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TACKIFIER FOR ADDITION POLYIMIDES

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INTRODUCTION

The use of polyimide resin matrices for advanced composite materials has shown a continuous increase in the aerospace industry. The ubiquitous problem associated with this type of material is the lack of "tack and drape" after prepregging solvent is lost. The loss of solvent in high molecular weight systems which use the polyamic acid approach to polymerization leaves a tough "boardy" material that is difficult to fabricate. For low molecular weight addition systems which use the monomeric approach, some solvent must be retained to prevent a grainy deposit of monomeric solids from forming on the reinforcement. The aromatic amine monomer is usually responsible for the granular texture.

A new polyimide formulation, LaRC-160B1, has been developed to minimize these problems. This polyimide resin is a modification of LaRC-160 (Ref. 1), which was developed at NASA Langley Research Center. LaRC-160B1 neat resin is a liquid at room temperature made without the use of solvent. The resulting prepreg made from LaRC-160B1 is not "boardy" and has longer retention of tack and drape because of the incorporation of a high-boiling-point, liquid reactive plasticizer. The compound used to accomplish this was monoethylphthalate, an endcap which replaces ten percent of the conventional endcapping system. The preparation and physical properties of LaRC-160B1/graphite prepreg and the resulting laminates will be described.

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EXPERIMENTAL

Monomers

3,3',4,4'-Benzophenonetetracarboxylic acid dianhydride (BTDA), 5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride), and phthalic anhydride were obtained commercially and used as received. The diamine, Jeffamine AP-22, was obtained commercially from Jefferson Chemical Co., Inc., Houston, Texas.*

Resin Preparation

Stoichiometric amounts of diethylester of BTDA (BTDE) 0.67 mole, and the monoethylesters of nadic anhydride (NE) 1.10 mole, and phthalic anhydride (PE) 0.12 mole were prepared by refluxing at 351K (172°F) the corresponding anhydrides with an excess of ethanol (2.69 mole). The esterification reaction was carried out in a three-neck round bottom flask equipped with a mechanical stirring device. When all the monomers had gone into solution, the refluxing was continued for 1/2 hour longer. The solution was allowed to cool to 310K-320K (°F) and then mixed with Jeffamine AP-22 (2.56 molar equivalents of amine) which had previously been warmed to 310K-320K.

The solution was cooled, bottled and refrigerated since the ester-acids tend to disproportionate on standing; the refrigeration helps extend solution stability.

The original version of LaRC-160 contained BTDE (0.67 mole), NE (1.22 mole), ethanol (2.69 mole) and Jeffamine AP-22 (2.56 mole).

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*Use of trade names or names of manufacturers in this report does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

The process for preparation was the same as previously described(Ref. 1). The amount of ethanol and Jeffamine AP-22 remained the same. For LaRC-160 and LaRC-160B1 the mixtures stayed liquid and did not turn granular after the solvent was evaporated.

Prepregging

A resin of LaRC-160B1 was prepared at a ratio of 50% solids by weight in ethanol. It was brushed onto Hercules HT-S graphite fiber which had been drum wound at a spacing of 5 1/2 tows per inch. The resulting prepreg had a 50% fiber content by weight. The solvent content was reduced to about 10% by allowing it to evaporate for 8-16 hours after being coated. The resulting prepreg with good tack and drape was then removed from the drum and could be easily cut and formed into shaped lay-ups.

Laminate Preparation

The prepreg was cut into 7.6 cm by 17.8 cm (3 in by 7 in) sections and stacked into 17-ply unidirectional preforms. The preformed billet was subjected to the first stage in the curing process. This required the preform to be vacuum bagged at 7-14 kPa, gauge (2-4 in Hg, gauge). The billet was then heated from ambient at a rate of 2.8K (5°F) per minute to 436K (325°F) and held at that temperature for one hour, then cooled under vacuum to room temperature. This step is a consolidation and imidization step which results in about a 25% weight loss and a well-formed billet averaging 36% resin by weight.

Molding of Laminates

The molding procedure was done using a flat matched-metal mold which had open ends. The consolidated billet was trimmed to fit the mold with the fiber in the 0° direction of the open ends, thus allowing observation of the resin flow during molding. The platens of the press were preheated to 478K (400°F), the mold containing the billet was introduced and contact pressure applied. A heating rate was established at 2.8K (5°F) per minute. When a temperature of 547 (525°F) was reached, the pressure was increased to 1.4 MPa (200 psig) over a 1 minute span, held for 1 minute, decreased to zero (gauge) for 15 seconds (a bumping action) and then reapplied at 1.4 MPa (200 psig). A maximum curing temperature of 603K (625°F) was then attained and held for two hours. The panel was cooled at 2.8K (5°F) per minute under full pressure and removed at a temperature below 366K (200°F).

Thermooxidative Aging

The laminate panels were trimmed and cut into specimens for both short beam shear (SBS) and flexural strength measurements. The press-molded SBS samples were aged at a temperature of 589K (600°F). Each test group consisted of four SBS samples that were randomly selected and weighed as a unit before and after aging. The flexural samples were tested without aging.

Air Aging

The groups of specimens were isothermally aged at 589K (600°F) and removed for testing after 250 and 500 hours of exposure. Forced air ovens with an air-change rate of 75 cc/min (4.6 in^3/min) were used. The temperature of the specimens was monitored by prepositioned thermocouples and also by the separate oven controls.

Testing

The mechanical testing data were obtained using an Instron Testing Machine Model TT-6, equipped with an Instron Environmental Chamber for the elevated temperature tests. Flexural strength and moduli were determined according to ASTM D790. Short beam shear strengths were determined using a span to thickness ratio of 4. Each specimen was held 15 minutes at test temperature prior to testing. Ultrasonic "C" scans were performed prior to testing with a Nano-scope Model 414 instrument.

Results and Discussion

Processing Conditions

The procedure used in making the prepreg and laminates can be considered a successful technique, based the fact that the polyimide resin can be either applied to the fibers by brush coating or immersion in a resin bath with good results (Ref. 2). Both methods leave a flexible and tacky prepreg following evaporation of the solvent. The laminates can be either autoclave processed or molded with matched metal dies (Ref. 1). Both the prepreg and laminates have been commercially prepared using the original formulation of LaRC-160. The mechanical properties of graphite laminates prepared from these prepregs were also equal to or better than those prepared from lab scale runs (Ref. 2). The LaRC-160B1 resin system press molds very well with adequate flow. Like LaRC-160, the LaRC-160B1 is processable under low pressure and at a moderate heating rate. The graphite-reinforced panels were post cured at 589K (600°F) 16 hours in air with no blistering and a weight loss of less than 0.1%. A typical cure cycle for LaRC-160 or LaRC-160B1 is shown in Figure 1.

Weight Loss

Figure 2 shows the weight loss curves for the short beam shear (SBS) specimens (8-sample average per data point) aged in air at 589K (600°F). There was no discoloration of the LaRC-160B1 specimens, even the ones aged up to 500 hours, thus indicating this resin system to be of comparable thermooxidative stability to LaRC-160. Approximately 2 percent laminate weight loss after 500 hours was recorded for each of these exposure conditions which translates into a significant resin loss of 6 percent (fiber oxidation considered minimal).

Short Beam Shear Tests

The short beam shear (SBS) strengths (8-sample average per data point) are shown in Figure 3 for LaRC-160B1. Aging was performed at 589K (600°F) and the testing done at various indicated temperatures. The initial increase in strength during the first 200 hours shows a definite postcuring effect. The percent retention of the SBS with 589K (°F) aging is shown in Figure 4. There was no significant difference in weight loss for these resin formulations.

Flexural Test

The flexural data (4-sample average) is presented in Table 1; the specimens were not aged but tested at room temperature and 561K (550°F). The results show that LaRC-160 and the modified version LaRC-160B1 had almost identical values.

Conclusions

The tack and drape characteristics of LaRC-160 polyimide/graphite prepreg has been significantly improved by the addition of a non-toxic, reactive, high-boiling-point phthalic ester tackifier. The modified resin designated LaRC-160B1 has an out-time of more than six months compared to about two days for LaRC-160. Laminates made from the LaRC-160B1 prepreg had excellent strength retention at temperatures up to 589K (600°F) and showed slightly improved oxidative stability over laminates made from LaRC-160 for up to 500 hours aging at 589K (600°F). The ester additive does not add to the cost of the resin system and the prepreg retains the good fabricability of the base LaRC-160 system. The use of an ester additive that is liquid at room temperature is a concept that may have application to other addition polyimide systems.

References

1. T. L. St. Clair and R. A. Jewell: LaRC-160: A New 550°F Polyimide Laminating Resin. Preprints, 8th National, SAMPE, Technical Conference, vol. 8, p. 82, Seattle, WA, October 12-14, 1976.
2. T. L. St. Clair and R. A. Jewell: Solventless LaRC-160 Polyimide Matrix Resin. 23rd National SAMPE Symposium, Anaheim, California, May 2-4, 1978.

Table 1. Laminate flexural data for LaRC-160B1

	FLEX STRENGTH MPa (ksi)	FLEX MODULUS GPa
R T TEST		
LARC-160	1900 (276)	124
LARC-160B1	1760 (259)	124
561K TEST		
LARC-160	1200 (175)	124
LARC-160B1	1095 (161)	124

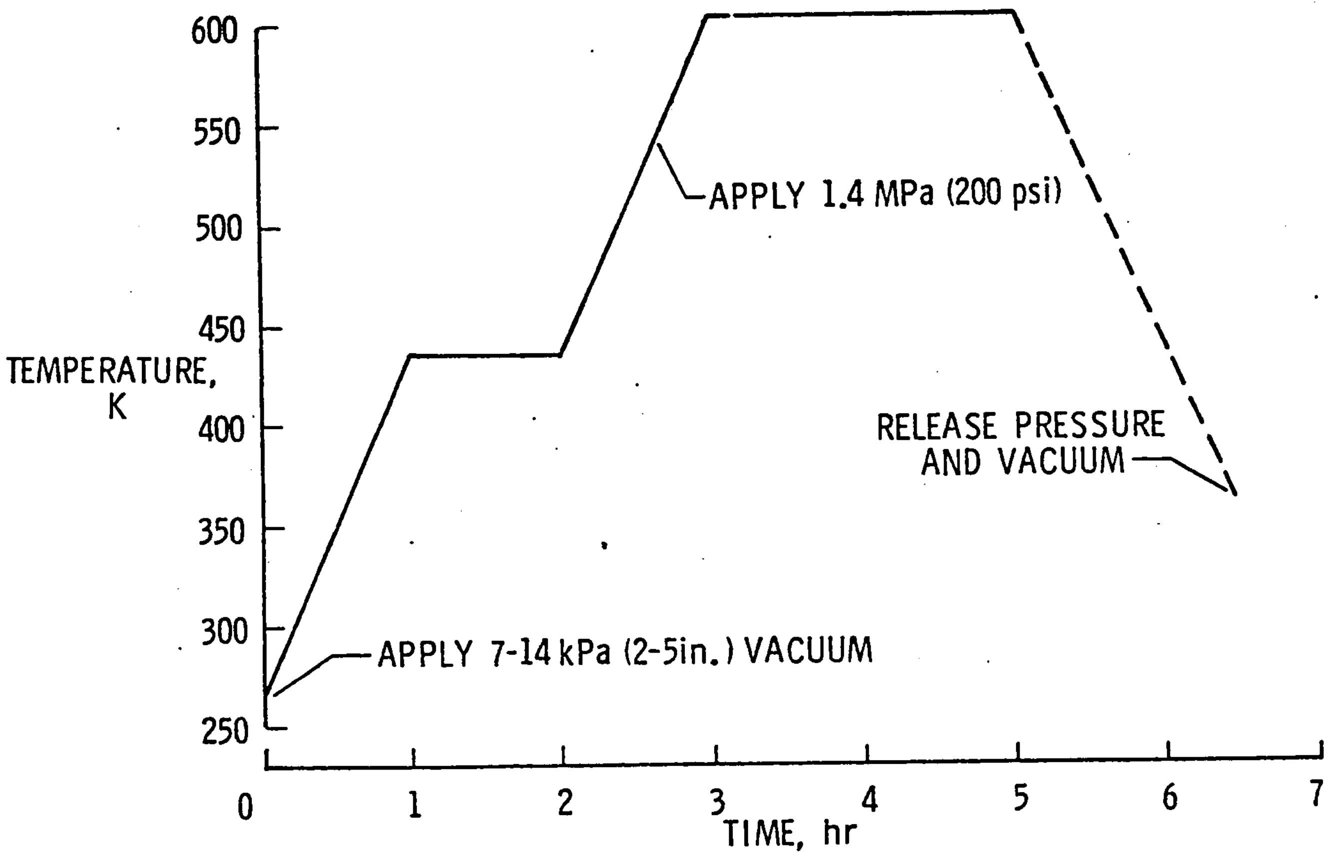

Figure 1. Cure cycle for LaRC-160 and LaRC-160B1

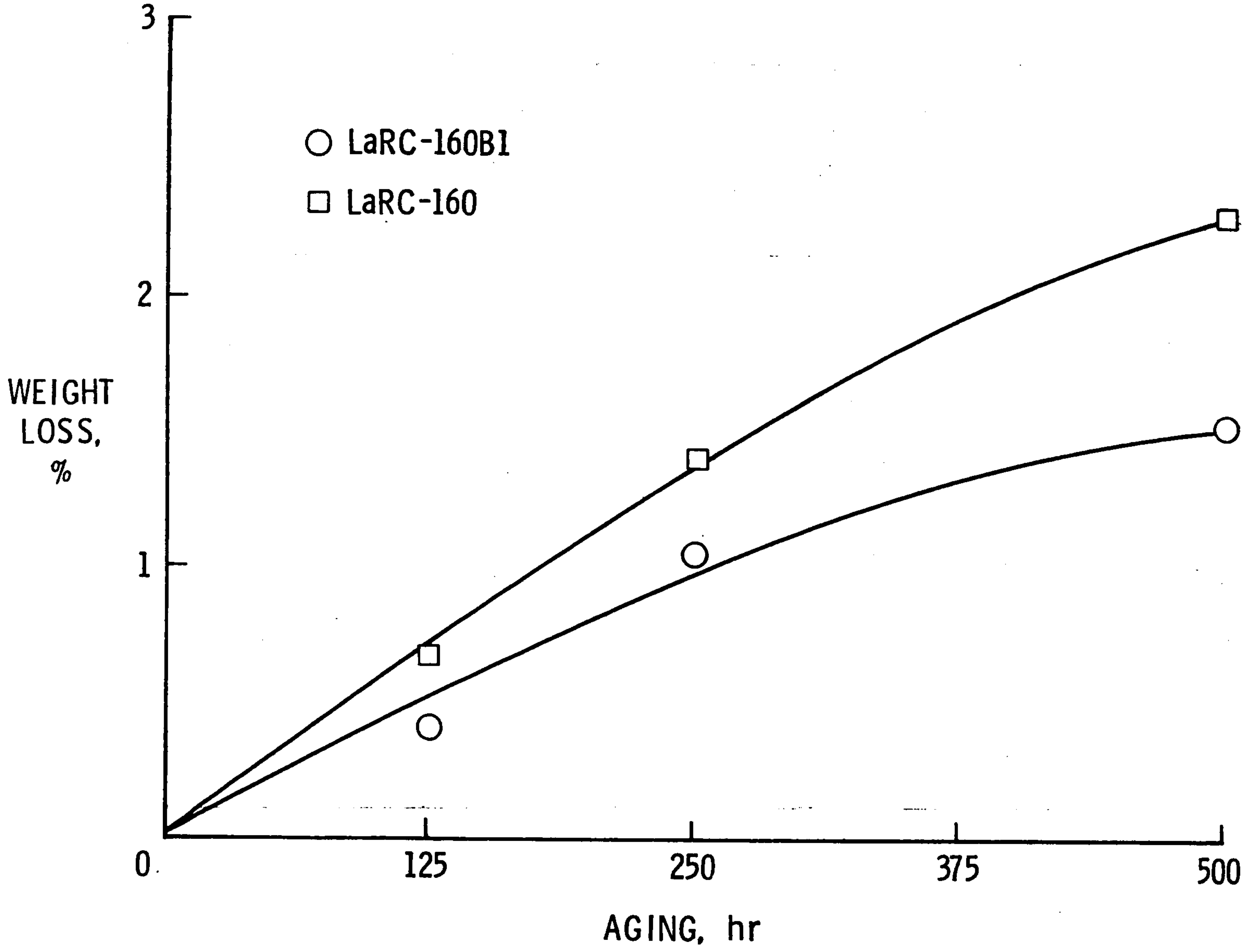

Figure 2. Comparative percent weight loss for LaRC-160 systems aged in air at 589K

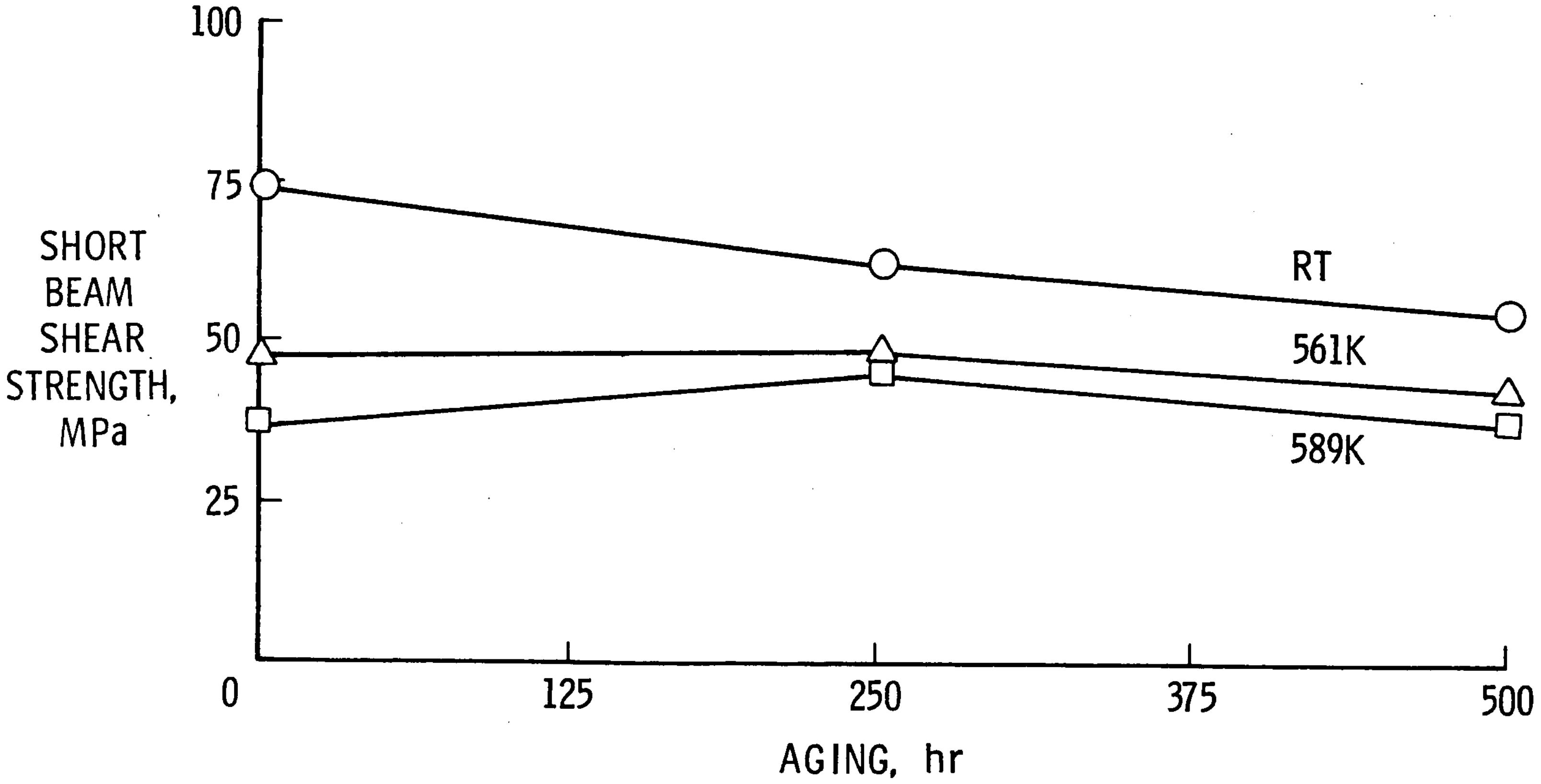

Figure 3. Short beam shear strengths as a function of ageing time at 589K at three test temperatures for LaRC-160B1

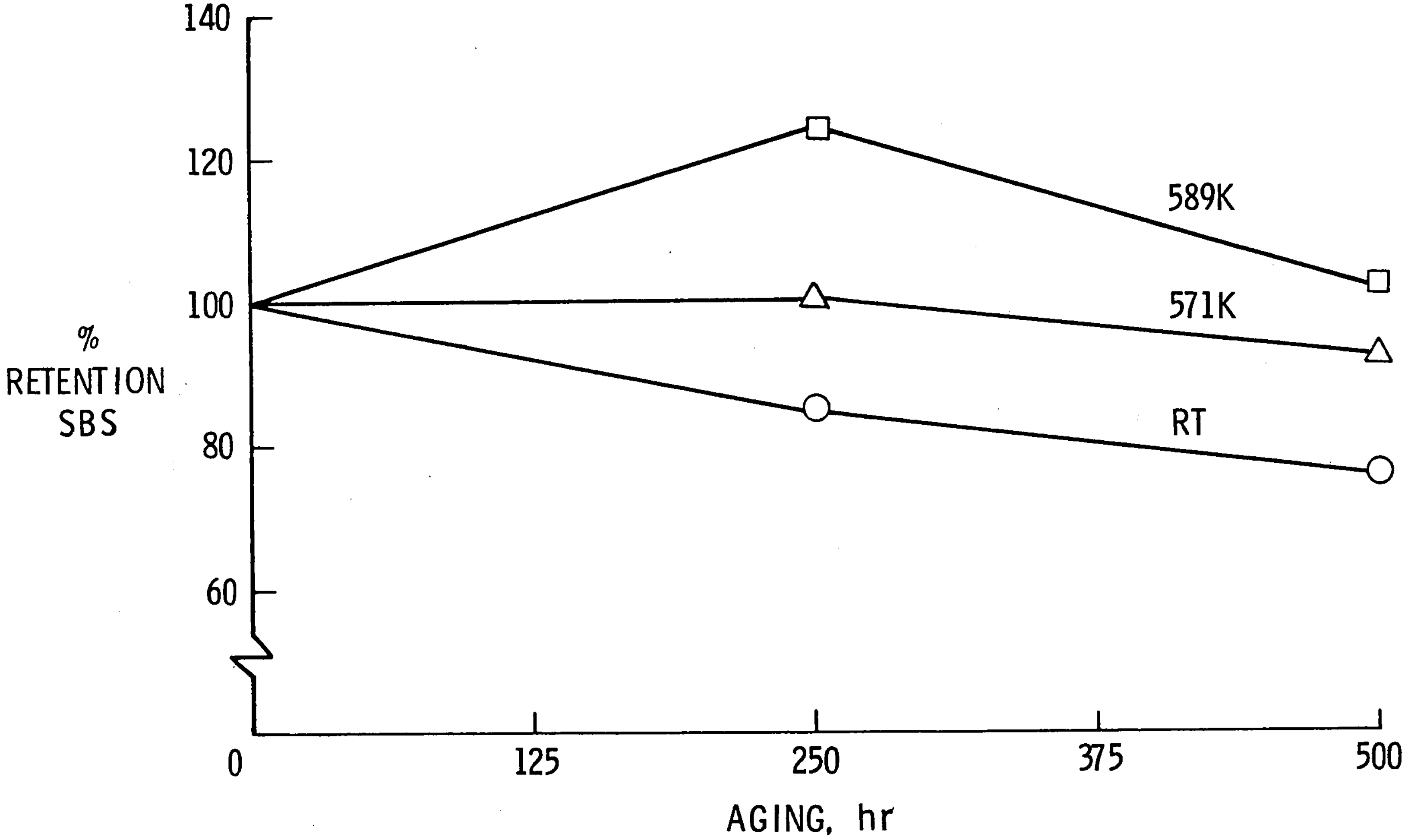

Figure 4. Percent retention of short beam shear strengths as a function of aging at 589K for LaRC-160B1

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16. Abstract

A modification to the addition polyimide, LaRC-160 has been prepared to improve tack and drape and increase prepeg out-time. The essentially solventless, high viscosity laminating resin is synthesized from low-cost liquid monomers. The modified version takes advantage of a reactive, liquid plasticizer which is used in place of solvent and helps solve a major problem of maintaining good prepeg tack and drape, or the ability of the prepeg to adhere to adjacent plies and conform to a desired shape during the lay-up process. This alternate solventless approach allows both longer life of the polymer prepeg and the processing of low-void laminates. This approach appears to be applicable to all addition polyimide systems.

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