EVALUATION OF EXPERIMENTAL EPOXY MONOMERS

W. T. HODGES, T. L. ST. CLAIR, J. R. PRATT* AND ROBIN FICKLIN*
NASA LANGLEY RESEARCH CENTER
HAMPTON, VA 23665

ABSTRACT

Three experimental epoxy monomers were cured with two isomeric curing agents and compared to a well documented standard epoxy system. The experimental epoxy monomers were, the 3,3'- and 4,4'-isomers of tetraglycidylsulfonyldianiline (TGDDS) and the 3,3'-isomer of tetraglycidlymethylenedianiline, (TGMDA). The 3,3'- and 4,4'-isomers of diaminodiphenylsulfone (DDS) were used as the curing agents with the epoxy monomers. The standard epoxy monomer used in this study was the 4,4'-isomer of TGMDA, Araldite MY-720. This standard epoxy monomer was also cured with both isomers of DDS. All of the systems were mixed ultrasonically for uniformity of constituents. Neat resin moldings were cast and cured for each system, and their physical and mechanical properties were compared.

*Miss. Univ. for Women, Columbus, MS 39701

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W. T. Hodges*, T. L. St. Clair, J. R. Pratt**, and Robin Ficklin**
NASA Langley Research Center
Hampton, Virginia 23665

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*Structures Laboratory, U.S. Army Research and Technology Laboratories (AVSCOM), Hampton, VA 23665.

**Mississippi University for Women, Columbus, MS 39701.

1. Introduction

Future generation aircraft need higher performance polymer matrices to fully achieve the weight savings possible with composite materials.[1] New resins are being formulated in an effort to understand basic polymer behavior and to develop improved resins.[2-5] Some polymer/curing agent combinations that could be useful are difficult to process. In the area of epoxies, a major problem is that some components have physical properties which make them difficult to utilize as matrix resins. A previous study in our laboratory has shown that the use of ultrasonic energy can be advantageous in the mixing of curing agents into a standard epoxy resin, such as MY 720 (Ciba-Geigy designation).[6] In the present study we have expanded this work to include three novel epoxides.

2. Experimental

Processing and Characterization Equipment

The ultrasonic unit used in the mixing was a Dukane Model 40A305A generator with 43A5 transducer and model 113 horn, rated at 300 watts output power. Glass transition temperatures by probe penetration of cured samples were measured on a DuPont Model 943 thermomechanical analyzer, with a heating rate of 5°C/min and a penetration load of 15 grams. Thermogravimetric analyses (TGA) were run on a Perkin Elmer TGS-2 system with an AR-2 autobalance and a UU-1 temperature program controller at a heating rate of 2.5°C/min. Dynamic mechanical analyses (DMA) were performed on a DuPont Model 982 DMA unit with a Model 1090 thermal analyser at a heating rate of 5°C per minute on a polymer specimen with 3.34 mm x 6.37 mm x 12.2 mm dimensions.

A DuPont 990 thermal analyser was used for the differential scanning calorimetry (DSC) measurements, at a temperature program of 10°C/min. Flexural strength and moduli of the specimens were determined in accordance with ASTM procedure D790 using an Instron TTC M1 testing machine.

Polymer Synthesis

The experimental epoxy monomers used are illustrated in Figure 1.

Figure 1 - Experimental Epoxy Monomers

The experimental epoxy systems were compared to a standard epoxy system based on the 4,4'-tetraglycidylmethylenedianiline (TGMDA) monomer. The experimental epoxides with the $-SO_2-$ bridge were the 3,3'- and 4,4'-isomers of tetraglycidylsulfonyldianiline (TGDDS) and the 3,3'-isomer of TGMDA.

The standard TGMDA epoxy system used in this study was acquired from Ciba-Geigy Corporation as Araldite MY-720 with an epoxy content[7-9] of 97%. The major constituent of MY-720 is 4,4'-TGMDA (Figure 2).

Monomer Synthesis

4,4'-Sulfonylbis[N,N-bis(2,3-epoxypropyl)]aniline, 4,4'-TGDDS

A mixture of bis(4-aminophenyl)sulfone (101g, 0.407 mol), 22 ml of glacial acetic acid, and epichlorohydrin (400 ml, a 212% excess) was heated in a 3-neck flask equipped with a Trubore stirrer for 27 hours at 48-60°C. The solvent and excess epichlorohydrin were removed on a flash evaporator for 2 hours at 55°. Methyl ethyl ketone (300 ml) was added, and the resulting solution was treated with 299g of aqueous 45% NaOH solution (a 10% excess). The NaOH solution was added incrementally during 1 hour while refluxing, and the reflux was maintained for 1 hour. On cooling, a small amount of white, low molecular weight polymer was removed by filtration, and the pH of the filtrate was adjusted to 7 with a small amount of HCl. After drying with anhydrous $MgSO_4$, the methyl ethyl ketone was removed in vacuo for 2 hours at 57°C. The yield was 114 g (59%); the average epoxy content was 74%.

3,3'-Sulfonylbis[N,N-bis(2,3-epoxypropyl)]aniline, 3,3'-TGDDS Modified Procedure

The bis(3-aminophenyl)sulfone (131 g, 0.528 mol) was dissolved in 550 ml epichlorohydrin and 30 ml glacial acetic acid. The mixture was heated for 30 hours at 55-60°C before the volatiles were removed in vacuo at 60° for 2 hours. Methyl ethyl ketone (300 ml) was added and the solution was treated at once with 262 g of 50% aqueous NaOH solution (a 100% excess). A temperature of 50-60°C was maintained for 2.5 hours before a white polymer was filtered and discarded. The filtrate was washed with water and then with HCl to adjust the pH of the aqueous layer from 14 to 5. After separation of the layers, the methyl ethyl ketone solution was dried, and the solvent was removed on the flash evaporator. The final heating stage was 0.5 hour at 78°C. The yield of viscous, amber oil was 216 g (87%). The epoxy content was 93%.

3,3'-Methylenebis[N,N-bis(2,3-epoxypropyl)]aniline, 3,3'-TGMDA

Using a similar procedure as in the previous examples a sample of this monomer was prepared from 3,3'-methylenedianiline and epichlorohydrin in aqueous ethanol at reflux for 20 hours; 50% NaOH solution was used to cyclize the chlorohydrin intermediate. After removal of the ethanol in vacuo, methylene chloride was added, and the aqueous layer was neutralized with HCl. The methylene chloride layer was washed with water and dried with anhydrous $MgSO_4$ before the solvent was removed in vacuo to yield 85 g (90%) of product having an average epoxy content of 75%.

The experimental monomers and the baseline MY-720 resin were cured with both the 3,3'- and 4,4'-isomers of DDS. All samples were mixed ultrasonically until they were transparent, as described in reference 6.

Sample Cure

After ultrasonic mixing, the resins were poured into flat bottomed aluminum pans 57 mm in diameter. All samples were placed in an oven and cured according to the cycle illustrated in Figure 3.

3. Results and Discussions

Polymer Characterization

Apparent glass transition temperature (Tg) measurements by the penetration method are listed in Table 1 along with TGA data. The Tg's for the systems that were studied ranged from 183°C to 265°C. In the case of the 4,4'-TGDDS cured with 4,4'-DDS, the lower epoxide equivalent system (63%) had a Tg of 213°C, verses 265°C for the higher epoxide equivalent (74%) system. The TGA data shows the temperature at which each sample had lost 50% of its original weight, when heated in static air at a 2.5°C/min.

Weight loss TGA data is illustrated in Figure 4. All of the systems showed similar behavior with decomposition beginning around 250°C. Figure 5 compares the DMA behavior of each system. All systems showed a transition around -40°C; however, the high temperature transitions began at different temperatures from 150°C to 300°C. DSC curves in Figure 6 show the exothermic behavior of each cured material. The presence of an exotherm indicates that a complete cure had not occurred. This was evident in all except two cases. Based on previous studies in this laboratory these residual exotherms are no more than artifacts of the original cure.

Mechanical Testing

Flexural strengths (Table 2) were good in comparison to the standard system for the experimental polymers, especially for the 4,4'-TGDDS systems. Baseline MY-720 strengths were comparable with those in reference 6.

As can be seen in Tables 1 and 2, there is a difference in the mechanical properties of the two samples of 4,4'-TGDDS that were cured with 4,4'-DDS. The sample with the lower epoxide content exhibited lower strength and modulus than the sample made with higher epoxide content. This may be attributed to a lower crosslink density in the 63% epoxide material.

The exceptionally high modulus value for the 3,3'-TGMDA epoxide cured with 4,4'-DDS can most likely be attributed to a more complete cure. This material exothermed severely during its cure cycle. In one case the exotherm was so intense that the sample burned and was discarded. Excessive curing of crosslinking systems generally leads to high moduli with accompanying losses in strength.

Particularly noteworthy are the properties obtained from the TGDDS epoxides. In all cases the moduli are higher than for the standard MY-720/4,4'-DDS system. For structural resins, modulus is very important. In particular, the 4,4'-TGDDS cured with 3,3'-DDS had a 29% higher modulus and also a 12% higher flexural strength.

Another structure-property relationship that is evident from Table 1 is that the 3,3'-epoxide always afforded a lower glass transition temperature than the corresponding 4,4'-epoxide. This was true for the TGMDA and TGDDS systems.

Conclusions

Three novel epoxides were prepared and cured with two standard curing agents. The properties of the experimental systems compared favorably to a standard epoxide system (MY-720/4,4'-DDS). All of the experimental systems exhibited higher flexural moduli than the standard. This is an important property for structural resins. There were some differences in glass transition temperatures with the 3,3'-epoxy system always having a lower transition than the corresponding 4,4'-epoxy system. The polymer decomposition temperatures were all quite similar. In all cases the ultrasonic mixing technique afforded very uniform, homogeneous mixtures. However, during subsequent cures some systems tended to exotherm more than others. Results of this research indicate that the 4,4'-TGDDS is a promising system and is worthy of additional study because of higher glass transition temperatures and good mechanical properties.

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Table 1
Physical Properties of Epoxy Formulations

Epoxy Monomer	4,4'TGMDA (MY-720)	4,4'TGMDA (MY-720)	3,3'TGDDS	3,3'TGDDS	4,4'TGDDS	4,4'TGDDS	3,3'TGMDA	4,4'TGDDS
Curing Agent	3,3'DDS	4,4'DDS	3,3'DDS	4,4'DDS	3,3'DDS	4,4'DDS	4,4'DDS	4,4'DDS
Apparent Glass Transition Temperature Tg (TMA)	217°C	213°C	193°C	207°C	237°C	265°C	183°C	213°C
Temperature for 50% Weight Loss	456°C	468°C	468°C	467°C	475°C	473°C	454°C	473°C
Epoxide Equivalent, %	97	97	93	93	74	74	75	63

Table 2
Mechanical Properties of Epoxy Formulations

Epoxy Monomer	4,4'TGMDA (MY-720)	4,4'TGMDA (MY-720)	3,3'TGDDS	3,3'TGDDS	4,4'TGDDS	4,4'TGDDS*	3,3'TGMDA	4,4'TGDDS**
Curing Agent Flexural	3,3'DDS	4,4'DDS	3,3'DDS	4,4'DDS	3,3'DDS	4,4'DDS	4,4'DDS	4,4'DDS
Flexural Pa Strength, (ksi)	164 (23.8)	155 (22.5)	139 (20.2)	135 (19.6)	174 (25.2)	143 (20.8)	136 (19.7)	135 (19.6)
Standard Deviation	23 (3.3)	13 (1.9)	10 (1.4)	14 (2.0)	14 (2.0)	38 (5.5)	10 (1.4)	23 (3.3)
Flexural Pa Modulus, (ksi)	4070 (590)	3670 (532)	5220 (757)	5230 (758)	4720 (685)	4190 (607)	5050 (733)	3930 (570)

*Epoxide Equivalent - (74%)
**Epoxide Equivalent - (63%)

Figure 1 - Experimental Epoxy Monomers

Figure 2 - Standard Epoxy Monomer: 4,4'-Tetraglycidylmethylenedianiline (TGMDA)

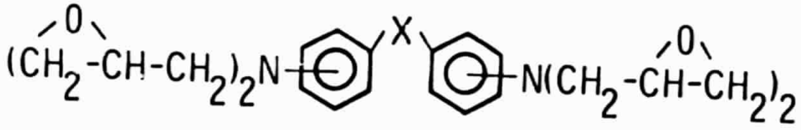
Figure 3 - Cure Cycle for Resin Disks

Figure 4 - Thermogravimetric Analysis (TGA) of Cured Epoxy Systems

Figure 5 - Dynamic Mechanical Analysis (DMA) of Cured Epoxy Systems

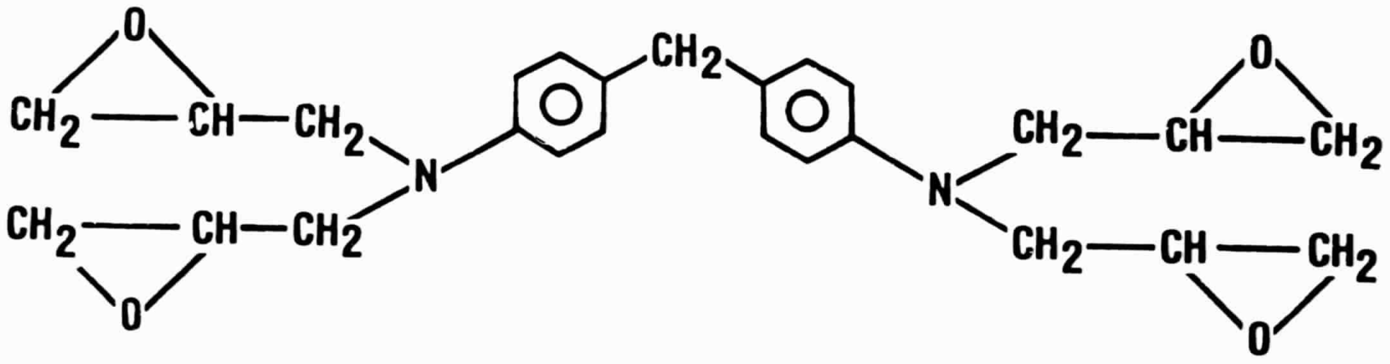
Figure 6 - Differential Scanning Calorimetry (DSC) of Cured Epoxy Systems

Fig 1



X = -CH_2- and -SO_2-
with 3, 3'- and 4, 4'- attachments

Fig 2



APPEARANCE: VISCOUS AMBER LIQUID

Fig 3

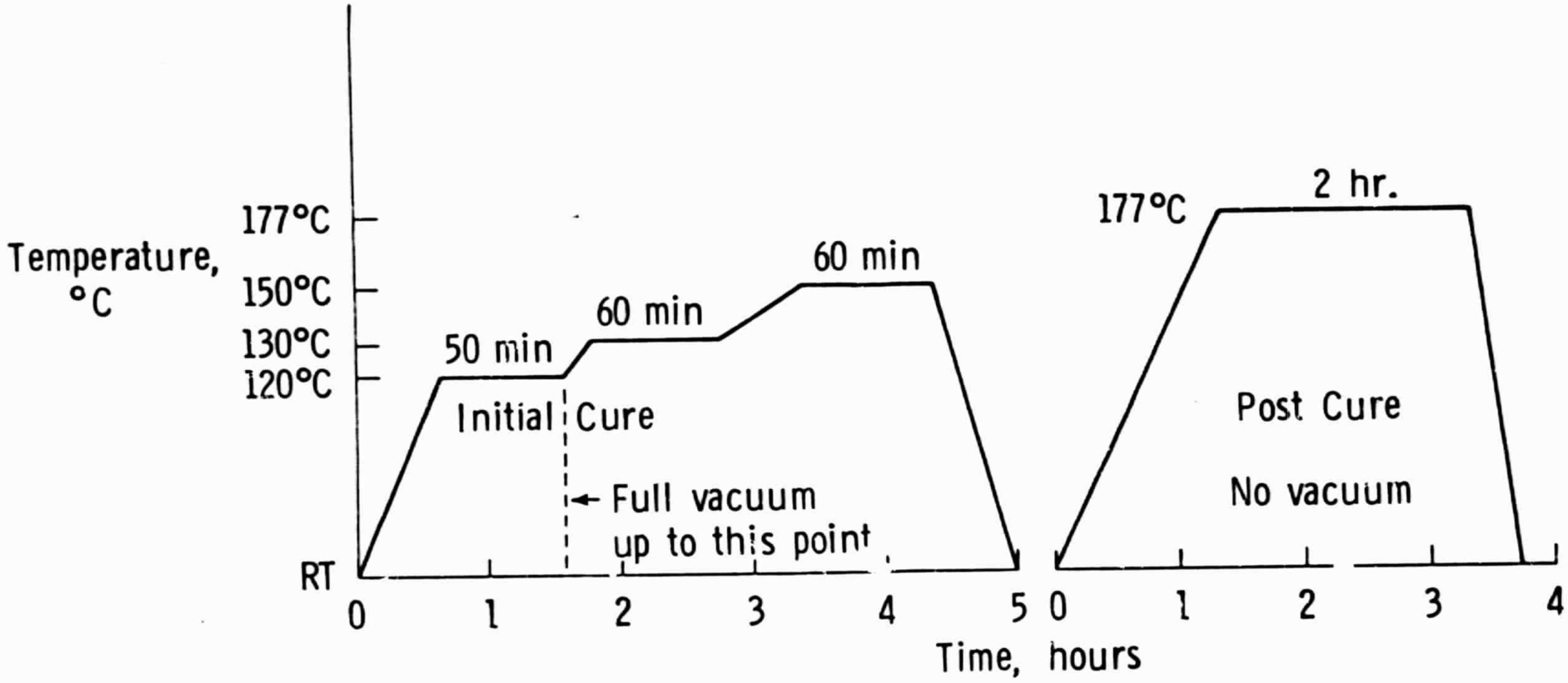

Temperature, °C
177°C
150°C
130°C
120°C
RT
50 min
60 min
60 min
Initial
Cure
← Full vacuum up to this point
177°C
2 hr.
Post Cure
No vacuum
0
1
2
3
4
5
0
1
2
3
4
Time, hours

Fig 4

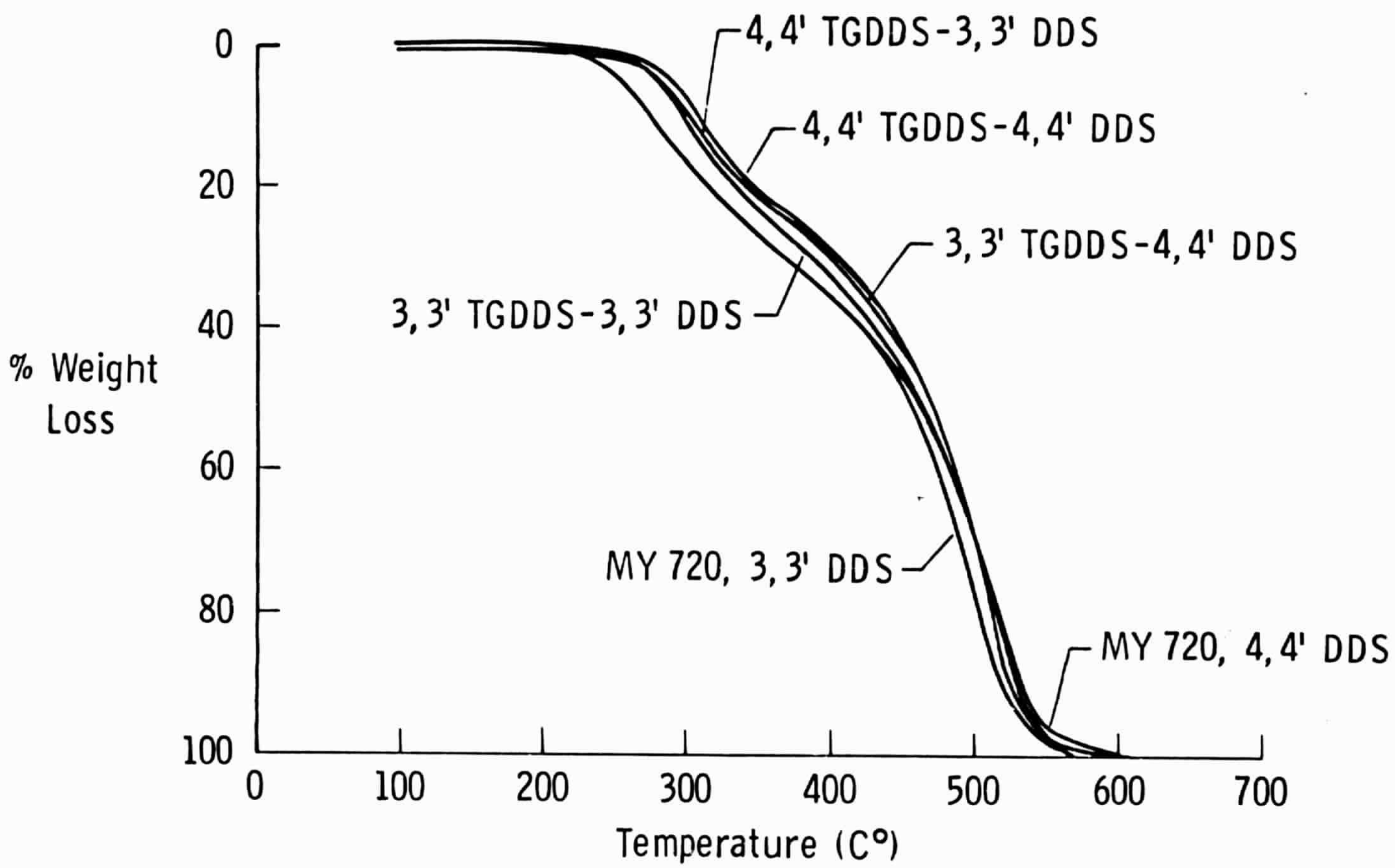

4,4' TGDDS-3,3' DDS
4,4' TGDDS-4,4' DDS
3,3' TGDDS-4,4' DDS
3,3' TGDDS-3,3' DDS
MY 720, 3,3' DDS
MY 720, 4,4' DDS
% Weight Loss
0
20
40
60
80
100
0
100
200
300
400
500
600
700
Temperature (C°)

Fig. 5

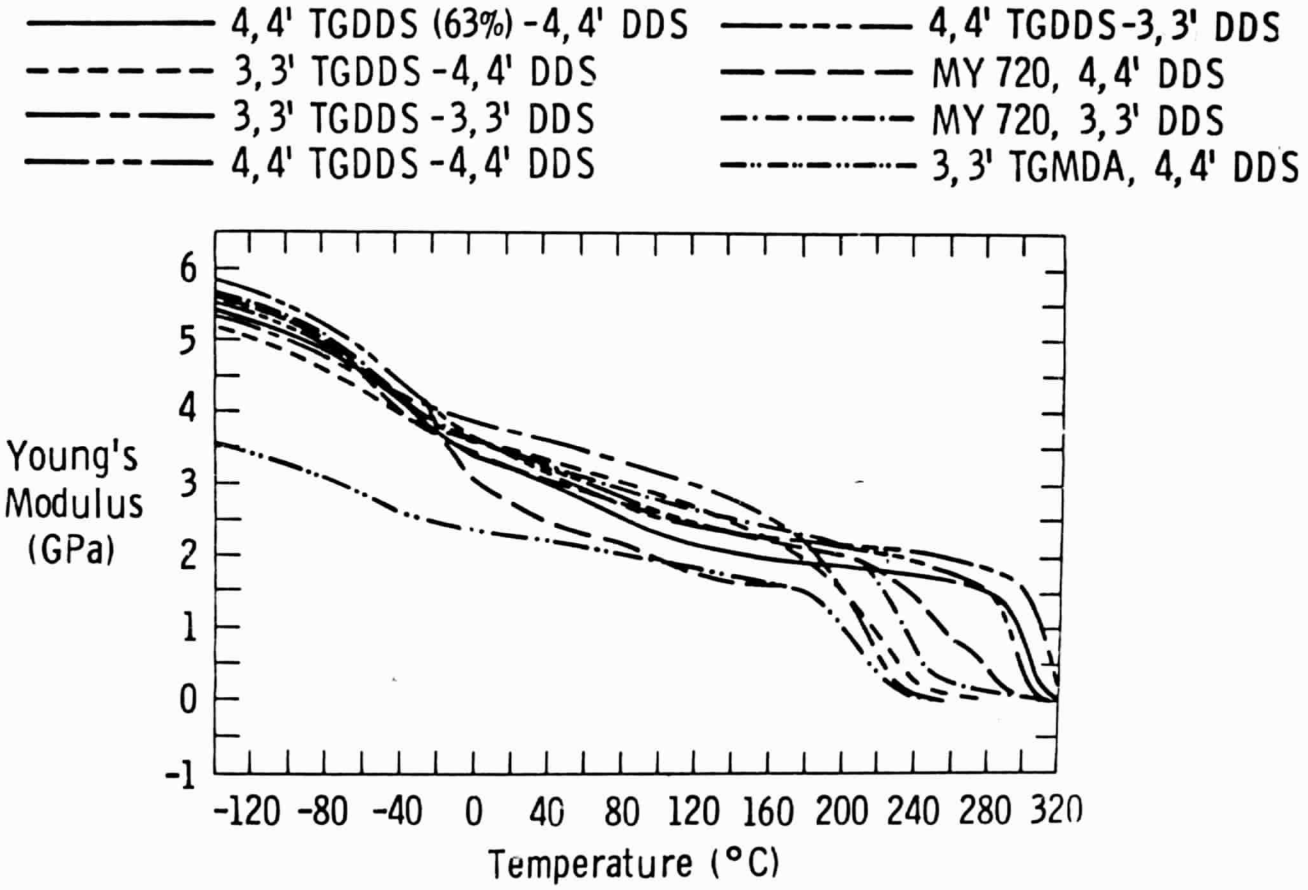
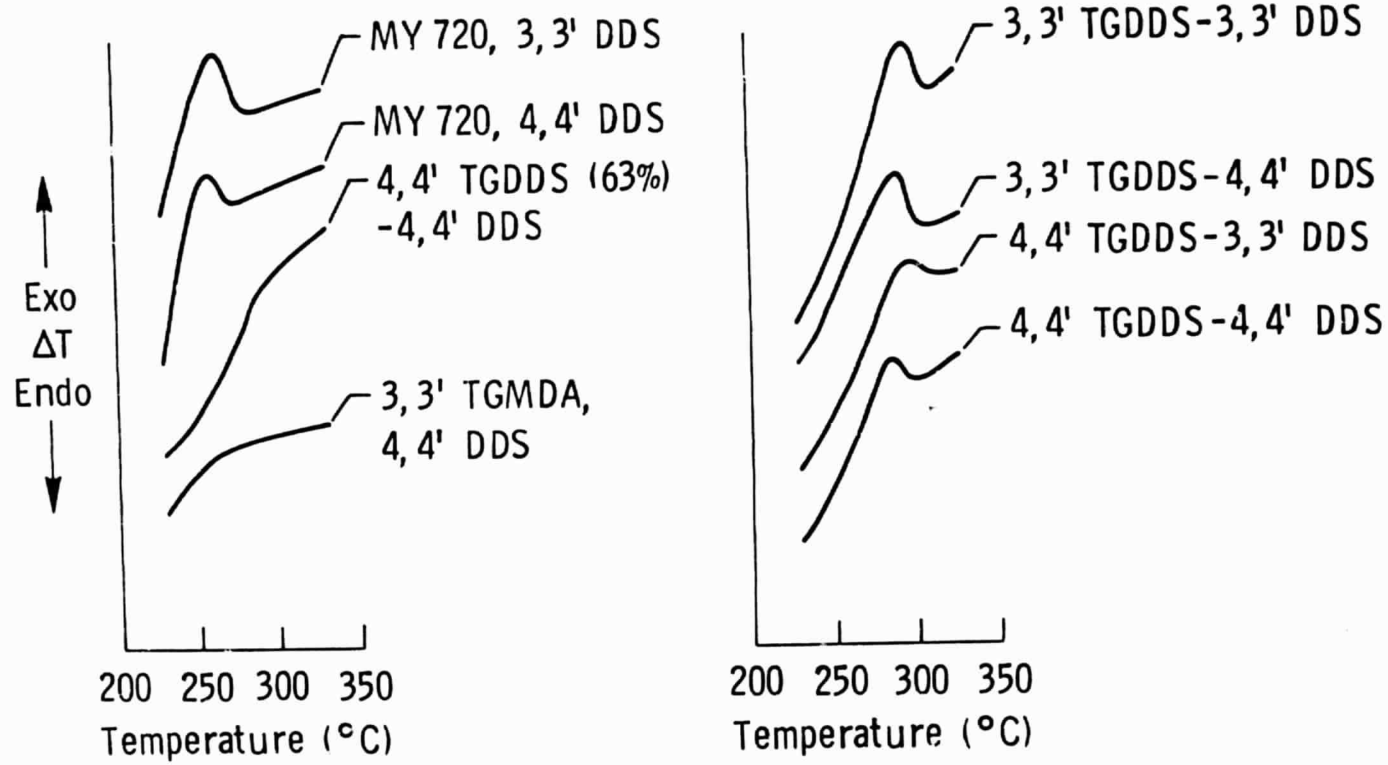

4,4' TGDDS (63%) -4,4' DDS
3,3' TGDDS -4,4' DDS
3,3' TGDDS -3,3' DDS
4,4' TGDDS -4,4' DDS
4,4' TGDDS-3,3' DDS
MY 720, 4,4' DDS
MY 720, 3,3' DDS
3,3' TGMDA, 4,4' DDS
Young's Modulus (GPa)
6
5
4
3
2
1
0
-1
-120
-80
-40
0
40
80
120
160
200
240
280
320
Temperature (°C)

Fig. 6


MY 720, 3,3' DDS
MY 720, 4,4' DDS
4,4' TGDDS (63%) -4,4' DDS
3,3' TGMDA, 4,4' DDS
Exo
ΔT
Endo
200
250
300
350
Temperature (°C)
3,3' TGDDS-3,3' DDS
3,3' TGDDS-4,4' DDS
4,4' TGDDS-3,3' DDS
4,4' TGDDS-4,4' DDS
200
250
300
350
Temperature (°C)