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### Some Effects of Structure on a Polymer's Performance as a Cryogenic Adhesive

Rex B. Gosnell<sup>a</sup>; Harold H. Levine<sup>a</sup>

<sup>a</sup> Whittaker Corporation, Research & Development/San Diego, San Diego, California

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## Some Effects of Structure on a Polymer's Performance as a Cryogenic Adhesive

REX B. GOSNELL and HAROLD H. LEVINE

*Whittaker Corporation  
Research & Development/San Diego  
San Diego, California*

### SUMMARY

The results of an evaluation of polymers as cryogenic adhesives are presented. It was observed that polyether-based polyurethanes provided the most attractive capability as adhesives for use at liquid hydrogen temperatures.

The polyether-polyurethane is pursued by introducing fluorine to bring about resistance to oxidizers. This extrapolation was possible while retaining the utility of the polyether-polyurethane.

The above observations provided the first clue that some segments of a polymer with a relatively high  $T_g$  could be available for work at temperatures down to those approaching the temperature at which secondary transition phenomena could be detected.

The polybenzimidazoles also demonstrate good cryogenic properties as a result of their completely aromatic-heterocyclic chains. This cryogenic integrity could not be observed if the polymer displayed brittle failure.

The polybenzimidazoles, polyquinoxalines, and polyimides can have a  $T_g$  of about  $400^\circ\text{C}$ . It appears that a combination of linearity, high density, and high  $T_g$ , which are consequences of the aromatic-heterocyclic structure, makes possible a stress-release mechanism at low temperatures.

The objective for research is to design polymers for cryogenic adhesive application with a flat temperature vs. elongation curve with higher elongation.

## EXPERIMENTAL AND RESULTS

There has been increasing interest in the use of polymers at very low temperatures, including the area of cryogenic adhesives. However, little consideration has been directed toward assessment of the relationship of the polymer's structure to its performance at very low temperatures. This paper presents some observations that we have made and the important conclusions which can be drawn.

At the outset, a study was made of the utility of polymeric adhesives at  $-320^{\circ}\text{F}$ . The tensile strength of shear specimens was measured at  $-320^{\circ}\text{F}$ . Figure 1 is a bar graph of the observed lap shear strengths for several available adhesive systems. The specimens were prepared using accepted practices for 7075-T6 aluminum and the bonding schedules recommended by the manufacturers. Each bar represents the average of several specimens prepared with one adhesive belonging to the indicated family.

The first group, the nylon-epoxy shown in Fig. 1, demonstrates that hydrogen bonding contributes to the toughness of a polymer and is a desirable structural feature in cryogenic adhesives. The nylon content in these adhesives is considerable. The improvement over the unmodified epoxies is shown in the graph. Unfortunately, there are processing problems inherent in the nylons which limit the types of nylon polymers that can be added to epoxies for this type of adhesive.

All three of the other epoxy-containing systems exhibit brittleness at  $-320^{\circ}\text{F}$ . Some epoxy systems (not shown in the figure) are so brittle that failure in the glue line occurs with no applied load. Failure occurs because of inability to withstand internal stresses due to differences in thermal contraction.

The rubber phenolic and vinyl phenolic adhesives are also quite brittle at low temperature. Although one such adhesive demonstrated fairly good strength in lap shear, this improved behavior was attributed to a nylon scrim which served as a support for the film.

The problems encountered with epoxy- and phenolic-based systems suggest that higher cross-link densities are not attractive at low temperature. In contrast to the formal cross-link is the hydrogen bond which permits more energy absorption (work) by the adhesive; it is suggested that these bonds contribute by a "make and break" capability.

It is desirable to spend more time discussing the structural features of the polyurethanes and the heterocyclic aromatic polymers shown to be most acceptable in lap shear strength at  $-320^{\circ}\text{F}$ .

In polyurethanes, three basic types of materials were studied. Poorest

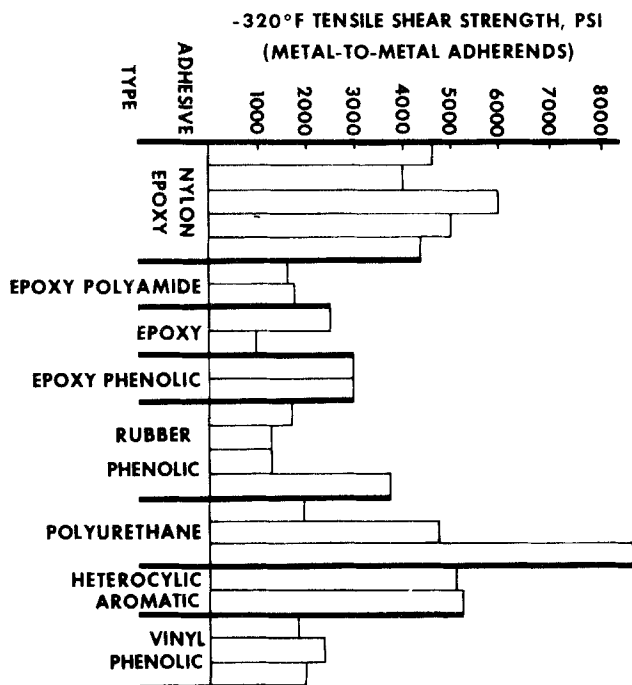
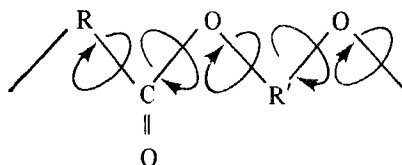


Fig. 1. Lap shear strength of adhesives at  $-320^{\circ}\text{F}$ .

performance was observed where the prepolymer was based on a polyester, acceptable performance was observed with propylene oxide-based polyethers, and outstanding performance was found with tetrahydrofuran-based polyethers.

These polymers are typically prepared from trifunctional hydroxyl-terminated polyesters or polyethers. A general polyester formula and its conversion to final polymer is shown in Fig. 2.

While the urethane and urea functions can contribute to toughness by hydrogen bonding, it is important to note that a significant part of the polymer consists of polyester because the values for X are typically from 8 to 12. Consequently, the degree of flexibility probably is in large part due to the rotational freedom available in the polyester portion of the molecule.



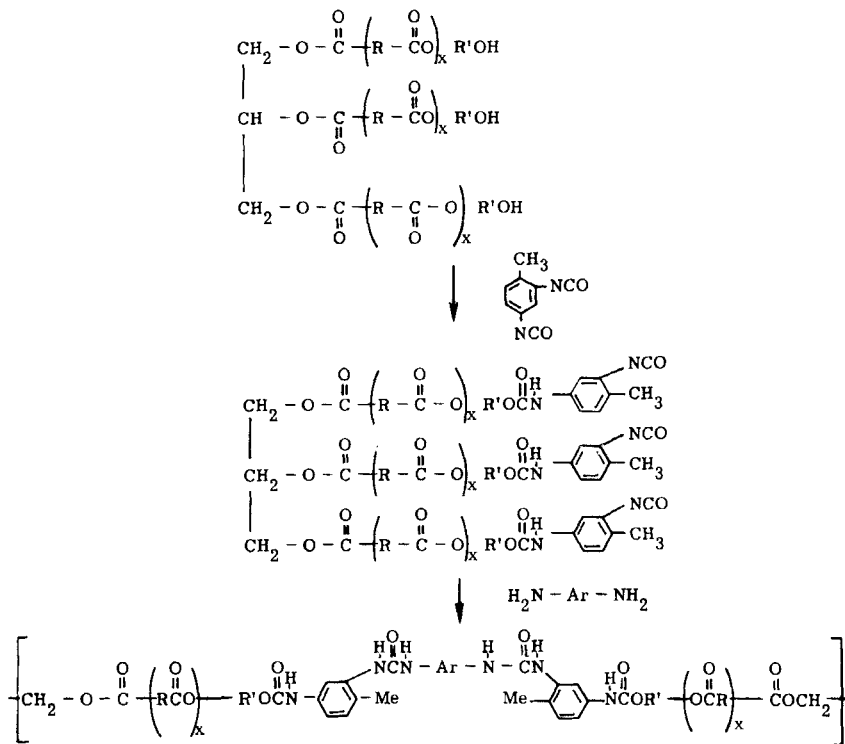
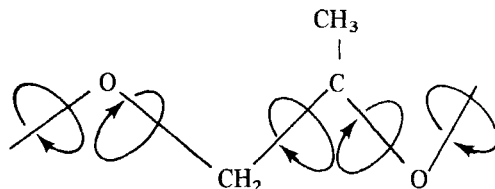


Fig. 2. Polyurethane formation.

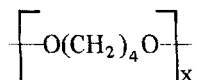
Similarly, the polyethers from propylene oxide-based systems would have the generalized structure as shown on the following page. Here again, a significant portion of the polymer is comprised of the polyether, and the flexibility of the polymer is due in large part to the rotational freedom in the polyether.



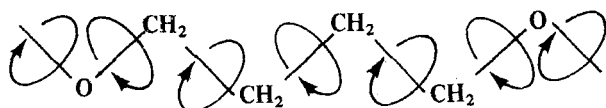


Since the propylene oxide-based polyurethanes are fairly good, it seems that not all rotational freedom is frozen out at  $-320^{\circ}\text{F}$ .

Outstanding results are observed when all structural features are constant, except that the polyether is derived from tetrahydrofuran resulting in the repeating unit:



It is accepted that the rotational freedom represented by



is essentially frozen out at the glass transition temperature, as is this same type of rotation in the aforementioned cases of the propylene oxide polyethers and the polyesters. This restriction of gross rotational freedom occurs at the glass transition temperature ( $T_g$ ).

It has been determined that peel is a critical test of adhesives for use at very low temperatures. This test is very sensitive to the polymer's ability to do work. Shown in Fig. 3 is an exaggerated representation of the configuration of a polymer in peel. Note that the work required to peel the upper metal surface is equal to the work done in the adhesive, which is proportional to the displacement from the original position and the tension on the polymer.

Because the stress on the polymer is expressed by  $P_s = L/A$ , where  $P_s$  is the peel stress,  $L$  is the load, and  $A$  is the area [(width of specimen)( $Y$ )], the value for  $Y$  and  $A$  are consequently very sensitive to the elongation of the polymer possible at load  $L$ . At cryogenic temperatures, brittle materials result in high peel stress at the line of failure. Additional poor performance in brittle adhesives is observed because of the analogy to notch sensitivity, resulting in a typical behavior of "break and run" at low temperature.

In testing lap shear specimens with relatively thin adherends, it is recognized that some peel failure mode is possible at higher load levels due to displacement of the glue line (see Fig. 4). It is then possible that the peel characteristic is evaluated to some extent in lap shear specimens tested at low temperature on thin adherends.

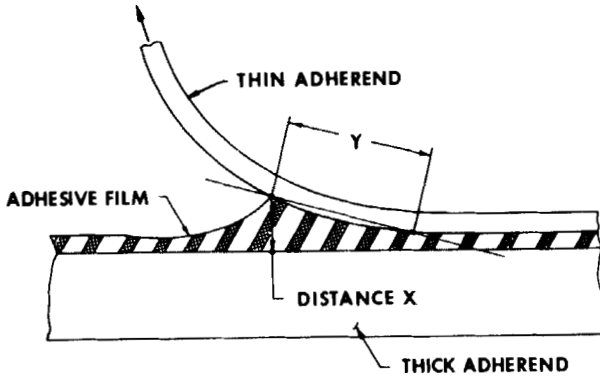


Fig. 3. Glueline configuration in peel failure.

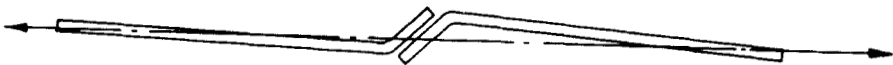


Fig. 4. Peel introduced to lap shear specimens at high loads with thin adherends.

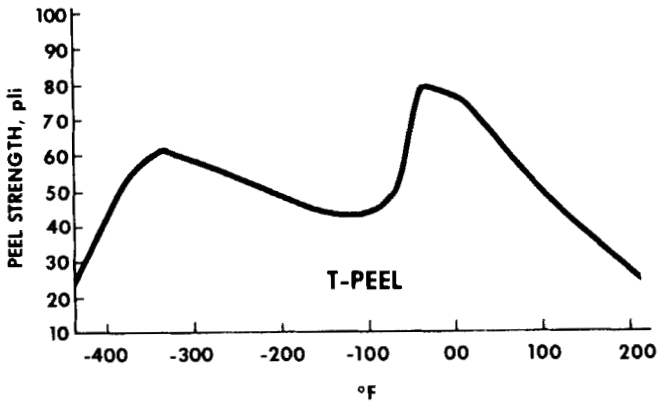
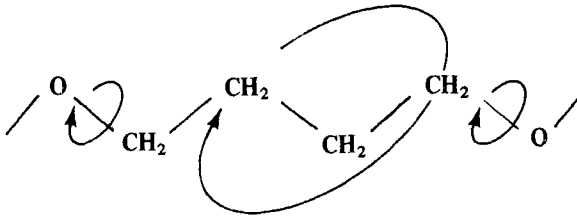


Fig. 5. Peel strength of polyurethanes based on tetrahydrofuran polyethers.



The pure peel configuration is the method to be considered in critical evaluation of cryogenic adhesives. For example, the peel data collected for the tetrahydrofuran-based polyurethanes are shown in Fig. 5. The figure demonstrates very well the glassy transition which is reported for these polymers at  $-50^{\circ}\text{F}$ .

Most important is the fact that another similar pattern was observed between  $-350$  and  $-423^{\circ}\text{F}$ . It is our belief that this behavior is due to residual segmented rotational freedom due to the entire movement of the tetramethylene unit.



Furthermore, this break in the peeling strength of the adhesive between  $-350$  and  $-423^{\circ}\text{F}$  represents this secondary transition in that region.

The elements of these concepts have been applied to fluorinated polyurethanes with some success. It is remarkable that these concepts can be extrapolated to such an extent.

The first hint that poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole, synthesized for high thermal and oxidative stability, had unusual behavior at low temperature was obtained during attempts to pulverize high-molecular-weight samples for infrared spectroscopy. It was not possible, in many instances, to reduce the particle size in a Wiley mill even when the polymer was mixed with pulverized dry ice.

Subsequent evaluations on adhesives and laminates, using this polymer, down to  $-320^{\circ}\text{F}$  showed that PBI did not embrittle at very low temperatures [1]. Test data are shown in Tables 1 and 2.

Supporting data were obtained on the polymer as a laminating resin.

These data indicated the polymer's resistance to brittle fracture at the high loads sustained. The modulus of  $6.6\text{--}7.0 \times 10^6$  psi is particularly relevant because this increase in modulus is least likely due to increased polymer modulus. Rather, the polymer's resistance to brittle fracture permits it to function at higher loads while transmitting stresses from

**Table 1.** Tensile Shear Strength of PBI Adhesives (17-7PH 950 Annealed Stainless-Steel Substrate)

| Test temperature, °C | Tensile shear strength, psi |
|----------------------|-----------------------------|
| Room temperature     | 3800                        |
| -170                 | 4820                        |
| -252                 | 5690                        |

**Table 2.** Flexural Strength and Modulus of PBI Laminates (AF-994 Fabric, HTS Finish, 1581 Style)

| Test temperature, °C | Flexural strength, psi | Modulus psi × 10 <sup>6</sup> |
|----------------------|------------------------|-------------------------------|
| Room temperature     | 100,000                | 4.1                           |
| -170                 | 181,000                | 7.0                           |
| -252                 | 176,000                | 6.6                           |

**Table 3.** Izod Impact Strength

| Polymer                  | Impact strength, lb/in. notch |        |
|--------------------------|-------------------------------|--------|
|                          | Room temperature              | -320°F |
| Epoxy, high temperature  | 0.2-1.5                       | —      |
| Phenolic, molded         | 0.2-0.5                       | —      |
| Polyester                | 0.2-0.4                       | —      |
| Nylon 6                  | 1.2-3.6                       | —      |
| Polystyrene, high impact | 1.0-3.0                       | —      |
| PBI                      | 1.5                           | 1.5    |

glass fiber to glass fiber in a more efficient manner. Consequently, the high modulus of the glass is much more completely utilized. Brittle polymers do not perform in this manner.

Two of the bulk properties of the PBI are especially pertinent to this discussion. Moldings had a density of 1.33-1.35 and Izod impact values of 1.5 ft-lb/in. of notch at room temperature and -320°F. The room temperature value is superior to conventional high-temperature polymers that depend

on cross-linking for elevated temperature strength (see Table 3). Even more significant was the retention of strength at liquid nitrogen temperatures indicating absence of embrittlement.

Such performance led to the question, "Why does the glassy, amorphous PBI have good mechanical properties at  $-320^{\circ}\text{F}$  despite its very rigid backbone and, consequently, a glass transition temperature ( $T_g$ ) over  $600\text{-}700^{\circ}\text{F}$  higher than conventional cryogenic polymers?"

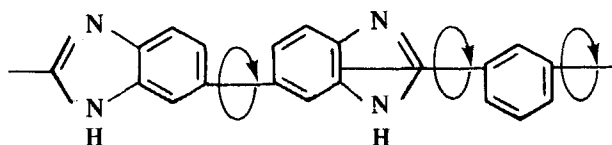
It is proposed that the "unusual" behavior of the PBI is due primarily to the following combination(s) of reasons: (1) High polymer density, (2) strong intermolecular attractions emanating from hydrogen bonding and van der Waal forces, and (3) stress-release mechanisms most probably due to secondary transition phenomena much below  $T_g$ .

The completely aromatic heterocyclic structure results in a very rigid, rod-like backbone which, in turn, results in a very high  $T_g$ . Consequently, more energy is "frozen in" when the polymer is cooled below its  $T_g$  and is converted into potential mechanical energy in the form of induced stresses. The glassy, amorphous PBI is able to withstand these extra stresses because it is stronger since its high density provides more polymer per unit volume.

It is interesting to consider that at room temperature, the PBI is already about  $600\text{-}700^{\circ}\text{F}$  below its  $T_g$ . Further cooling to cryogenic regions can hardly be expected to cause any drastic changes in properties. With almost all polymers, it would be impossible to achieve  $600\text{-}700^{\circ}\text{F}$  below their  $T_g$  since this would be below absolute zero. Therefore, since the PBI is not brittle at room temperature, it should not be brittle at cryogenic temperatures.

It should be pointed out that as the polymer is cooled to very low temperatures, only a very small decrease in free volume would be needed to increase intermolecular forces since these vary inversely with distance raised to the seventh power, and this could serve to increase the tensile strength and the "make and break" capability of these intermolecular forces, contributing to toughness.

Examination of the PBI structure indicates that secondary transitional



motion must involve a large group (m-phenylene), larger benzimidazole moieties, or still larger chain segments, all favoring toughness.

Gillham [2], using torsional braid analysis, provided experimental evidence of a stress-release mechanism by a damping peak at  $-70^{\circ}\text{C}$  (see Fig. 6).

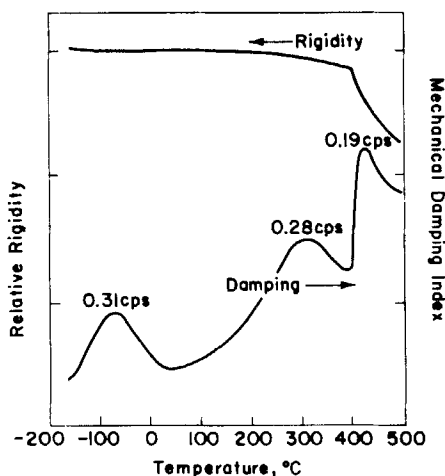


Fig. 6. Torsional braid analysis of PBI.

The properties of PBI at  $-252^{\circ}\text{C}$  strongly suggest the need to look for another damping peak below  $-70^{\circ}\text{C}$ , using torsional braid or torsional pendulum analysis from liquid hydrogen or helium temperature.

The implications of the foregoing discussion are interesting, but most significantly it means that it is possible to utilize secondary transitions below  $T_g$  as a means of obtaining toughness. Toughness can be reasonably anticipated from other completely aromatic heterocyclic polymers since they also have most or all of the properties given earlier.

It has been shown in recent work that a modified benzimidazole, Whittaker 820, is able to perform at fairly high temperatures and demonstrates the excellent  $-320^{\circ}\text{F}$  properties of 5000 psi in lap shear and 8.5 lb/in. peel. The polymer which has a  $T_g$  of  $\sim 450^{\circ}\text{F}$  has higher elongation at room temperature than unmodified PBI and apparently is able to retain this elongation to low temperatures.

Similar outstanding performance at  $-320^{\circ}\text{F}$  has been observed for polyimides and polyquinoxalines. Segmented residual chain motion is

possible in these polymers, and low-temperature secondary transitions can be determined by torsion methods.

In summary, it has been indicated that a new approach to the problem of cryogenic adhesives or polymers, and particularly to the problem of using such adhesives or polymers at elevated temperatures, consists of designing polymers with segmented chain motion which is not frozen out below the glass transition temperature. This has been shown to be feasible in polymers with very high  $T_g$ , demonstrating this new approach to wide-temperature-range polymers.

### REFERENCES

- [1] H. H. Levine et al., ASD-TDR-63-48 (1963).
- [2] J. K. Gillham, *Polymer Preprints*, 7, 513 (1966).

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#### Discussion of Paper by Rex B. Gosnell and Harold H. Levine

##### Some Effects of Structure on a Polymer's Performance as a Cryogenic Adhesive

- J. K. Gillham: In good low-temperature adhesives is the failure always cohesive rather than adhesive?
- R. Gosnell: In good cryogenic adhesives the failure is cohesive. It has been our observation that adhesion, per se, is not decreased as the temperature is reduced.
- S. M. Toy: How do you translate ft-lb energy to strength units (psi)? Table 3 reports only lb/in. notch, yet strengths are usually reported in terms of lb/in.<sup>2</sup>.
- R. Gosnell: The impact "strength" should be expressed in ft lb/in. of notch. This represents the energy level which can be absorbed by the polymer before failure.
- R. Landell: I have heard that polyphenylene oxide has no reported

glass transition temperature. Have you looked at this material at low temperatures?

- R. Gosnell: No, we have not. I would expect that the segmented rotation represented by the phenylene group would evidence itself in some transitional phenomena at  $-250$  to  $-300^{\circ}\text{F}$ . If, however, the polymer has methyl groups in 2,6 positions, this can introduce an added steric factor into secondary transitional behavior.