NASA CONTRACTOR REPORT

NASA CR-2718

STRUCTURE-PROPERTY RELATIONSHIPS IN LOW-TEMPERATURE ADHESIVES

C. K. Schoff, K. Udipi, and J. K. Gillham

Prepared by
PRINCETON UNIVERSITY
Princeton, N. J. 08540
for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MARCH 1977

1. Report No. NASA CR 2718	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle STRUCTURE-PROPERTY RELATIONSHIPS IN LOW-TEMPERATURE ADHESIVES		5. Report Date March 1977
		6. Performing Organization Code
7. Author(s) C. K. Schoff, K. Udipi and J. K. Gillham		8. Performing Organization Report No.
9. Performing Organization Name and Address Department of Chemical Engineering Princeton University Princeton, NJ 08540		10. Work Unit No.
		11. Contract or Grant No. NGR 31-001-272
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546		13. Type of Report and Period Covered Contractors Report 1972-1976
		14. Sponsoring Agency Code

15. Supplementary Notes

Langley Technical Monitor: Austin D. McHatton

Final Report

16. Abstract

New adhesive materials of aliphatic polyester, linear hydroxyl end-capped polybutadienes, or SBS block copolymers are studied with the objective to replace conventional partially aromatic end-reactive polyester-isocyanate adhesives that have shown undesirable enbrittlement in balloon applications at the service temperatures of -70°C.

17. Key Words (Suggested by Author(s)) New adhesive materials Adhesive systems for balloons Low temperature adhesives Polybutadiene adhesives	18. Distribution Statement Unclassified - Unlimited Subject Category 37

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 90	22. Price* $4.75

* For sale by the National Technical Information Service, Springfield, Virginia 22161

FOREWORD

This report was prepared by C. K. Schoff, K. Udipi and J. K. Gillham of the Chemical Engineering Department of Princeton University under NASA Research Grant NGR 31-001-272 and is based on work performed between April 1, 1972 and October 1, 1974. The work was directed and monitored by the NASA Langley Research Center under the technical direction of Mr. V. L. Alley, Jr., of the Directorate for Systems Engineering and Operations and Mr. Austin McHatton, the Technical Representative of the Contracting Officer, Systems Engineering Division. Funds for this research were provided for NASA by the Advanced Research Planning Agency (ARPA) of the Department of Defense.

The authors acknowledge the presence of numerous contributions to the text pertaining to applications, mechanical performance, and industrial features that have been supplied to the authors by the courtesy of NASA monitors, or were forwarded for inclusion by the University by NASA from related research obtained from a NASA contract with the G. T. Sheldahl Co., Northfield, Minnesota. It is the belief of all involved that such contributions would better relate the subject paper to the inflatable structures segment of the aerospace community, which is not generally "chemistry" oriented. In strict accordance with the desires of the monitors to avoid undesirable encumberance of the paper, the usual use of foot notes, acknowledgments, and references to these dispersed contributions is omitted.

SUMMARY

Developments and testing are documented herein of new adhesive systems for use in balloons or other inflatable devices fabricated of polyester films or laminates. Conventional adhesives experience severe embrittlement and loss of toughness at service temperatures of -70°C in the tropopause.

Procured and/or synthesized candidate adhesives were characterized by determining their thermomechanical properties through use of Torsional Braid Analyses (TBA). Materials with the lowest transition temperatures (primary and secondary glass transitions and minimum damping) were tested further for blocking, tackiness, bonding, cure complexity, shelf-life, tensile strength, and compatibility with industrial equipment and practices.

The investigation included characterization of current balloon adhesives (partially end-reactive aromatic polyesters cross-linked with isocyanates), synthesis of low molecular weight hydroxyl end-capped aliphatic polyesters, characterization of polybutadienes and butadiene-acrylonitrile copolymers, and the analysis of two styrene-butadiene-styrene block copolymers.

The aliphatic polyesters show considerable improvement over conventional partially aromatic adhesives. Moreover, the linear hydroxyl end-capped amorphous polybutadienes show superior thermomechanical characteristics over the aliphatic materials. However, Shell Kraton™ 1101 and Phillips Solprene™ 406 SBS block copolymers appear the most promising if antioxidant and ultraviolet additives can be developed.

Curing behavior was studied in depth with respect to functionality of isocyanate, temperature, time, pressure, catalyst types, and backing paper. The polybutadienes display no difficult curing characteristics although adhesive strength decays with aging and shelf life and the materials are thermosetting. Cure is sensitive to hydroxyl number, is reactive to atmosphere, and is subject to volatility of solvents, thickness of coating, and characteristics of backing paper. Lowest tack was experienced using tin octoate and dibutyltin diacetate as catalysts. Curing was found to be relatively insensitive to pressure, although pressure is useful for dimensional control.

The upper values of peel strength were found to be comparable to the typical minimum values of conventional adhesives. The polybutadiene adhesives do not degrade the tensile strength of base films even at the low limit of use, -70°C; however, care must be exercised in gripping amorphous materials to preclude misleading downgraded tensile test data.

The achievement of adhesives with desired thermomechanical characteristics, with near conventional peel, ease of cure, and production compatibility, justifies further research to obtain a useable commercial product that is nonreactive, has slightly improved peel strength, and preferably is thermoplastic.

INTRODUCTION

Fabrication of polyester films and fibers is used extensively in the manufacture of balloons and other light weight devices for use by the aerospace agencies, the Department of Defense, and industry. Research balloons are used to monitor the ecology, to make meterology measurements, to serve as launch platforms for reentry tests, and are used as decelerators for atmospheric entry. Military applications include navigation aids, pilot rescue and recovery, border surveillance, and cargo carriers. Industrial uses involve recreational ballooning, sails, gas liners, sky-hooks for harvesting timber, hang gliders, wind and weather barriers, micro-wave relay and communication platforms, and fish spotting. Other prospective applications are in new generation airships and semi-bouyant aircraft.

In most of these applications, the materials fabrications are dependent upon constructing and assembling composites of films, fibers, and fabrics by use of suitable adhesives. Figure 1 shows typical fabrications of contemporary light weight and heavy weight balloon materials. The Dacron yarn reinforced Mylar film shown in figure 1a weight approximately 41 gm/m^2 (1.2 oz/yd^2) and is a typical light weight material used in natural shaped (onion shape) high altitude balloons of sizes up to 1 x 10^{6}m^3 (35 x 10^{6}ft^3). Figure 1b shows a multi-constituent lamination used for aerodynamic shaped tethered balloons (blimp shape) that range in size up to 5.7 x 10^{3}m^3 (2 x 10^{5}ft^3). Adhesives are used to attach the reinforcement fibers or to combine the films and encapsulate the structural fabric as in the case of the heavy weight laminate.

For high altitude and polar uses, these composite materials are subjected to a severe environment of winds, ultra-violet radiation, and temperature ranges from 100°C down to -50°C in the artic and -70°C in the tropopause region of the upper atmosphere.

Both flight experience and laboratory experiments have indicated that the structural integrities of such fabrications are greatly degraded by material embrittlement at low temperatures. Furthermore, it has been found that the adhesives show embrittlement far in excess of the base films and are suspected of initiating material failures. For example, figure 2a shows microscopic photography of a polyester film precoated with an adhesive. Figure 2b shows a similar film with reinforcement yarns attached with an adhesive. In both cases, the lack of continuity and homogeneity in the application of adhesive is apparent. In room temperatures, these features are of trivial effects; however, in sub-zero environments, the discontinuities, notches, geometric changes, combined with the fracture sensitive embrittled adhesive, produce premature stress failure that propagates into the film. Figure 2c shows another subtle feature of an adhesive coat on film. Diagonal and vertical Dacron fibers have been attached to a polyester film by hot rolling to a precoated adhesive film. An undesirable impression resulted from a fabric liner on the hot roller of the industrial fabricator. Again, these impressions are of little consequence when the film is amorphous, but they significantly reduce the film's tolerances to stress when

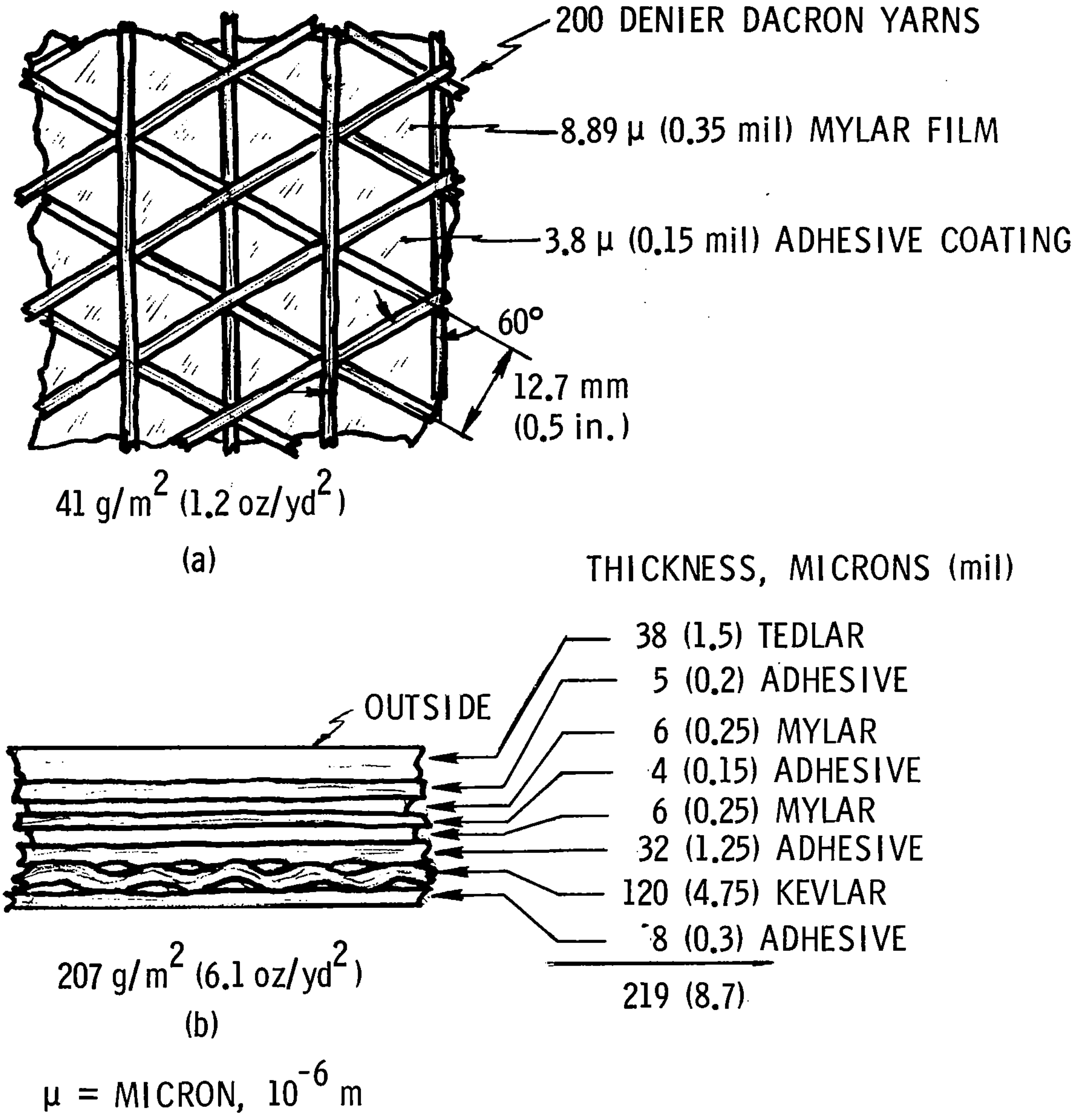
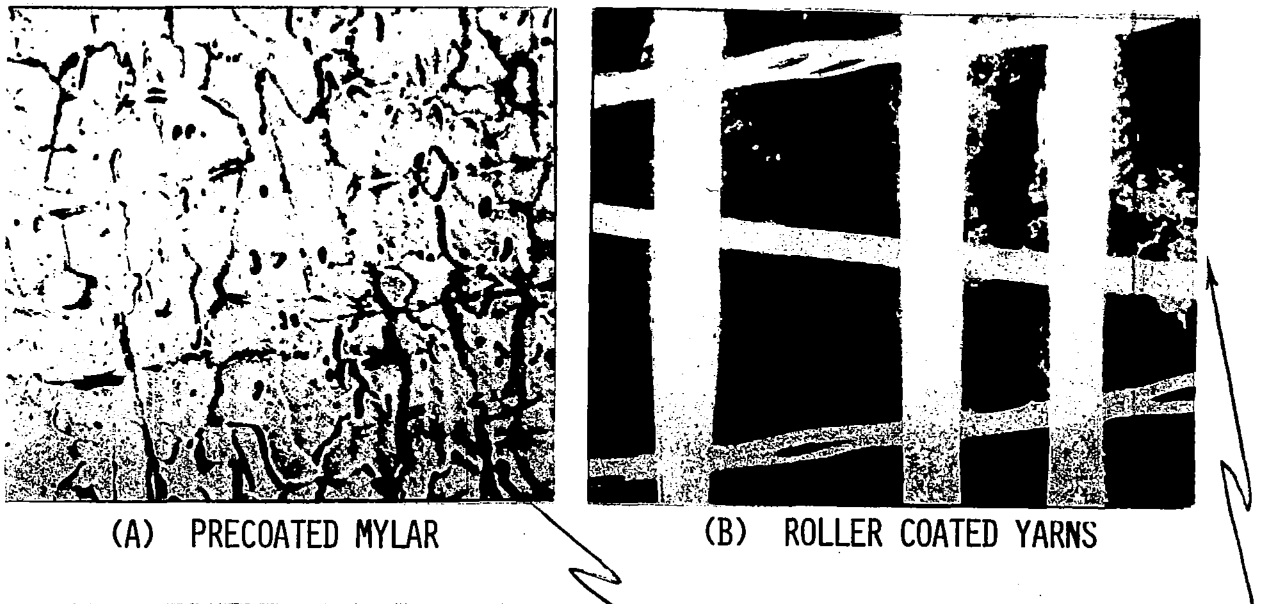
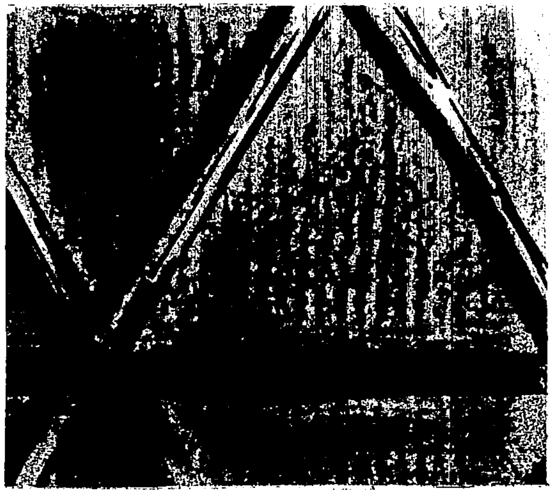


FIGURE 1.- Typical fabrication of material for inflatable structures.



(A) PRECOATED MYLAR

(B) ROLLER COATED YARNS



(C) ROLLER IMPRESSIONS

FIGURE 2. - ADHESIVE COATS AND GLOBULES AND FABRICATION IMPRESSIONS ON FILMS

the environmental temperature is below the glass transition temperature of the adhesive.

In light of these types of adverse involvement of adhesives in composite fabrications, and in view of the increasing uses of such materials in high altitude applications, the need is apparent for acquiring or developing a specific adhesive of compatible mechanical performance to the usual film constituents of the contemporary balloon materials.

It is the purpose of this paper to report and record the research effort that has been made to develop or acquire an adhesive with improved low temperature properties suitable for bonding polyester fibers or films to polyester films within the specific environments and constraints of balloon applications. Most of low-temperature adhesive references found in the literature deal with cryogenic ($T < -150^\circ C$) applications, usually involving metal-metal bonding. However, references 1-3 do include information, references, and techniques useful for somewhat higher temperatures. Due to the lack of applicable data in the literature and the strong interest of the University laboratory in thermomechanical studies, the development of the adhesive project was directed primarily by knowledge and application of the principles of thermomechanical behavior of polymers. For example, embrittlement observed in polymeric materials is closely related to relaxational processes which in turn are dependent upon molecular structure, temperature, and the time scale of perturbations. Embrittlement of the balloon adhesive at low temperatures presumably arises out of frozen relaxations. One solution to this problem would be to use polymers which have more flexible backbones and, therefore, lower glass transition temperatures (Tg). It would be possible to use polymers with very high Tgs as low temperature adhesives as long as relaxation giving mechanisms for release of stress occurred in the region of the use temperature. Examples (ref. 3) include tetrahydrofuran-based polyether-urethanes and polybenzimidazoles (PBI), one of the latter being of particular interest because it shows a secondary relaxation at $\sim -70^\circ C$ (ref. 4). However, most high Tg materials would create severe processing problems due to high working temperatures, low solubilities, etc., and it is doubtful whether most of these polymers would show sufficient elongation for use in balloon laminates. Therefore, it was decided to limit the investigation to low Tg polymers (preferably with Tg below $-70^\circ C$); i.e., materials that would be flexible and rubbery at the minimum use temperature.

Elimination of embrittlement would not, however, solve the problem completely. In addition to flexibility, a suitable adhesive must show good adhesion! This occurs when there are sufficient numbers of polar groups, such as esters, ethers, or urethanes, along the polymer chains. The adhesive must also have dimensional stability and good non-blocking (tack-free) properties. Some of the balloons are of unusually large dimensions (volume $\sim 10^6$ m^3) and must be folded during and after fabrication. Since the adhesive layer in the fiber/film laminate used for the balloon panels is not completely covered, a tacky adhesive would cause the layers of balloon material to stick together (block) on being folded. Therefore, it is imperative that the adhesive be tack-free. Good non-blocking properties and dimensional stability are found when the polymer molecules comprising the adhesive are partly crystalline or are crosslinked (or both). Although crystallization is helpful in conferring non-blocking properties and dimensional stability at temperatures in excess of Tg, it can be highly detrimental at temperatures below Tg by causing excessive embrittlement.

End-reactive aromatic polyesters, crosslinked with isocyanates, are widely used as adhesives in the manufacture of balloons. However, due to their having glass transition temperatures of $\sim -10^\circ C$, such materials are not likely to be very effective adhesives in the temperature region of $-70^\circ C$. Aliphatic polyesters are more flexible than their aromatic counterparts and have lower Tgs. Polybutadienes show even greater superiority in these respects. Therefore, it was decided that amorphous end-reactive (hydroxyl end-capped) aliphatic polyesters or end-reactive polybutadienes, crosslinked with multifunctional isocyanates would be good candidates for meeting the requirements for balloon adhesives. When cured (crosslinked) these polyester- and polybutadiene-urethanes would be expected to show excellent high temperature stability as well, i.e. stability equal to or greater than the aromatic polyester film on which they would be coated.

Later in the project, systems which do not need a reactive (chemical) curing process were considered, particularly "thermoplastic elastomers" such as styrene-butadiene block copolymers. These block copolymers are of considerable interest in that they are thermoplastic but the copolymer segments have distinct and very different glass transitions. Above $\sim 100^\circ C$, the Tg of polystyrene, the material is relatively liquid, while below that temperature the material is rubbery and flexible with the glassy polystyrene aggregates acting as crosslinks to immobilize the ends of the polybutadiene rubber chains. The copolymer retains its flexibility to very low temperatures. These materials appear to be excellent candidates for balloon adhesives.

TEST APPARATUS

The candidate adhesives were selected first by examining their thermomechanical spectra. The most likely materials then were tested for compatibility with films, curing characteristics, blocking, peel, and suitability for industrial processes.

Torsional Braid Apparatus

The low temperature properties of the various polymers were evaluated by monitoring thermomechanical behavior using torsional braid analysis (TBA) (ref. 5-9). This technique uses a torsional pendulum capable of examining small amounts of materials and is unique in that the preparation of specimens is simple and polymers can be examined throughout the spectrum of mechanical states (glassy, rubbery, fluid). A composite specimen is prepared simply by soaking a multifilamented glass braid (shown in Fig. 3) in a solution of the polymer (concentration, 5-100%) and removing the solvent

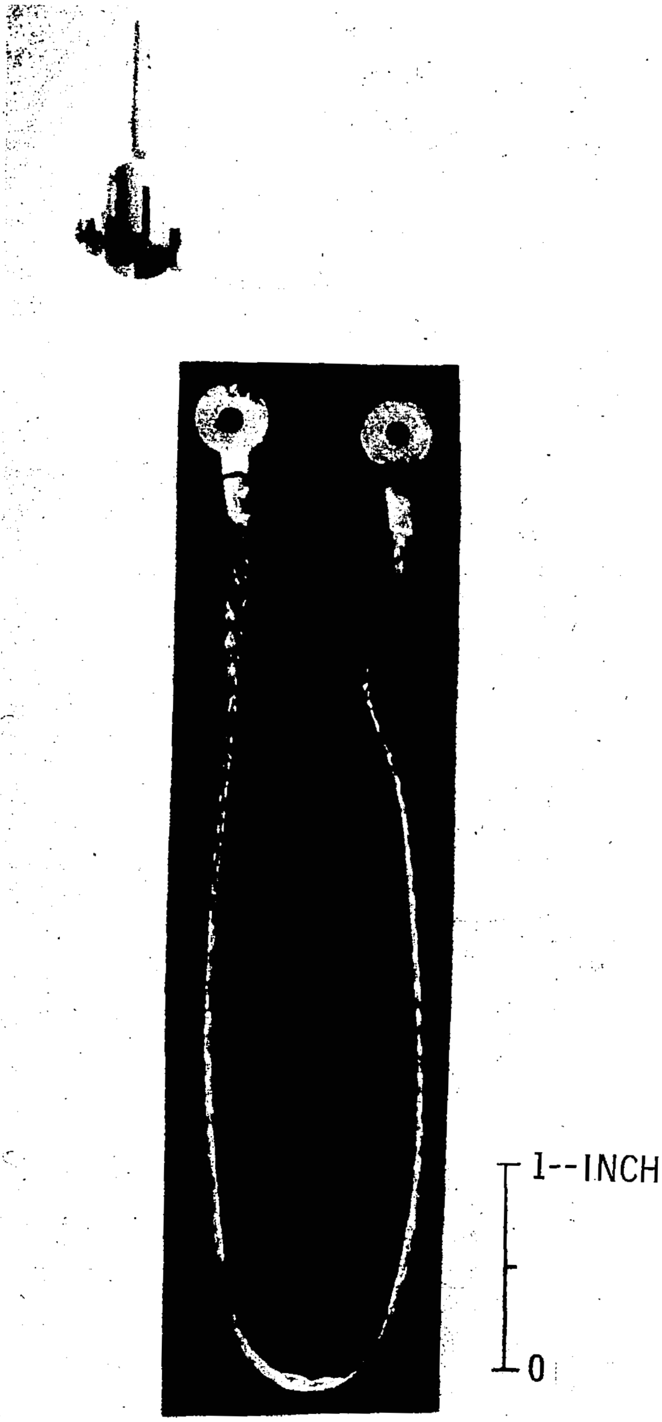


FIGURE 3. --MULTIFILAMENTED GLASS BRAID

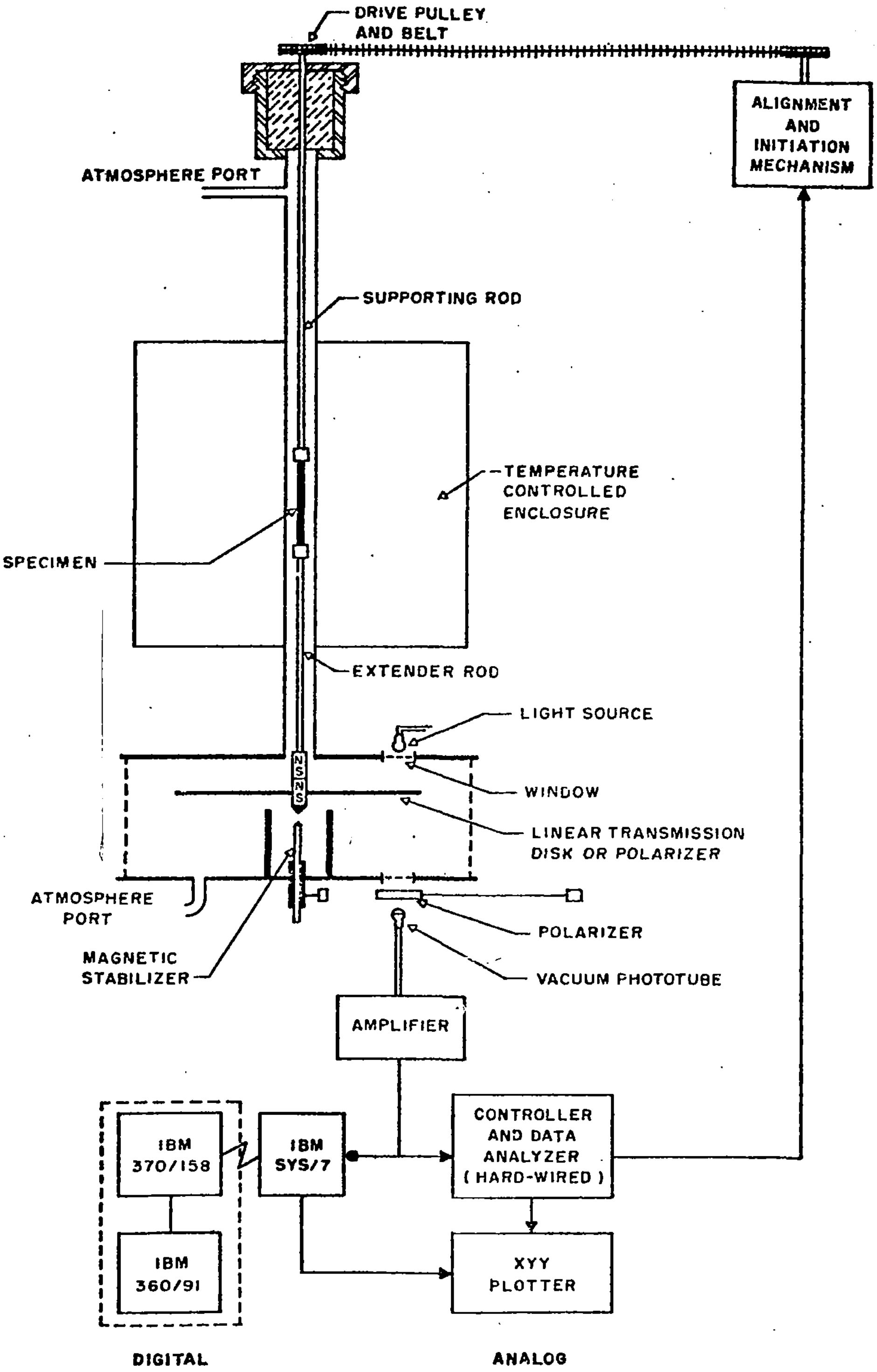


Figure 4. Torsional Braid Analysis Apparatus.

by heating in the apparatus. The technique is particularly useful for the thermomechanical characterization of non-selfsupporting polymers.

The apparatus is shown in Figure 4. It is essentially a stainless steel tube surrounded by a heating mandrel and fluidized bed (for heat transfer). It operates over a temperature range of -190°C to +600°C with a temperature spread of ± 1°C over an 8 in. sample. Through the use of a suitable controller/programmer the apparatus can be programmed for increasing, decreasing, and isothermal modes of temperature. The atmosphere is tightly controlled; inert or reactive gases or a vacuum may be used.

The pendulum is activated by turning the rod which supports both the specimen and the inertial mass. This is performed by a displacement of the upper lever through a small angle. The mechanical oscillations thus generated are converted linearly to a convenient electrical analogue using a friction-free transducer. Light from a constant source is attenuated in passing through the linear-with-angle region of a pair of polarizers, one of which serves as the inertial mass of the pendulum; the attenuated light is sensed by a linearly responding vacuum phototube.

Many of the thermomechanical experiments described below and some of those carried out specifically for this study involved the use of an automated torsional braid analysis instrument. This apparatus uses an analog minicomputer (designed and built in the Princeton laboratory) to control a repetitive sequence consisting of alignment of the optical transducer by rotation of the pendulum head, initiation of free oscillations, collection of data from the oscillations, and computation and simultaneous print-out of temperature, logarithmic decrement, and period for each damped curve (ref. 8). The TBA apparatus has also been connected to a hierarchical system of computers (refs. 10-12) employing an interactive computer in the laboratory as the digital front end. This system is a flexible and powerful tool and for analysis and presentation of data and development of instrumentation. Because of a number of initial difficulties this system was not used in the balloon project.

Preparation of Braid - In the study, glass braids were impregnated with 10 or 15% polymer solution. Solvent was removed from the specimen by heating ($\Delta T/\Delta t$ = 3°C/min) to 120°C. In the case of an adhesive composition, the glass braid was impregnated with a solution (15% solids, usually in methylene chloride) of stoichiometric proportions of prepolymer, curing agent and a catalyst. The specimen was then mounted in the instrument and cured at 65°C for 16 hours in air. Similar braids involving only polymer and without curing were prepared from styrene-butadiene-styrene (SBS) block copolymers. All thermomechanical experiments were performed in dry nitrogen at heating and cooling rates of 3°C/min above room temperature and 1°C/min below room temperature.

Roller Coating Apparatus

In order to perform additional mechanical tests on the most promising adhesive candidates it was necessary to fabricate adhesive coated film of controlled thickness and under controlled cures. Materials were manufactured, test specimens fabricated, and test results were provided the University under a complementing NASA contract with the G. T. Sheldahl Co., Northfield, Minnesota. This contract was let to provide the University access to the industrial expertise and facilities for handling, controlling, manufacturing and curing of bulk polyester products.

Coated films were manufactured by applying various adhesive formulations to .009 mm (0.35 mil) polyester film substrate using an industrial roller coater for which the schematic is shown on Figure 5. The coating thickness was adjusted to approximately .005 mm (0.2 mils) and .010 mm (0.4 mils) for each adhesive candidate by varying the solution viscosity and coating speed. Thickness was monitored by direct gauging and by weight.

Coating small quantities of films with the various adhesives was carried out on a qualitative basis in the University laboratory. This involved casting thin adhesive films on aromatic polyester film from formulations containing stoichiometric mixtures of polyester (or polybutadiene), isocyanate, solvent, and catalysts. The adhesives were allowed to dry for 5 minutes in an exhaust hood and then a coated film was placed between two PTFE sheets which in turn were sandwiched between two aluminum plates, each 3 mm thick. The sandwiches were transferred to a heated (60, 80, or 150°C) platen press and the adhesives cured for different periods of time at different pressures. No curing was necessary in the case of the SBS polymers. Tack was evaluated after adhesive films cast on polyester film had been dried and annealed in an oven at 80 or 120°C. In other experiments uncoated strips of polyester film were bonded to adhesive-coated film and heated in the platen press after which qualitative determinations of the bonding ability of the adhesive were made.

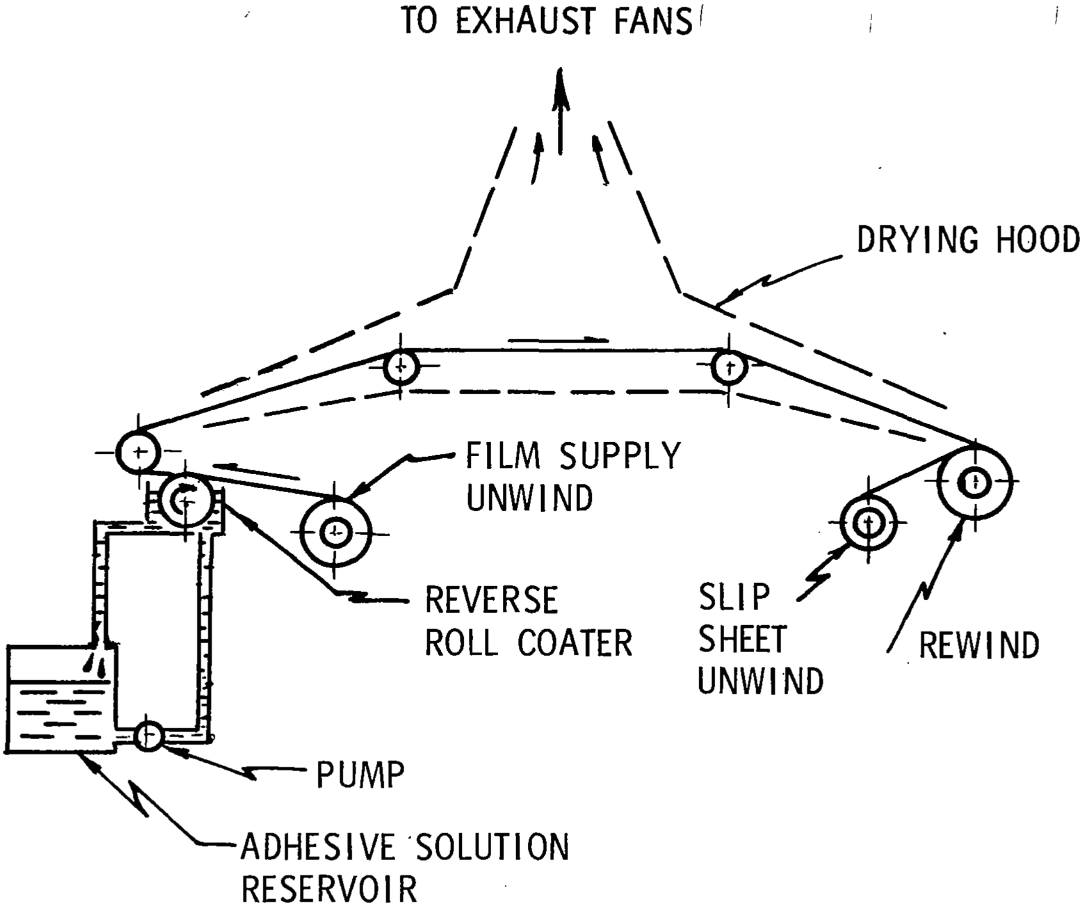


FIGURE 5. - SCHEMATIC OF THE ROLLER COATER PROCESS.

Tensile Test Apparatus

As previously mentioned, both flight experience and laboratory experiments have indicated that the conventional adhesives degrade the strength of the film substrate. A goal of the adhesive research was to acquire an adhesive that would not degrade and perhaps improve the membrane strength of the control film. Uniaxial tensile tests were made to acquire quantitative data on the adhesive-film compatibility. Standard tensile test specimens of .025 meter (1 inch) width and .051 mils (2 inch) gage length were prepared from the bulk adhesive coated film.

Tensile data were determined for those specimens at the Sheldahl Co. using the Model 114 Instron Testing Machine equipped with a liquid nitrogen cooled Missimers environmental chamber as shown in Figure 6.

Break tensile strength and elongations were obtained at 23°C and -68°C using ASTM method D882. The strain rate unless otherwise stated was standardized at 100% strain per minute. As a prerequisite to testing, an investigation was made to determine jaw effectiveness on these visco-elastic or glasseous films. The analysis of the various clamping techniques showed that the rubber-faced pneumatically operated jaws supplied by Instron provide the most uniform specimen loading. Those jaws were used for all subsequent film testing for this project.

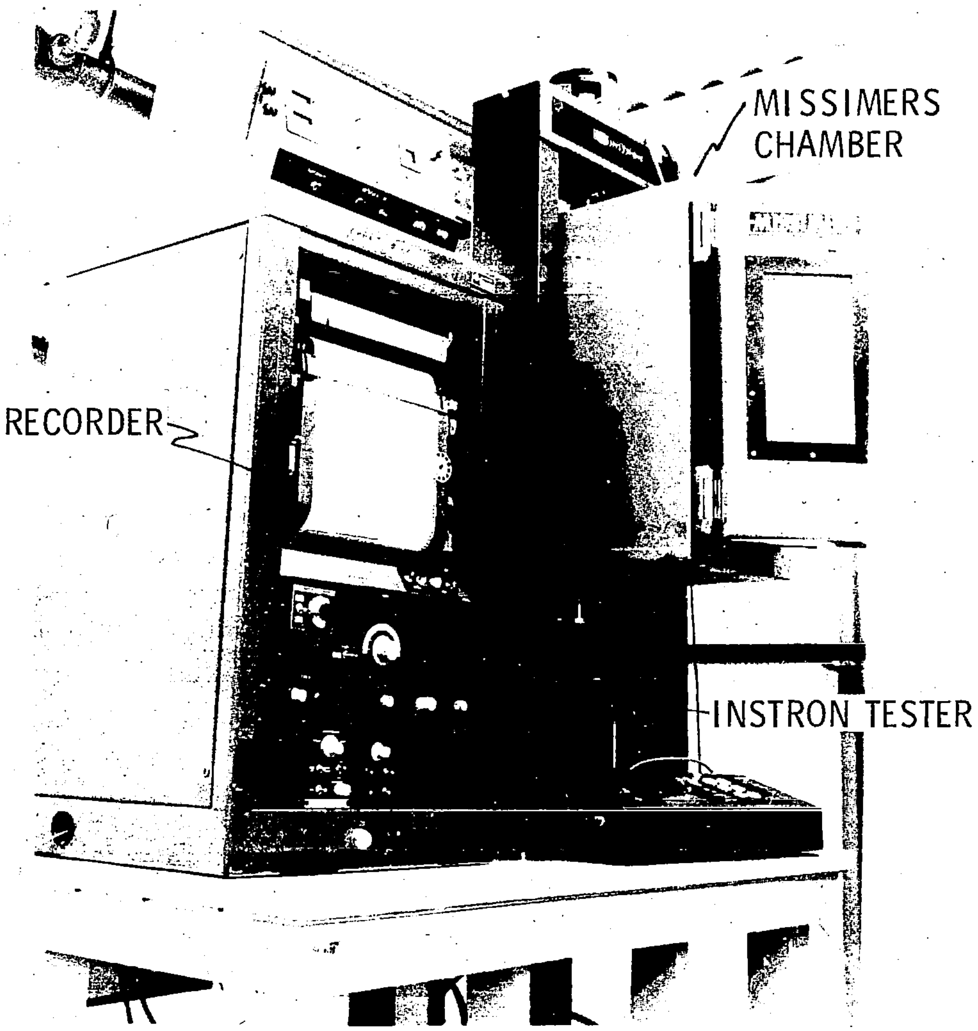


FIGURE 6. - UNIAXIAL TENSILE TEST APPARATUS

Peel Test Apparatus

Peel strength measurements of adhesive-film-adhesive sandwich specimens were made in accordance with ASTM specifications D1876. The 114 Instron console shown on Figure 6 was used for these tests. Each of the film adherends was gripped in the Instron jaws and both adherends were allowed to freely flex near the line of bond failure through angles of approximately 90 degrees. Film to adhesive peel was run at 0.305 meters (12 inches) per minute. A typical peel test installation is shown in Figure 7. The intact sandwich is shown standing free behind the peel parting line. The two parted adherents are shown, one to the upper Instron jaw, and one to the lower jaw.

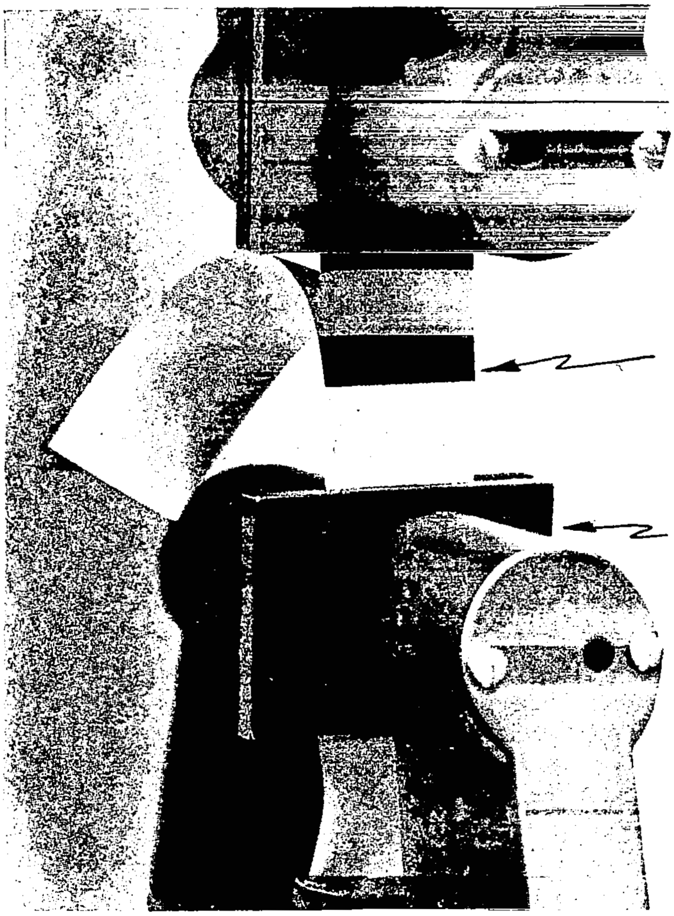


FIGURE 7. - PEEL TEST ASSEMBLY

SYMBOLS AND ABBREVIATIONS

f	Functionality also, peel force
°C	Temperature, deg. centrigrade
DTA	Differential thermal analysis
G'	Storage modulus
K"G"	Relative loss modulus
MD	Machine direction of structurally oriented film
1/n	Mechanical damping index
$1/p^2$	Relative rigidity index
Q	Weight/unit area of the composite; film plus adhesive coat
RT	Room temperature
SG	Specific gravity
T	Temperature
TGA	Thermogravimetric analysis
TBA	Torsional Braid analysis
TD	Transverse direction of structurally oriented film
T_{min}	Temperature of minimum mechanical loss
T_β	Temperature of secondary state transitions
Tg	Glass transition temperature
T_{crys}	Temperature of crystallization
t_a	Average thickness of the adhesive coat
t_f	Thickness of the base film
W_i	Weight of the ith constituent of a solution
Δ	Logarithmic decrement of damped wave
β	Secondary glassy-state transition
δ_w	Density of fresh water (1 gram/cc)

METHODS OF ANALYSES

The method of selecting candidate adhesives has been through an analysis of the thermo-mechanical characteristics of the polymeric materials. This technology will be discussed in detail in the following section. In addition, the method for determining molecular weight by analysis of hydroxyl end groups will be delineated in a subsequent section.

Thermomechanical Spectral Characteristics

By exciting the Torsional Braid Apparatus previously defined, the natural torsional oscillation and its damped decay are induced and recorded against time for a range of environmental temperatures.

The logarithms of two parameters, one relating to the storage of energy (relative rigidity, $1/p^2$) and the other to the dissipation of energy on mechanical deformation (mechanical damping index, $1/n$, logarithmic decrement, Δ, or relative loss modulus, K"G") are plotted versus temperature or time to form mechanical spectra (Fig. 8). These parameters are comparable to the commonly used storage modulus, G', and loss tangent, tan δ. The plots are relative and do not give absolute modulus values. The loss (damping) spectrum is characterized by a series of peaks each of which is attributed to the onset of motion of internal structural elements of the material. These loss peaks define the phase transitions and are accompanied by changes in the storage (rigidity) spectrum.

Mechanical spectra are of considerable theoretical interest, but are even more important for determining properties of and applications for polymeric materials. One way in which this is being done is by relating the damping (loss) peaks of the spectra both to the onset of particular localized inter- and intramolecular motions and to changes in bulk properties. For example (ref. 12), the thermomechanical loss spectrum of each of the amorphous polymethylmethacrylates of Figure 9 displays a sharp peak at the glass transition (Tg) and a less intense secondary or "β" transition (T_{sec} or T_β) in the glassy state. The latter is associated with the onset of motions of the ester side groups with increasing temperature, whereas the glass transition is associated with the onset of longer range cooperative torsional motions of extended segments of the polymer chains. In terms of bulk properties, materials tend to be brittle at temperatures below the β-peak, tougher above it, and no longer solid above the glass transition. A major use of the torsional pendulum is to characterize phase transitions in solid polymeric materials. By using a supported polymer as in TBA, measurements can be made through the load-limiting transitions (Tg for amorphous polymers; melting and crystallization transitions, Tm and Tcrys, for semicrystalline polymers).

It should be pointed out that although a low glass transition temperature is necessary for a polymer to qualify as a potential candidate for a low temperature adhesive, the temperature at which the polymer in the solid exhibits a minimum damping or loss level (T_{min}) may be of greater significance.

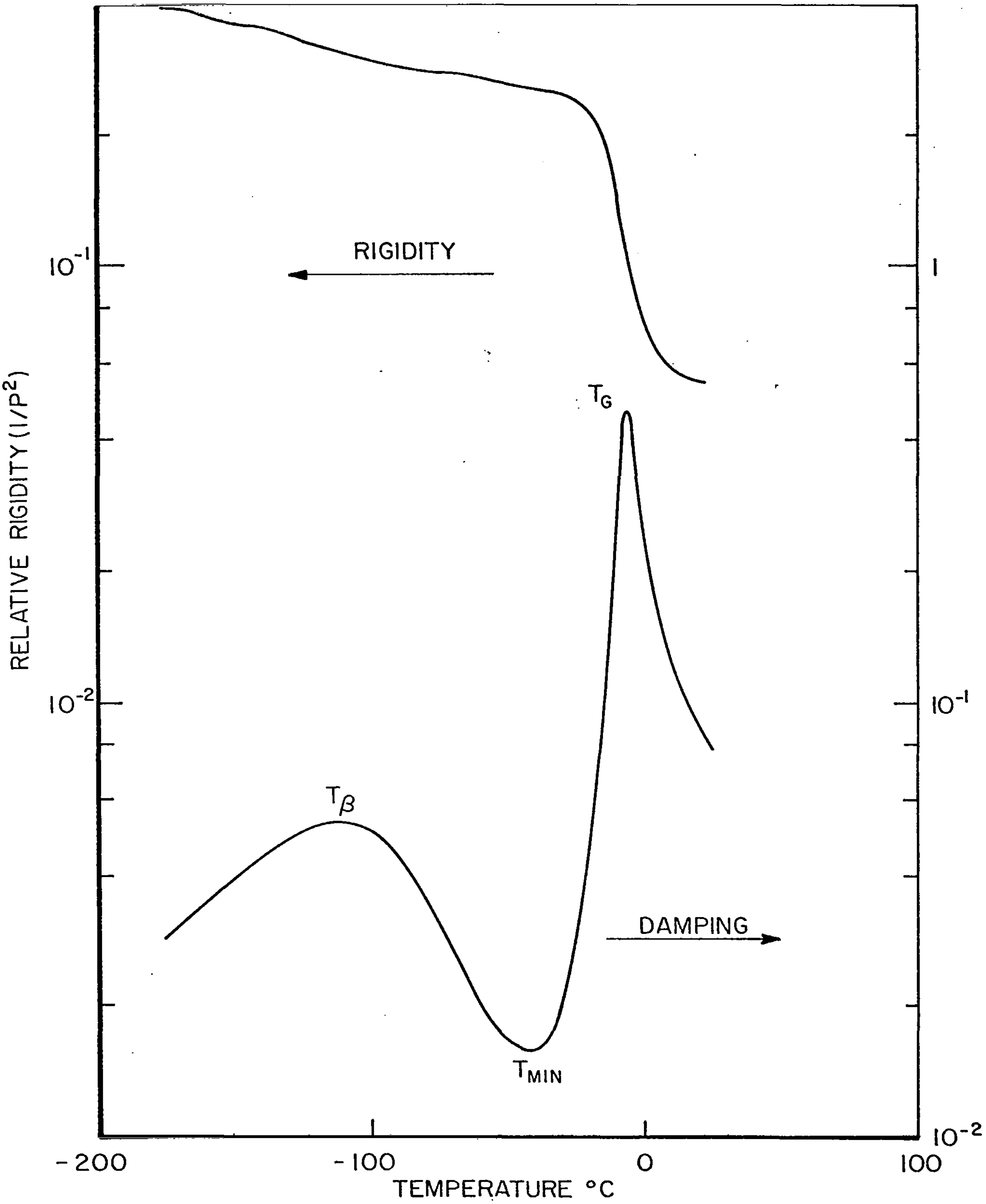


Figure 8. Thermomechanical Spectra in Nitrogen of Polyester Used in Balloon Adhesives (A002800, G.T. Sheldahl Co.), Drying: RT → 100°C → RT, Experiment: RT → -175°C → RT.

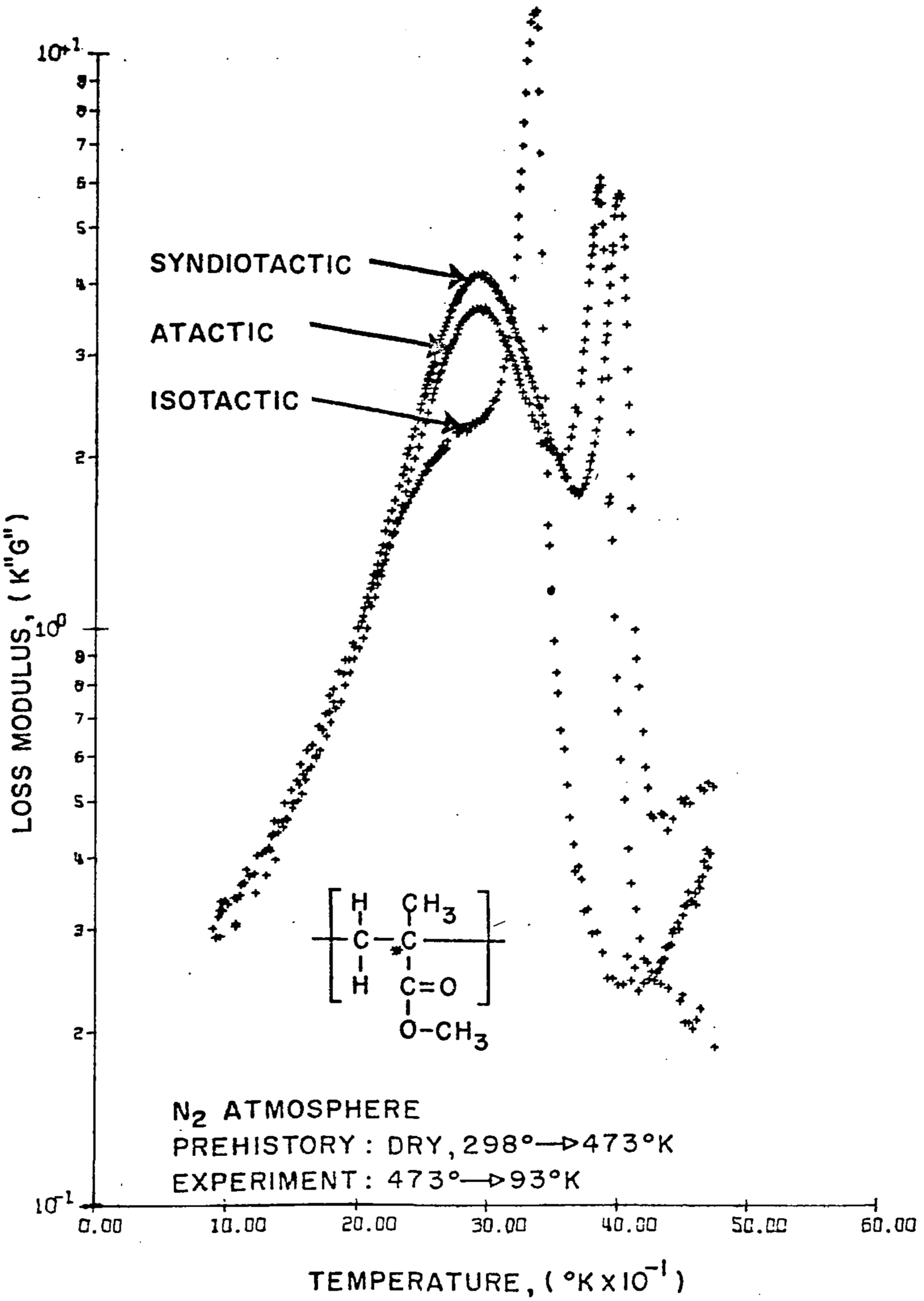
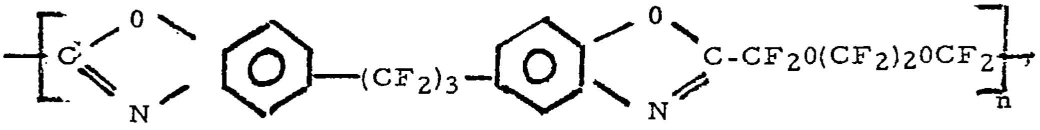


Figure 9. Computer Processed Data for Three Polymethylmethacrylates.

Minimum loss in the solid state is directly related to brittleness, and above T_{min} the polymer would be expected to be tough and somewhat flexible. Therefore, it is necessary that the adhesive have a low temperature of minimum mechanical loss, certainly lower than the use temperature of $\sim -70°C$.

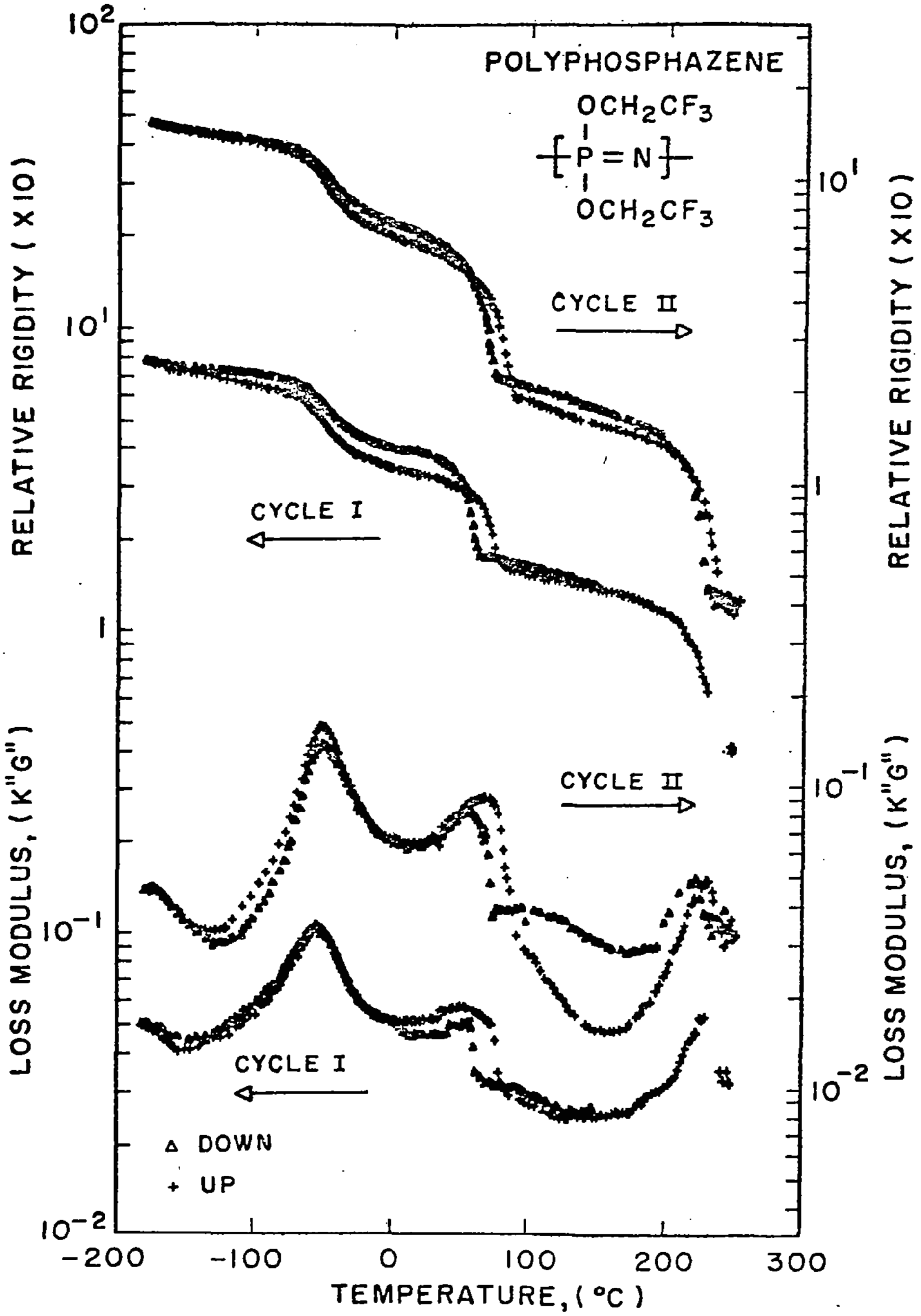
The ability to obtain data throughout load-limiting first order transitions is exemplified by the thermomechanical spectra for a polyphosphazene with repeat structure $-P(OCH_2CF_3)_2N-$ (Fig. 10). [The spectra are for the continuous sequence 150 → -180 → 250 → -180 → 250°C (ref. 13); they are separated into two parts for reasons of clarity.] The following transitions are observed: a single glassy-state relaxation at -175°C, a glass transition at -49°C, a first order crystal to crystal transition with the transition measured at 58°C on cooling and at 68°C on heating, and a first order crystal/melting transition with crystallization occurring at 233°C (Tcrys) and subsequent melting occurring at 238°C (Tm).

Many polymers with complicated structures give more than one glassy-state secondary transition. Good examples of this are shown by the members of a series of fluorocarbon bibenzoxazole polymers (ref. 14). The mechanical spectra of one of these polymers,



is presented in Figure 11. The results from these polymers are noteworthy in that definite correlations have been made between each of the secondary transitions and the onset of motion in particular fluorocarbon linkages. The secondary transition in the region of -40°C (Tsec') noted for each polymer was assigned to the onset of motion in the $-(CF_2)_3-$ chain segment. The lower temperature secondary transitions (Tsec") were assigned to motion in the other fluorocarbon linkages, i.e. $-CF_2O(CF_2)_2OCF_2-$ in the case of the polymer shown in Figure 11.

Thermomechanical measurements are inherently more sensitive than the more usual thermal techniques for investigating temperature dependent properties, and, in revealing changes in mechanical terms, are of special interest to applied polymer scientists. As an example of sensitivity and correlation with other techniques, the thermomechanical spectra of a specimen of highly acetylated cellulose triacetate, together with the corresponding results for thermogravimetric analysis (TGA) and differential thermal analysis (DTA), are presented in Figure 12 (ref. 5). The T_g in the vicinity of 190°C is accompanied by a drastic decrease in rigidity, a prominent maximum in damping, and an endothermic shift in DTA. The subsequent increase in rigidity at temperatures above 200°C is attributed to crystallization and/or chain-stiffening processes and is accompanied by an exothermic maximum (DTA). Tm at 290°C is accompanied by an abrupt decrease in rigidity, a maximum in damping, and an endothermic maximum (DTA). The subsequent increase in rigidity, decrease in damping, exotherm (DTA) and weight loss (TGA), are attributed to crosslinking and/or chain stiffening processes.



He ATMOSPHERE

PREHISTORY : DRY, 25 ⟶ 150°C

EXPERIMENT :

150 ⟶ -180 ⟶ 250 ⟶ -180 ⟶ 250°C

Figure 10. Thermomechanical Spectra for a Polyphosphazene, Data from TBA Data Analyzer.

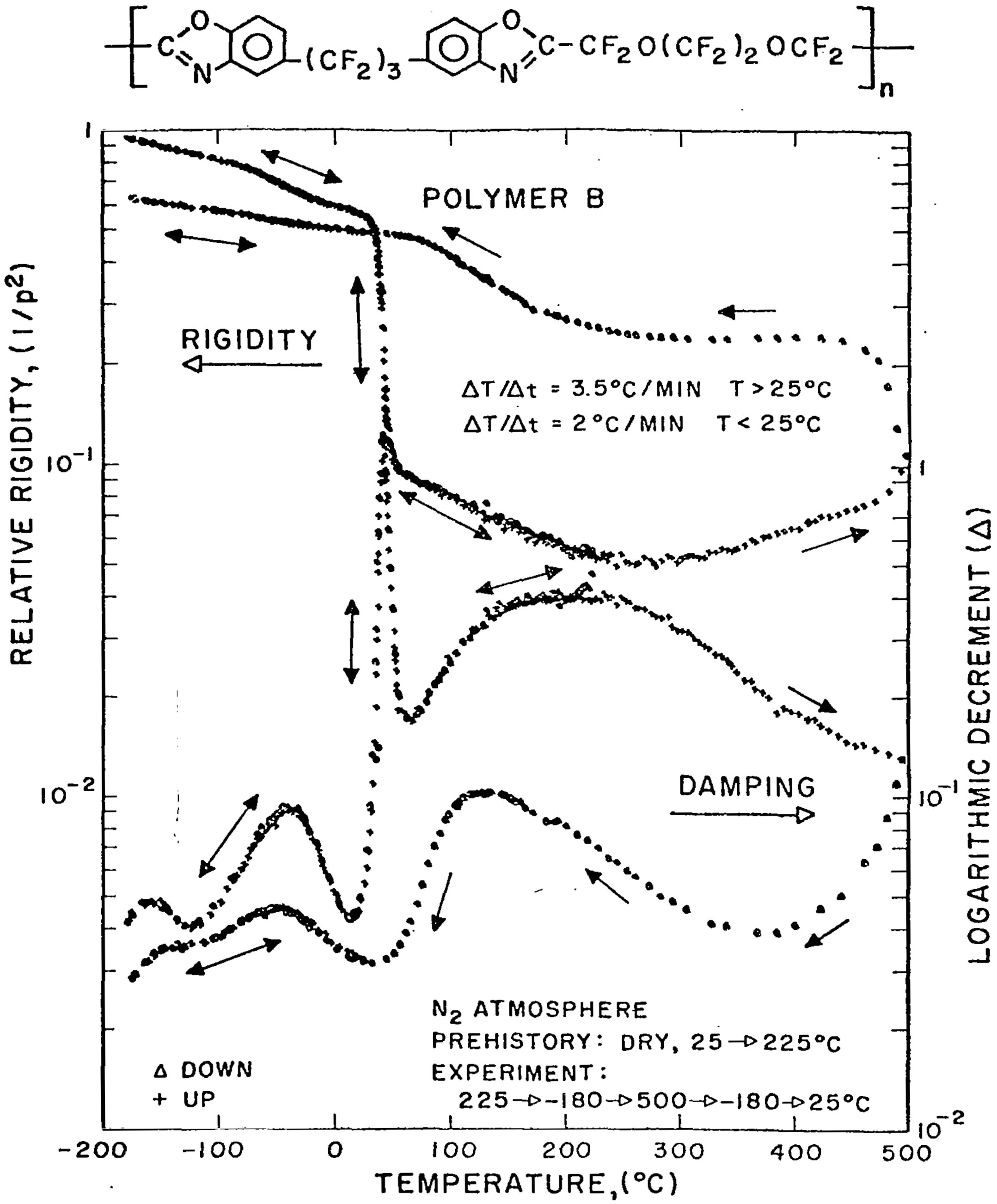


Figure 11. Thermomechanical Spectra in Nitrogen of a Fluorocarbon Bibenzoxazole Polymer.

The bottom diagram of Figure 12 shows the drift of the neutral position of the inertial mass versus temperature for a cellulose triacetate/glass braid specimen. The specimen was not oscillated. The motion is a consequence of stresses which develop in the composite specimen. The sense of the drift correlates with expansion or contraction of the matrix. It is observed that drifts which correspond to T_g and T_m are in the opposite sense to the processes corresponding to crystallization and crosslinking. (It is the occurrence of this phenomenon which necessitated the incorporation into the instrumentation of a self-aligning mechanism for the optical transducer (ref. 8).

There are many advantages of working with small specimens with an essentially nondestructive technique. Among these is the relatively rapid thermal equilibrium of the specimen with the environment. This permits thermomechanical experiments to be undertaken over extended ranges of temperatures in a reasonable time scale. It allows the taking of data at both increasing and decreasing temperatures which often reveals features which might be ignored by a unidirectional experiment. (Most mechanical apparatus operate in one direction of temperature change.) Thermohysteresis may indicate physical time-dependent phenomena such as crystallization/fusion, dry atmosphere/water vapor, annealing/cracking and chemical reactions, not to mention incorrect assignments of temperature. Lack of thermohysteresis is a good test of reversibility and also often distinguishes amorphous from semi-crystalline materials. A more subtle advantage in using small specimens is the ability to remove (by heating the polymeric matrix to a fluid state) tenaciously held foreign materials such as water and solvent, the presence of which alters the mechanical spectra. Working with small samples also presents problems. Development of instrumentation required the innovation of a no-drag transducer for converting the mechanical oscillations into an electrical analog, while the use of nitrogen as an inert atmosphere must be accompanied by careful drying since water vapor can condense at low temperatures and affect the data.

A considerable literature on mechanical spectroscopy exists. An extensive review of the literature emphasizing the molecular basis of mechanical spectra but also reviewing the theory of the experimental methods was published by McCrum, Read, and Williams in 1967 (ref. 15), whereas several important papers emphasizing engineering properties as the manifestation of the mechanical spectra have been published by Boyer (refs. 16-18).

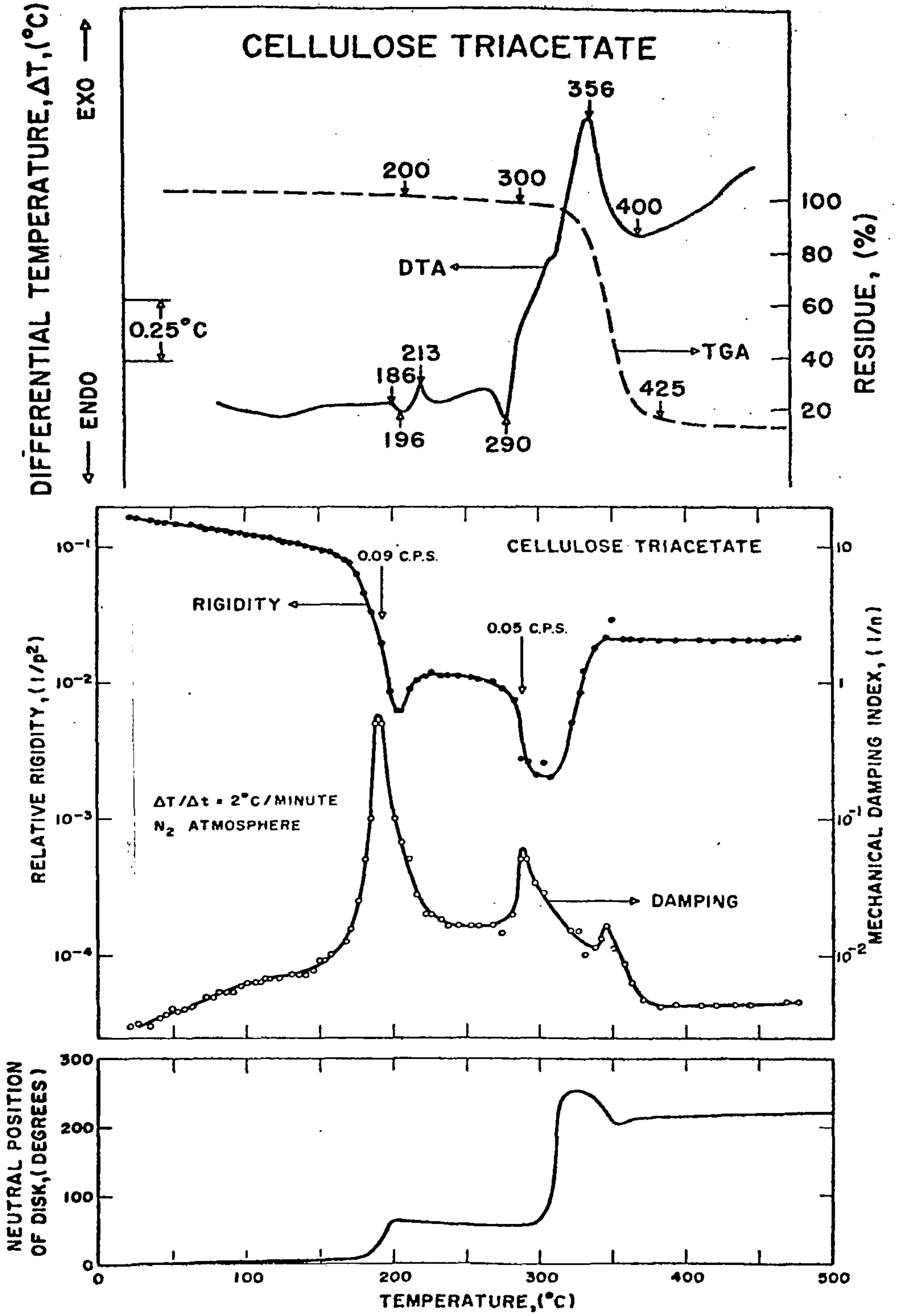


Figure 12. Comparison of Thermomechanical (TBA), Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) Data for Cellulose Triacetate.

Determination of Molecular Weight by the Analysis of Hydroxyl End Groups

The following procedure (ref. 19) was used to determine molecular weight by end group analysis. About 1 gram of polyester was weighed to the nearest mg. into a 100 ml. round-bottom flask. To dissolve the sample, 25.0 ml. of a mixture of 12.0 ml. acetic anhydride and 50 ml. dry pyridine was added by pipet. The solution was refluxed for 1 hr. The condensor was then washed out by the addition of about 5 ml. water through the top and the heating was continued for 5 minutes. The heat was then removed, the condensor tube and tip were washed with 25 ml. of methanol which was added to the total. When the mixture had cooled to room temperature, it was titrated with approximately 0.5 N standard potassium hydroxide solution to a phenolphthalein end point. The amount of KOH (mg) necessary for neutralization was called value A.

A blank titration was then run against a mixture of acetic anhydride-pyridine reagent and water in the same volumes as above, which had been allowed to stand for 15 minutes. 25 ml. of methanol was added, as in the preceding case, just before titrating. This blank value, in mg. KOH, was called value B. (If value A is less than 65% of value B, it indicates that insufficient acetic anhydride was added for complete acetylation in which case the experiment should be repeated with a larger excess of acetic anhydride.)

Another sample of polymer, of about the same size as the first, was dissolved in 25 ml. pyridine and the solution titrated against 0.5N KOH to a phenolphthalein end point. Here, the number of mg. KOH per g. polymer, value C, gave the acid number of the polyester.

The hydroxyl number of the polyester = (C + B - A) mg KOH/g polymer. Because there are two ends per molecule, the total of hydroxyl and carboxyl ends equals twice the number of polymer molecules. Therefore, the sum of the acid and hydroxyl numbers may be used to calculate the number average molecular weight:

$$\frac{(\text{Acid No. + Hydroxyl No.})}{2 \times 56.1} = \text{moles of polymer per gram,}$$

$$\text{Molecular Weight} = \frac{1}{\text{moles of polymer per gram}} .$$

CANDIDATE ADHESIVES

In selecting candidate adhesives, initially a conventional balloon adhesive and four candidate industrial adhesives were studied to provide base line characteristics. Additional candidates were obtained by synthesizing and/or procuring other molecularly suitable materials.

Industrial Adhesives

Four readily available industrial adhesives used in balloon application and characterized under this University effort were as follows:

Adhesive A. - A formulation of a 50-50 mixture of two solutions. The first solution is 15 wt. percent B. F. Goodrich Estane 5712 polyurethane resin in a 50-50 mix of tetrahydrafuran and methyl ethyl ketone. The second solution is 15 wt. percent A-102 resin in methylene chloride. A-102 is a Sheldahl Company proprietary thermoplastic polyester.

Adhesive B. - A solution of 15 wt. percent of A-103 resin in methylene chloride. A-103 is a Sheldahl Company proprietary thermoplastic polyester.

Adhesive C. - A solution of 15 wt. percent Bostik 7925 polyester in methylene chloride.

Adhesive D. - A solution of 15 wt. percent solids in methylene chloride. The solids are 80 parts A-102 resin, 20 parts microthene (polyethylene powder), and 0.5 parts silane coupling agent.

Synthesis of Low Molecular Weight Hydroxyl End-Capped Aliphatic Polyesters (Ref. 19)

A second phase of the study was to synthesize and/or purchase amorphous low molecular weight hydroxyl end-capped aliphatic polyesters and polybutadienes. The molecular design of the adhesive was to be such that the low molecular weight end-reactive flexible prepolymer could be (1) chain extended with a difunctional (functionality, f, = 2) isocyanate which would simply increase the molecular weight of the linear polymer or (2) crosslinked with trifunctional (f = 3) isocyanate to produce a network. The crosslink density of the network could be varied by using a mixture of di- and trifunctional isocyanates.

Experimental conditions were standardized to produce amorphous hydroxyl end-capped aliphatic polyesters and copolyesters with number average molecular weights in the region of 2000-3000. Such a molecular weight was considered to give an optimum chain length between crosslinks so as to impart dimensional stability and yet not affect the flexibility of the resultant product. Preliminary synthetic work was carried out using adipic acid and 1,2 propane diol. The effect of varying stoichiometry and reaction temperature, and removal of water formed in the reaction were studied to arrive at the most suitable reaction conditions. Polyesters of azelaic acid and adipic acid with various diols of symmetric and asymmetric structures (ethylene glycol, 1,2 propane diol, 1,3 butane diol and polyethylene glycols of different molecular weights) were then synthesized. Details of the constituent diacids and diols, the acid and hydroxyl numbers, and the number average molecular weights of the synthesized polyesters are all summarized in Table 1.

The low molecular weight hydroxyl end-capped aliphatic polyesters and copolyesters were synthesized in a 4-necked, 100 ml glass kettle equipped with a glass stirrer, reflux condensor with a Dean & Stark distilling receiver, thermometer, and an inlet for nitrogen gas. Calculated amounts of diol(s), dibasic acid, catalyst, and solvent were placed in the resin kettle (for details of the various ingredients, see Appendix A). The reactants were slowly heated (by means of a heating mantle) and stirred under a steady stream of nitrogen to produce a homogeneous, clear solution. Condensation was carried out in two steps: (i) preliminary condensation at ∿ 140°C and (ii) main condensation at a higher temperature (∿ 220°C) and under vacuum (10^{-2} mm). Preliminary condensation was carried out until a major fraction (∿ 80-90%) of the theoretical water yield had distilled over into the receiver. Then the solvent was distilled out of the reaction kettle and the temperature was raised to ∿220°C with a simultaneous application of vacuum. The main condensation was continued under these conditions for several hours until the reaction mass turned thick and syrupy and the product had a molecular weight of about 2000-3000 as determined by end group analysis (ref. 19).

Efforts were made to procure commercial polyesters similar in structure to those synthesized. Although azelaic acid polyesters and copolyesters

TABLE 1. POLYESTER DATA

Polyester	Diacid	Diol(s)	Acid Number mg KOH/g	Hydroxyl No. mg KOH/g	Number Ave.* Molecular Wt.
Polyester DE	Adipic Acid	Ethylene Glycol	1.2	55.0	2000
Polyester DP	Adipic Acid	1,2 Propane Diol	4.9	27.0	3500
Polyester DBP	Adipic Acid	1,4 Butane Diol & Dipropylene Glycol (1:1)	0.9	56.0	2000
Polyester DP4	Adipic Acid	Polyethylene Glycol (mol. wt. 400)	<0.5	16.7	6700
Polyester DB2	Adipic Acid	1,3 Butane Diol	0.8	38.0	3000
Polyester ZP2	Azelaic Acid	Dipropylene Glycol	<0.5	17.0	6600
Polyester ZP4	Azelaic Acid	Polyethylene Glycol	<0.5	27.0	4150
Multrathane F-222	Adipic Acid	1,4 Butane Diol & Dipropylene Glycol	1.51	55.0	2000

*By end group analysis (ref. 19).

appeared slightly more promising, no commercial azelaic acid polyesters were available (most are based on adipic acid). The copolyester chosen for study was based on a combination of dipropylene glycol 1,4 butanediol, and adipic acid (Multrathane F-222 from Mobay Chemicals, Pittsburgh, Pa.) and was selected because of its similarity in chemical composition and properties to one of the polyesters that was synthesized (DBP) which had a relatively low Tg (-48°C) and a suitable hydroxyl content for reacting with isocyanates.

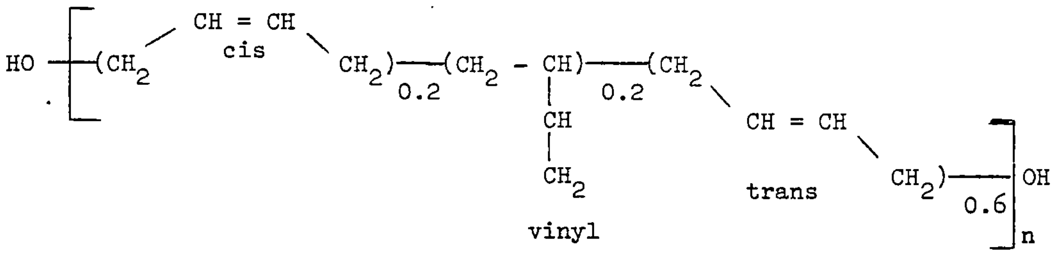
Linear Hydroxyl End-Capped Amorphous Polybutadienes

Efforts were made to find polymeric materials with transitions lower than those of the aliphatic polyesters studied. Polybutadienes are known to exhibit low glass transition temperatures (-78°C to -103°C) and in the last few years, certain low molecular weight (Mn ∿ 3000-5000), hydroxyl or carboxyl end-capped polybutadienes and butadiene-acrylonitrile copolymers have been made available by several manufacturers. Hydroxyl end-capped polybutadienes can be made to react with polyfunctional ($f \geq 2$) isocyanates in a manner similar to the polyesters referred to earlier. It was expected that the resulting polyurethanes would have low glass transition temperatures.

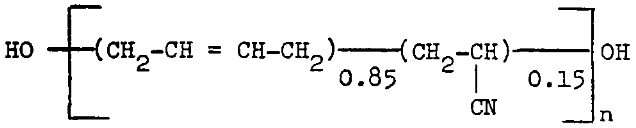
The following polybutadienes and butadiene-acrylonitrile copolymers were obtained from ARCO Chemical Co:

Polybd™ R-45 M (degree of polymerization, n, = 55
hydroxyl number = 0.75)

Polybd™ R-45 HT (n = 50, hydroxyl number = 0.83).



Polybd™ CN-15 (n = 78-87, hydroxyl number = 0.60).



$$HO\left[(CH_2\text{-}CH = CH\text{-}CH_2)_{0.85}(CH_2\text{-}\underset{\displaystyle CN}{CH})_{0.15}\right]_n OH$$

Nonreactive Systems

A third phase of selection of candidates considered linear polymers with low glass transition temperatures. This would eliminate systems that need reactive (chemical) curing processes. (It is noteworthy that most of the difficulties in fabricating adhesives are associated with the chemical reactions of the process.) The linear systems were to include thermoplastic elastomers such as styrene-butadiene-styrene block copolymers, and other materials such as silicones, polypentenamers, and polyphosphazenes.

As the work on the development of good low-temperature adhesives progressed it became obvious that commercial processing and fabricating techniques and equipment had to be taken into account. This caused problems especially with regard to the fact that the systems being considered were thermosets. In order to provide the necessary tack-free surface, a combination of an isocyanate curing agent and a catalyst must be used in carefully calculated amounts. However, due to its reactivity and moisture sensitivity, this system will cause the adhesive film to undergo a surface cure in air. The film tends to lose its bonding ability with aging because the bonding surface becomes cured and no longer has adhesive properties. In consequence, the adhesive/polyester composite cannot be stored for use at a later time.

The solution to the above problem is to find a material that does not need a reactive (chemical) curing process, yet remains flexible at low temperatures and shows good adhesive properties. Several possibilities were considered, including polypentenamers, polyphosphazenes, silicones, and styrene-butadiene block copolymers. The latter appeared to be particularly interesting in that they show both rubbery and thermoplastic behavior. The unique properties of these "thermoplastic elastomers" arise from a network structure held together by physical crosslinks which melt on heating and reform on cooling. The structure is made up of rigid polystyrene end blocks joined by elastomeric polybutadiene center blocks. The polystyrene blocks associate with each other to give large aggregates. Above $\sim$ 100°C, the Tg of polystyrene, the polystyrene aggregates soften and the polymer can flow. At lower temperatures the glassy polystyrene aggregates act as crosslinks to immobilize the ends of the otherwise mobile polybutadiene rubber chains. The material is flexible and rubbery, yet no vulcanization has been necessary. Flexibility is retained to very low temperatures due to the low Tg of the polybutadiene segment ($\sim$ -90°C). There is a considerable literature concerning SBS and other thermoplastic elastomers, a small part of which is listed as references 20 to 30.

SBS block copolymers dissolve readily in a number of solvents and this plus high tensile strength without need for vulcanization would indicate their possible use as adhesives where a strong and flexible bond is needed. In fact, these materials have been used to make excellent contact cements, pressure-sensitive adhesives, and hot melt adhesives (ref. 30). All of these formulations involved the addition of resinous tackifiers, however, in order to guarantee high tack and peel strength. For this reason, it was not certain that the SBS block copolymers would be suitable as low-tack adhesives.

Two different SBS block copolymer candidates were studied. One was a series of Solprene^{TM} radial block copolymers supplied by the Research and Development Division of the Phillips Petroleum Company. These copolymers have the general structure $(S\text{-}B)_nX$ where X is a coupling agent and $n > 2$. The other was from a series of Kraton^{TM} thermoplastic rubbers which are linear block copolymers of the type S-B-S. Some of the properties of these polymers have been acquired from the manufacturers and are listed in Tables 2 and 3. It should be noted, that all of the samples contained 1% antioxidant. The samples were used as 10% (W/V) solutions in benzene which was chosen for the preliminary studies because it is a good solvent for both the polystyrene and polybutadiene domains (segments).

TABLE 2. PROPERTIES OF PHILLIPS RADIAL BLOCK COPOLYMERS

Solprene^{TM} Polymer (Phillips R&D Sample No.)	411 (49985)	406 (49986)	414 (49988)	(49987)
Butadiene/Styrene Ratio	70/30	60/40	60/40	60/40
Polystyrene %	30	40	40	40
Molecular Weight { $\overline{M}w$	3×10^5	2.5×10^5	1.3×10^5	1.6×10^5
$\overline{M}n$	2×10^5	1.8×10^5	1×10^5	1.2×10^5
Specific Gravity	0.94	0.95	0.95	
Tensile Strength, PSI at 80°F	2800	3800	4000	
Elongation, %	700	700	750	
Hardness, Shore A	80	90	90	
Glass Transition, Tg (lower) °C	-87	-92	-92	
Tg (upper) °C	110	102	102	

(temp. of loss modulus maximum at 35 Hz)

Data from ref. 30 and private communication from Dr. H. L. Hsieh of the Phillips Petroleum Company.

TABLE 3. PROPERTIES OF SHELL LINEAR BLOCK COPOLYMERS

Kraton™ 1000 Series Rubbers	
Specific Gravity	0.92 to 0.94
Tensile Strength, PSI @ 74°F	3100 - 4600
Elongation, %	880 - 1300
Hardness, Shore A	35 - 70
Glass Transition, Tg (lower) °F	∿ -90
Tg (upper) °F	
(from viscous damping peaks)	

Data from Shell technical publication (see Appendix E).

Kraton™ 1101	
Butadiene/Styrene Ratio	74/26
Polystyrene, %	26
Molecular Weight, $\overline{M}_w$	8.4×10^4

Data from ref. 29.

DATA ON THERMOMECHANICAL CHARACTERISTICS

Results from the torsional braid analysis for the industrial adhesives, Hydroxyl End-Capped Aliphatic Polyesters, Polybutadienes, and Block Copolymers are furnished, discussed, and compared in this section. With the exception of the industrial adhesives and non-reacting Block Copolymers, the adhesive data are provided for the materials, with and without curing agents.

Data on Thermomechanical Characteristics

In the section on METHOD OF ANALYSIS, loci of "Rigidity" and "Damping" indicies were displayed on Figure 8 for an uncured conventional balloon material adhesive (Polyester A-002800, Sheldahl Co.). These data were acquired using the Torsional Braid Analysis technique discussed in the section on TEST APPARATUS.

This adhesive material is a polyester-urethane and has been used widely in balloon applications. Experiences and laboratory tests with this adhesive have indicated deleterious effects from embrittlement that initiates at -7°C and below for the uncured adhesive and becomes critical below -40°C. This material has good bonding and non-blocking properties and has been used extensively because of these favorable mechanical qualities. Its successful use is dependent upon maintaining quiescent loading and low stress states in unfavorable thermal environments such as the tropopause.

The thermomechanical spectra of the same adhesive after curing with the vendor's recommended isocyanate curing agent are given on Figure 13. These data indicate that the Tg is raised to 13°C on curing. The glassy-state relaxation temperature (β transition) that is associated with the movement of short segments of the polymer chains increases from -114°C to -100°C on curing. The uncured polyester urethane exhibits minimum damping at -42°C (T_{min}) and upon curing this is raised to around -35°C. For solid state materials, a drastic decay in toughness is encountered for temperatures below the T_{min}. These thermomechanical properties appear to be consistent with the reported difficulties encountered with applications of this adhesive when exposed to tropopause temperatures.

Structure-property correlations for embrittlement for the adhesives currently in use would have been particularly helpful in directing the efforts to design more flexible adhesives. However, very little information was available regarding the chemical structure of these adhesives, other than the fact that they were partially aromatic, hydroxyl terminated polyesters either used without curing or cured with a multifunctional ($f \geq 2$) isocyanate. Aromatic constituents, due to their rigid configuration, are known to raise the glass transition temperature of polymers and in this connection it was felt that amorphous hydroxyl end-capped aliphatic polyesters and copolyesters of suitable molecular weights, cured as above should provide better performance due to the flexible carbon linkage.

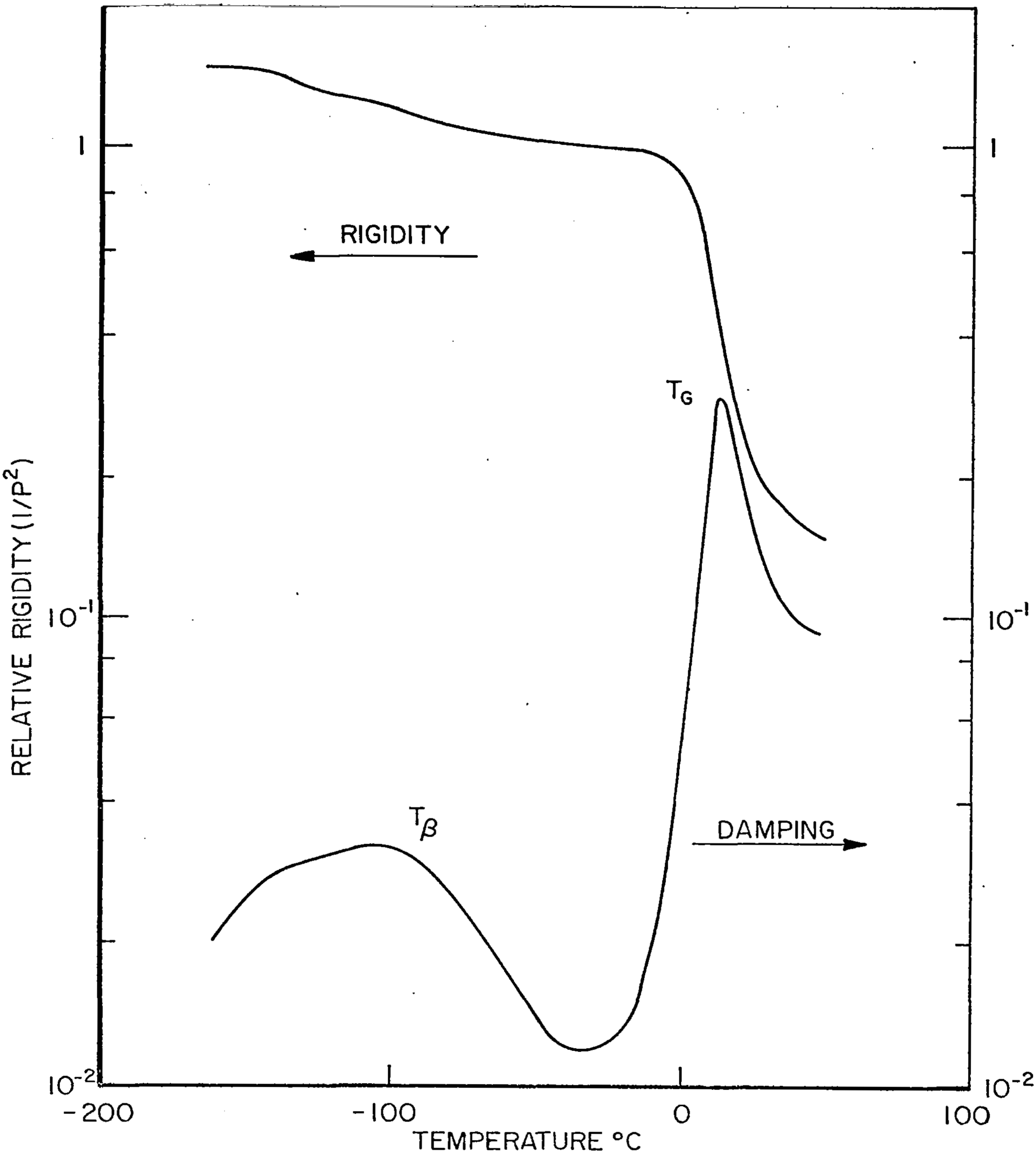


Figure 13. Thermomechanical Spectra in Nitrogen of Cured Polyester Used in Balloon Adhesives, RT > -160°C > RT.

The thermomechanical behavior of four other industrial adhesives (samples A, B, C, and D) were determined. These samples and their solvents were previously defined in the section on CANDIDATE ADHESIVES. Glass braids impregnated with these solutions (5% wt/wt) were dried in nitrogen atmosphere by heating to 100°C and then cooling to room temperature. All the experiments were run in the temperature range 25°C → -180°C → 25°C. It was assumed that the adhesives were thermoplastic. The thermomechanical spectra of the four polymer samples are shown in Figures 14-17.

Sample A exhibited glass transitions of two temperatures, -10°C and -40°C. This is not surprising in view of the fact that the sample is a physical mixture of two polymers. However, only one β-transition temperature was observed for this sample (-130°C). Although sample D is also a physical mixture of two polymers, only one glass transition temperature was observed (-7°C). According to the information received from G. T. Sheldahl Co., Sample A and D have one polymer in common, Resin A-102. From the data obtained for these two samples it appeared that the transition observed for sample A at -10°C was due to resin A-102 and the transition at -40°C was due to Estane 5712.

The glass transition temperatures, β-transition temperatures, and the temperatures of minimum mechanical loss obtained from the thermomechanical spectra are tabulated in Table 4.

Of the four industrial adhesives the one that appeared to be most suitable for use as a baloon adhesive was sample B (Sheldahl A-103). The glass transition (∿ -25°C) of this adhesive was much higher than the tropopause temperature of -70°C, but Tmin was below that temperature.

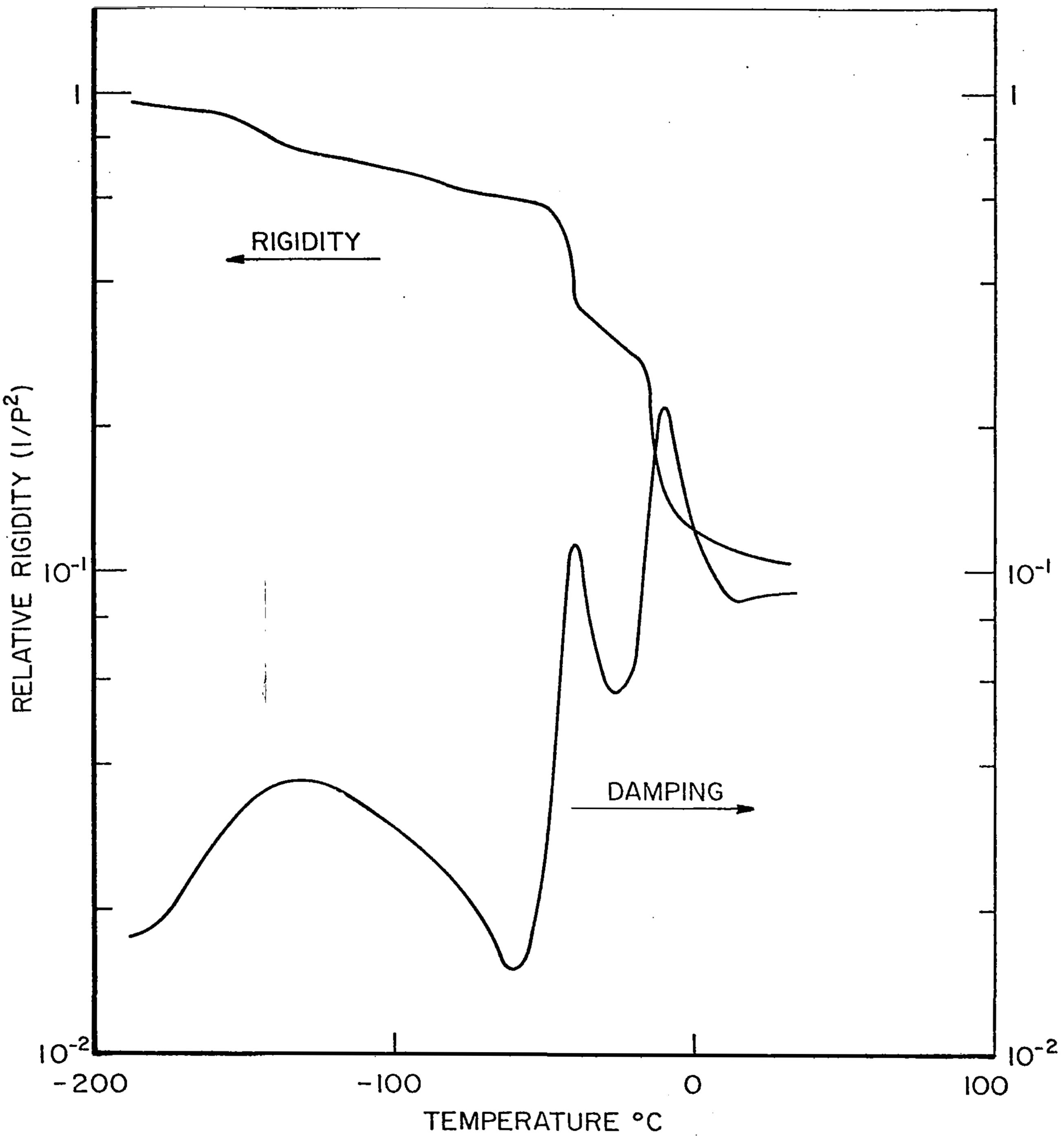


Figure 14. Thermomechanical Spectra in Nitrogen of Adhesive Sample A, Drying: RT → 100°C → RT, Experiment: RT → -180°C → RT.

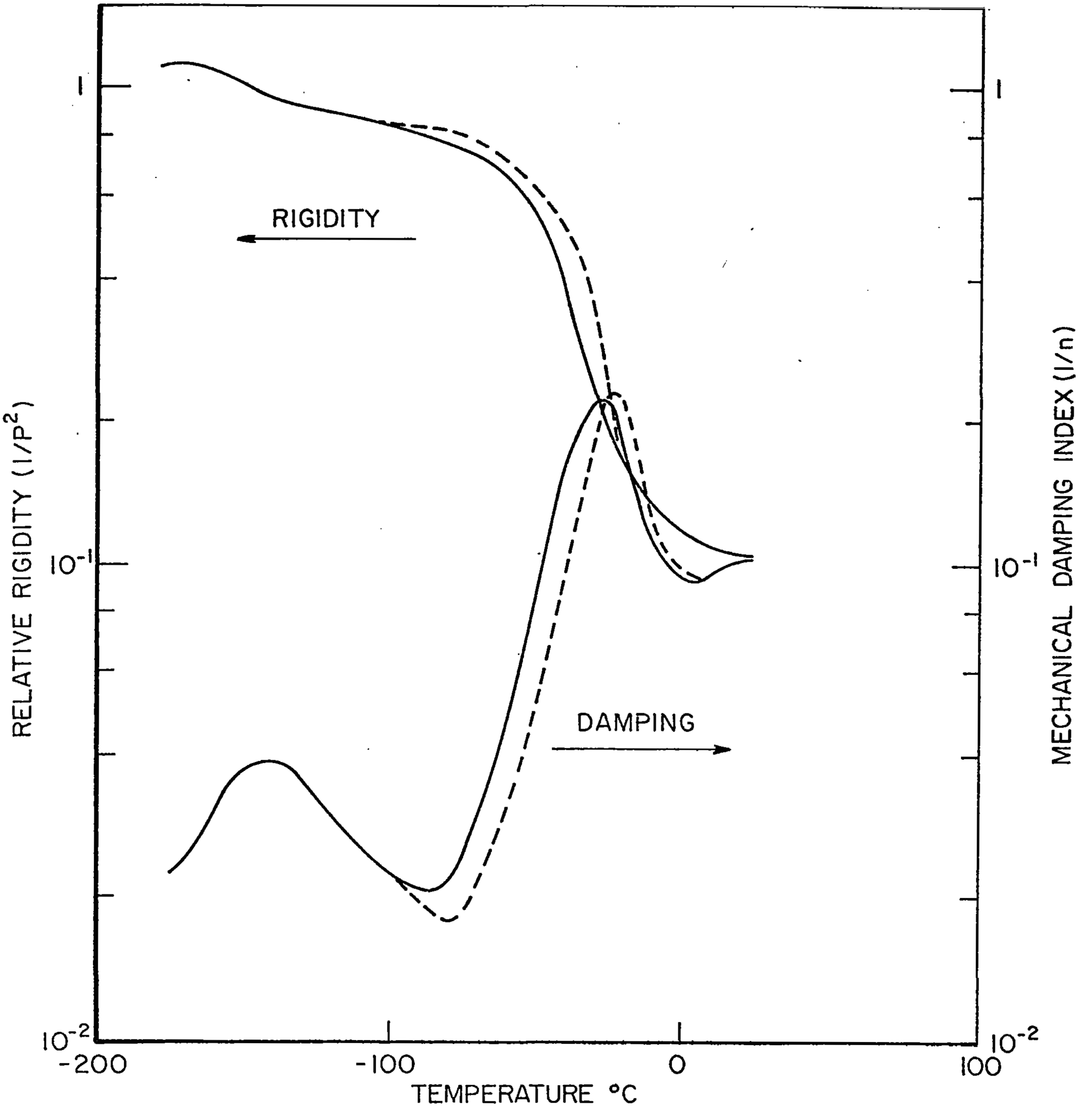


Figure 15. Thermomechanical Spectra in Nitrogen of Adhesive Sample B, Drying: RT → 100°C → RT, Experiment: RT → -180°C → RT.

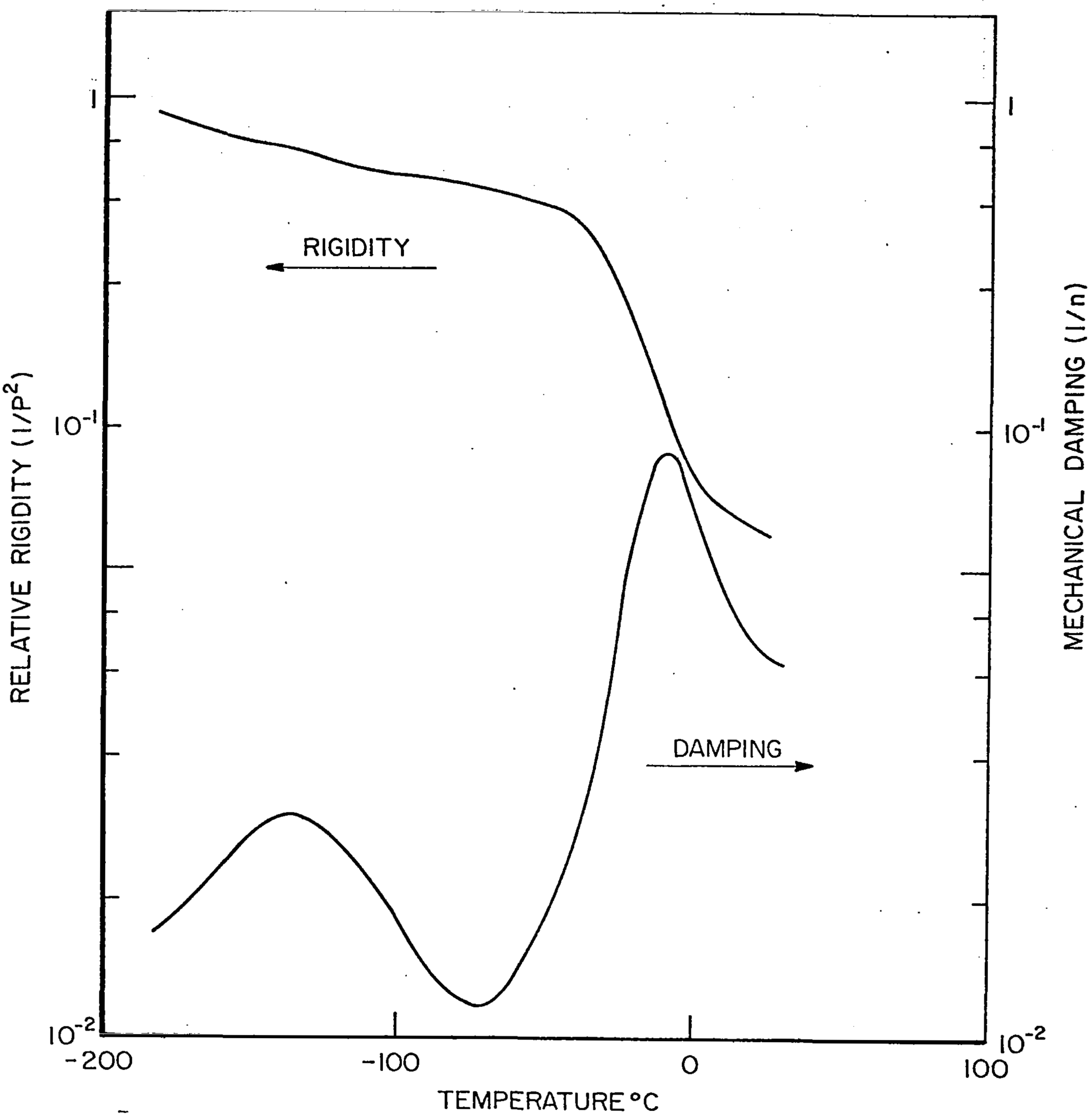


Figure 16. Thermomechanical Spectra in Nitrogen of Adhesive Sample C, Drying: RT → 100°C → RT, Experiment: RT → -180°C → RT.

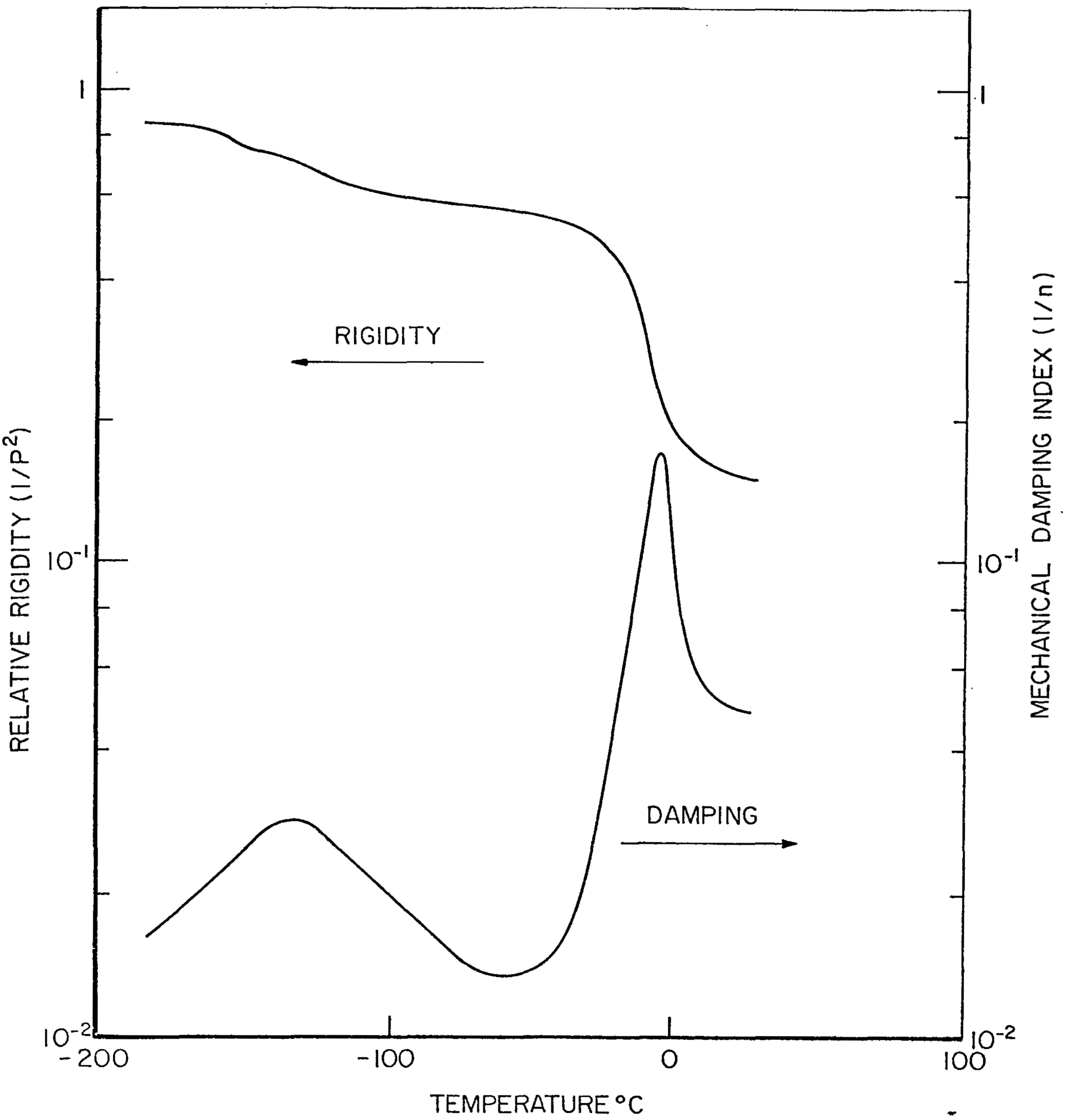


Figure 17. Thermomechanical Spectra in Nitrogen of Adhesive Sample D, Drying: RT → 100°C → RT, Experiment: RT → -180°C → RT.

TABLE 4. TBA RESULTS FOR INDUSTRIAL ADHESIVE SAMPLES

Code	Sample Components	T_g^a °C	T_β °C^b	T^c_{min} °C
A	50-50 mixture of A-102 and Estane 5712	-10, -40	-130	-60
B	A-103	-25	-136	-79
C	Bostik 7925	-6	-140	-70
D	80 Parts A-102 20 Parts Microthene	-7	-130	-57

a) Glass transition temperature
b) β-transition temperature
c) Temperature of minimum mechanical loss

Thermomechanical Spectra on Hydroxyl End-Capped Aliphatic Polyester

The synthesized or procured aliphatic polyester and copolyesters listed in TABLE 1 were analyzed by the Torsional Braid Technique to obtain their thermomechanical characteristics. The thermomechanical spectra of some of these polyesters without curing agents are shown in Figures 18-22. As can be seen, the glass transitions of the various aliphatic polyesters and copolyesters are considerably lower than those of the industrial adhesives and the conventional balloon adhesive as presented in the preceding paragraphs. However, the Tmin characteristics are not appreciable improvements over the best of the industrial adhesives. The glass transition temperature (Tg), glassy state relaxation temperature (T_β) and the temperatures of minimum mechanical loss (Tmin) of all of the Hydroxyl End-Capped Aliphatic Polyesters studied are tabulated in TABLE 5.

Also, for comparative purposes, the characteristics of the uncured conventional partially aromatic balloon adhesive are shown on the bottom of the tabulation. It is readily apparent that the aliphatic polyesters show good improvements over the conventional adhesive in the three characteristics shown. However, the temperatures of minimum loss (Tmin) for all the aliphatic polyesters are near the minimum use temperature of -70°C. It would be more preferable to acquire an adhesive with a Tmin well below -70°C.

Since Multrathane F222 showed typical properties of the synthesized aliphatic materials and because it was commercially available it was studied with several curing agents. Multrathane F 222 based adhesives were cured on TBA glass braids using the following curing agents:

1) Mondur CB-75

2) Equal parts of Mondur CB-75 and E-323

3) E-323

The curing reactions were carried out at 65°C for 16 hours, A combination of tin octoate and DABCO (0.3% each of the total weight of adhesive solids) was used to catalyze the reaction. The temperature and time period for curing were chosen on the basis of recommendations from the Sheldahl Co. In the absence of any kinetic data, it was presumed that the reactions were complete by the end of the time of cure. The thermomechanical spectra of one of the cured adhesives is shown in Figure 23. The spectra for the other two were very similar and are not shown. The two transitions Tg and T_β and the T_{min} for these systems are compared with the cured and uncured conventional balloon adhesives in Table 6. The curing of the Multrathane polyesters raised the glass transition temperatures by 10 to 20°C depending on which curing system was used. The Tg increased in a direct relationship with the increase in the functionality of the curing agent. Increases of about 7 to 10°C were also noted for the glassy state relaxation temperature (T_β). There was no relationship between this change and the functionality of the curing agent. Unfortunately, the temperatures of minimum mechanical loss of the cured Multrathane polyester adhesives are in the region of the tropopause temperature of $\sim -70°C$.

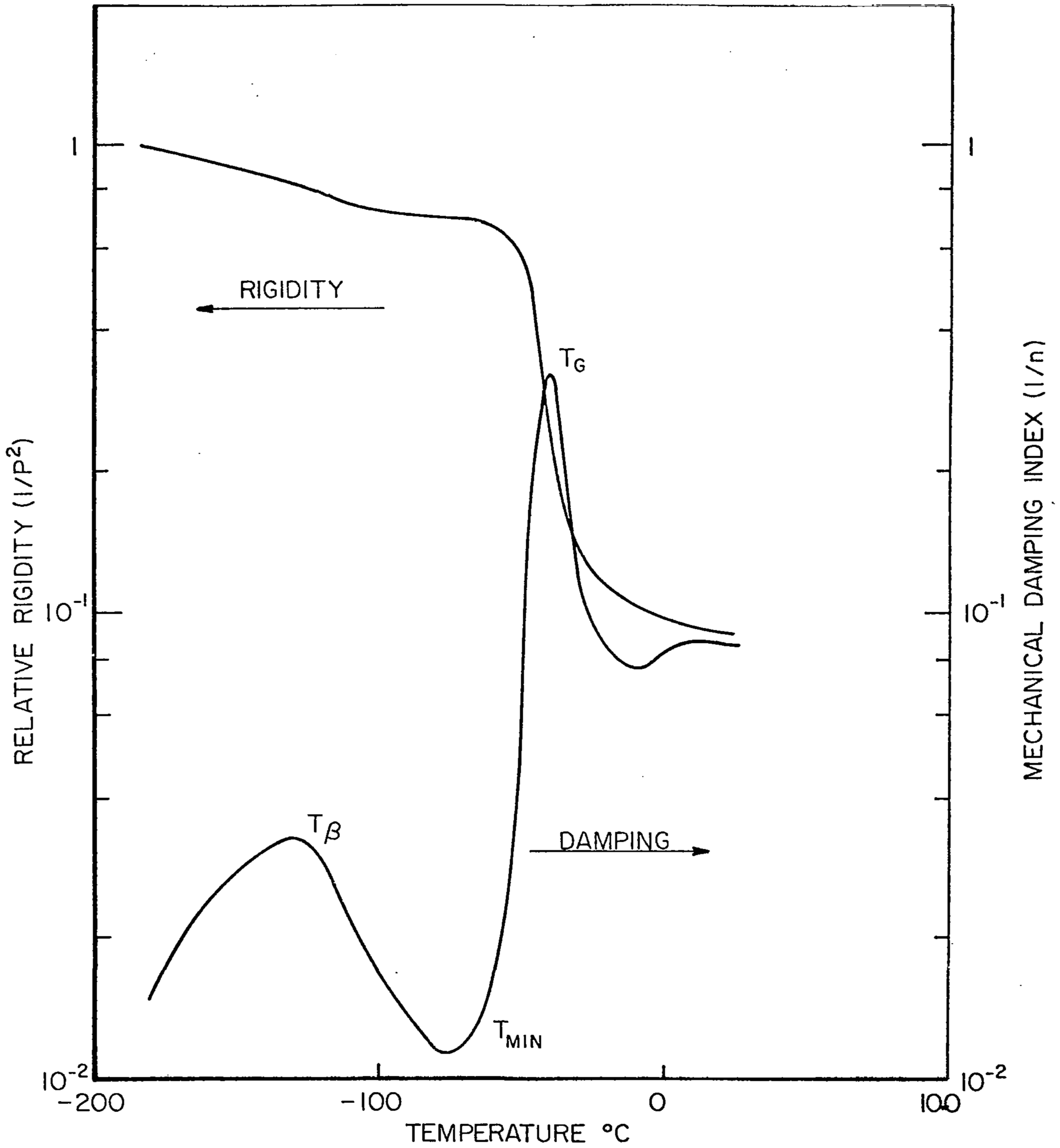


Figure 18. Thermomechanical Spectra of Aliphatic Polyester DP (Adipic Acid + 1,2 Propane Diol), Drying: RT → 120°C → RT, Experiment: RT → -180°C → RT.

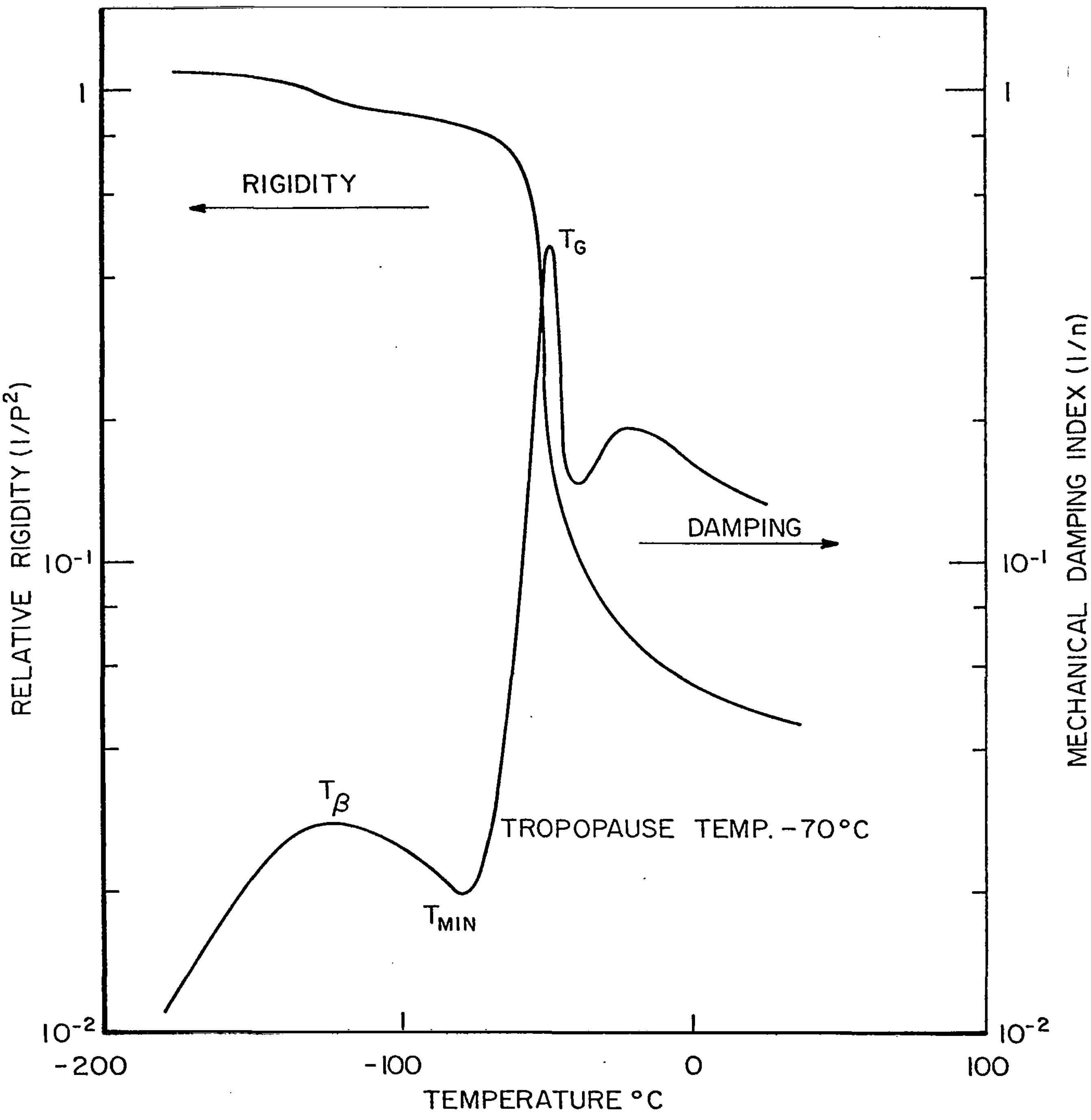


Figure 19. Thermomechanical Spectra in Nitrogen of Aliphatic Polyester DBP (Adipic Acid + 1,4 Butane Diol/Dipropylene Glycol), Drying: RT → 120°C → RT, Experiment: RT → -180°C → RT.

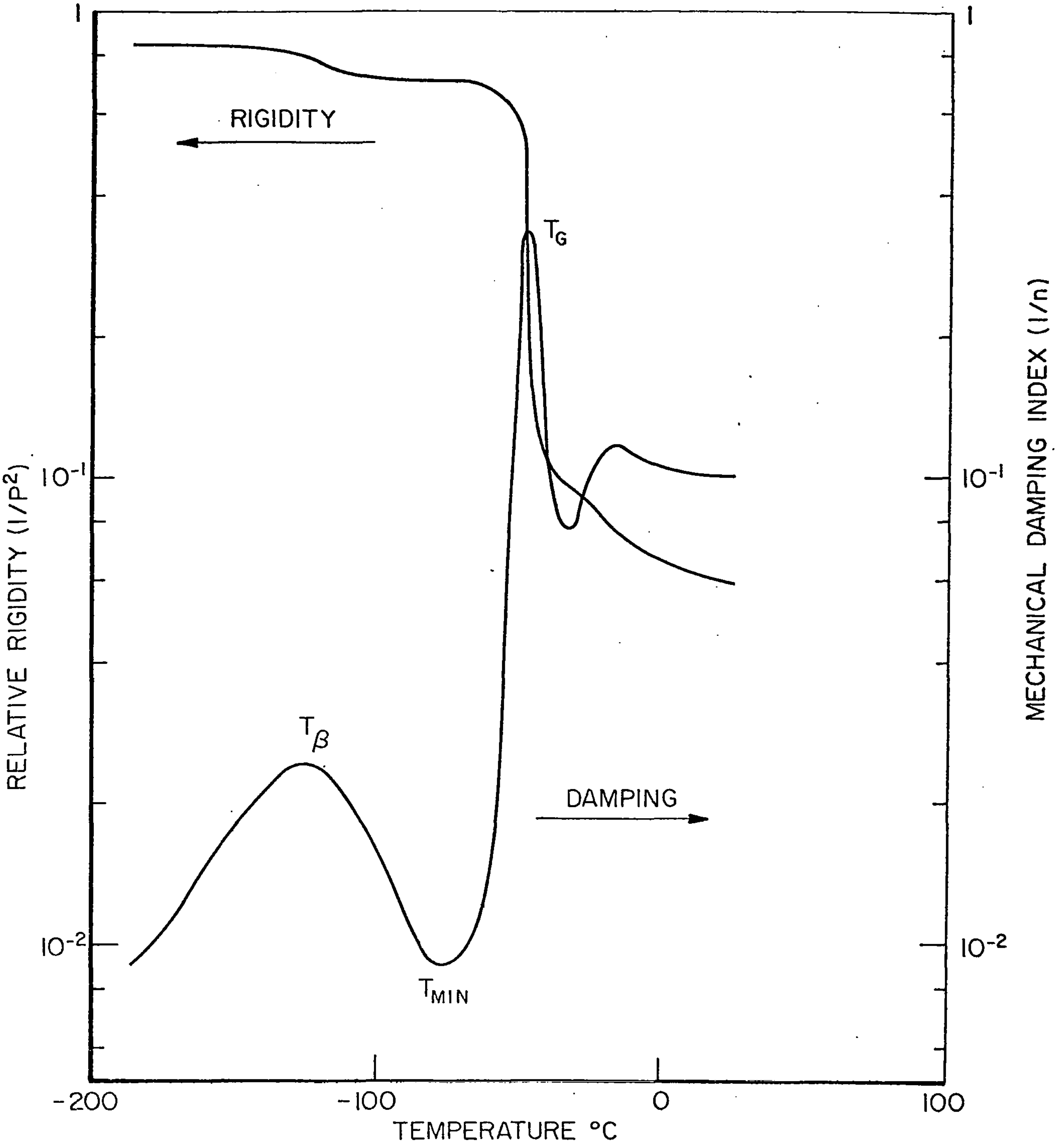


Figure 20. Thermomechanical Spectra in Nitrogen of Aliphatic Polyester DP-4 (Adipic Acid + Polyethylene Glycol 400), Drying: RT → 120°C → RT, Experiment: RT → -180°C → RT.

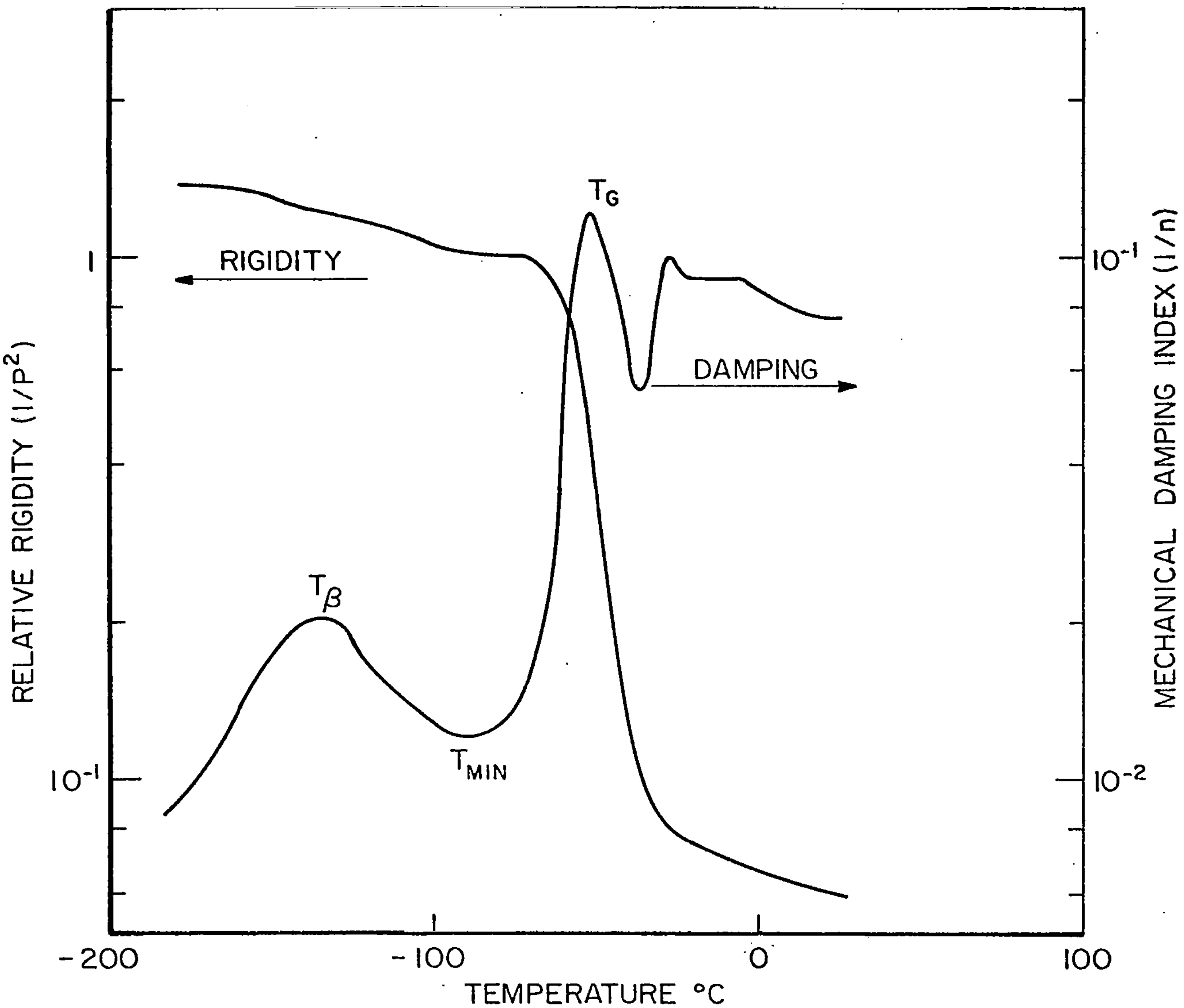


Figure 21. Thermomechanical Spectra in Nitrogen of Aliphatic Polyester ZP-4 (Azelaic Acid + Polyethylene Glycol 400), Drying: RT → 120°C → RT. Experiment: RT → -180°C → RT.

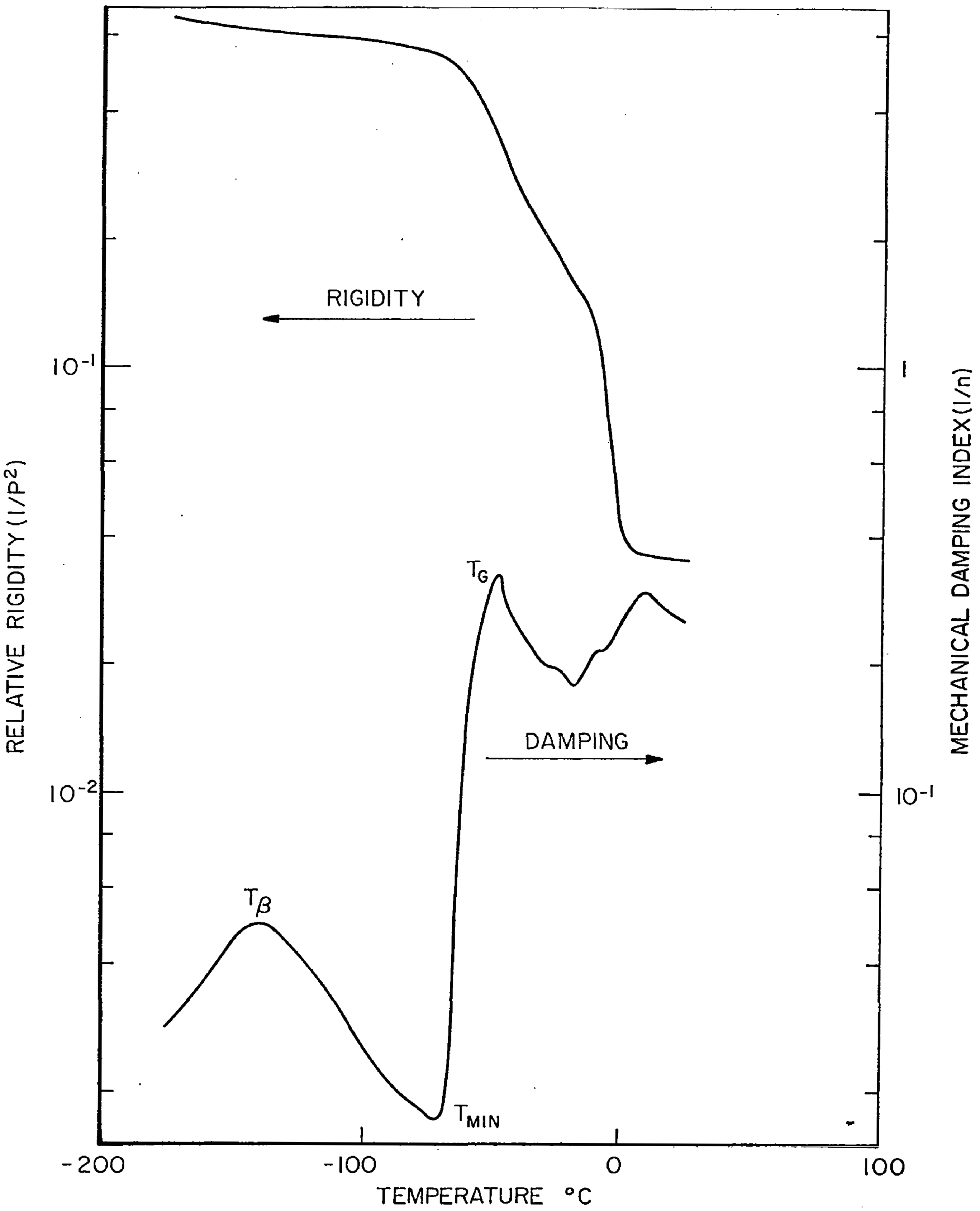


Figure 22. Thermomechanical Spectra in Nitrogen of Aliphatic Ester Multrathane-F222 (1,4 Butane Diol Dipropylene Glycol Adipate), Drying: RT → 100°C → RT, Experiment: RT → -175°C → RT.

TABLE 5. HYDROXYL END-CAPPED ALIPHATIC POLYESTER TRANSITIONS (UNCURED)

Polyester	T_g °C	T_β °C	T_{min} °C
Polyester DE	-40	-120	-75
Polyester DP	-40	-130	-75
Polyester DBP	-50	-130	-80
Polyester DP4	-50	-125	-80
Polyester DB2	-55	-110	-70
Polyester ZP2	-55	-139	-80
Polyester ZP4	-52	-133	-85
Multrathane F222 (Mobay Chemicals, Pittsburgh, Pa.)	-48	-140	-70
Uncured Conventional Balloon Adhesive (Partially Aromatic)			
Polyester A-002800 (Sheldahl Co., Northfield, Minn.)	-7	-114	-40

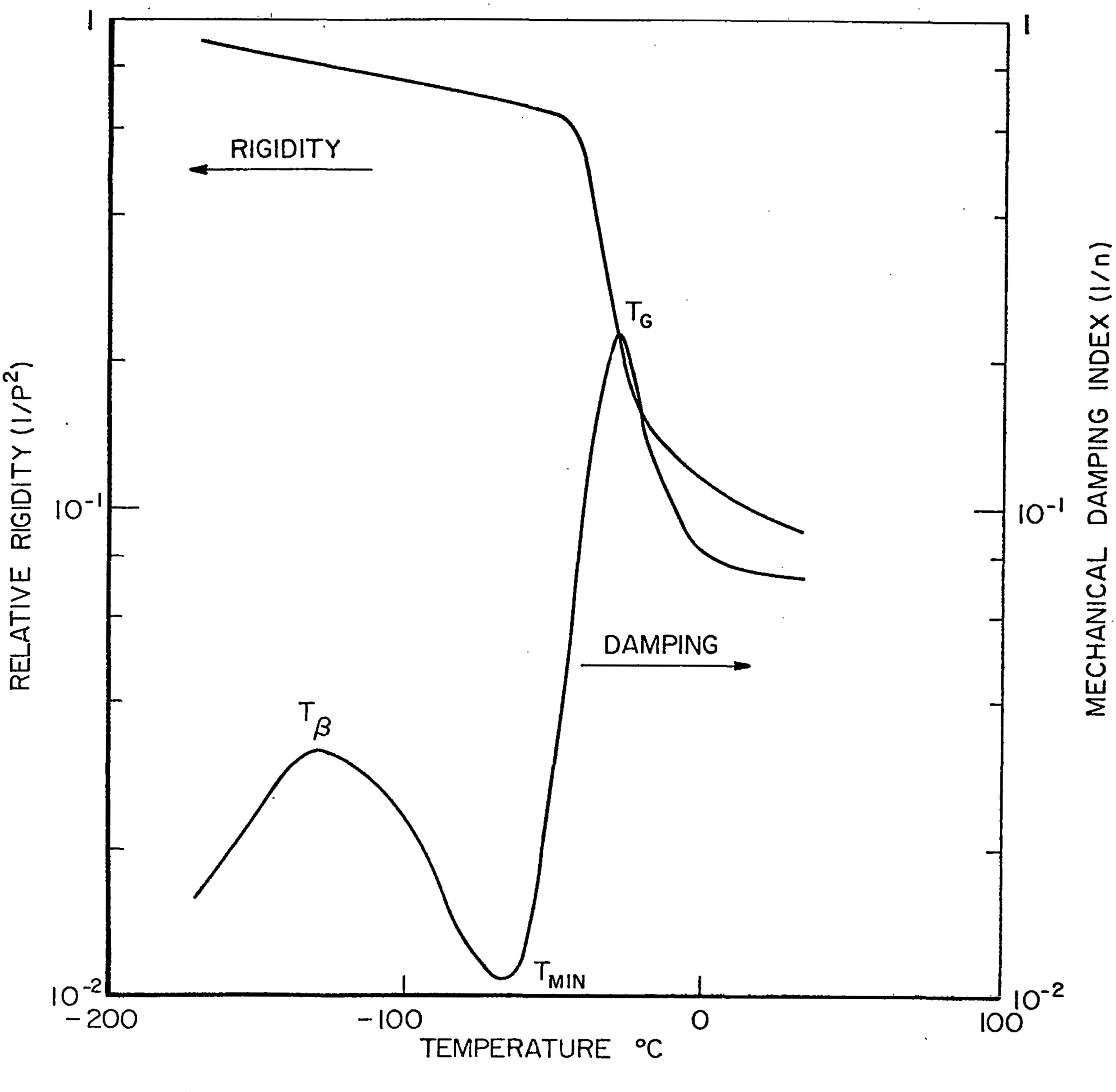


Figure 23. Thermomechanical Spectra of Polyester Resin Multrathane-F222 Cured with Mondur CB-75, Experiment: RT → -160°C → RT.

TABLE 6. POLYESTER ADHESIVES AND THEIR TRANSITIONS

Polyester	Curing Agent(s)	Curing Conditions		T_g °	Increase in T_g °C	T_β °C	T_{min} °
		Temperature °C	Time Hr				
A-002800*	Uncured	-	-	-7	-	-114	-40
A-002800*	A-010000*	65	16	13	20	-90	-36
Multrathane F-222	Uncured	-	-	-50	-	-140	-70
Multrathane F-222	Mondur CB-75 (f=3)	65	16	-30	20	-130	-65
Multrathane F-222	Mondur CB-75 and E-323 (1:1 mixture) (f=2.5)	65	16	-35	15	-133	-70
Multrathane F-222	E-323 (f=2)	65	16	-40	10	-130	-70

---

*Supplied by Sheldahl Co., Northfield, Minnesota.

Thermomechanical Data on Linear Hydroxyl End-Capped Amorphous Polybutadienes

TBA were performed on the three polybutadienes and butadiene-acrylonitrile copolymers obtained from the ARCO Chemical Co. and the spectra of the uncured materials are furnished on Figures 24 through 26. Their glass transition temperature (T_g), glassy-state relaxation temperatures (T_β) and temperature of minimum mechanical loss (T_{min}) are given in Table 7. These materials proved to be substantially superior to the aliphatic polyesters in terms of transitions. Polybd^{TM} R-45M has the lowest transitions of the three polybutadienes (T_g = -80°C, T_{min} = -108°C).

Thermomechanical spectra of the polybutadiene Polybd^{TM} R-45M, cured with Mondur CB-75 under conditions similar to those described for the aliphatic adhesives, but using tin octoate catalyst (0.2% by weight of adhesive solids), are shown in Figure 27. The curing process increased the T_g of the butadiene from -80°C to -68°C and T_β from -130°C to -125°C. However, no change was observed in the T_{min} of -100°C after curing. The polybutadiene-urethane adhesive produced moderate bonds, was tack-free when cured, and showed very low transition temperatures, including a T_g at -68°C, approximately the tropopause temperature.

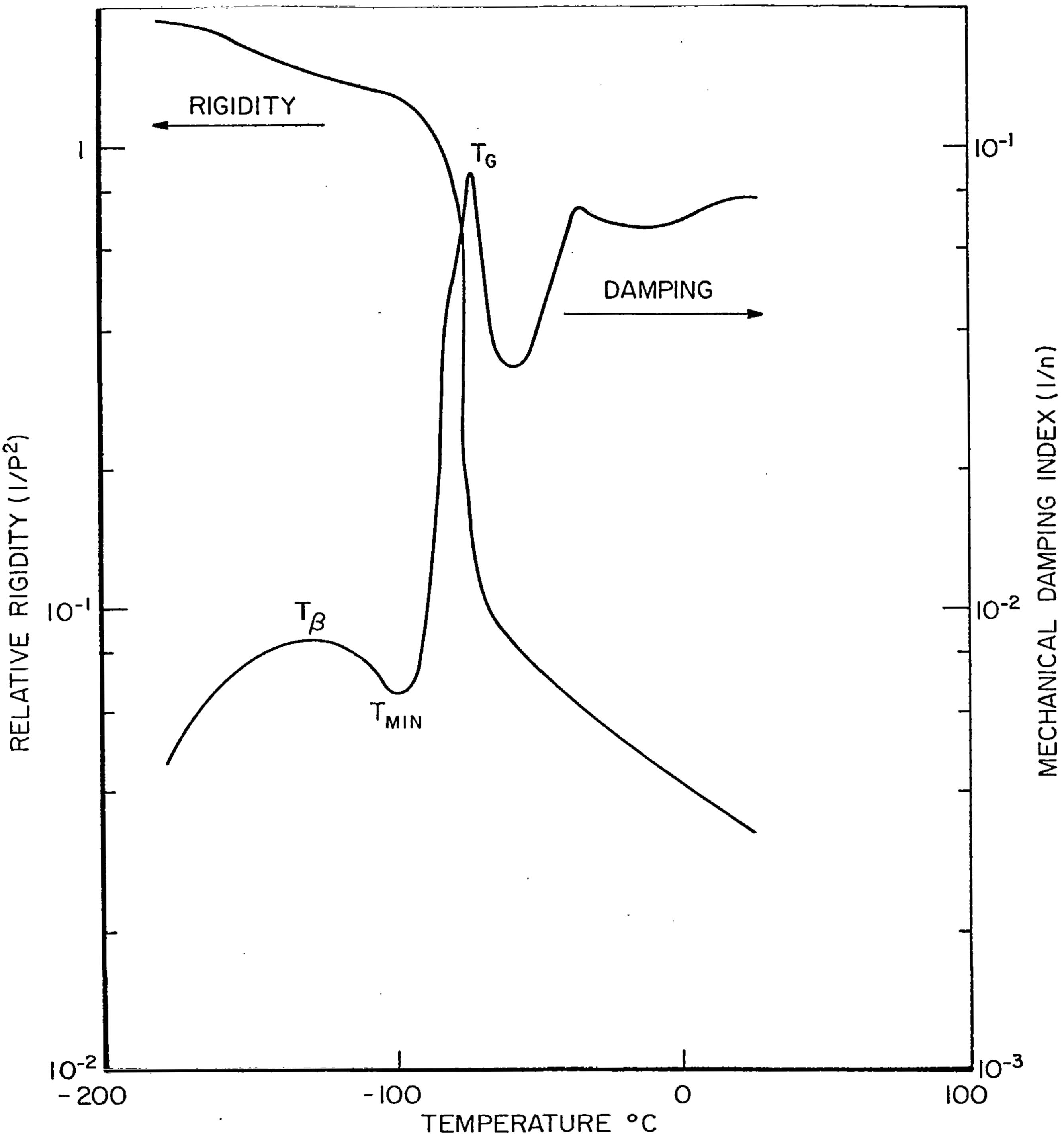


Figure 24. Thermomechanical Spectra in Nitrogen of Polybutadiene Resin R-45HT, Drying: RT → 65°C → RT, Experiment: RT → -180°C → RT.

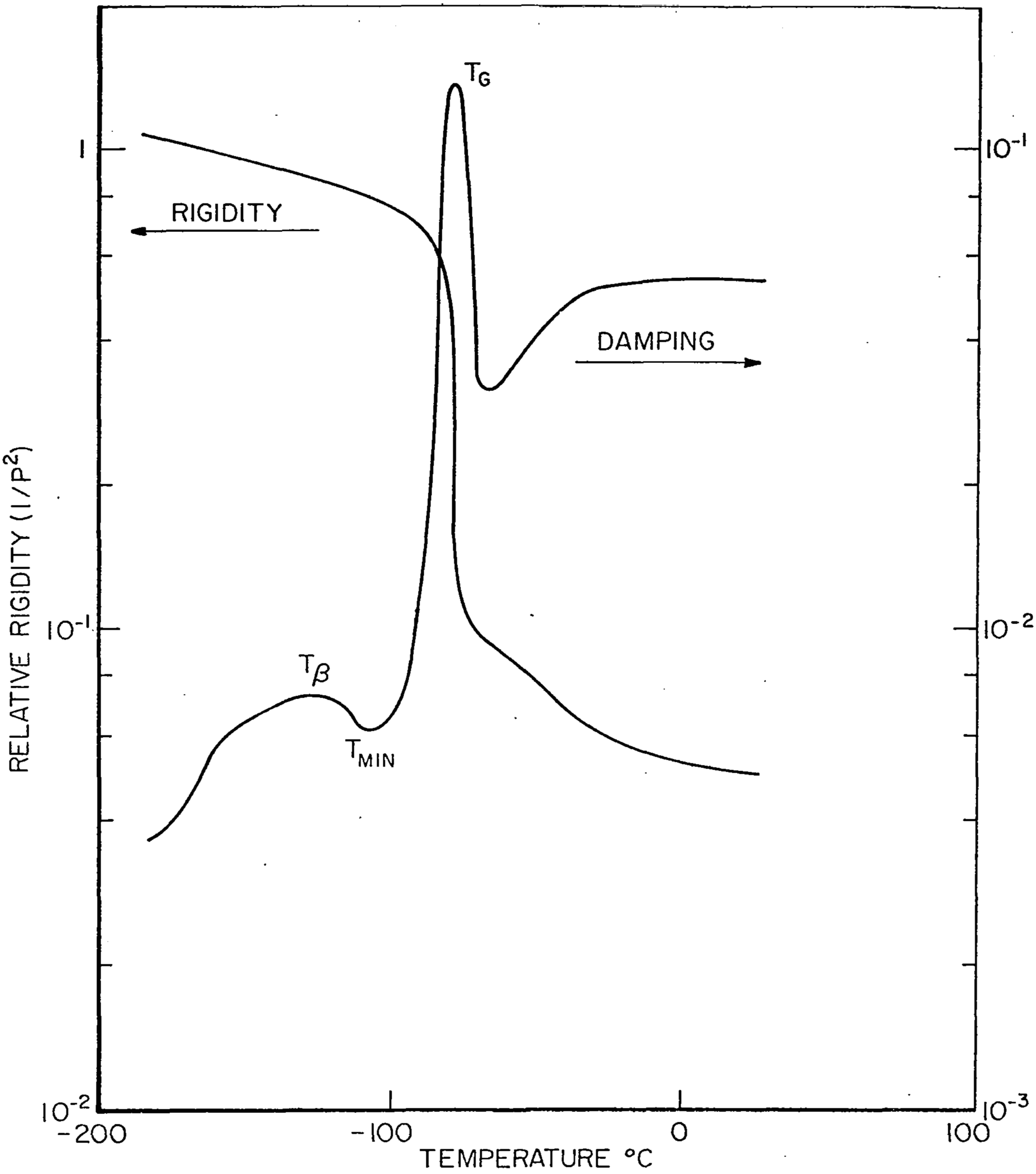


Figure 25. Thermomechanical Spectra in Nitrogen of Polybutadiene Resin R-45M, Drying: RT → 65°C → RT, Experiment: RT → -180°C → RT.

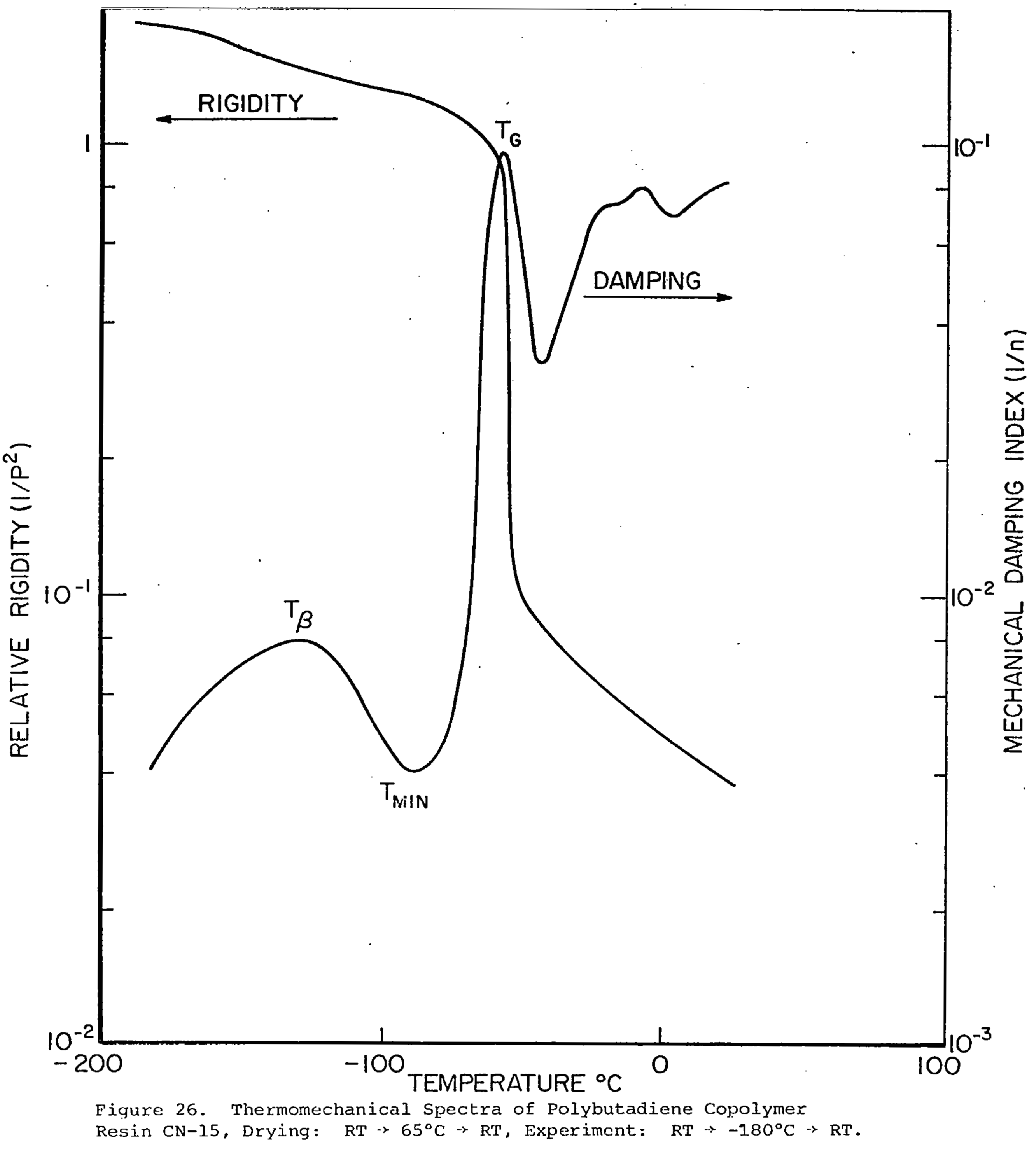


Figure 26. Thermomechanical Spectra of Polybutadiene Copolymer Resin CN-15, Drying: RT → 65°C → RT, Experiment: RT → -180°C → RT.

TABLE 7. POLYBUTADIENE TRANSITIONS

Polymer	T_g °C	T_β °C	T_{min} °C
Polybd^{TM} R-45HT	-75	-125	-98
Polybd^{TM} R-45M	-80	-130	-108
Polybd^{TM} CN-15	-56	-125	-85

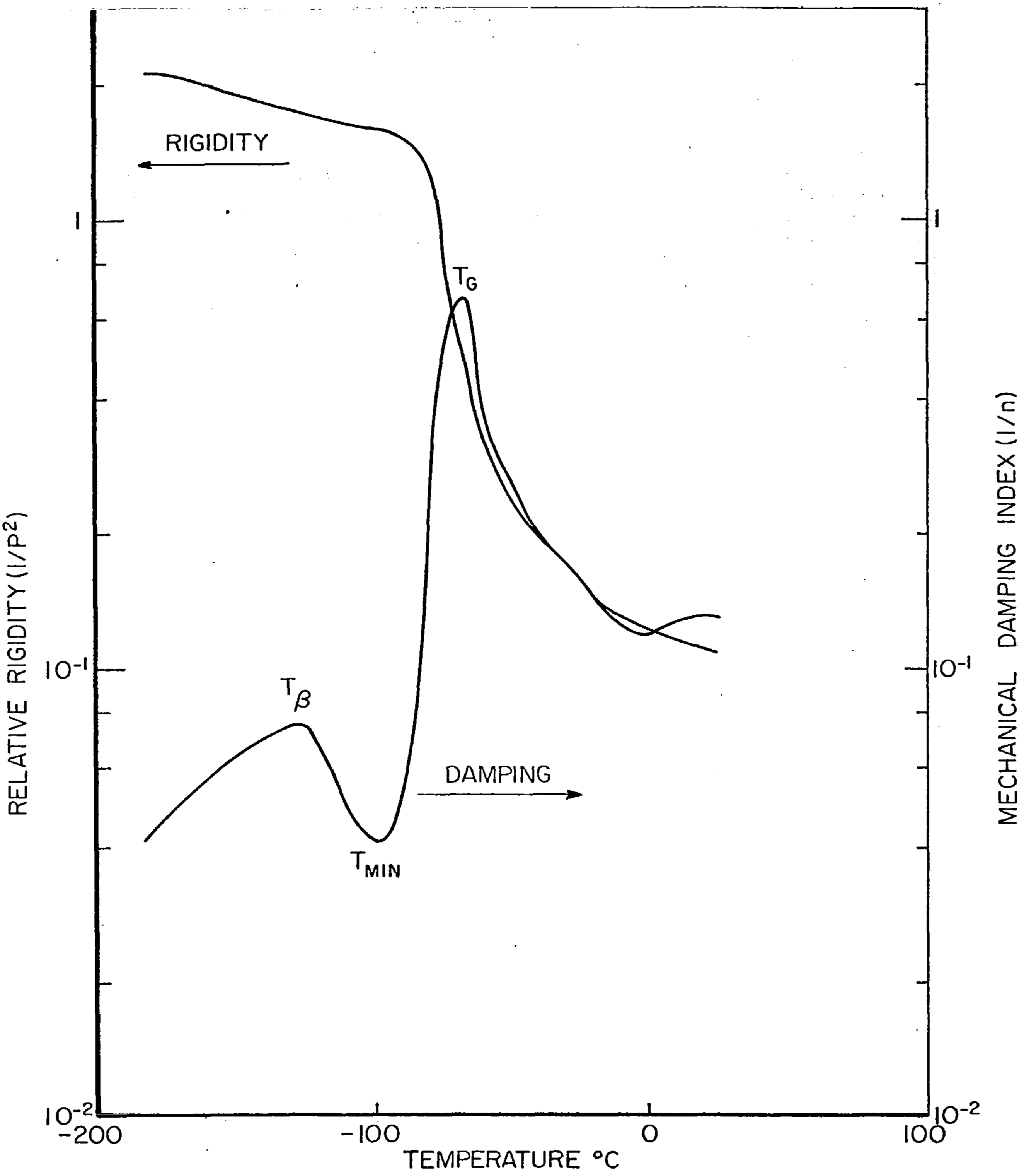


Figure 27. Thermomechanical Spectra in Nitrogen of Polybutadiene Resin R-45M Cured with Mondur CB-75, Experiment: RT → -180°C → RT.

Thermomechanical Data on Block-Copolymer Styrenes

Physical transitions were determined from mechanical spectra generated in dry nitrogen by Torsional Braid Analysis. The experiments were carried out over the temperature range 150 → -180 → 150°C after the specimens had first been dried to 150°C in the apparatus. The rate of change of temperature was ± 3°C/min above room temperature and ± 1°C/min below room temperature. The mechanical spectra for Shell Kraton™ 1101 are given in Figure 28 and for Phillips Solprene™ 406 (Sample No. 49986) in Figure 29. Note the two distinct glass transition regions (denoted by damping peaks and rigidity changes), particularly in the case of the Phillips sample. Only one of the Phillips polymers is shown because the plots obtained were so much alike. The transitions for the polymers are listed in Table 8. Both types of SBS block copolymers, linear and radial, are flexible to very low temperatures (∿ -90°C), well below the minimum working temperature for balloon adhesives.

It should be pointed out that these results were gained using benzene as the solvent. Experiments carried out with methylene chloride, the usual balloon adhesive solvent, could give somewhat different results. The polybutadiene domains are relatively insoluble in methylene chloride, but the polystyrene domains are quite soluble. This results in a suspension of precipitated rubber particles surrounded by polystyrene end blocks still in solution. As the solvent evaporates, rubber will precipitate first, the polystyrene domains last, and a continuous plastic phase will be favored. The resulting film has a higher modulus and lower elongation. (Reference: Shell technical literature.) Annealing (as in forming a bond under pressure at 80 or 120°C) will allow movement of polybutadiene domains as well as polystyrene. This makes up for the lack of solution of polybutadiene above. The film will have a lower modulus, but higher elongation. The rate at which the film anneals is temperature dependent. Some annealing could be carried out by passing the film through a high-temperature drying tunnel. Further study is needed on polybutadiene based adhesives cast from methylene chloride solutions.

All polybutadiene-based materials suffer from oxidative and photo degradation. This is due to the unsaturation in the polymer molecules. The SBS adhesives would need antioxidant and UV protecting additives in order to be used as balloon adhesives.

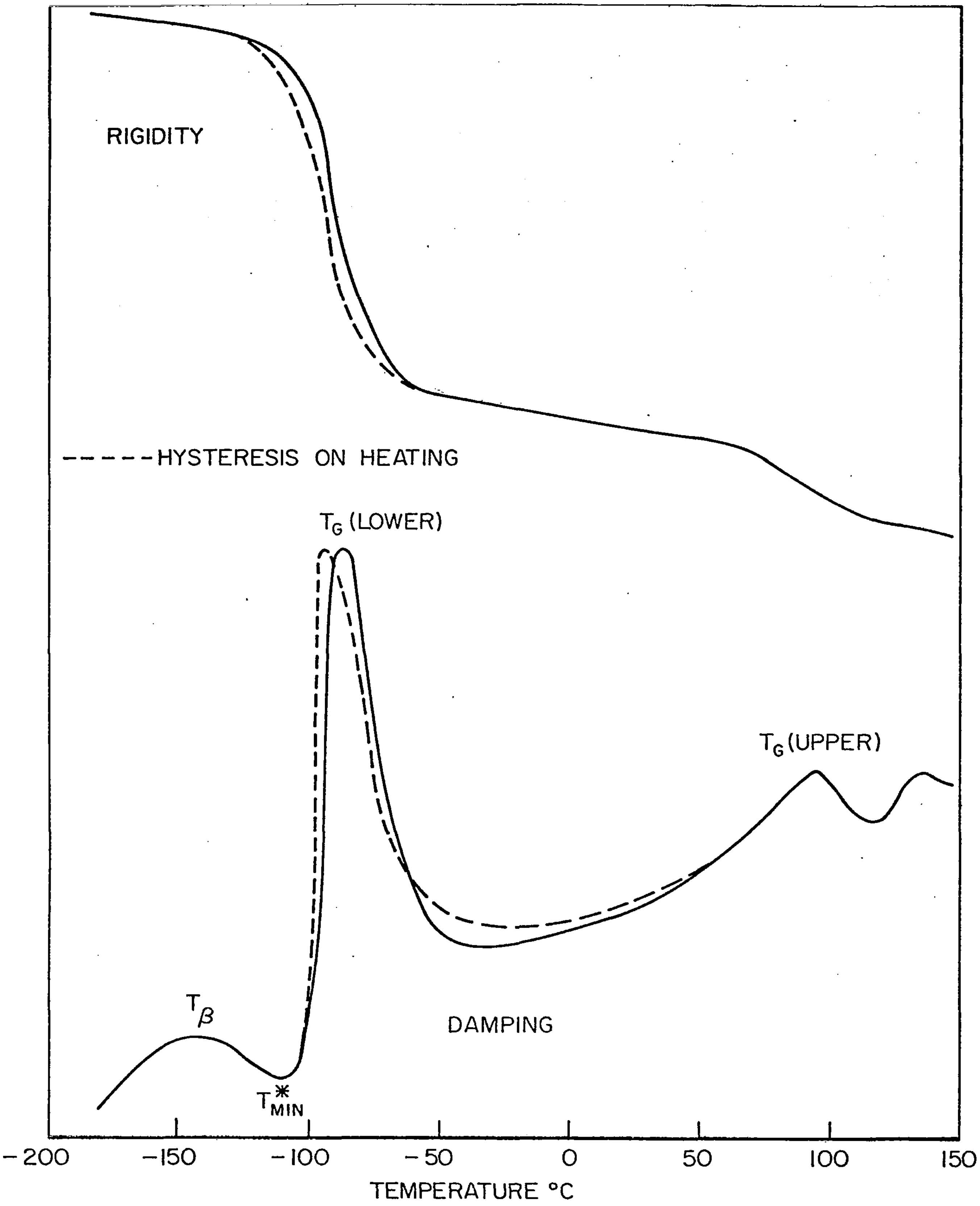


Figure 28. Thermomechanical Spectra in Nitrogen of SBS Linear Block Copolymer, Drying: RT → 150°C, Experiment: 150° → -180° → 150°C.

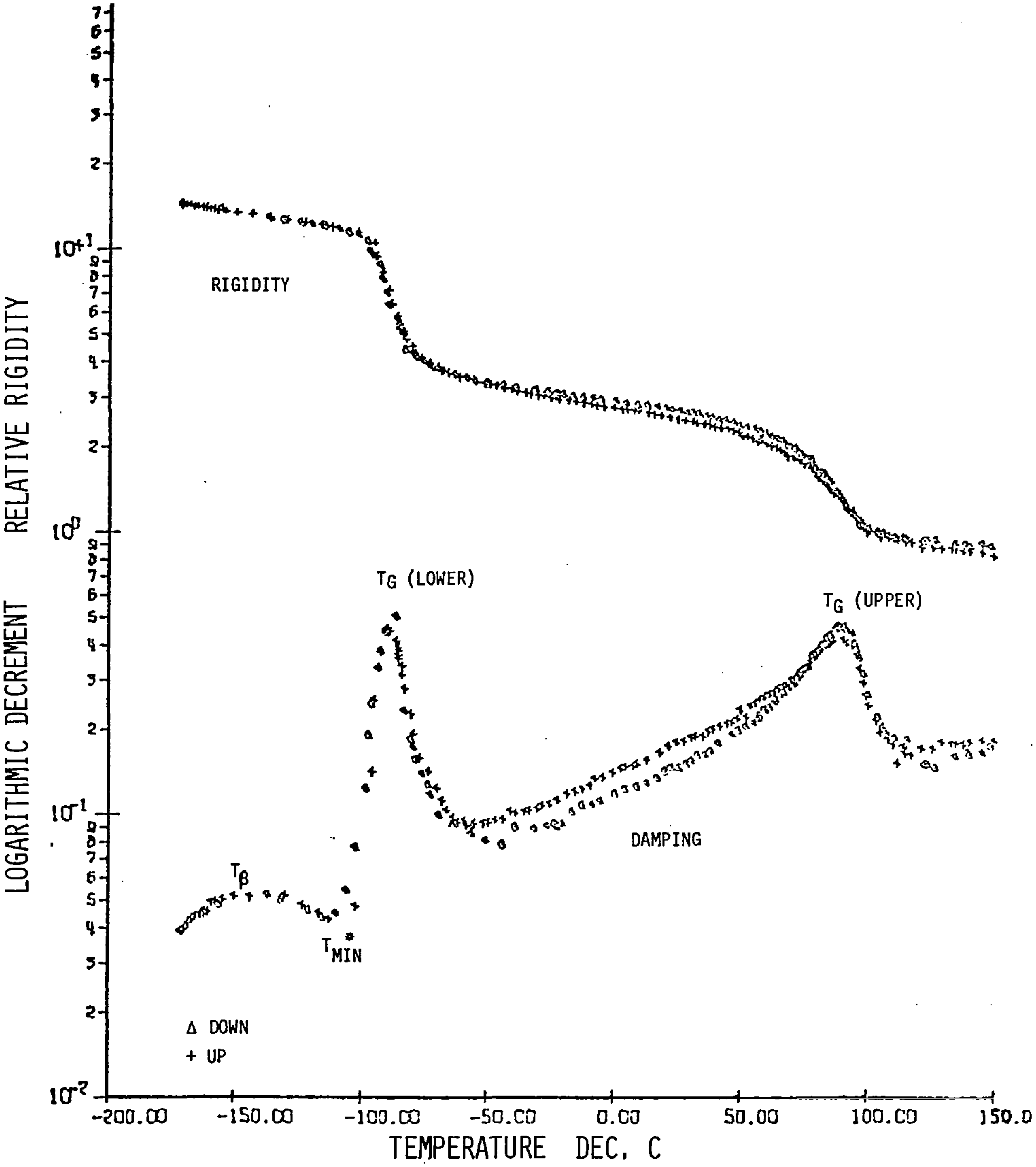


Figure 29. Thermomechanical Spectra in Nitrogen of SBS Radial Block Copolymer, Drying: RT → 150°C. Experiment: 150°→ -180°→ 150°C.

TABLE 8: TRANSITIONS OF SBS BLOCK COPOLYMERS BY TBA (∿1 Hz)

Polymer	Transitions, °C Tg(upper)	Tg(lower)	Tmin*	T_β
Kraton^{TM} 1101	95	-92	-111	-142
Solprene^{TM} 411 (Sample No. 49985)	87	-90	-115	-145
Solprene^{TM} 406 (49986)	91	-90	-112	∿-130
Solprene^{TM} 414 (49988)	84	-91	-111	∿-140
Solprene^{TM} (49987)	80	-91	-111	-135

---

*Somewhat different from Tmin discussed previously. This is the relative minimum between Tg (lower) and T_β.

DRYING, AGING, AND CURING

In addition to having desirable thermomechanical and adequate physical properties a practical adhesive must be compatible with production processes, production machinery, storage procedures, and must remain an active adhesive for extended periods of time. Reactive curing techniques, thermoplastic, or thermoelastic characteristics, toxic properties, flammability and sensitivity to processing contaminants are some important characteristics. Criticality, in mixing and applying, homogeneity of film adhesives, size and quantity effects on handling and curing, the effects of backing paper, shelf-life, storage environment and quality control are a number of other factors that must be considered in adapting an adhesive to a production process. Many of these features are related to the curing chemistry and the controlling parameters effecting cures such as temperature, pressure, time, vapor barriers, solvents, humidity, and gaseous environment.

It has been suspected that misleading mechanical properties on polymeric fabrications have resulted from subtle errors from grip slippage in testing tensile specimens that are only partially cured. Amorphous and/or viscoelastic specimens or specimens containing solvents, or that are tacky, appear to present different test problems than crystalline non-tacky, elastic specimens. Care must be exercised in comparing properties above or below the glass transition temperature to assure against non-uniform gripping producing misleading conclusions.

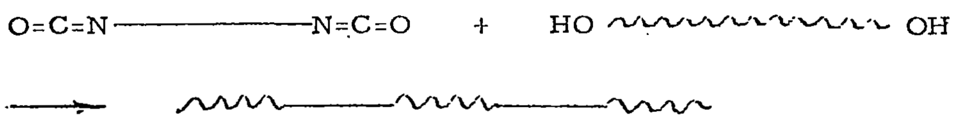
Cure times and/or variations in homogeneity of adhesive coatings are characteristics having dependency on production size and process kinematics; such as, the ratio of perimeter to surface area, production rates, nip roll wrap, temperature, pressure, and roller surface treatment.

Some considerations and experiments have been carried out in regard to a few of these factors for the prime adhesive candidates and are discussed in the following paragraphs.

Curing Agents and Formulations

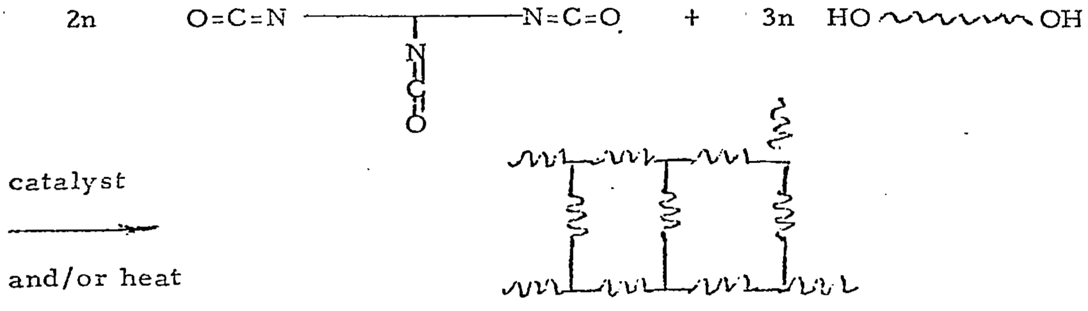
Several types of isocyanate curing agents, each differing in chemical composition and functionality, are available. Although, according to theory, a thermosetting system results whenever the constituent reactants have an average functionality greater than 2.0, the physical properties of the resulting product will depend on the particular chemical structures of the reactants.

The chemical reaction between a difunctional isocyanate and a difunctional hydroxyl compound such as a hydroxyl end-capped polyester or polybutadiene can be represented as follows:

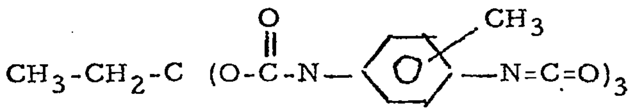


The difunctional isocyanate acts as a chain extender. The molecular weight is increased, but no network is formed. The difunctional isocyanate used in this work was modified p-p'-diphenyl methane diisocyanate (E-323, Mobay Chemical Co., Pittsburgh, Pa.).

A trifunctional isocyanate and a difunctional hydroxyl end-capped polyester or polybutadiene react to form a network in the following manner:



The trifunctional isocyanate chosen (Mondur CB-75 from Mobay Chemical Co.) was an adduct of trimethylol propane with tolylene diisocyanate with the following approximate structure:

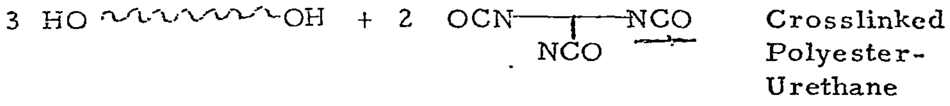


Catalysts. - Isocyanate groups are reactive towards compounds containing active hydrogen atoms such as those in hydroxyl, carboxyl, amine, and amide groups, The relative reactivity of an isocyanate group with a hydroxyl group is in the following order:

primary OH > secondary OH > tertiary OH.

The polyesters studied have primary and/or secondary hydroxyl groups, but the polybutadiene contained mainly primary OH groups. Uncatalyzed reactions between isocyanate and hydroxyl groups often have been found to be too slow for commercial curing operations. Therefore, several types of catalysts were considered for use in the reactions, particularly organotin compounds, such as dibutyltin dichloride, dibutyltin diacetate, dibutyltin dilurate, tin ocotate, and tin 2-ethyl hexoate. Amines are sometimes used in conjunction with organotin catalysts to accelerate reactions; the most effective amine has proved to be triethylene diamone, often referred to as DABCO (1, 1 diazo, 2, 2, 2, bicyclo octane).

Stoichiometric calculations for polyester-isocyanate reactions. - In a curing reaction involving a hydroxyl end-capped linear polyester and an isocyanate, 3 moles of the polyester are required to react with 2 moles of a triisocyanate to give a crosslinked polyester-urethane network.



The quantities of the reactants required to react can easily be calculated from their molecular weights. Quite often, however, a manufacturer prefers not to divulge the molecular weight of a material but instead provides the equivalent weight which is the ratio of molecular weight to functionality. Thus the reactants can be mixed in the ratio of their equivalent weights. From the manufacturer's technical literature:

Equivalent weight of polyester Multrathane F-222	= 1000

and

Equivalent weight of isocyanate curing agent Mondur CB-75	= 325

Therefore, 32.5 parts of Mondur CB-75 Solution (75%) are required to cure 100 parts of Multrathane F-222. This would give a ratio of NCO/OH = 1.0.

A 10% excess of isocyanate content (NCO/OH = 1.1) is generally recommended in such reactions to account for any loss of isocyanate groups due to attack by atmospheric moisture, etc. A large excess (NCO/OH greater than 1.4) should be avoided, however, since it could lead to rigid allophonate and biuret linkages during crosslinking. On the basis of the sample calculation described above, quantities of other curing agents required to crosslink end-reactive polyesters can also be determined.

Polybutadiene-isocyanate reactions. - Although the curing of a hydroxyl end-capped polybutadiene by an isocyanate is similar to that of a hydroxyl end-capped polyester, the stoichiometric calculations are slightly different since the polybutadienes have an average of 2.2 to 2.4 OH groups per molecule. For such calculations, it is convenient to express the reactive group concentrations of the reactants in terms of a common parameter such as mg of KOH per gram of the reactant. For example, the average hydroxyl value of the ARCO R-45M polybutadiene is specified as 0.75 meq/g (individual batches vary) which may be expressed as 0.75 x 56.1 = 42.1 mg KOH/g. Although a polyfunctional isocyanate does not contain hydroxyl groups, the isocyanate content may be expressed in terms of mg KOH/g. Mondur CB-75 has an isocyanate content of 13% which can be expressed as:

$$\frac{13}{100} \times \frac{56.1}{30.3} \times 729 = 175.6 \text{ mg KOH/g}$$

where 30.3 is the percent OH in KOH and 729 is the molecular weight of Mondur CB-75. The latter was calculated from the facts that Mondur CB-75 is supplied as a 75% solution, has an equivalent weight of 325, and functionality of 3 (data from manufacturer's technical literature).

Therefore,

$$\text{Molecular Weight} = 325 \times 3 \times 0.75 = 729.$$

Given the isocyanate content, 175.6 mg KOH/g, the quantity of Mondur CB-75 required to cure 100 parts of the given polybutadiene (OH value = 42.1 mg KOH/g):

$$= \frac{42.1 \times 100}{175.6}$$

$$= 24.0 \text{ parts } (NCO/OH = 1.0)$$

$$= 26.4 \text{ parts } (NCO/OH = 1.1)$$

Qualitative Curing Tests

The selection of adhesives for quantitative evaluation was based primarily upon thermomechanical results. However, prior to studying the thermomechanical behavior of the cured adhesives, the field had been narrowed down through qualitative adhesive and curing tests which were used to test bonding and blocking properties and to arrive at suitable curing conditions. For balloon applications, the non-blocking (tack-free surface) characteristics of the adhesives are considered very necessary and actually more important than the bonding abilities.

All the preliminary tests were carried out on adhesives based on Multrathane F-222 polyester and Polybd^{TM} R-45M polybutadiene resin. These polymers were used as 15% solutions in methylene chloride. The effect of reaction variables such as average functionality of isocyanate (i.e., ratio of tri/di isocyanate), temperature, cure time, pressure, catalyst type and concentration on the properties of the adhesive film were studied qualitatively.

Pre-cure aging. - Experiments were run to determine the effect of "drying" or aging the adhesive films prior to curing. Cast films were exposed to the atmosphere for varying periods of time and then cured. An exposure of 15 minutes or more gave a slightly foamy appearance to the adhesive film on curing. This was particularly noticeable in thicker adhesive films [> 1 mil (2.5 x 10^{-5} m)]. These observations may be explained by the fact that isocyanate groups react with atmospheric moisture. The foamy appearance of the cured film probably was due to decarboxylation resulting in the formation of polyureas. These reactions are undesirable and would lead to a brittle adhesive and poor or nonexistent bonding. Therefore, it is important that the wet adhesive film be exposed to atmosphere for a short time only, just long enough to facilitate the evaporation of the solvent. The solvent must be removed before bonding to another sheet of polyester film or winding up in a roll, however. In the laboratory experiments, "drying" the wet films for a period of about 5 minutes before curing seemed to give an adhesive with satisfactory properties. On a commercial scale, such a drying period could be varied depending on the size of the coating set-up, relative humidity, etc. A highly volatile solvent such as the methylene chloride used in these tests aids in rapid drying. Using a minimum adhesive film thickness would also allow the solvent to vaporize rapidly.

Cure Time and Temperature - In the initial set of curing experiments, the temperature of cure was set at 150°C in order to simulate the temperature of a laminator hot-roll. A cure time of 5 minutes appeared to be sufficient. Subsequent experiments were made by varying the hot-roll temperature and tests were carried out at 60 and 80°C. At these lower temperatures, however, a longer cure (~10 min) was needed in order to produce tack-free films. It should be pointed out that the films studied were quite thick [$\geq$ 1 mil (2.5 x 10^{-5} m)] and that shorter cure times would be needed for thinner films.

NCO/OH ratio. - The effect of variation of stoichiometry (NCO/OH ratio) and cure time on the properties of polyester cured adhesive films was studied. Multrathane F-222 was cured with Mondur CB-75 using stannic chloride, $SnCl_4$, (0.20% by weight of total adhesive solids) as a catalyst. The adhesive films were cured at NCO/OH ratios of 2, 1.5, 1.1, and 1.0 at 150°C and 200 psi (1.4 x 10^6 nm^{-2}) pressure for 1, 3, and 5 minutes. The five minute cure appeared to produce a film with very low tack, while shorter times produced tacky, unacceptable films. The cured adhesive films appeared brittle at a NCO/OH ratio of 2, but were much less so at a ratio of 1.5. This difference was particularly noticeable in thicker adhesive films. The brittle nature of the cured adhesives at higher NCO/OH ratios was not unexpected for reasons stated earlier. At NCO/OH ratios of 1.1 and 1.0 the cured adhesive films appeared to be flexible, even at relatively high thickness. A series of experiments was carried out in which the adhesive films were cured between strips of polyester film to determine the bonding properties. All the samples exhibited satisfactory bonding, but it must be pointed out that these tests were not quantitative.

Cure pressure. - In order to look into the effect of pressure on curing, the Multrathane F-222/Mondur CB-75 system with a NCO/OH ratio of 1.1 was cured for 5 minutes at pressures of 100, 150 and 200 psi (6.9, 10.3, and 13.8 x 10^5 nm^{-2}). Although pressure did seem to be necessary to prepare a good laminate (two polyester films bonded to each other by an adhesive layer) it did not appear to have any effect on the curing of an open-sandwich type of specimen (polyester film coated on only one side with adhesive). However, so as to maintain a uniform, reproducible adhesive film thickness in subsequent tests, it was decided to use an arbitrary pressure of 200 psi (1.4 x 10^6 nm^{-2}).

Catalysts. - The effects of different types of catalysts and their concentrations on the properties of cured adhesive films were studied. One percent solutions of tin octoate, dibutyltin dichloride, dibutyltin diethylhexoate, dibutyltin diacetate were added separately to mixtures of Multrathane F-222 and Mondur CB-75 (NCO/OH = 1.1) to give catalyst concentrations of 0.2, 0.4, and 0.6 weight percent of adhesive solids. Films cast from these solutions onto polyester film were allowed to dry for 5 minutes and cured for 5 minutes in a platen press at 150°C at a pressure of 200 psi (1.4×10^6 nm^{-2}). In another set of experiments the same catalysts were used in combination with an accelerator, triethylene diamine, at two concentration levels: 0.1% catalyst, 0.5% accelerator and 0.3% catalyst, 0.3% accelerator. Results of the above tests indicated the following:

a) The tackiness of the cured adhesive film decreased with increasing catalyst concentration.

b) From among the catalysts investigation, tin octoate and dibutyltin diacetate produced the cured adhesive films with the lowest tack.

c) Although higher levels of catalyst or accelerator provided film with very satisfactory tack-free films,

the pot-lives of such mixtures were unsuitable for easy handling. Higher levels of accelerators, in particular, seemed to cause a rapid increase in viscosity of the adhesive solution leading to gelation in about 2 hours. Catalyst and accelerator levels of 0.3% each proved to be satisfactory in terms of tack-free properties of the resultant adhesive film and satisfactory pot lives of the adhesive mixtures.

Difunctional Curing Agents. - Attempts were made to look into the feasibility of using a difunctional chain extender such as E-323 in lieu of or in combination with Mondur CB-75. The difunctional curing agent would increase the molecular weight but not make a network, while the mixture would give a lower crosslink density in the cured adhesive than would Mondur CB-75 alone. It was felt that a more flexible adhesive could be produced by these means. The reaction conditions employed were 150°C, 200 psi (1.4×10^6 nm^{-2}), 4 minutes cure time, and a combination of 0.3% tin octoate and 0.3% triethylene diamine as the catalyst. While the adhesive films so obtained displayed a faint tack, no tendency for films to stick together was noticed. A qualitative determination of bonding properties by curing the adhesives between strips of Mylar film indicated moderate bonding strength using this system.

Polybutadiene (Polybd R45M) was then studied in a manner similar to Multrathane F 222 but using only Mondur CB-75 as the curing agent.

Curing reactions were carried out for 5 minutes at 150°C and 200 psi (1.4 x 10^6 nm^{-2}) pressure. Tin octoate was used to catalyze the reaction. Tack-free adhesive films with moderate bonding properties were produced.

SBS Block Copolymers. - Qualitative tack and bond testing were carried out on the various SBS block copolymer samples. Tack was evaluated after adhesive films cast on polyester film had been dried and annealed in an oven at 80 or 120°C (i.e. both below and above the Tg of the polystyrene segments). After uncoated strips of polyester film had been bonded to adhesive coated film and heated at 80 or 120°C at 200 psi (1.4 x 10^6 nm^{-2}) in the platen press rough evaluations of bonding were made. In these very qualitative tests both types of material showed no or low tack, but the Kraton 1101 sample appeared to give much better bonding. Further testing is necessary before any real choice can be made between the two block copolymer systems.

Industrial Testing

A series of adhesive tests were carried out in October 1973 using production equipment at the G. T. Sheldahl Co., Northfield, Minnesota. Polyester film was coated in bulk quantities with an experimental adhesive and the process was studied in light of stoichiometry (NCO/OH ratio), film thickness, removal of solvents, temperature effects, and backing materials, aging, batch life, solid content, and drying time. These experimental production runs were made using the basic polybutadiene resin and the trifunctional isocyanate curing agent, Mondur CB-75 with dibutyltin diacetate as the catalyst.

Production material. - A 40 lb mixture (18.2 kg), 4 gal (0.15 m^3), of the adhesive components was prepared using the following amount and order:

Methylene Chloride (solvent)................	33.35 lb (14,345g)
Polybd R-45M (resin).......................	5.15 lb (2,338g)
Mondur CB-75 (curing agent).................	1.50 lb (681g)
Dibutyltin diacete (catalyst).................	0.0176 lb (8g)

The proportion of Polybd R-45M to Mondur CB-75 was such that the NCO/OH ratio was $\sim$ 1.1; the catalyst concentration (percent of total solids) was $\sim$ 0.3%. These proportions were necessary in order to produce a satisfactory adhesive film.

This mixture had a specific gravity of 1.244 and contained 15.5 percent solid content (15.72 percent theoretical solid content). The solution was applied to a 9 x 10^{-3} mm (0.35 mil) polyester film substrate using a roller coater running at a speed of 1.2 to 1.5 m/min. (4 to 5 ft/min). A wet film thickness of 13 x 10^{-3} mm (0.5 mils) resulted.

Control of film thickness: - In order to control the adhesive film thickness to a desired value, the solid content of the adhesive solution is varied by successive additions of methylene chloride. Measurements show that evaporation of solvent from the adhesive supply produces a gradual increase in solid content, an increase in viscosity of the solution, and a gradual increase in adhesive film thickness. For example, for an initial 5 x 10^{-3} mm (0.2 mils) adhesive thickness, it was observed that the thickness increased to 6.8 x 10^{-3} mm (0.27 mils) at the middle of a run, as a result of evaporation.

Determining and adjusting the solids content to produce a specified film thickness proved difficult by virtue of both the evaporation and the nonlinear relationship that exists between the percent solids and the adhesive coating thickness. Experimental data obtained and furnished as figure 30 show clearly the nonlinear relationship.

The thickness of the adhesive coating was measured with a sensitive micrometer and through a weighing technique. The micrometer was used for nearly all initial measurements of thickness. More exact thicknesses for given test specimens were determined later by the weighing technique after an accurate value for the density of the adhesive coating had been determined.

The density of the adhesive coating is determined from the knowledge of the weights and specific gravities of the "n" constituents solids in the compound, that is:

$$SG_a = \frac{\sum_{i=1}^{n} W_i}{\sum_{i=1}^{n} \frac{W_i}{SG_i}}$$

where W_i is the weight of the ith constituent

SG_i is the specific gravity of the ith constituent

SG_a is the average specific gravity of the adhesive coat.

The average thickness of the adhesive coat can be computed by:

$$t_a = \frac{SG_f}{SG_a}\left(\frac{Q}{\sigma_w SG_f} - t_f\right)$$

where t_a = average thickness of the adhesive coat.

t_f = thickness of the base film

SG_f = specific gravity of the film

σ_w = density of fresh water

Q = weight/unit area of the composite (film + adhesive coat)

For example, consider the initial mixture of two (n = 2) constituents:

	Weight, kg	Specific gravity
Polybd - 45M	9.34	0.90
Mondur CB-75 (solid)	2.04	1.29

$$SG_a = \frac{9.34 + 2.04}{\frac{9.34}{0.90} + \frac{2.04}{1.29}} = 0.952$$

If the specific gravity of the film is 1.39 and the thickness is 8.89 x 10^{-4} cm (.35 mils), and recalling that the density of water is 1 gr/cm^3 then for a composite weighing 17.15 x 10^{-4} gr/cm^2 the average thickness of the adhesive is:

$$t_a = \frac{1.39}{.952}\left(\frac{17.15 \times 10^{-4}}{1 \times 1.39} - 8.89 \times 10^{-4}\right) = 5.03 \times 10^{-4} \text{ cm}$$
(.20 mils)

Quantities: - Four quantities of adhesive coated polyester film were produced under the conditions noted below:

a) About 18 meters of the Mylar film were coated at room temperature with the drying tunnel exhaust fan on and the coated film was wound on a roll with silicone treated Kraft paper as the backing material.

b) A section of about 8 meters of the Mylar film was coated under similar conditions as in (a) but was wound on a roll with "Armalon" (Teflon coated glass-fiber fabric) as the backing material.

c) About 18 meters of the Mylar film were coated with the drying tunnel lights on (temperature of the Mylar Surface ~ 27°C) and wound on a roll with silicone treated Kraft paper as the backing material.

d) About 18 meters of the Mylar film were run under similar conditions as in (c) but with the exhaust fans shut off. Temperatures of the Mylar Films in this case rose to ~ 90°C.

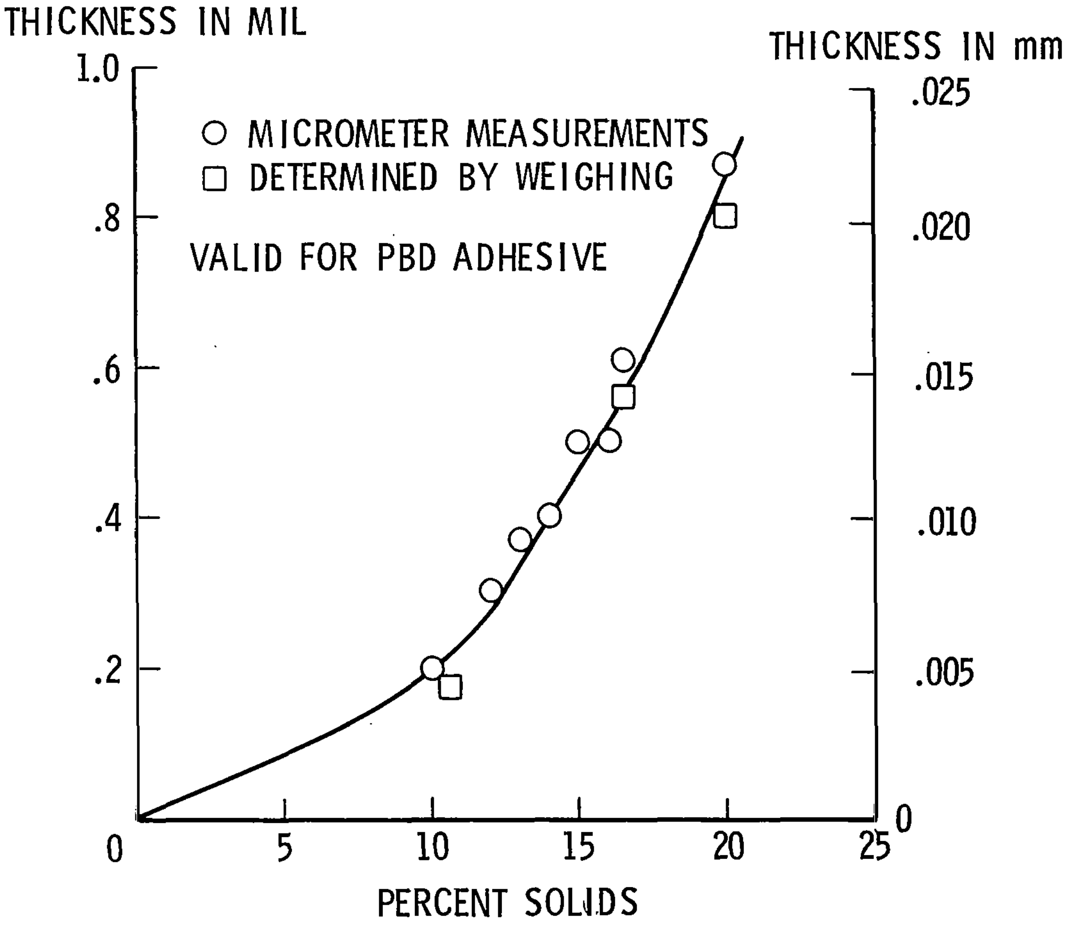


FIGURE 30. — COATING THICKNESS VERSUS PERCENT SOLIDS

Industrial cures: Coated film batches (a) and (b) received essentially a slow drying over-night and at room temperature. Batches (c) and (d) were forced dried at film temperature of 27°C and 90°C, respectively. In addition, coated film specimens from batches (c) and (d) were cured further in the laminator (see figure 5) at temperatures of 82°, 104°, and 171°C and with combinations of pressures of 27.6 and 55.2 N/cm^2. Also the roll speeds were varied from 1.2 m/min and 3.0 m/min to vary the pressure and temperature dwell times from 4-5 secs and 2 secs, respectively.

Surface tack: Evaluation of these various specimens consisted only of qualitative analysis of the film tack. All of the specimens were judged relatively tack-free. Differences were not discernable between the "apparent cure" that occurred on rapid drying in the heat-tunnel (batches (c) and (d), or slow drying overnight at room temperatures (batches (a) and (b), and the "true cure" produced by passing the composite film and adhesive through the laminator under temperature and pressure.

Operating personnel were impressed by the ease of cure of the adhesive using the existing hot roll/nip roll techniques.

Thermosetting: It was noted that the adhesion ability of the adhesive coated film decayed sharply with aging time. The casting of the adhesive film and adhesive bonding in a fabrication should be done as part of a single process. The adhesive film cannot be coated on polyester and stored before further application in a fabrication process. This is a constraint characteristic of a thermosetting adhesive and indicates the desirability of process flexibility that can be gained from thermoplastic adhesives.

Criticality of Hydroxyl Number: Due to an incorrect assumption as to the hydroxyl number of the polybutadiene resin batch used in one experiment, the proportion of isocyanate to polybutadiene in the adhesive mixture was such that the NCO/OH ratio was 1.2 rather than the desired 1.1. This difference should not have affected the properties of the adhesive, although it is possible that more surface cure might have occurred, resulting in lower tack and a slight decrease in bonding ability.

This discrepancy pointed up the fact that the hydroxyl number for the resin may vary and, therefore, this value should be obtained from the supplier before formulation and mixing. This means that fresh calculations for the proportion of isocyanate to polybutadiene in the adhesive formulation should be made whenever a new batch of polybutadiene resin is used.

Backing paper: Coated film batches (a) and (c) and batch (b) were rolled and stored on silicone treated Kraft paper and on Armalon (Teflon coated glass-fiber fabric), respectively. It was observed that 5 x 10^{-4} cm (0.2 mil) thick adhesive films were not uniform, had visible discontinuities, and considerable surface area of the base film remained uncoated. These defects were more pronounced when rolling and storing between silicone treated Kraft paper then when rolled with "Armalon" backing material.

A continuous adhesive layer on Mylar film is a definite necessity for good performance. Consideration should be given to using thicker adhesive layers than 5 or 10 x 10^{-3} mm as well as smoother and less absorvent backing material such as Teflon film. A thicker film of the adhesive will not necessarily cause an increase in the weight of the balloon since the polybutadiene-based adhesive has a lower specific gravity than the polyesterurethane adhesive currently being used. A slightly greater adhesive thickness probably would lead to a better peel strength when Dacron fibers are bonded to the Mylar film.

Peel tests. - Peel tests were made by the G. T. Sheldahl Co. to investigate the bonding ability of the polybutadiene-based adhesive. In addition, this mechanical property was used to assess the effects of the temperature and time parameters on laminating. Peel tests were made using the apparatus and procedure relating to figure 7. Specimens were fabricated of the 5 and 10 x 10^{-6} m adhesive coated bulk material bonded to a second uncoated Mylar film. A controlled bonding process was made possible on the laminator (fig. 5) by varying web speed and the hot-rod temperature. Peel strength data from these various specimens are shown on figure 31 and were provided through the supporting contract between the NASA and G. T. Sheldahl. Peel strength is plotted against the hot roll temperature for families of temperature dwell times. Two data points have been disregarded in fairing the data of figure 31 since they appear to be inordinate. The major significance of the peel data is at the upper test temperature (166°C) since consistent improvement in peel strength appears with increasing roll temperatures. However, there is consistant evidence from the data that peel forces are increased with decreasing dwell time. The thick adhesive film appears more tolerant to long dwell times than the thin film. The indications are that the thin film (5 x 10^{-6} m thick) should be cured at temperatures around 160°C but for dwell times less than 1 second. The thick film (10 x 10^{-6} m thick) appears to achieve maximum peel forces for dwell times between

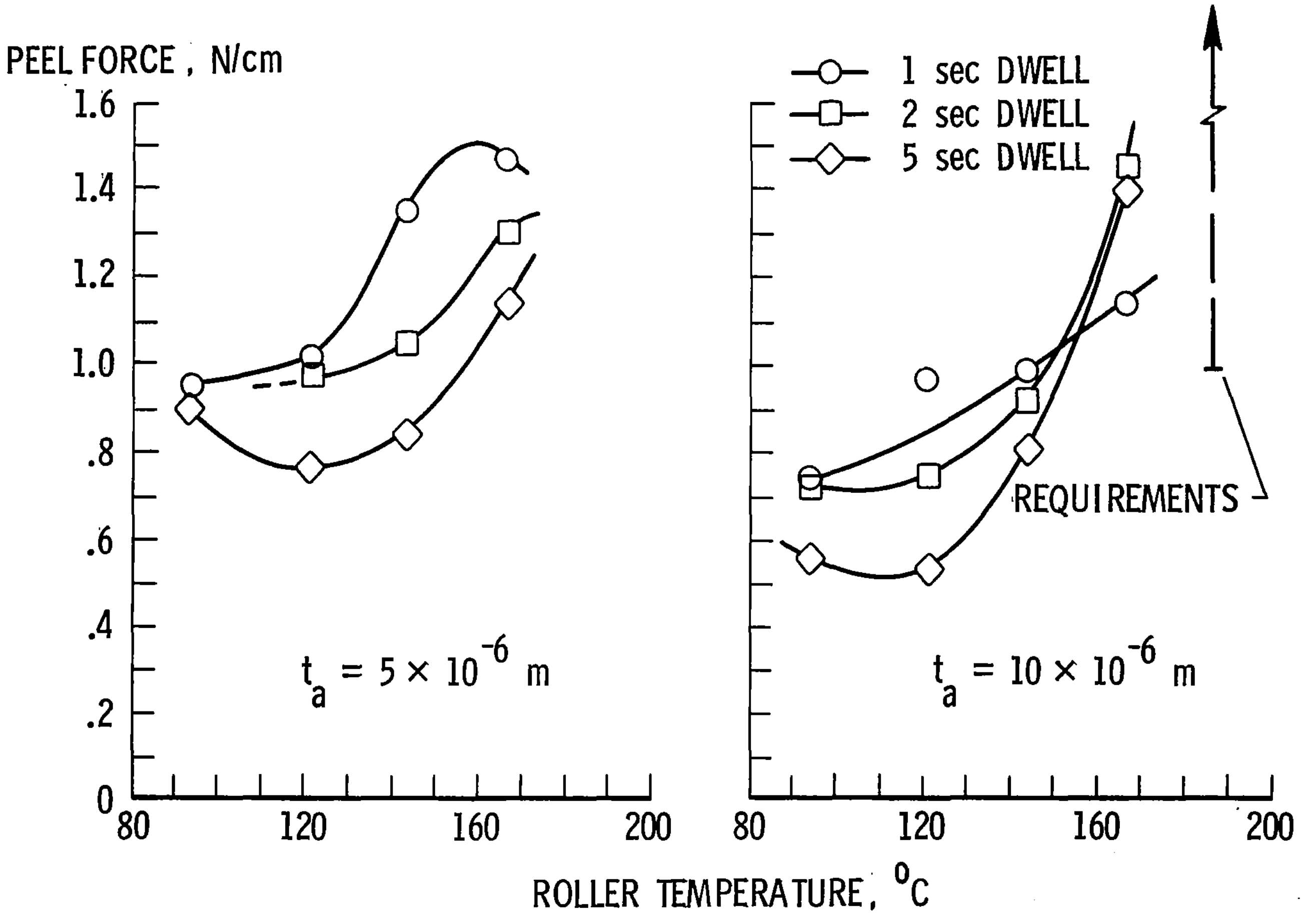


FIGURE 31. — PEEL STRENGTH AS A FUNCTION OF HOT ROLL TEMPERATURE AND DWELL TIME

2 and 3 seconds at the maximum test temperature of 166°C. There is an indication from the data of figure 31 that higher roller temperatures with optimum dwell times could yield slightly greater peel forces.

It is generally concluded that for even thick coats of adhesives in Mylar laminations, the fabrication cannot be subjected to roll temperatures in excess of 200°C. At this upper temperature, the Mylar film loses strength and structural orientation, dimensional stability is lost, and transport of materials becomes a problem. The conventional hot roll lamination process generally is limited to temperatures in the vicinity of the maximum test temperature of 166°C. Hence, it is speculated that only small improvements from slightly increased roll temperature can be anticipated.

The data of figure 31 indicates that maximum peel for the polybutadiene based adhesive under optimum aging and curing will be approximately 1.5 N/cm (0.86 lb/in). This value is within the average range of peel values for conventional polyester-urethane adhesives. For example, peel values on thin homogeneous laminates of Mylar-adhesive-Mylar construction are:

$f \leqq$ 0.8 N/cm (0.5 lb/in.) for 2.5 x 10^{-3} mm (0.1 mil) adhesive thickness

$f \geqq$ 1.8 N/cm (1.0 lb/in.) for 25 x 10^{-3} mm (1.0 mil) adhesive thickness

$f =$ 3.2 N/cm (1.8 lb/in.) at a Mylar-adhesive-Mylar interface in a 1.7 N/m^2 (5 ounce/yd^2) fabric reinforced lamination for an adhesive thickness of 5 x 10^{-3} mm (0.2 mils)

In view of the above, it is concluded that the peel strength of the polybutadiene adhesive is on the low range of acceptability. Its use should be for low stress applications or will depend upon reassessment and reduction in peel criteria in some cases.

Further research appears desirable and justified to work to increase the maximum peel level of the polybutadiene product to approximately 3.2 N/cm (1.8 lb/in.).

Shelf life. - Since the polybutadiene adhesive is a thermosetting adhesive, it must be used for bonding shortly after application. Experiments were made by the G. T. Sheldahl Co. to determine the loss

in adhesive ability of the product as a result of shelf life or time lag between initial coating of a film and its subsequent bonding to a second film. Specimens were prepared of 5×10^{-6} m and 10×10^{-6} m adhesive films on a 9×10^{-6} Mylar base film using both whalehide backing paper and polyethylene backing film. Peel force was used as the indicator of bond degradation with shelf life. These data are shown on figure 32 for a range of shelf life value up to 500 hours. Bonding of test specimens was effected on a tape sealer using a wheel temperature of 165°C, a pressure of 70 N/cm^2 (100 psi) and a temperature dwell time of 2 seconds.

Inspection of figure 32 indicates that varying the adhesive thickness or changing the release paper has no pronounced effect on performance. The loss of bonding ability with aging was clearly shown by the drop-off in peel strength with increasing time from coating to bonding. For example, bonding within one hour of coating gave a peel strength in the region of 1.60 N/cm (0.9 lb/in) which fell rapidly after 3-4 hours, being half the original value after aging for ten hours before bonding, and dropping to around 18 N/cm (0.1 lb/in) after a week. However, a sample kept dry and under cold storage (below 0°C) for the same period before bonding showed a peel strength of over 0.9 N/cm (dash) curve). The decrease in peel strength after aging presumably is due to overall slow curing of the adhesive plus surface curing through contact with moisture in the air. Keeping the adhesive dry and at a low temperature retards curing and allows better bonding.

Tensile strength. - An initial stimulus to this adhesive research was random evidence of cold temperature film strength degeneration as a result of the adhesive coat. Hence, a prime goal was to develop an adhesive that would not degenerate the film. An enhancement to film strength was not considered a goal; however, if it could be acquired as a bi-product it would be desirable; if otherwise without deleterious consequences.

Exhaustive studies were performed by the G. T. Sheldahl Co. to determine the influence of polybutadiene adhesive on Mylar film substrates. In general it can be concluded that the adhesive neither enhances nor degrades the base film. This result is as expected by virtue of the amorphous and low modulus characteristics of the adhesive, at both room or tropopause temperatures. Some experiences to the contrary are thought traceable to grip slippage in the tester. Slippage is aggravated by the viso-elastic and amorphous state of the polybutadiene adhesive, and this is particularly true if the adhesive is not completely cured.

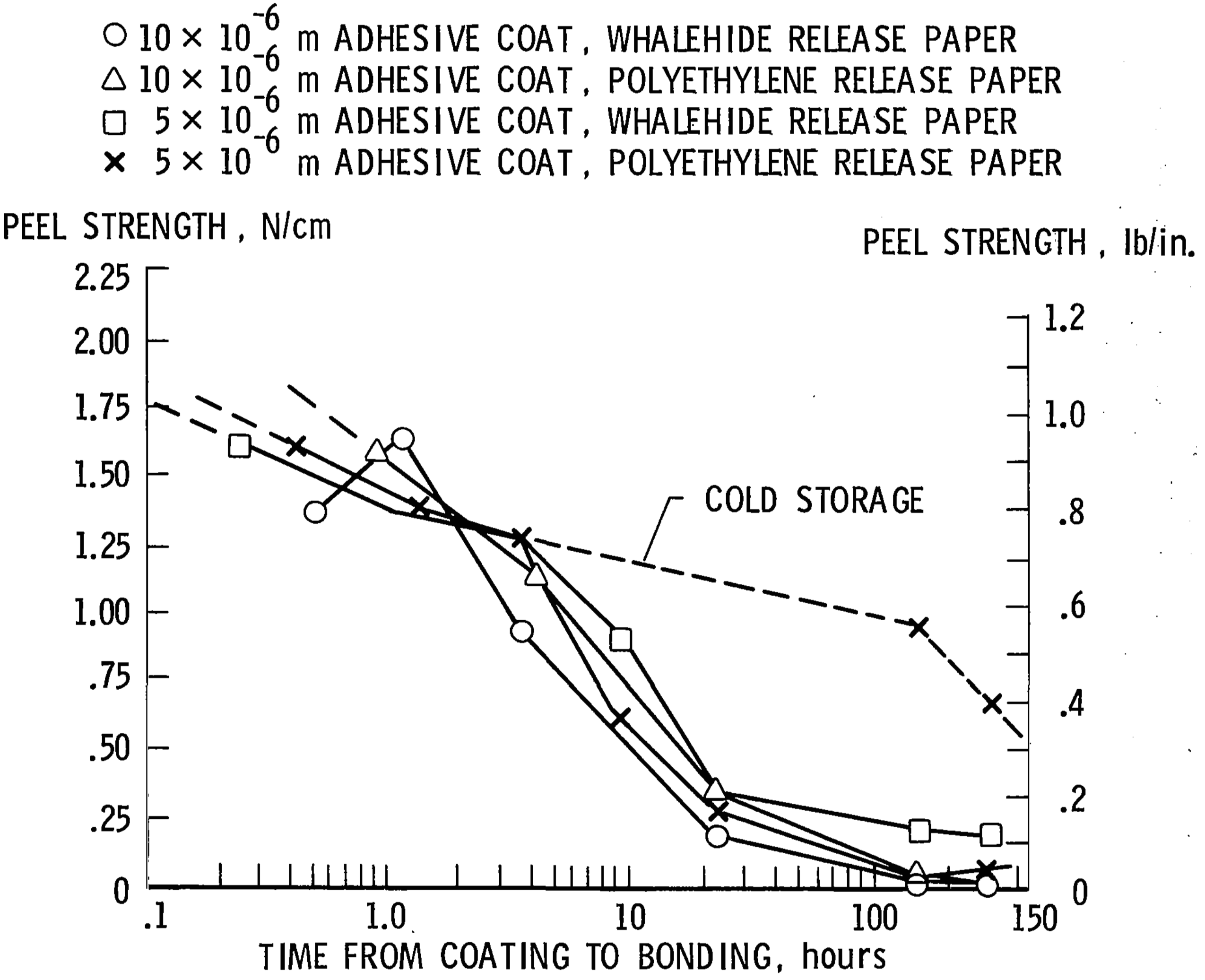


FIGURE 32. — PEEL FORCE DEGRADION WITH SHELF LIFE

Concern was had regarding the possible degrading effects of adhesive solvents on stress oriented Mylar. The film is exposed to these solvents during coating and curing and in certain lamination of metallic foils there has been evidence of entrapped solvent. Studies to determine the effects of methylene chloride on polyester film show that the film is highly plasticized in the presence of the solvent but fully recovers its strength after completely drying.

In general, the conventional glasseous adhesives show enhancement of the strength of mylar at the tropopause temperatures. Offhand, this is as would be expected for homogeneous test specimens with a higher modulus coating. This enhancement might appear as desirable until it becomes apparent that it is this structural participation between the film and the adhesive that produces the complex stress paths and stress concentrations that precipatate brittle failure at temperatures below the glasseous transitions. To fully assess the degenerative potential of the glasseous adhesives at low temperatures, it would be necessary to use notched specimens. Perhaps, more realistic to actual experience would be studies with adhesive splotched specimens.

Experiences had during the design, development, and manufacture of the material for the Viking Balloon Launch Decelerator test (BLDT) had shown significant degeneration in strength due to inordinate, splotchy, or inhomogeneous adhesive coating.

To illustrate the non-reactive or passive character of the polybutadiene adhesive coating, typical stress strain data are provided on figure 33. The membrane loads (ordinate) versus the percent strain (abscissa) are compared for uncoated mylar film and film coated with polybutadiene adhesive. The comparison is made for films loaded parallel to the machine and transverse directions and for room temeprature, 22°C, and the tropopause temperature, -68°C.

It can be seen that only small departures exist between the characteristics of the coated and uncoated materials. The larger variations are apparent for room temperatures and these are best accounted for as resulting from grip behavior. The grip problem diminishes at the cold test temperatures and lower percent variations in the curves and closer agreements between rupture values are seen to occur.

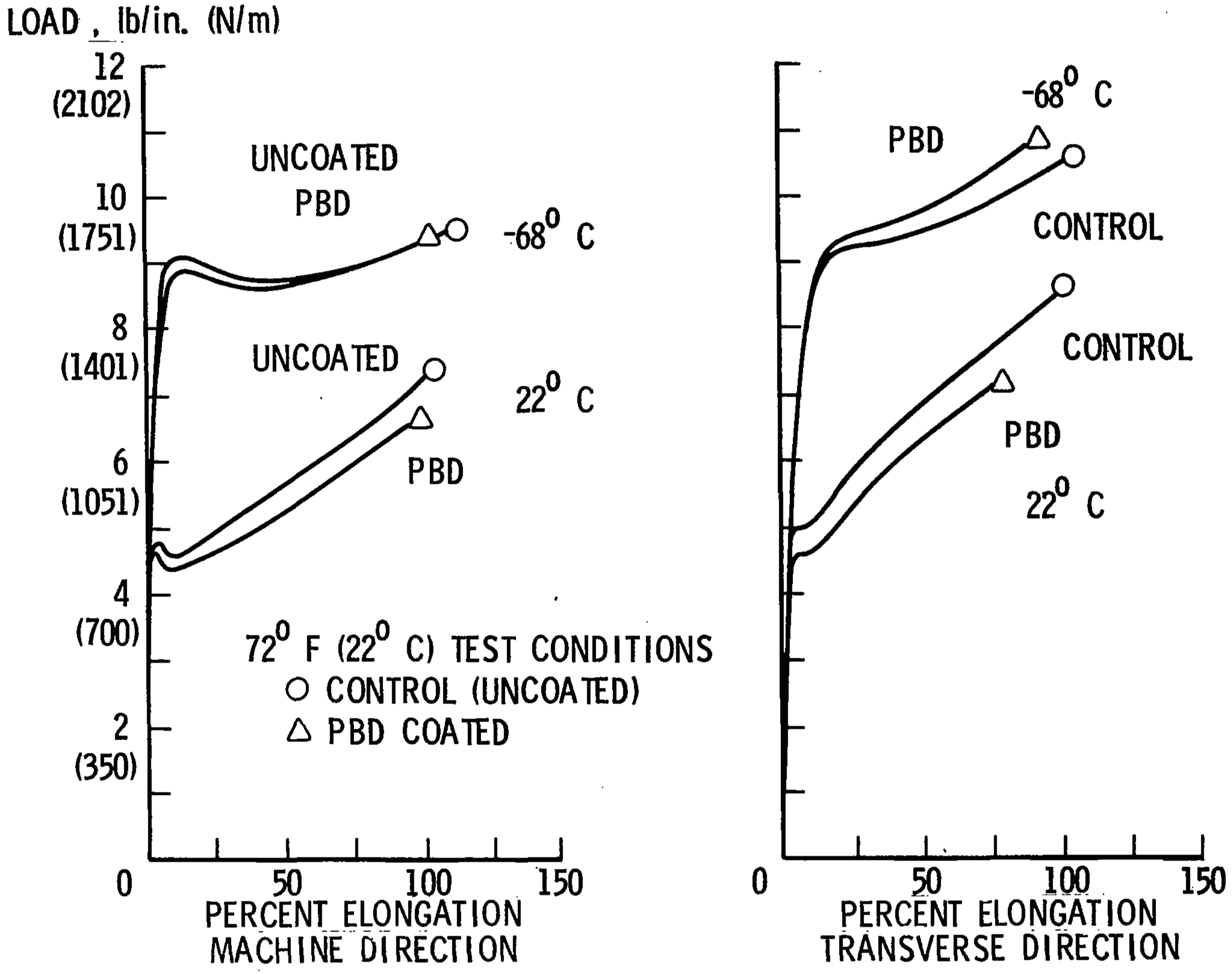


FIGURE 33. — LOAD ELONGATION CURVES

CONCLUSIONS

Fabrication of films and fibers for use as structural materials is a rapidly growing industry with increasing numbers of applications in many fields. Improvement in the performance of these materials will significantly impact the functionality, life, cost effectiveness, limitations, as well as scope of applications. A specific need for improvement has been identified in increasing the tolerance to sub-zero temperatures by reducing the embrittlement of constituents of the fabrications. A concerted study is recorded in this paper to reducing the embrittlement of a basic constituent to all such fabrications, the bonding adhesive.

The principal approach to this study, which involves procurement and synthesis of adhesives, candidate selections, curing techniques, and mechanical testing, is the determination of the thermomechanical characteristics of the materials by use of the Torsional Braid Analysis. Secondary evaluations of bonding ability thru peel tests, qualitative tack tests, and tensile tests are used to evaluate compatible adhesives practical for normal industrial processes.

Thru a NASA supporting contract, adhesive coated films and test specimens were fabricated with candidate adhesives using Industrial Roller Coating and Laminating equipment at the G. T. Sheldahl Co., Northfield, Minnesota. In addition, curing techniques, peel tests, and tensile tests were performed by Sheldahl in cooperation with the University efforts.

The widely used end-reactive aromatic polyesters, crosslinked with isocyanates were tested and found to have glass transition temperatures as high as +13°C after curing and temperatures of minimum mechanical damping at -35°C. For good solid state material toughness, these characteristic temperatures should be lower than the temperature of use. For high altitude balloon applications, the use temperature is -68°C (-90°F).

The scope of the investigation included study of four commercially available adhesives, synthesis and study of eight low molecular weight hydroxyl end-capped aliphatic polyesters, procurement and study of three polybutadienes and butadiene-acrylonitrile copolymers, and the procurement and study of two styrene-butadiene-styrene block copolymers.

In general, thermomechanical spectra are provided in the text for most of the adhesives for both the uncured and cured conditions. Tabulations are submitted of the characteristic glass transition temperatures (T_g), the temperature of minimum mechanical damping ($T_{min} < T_g$), and the temperature of secondary glassy-state transition (T_β) for all of the adhesives studied.

Of the four industrial adhesives tested, the G. T. Sheldahl candidate B formulation appeared to be most suitable for balloon applications having a glass transition at -25°C and a minimum damping temperature below the -70°C use temperature (i.e., tropopause temperature).

The thermomechanical characteristics of the aliphatic polyesters show vast improvements over the conventional partially aromatic balloon adhesive as well as the four industrial adhesives. However, the temperatures of minimum damping of the aliphatic materials are found to be near the minimum use temperature (-70°C), whereas it is preferable to acquire adhesives with T_{min} well below -70°C.

The linear hydroxyl end-capped amorphous polybutadienes show thermomechanical characteristics substantially superior to the aliphatic polyesters. Polybd^{TM} R-45M procured from the ARCO Chemical Co. has the most promising characteristics. After curing, the material exhibited a T_g of -68°C, T_{min} of -100°C, and a T_β of -125°C. The material was tack-free, cured easily, and provided a T_g at approximately the tropopause temperature.

The two SBS block copolymers (Shell Kraton^{TM} 1101 and Phillips Solprene^{TM} 406) had glass transitions temperatures (-92° and -90°C) well below the use temperature (-70°C). These results are for materials using benzene as the solvent. Further study is needed using methylene chloride as the solvent since it is more compatible to industrial use. In addition, the SBS adhesives would require antioxidant and UV protecting additives in order to be used in balloon applications.

The reactive adhesives investigated were all thermosetting, whereas thermoplastic adhesives are more versatile and amenable to existing industrial practices.

The quality, complexity, and sensitivity of the curing process are important to the application of an adhesive. Multrathane F-222 polyester and Polybd^{TM} R-45M polybutadiene resin were studied extensively for cure behavior relative to average functionality of isocyanate, temperature, time, pressure, catalyst type, and backing papers.

The polybutadiene adhesives react with the atmosphere and should not be allowed to age during drying in excess of 5 minutes before curing, depending upon quantity, humidity, volatility of solvent, and thickness of coating.

Stoichiometry (NCO/OH ratio) and cure time were investigated for the polybutadiene adhesives. NCO/OH ratios larger than 1.5 with 5 minutes cure at 150°C and 140 N/cm (200 psi) pressure appear to produce brittle adhesive films.

Pressure does not appear to be a significant parameter in the curing process of polybutadiene based adhesives.

Studies of effects of catalysts on curing indicate that the tackiness decreases with increased catalyst concentration. Tin octoate and dibutyltin diacetate produced the lowest tack with the polybutadiene adhesives. Catalyst and accelerator levels of 0.30% each proved satisfactory in terms of tack-free properties and satisfactory "pot lives" of the adhesive mixtures.

The Kraton^{TM} 1101 SBS block copolymers after drying and annealing at 80 or 120°C and bonded to uncoated polyester film at similar temperatures and under 140 N/cm^2 pressure, showed no tack and better bonding than the other adhesives, with the exception of the conventional and industrial products.

In general, bulk material of Polybd R-45M resin, Mondur CB-75 curing agent, dibutyltin diacetate catalyst, and methylene chloride solvent, coated on Mylar film showed little sensitivity to rapid drying in a heat tunnel, or slow drying at room temperature over night, or cures produced under temperature and pressure in a laminator. The polybutadiene adhesives exhibit ease of cure using existing hot roll/nip roll techniques.

The bonding ability of the polybutadiene adhesive decays sharply with aging. Shelf life can be increased by maintaining material in a dry-cold storage below 0°C.

In laminating adhesive coated film to film, peel strength appears to increase with decreasing dwell times and increasing temperature.

Maximum peel strengths of the polybutadiene adhesives as studied are not in excess of 1.8 N/cm (1 lb/in). Higher values are anticipated for the SBS block copolymers although these data were not within the scope of this contract effort. These upper values of peel strength are comparable to the typical minimum values of specifications for conventional thin film balloon applications.

In general, the polybutadiene adhesives displayed marginal peel strength but excellent thermomechanical characteristics.

Coupon studies on uncoated film and film coated with polybutadiene adhesive show that the PBD adhesive neither enhances or degrades the basic strength of the polyester film for temperatures ranging from room values to tropopause conditions.

The most promising non-reactive adhesive system appears to be the styrene-butadiene-styrene (SBS) block copolymers. These materials require no reactive (chemical) curing process, have the most suitable thermomechanical properties, and are anticipated to give low tack and peel in excess of 1.8 N/cm (1 lb/in). Considerable work is needed to evaluate these adhesives and make improvements for balloon applications.

Undesirable imprints and discontinuities in adhesive coatings can be produced by the backing film or lifting paper. A smooth backing material such as "Armalon" provides more homogeneous coatings than Kraft paper.

Due to the criticality of the hydroxyl number of the resin in the curing process, the value should be obtained for each batch mixed for production purposes.

The project to investigate adhesives suitable for low temperature applications was successful in converging on classes of adhesives that provided appropriate thermomechanical characteristics, low tack, and ease of curing. However, these materials, in general, provide only the minimum bonding strength that the balloon industry is accustomed to; they would be more suitable if thermoplastic, and would simplify production control if reactive curing process could be avoided. Further research on these features appears needed and worthwhile.

REFERENCES

1. A. H. Landrock, "Cryogenic Properties of Polymers", in "Encyclopedia of Polymer Science and Technology", Vol. 4, p. 415, Interscience, New York, 1966.

2. R. F. Robbins, "Cryogenic Properties of a Polyurethane Adhesive", in "Polymers in Space Research" (C. L. Segal, M. Shen, and F. N. Kelley, eds.), p. 331, Marcel Dekker, New York, 1970.

3. R. B. Gosnell and H. H. Levine, "Some Effects of Structure on a Polymer's Performance as a Cryogenic Adhesive", in "Polymers in Space Research", p. 345, Marcel Dekker, New York, 1970.

4. J. K. Gillham, Amer. Chem. Soc., Polymer Preprints, 7, 513 (1966).

5. J. K. Gillham, Critical Rev, Macromolec. Sci., 1, 83 (1972).

6. J. K. Gillham, "Torsional Braid Analysis", in "Encyclopedia of Polymer Science and Technology", Vol. 14, p. 76, Interscience, New York, 1971.

7. J. K. Gillham and M. B. Roller, Polym. Eng. Sci., 11, 295 (1971).

8. C. L. M. Bell, J. K. Gillham, and J. A. Benci, Amer. Chem. Soc., Polymer Preprints, 15(1), 542 (1974).

9. J. K. Gillham, A.I.Ch.E. J., 20(6), 1066 (1974).

10. Y. Hazony, S. J. Stadnicki, and J. K. Gillham, Amer. Chem. Soc., Polymer Preprints, 15(1), 549 (1974).

11. S. J. Stadnicki, J. K Gillham, and Y. Hazony, Amer. Chem. Soc., Polymer Preprints, 15(1), 556 (1974).

12. J. K. Gillham, S. J. Stadnicki, and Y. Hazony, Amer. Chem. Soc., Polymer Preprints, 15(1), 562 (1974).

13. T. M. Connelly, Jr., and J. K. Gillham, Amer. Chem. Soc., Polymer Preprints, 15(2), 458 (1974).

14. C. K. Schoff and J. K. Gillham. Amer. Chem. Soc., Polymer Preprints, 15(2), 451 (1974).

15. N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", John Wiley, New York, 1967.

16. R. F. Boyer, Rubber Chem. Tech., 36, 1303 (1963).

17. R. F. Boyer, Polym. Eng. Sci., 8, 161 (1968).

18. R. F. Boyer, "Multiple Transitions in Semi-Crystalline Polymers" (Swinburne Award Address), Plastics Institute, London, 1973.

19. W. R. Sorenson and T. W. Cambell, "Preparative Methods of Polymer Chemistry", Interscience, New York, 1968.

20. P. E. Pierce, "Mechanical Properties of Coatings" in "Treatise on Coatings", Vol. 2 (Part I), p. 99, Marcel Dekker, New York, 1969.

21. R. J. Angelo, R. M. Ikeda, and M. L. Wallach, Polymer, 6, 141 (1965).

22. J. T. Bailey, E. T. Bishop, W. R. Hendricks, G. Holden, and N. R. Legge, Rubber Age, 98, 69 (1966).

23. G. Krans, C. W. Childers, and J. T. Gruver, J. Appl. Polym. Sci., 11, 1581 (1967).

24. G. Krans and J. T. Gruver, J. Appl. Polym. Sci. 11, 2121 (1967).

25. R. P. Zelinski and C. W. Childers, Rubber Chem. Tech., 41, 161 (1968).

26. J. Moacanin, G. Holden, and N. W. Tschoegl, Eds., "Block Copolymers", J. Polym. Sci. C, 26, (1969).

27. K. R. Arnold and D. J. Meier, J. Appl. Polym. Sci., 14, 427 (1970).

28. O. L. Marrs, F. E. Naylor, and L. O. Edwards, J. Adhesion, 4, 211 (1972).

29. M. Shen, V. A. Kaniskin, K. Biliyar, and R. H. Boyd, J. Polym. Sci., Polym. Phys. Ed., 11, 2261 (1973).

30. J. R. Haws, Amer. Chem. Soc., Coatings and Plastics Preprints, 34, (1), 114 (1974).