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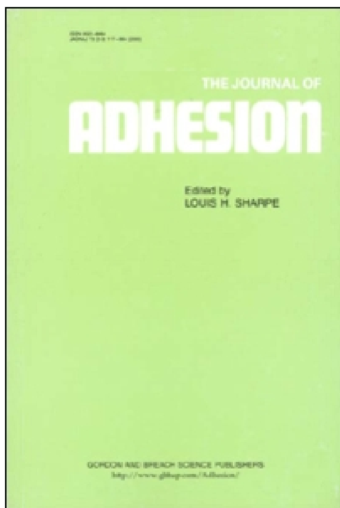

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Patrick E. Cassidy[a,b]; James M. Johnson[a,c]; Carl E. Locke[a,c]
[a] Tracor, Inc., Austin, Texas, U.S.A. [b] Department of Chemistry, Southwest Texas State University, San Marcos, Texas, U.S.A. [c] Chemical Engineering Department, University of Texas, Austin, Texas, U.S.A.

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The Relationship of Glass Transition Temperature to Adhesive Strength

PATRICK E. CASSIDY†, JAMES M. JOHNSON,* and CARL E. LOCKE*

Tracor, Inc. Austin, Texas, U.S.A.

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The effects of glass transition temperature (T_g) on mechanical properties have been further demonstrated by the observation of a direct relationship between the T_g of an epoxy adhesive and its lap shear bond strength to metal at elevated test temperatures. An additive (coupling agent) which lowers the T_g from a point near or above the test temperature to below it causes a subsequent decrease in the strength of the system and generally increased cohesive failure. Therefore effects on the T_g of the adhesive are more important than on interfacial properties. The end result is that differential thermal analysis (DTA) can be utilized as a effective screening method for adhesives and additives, and can be a good indicator of maximum use temperature. From these data T_g can also be used to estimate adhesive strength at a given use temperature.

INTRODUCTION

Relationships between numerous mechanical properties and macromolecular structure (intra- and interchain) have been well known for some time.[1] And, since this structure (or interchain forces or molecular motion[2]) in the amorphous region is indicated by T_g, the mechanical property/T_g relationships can be considered.

Some of the physical properties which have been studied in conjunction with T_g are solubility parameters, modulus,[1,3] diffusion, abrasion, tear strength,[4] creep, impact,[5] stress relaxation, flexural strength, and, of course, tensile strength.[6] In most cases the property (strength, modulus, etc.) will increase slightly with the test temperature until the T_g is reached, at which

† Present address: Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666, U.S.A.
* Present address: Chemical Engineering Department, University of Texas, Austin, Texas 78712, U.S.A.

time a rapid decrease is observed. Also T_g has been shown to correspond to heat deflection temperature[7] (HDT) which is to be expected since both properties relate to interchain forces, either secondary bonds or covalent crosslinks, and to molecular flexibility.

From the above discussion a relationship between apparent adhesive strength of a polymer and T_g may be expected. This becomes a more complex problem than those properties discussed above since an interface between the organic adhesive and the metallic substrate must be considered, so that more is involved than the bulk properties alone. If the bulk properties are the controlling factor in bond failure (that is, cohesive failure rather than adhesive failure occurs), the usual strength *vs* T_g relationships should be found.

A study has been completed in this laboratory which required the comprehensive testing of a wide variety of coupling agents as adhesion promoters.[8] This program involved two adhesives (urethane and epoxy), four substrates (aluminum, mild steel, stainless steel, and glass), and 16 coupling agents (silanes, phosphorous esters, chromium complexes, and alicyclic amines). The significance of this work was in the fact that the agents were incorporated into the uncured adhesive mixture with the curing agent before application to the surface. Considerable improvements were realized by the proper selection of agent.

A part of the program involved testing selected compositions at cryogenic (−196°C) and elevated (+93°C) temperatures after screening at room temperature using lap shear testing methods. It was discovered during the comprehensive testing of the epoxy adhesive that while many agents effected an increased lap shear strength at room temperature, many of these same agents lowered lap shear strength at elevated temperatures. And, conversely, several agents which produced no increase in lap shear strength at room temperature, increased shear strength markedly at elevated temperatures compared to the control value. It was postulated that the use of some additives lowered the T_g from near the test temperature to far below it while other additives raised the T_g, resulting in a change in mechanical properties (modulus, hardness, elasticity, etc.) at 93°C. That is, with detrimental agents, the amorphous region of the epoxy at 93°C was well into the rubbery state and bond failure was cohesive. With beneficial agents, however, the epoxy was near the point where its mechanical properties approached those of the glassy state and adhesive bond failure became important. At room temperature, of course, all compositions were far into the glassy state (all adhesive failure), and no detrimental agent effect was seen. On the contrary, improved the situation some agents since interfacial forces played a more important role.

To investigate these agent effects, differential thermal analyses (DTA) were performed upon the bulk adhesive with and without coupling agents, and the

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results of these analyses were compared to corresponding lap shear strengths at various test temperatures.

EXPERIMENTAL

1.0 Adhesives

Epon VIII (Shell Chemical Company) was utilized with 6% by weight curing agent "A". The resin was mixed with the coupling agent, then with 0.2% glass beads (2.3–3.4 mil diameter for bondline thickness control), then with the curing agent, applied to the bonding surfaces and cured under pressure for 90 minutes at 93°C. After flash removal the bond was tested in tension as prescribed in ASTM D1876-61T. These test methods have been discussed in a NASA report.[8]

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2.0 Substrates

Preparation of the bonding surface was well defined and controlled throughout the test program. It should be noted that considerable effort was expended optimizing this treatment and controlling bond lines for the maximum and most reproducible bond strength.

Aluminum coupons (2024-T3) were wiped with trichloroethylene, vapor degreased with the same for 10 minutes at 87°C, etched for 20 minutes at 66°C (composition of etchant: 65.4 wt-% water, 26.9 wt-% sulfuric acid, and 7.7 wt-% sodium dichromate dihydrate), washed with tap water and distilled water, dried at 66°C for 10 minutes and stored in a desiccator until use.

Mild steel coupons were wiped and vapor degreased as above, sanded with #180 grit paper, degreased again and used immediately.

3.0 Thermal Analysis

The differential thermal analyses (DTA) were performed on the following TRACOR-Robert L. Stone equipment: an SH-11BR2-A1 (aluminum) sample holder, an F-1DF furnace, a DTA Furnace Platform (Model JP-202), and a Stone LB-202 Recorder-Controller. The SH-11BR2-A1 sample holder contained a Platinel II ring differential thermocouple and a Chromel-Alumel reference thermocouple. The Platinel II ring differential thermocouple proved to be highly sensitive, and in conjunction with the aluminum sample holder, provided excellent thermal properties with low drift.

The samples, ranging in weight from two to six milligrams, were contained in small aluminum foil dishes that sat on the sample holder rings (the ring

differential thermocouples). Alumina was used as a reference and the sample and reference weights were balanced according to the following formula to effect zero drift:

$$\text{Weight of Reference} = \frac{\text{Weight of Sample} \times \text{Specific Heat of Sample}}{\text{Specific Heat of Reference}}$$

A programmed heating rate of 10°C per minute was maintained throughout the test as was an amplifier gain setting of 20 μV for full scale deflection. All samples were run statically in air.

RESULTS AND DISCUSSION

For this program a number of coupling agents were mixed with epoxy resin in an effort to find some which lowered and others which raised the T_g of the resin. Given in Table 1 are the nine agents used, their structure, concentration in the adhesive and T_g of the epoxy resin when they are incorporated. These concentrations were chosen for extensive testing because they were optimum in room temperature tests. The concentrations of the agents range from 1%

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TABLE I

Glass Transition Temperatures of Adhesive—Agent Compositions

Coupling agent	Nomenclature and structure	T_g and agent concentration
None (Control)	—	82°C
HFS-2	Hydroxy functional silane (exact structure unavailable) (Dow Corning Corp., XZ-8-5062)	55°C @ 10%
PE	A tri-functional phosphorus ester (exact structure unavailable) (Weston Chemical Co., Weslink E)	63°C @ 10%
4-AMPIP	4-Aminomethyl-piperidine	70°C @ 15%
MO-1	Solvent-dispersed metallo-organic (exact structure unavailable) (Stauffer-Wacker Silicone Corp., SWS-401)	71°C @ 5%
MO-2	Solvent-dispersed metallo-organic (exact structure unavailable) (Stauffer-Wacker Silicone Corp., SWS-403)	73°C @ 1%
MCrCl	Methacrylo Chromic Chloride (DuPont, VOLAN)	73°C @ 1%
CHA	Cyclohexylamine	80°C @ 3%
DMDCS	Dimethyldichlorosilane $(CH_3)_2SiCl_2$ (Stauffer-Wacker Silicone Corp., SWS-441)	91°C @ 1%
MTCS	Methyltrichlorosilane CH_3SiCl_3 (Stauffer-Wacker Silicone Corp., SWS-442)	105°C @ 1%

to 15% by weight; but since the actual mechanism or the role of each additive is unimportant here, the relative concentrations are of no real concern. That is, the only effect of the additive which is being monitored is the T_g. It is important, of course, to note that decreases in T_g caused by coupling agents overshadow any interfacial effects since cohesive failure is promoted. Some of these coupling agents were of unknown structure but again for the purpose of this program this information was not essential. It can be seen that two of these raise the T_g significantly (by 25°C), one causes no change, and six lower the T_g to as much as 25°C below the control.

Since the cure and post cure schedule of the test bonds was adhered to rigidly, the thermal history of all test bonds was the same, and the DTA data reflected this in nearly identical trace patterns (except for the shift in position of T_g). The few exceptions were apparently brought about by rather drastic agent effects on the polymerization characteristics of the resin. Some "relaxation peaks"[9,10] were evident in these materials and had to be distinguished from T_g.

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Figure 1 is a plot of lap shear strength at 93°C *vs* T_g for the compositions tested, and shows the direct relation between the two parameters for both aluminum and mild steel substrates. As can be seen from the graph, the epoxy-aluminum system demonstrated an almost linear lap shear strength/T_g relationship while the epoxy-mild steel system did not demonstrate linearity so clearly. It must be noted before comparing the two systems, however, that the epoxy-aluminum system experienced essentially total cohesive failure at the test temperature while the epoxy-mild steel experienced a combination of cohesive and adhesive failure, and these two factors probably have different relationships to T_g.

The leveling off of the curves at high strengths may be a real effect and can be explained in a number of ways. First, as the glass transition of the system departs from the test temperature, there is less sensitivity to and dependence upon T_g. The second way to express this is to say that as the T_g increases, the cohesive strength approaches asymptotically a limited maximum value which is the maximum bulk strength to be expected. Of course, it is probable that as this point is approached, more adhesive failure would be realized. There is, however, a third explanation: the T_g of the MTCS mixture is above the test temperature and therefore the adhesive was in the glassy state, and, as a result, the two types of data points may not be directly comparable. That is to say, separate effects are being tested.

It was further postulated that the shear strength should show a distinctive behavior as the test temperature varies, particularly in the region of the T_g. Figure 2 presents three typical shear strength versus test temperature plots for the EPON VIII-aluminum system. One curve is a control while the other two are for the cases with 1% MTCS or 10% PE additives. The glass

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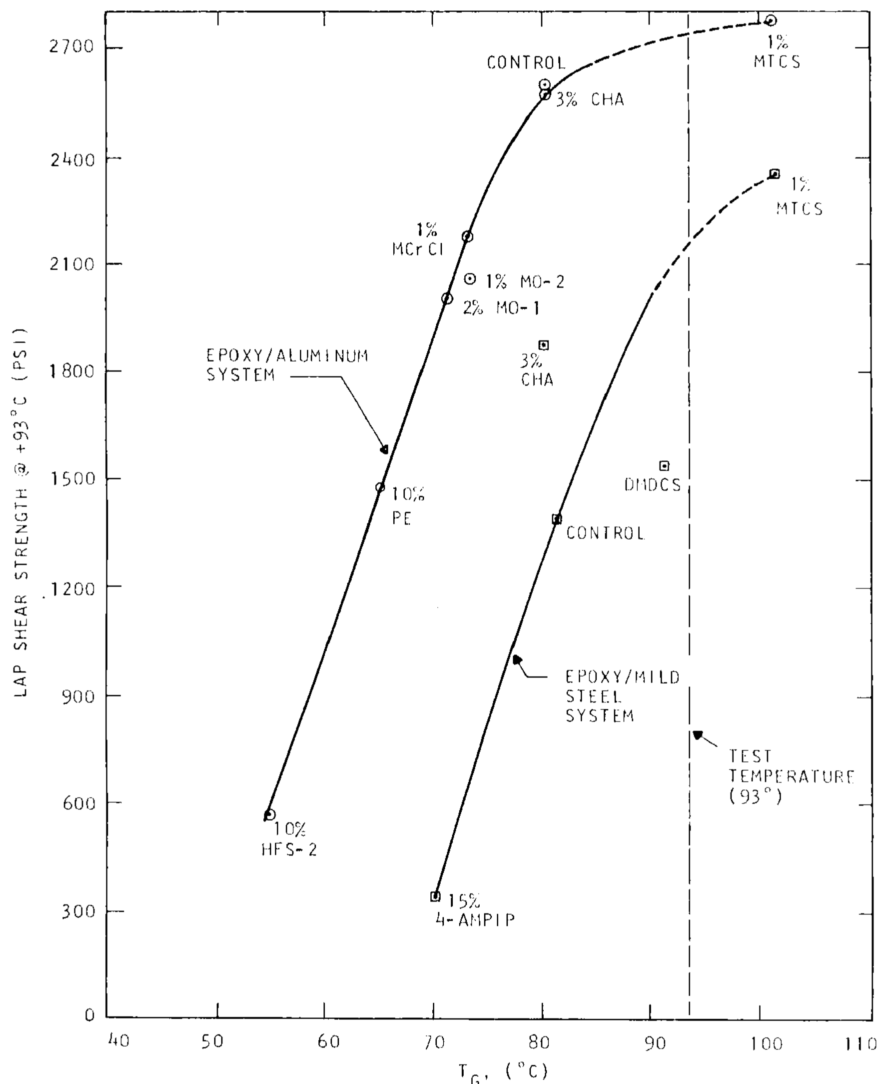

FIGURE 1 Lap shear strength/T_g relationship at 93°C test temperature.

transition temperatures determined by this mechanical method (indicated T_gs are in parentheses) agree favorable with those established by DTA. A table for comparison is also shown in Figure 2. It can be seen that at low temperatures, shear strengths tend to be retained and, in some cases, to increase as the test temperature increases. However, at or very near the glass transition temperature of the resin, the test bonds suffered severe degenera-

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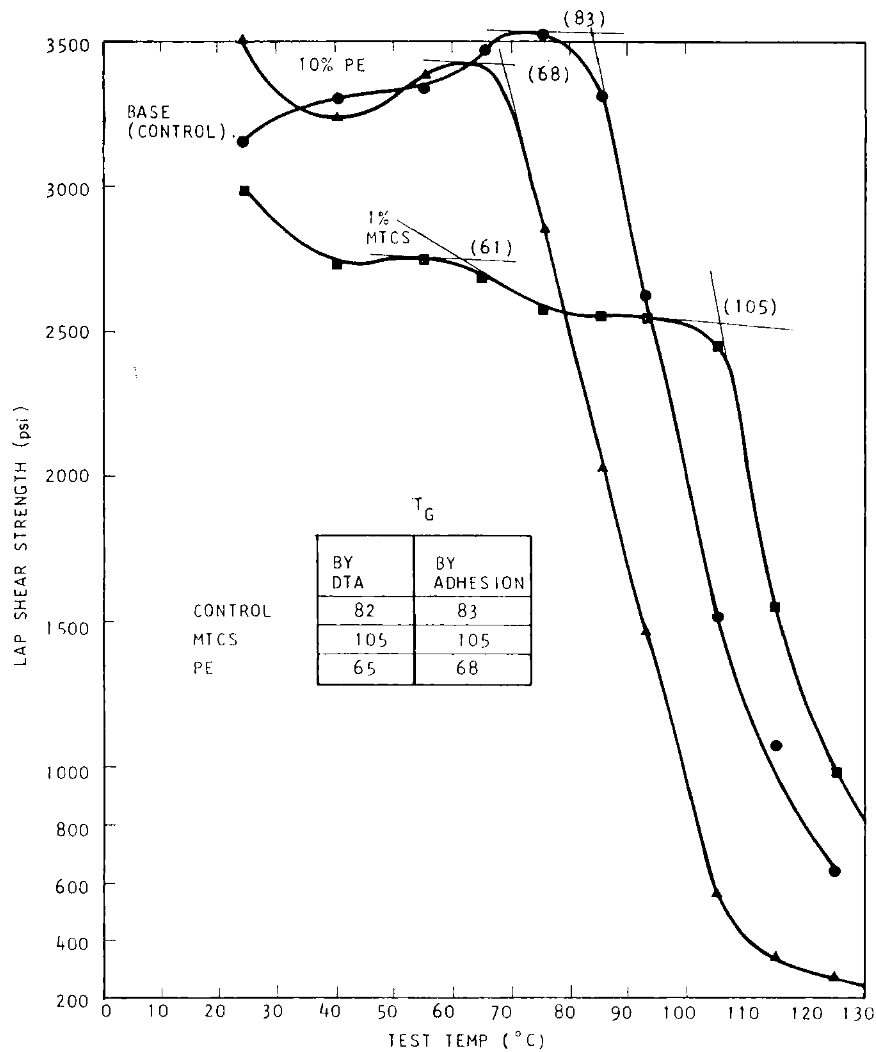

FIGURE 2 Lap shear strength/test temperature relationships for three adhesive systems.

tion of shear strength and tended to establish a discernible relationship concerning that deterioration of strength and test temperature. Since all test bond failures in this system were cohesive in nature at or above the T_g, a linear relationship between the T_g and bulk properties (in this case, shear strength) of the resins was established for test temperatures at or above the glass transition temperatures of those compositions.

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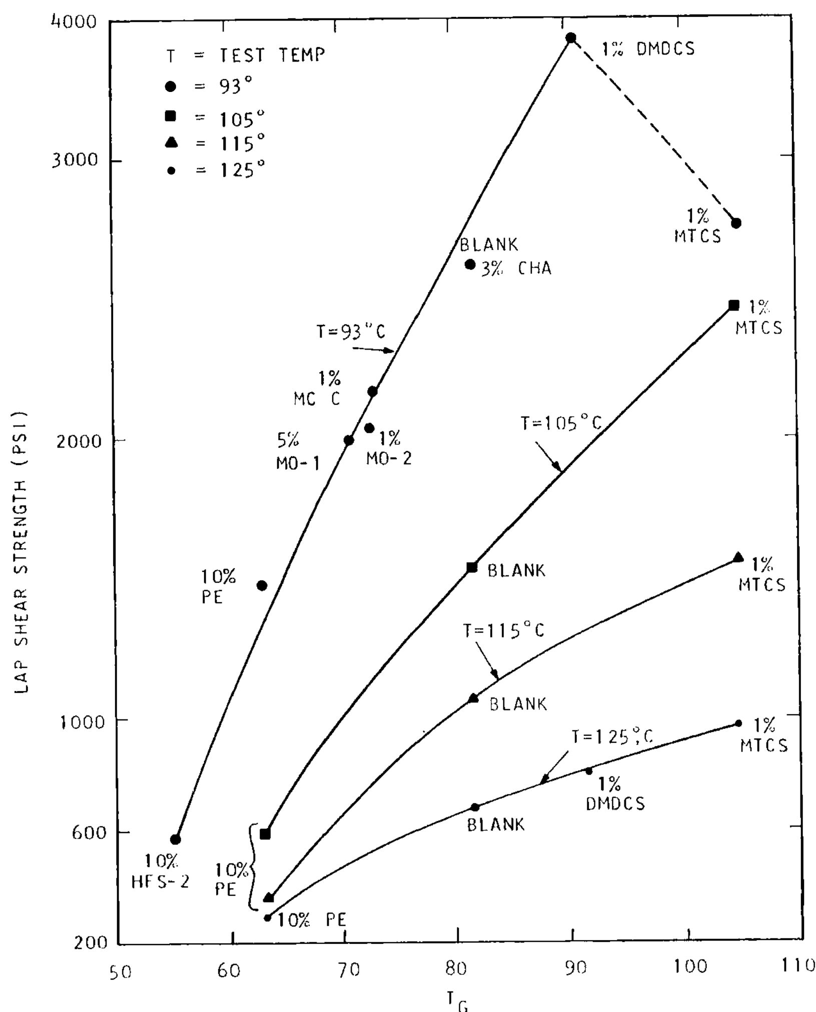

FIGURE 3 Lap shear strength/T_g relationships at four test temperatures.

Figure 3 presents more clearly the meaning of that relationship by plotting lap shear strength versus T_g at four specific test temperatures. While a plot such as illustrated in Figure 2 shows complete shear strength data over a specific temperature range, each curve relates to only one epoxy-agent combination. In contrast, each curve of the type illustrated in Figure 3 is representative of all agent-resin combinations at a single test temperature. This means that the bond strength of any composition utilizing EPON VIII can be estimated for any test temperature (at or above the T_g) covered by the

span of available curves from the T_g. It must be remembered however, that the type failure (cohesive *vs* adhesive) must be considered before the T_g/lap shear strength relationship of the resin can be determined. The greater the degree of cohesive failure of the resin involved, the more accurately shear strength can be estimated for a known T_g from curves like those in Figure 3.

An intimate knowledge of the thermal history of the resin comprising the bond in question is also necessary before an accurate shear strength estimation is possible. The "elevated" cure schedule involved and any subsequent elevated thermal history of the resin directly affects its T_g which, in turn, affects shear strength. For instance, EPON VIII epoxy with 1.0 wt-% MTCS cured ninety minutes at 93°C has a T_g of approximately 105°C. If this epoxy (cured as above) is heated at 10°C/min until 121°C is reached and then air quenched, the resulting T_g of the resin is approximately 87°C. An elevated cure schedule variation or thermal history will not necessarily always affect resin T_g adversely (lower it, as in the above case), for just as surely as there is an optimum cure schedule to establish maximum bulk properties in the resin at room temperature, there is one to establish maximum bulk properties in the resin at elevated temperatures (impart a maximum T_g of which the improved bulk properties of the resin at an elevated temperature would be a result). There is no guarantee that the two coincide.

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