms of a decrease in the air content in the polymer which in turn means a reduction in defects in the polymer. The explanation for the behavior of σ_f with pressure in Cycle IV is the same as that given for the behavior of the butt joints exposed to Cycle IV.

The modulus of elasticity of the pure polystyrene specimens did not change with P-T history to any significant extent. Its average value was computed as 4.1×10^5 psi.

C. Fractography

1. *Non-Fractured butt joints* Because of the transparency of both Pyrex glass and polystyrene to visible light, the bonding interfaces of non-fractured butt joints could be directly observed in the optical microscope. A qualitative relationship was established between debonding of non-fractured butt joints, and fracture stress.

Some selected pictures are shown in Figures 11 and 12. The black lines correspond to debonding of the polymer from the Pyrex glass surface. These lines lie in the plane of the interface and run parallel to the radial direction and perpendicular to it. The extent of the debonding lines depends upon the magnitude of the residual stresses caused by contraction of the polymer. In general, the radial lines penetrate more to the center of the adhesive layer than do the tangential lines, suggesting that the tangential (or hoop) component of the stress is greater than the radial component.

Figure 11 compares the debonding lines observed for specimens subjected to Cycle II and molding pressures of 1 bar (the control), 500 bars and 1500 bars. Fracture stresses for other specimens subjected to these same molding conditions were 2000 psi, 3150 psi and 1000 psi, respectively. It will be noted that molding conditions which lead to maximum fracture stress lead to a decrease in the number and length of both the radial and tangential debonding lines. However, even for the sample molded at 500 bars, which yielded the maximum fracture stress in Cycle II, these debonding lines are still present to some extent. The residual debonding lines are attributed to transient stresses which are never eliminated when molding according to this cycle.

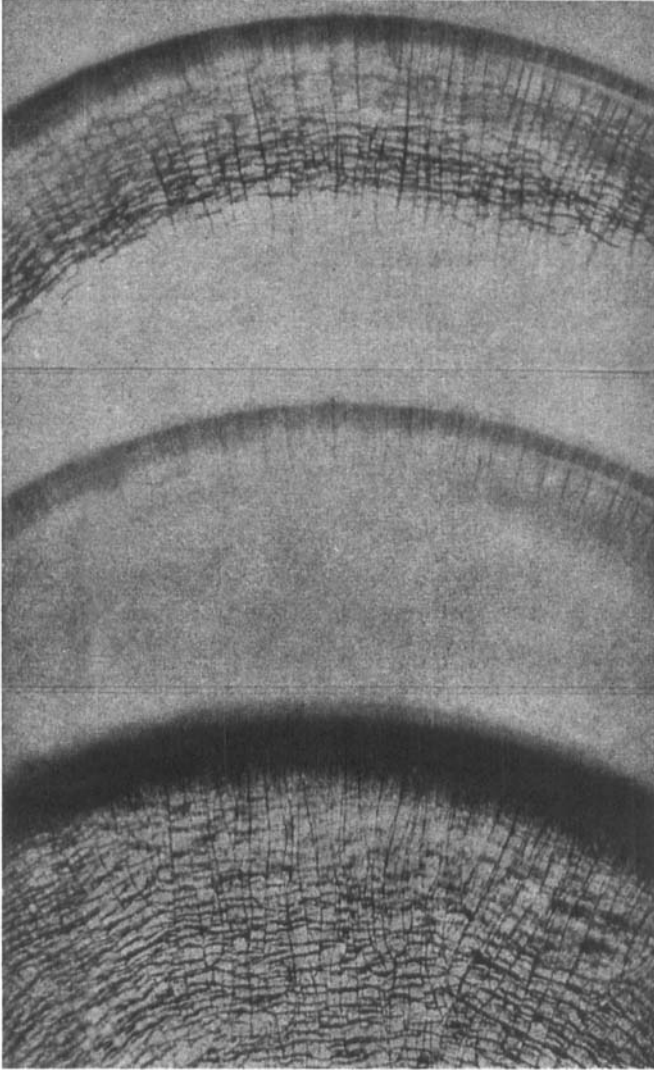


FIGURE 11 Micrographs of bonding interfaces in non-fractured butt joint specimens subjected to Cycle II and (a) molding pressures of 1 bar; (b) molding pressures of 500 bars and (c) molding pressures of 1500 bars.

Figure 12 compares the debonding lines observed for specimens subjected to Cycle I at 500 bars, to Cycle III at 1000 bars and to Cycle IV at 1000 bars. The extent of debonding of the specimen subjected to Cycle I is greater than that observed for the specimen subjected to Cycle II at 500 bars. In addition, at some points the debonding lines cross in directions other than the radial

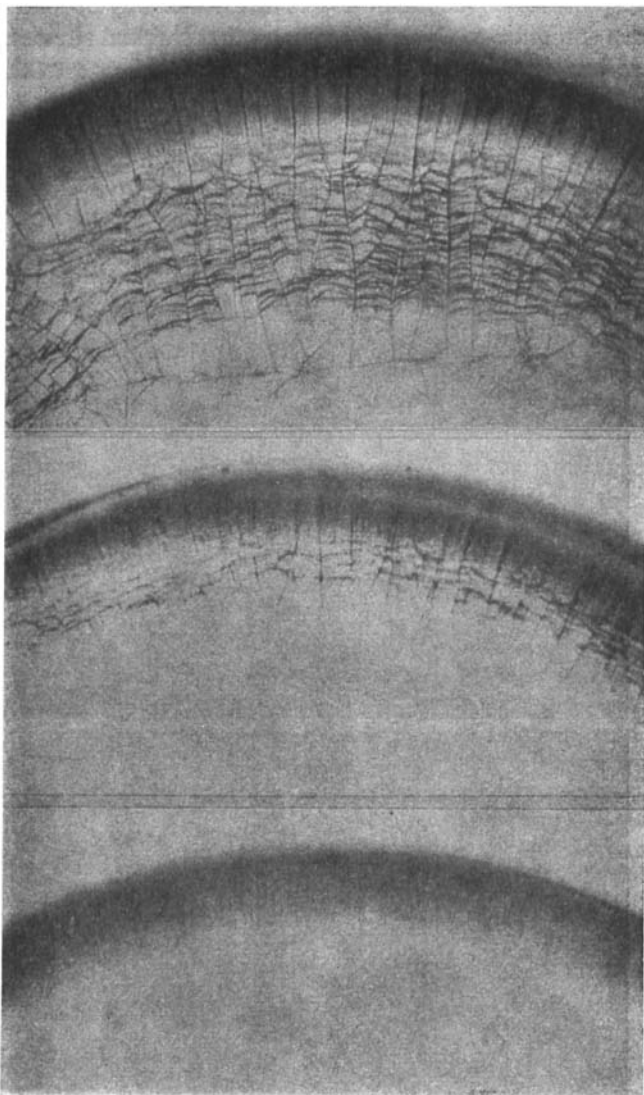


FIGURE 12 Micrographs of bonding interfaces in non-fractured butt joint specimens subjected to (a) Cycle I and a molding pressure of 500 bars, (b) Cycle III and a molding pressure of 1000 bars and (c) Cycle IV and a molding pressure of 1000 bars.

and tangential. These off pattern lines probably indicate points where concentrations of stress occurred because of microcracks at the Pyrex glass surface. The debonding line pattern in the specimen subjected to Cycle III is very similar to that in the control specimen indicating that thermal stresses

are most responsible for debonding. The absence of any debonding lines in the specimen subjected to Cycle IV indicates that residual stresses, if present at all, were too small to cause permanent visible damage to the bonding surfaces of this sample.

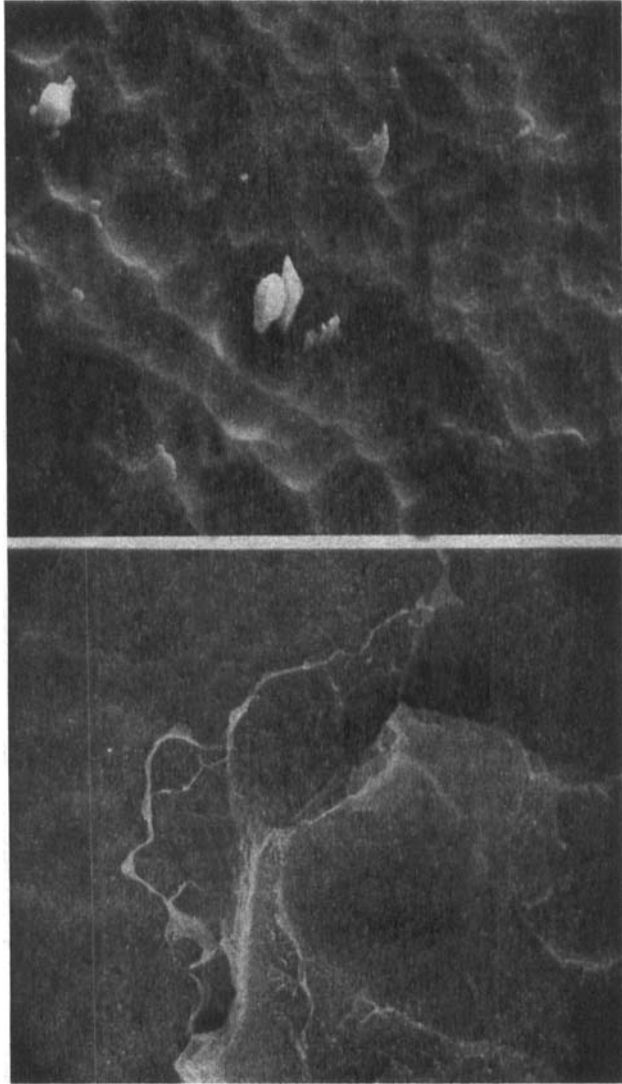


FIGURE 13 Micrographs of fracture surfaces of butt joints showing (a) apparent adhesive fracture and (b) partial cohesive fracture in the polymer.

2. *Fractured butt joints* The fracture surfaces of butt joints tested in uniaxial tension were observed in both the optical and scanning electron microscopes to study the effect of P-T history on the mode of fracture. Typical observed behavior is shown in Figure 13.

In general, the fracture surfaces of the specimens that yielded low tensile strengths showed apparent adhesive fracture. As joint tensile strength increased, the crack front appeared to propagate at one of the bonding interfaces only to a limited extent, then moved to the other bonding interface splitting the polymer layer into two parts. The crack front then continued to propagate at the second interface. The specimens yielding maximum joint strengths showed cohesive failure in some regions of the fracture surface in the polystyrene layer as well as some apparent adhesive fracture. Figure 13a is a micrograph of a specimen showing apparent adhesive fracture. Figure 13b is a micrograph of a specimen showing partial cohesive fracture.

V. Acknowledgement

The authors acknowledge U.S. Army Research Office - Durham Contract DAHCO 4-72-C-0042 which partially supported this work.

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