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AUG 76　G L BALL, D W WERKMEISTER, I O SALYER　F33615-75-C-5090
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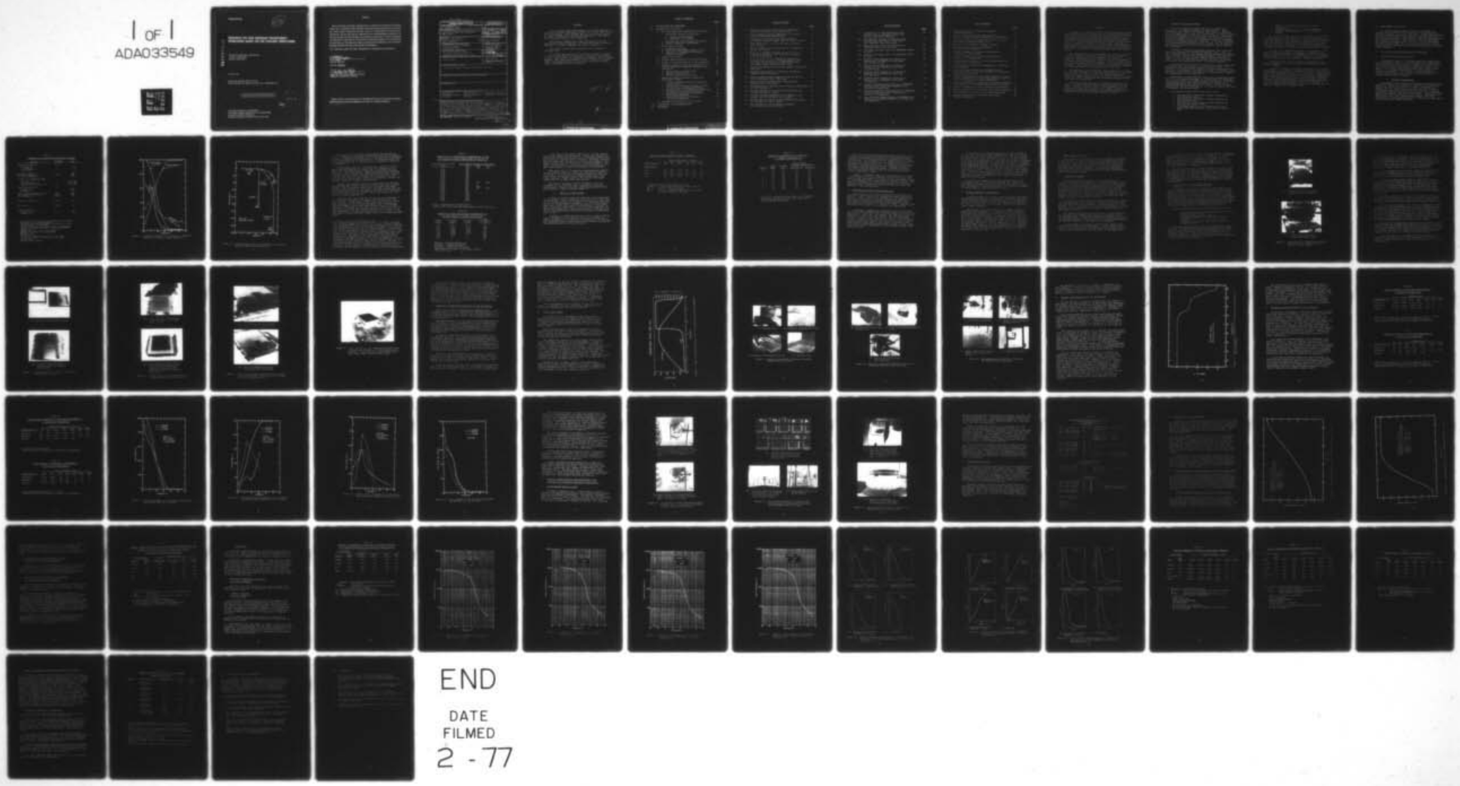

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# RESEARCH ON HEAT RESISTANT TRANSPARENT INTERLAYERS BASED ON THE ETHYLENE TERPOLYMER

*MONSANTO RESEARCH CORPORATION*
*DAYTON LABORATORY*
*DAYTON, OHIO 45407*

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

# NOTICE

This technical report has been reviewed and is approved for publication.

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FOR THE COMMANDER

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

An ethylene terpolymer aircraft glazing interlayer, designated ETAXXX032, was developed that has reasonable strength to 350°F while retaining excellent high elongation down to -65°F. The high temperature performance was achieved while retaining thermoplastic sheet formability at 250°F required for polycarbonate. The improved mechanical performance to 350°F introduced no changes in the basic (550°F) thermal stability or transparency of the ethylene terpolymer

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# FOREWORD

This technical report was prepared by Monsanto Research Corporation, Dayton Laboratory, Dayton, Ohio under USAF Contract F33615-75-C-5090. This contract was initiated under Project No. 2914, "Non-metallic and Composite Materials," and Task No. 03, "Structural Plastics and Composites".

The work was administered under the direction of the Nonmetallic Material Division, Air Force Materials Laboratory, with Mr. E. A. Arvay (AFML/MBC) as Project Engineer.

This report covers work performed from 2 January to 2 December 1975.

The report was authored by the Project Leader Mr. George L. Ball III and Dennis W. Werkmeister, Principal Investigator in the Polymer Physics and Applications Section, Ival O. Salyer, Manager. The report was submitted by the authors in January 1976. Extensive revisions to the report were made in April 1976 at the request of the Air Force.

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# SUMMARY

An ethylene terpolymer aircraft glazing interlayer, designated ETAXXX032, was developed that has reasonable strength to 350°F while retaining excellent high elongation down to -65°F. The high temperature performance was achieved while retaining thermoplastic sheet formability at 250°F required for polycarbonate. The improved mechanical performance to 350°F introduced no changes in the basic (550°F) thermal stability or transparency of the ethylene terpolymer. The most significant improvement in thermal-mechanical properties occurred between +165°F and 350°F, where no measurable performance had existed before.

The improved mechanical performance to 350°F was achieved through a "controlled limited crosslinking" of the basic ethylene terpolymer system (containing 3.2% hydroxyl). It was shown that this improved form stability could be provided by any one of three crosslinking systems. The crosslinking could be conducted during or after formation of the ethylene terpolymer sheet. The crosslinking is taken to completion, therefore the interlayer sheet is completely stable with time.

In addition to the significant high temperature improvement in mechanical performance, ultimate elongations of up to 200% were retained at -65°F. Tensile and tear strengths were increased slightly between -65°F and +165°F, while both tensile impact and tensile elongation were decreased slightly between -65°F and room temperature.

ETAXXX032 bonded laminates of glass/polycarbonate were shown to survive repeated thermal cycling between -65°F and 300°F. Failures occurred only in the polycarbonate, which softened and bent, as expected, at the higher temperature. Glass/glass laminates containing the ETAXXX032 survived this thermal cycling and also thermal soaking at 350°F.

# I. INTRODUCTION AND BACKGROUND

Aircraft windshield temperatures of up to 350°F are anticipated for high performance military aircraft. These windshields must resist bird impacts, which makes it desirable to use bonded plies of glass and polycarbonate (or other plastics). Effective utilization of these materials requires a transparent interlayer, compatible with both glass and polycarbonate, that will be elastomeric over a wide temperature range to accommodate a variety of thermal expansion conditons. It is also desirable, from a windshield fabricator's point of view, that the material be capable of being processed by thermoplastic (sheet) laminating techniques.

A family of ethylene terpolymer adhesives (ETA) exist that have been developed for aircraft interlayers (Ref. 1 thru 5). The unmodified ethylene terpolymers lack any measurable strength above 125°F but have inherent thermal stability well into the range of 550°F. Mechanical performance had been improved to +165°F by chemical modification, without affecting the ability to laminate as a sheet below 250°F, in previous programs.

This program was conducted to incorporate useful mechanical performance into the ethylene terpolymer up to +350°F. Its otherwise excellent aircraft glazing interlayer characteristics were not to be impaired. This was to be done, if possible, while retaining thermoplastic processability at polycarbonate compatible temperatures of less than 275°F.

Enhancement of these elevated temperature mechanical properties was to be achieved through (a) crosslinking, (b) grafting, or (c) polyblending of the basic ethylene terpolymer. Controlled crosslinking, using fractional stoichiometric quantities of crosslinking agents, was expected to provide the most practical approach, but required defining the exact type and amount of crosslinking agent and new processes.

The program included seven tasks, which were:

1. Form stability improvement through crosslinking the ETA (major effort).
2. Form stability improvement through grafting the ETA (minor effort).
3. Form stability improvement through polyblending with the ETA (minor effort).
4. Processing studies on the preparation of the high temperature interlayer and laminates therefrom.

5. Thermal and physical screening and system optimization.
6. Preparation of up to 12 x 12 inch laminates.
7. Detailed characterization of the optimized system.

All of the ethylene terpolymer interlayers are described by a nine character code that starts with ETA for Ethylene Terpolymer Adhesive. The second set of three characters indicates the nature of high temperature modification, if any. Those used are NOX, indicating no crosslinking or no modification and XXX indicating a crosslinking modification, by any number of means, to achieve an interlayer useful to 350°F.

The last three characters indicate the hydroxyl content to one tenth of a percent. Accordingly, ETANOX032 is an ethylene terpolymer adhesive, unmodified, with 3.2% hydroxyl. This was the single starting material used in all the experimental effort, except measurement of optical properties.

Exceptions exist to this code (i.e., ETA138200) that intentionally do not reveal unpublished information for proprietary reasons.

In order to maintain uniformity throughout this program with regard to the ethylene terpolymer used, a 100 pound batch of ETANOX032 was synthesized in our pilot plant. Unfortunately some of the reactants contained minor amounts of contamination which caused the final products to have an above average haziness. This actually was no problem since we were concerned primarily with thermal properties and any changes that might occur in optical properties as a result of treatments to increase thermal form stability. Therefore, relative and not absolute numbers were of significance.

## II EXPERIMENTAL DISCUSSION

The experimental discussion describes in detail the approach taken to achieve high temperature mechanical performance, required processing conditions, thermal characteristics and durability of an optimized ethylene terpolymer which is identified as ETAXXX032. The resultant physical characteristics are summarized in Table 1 and Figure 1. Data on ETA 138200 (an ethylene terpolymer useful to +165°F) and aircraft-grade polyvinylbutyral (PVB-3 GH) is also described in the text to illustrate the improvement and provide a comparison to a better known reference.

### A. The High Temperature Modification Technique

### 1. Controlled Limited Crosslinking

The physical result of the high temperature modification is illustrated in Figure 2, Creep Elongation Vs. Temperature. Chemically what is done is chain extension followed by limited crosslinking. The crosslinking is introduced either (1) by addition of chemical crosslinking agents with thermal initiation or (2) through the generation of free radicals by electron bombardment. *The ethylene* terpolymer adhesive has these groups, through other segments in the structure, or through a carbon-carbon backbone.

#### a. Chemical Crosslinking

Development of the ethylene terpolymer to achieve the high temperature properties involved (a) identifying crosslinking agents that would be effective in partial stoichiometric amounts, and (b) establishing a suitable process to achieve the desired improvement in mechanical properties at elevated temperatures without causing intractability. Two crosslinking agents were selected and shown to be useful; isophthaloyl bis-caprolactam (ipbc) and vinyltriethoxy silane. They were selected due to their known ability to crosslink the ETA system and expected good thermal stability.

## Table 1

## ENGINEERING DATA ON ETHYLENE TERPOLYMER ADHESIVE ETAXXX032

| Property | ASTM METHOD | Value |
|---|---|---|
| Temperature at Modulus of | D1043 | |
| 45,000 psi, °F | - | -27 |
| 675 psi, °F | - | +17 |
| Stifflex Range, °F | -[1] | 44 |
| Resistance to heat, °F | -[2] | 450 |
| Zero Tensile Strength, °F | D1637[3] | 380 |
| Zero Tensile Elongation, % | -[3] | 2000 |
| Laminate Utility Temperature Range | | |
| Glass-Glass, °F | -[4] | -65 to +350 |
| Glass-Polycarbonate, °F | - | -65 to +270 |
| Polycarbonate-Polycarbonate, °F | - | -65 to +270 |
| Tensile (Room Temperature) | D412[5] | |
| Strength, psi | - | 4300 |
| Elongation, % | | 1400 |
| Impact (Tensile) Strength, ft lb/in.$^2$ | D1822[6] | 580 |
| Tear Strength, lb/in. thickness | D1004[7] | 350 |
| Shear Strength, psi | D1002[8] | 300 |
| Transmission (laminate), % | D1003[9] | >85 |
| Haze (laminate), % | D1003[9] | <3.6 |
| Laminating Conditions | | |
| Temperature, °F | -[10] | 250 |
| Pressure, psi | - | 45 |

[1] Stifflex Range is difference between temperatures at two modulis.
[2] Zero weight loss in an inert atmosphere.
[3] Indicates temperature and elongation at break with ∿3 psi load upon heating at a rate of 10°C/min.
[4] Based on thermal cyclic exposure of 5 in. x 5 in. glass-glass and glass-PC laminates with 0.03 in. adhesive layer. Plies 0.25 in. thick.
[5] Specimen C, 0.03 in. thick, 2 ipm crosshead.
[6] Specimen - Type 412 C; 24 in. drop height.
[7] Thickness 0.03 in.
[8] Aluminum tabs.
[9] Determined on WPAFB Spectrophotometer, 0.03 in. thick adhesive layer between plies of 0.125 in. thick glass. Reference air.
[10] Typical maximums required.

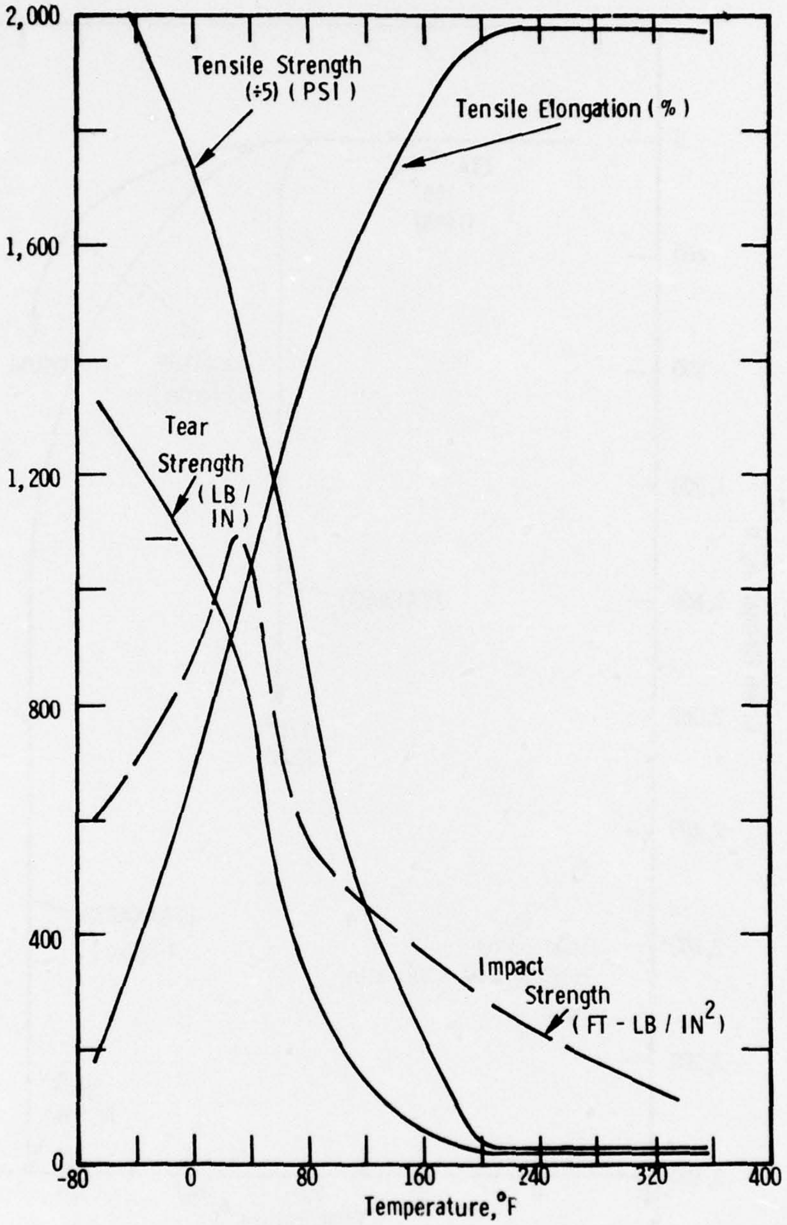

Figure 1. Summarized Mechanical Properties of ETAXXX032 Aircraft Interlayer Versus Temperature

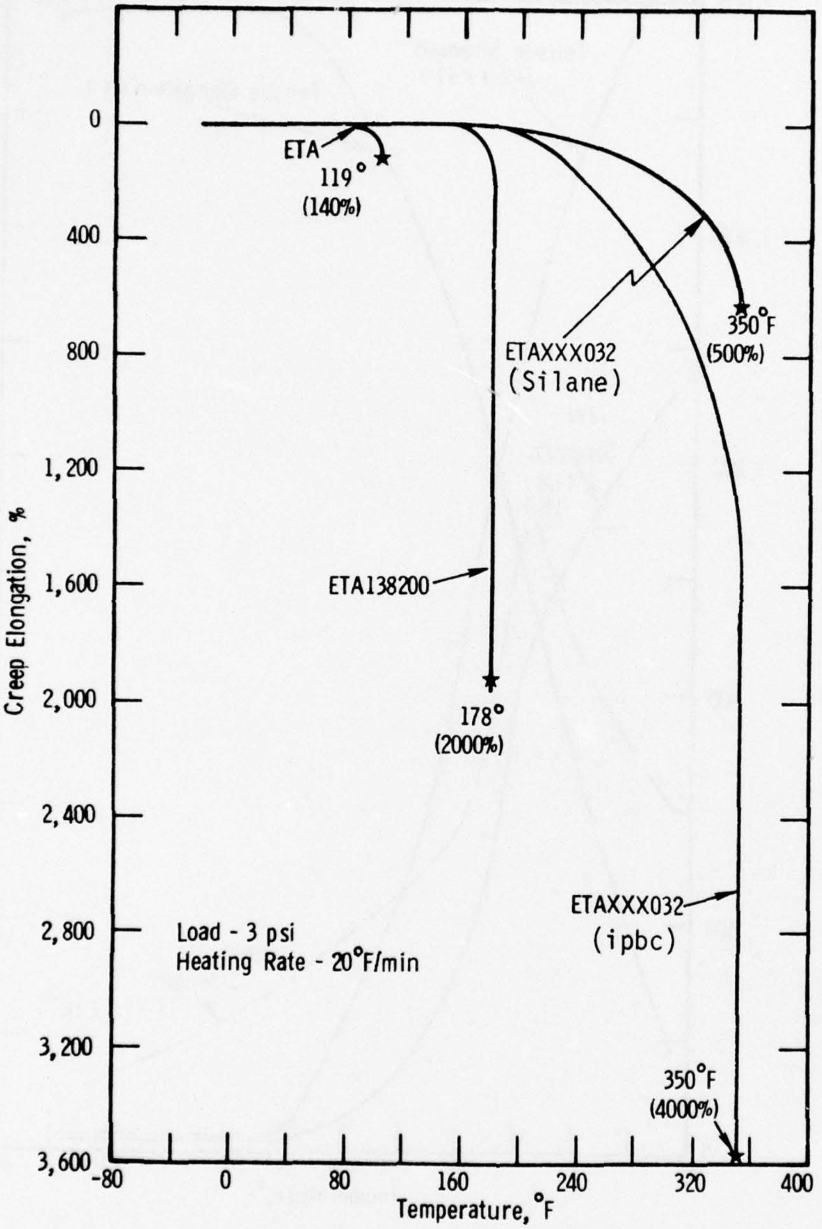

Figure 2. Creep Elongation Versus Temperature for Various Ethylene Terpolymer Compositions

The need to fine tune the system may not be apparent at first. Consider the fact that the material must be processable,. in terms of making a laminate, after it is partially crosslinked. This necessitates that a minimum amount of crosslinking be done to the material so as to retain as much thermoplastic character as possible.

Crosslinking (limited) of the ETA with either of the two agents was achieved by (a) compounding the ingredients on a mill roll, (b) compression molding and curing under pressure, and (c) at times post-curing. Experimental work was performed to arrive at the optimum concentration of crosslinker, which is 0.2% for ipbc and 1.0% for silane; the concentration of the chemical crosslinking agents needed to be present to effect the desired increase in thermal form stability.

Samples were prepared on a mill roll using 100 g batches. The material was first hot milled to remove volatiles and then cooled. The crosslinking agent and/or catalysts were added and thoroughly milled in. The sample was then removed from the mill and a portion of it was compression molded into thin sheets at 400 psi for 5 hours at +325°F. These were tested for zero tensile strength temperature.

Tables 2 and 3 are lists of the various concentrations of the chemical crosslinkers and appropriate accelerators that were studied. In the case of ipbc, there seems to be a fairly wide variation in Zero Tensile Strength* (ZTS) temperatures. This was probably due to the small sample size, a few impure crystals or the loss of a few crystals upon addition of ipbc to the mill roll, which could cause a significant decrease in the ZTS temperature. It was felt that at the 0.3 phr level a material could be made that would always have a ZTS temperature above 350°F.

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*Zero Tensile Strength Temperature (ZTS) - A useful screening test (modified ASTMD 1637) is the zero tensile strength temperature determination. The test as used only required a forced air oven capable of reaching 410°F and simple grips. A simple support is placed in the oven and a sample 15 mils thick by 1/8 inch long by 1/4 inch wide is suspended from the support using clips (3 psi load). The oven door is closed and the temperature increased until the sound of the lower sample clip hitting the oven bottom is heard; at this point the oven temperature is recorded as the ZTS temperature. The ZTS determination is rapid (less than 30 min) and quite reproducible (±5°F). The test quickly determines if crosslinking or other treatments have had any effect on the thermal form properties of the material by indicating creep elongation and fracture at elevated temperatures.

## Table 2

## EFFECT OF ipbc[1] CROSSLINKER CONCENTRATION ON THE ZERO TENSILE STRENGTH TEMPERATURE OF ETAXXX032

| Concentration of ipbc (phr) | Zero Tensile Strength Temperature °F (a)[2] | °F (b)[2] | °F (c)[2] |
|---|---|---|---|
| 0.00 | 140 | | |
| 0.10 | 186 | | |
| 0.15 | 221 | | |
| 0.20 | 332 | | |
| 0.21 | 309 | | |
| 0.22 | 302 | | |
| 0.23 | 305 | | |
| 0.25 | 401 | 368 | 339 |
| 0.27 | 401 | | |
| 0.29 | 365 | 401 | |
| 0.30 | 361 | 384 | 393 |
| 0.31 | 392 | | |
| 0.32 | 392 | | |
| 0.34 | 401+ | | |
| 0.35 | 401+ | | |
| 0.40 | 401+ | | |
| 0.45 | 401+ | | |
| 0.50 | 401+ | | |

[1] ipbc - isophthaloyl biscaprolactam

[2] Sample from completely new batch cured at 325°F for 5 hr.

## Table 3

## EFFECT OF SILANE CROSSLINKER CONCENTRATION ON THE ZERO TENSILE STRENGTH TEMPERATURE

| Silane[1] (phr) | Peroxide[2] (phr) | Catalyst[3] (phr) | ZTS[4] Temperature (°F) |
|---|---|---|---|
| 0.0 | 0.0 | 0.0 | 140 |
| 0.1 | 0.01 | 0.01 | 158 |
| 0.2 | 0.02 | 0.02 | 172 |
| 0.6 | 0.06 | 0.06 | 357 |
| 0.8 | 0.08 | 0.08 | 374 |
| 0.8 | 0.08 | - | 289 |
| 0.8 | - | - | 381 |
| 1.0 | - | - | 401 |

[1] Silane - vinyltriethoxysilane.

[2] Peroxide - dicumyl peroxide.

[3] Catalyst - dibutyltin dilaurate.

[4] Zero Tensile Strength of specimens cured at 325°F for 5 hr.

In the case of the silane (Table 3), a 1.0 phr concentration was chosen for two reasons. First, the required ZTS temperature for the interlayer could be achieved without adding a peroxide initiator or tin catalyst. Secondly, extensive physical tests with 0.8 phr and 1.0 phr silane showed no difference between the two other than the ZTS temperature. The higher concentration of 1.0 phr was therefore chosen so as to add a small margin of safety with respect to processing.

Some difference in the physical characteristics between the two systems resulted. These are reflected in Figure 2 and Table 4. The two creep elongation-fracture curves that reach 350°F resulted from these chemical additives. The lower elongation (500%) result is for silane; the higher (4000%) is for the ipbc type cured product.

The tensile strength, tensile elongation, and tear strength, as will be shown, were comparable for the two compositions. However, the ipbc cured system appeared best with respect to impact strength (Table 4).

### b. Radiation Crosslinking

A study of electron beam crosslinking on preformed sheet was conducted. Table 5 shows the effect of the electron beam on the thermal properties of sheets after they have been subjected to various doses of radiation. At 180 KV the samples were about 30 mils thick and were irradiated on both sides; thus, an uncrosslinked center of about 10 mils remained. At 300 KV the samples were fully cured; however, bubbling occurred and was progressively worse as doses above 10 Mrads were used to cure.

A quantity of sheet material was molded, cured at 300 KV with a 10 Mrad dose, and tested for tensile strength and tensile elongation as a function of temperature. The results were equally as good as the chemically crosslinked system and are disclosed later in Tables 13 and 14.

Table 4

## EFFECT OF CROSSLINKING ON IMPACT STRENGTH[1]

| Temperature, °F | Impact Strength, ft.lb/in.$^2$ -65 | -40 | +32 | +74 | +200 | +350 |
|---|---|---|---|---|---|---|
| Crosslinker[2] | | | | | | |
| none | 600 | 850 | 1,150 | 530 | 0 | 0 |
| Silane | 380 | 600 | 1,100 | 610 | 180 | 90 |
| ipbc | 960 | 850 | 1,390 | 650 | 310 | 140 |

[1] ASTM D1822 with D412 tensile specimen.

[2] Silane - 1.0 phr vinyltriethoxy silane cured at 325°F, 5 hours, 400 psi.
ipbc - 0.3 phr isophthaloylbiscaprolactam cured at 325°F, 5 hours, 400 psi.

Table 5

## EFFECT OF ELECTRON CURE OF ETANOX032 ON THERMAL FORM STABILITY

| Sample[1] | Dose[2] Mrad | Voltage KV | Zero Tensile Strength Temperature Initial, °F | Final, °F |
|---|---|---|---|---|
| 1 | 20 | 180 | 134 | 293 |
| 2 | 30 | 180 | 134 | 348 |
| 3 | 10 | 300 | 134 | 354 |
| 4 | 15 | 300 | 134 | 366 |
| 5 | 20 | 300 | 134 | 374 |
| 6 | 45 | 300 | 134 | 400+ |
| 7 | 60 | 300 | 134 | 400+ |

[1] 25-30 mil compression molded sheets of ETANOX032

[2] Applied by Energy Sciences, Inc. using their Electrocurtain Processor.

An electron cured system is partially attractive, since no addition of material to the ETA is required, which may otherwise affect its processability or durability in an aircraft window. The electron cure is accomplished after sheets are made, thus simplifying the sheet making operation by eliminating one processing step. It likewise gives the user the option of making several thermal performance grades of interlayer from the same base sheets. Thermal performance could be controlled within limits by merely adjusting the electron dose given a sheet.

Samples of ETANOX032 which had unreacted ipbc or silane as accelerators were also subjected to electron beams. The samples were crosslinked to a higher degree than samples given the same radiation dose without either chemical present. Thus degree or unformity of crosslinking through the interlayer thickness could advantageously be controlled, but with the addition of one process step.

## 2. Grafting and Polyblending Modification

Caprolactam was the monomer selected for grafting onto ETANOX032. There were several reasons for using caprolactam monomer. First, to gain high temperature form stability the graft must itself have a high heat distortion temperature. Caprolactam polymer, more commonly known as Nylon 6, has a heat deflection temperature at 66 psi of 365°F. Secondly, ipbc reportedly can be used as an initiator for caprolactam.

Accordingly, samples were prepared in which caprolactam was milled into the ETANOX032 at concentrations of 5 and 10 phr along with 0.1 phr ipbc. The samples were then oven cured at 257°F for 16 hours. In both samples. the ZTS temperature remained at 175 to 185°F which is the value for ipbc alone at 0.1 phr. Because of this, it was felt that it was not worthwhile pursuing this approach any further, especially since several good crosslinking systems were already in hand. These alone would require the majority of the effort available for detailed study.

Polyblending was attempted using Kraton GX6500, which is a clear rubber block copolymer made by Shell Chemical Company. The material has a ZTS temperature of 291°F. The Kraton polymer alone forms a very poor bond to glass and is quite unsuitable as an interlayer material. The idea was to make a polyblend of the Kraton and ETANOX032 in an attempt to combine the higher temperature properties of the Kraton with the excellent adhesion of the ETANOX032 material. A polyblend was prepared using a 50/50 mixture of the polymers. The resulting blend had a ZTS temperature of 225°F. The blend was not clear at room temperature. A laminate was prepared in order to observe how severe the haze was. At room temperature, the laminate with a 30 mil interlayer appeared translucent. The laminate also showed signs of poor bonding.

From this one sample it was concluded that while some increased thermal form stability resulted from a blend of ETANOX032 and Kraton, the loss in clarity and adhesive properties outweighed the benefits obtained. For the above reasons, no further work in this area was performed.

### 3. Thermal Oxidative Crosslinking

A marked increase in the zero tensile strength temperature (ZTST) had been noted in a terpolymer containing 6% OH. This resulted when the terpolymer was subjected to long periods of time in a toluene solution at 35°C and subsequently annealed at 110°C in an oven for 4 to 8 hours. This was attributed to ether linkage formation.

The ability of the 3% OH material to behave in the same manner was then investigated. A sample of 3% OH ethylene terpolymer was dissolved in toluene and maintained at 35 to 40°C with constant agitation. A capillary tube was inserted into the solution and oxygen was bubbled through at the rate of 20 cc per minute. Samples were taken at regular intervals for 2 weeks. These were dried at 110°C for either 4 hours or 16 hours and then tested for ZTS temperature. In no case was any appreciable change in the ZTS temperature of the material observed. The experiment was discontinued after two weeks. It was felt that any change which might occur after this time would be of dubious value.

## B. Sheet Making Processes

In the making of a muliply transparent laminate containing an interlayer, it is desirable that an interlayer sheet first be fabricated with near the desired final thickness (usually 20-30 mils). This sheet is then plyed with other transparent materials and laminated (Section C). Processes examined for achieving these sheets included: compression molding (with simultaneous curing), the block and skive method, and extrusion (with simultaneous curing).

### 1. Compression Molding

Compression molding consists of the application of elevated temperature and pressure to a material within a mold, whereupon it takes the size and shape of the mold. The molding is usually accomplished with a thermoplastic by first heating the plastic to a melt, applying pressure, and then cooling. A thermosetting plastic will require a specific time at an elevated temperature to cure, i.e. allowing a chemical in addition to just a physical change to occur. If curing is extensive, cooling is usually not required since the part would be form stable and easily removed from the mold.

In the case of the ethylene terpolymer (ETANOX032) containing a crosslinking agent molding is conducted to provide both the form (thin sheet) and introduce a limited degree of crosslinking. Thus it is molded as a thermosetting plastic, but must be cooled to be removed since it remains a thermoplastic (of much higher viscosity).

The particular molding and simultaneous curing conditions for the resultant ETAXXX032 interlayer are dependent on the crosslinking agent. These were discussed in Section A.1.a. for the individual systems (either the ipbc or silane crosslinkers) and are very sensitive to the amount of crosslinker.

A slow curing is desired to introduce the limited crosslinking agents thus the molding time is usually long and/or followed by extensive oven (or autoclave) post-curing so additional chemical conversion does not occur in time with use.

A typical compression molding cycle consists of a molding stage where pressures of 300 psi are applied to the material at 325°F for 3 hours. This is followed by a low pressure post cure stage of heating the interlayer up to 250°F for up to 6 hours (usually during the laminating process itself). This cycle was convenient in the laboratory, however shorter post cures are possible, if desired.

The mold used was only a sample picture frame type (20-30 mils thick) placed between two 15 in. x 15 in. Teflon coated caul sheets. Thus the pressure reduces to nearly zero during the operation when the frame is contacted. The mold is always cooled before removing the part. Sand blasted Teflon coated mold surfaces are recommended to prevent sticking and provide a rough molded surface from which air can readily be expelled in laminating.

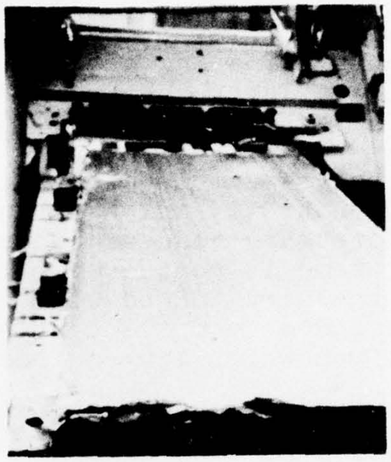
## 2. Block and Skive Sheet Making Process

A convenient way to process polymers into sheets is to utilize the skiving technique. This process consists of two separate operations--first, fusion of the polymer into a block bonded to a steel plate and second, the cutting off of thin layers of this block to yield sheet of the desired thickness. Figure 3(a) shows a full size block mounted on a skiving machine. The knife is fixed to an arm that can be indexed down to cut off sheets of the desired thickness from the block. The table that the block is mounted on moves back and forth under the knife thus cutting off sheet as shown in Figure 3(b).

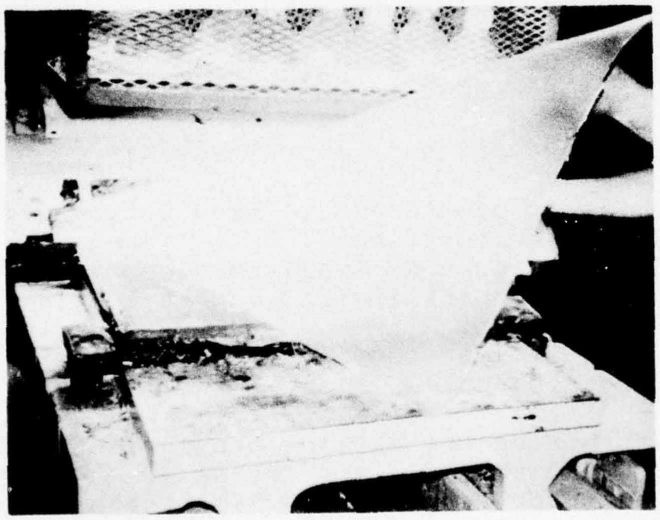
This sheeting process has several advantages such as:

- ability to handle crosslinked material (i.e. materials with poor flow)
- ability to process small samples
- ease and versatility of gauge selection and control
- relatively low cost on small and intermediate production scales

The logic for using the skiving process is as follows: it allows us to compound the ETA with the desired crosslinking material and then to perform the crosslinking of the polymer during the block formation, which is done under heat and pressure conditions. Thus, the sheets that are skived off the block should be crosslinked and capable of high temperature vacuum drying before lamination.



(a) Formed block (~6 in. thick) mounted on skiving apparatus



(b) Sheet (~0.03 in. thick) being skived from block

Figure 3. Illustration of Large-Scale Block and Skive Interlayer Sheeting Process (30 in. x 60 in. sheet)

In light of these advantages, it was decided to use this processing technqiue to prepare 8 inch x 10 inch samples. A small block mold was constructed. The mold consists of a steel base plate with grooves cut in it, to provide a mechanical tie for the polymer, removable sides and a top insert. Figure 4(a) shows the base plate and sides of the mold disassembled. Figure 4(b) shows a close-up of the grooved base plate.

A block is made by placing about 4 pounds of ETANOX032 on a mill and compounding in the desired amount of crosslinker. The material is then removed from the mill and laid onto the base plate of the block mold as shown in Figure 5(a).

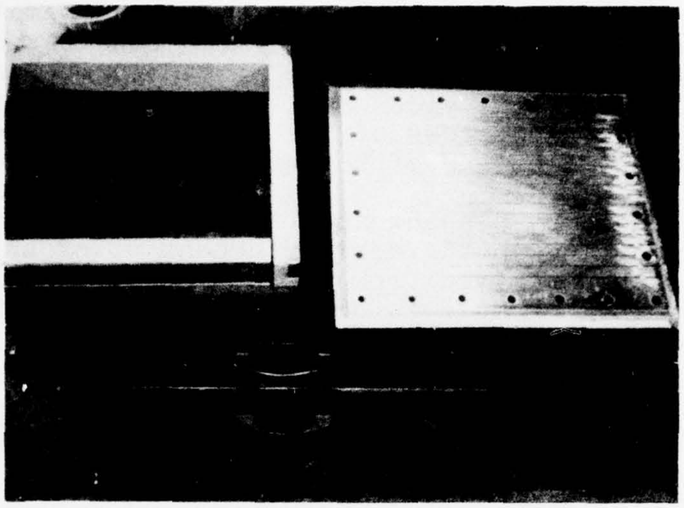
A fine weave nylon bleeder cloth was then laid over the top and sides of the slabs, in order to allow air to escape during the fusion of the block; then the sides of the mold were fastened on as shown in Figure 5(b). A top plate was then placed on the mold and the mold subjected to 50 psi at 320°F for 4 hours. The mold was then cooled and the top and sides removed. The result was a well-fused block as shown in Figures 6(a) and 6(b).

The white appearance of the blocks in Figure 5 is due to the nylon bleeder cloth which becomes embedded in the polymer during the molding operation. This presents no problems as it is easily skived off with the first sheet or two of material.

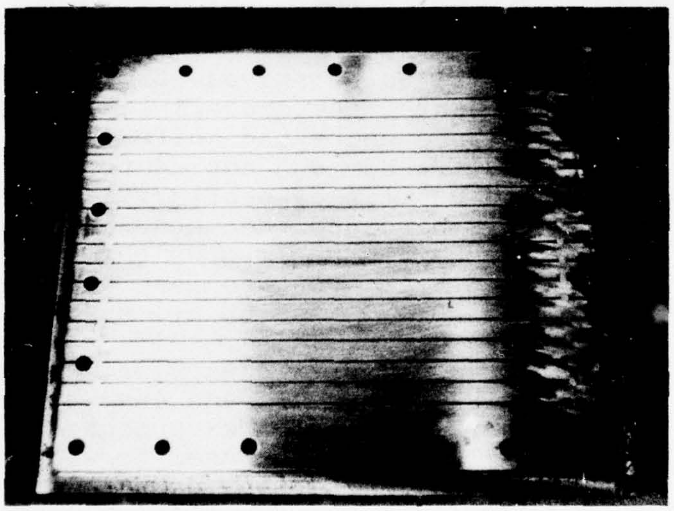
In order for a material to be skived it must have a certain rigidity. At room temperature, the crosslinked ETANOX032 was too rubbery and it would bend under the knife rather than cut. The block was placed in a freezer and cooled to -20°F, however, it was still too tough to cut. A cake of dry ice was then placed on the block. This hardened the material sufficiently so that it could be skived. Figure 7 shows the block mounted on the skiving machine as it is about to pass under the knife. The block was skived into 10, 30, and 50 mil sheets.

Laminates of glass/glass, acrylic/acrylic, and acrylic/polycarbonate were made from skived sheets and checked for clarity. It was noted that boundary lines or marks appeared in the skived sheets where the mill roll slabs were fused together during the block making process. It seems that the ethylene terpolymers cannot be fused optically without using melt shearing.

A second problem was encountered in the skived blocks, which was non-uniformity of curing throughout the block. For example, a block was prepared using 0.8 phr silane as the crosslinking agent.

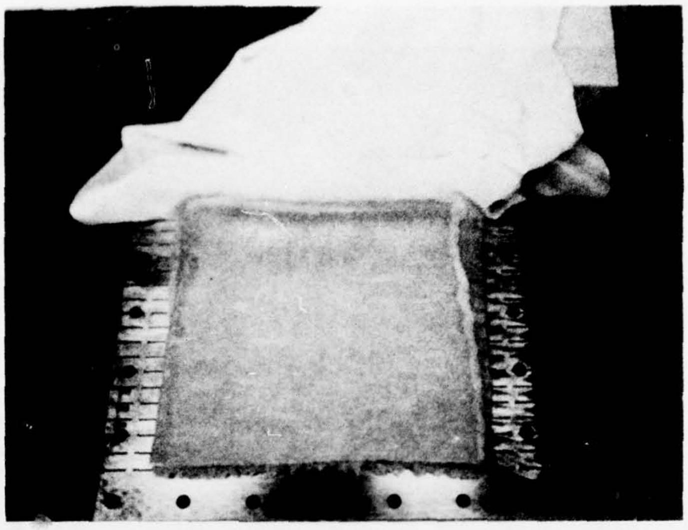


(a) Base Plate and removable sides

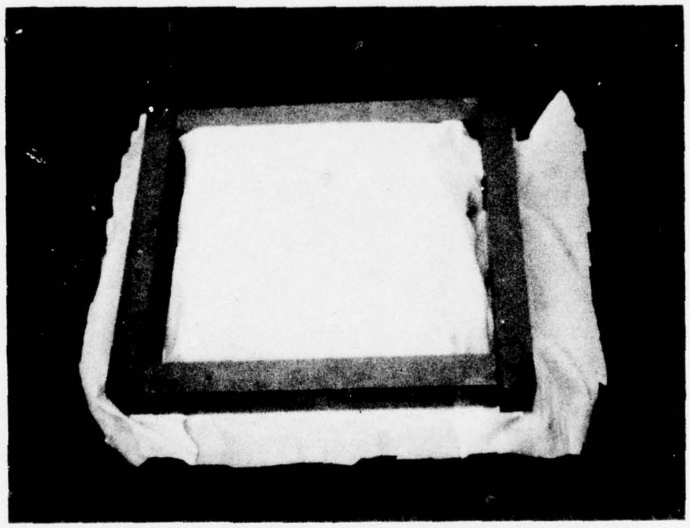


(b) closeup of the base plate showing channels to improve bonding area

Figure 4. Block Mold (8 in. x 10 in.) For Use in Skiving Sheet Process

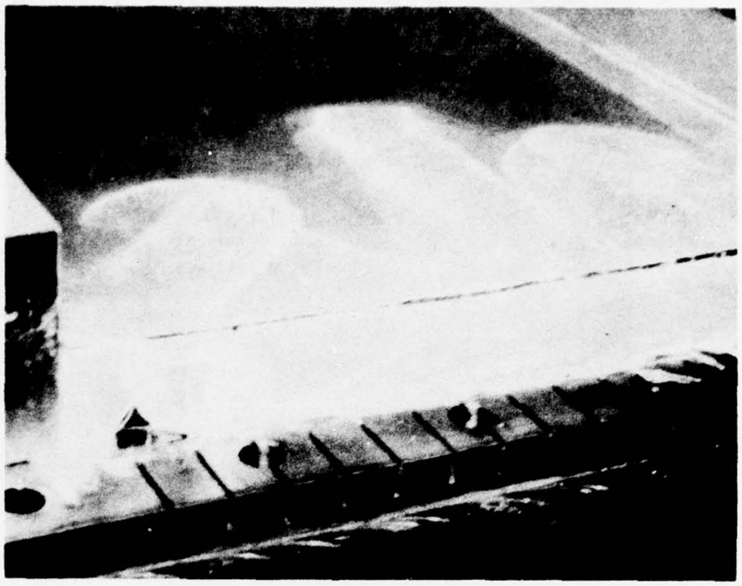


(a) Milled compounded interlayer slabs layed up on the block mold base plate

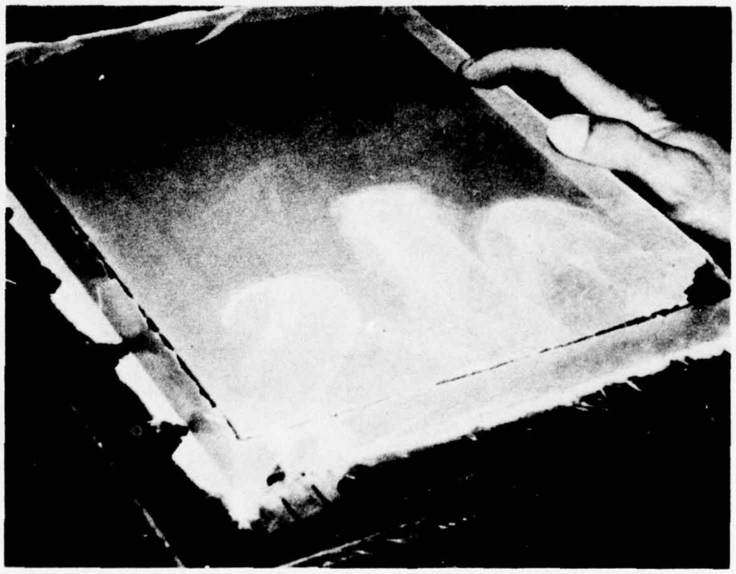


(b) Block mold with nylon bleeder cloth over the milled slabs. Sides bolted into position ready for compression molding and curing.

Figure 5. Initial Steps in the Preparation of a Limited Cure Molded Skive Block



(a) With one side of mold removed



(b) Block of ETANOX032 cured in place with ipbc crosslinker

Figure 6. Block of Interlayer Material (8 in. x 10 in.) Compression Molded to Base Plate for Attachment to Skiving Apparatus.

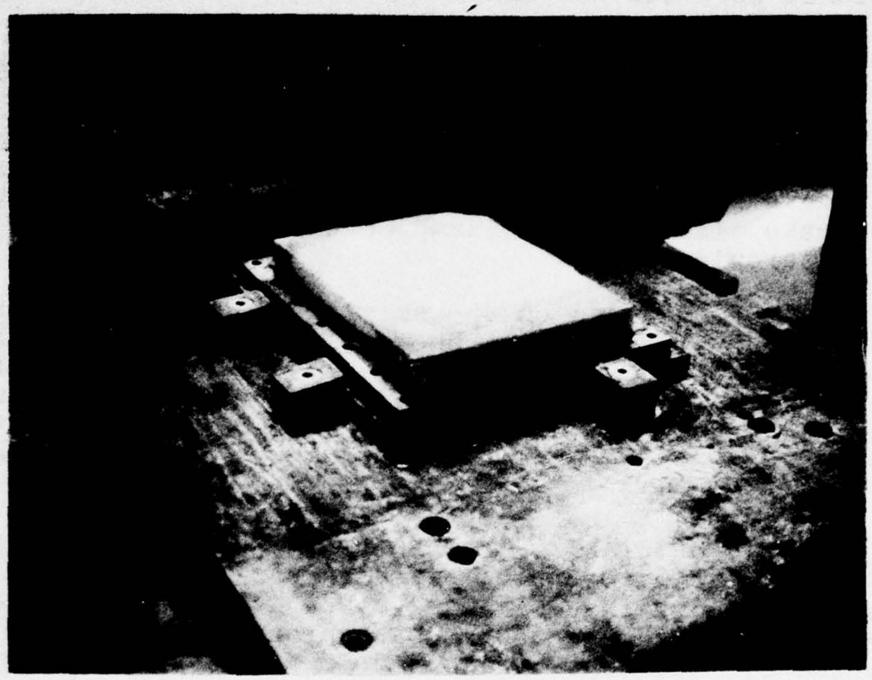


Figure 7. 8 in. x 10 in. x 1 in. Compression Molded Block of Interlayer Attached to Skiving Apparatus for Sheeting. Block attached to oscillating table that passes under indexing knife (rear).

The block mold was cured in the press for 16 hours at 320°F and 50 psi. Once the block was removed, a corner through the thickness was cut off. ZTS temperatures were determined on material at three depths on this corner. The results were: top 309°F, middle 347°F, and bottom 255°F. The block was then skived. The resulting sheets were tested for ZTS temperature and found to be: top 160°F, middle 186°F, and bottom 282°F. These results indicated that the curing was not uniform throughout the block so the process would require further extensive development. Since process development was not a major task additional work was not done.

## 3. Extrusion of ETANOX032 Containing Silane Crosslinker

The data on partial crosslinking of ETANOX032 with vinyltriethoxy silane (A.1.a.) indicated the reaction goes rapidly in thin sheets which are press cured. The data also indicated no curing rate difference for samples which contained an initiator such as peroxide.

The data obtained on the skiving block indicated something quite different. The block showed little or no crosslinking had occurred in the center of the block (after 16 hr at 320°F and 50 psi). The cure result demonstrated that there was a reasonable chance for extruding the material, i.e. that sufficient time was available to extrude to form before curing prevented flow.

A sample of ETANOX032 containing 1 phr of silane was compounded for extrusion. The extruder was fitted with a sheet die and run under the following conditions--barrel temperature 250°F, die temperature 260°F, back pressure 1000 psi at 40 rpm. The sheet die was set for about 40 mils. Good quality sheet was easily extruded. A sample of the sheet was checked for ZTS temperature and it was 167°F. This indicated very little crosslinking had occurred during extrusion since the starting material had a ZTS temperature of 140°F.

A piece of the extruded sheet was placed in a vacuum oven at 330°F for 3 days after which time the ZTS temperature was measured to be 187°F - a rather insignificant change. It was decided that perhaps the peroxide catalyst is necessary when samples are to be extruded.

A second extrusion run was made using ETANOX032 compounded with 1 phr vinyltriethoxysilane, 0.1 phr dicumyl peroxide, 0.1 phr dibutyltin dilaurate. The addition of the catalyst made a dramatic change in the way the material handled in the extruder. With the extrusion conditions the same as before the back pressure increased to 2000-2500 psi. The extruded sheet was very non-uniform in thickness and width. Increasing the final temperature caused the problem to worsen. This indicated that an increase in temperature caused more rapid crosslinking of the material rather than increasing melt flow. A sample of the extruded sheet showed a ZTS temperature of 310°F. A decrease in the amount of catalyst or the use of a peroxide with a longer half life (di-*t*-butyl peroxide) at 260°F might solve the problem and give an extrudable formulation.

Similar experiments were run using ipbc in place of the silane. In general, the ipbc crosslinking reaction was so rapid that the material could not be extruded.

## C. Laminating Process

The ETAXXX032 is a thermoplastic sheet that can be assembled with plates of any known glazing material to bond them together using moderate temperature and low pressure. It has been specifically tailored to be usable with polycarbonate, where laminating temperatures of less than 250°F are desirable.

The fabrication cycle used in our laboratory for the preparation of laminates is shown in Figure 8. Whereas this cycle is known to work, it is expected that much shorter times can be used if heat transfer were better than that provided in the air-type autoclave used.

The laminating technique is a multi-phase process which can be described through the use of photographs. Figures 9 thru 11 illustrate an acceptable procedure for laminating a 5 inch x 5 inch glass-polycarbonate laminate. The laminating cycle consists simply of heating the entire vacuum bagged composite to 250°F, applying a pressure of 30 psi ($\Delta P = 45$ psi because of a vacuum applied to degas) and cooling the part down. This low pressure cycle is especially attractive for minimizing residual strains. It is also almost identical to that previously described for the ETA 138200 material (Ref. 1) except that the pressure has been increased by 15 psi.

Materials such as glass, that can take temperatures greater than 250°F, are best laminated at 300°F. Laminating temperatures greater than 300°F are acceptable but usually of little increased value since care in preventing degradation of the interlayer or other plys becomes a problem.

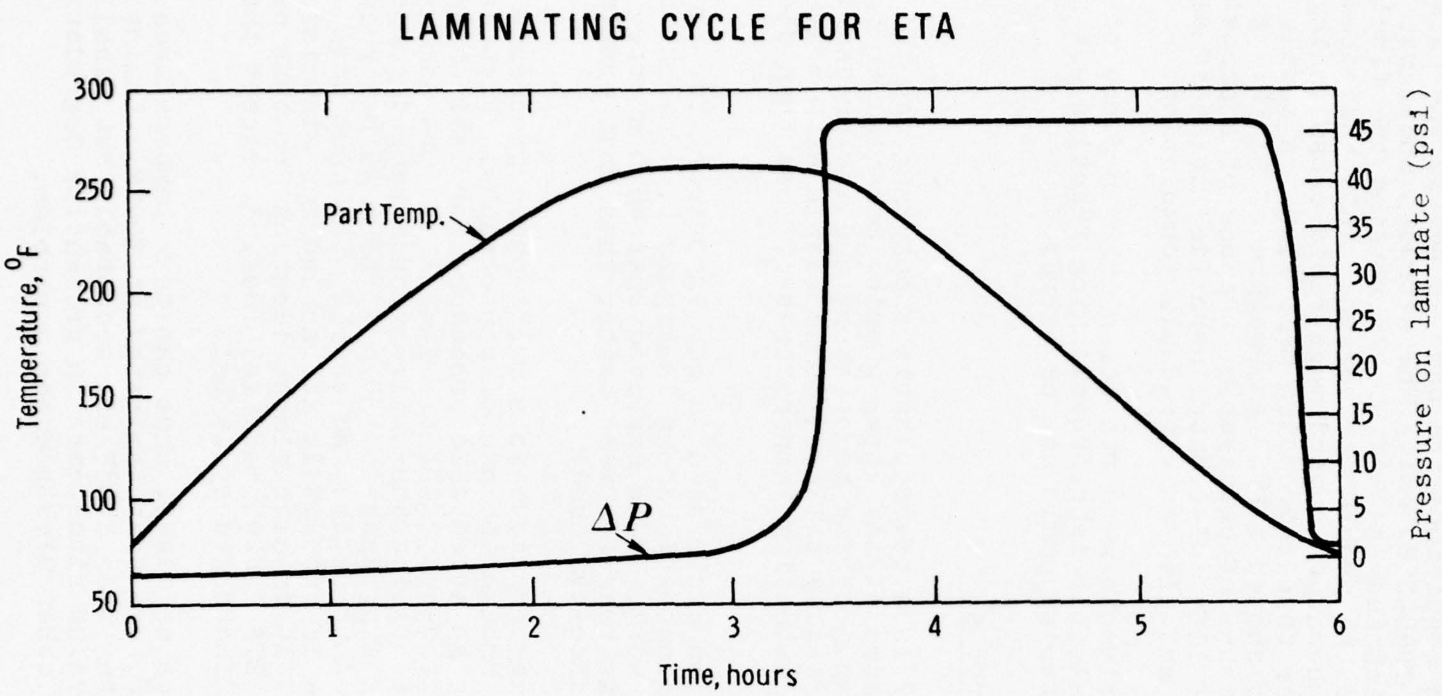
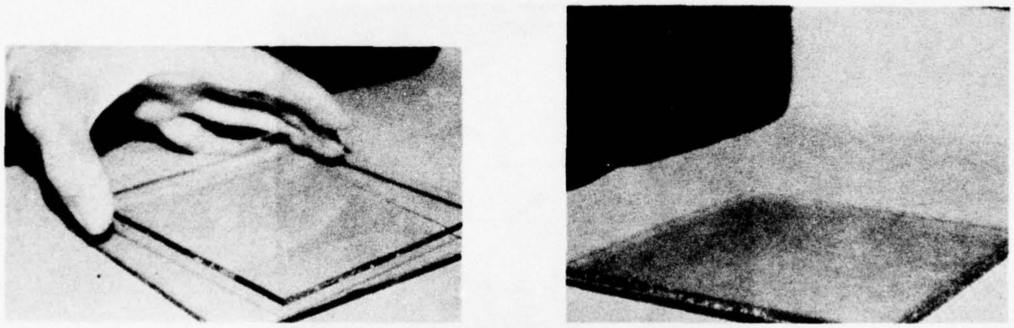


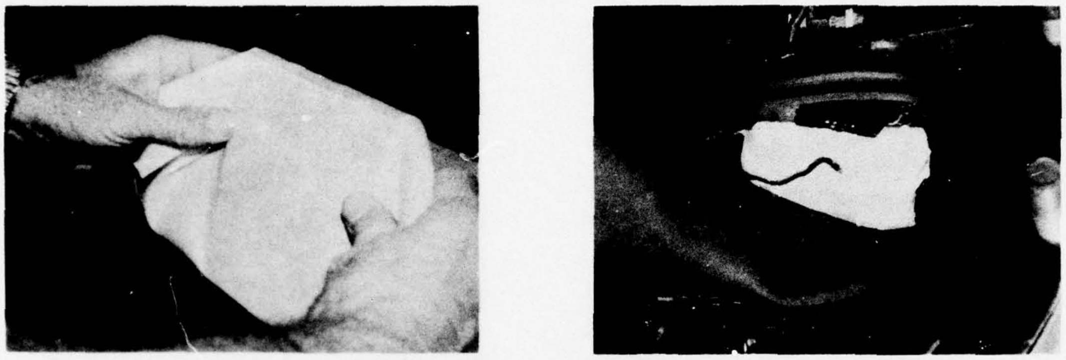
Figure 8. Typical Laminating Cycle for the Ethylene Terpolymer, ETAXXX032

(a) Detergent Wash (b) Interlayer and glass cut to size



(c) Interlayer placed between glass ply (d) Layed-up plies

Figure 9. Cleaning and Laying Up of Laminates Containing ETAXXX032 Sheet Interlayer

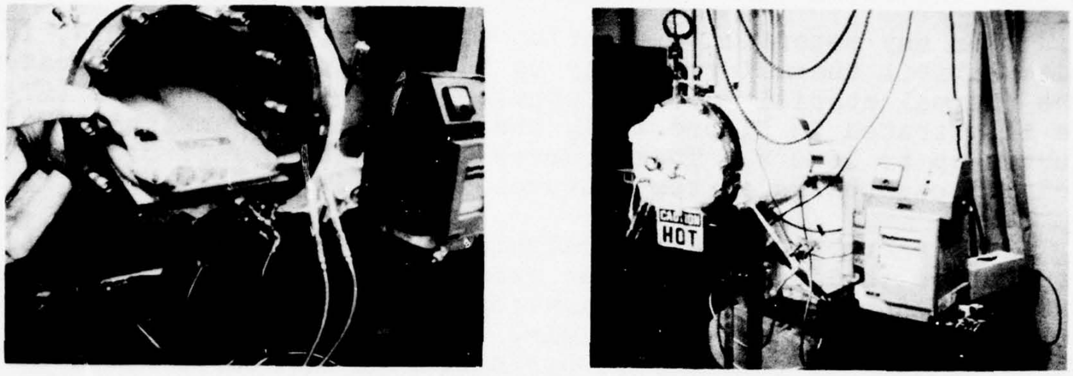


(a) Wrapping with porous nylon bleeder cloth

(b) Covering lay up with silicone bag

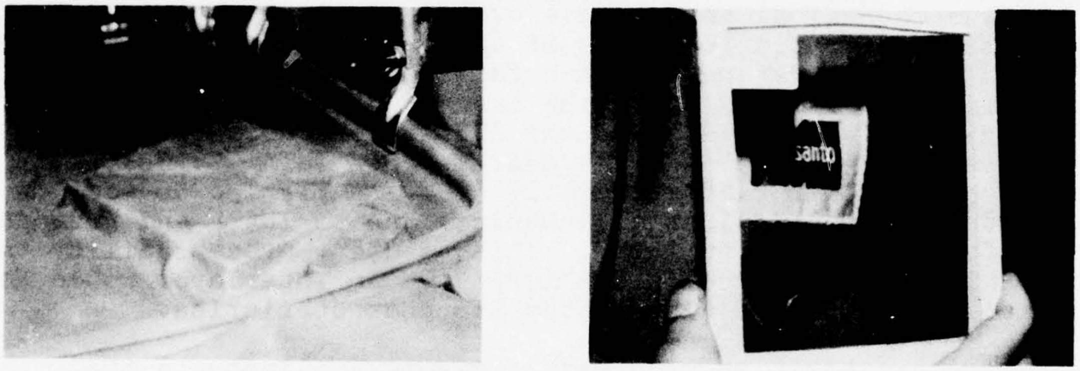
(c) Sealing the silicone sheet with rigid base

Figure 10. Wrapping and Autoclave Bagging of the Lay Up Containing ETAXXX032 Sheet Interlayer



(a) Vacuum bag in autoclave

(b) General view of autoclave during operation



(c) Bagged laminate just prior to removal with vacuum still applied

(d) Fabricated laminate

Figure 11. Autoclaving and Finished Part Containing the ETAXXX032 Sheet Interlayer

The laminating cycle shown in Figure 8 illustrates the application of a vacuum to a bagged laminate during processing. It is desirable to minimize the possibility of any entrapped vapors. If routine aircraft windshield pre-drying procedures are used, however, vacuum is probably not necessary.

## D. Thermal Characteristics of the Interlayers

For any material to function mechanically up to 350°F, it must exhibit thermal stability up to and beyond that temperature. The thermal stability of the ethylene terpolymer adhesive (ETA) is illustrated in Figure 12 by thermogravimetric analysis (TGA) curves up to 1000°F. These curves show that no appreciable weight loss occurs at temperatures below 550°F.

The thermogravimetric analysis was conducted in an inert atmosphere (helium) to prevent oxidation at the higher temperatures. Interlayers usually are contained between plies of other materials that exclude air. These data are thus valid for this type of configuration. A similar TGA curve would be expected if air were present, but generation of color (due to oxidation) would be expected at temperatures in the region of 300°F.

The mechanical performance over a similar temperature range is well illustrated in graphs of creep as a function of temperature. The temperature at which failure occurs under a 3 psi test load is referred to as the zero tensile strength (ZTS) temperature. Figure 2 shows the ZTS temperatures of the unmodified ETA (119°F) and of a modified ETA (ETA 138200) developed earlier (178°F; Ref. 1, 4). The ETA 138200 was reported to be useful as an interlayer up to 165°F and processable for laminating at 250°F. This adequate processability and mechanical performance of ETA 138200 as an interlayer would be anticipated from the illustrated ZTS characteristics.

The two additional curves in Figure 2 illustrate the performance of the newly developed material referred to as ETAXXX032 (two variations) to 350°F. These curves show that these materials would have some, albeit minimal, useful mechanical properties at 350°F. However, it is not entirely obvious that this material is processable at 250°F. These data illustrate a point that must be considered to resolve what may seem to be a contradiction in properties versus processability. ETAXXX032 has a limited degree of thermoplasticity at 250°F, which provides sufficient flow for laminating of plies of glass or plastic. It is not a thermoplastic in the usual sense since it can not flow into a cavity to make a part, nor does it contain thermally reversible chemical bonds such as those available in some urethanes.

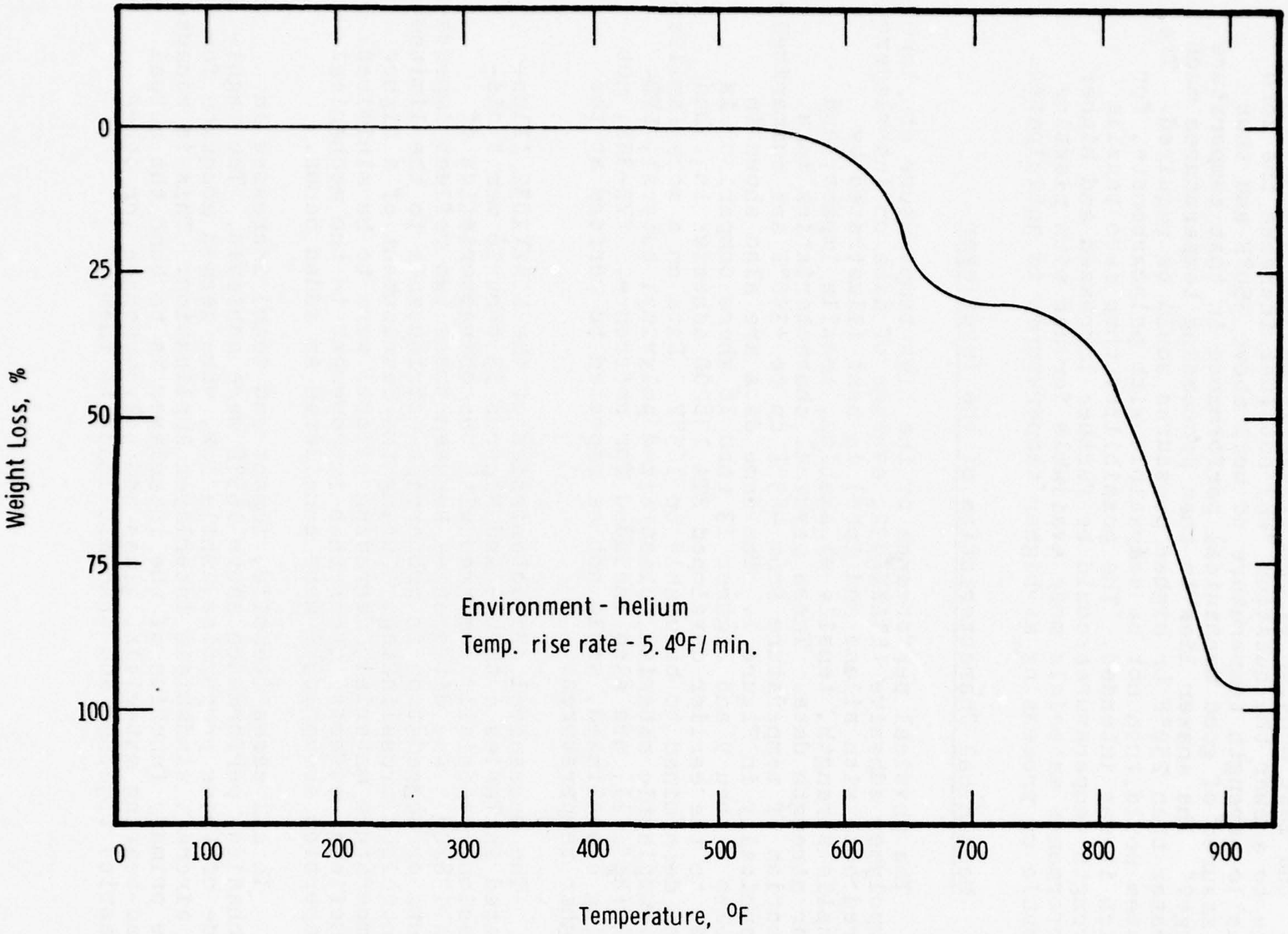


Figure 12. Thermogravimetric Analysis of All Ethylene Terpolymers in Inert Atmosphere

One last mention of the creep elongation data must be made to answer the question "Why not just increase the zero tensile strength temperature to well above 350°F and thus be assured of good mechanical performance in that temperature range?" The answer lies in that processing temperatures much greater than 250°F or higher pressures would be required. The system would then not be compatible with polycarbonate, for which it was intended. The possibility that zero tensile strength temperatures could be further increased and higher performance materials made available for use with plastics capable of processing at higher temperatures is anticipated.

## E. Mechanical Characteristics of the Interlayer

The physical performance of the high temperature ethylene terpolymer adhesive (ETAXXX032, average of data on interlayers cured both with silane and ipbc) is best illustrated by tensile strength, tensile elongation, tensile impact, and tear strength data. These physical characteristics as a function of temperature from -65°F up to +350°F are summarized graphically in Figure 1. The same data are also shown in Tables 6 thru 9 and Figures 13 thru 16 where comparison is made to the earlier developed ETA 138200 adhesive that had been determined to be usable to 165°F. Data on a more familiar thermoplastic material, plasticized polyvinyl butyral, PVB-3GH (Ref. 1), are also included for reference. PVB-3GH, not being crosslinked, would not be expected to perform at the higher temperatures.

The mechanical characteristics of the ETAXXX032 illustrated in Tables 6 thru 9 and Figures 13 thru 16 merit discussion, especially compared with the characteristics of ETA 138200. Any differences between these two reflect improvements or degradation in properties attributable to the limited controlled crosslinking. During the development of a higher temperature material, degrading effects were to be minimized. Beneficial effects, other than improvement in the mechanical properties above 165°F were considered an added bonus.

In all cases (tensile, impact and tear) increases in mechanical performance above 165°F were achieved. The magnitude of these properties, while low, were deemed adequate for an aircraft windshield interlayer application. This is because the primary function of the interlayer is to bond the actual load-bearing materials, glass and polycarbonate (or other plastic) together and transmit loads to them.

## Table 6

## TENSILE STRENGTH[1] OF ETHYLENE TERPOLYMERS AS A FUNCTION OF TEMPERATURE

| | Strength, psi | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature, °F | -65 | -40 | +32 | +74 | +165 | +200 | +350 |
| ETA138200 | 8,200 | 8,800 | 6,000 | 3,600 | 20 | 0 | 0 |
| ETAXXX032[2] | 10,500 | 10,000 | 7,000 | 4,300 | -[3] | 24 | 2 |
| PVB-3GH | 8,900 | 7,400 | 5,600 | 4,300 | 195 | - | - |

[1] ASTM D412, Specimen C, 2 in./min crosshead, ~0.03 in. thick.
[2] Micro tensile specimens used due to high elongation.
[3] Indicates data not obtained or available in literature.

## Table 7

## TENSILE ELONGATION[1] OF ETHYLENE TERPOLYMERS AS A FUNCTION OF TEMPERATURE

| | Elongation, % | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature, °F | -65 | -40 | +32 | +74 | +165 | +200 | +350 |
| ETA138200 | 460 | 570 | 1,400 | 1,200 | 600 | 0 | 0 |
| ETAXXX032[2] | 220 | 360 | 900 | 1,400 | -[3] | >2,000 | >2,000 |
| PVB-3GH | 10 | 210 | 420 | 320 | 1,100 | - | - |

[1] ASTM D412, Specimen C, 2 in./min crosshead, ~0.03 in. thick.
[2] Micro tensile specimens used due to high elongation.
[3] Indicates data not obtained or available in literature.

## Table 8

## TENSILE IMPACT STRENGTH[1] OF ETHYLENE TERPOLYMERS AS A FUNCTION OF TEMPERATURE

| | Impact Strength, ft lb/in.$^2$ | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature, °F | -65 | -40 | +32 | +74 | +165 | +200 | +350 |
| ETA138200 | 360 | 890 | 1,100 | 1,100 | 135 | 0 | 0 |
| ETAXXX032 | 600 | 670 | 1,100 | 580 | -[2] | 300 | 120 |
| PVB-3GH | 100 | 220 | 1,510 | 1,290 | 410 | - | - |

[1] ASTM D1822, Specimen Type

[2] Indicates data not obtained or available in literature.

## Table 9

## TEAR STRENGTH[1] OF ETHYLENE TERPOLYMERS AS A FUNCTION OF TEMPERATURE

| | Tear Strength, lb/in. | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature, °F | -65 | -40 | +32 | +74 | +165 | +200 | +350 |
| ETA138200 | 1,100 | 1,000 | 410 | 180 | 5 | 0 | 0 |
| ETAXXX032 | 1,300 | 1,150 | 780 | 350 | -[2] | 10 | 3 |
| PVB-3GH | 1,800 | 1,300 | 790 | 340 | 23 | - | - |

[1] ASTM D1004, Specimen ~0.03 in. thick.

[2] Indicates data not obtained or avilable in literature.

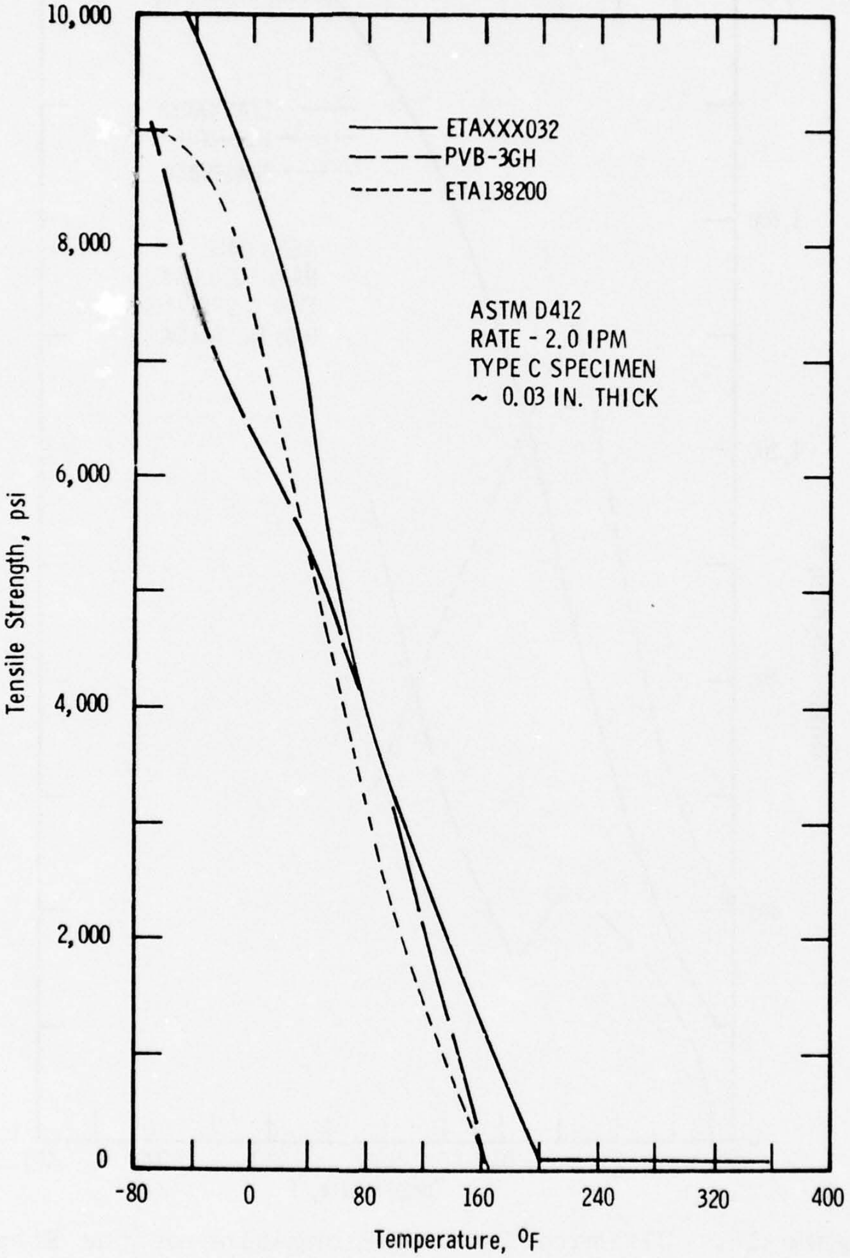


Figure 13. Tensile Strength of the Ethylene Terpolymers and PVB-3GH from -65 to +350°F

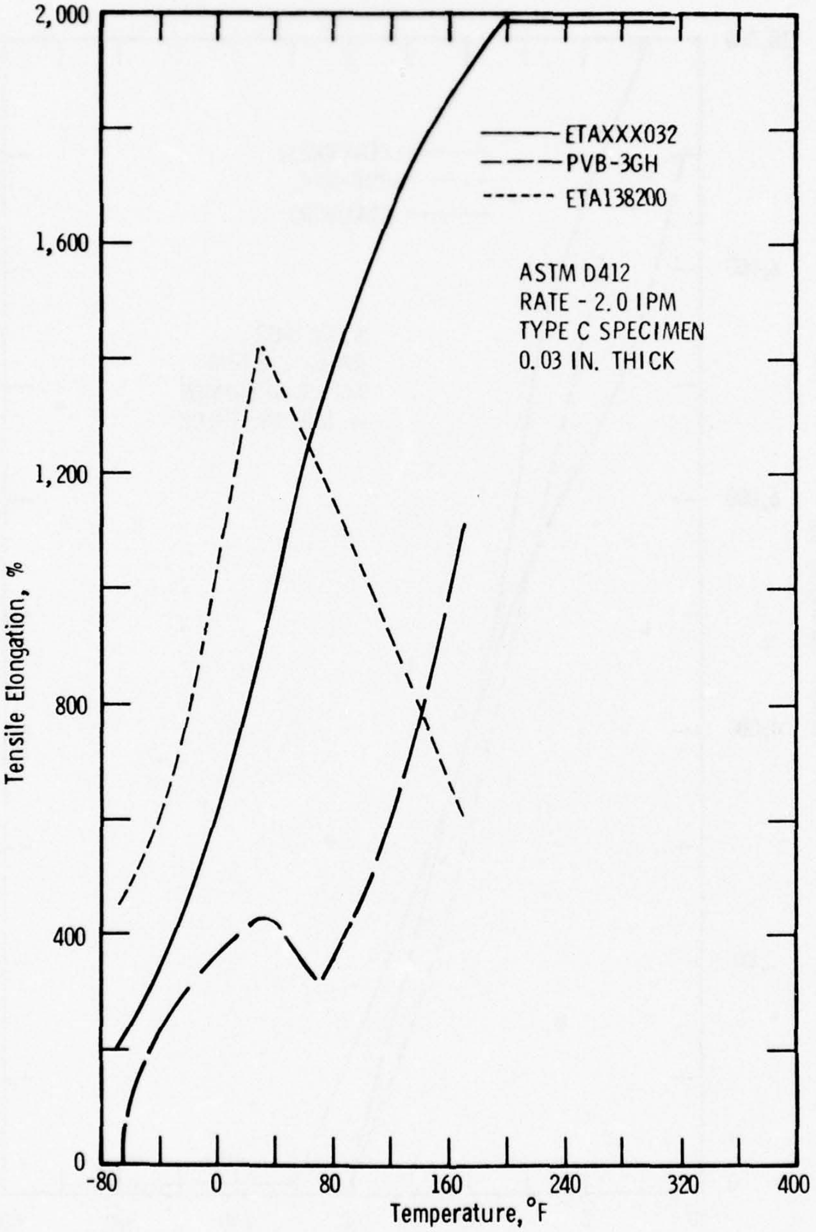


Figure 14. Ultimate Tensile Elongation of the Ethylene Terpolymers and PVB-3GH from -65 to +350°F

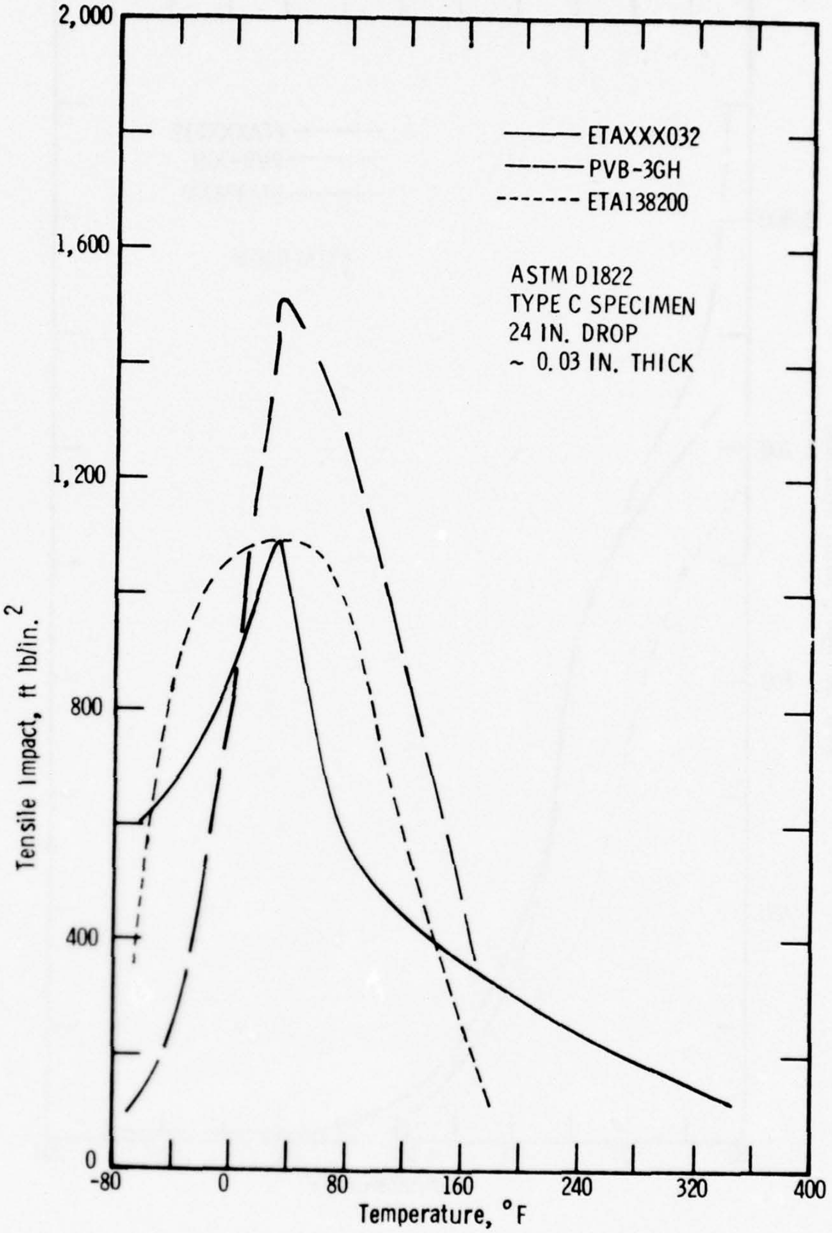


Figure 15. Tensile Impact Strength of the Ethylene Terpolymers and PVB-3GH from -65 to +350°F

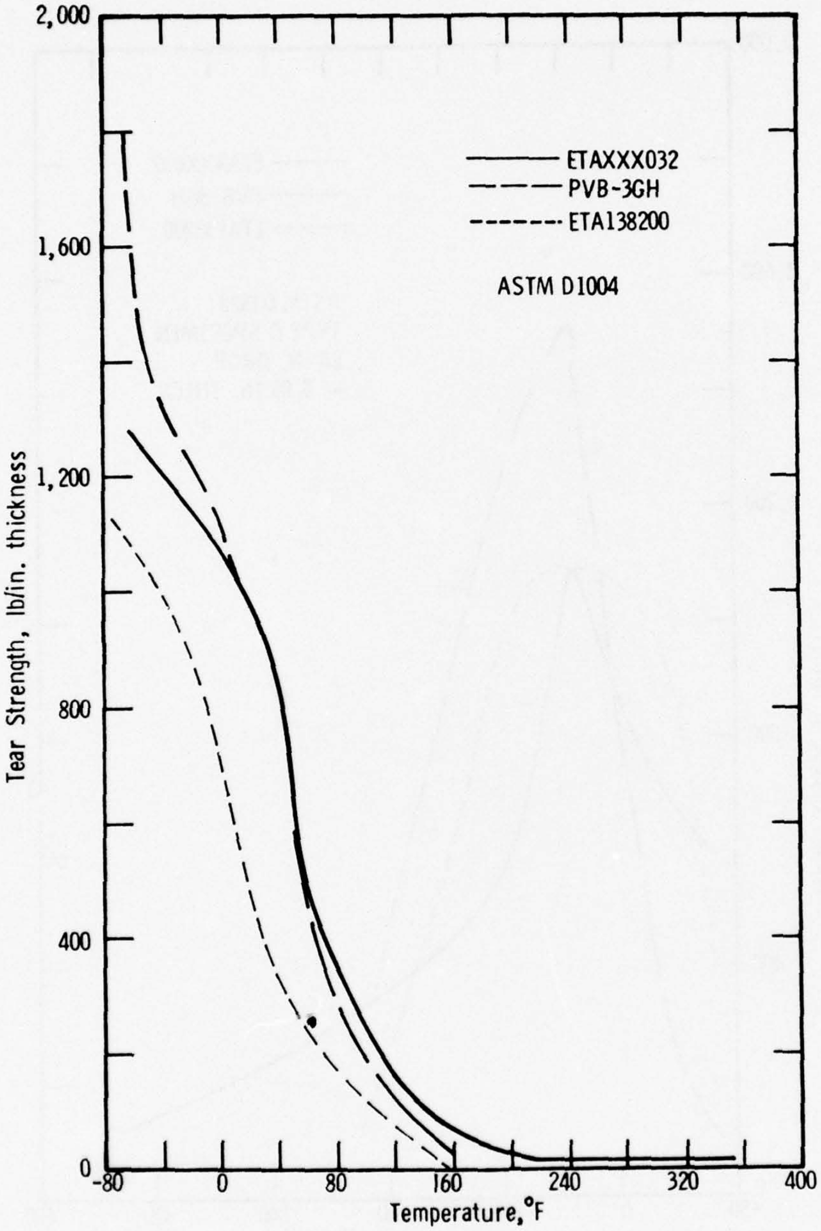


Figure 16. Tear Strength of the Ethylene Terpolymers and PVB-3GH from -65 to +350°F

The biggest difference in properties between the two materials occurred between room temperature and -65°F. Increases in tensile and tear strength, illustrated in Figures 13 and 16 were achieved. Over the same temperature range, decreases in tensile elongation and tensile impact were exhibited. While some decreases in tensile elongation were anticipated due to the modification, the low temperature elongations were still quite substantial, being as high as 220% at -65%. In both materials, the elongation at yield was about 10% of the ultimate elongation.

The shear strength of the ethylene terpolymer adhesive at 350°F was demonstrated by heating 5 inch x 5 inch laminates to 350°F with one of the plies clamped in a vertical position. A shear force consisting of the weight of the other 1/4-inch thick glass ply (0.02 psi) was exerted on the adhesive. Upon heating, a slight deflection (1/16 inch) of the suspended ply of glass was noted and could be related to the expected change in modulus. Also, no creep was found following 48 hour exposure to this temperature.

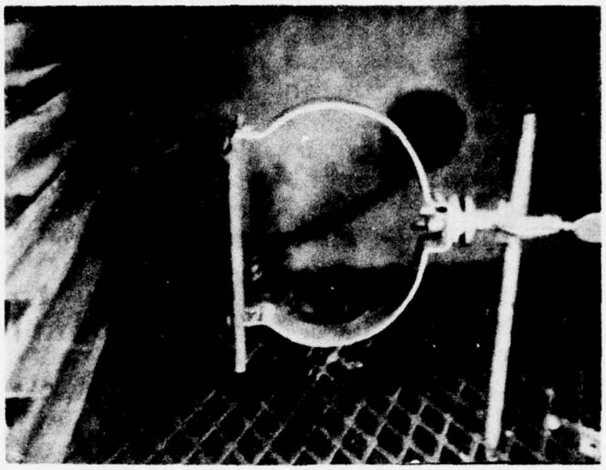
Similar experiments were conducted with a glass/polycarbonate laminate to temperatures of 300°F, as shown in Figure 17. In this case, the clamp caused compression and bending of the polycarbonate ply, but still no sliding or separation of the glass ply resulted.

Tensile lap shear strength properties of partially crosslinked ETAXXX032 were determined at room temperature using ASTM D-1002 test procedure. Aluminum tabs were used which were sandblasted and, washed in hydrochloric acid, rinsed and dried. The data showed the tabs, bonded with the partially crosslinked interlayer under typical laminating conditions, to have a cohesive shear strength of 300 to 400 psi while the uncrosslinked material was 150 psi.

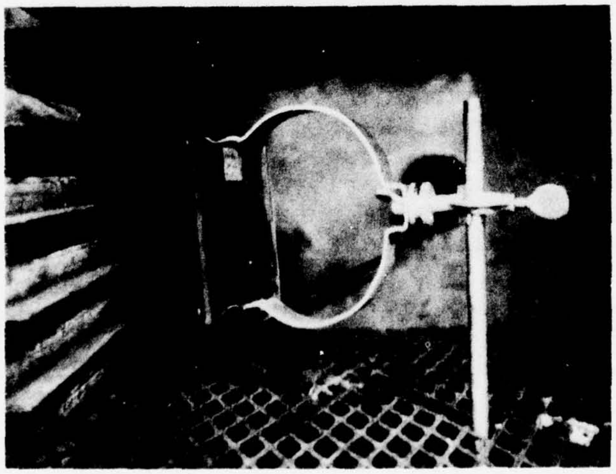
## F. Physical Characteristics and Durability of the Interlayer and Composite Laminates Containing It

### 1. Environmental Exposure Tests

A number of laminates (31) of glass/glass, glass/polycarbonate and acrylic/polycarbonate were prepared using various types of the ETAXXX032 interlayer. Included were ETAXXX032 cured with ipbc (0.3 phr) or silane (1.0 phr) and controls which were not crosslinked. The laminates underwent three types of exposure, as pictured in Figures 18 and 19. The first was

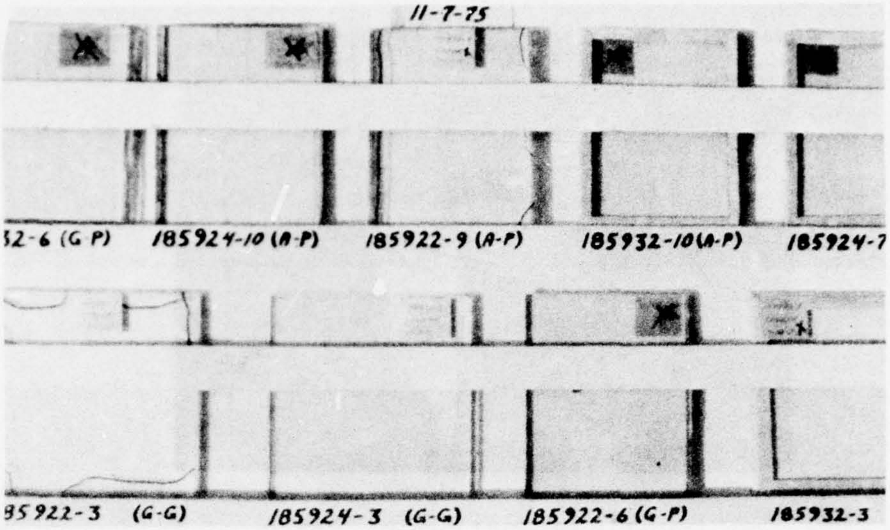


(a) Laminates held by a clamp attached to the polycarbonate ply only. Shear introduced through weight of glass ply. No creep at temperature of 250°F.

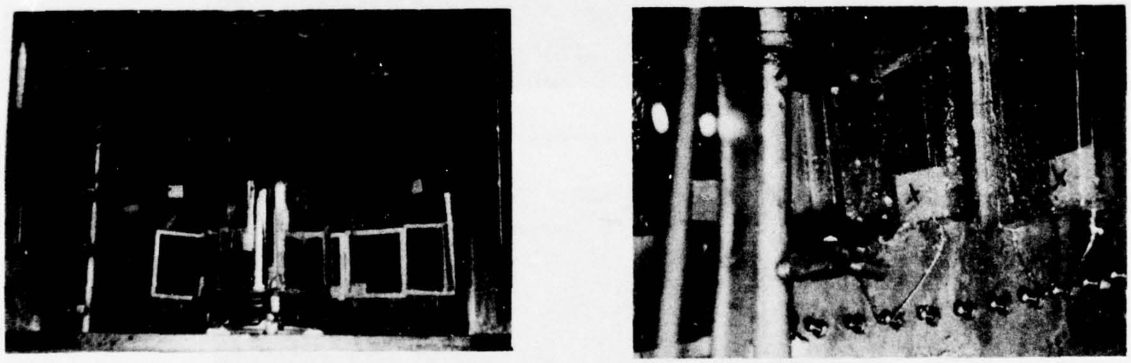


(b) Clamp sinking into polycarbonate at 300°F. Maximum deflection of interlayer 1/16 inch. No creep.

Figure 17. Illustration of High Temperature Shear Strength Test on Laminates Bonded with Ethylene Terpolymer ETAXXX032



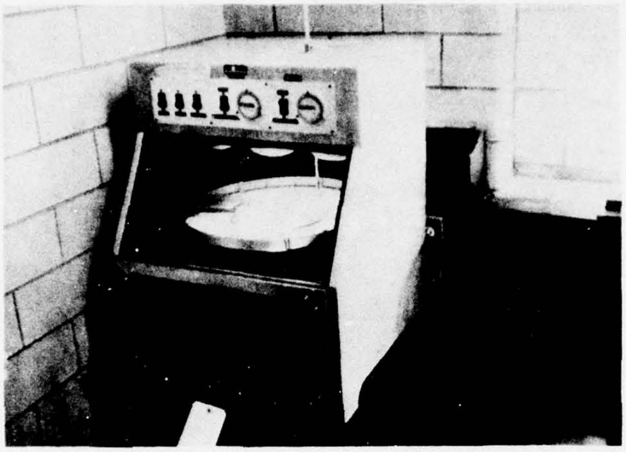
(a) Laminates positioned in the outdoor weathering rack at Dayton, Ohio, facing south, inclined 45°.



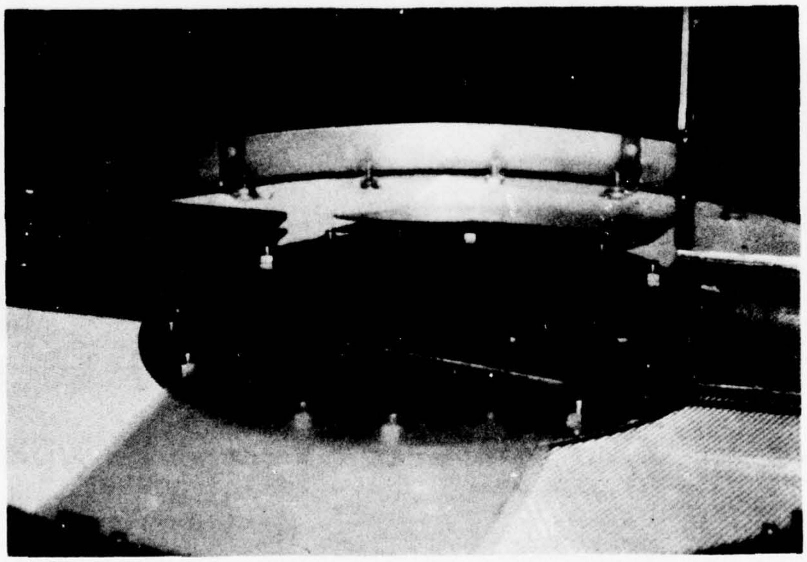
(b) Laminates fixed in the Atlas weatherometer to be exposed to carbon arc ultraviolet light and water spray.

(c) Water spray cycle in the weatherometer.

Figure 18. Environmental Testing of Laminates with Various Glass and Plastic Plies Bonded with ETAXXX032 Sheet Interlayer



(a) Sunliner Instrument which uses three G.E. RS-4 sunlight bulbs for accelerated rate of 100X (1 week exposure - 3 years).



(b) Samples of ETAXXX032 in position on the turn table of the Sunliner Instrument.

Figure 19. High Intensity Ultraviolet Exposure of ETAXXX032 Sheets and Laminates

outdoor weathering during the months of November, December, and January in Dayton, Ohio. Second was accelerated weathering in an Atlas Weatherometer. Third was high intensity (100X) ultraviolet exposure in a Sunliner, shown in Figure 19, containing three G.E. RS-4 sunlight bulbs.

Table 10 gives the details of the specimens, exposure conditions, and results at the conclusion of the test. In general, all of the laminates containing a partially crosslinked interlayer did well. The acrylic/polycarbonate laminates were the most sensitive. A large number of bubbles (see Table 10) formed in these laminates exposed in the weatherometer that was at a relatively higher temperature (140°F) during the exposure period. Penetration of moisture through the acrylic or polycarbonate is the suspected problem.

The crosslinked interlayer material exposed directly to high intensity UV, as expected, was severely degraded. The ZTS temperature of this unstabilized interlayer was lowered below 145°F. The specimens melted and flowed out of the supporting holders. Laminates of the same material survived the high UV conditions without any noticeable change. The glass or plastic plies screened out the detrimental UV radiation, as expected.

## 2. Thermal Cycling Tests

The physical integrity and functioning of the ETAXXX032 was further illustrated through the thermal cycling of glass/polycarbonate, glass/glass, and polycarbonate/acrylic laminates containing the ETAXXX032. 5 inch x 5 inch three ply laminates were prepared using 1/4-inch plies of glass, polycarbonate, or acrylic and 0.030 inch of interlayers. These laminates were repeatedly thermal cycled (100) between -65 and +165°F with occassional (4) excursions to 350°F (for glass/glass), or 300°F (for laminates containing polycarbonate).

Repeated thermal cycling of the ETA bonded laminates described above resulted in no visible failures of any sort to the ethylene terpolymer adhesive, or to its bond with any of the laminate plies. The only degradation occurred with the polycarbonate due to the softening and deforming during excursions to 300°F, which is above its 277°F glass transition temperature.

# Table 10

## DATA ON LAMINATES BONDED WITH ETAXXX032 SHEET INTERLAYER AND ITS PRECURSOR EXPOSED TO ACCELERATED AND OUTDOOR ENVIRONMENT

### Atlas Weatherometer[1]

Time - 630 hours of light, 796 hours total weathering
*Maximum Temperature = 140°F

| Sample No. | Interlayer | Surfaces[2] | Edges[3] | Condition (unchanged unless noted) | Time at Which Changes Noted |
|---|---|---|---|---|---|
| 185922-1 | 3.2% OH (starting material) | G-G | S | large bubbles at 2 edges, intrusion of caulking | at end of test |
| 185922-2 | 3.2% OH (starting material) | G-G | U | | |
| 185922-4 | 3.2% OH (starting material) | G-P | S | | |
| 185922-5 | 3.2% OH (starting material) | G-P | U | some material squeezed out at edges | after 254 hr |
| 185922-7 | 3.2% OH (starting material) | A-P | S | many bubbles, intrusion of of caulking | after 796 hr |
| 185922-8 | 3.2% OH (starting material) | A-P | U | (a) redistribution of bubbles<br>(b) interlayer squeezed out<br>(c) dozen bubbles, much squeeze out at edge | after 254 hr<br>after 254 hr<br>after 796 hr |
| 185924-1 | 3.2% OH + 1.0 phr Silane | G-G | S | | |
| 185924-2 | 3.2% OH + 1.0 phr Silane | G-G | U | | |
| 185924-5 | 3.2% OH + 1.0 phr Silane | G-P | S | | |
| 185924-6 | 3.2% OH + 1.0 phr Silane | G-P | U | | |
| 185924-8 | 3.2% OH + 1.0 phr Silane | A-P | S | 4 bubbles (1/8" diameter) | between 254 and 796 hours |
| 185924-9 | 3.2% OH + 1.0 phr Silane | A-P | U | some squeeze out at edges | |
| 185932-1 | 3.2% OH + 0.3 phr ipbc[4] | G-G | S | | |
| 185932-2 | 3.2% OH + 0.3 phr ipbc | G-G | U | | |
| 185932-4 | 3.2% OH + 0.3 phr ipbc | G-P | S | | |
| 185932-5 | 3.2% OH + 0.3 phr ipbc | G-P | U | | |
| 185932-8 | 3.2% OH + 0.3 phr ipbc | A-P | S | bubbles throughout top 2/3 | (a) at edges after 254 hours<br>(b) throughout after 796 hours |
| 185932-9 | 3.2% OH + 0.3 phr ipbc | A-P | U | bubbles throughout | (a) a few after 254 hours<br>(b) throughout after 796 hours |

### SUNLINER (High Intensity Ultraviolet)

Sunliner Time - 18.7 Days (8 year equivalent)
*Maximum Temperature* = 140°F

| Sample No. | Interlayer | Surfaces | Edges | Condition | Time at Which Changes Noted |
|---|---|---|---|---|---|
| 185924-4 | 3.2% OH + 1.0 phr Silane | G-G | U | | |
| 185924-4A | 3.2% OH + 1.0 phr Silane | none | - | completely degraded | |
| 185932-7 | 3.2% OH + 0.3 phr ipbc | G-P | U | redistribution of a few bubbles | (a) present at edges initially |
| 185932-7A | 3.2% OH + 0.3 phr ipbc | none | - | completely degraded | |

### ROOF - Dayton, Ohio

Time - 68 days (Nov. 1975 - Jan. 1976)
45° South Exposure

| Sample No. | Interlayer | Surfaces | Edges | Condition |
|---|---|---|---|---|
| 185922-3 | 3.2% OH (starting material) | G-G | U | no effect after 68 days |
| 185922-6 | 3.2% OH (starting material) | G-P | U | |
| 185922-9 | 3.2% OH (starting material) | A-P | U | |
| 185924-3 | 3.2% OH + 1.0 phr Silane | G-G | U | |
| 185924-7 | 3.2% OH + 1.0 phr Silane | G-P | S | |
| 185924-10 | 3.2% OH + 1.0 phr Silane | A-P | U | |
| 185932-3 | 3.2% OH + 0.3 phr ipbc | G-G | S | |
| 185932-6 | 3.2% OH + 0.3 phr ipbc | G-P | U | |
| 185332-10 | 3.2% OH + 0.3 phr ipbc | A-P | S | |

Note: July 1976. After 160 non-consecutive days no visible changes except in 185922-4, which has small bubbles around unsealed edges.

---

[1] *Cycle - 4 hr light (carbon arc)
5 hr 57.5 min water spray
2.5 min rest

[2] A - Acrylic
G - Glass
P - Polycarbonate

[3] S - Sealed with butyl caulk
U - Unsealed

[4] ipbc = isophthaloylbiscaprolactam

### 3. Thermal Shock and Soak Tests

A sample of ETANOX032 was compounded with 0.29 phr of ipbc. The sample (30 mil thick) was cured into a sheet for 2 hours in the press at 320°F. The ZTS temperature was 400°F. This sheet was vacuum dried overnight at 158°F and then laminated between glass. A few small bubbles were noted near the edges. The sample was then aged for 24 hours at 350°F, whereupon all bubbles disappeared.

The above laminate was held in a vertical position and attached to a support by only one pane of glass. The sample was then abruptly immersed into an oven at 400°F and held for 24 hours. The glass plate, which was free to move, did not. The laminate was then placed in the low temperature environmental chamber and cycled eight times per 24 hour period between -60°F to 160°F (160 to -60 in 1.5 hour, -60 to 160 in 0.5 hour, soak at 160 for 1 hour). The laminate survived all tests perfectly and the original bubbles never did reappear.

A second cured sample containing 0.32 phr ipbc was subjected first to a 24 hour 350°F exposure and then thermocycled from -60 to +160°F. The interlayer had a ZTS temperature of 360°F. A bubble-free laminate was obtained. This laminate was subjected to 24 hours at 350°F and then 30 days of thermocycling from -60 to +160. The laminate remained bubble-free with no movement of the glass.

## G. Analytical Results Achieved During the Development Effort

In this section, certain analytical data which were generated as a part of the development effort, but which have not specifically been included previously, are given and discussed. These include: (1) Rheometer curing of ETA; (2) differential scanning calorimetry (DSC) data on partially crosslinked ETA; (3) Clash-Berg data on the partially crosslinked ETA; and (4) tensile, elongation, and tear strength data on the same material. Each of these will be described separately in detail.

### 1. Instron Capillary Extrusion Rheometer Curing Studies

Several samples of the ETA terpolymer were blended with ipbc in order to establish a curing cycle for the material. Figures 20 and 21 show the results of cold blending ipbc at 0.5 phr into ETA and curing it in the extrusion rheometer. The load to extrude at a constant rate thru a 1.00 inch long x 0.06 inch diameter (L/D = 16.67/1, rate = 0.02 ipm) orifice

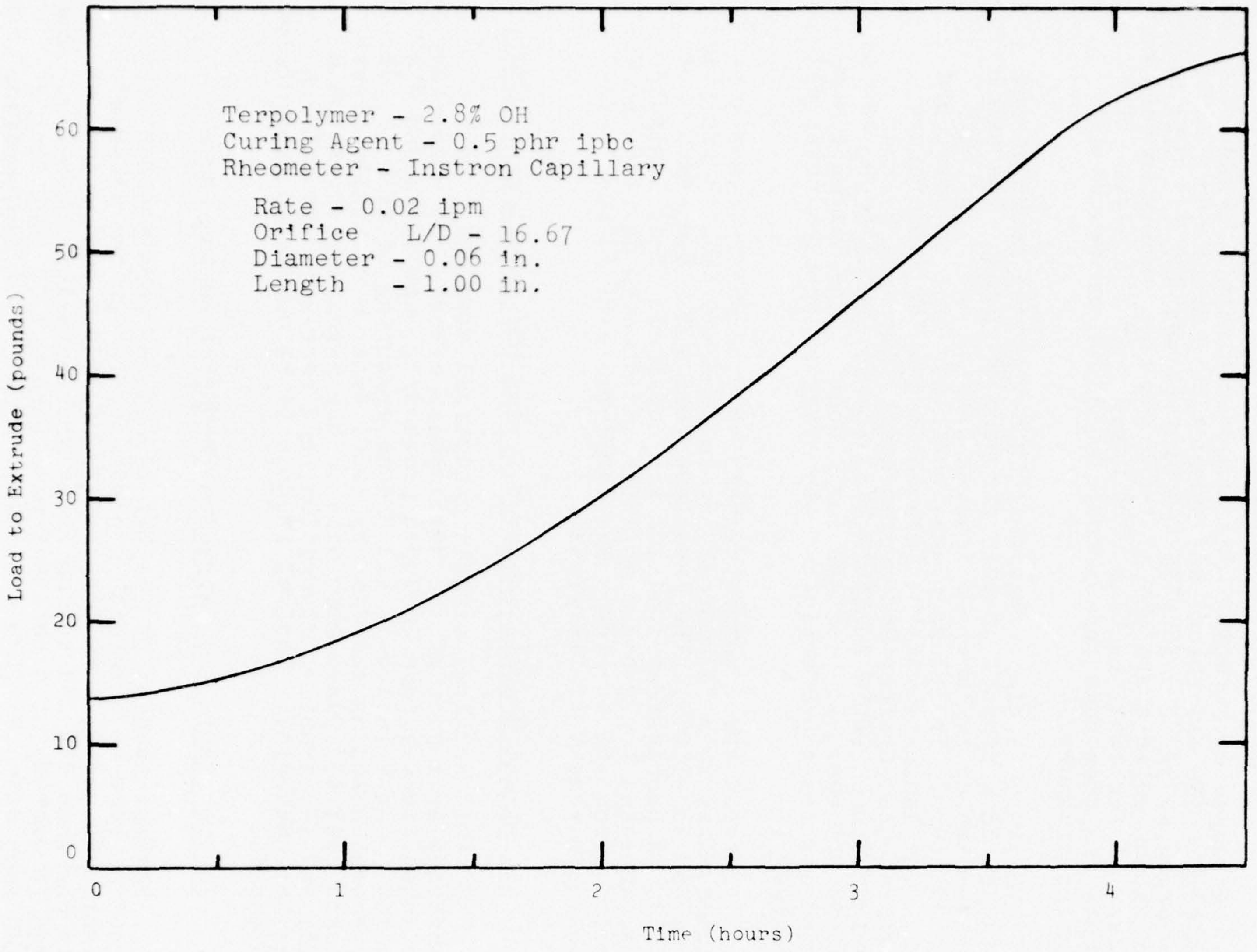


Figure 20. Capillary Extrusion Curve for ETANOX028 Curing at 125°C

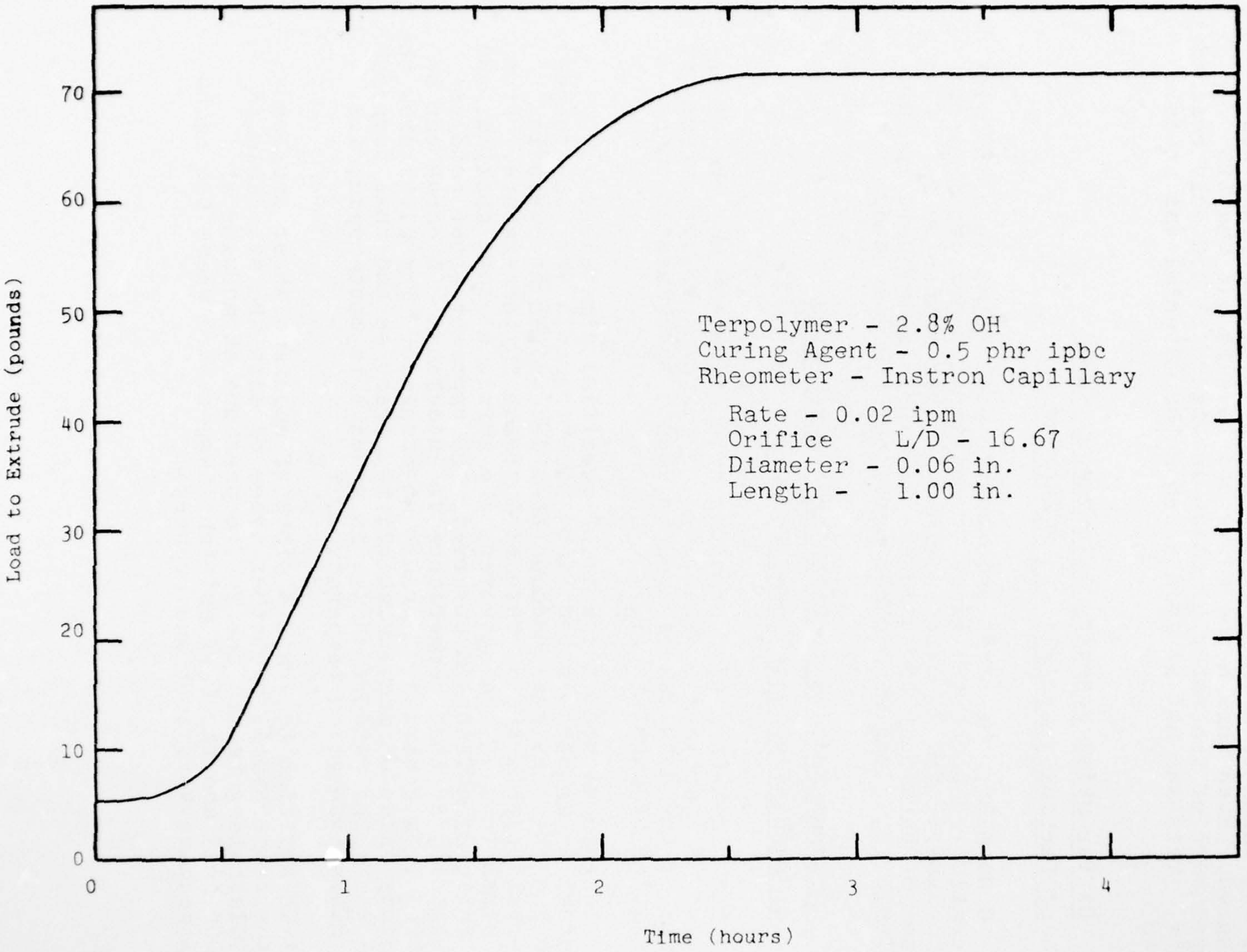


Figure 21. Capillary Extrusion Curve for ETANOX028 Curing at 150°C

was continuously monitored. After 5 hours, the remaining material was taken from the barrel and the ZTS temperature was measured. Even though the curve had leveled out the ZTS temperature of the material shown in Figure 21 had only reached 320°F. This was not as good as when the material was press cured.

## 2. Differential Scanning Calorimetry (DSC) of Partially Crosslinked ETANOX032

Generally, the first endothermic peak noted in a DSC plot is considered to be the glass transition temperature ($T_g$) of the polymer. The $T_g$ data obtained in this manner on a series of partially crosslinked ETANOX032 interlayers appears in Table 11, along with other pertinent thermal data.

## 3. Apparent Modulus of Rigidity (Clash-Berg) of Partially Crosslinked ETANOX032

The Clash-Berg test provides a quantitative measure of the modulus of a polymer over a range of temperatures. Analysis of graphs of the data can be used to locate its glass to rubber transition temperature ($T_g$).

In this method, a sample of specified dimensions is immersed in a thermostated bath, starting at a very low temperature and the torsional modulus then determined at periodic intervals with a steady rate of increase in temperature. From the dimensions of the specimen, the torsional load applied, and the angle of deflection observed, the apparent shear modulus of rigidity at that temperature is calculated. A curve can be plotted from a series of points so obtained. The plots show the absolute value of modulus at all temperatures and that temperature where the rate of change in modulus is most rapid, i.e. the glass transition temperature, $T_g$.

In addition to graphic plots of apparent shear modulus versus temperature, two other types of data are available in the Clash-Berg test: the $T_f$ (temperature at modulus at 45,000 psi) and the $T_{675\text{ psi}}$ (the temperature where the material becomes very soft and rubbery).

Table 11

## THERMAL CHARACTERISTICS AND GLASS TRANSITION TEMPERATURES ($T_g$) -DETERMINED BY DIFFERENTIAL SCANNING CALORIMETRY OF PARTIALLY CROSSLINKED ETANOX032

| Crosslinker | | Temperature, °F | | | |
|---|---|---|---|---|---|
| Type(a) | Conc. (phr) | ZTS(b) Temperature | $T_{45,000}$(c) | $T_g$(d) | TGA(e) |
| Silane | 0.8 | 384 | -31 | -18 | 527 |
| Silane | 1.0 | 401+ | -32 | -24 | 527 |
| ipbc | 0.25 | 363 | -33 | -22 | 536 |
| ipbc | 0.30 | 381 | -27 | -20 | 536 |
| None | - | 140 | -31 | -29 | 545 |

---

(a) Silane - vinyltriethoxy silane press-cured at 325°F for 3 hours.
ipbc - isophthaloylbiscaprolactam cured at 325°F for 3 hours.

(b) Zero Tensile Strength Temperature.

(c) Temperature at Modulus of 45,000 psi.

(d) Glass transition temperature obtained by DSC.

(e) Zero weight loss up to this temperature.

## The Results

The sample identification and crosslinking concentrations along with the numerical apparent modulus (Clash-Berg) data of the $T_f$ and $T_{675}$, are summarized in Table 12. Graphic plots of the modulus versus temperature are shown in Figures 22 thru 25.

Examination of the data in Table 12 shows that the limited crosslinking of ETANOX032 using silane or ipbc had very little effect on the $T_f$, therefore the polymers should still show good low temperature properties. The fact that the skiving blocks which were made required dry ice temperature (-40°F) before they became hard enough to be skived, substantiates this data. As noted previously, form stability and ZTS temperature of these limitedly crosslinked materials is greatly increased over that of uncrosslinked controls.

## 4. Mechanical Properties of Partially Crosslinked ETANOX032

The efficacy of the chemically crosslinked ETANOX032 was determined as a function of temperature (-65 to 350°F) with the following tests:

- Tensile Strength
- Tensile Elongation
- Tear Strength

The tensile testing was done using a non-standard micro tensile specimen. It was necessary to use this small size specimen because the environmental chamber severely restricts the travel of the Instron testing machine. Even with the use of small specimens, the ultimate elongation of the samples at elevated temperatures could be measured to only 2000 percent (if the specimen did not fail - an elongation of >2000 was reported.

The results of the physical testing are presented in graphic form in Figures 26, 27 and 28, and in tabular form in Tables 13, 14 and 15.

Examination of the data makes it clearly evident that the partially crosslinked samples show the same excellent mechanical properties at low temperatures as the untreated ETANOX032. The significant difference, however, is that the partially crosslinked materials retained sufficient mechanical characteristics for an interlayer up to 350°F.

Table 12

## MODULUS OF RIGIDITY OF PARTIALLY CROSSLINKED ETANOX032 AS A FUNCTION OF CROSSLINKER TYPE AND CONCENTRATION

| Crosslinker | | ZTS(b) | | | |
|---|---|---|---|---|---|
| Type(a) | Conc. (phr) | Temperature (°F) | $T_{45,000}$(c) (°F) | $T_{675}$(d) (°F) | SR(e) (F°) |
| Silane | 0.8 | 384 | -31 | +13 | 44 |
| Silane | 1.0 | 401+ | -32 | +16 | 48 |
| ipbc | 0.25 | 363 | -33 | +15 | 48 |
| ipbc | 0.30 | 381 | -27 | +17 | 44 |

(a) Silane - vinyltriethoxy silane press-cured at 325°F for 3 hours.
ipbc - isophthaloylbiscaprolactam press-cured at 325°F for 3 hours.
(b) Zero Tensile Strength Temperature.
(c) Temperature at modulus of 45,000 psi.
(d) Temperature at modulus of 675 psi.
(e) Temperature range between modulus of 45,000 and 675 psi.

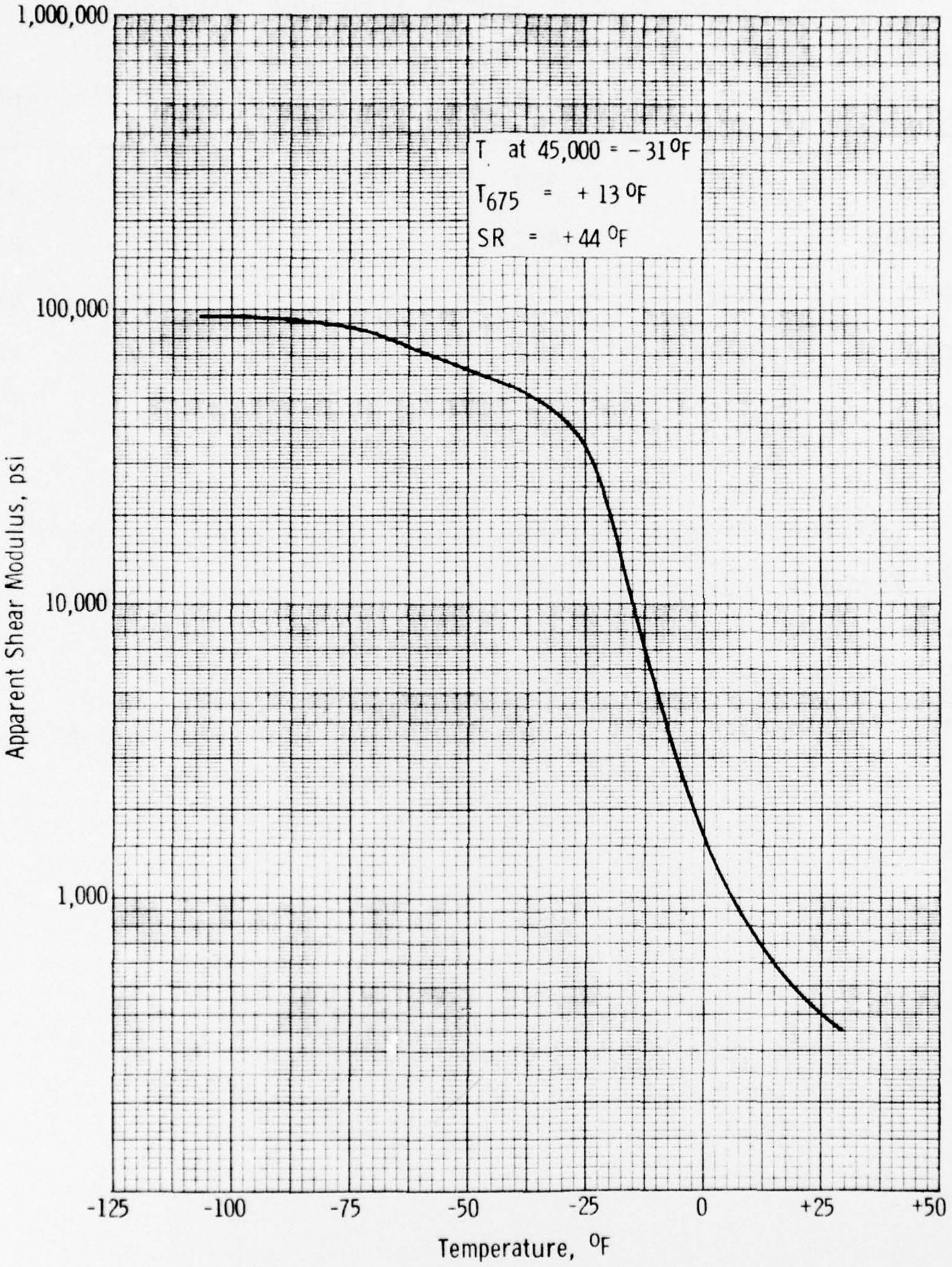


Figure 22. Apparent Shear Modulus as a Function of Temperature for ETANOX032 Crosslinked With 0.8 phr Silane.

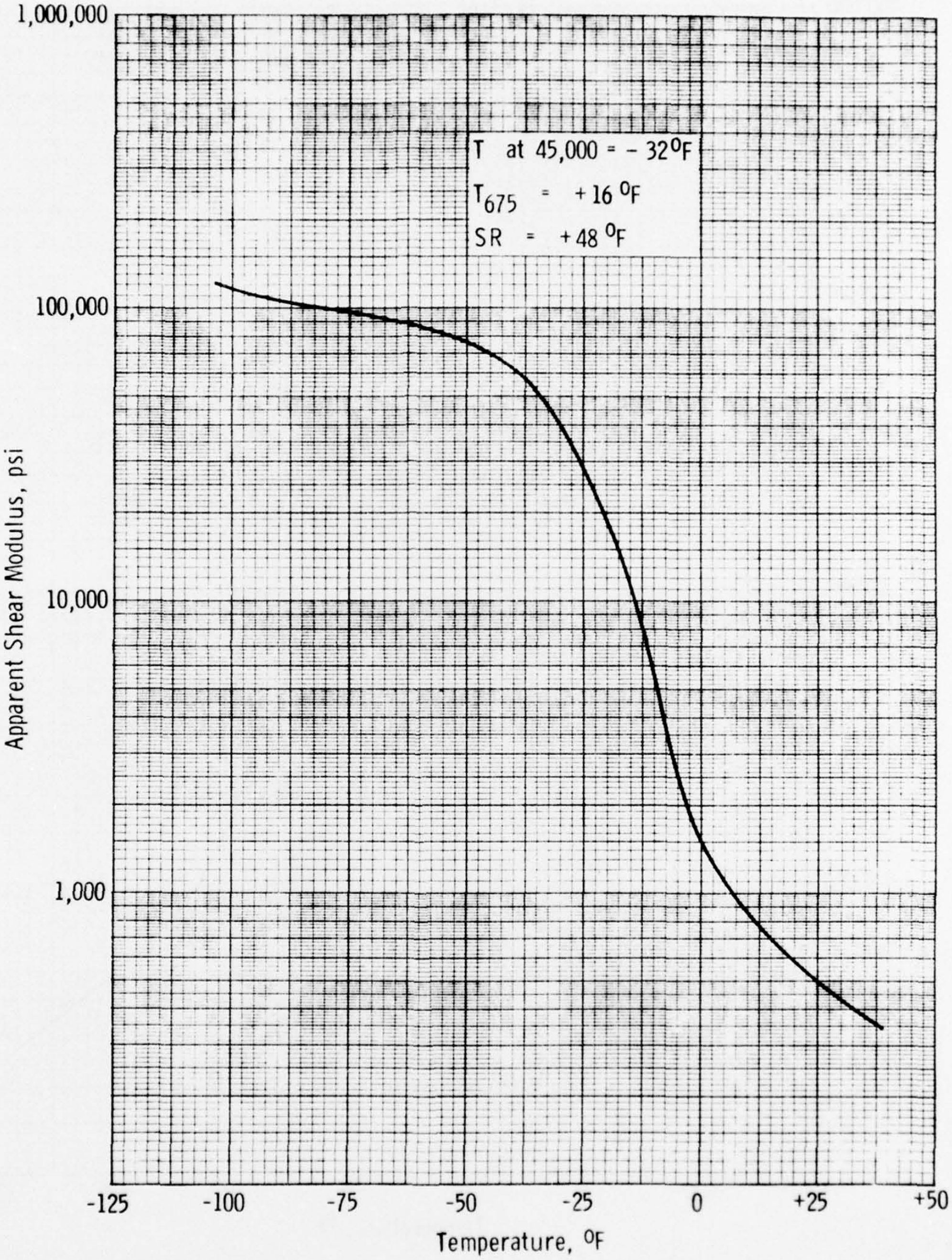


Figure 23. Apparent Shear Modulus as a Function of Temperature for ETANOX032 Cured With 1.0 phr Silane.

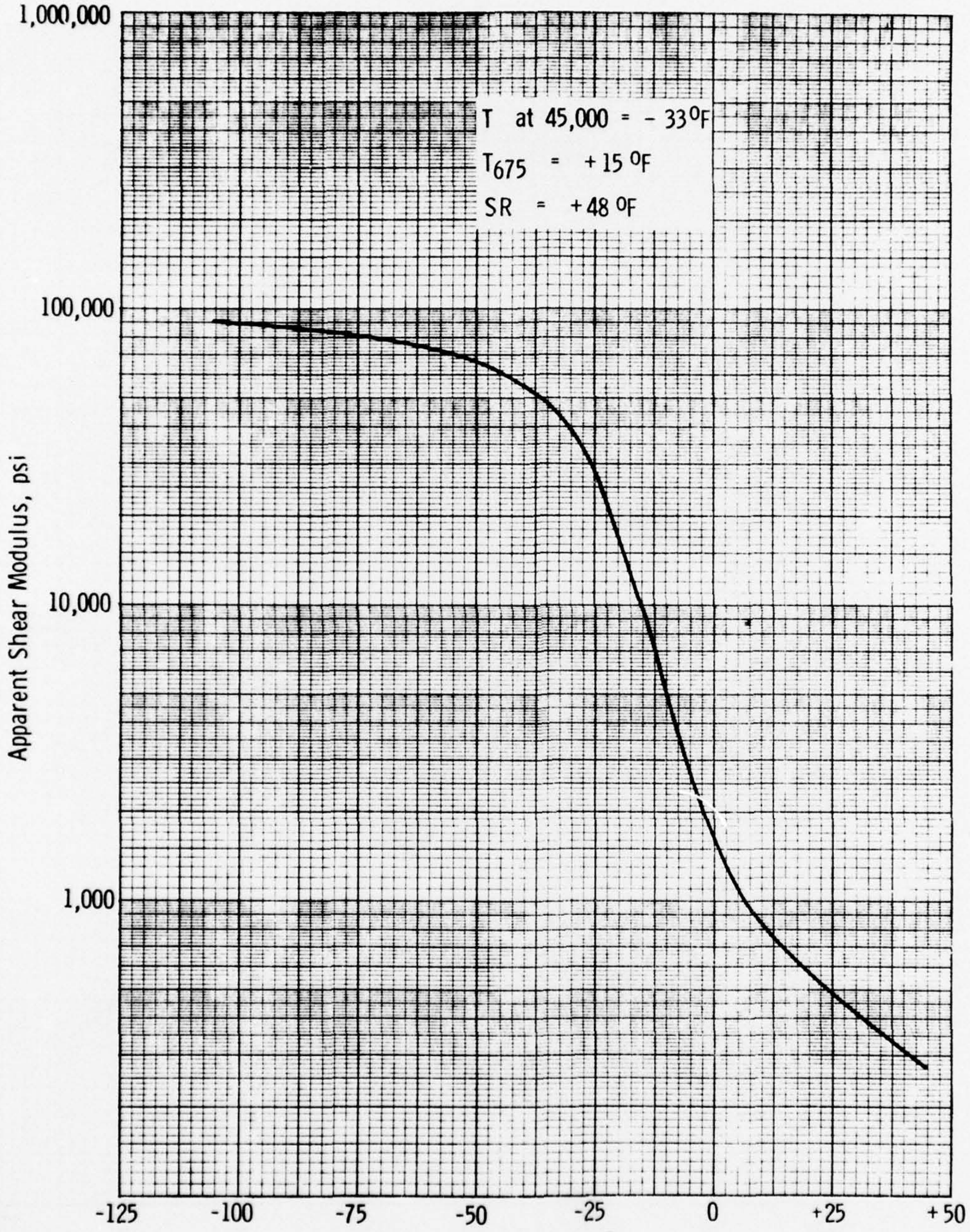


Figure 24. Apparent Shear Modulus as a Function of Temperature for ETANOX032 Cured With 0.25 phr ipbc.

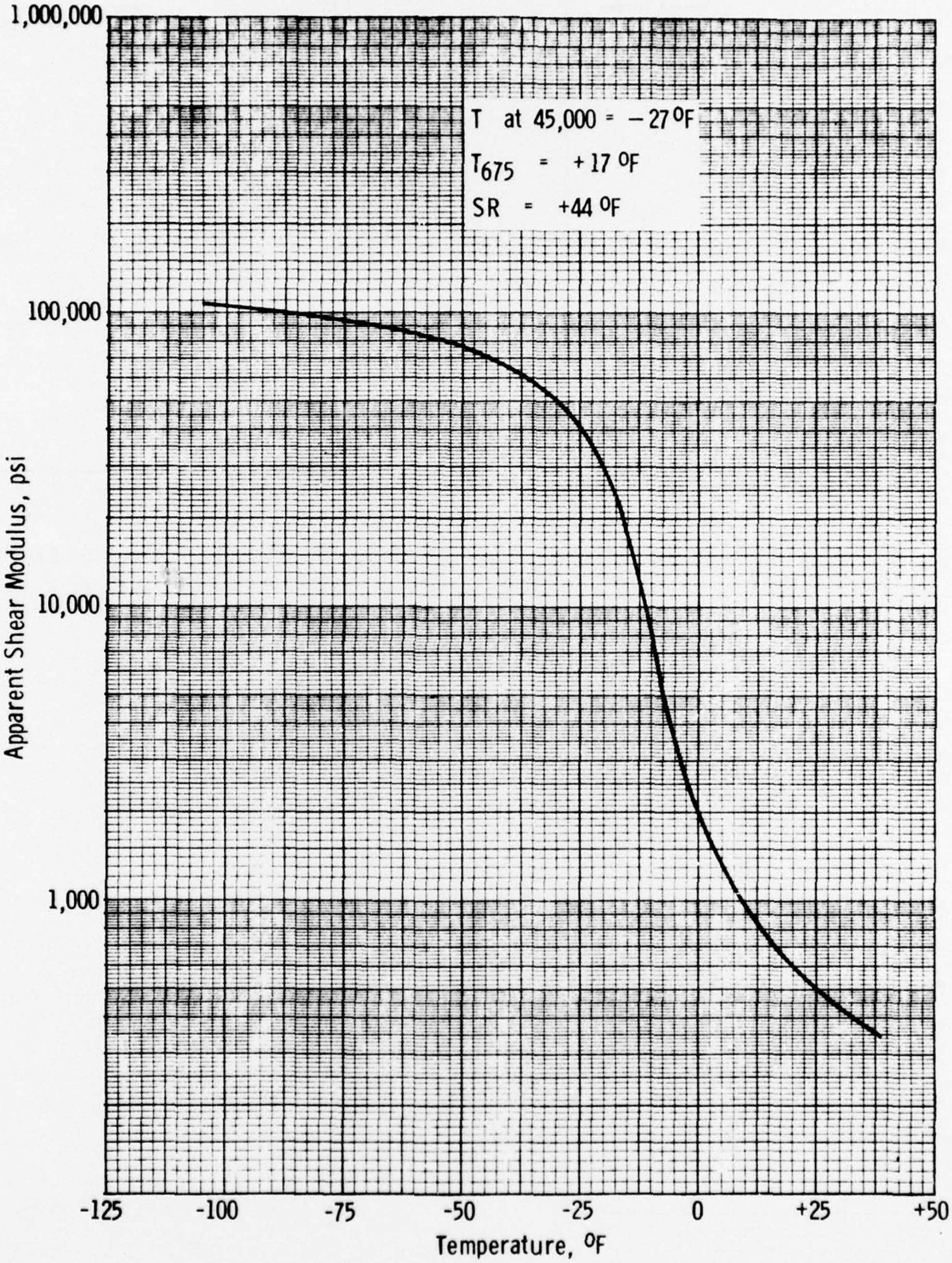
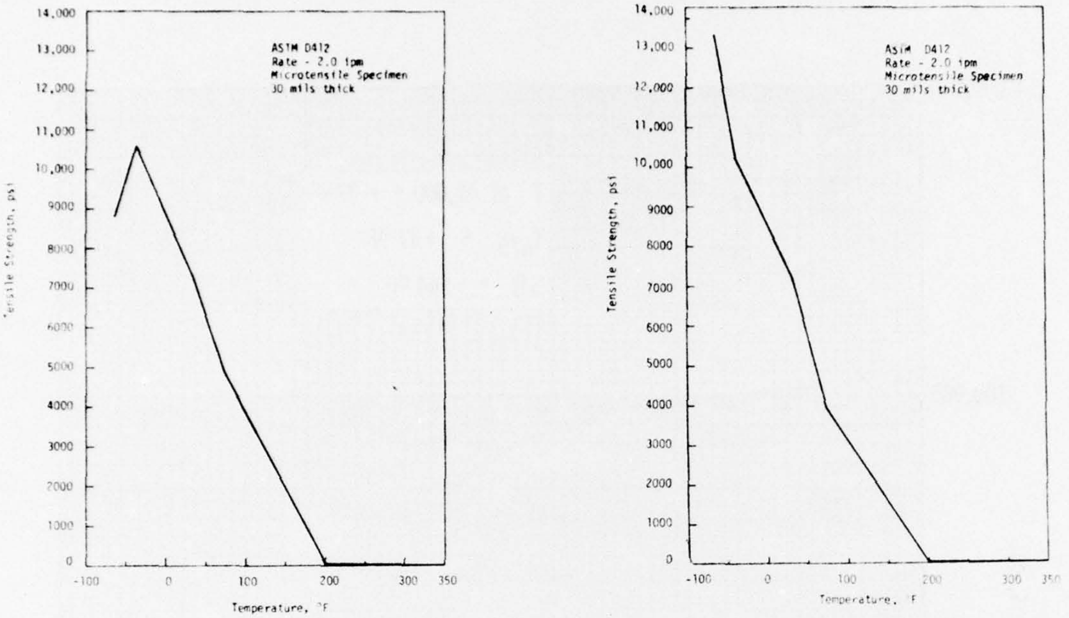
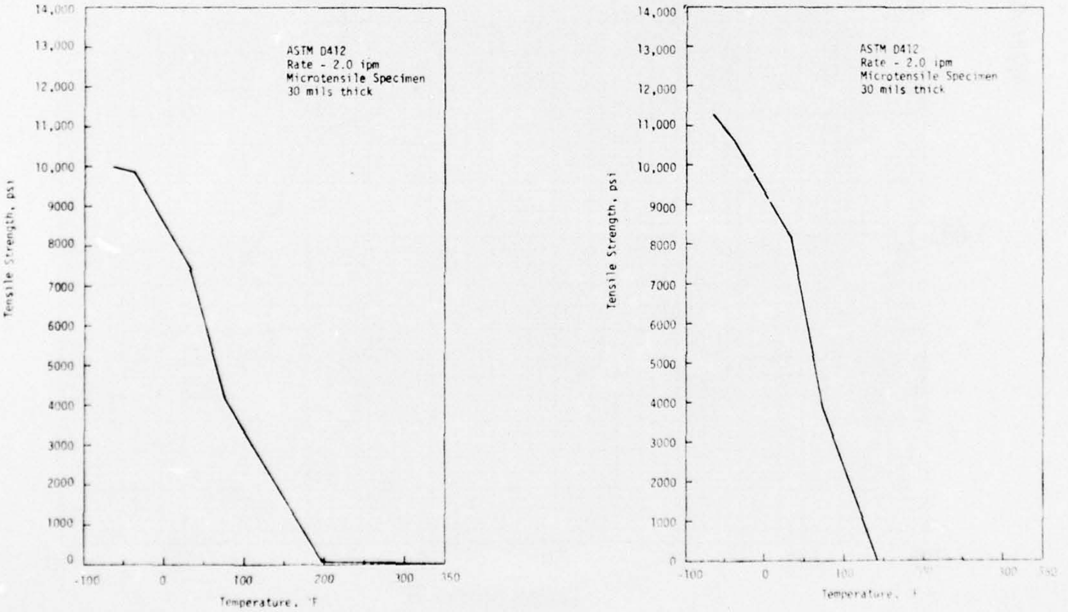


Figure 25. Apparent Shear Modulus as a Function of Temperature for ETANOX032 Cured With 0.30 phr ipbc.



(a) Partially Crosslinked ETANOX032 1.0 phr Silane

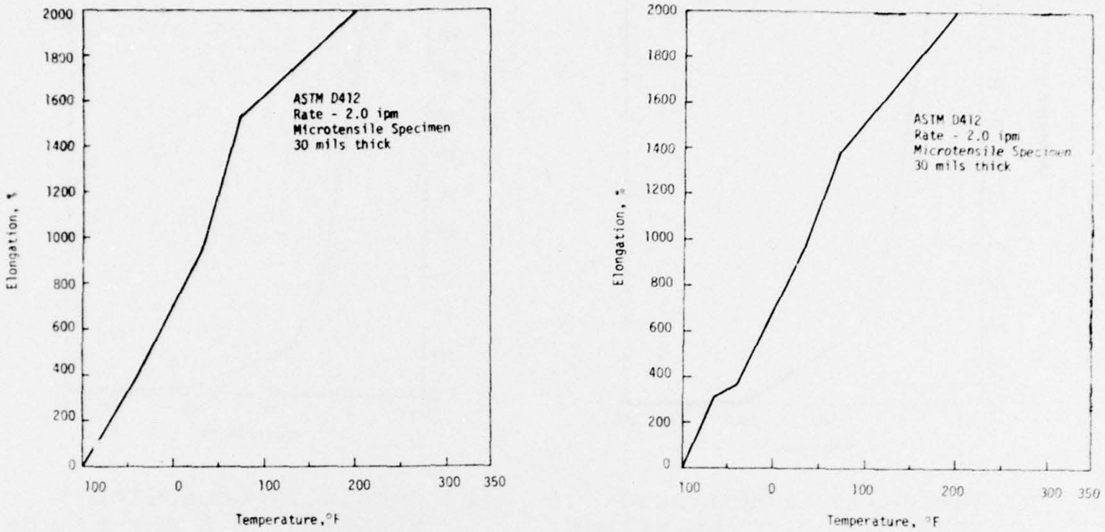
(b) Partially Crosslinked ETANOX032 0.8 phr Silane



(c) Partially Crosslinked ETANOX032 0.1 ipbc

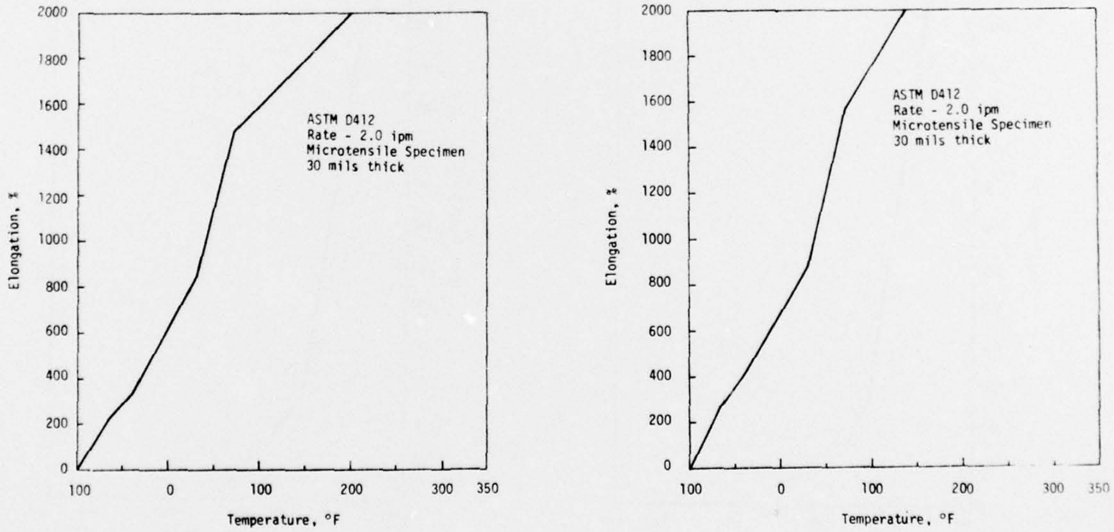
(d) ETANOX032

Figure 26. Tensile Strength Characteristics of ETANOX032 and Partially Crosslinked ETANOX032 as a Function of Temperature.



(a) Partially Crosslinked
ETANOX032 1.0 phr Silane

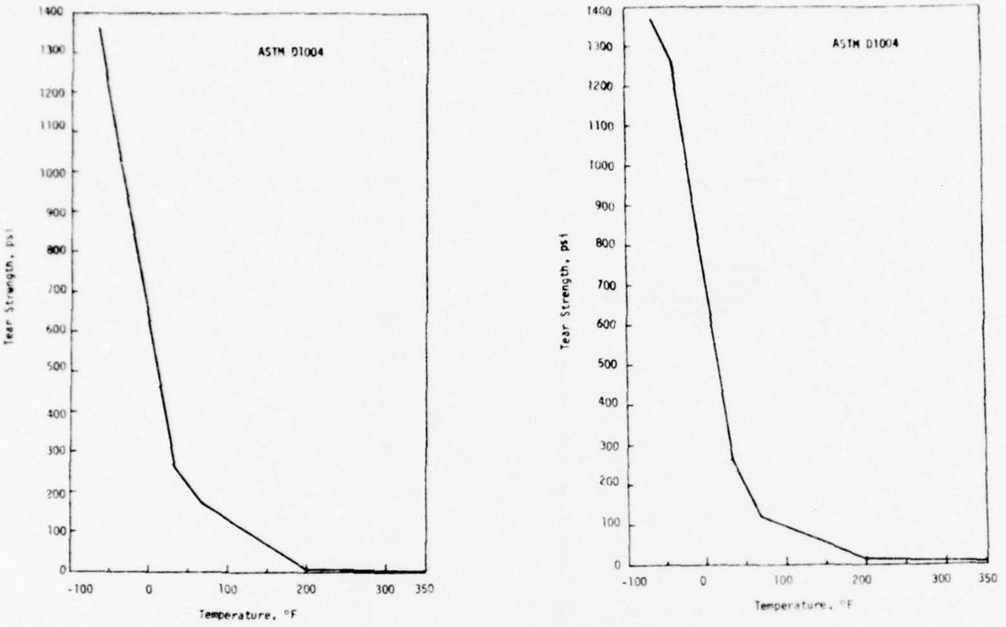
(b) Partially Crosslinked
ETANOX032 0.8 phr Silane



(c) Partially Crosslinked
ETANOX032 0.3 ipbc

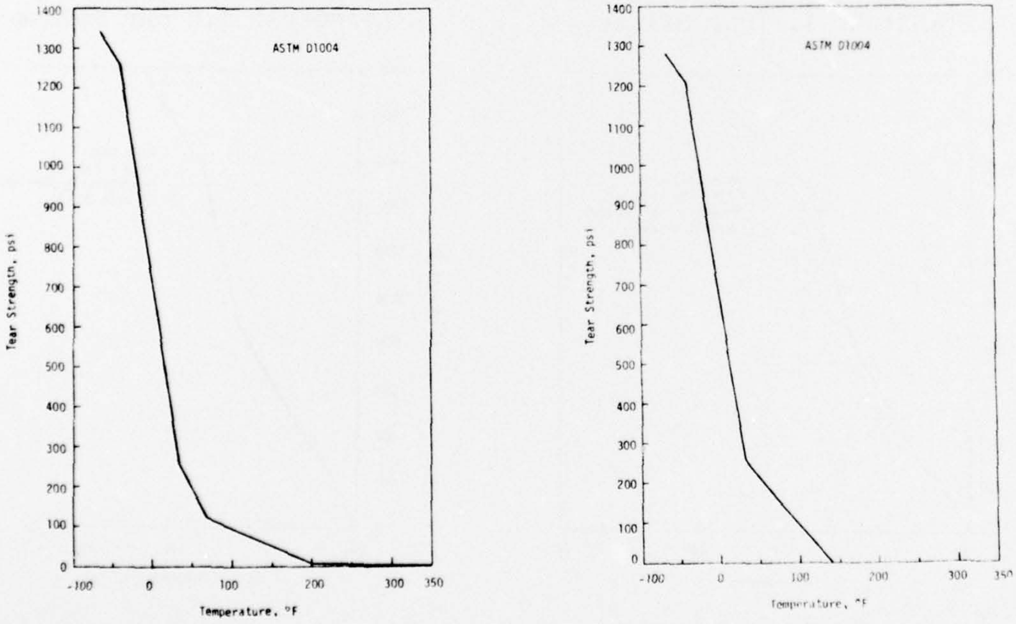
(d) ETANOX032

Figure 27. Tensile Elongation Characteristics of ETANOX032 and Partially Crosslinked ETANOX032 as a Function of Temperature.



(a) Partially Crosslinked ETANOX032 1.0 phr Silane

(b) Partially Crosslinked ETANOX032 0.8 phr Silane



(c) Partially Crosslinked ETANOX032 0.3 ipbc

(d) ETANOX032

Figure 28. Tear Strength Characteristics of ETANOX032 and Partially Crosslinked ETANOX032 as a Function of Temperature.

Table 13

## TENSILE STRENGTH OF PARTIALLY CROSSLINKED ETANOX032

| Crosslinker | | Tensile Strength, psi[2] | | | | | |
|---|---|---|---|---|---|---|---|
| Type[1] | Conc phr | -65°F | -40°F | 32°F | 73°F | 200°F | 350°F |
| silane | 1.0 | 8,870 | 10,600 | 7,320 | 4,900 | 44 | 2 |
| silane | 0.8 | 13,300 | 10,300 | 7,160 | 3,910 | 14 | 1 |
| ipbc | 0.3 | 9,990 | 9,860 | 7,440 | 4,310 | 13 | 3 |
| Radiation[3] | 0 | 8,800 | 10,500 | 8,100 | 2,800 | 29 | 4 |
| none | | 11,300 | 10,600 | 8,180 | 3,800 | 0 | 0 |

---

[1] Silane - vinyltriethoxy silane press-cured at 325°F for 3 hours at 300 psi.
ipbc - isophthaloylbiscaprolactam cured at 325°F for 3 hours at 300 psi.

[2] ASTM D412
Rate - 2.0 ipm
Microtensile Specimen
30 mils thick

Data average of 3 specimens

[3] 30 mil thick sheet given 10 Mrad dose on each side by 300 KV source.

Table 14

## TENSILE ELONGATION OF PARTIALLY CROSSLINKED ETANOX032

| Crosslinker[1] | | Elongation %[2] | | | | | |
|---|---|---|---|---|---|---|---|
| Type | Conc phr | -65°F | -40°F | 32°F | 73°F | 200°F | 350°F |
| silane | 1.0 | 233 | 394 | 944 | 1530 | >2000 | 1100 |
| silane | 0.8 | 305 | 366 | 944 | 1380 | >2000 | >2000 |
| ipbc | 0.3 | 222 | 327 | 850 | 1480 | >2000 | >2000 |
| Radiation[3] | 0 | 200 | 350 | 750 | 1450 | >2000 | >2000 |
| none | 0 | 278 | 405 | 878 | 1580 | 0 | 0 |

---

[1] Silane - vinyltriethoxy silane press-cured at 325°F for 3 hours at 300 psi.
ipbc - isophthaloylbiscaprolactam cured at 325°F for 3 hours at 300 psi

[2] ASTM D412 (ultimate elongation)
Rate - 2.0 ipm
Microtensile Specimen
30 mils thick
Data average of 3 specimens

[3] 30 mil thick sheet given 10 Mrad dose on each side by 300 KV source.

Table 15

## TEAR STRENGTH OF PARTIALLY CROSSLINKED ETANOXO32

| Crosslinker | | Tear Strength, psi[2] | | | | | |
|---|---|---|---|---|---|---|---|
| Type[1] | Conc phr | -65°F | -40°F | 32°F | 73°F | 200°F | 350°F |
| silane | 1.0 | 1360 | 1070 | 262 | 117 | 8 | 4 |
| silane | 0.8 | 1370 | 1260 | 261 | 120 | 14 | 6 |
| ipbc | 0.3 | 1340 | 1260 | 264 | 123 | 7 | 1 |
| none | 0 | 1280 | 1210 | 258 | 166 | 0 | 0 |

---

[1] Silane - vinyltriethoxy silane press-cured at 325°F
for 3 hours at 300 psi.
\- isphthaloylbiscaprolactam press-cured at 325°F
for 3 hours at 300 psi

[2] ASTM D1004, average of 3 specimens

### 5. Optical Properties of Partially Crosslinked ETANOX032

In order to determine the effect that crosslinking of the ethylene terpolymer has on optical properties, the % transmittance and the % haze of various samples were measured at WPAFB, according to ASTM D-1003-61. Included were samples crosslinked by electron beam radiation or by chemical means with silane or ipbc. Results obtained are given in Table 16. The total % transmittance of all samples tested was close to that of the control. There were some significant differences in % haze, however (the accuracy of the test is reportedly ±0.3% haze). All crosslinked ethylene terpolymer samples show at least a slight increase in % haze when compared to a control that was not crosslinked. For the 3.1% OH samples crosslinked with ipbc, this increase is quite small; it is somewhat greater for the silane crosslinked material (+1.8). The electron beam crosslinked material exhibits the largest increase in % haze of any tested, up to +4.8%. This much of an increase in % haze could be detrimental and would be an argument against use of the electron beam method of crosslinking the ethylene terpolymer for this application.

## H. Laminates Delivered to the Air Force

One foot square laminates were prepared and delivered to the Air Force as part of the program requirements.

These laminates were prepared using the vacuum bag autoclave technique. The first laminate consisted of polycarbonate (0.25 in.) and acrylic (0.25 in.) sheets bonded together with an interlayer of ETANOX032 (0.032 in.) partially crosslinked with 0.3 phr ipbc. A maximum temperature of 239°F and a total pressure differential of 45 psi was used in the laminating cycle.

The second laminate was prepared using glass (0.025 in.) and polycarbonate (0.25 in.) sheets. The 30 mil ETANOX032 interlayer was partially crosslinked with 1.0 phr silane (vinyltriethoxy silane). The maximum laminating temperature was 249°F with a 45 psi total pressure differential.

The third laminate was prepared using two sheets of glass (0.125 in.). The ETANOX032 interlayer (30 mils) was partially crosslinked with 0.5 phr ipbc. The laminating temperature was peaked at 336°F with a 45 psi total pressure differential to insure a good strain and bubble-free laminate.

All three laminates which were delivered to the Air Force were of good quality and bubble-free.

## Table 16

## OPTICAL PROPERTIES OF PARTIALLY CROSSLINKED ETANOX031 LAMINATES[1]

| Sample | Description[2] | % Transmittance | HR[3,4] | % Haze |
|---|---|---|---|---|
| 1 | uncrosslinked control | 85.2 | 1.5 | 1.8 |
| 2 | 1% Silane crosslinker | 83.5 | 3.0 | 3.6 |
| 3 | 0.3% ipbc crosslinker | 87.0 | 3.1 | 3.6 |
| 4 | 0.4% ipbc crosslinker | 86.4 | 2.0 | 2.3 |
| 5 | 0.5% ipbc crosslinker | 85.5 | 2.5 | 2.9 |
| 6 | 15 Mrads[5] electron beam crosslinked | 87.8<br>85.5 | 5.8<br>4.4 | 6.6<br>5.1 |

---

[1] 3 ply laminates consisting of 2 plys of 0.125 inch thick window glass bonded with 0.03 in. of the designated interlayer.

[2] Special optical clarity interlayer batch prepared with 3.1% OH, but required slightly higher levels of crosslinkers for desired form stability.

ipbc = isophthaloylbiscaprolactam cured at 325°F for 5 hours; Silane cured at 325°F for 5 hours.

[3] ASTM D-1003-61 performed at WPAFB.

[4] HR = Haze Reading from spectrophotometer, tests performed at WPAFB.

[5] Some minor bubbles apparently present, affect unknown.

## III. CONCLUSIONS AND RECOMMENDATIONS

An ethylene terpolymer aircraft glazing interlayer has been developed in the course of this project, which has reasonable strength up to 350°F while retaining high elongation down to -65°F as well as thermoplastic sheet formability at 250°F (required for polycarbonate). The improved thermal form stability to 350°F was achieved through "controlled limited crosslinking" of the ethylene terpolymer via one of three crosslinking systems.

Based on the results obtained in this study, the following recommendations are made for future work in this area;

1. that the electron beam method of crosslinking the ethylene terpolymer warrants further, more detailed study;

2. that the economics of the three crosslinking systems should be studied for comparative purposes;

3. that preparation of a substantially larger quantity of the best (and/or most economical) of the three crosslinked materials should be undertaken;

4. that a more extensive characterization of the engineering properties of both the crosslinked terpolymer material itself and laminates containing it should be performed; and

5. that further examination of the ethylene terpolymer system to achieve a potential 450°F modification (using crosslinking in place) should be done.

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5. Conference on Aerospace Transparent Materials and Enclosures; Atlanta, November 1975.

☆ U. S. GOVERNMENT PRINTING OFFICE: 1976 — 757-001/102