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# CRYOGENIC COMPRESSIVE PROPERTIES OF BASIC EPOXY RESIN SYSTEMS*

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September 1985

*Presented at the 1985 Cryogenic Engineering Conference and International Cryogenic Materials Conference, Massachusetts Institute of Technology, Cambridge, Massachusetts, August 12-16, 1985.

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## ABSTRACT

The compressive properties of short cylindrical samples of many different epoxy resin systems have been measured at ambient temperature and at 77 degrees Kelvin. These are pure resin systems of known chemistry, without the inorganic fillers or fibrous reinforcements needed in final cryogenic systems. Of course, chemically incorporated modifiers such as flexibilizing resins have been included. This data should make possible inferences about cryogenic properties from molecular structures and provide specific data useful to formulators and end users.

Measurements on some other plastics such as PTFE, Polyimides, and UHMWPE have been made for comparison purposes.

## INTRODUCTION

Epoxy resin systems have been widely used in the construction of superconducting coils and other cryogenic apparatus. Fiber reinforced laminates such as NEMA grades G-10 and G-11, heavily filled room cured putties, and "B-staged" adhesives have been popular. Studies of the mechanical cryogenic properties of many useful systems have been presented at these conferences.[1,2,3,4,5,6,7]

The practical focus of much testing has been on proprietary, commercial systems. There has been a need for additional data on simple matrix systems of known constituents.

## EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 shows the overall arrangement of the apparatus in the Instron testing machine. Everything is supported through an insulating rod of G-10 by the load cell on the stationary frame of the machine. The moveable crosshead of the machine applies the load through another insulating rod of G-10 to the sample clamped between steel plates. The surrounding foam insulated steel container can be filled with liquid nitrogen. Two glass tubes transmit relative motions to the linear variable differential transformer located above the crosshead. The inner tube rests on the lower steel compression member, and the outer tube rests on a thin steel washer on top of the sample. Figure 2 shows the details of the sample and its surroundings. The iron core of the LVDT may be adjusted for zero output with the plastic extension and the threaded attachment of the core to the inner glass tube. The output of the load cell amplifier and the LVDT read-out are connected to an analogue X-Y recorder. Data have been manually digitized and entered into the central computer for further manipulations and analysis. All stress-strain curves have a manually fitted slope and a subsequent shift of strain values to give a consistent 0,0 intercept. This procedure eliminates small effects of sample end deviation from a true flat and parallel condition.

The sample is loaded into the apparatus, and a room temperature stress-strain curve taken with care not to exceed the yield point. The load is then reduced to zero and the container filled with liquid nitrogen. A shrinkage measurement is taken before reloading. The springs between the steel plates assure contact with the sample during cooldown. These shrinkage measurements are reported here, but should be used with caution since the thermal-mechanical shock of filling can cause the glass tubes to move on their support areas with resulting errors.

When rapid boiling subsides in the liquid nitrogen, the sample is reloaded - this time it is taken to ultimate failure. The failure is sudden, and accompanied by a loud report. Failure often causes breaking of the glass tubes which is why quartz was not used. During loading, cracking noises are often heard and are accompanied by discontinuities in the stress measurement. The modulus measurement is not disturbed by these events, but they are probably responsible for the large variation in ultimate stress and strain values. They are most serious for the weak and brittle samples. Very careful machining of the samples may reduce their occurrence.

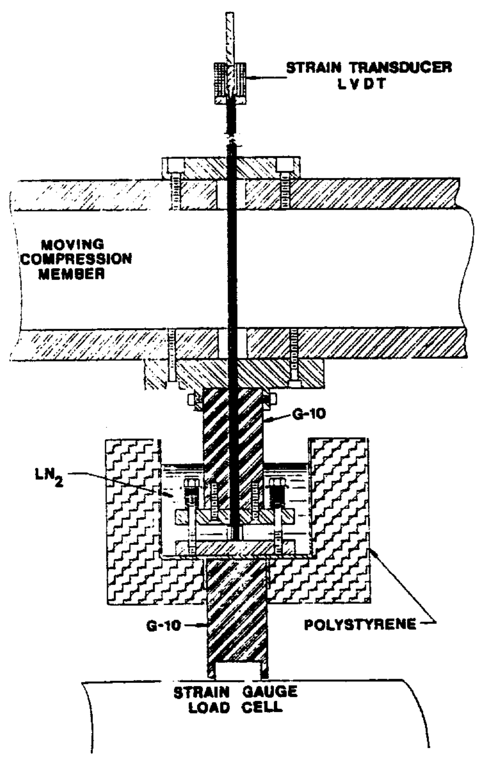



Fig. 1. Test apparatus

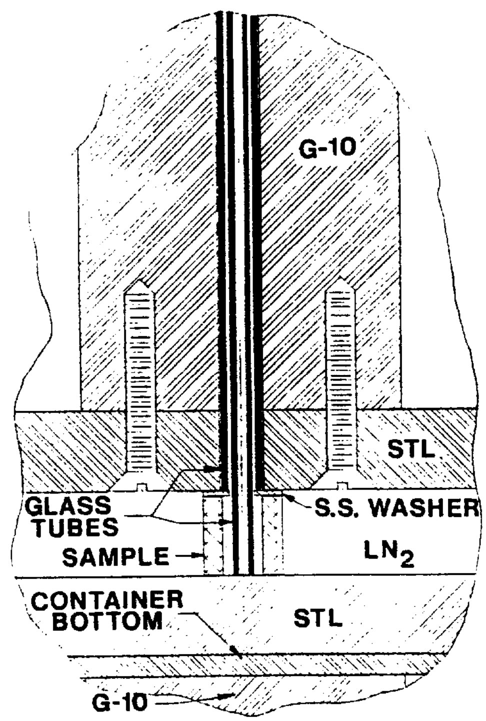



Fig. 2. Sample detail

## MATERIALS



The materials used in this study have been the standard commercial epoxy resin (DGEBA) and its minor variations, combined with many different curing agents. Each major chemical category of curing agent has been represented. The materials are identified in Table I by chemical name, by structure formula, and by a shorthand code, often an acronym. Only the hydrogen atoms active in the curing reactions are shown in the structural formulas. Epoxy resin and flexibilizing agent structural formulas are also shown. Inclusion of this detail should encourage analysis of the data in terms of chemical structure by the readers.

Figure 3 is a graph of the difference between the 77 K modulus and the 300 K modulus versus the 300 K modulus. It shows a general trend for the change in the modulus to be inversely proportional to room temperature modulus. The 77 K modulus tends to be constant and independent of the 300 K modulus. Flexibilizing agents that greatly reduce the warm modulus do not affect this cold modulus. In fact, they usually cause a slight increase in the cold modulus. Even the variations in warm modulus within a system are "frozen out" at low temperatures. Specifically DER 732 increases the cold modulus of a TETA cured system; castor oil increases the cold modulus of an EM 308 cured system; and EMPOL 1040 increases the modulus of a DDSA cured system. This is consistent with the observation reported by Elkin, et al.[7] in 1983 at these Conferences, "The addition of flexibilizers to the epoxy systems also produced no improvement in 4 K properties - - -."

## RESULTS AND CONCLUSIONS

Figures 4, 5, and 6 show the stress-strain curves grouped into general areas. Real differences between systems are apparent. The aromatic amine (Shell Z) gives greater elongations than the group of aliphatic amines. The aliphatic amine TETA gives a higher modulus and greater elongation than all the rest of the aliphatic amines, including the structurally similar DETA. Table 2 gives the actual measured data in detail for design use by the cryogenic materials engineer.

The catalytic curing agents give lower moduli and greater elongations than the aliphatic amines. BDMA is even better than DMP-30 in this regard. In fact, it gives the greatest elongations of any epoxy system. The catalyst BF3-400 showed a lot of scatter in modulus and elongation, but its room temperature latency can be so valuable as to commend it for further study. The catalyst Shell D should be similar to DMP-30. The amido-polyamines of low molecular weight behaved like the better aliphatic amines, while higher molecular weights gave lower moduli, but disappointingly smaller elongations.

The anhydrides have smaller elongations than the BDMA system, but also show a trend toward smaller moduli. The modulus of the HHPA, PA, and MTHPA systems equals that of the BDMA, but the NMA systems moduli are lower, and the DDSA gives the lowest modulus of any epoxy system. The anhydrides show more scatter than other systems. Perhaps this is due to the complexity of their chemical reactions. They should be sensitive to epoxy/anhydride ratio, type of catalyst, presence of -OH initiators including water, and cure schedule. However, they show a lot of promise should these variables be carefully controlled and studied.

Selected thermoplastics showed much lower moduli and very much greater elongations, but the rigid brittle nature of polymethylmethacrylate (PMMA) warns against any hasty conclusion that eliminating cross-links will give a flexible low temperature material.

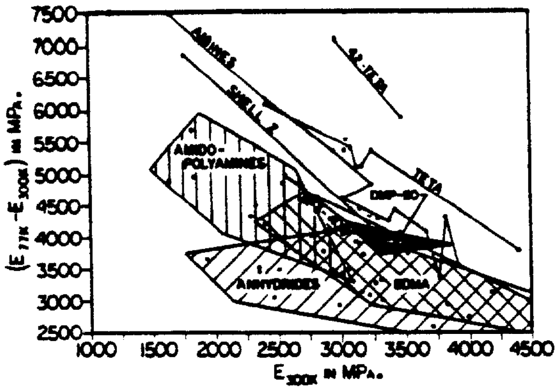



Fig. 3. Modulus change

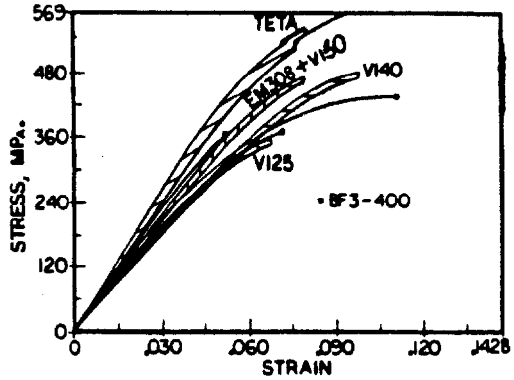



Fig. 4. TETA and amido amines

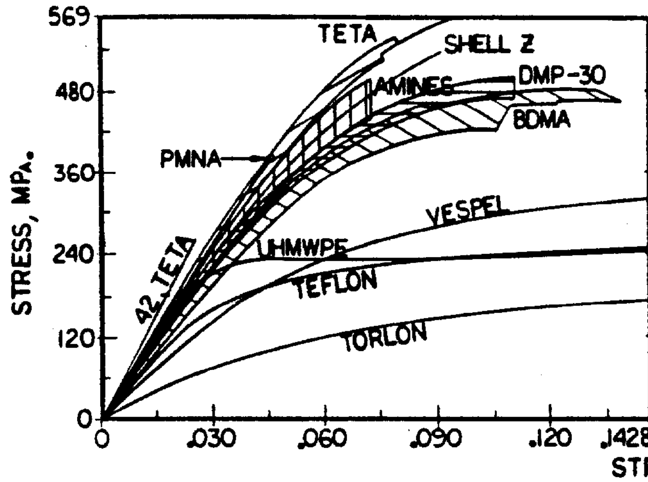



Fig. 5. TETA and miscellaneous systems

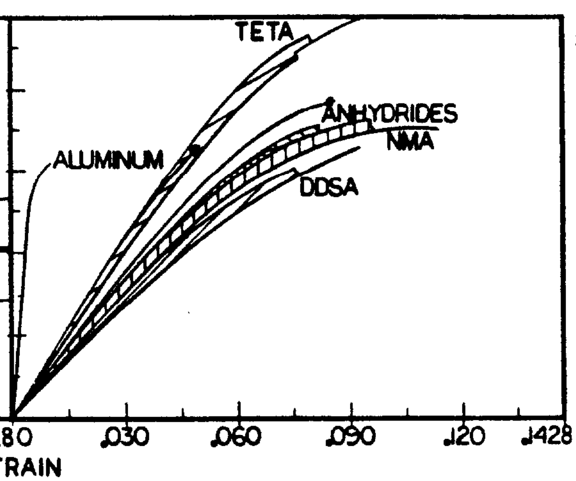



Fig. 6. TETA and anhydrides

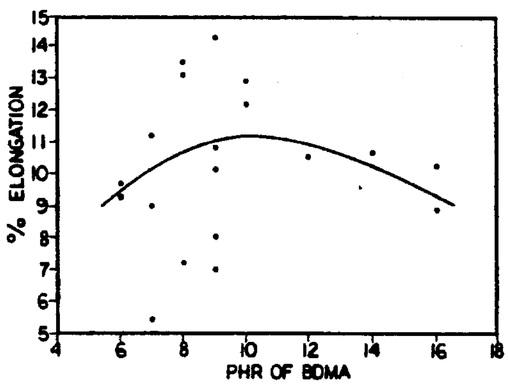



Fig. 7. Maximizing elongation

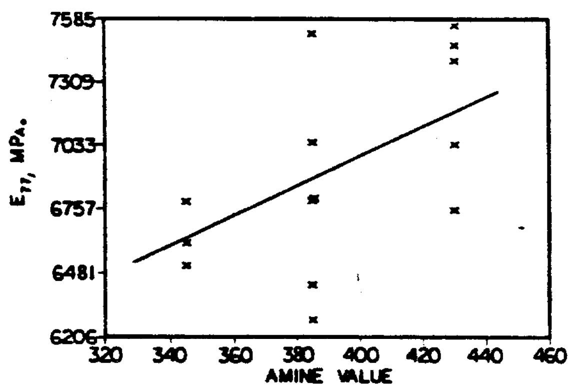



Fig. 8. Molecular weight influence

In fact, the two samples of 42 Phr TETA tested can be expected to give very low cross-link densities since the primary amine hydrogens are much more reactive than the secondary amine hydrogens. Their low elongations are probably only indicative of low molecular weight. However, their high moduli (like PMMA) again shows low cross-link density does not necessarily give high elongation. It is evident that the broad category of thermoplastics must be studied with reference to polarity, chain length, chain branching, chain structure and rigidity, crystality, and molecular weight. UHMWPE, polytetrafluoroethylene, and polymides should be very useful but difficult to use with fillers, or to mold, cast, use as adhesives, etc.

The aluminum curve is given for reference and was not taken to destruction. Figure 7 shows the variations of elongation with curing agent concentration for the catalyst BDMA. It has a broad curve with a peak around 10 Phr. Figure 8 gives the cold elastic modulus of the amido-polyamine systems versus amine numbers, which are inversely related to curing agent molecular weight. A reasonable correlation is shown. However, the high molecular weight resin 1001, when cured with PA, was not appreciably different from the low molecular weight resins cured with HHPA or MTHPA. In spite of their scatter the shrinkage measurements show a definite inverse relationship between shrinkage and 300 K elastic modulus.

SUMMARY

1. Adding 3 common flexibilizing agents actually causes slight increases in 77 K modulus.

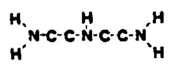
2. Epoxy systems ranked in order of decreasing modulus at 77 K are TETA > aliphatic amines and aromatic amines > DMP-30 > BDMA > most anhydrides > DDSA > selected thermoplastics.

3. Epoxy systems ranked in order of increasing elongation at 77 K are aliphatic amines < all others < BDMA < selected thermoplastics.

4. Improvements in cryogenic properties of epoxy resins can be achieved and additional research is encouraged.

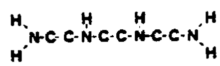
Table 1. Structural Formulas

DETA



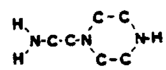
Diethylene triamine

TETA



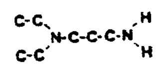
Triethylene tetramine

AEP



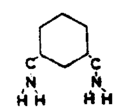
Aminoethyl piperazine

DEAPA



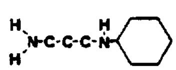
Diethyl aminopropyl amine

BAC



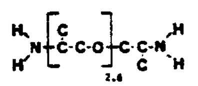
1,3-Bis (aminomethyl) cyclohexane

POLYCAT - 352



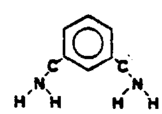
N (3 aminopropyl) cyclohexylamine

D230



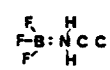
Polyoxypropylene diamine

MXDA



m-Xylylene diamine

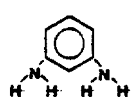
$BF_3$-400



Boron trifluoride-monoethylamine

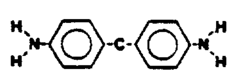
SHELL Z

MPDA 70%



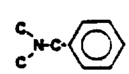
m-Phenylene diamine

MDA 30%



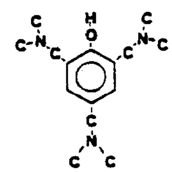
4,4'-Methylene dianaline

BDMA



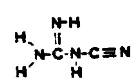
Benzyl dimethyl-amine

DMP 30



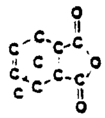
Tris (dimethyl-aminomethyl)-phenol

DICY



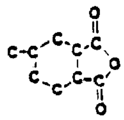
Dicyan-diamide

NMA



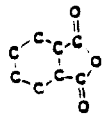
Nadic methyl anhydride

MTHPA



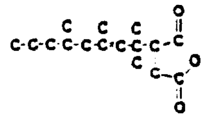
Methyl-tetrahydro-phthalic anhydride

HHPA



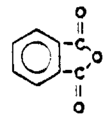
Hexahydro-phthalic anhydride

DDSA



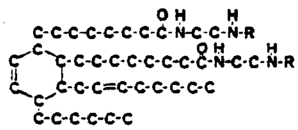
Dodecenyl-succinic anhydride

PA



Phthalic anhydride

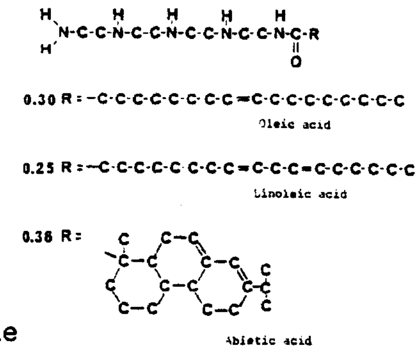
AMIDOPOLYAMINE V150
V140
V125



R=H or another dimer

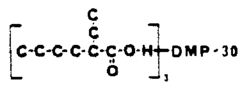
Dimerized linoleic acid & ethylenetriamine

AMIDOPOLYAMINE EM 308



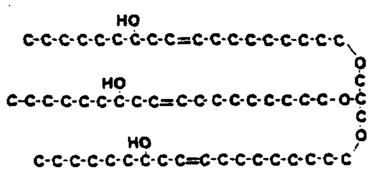

Tall oil fatty acid with tetraethylenepentamine

SHELL D



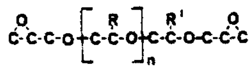

Tri(2 ethylhexoate) salt of tri[dimethyl(amino methyl)]phenol

CASTOR OIL



Triglyceride of ricinoleic acid

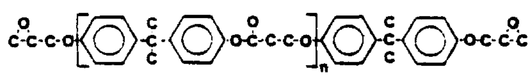
DER 732



R and R¹ may be methyl
n may be about 9

Diglycidyl ether of polypropylene glycol

DER 331, 332 and Shell 826, 828, 1001, and BIS-F



Diglycidylether of bisphenol A and higher homologues

For 332 and 826 n ≅ 0
For 331 and 828 n ≅ 0.13
For 1001 n ≅ 2.5

For BIS-F n ≅ 0 and the 3 carbon chain is reduced to 1

Table 2. Compressive Properties of Epoxy Resins

| Cure Agent/ Addit. | PHR Agent/ Addit. | 300 K Mod MPa | 77 K Mod MPa | σ Ult 77 K % | ε ULT 77 K | Λ L % | Resin/ Sample/ Addit. | °C-hr* /post Cure | ∫σdε MPa |
|---|---|---|---|---|---|---|---|---|---|
| Z | 20 | 3320 | 7380 | 523 | 10.2 | .73 | 332-1 | /65-2 | 32.4 |
| Z | 20 | | 7580 | 519 | 10.6 | .75 | 332-2 | /65-2 | 34.2 |
| Z | 20 | 1740 | 8620 | 516 | 7.4 | .70 | 826 | /65-2 | 20.2 |
| AEP | 24.7 | 2890 | 7510 | 416 | 6.6 | .79 | 332 | /65-16 | 14.0 |
| BAC | 16.0 | 3890 | 7450 | 415 | 6.6 | .77 | 332-1 | /65-21 | 14.9 |
| BAC | 16.0 | 3740 | 7100 | 407 | 6.0 | .75 | 332-2 | /65-21 | 13.2 |
| DEAPA | 6.0 | 3360 | 7580 | 425 | 7.1 | .86 | 332 | 72/65-24 | 17.0 |
| DETA | 12.1 | 3400 | 7860 | 361 | 4.9 | .90 | 332 | * | 9.0 |
| D230 | 30.0 | 3680 | 7790 | 459 | 7.4 | .84 | 332 | /65-4 | 18.7 |
| MXDA | 15.0 | 3810 | 8130 | 478 | 7.0 | .77 | 332 | /65-21 | 18.5 |
| POLYCAT | 30.0 | 2920 | 8270 | 275 | 4.0 | .75 | 332 | 16/100-3 | 5.8 |
| U | 25.0 | 2390 | 8550 | 563 | 10.3 | .77 | 332-1 | /65-16 | 36.3 |
| U | 25.0 | 3230 | 8070 | 426 | 6.1 | 1.76 | 331-2 | /65-16 | 13.2 |
| U/732 | 33/33 | 1630 | 9100 | 385 | 5.4 | 1.50 | 331-732 | /65-16 | 10.7 |
| TETA | 14.0 | 3061 | 8480 | 576 | 10.2 | .87 | 332-1 | 6/65-15 | 36.4 |
| TETA | 14.0 | 2410 | 8550 | 456 | 6.0 | .62 | 332-2 | * | 14.2 |
| TETA | 13.0 | 3100 | 8340 | 411 | 5.6 | | 331 | * | 13.6 |
| TETA | 15.4 | 3150 | 8410 | 492 | 2.7 | .74 | BIS-F | * | 21.5 |
| TETA732 | 15/33 | 3230 | 8620 | 540 | 7.8 | .76 | 331-732 | * | 4.6 |
| TETACGE | 17/33 | 4390 | 8200 | 428 | 5.8 | | 331 | * | 14.4 |
| TETA | 42.0 | 2910 | 10000 | 254 | 2.5 | .72 | 332-1 | * | 3.2 |
| TETA | 42.0 | 3440 | 9310 | 256 | 2.5 | .80 | 332-2 | * | 3.3 |
| BDMA | 6.0 | 3130 | 7030 | 443 | 9.3 | .84 | 332-1 | 64/65-4 | 25.2 |
| BDMA | 6.0 | 2760 | 6750 | 449 | 9.6 | .79 | 332-2 | 64/65-4 | 26.5 |
| BDMA | 7.0 | 4480 | 7100 | 345 | 5.4 | 1.59 | 332-1 | 4/65-4 | 10.3 |
| BDMA | 7.0 | 3990 | 7450 | 445 | 9.0 | .65 | 332-2 | 4/65-4 | 22.4 |
| BDMA | 7.0 | 2870 | 6960 | 443 | 11.3 | .64 | 332-3 | 4/65-4 | 30.0 |
| BDMA | 8.0 | 4180 | 7310 | 397 | 7.2 | .63 | 828 | 16/65-4 | 15.9 |
| BDMA | 8.0 | 3300 | 6300 | 464 | 13.1 | .81 | 332-1 | 16/65-4 | 41.1 |
| BDMA | 8.0 | 3040 | 6530 | 465 | 13.5 | .82 | 332-2 | 16/65-4 | 41.5 |
| BDMA | 9.0 | 3810 | 6740 | 376 | 7.0 | .79 | 332-1 | /65-4 | 14.8 |
| BDMA | 9.0 | 3100 | 7030 | 444 | 10.2 | .85 | 332-2 | /65-4 | 28.8 |
| BDMA | 9.0 | 3090 | 7170 | 450 | 14.2 | .67 | 332-3 | /65-4 | 45.0 |
| BDMA | 9.0 | 2390 | 6700 | 399 | 8.0 | .65 | 332-4 | /65-4 | 16.6 |
| BDMA | 9.0 | 2900 | 7170 | 447 | 10.8 | .62 | 332-5 | /65-4 | 30.3 |
| BDMA | 10.0 | 3030 | 8550 | 461 | 12.2 | .85 | 332-1 | 16/65-4 | 41.5 |
| BDMA | 10.0 | 3080 | 6960 | 440 | 12.9 | .80 | 332-2 | 16/65-4 | 37.3 |
| BDMA | 12.0 | 3400 | 7100 | 458 | 10.6 | .77 | 332 | 16/65-4 | 29.6 |
| BDMA | 14.0 | 2900 | 6960 | 439 | 10.6 | .88 | 332 | /80-1 | 30.1 |
| BDMA | 16.0 | 2800 | 7450 | 439 | 8.9 | .86 | 332-1 | 16/65-4 | 24.2 |
| BDMA | 16.0 | 2850 | 6630 | 410 | 10.3 | .89 | 332-2 | 16/65-4 | 28.11 |
| DMP-30 | 6 | 3170 | 7240 | 429 | 8.2 | .81 | 332 | /80-1 | 21.0 |
| DMP-30 | 8 | 3300 | 7030 | 450 | 10.3 | .69 | 332 | /80-1 | 28.7 |
| DMP-30 | 10 | 3040 | 7240 | 458 | 11.4 | .74 | 332 | /80-1 | 33.9 |
| DMP-30 | 12 | 3840 | 7720 | 448 | 9.5 | .70 | 332 | /65-1 | 29.6 |
| DMP-30 | 14 | 3160 | 7310 | 463 | 11.0 | .68 | 332-1 | /65-4 | 32.6 |
| DMP-30 | 14 | 3430 | 7520 | 465 | 10.5 | .84 | 332-2 | /65-1 | 33.4 |
| Shell-D | 12 | 3120 | 7580 | 417 | 6.9 | .78 | 332 | /150-2 | 15.9 |
| BF3-400 | 3 | 2550 | 7520 | 425 | 11.2 | .70 | 332-1 | 120-3 | 30.7 |
| BF3-400 | 3 | 3280 | 7580 | 356 | 5.5 | .76 | 332-2 | | 9.6 |
| BF3-400 | 3 | 3240 | 7100 | 336 | 6.6 | .64 | 332-3 | /200-1 | 11.4 |
| V 150 | 83.6 | 1810 | 7520 | 449 | 7.5 | 1.3 | 332 | 12/65-4 | 18.9 |
| V 140 | 50.0 | | 6280 | 270 | 4.6 | 5.9 | 331 | 24 | 5.8 |
| V 140 | 83.6 | 2990 | 6430 | 467 | 9.8 | 1.1 | 332-1 | 12/65-4 | 26.5 |
| V 140 | 83.6 | 2320 | 6810 | 401 | 8.1 | 1.7 | 332-2 | 24 | 18.8 |
| V 140 | 100.0 | | 7030 | 349 | 5.9 | .5 | 331 | 24 | 9.6 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| V 140 | 150.0 | | 6800 | 348 | 6.1 | | 331 | 24 | 11.3 |
| V 125 | 150.0 | 1830 | 6790 | 352 | 6.3 | | 331 | 24 | 11.7 |
| V 125 | 93.3 | 1610 | 6520 | 271 | 4.8 | 1.2 | 332 | 48 | 6.7 |
| V 125 | 100.0 | 2280 | 6610 | 290 | 4.8 | 2.4 | 331 | 24 | 7.4 |
| Em308 | 80.0 | 2520 | 7380 | 460 | 6.6 | 1.3 | 332 | 24 | 20.1 |
| Em308 | 180.0 | | | | | | 826 | 24 | |
| Em308C | 80/20 | | 7580 | 352 | 5.3 | 1.4 | 826-1-C | 24 | 9.4 |
| Em308 | 100.0 | | 6760 | 420 | 4.7 | | 826 | 24 | 6.7 |
| NMA 50-1.5DMP | | 3710 | 6300 | 384 | 7.4 | .90 | 332 | 143-24 | 15.2 |
| NMA 70-1.5DMP | | 3350 | 6220 | 404 | 8.9 | 1.03 | 332 | 143-24 | 21.6 |
| NMA 92-1.5DMP | | 2970 | 7030 | 449 | 8.6 | 1.04 | 332 | 143-26 | 21.9 |
| NMA 102-1.5DMP | | 2970 | 5910 | 410 | 11.3 | 1.09 | 332 | 143-24 | 29.9 |
| NMA 90-2BDMA | | 4000 | 6750 | 419 | 9.4 | .80 | 332-1 | 150-24 | 23.6 |
| NMA 90-2BDMA | | 4910 | 8270 | 371 | 4.8 | .96 | 332-2 | 150-1 | 9.0 |
| NMA 90-5DBVIII | | 200 | 6290 | 404 | 9.8 | .90 | 332-1 | 143-24 | 23.4 |
| NMA 90-5DBVIII | | 3500 | 7240 | 380 | 6.9 | .82 | 332-2 | 143-24 | 13.9 |
| HHPA 80-1.5DMP | | 3170 | 6900 | 412 | 7.9 | 1.04 | 332 | 148-2 | 18.7 |
| MTHPA | 84 | 3290 | 6630 | 411 | 9.5 | .78 | 332 | 79-4 | 19.9 |
| NMA DBVIII | | | | | | | 826 | 150-24 | 10.9 |
| DDSA 138-1.5 DMP | | 2470 | 5530 | 381 | 9.2 | 1.5 | 332 | | 20.2 |
| DDSA 116-201BDM | | 2340 | 5860 | 351 | 7.6 | 1.0 | 332-1-EM | 100-1 | 14.7 |
| DDSA 116-201BDM | | 1930 | 5590 | 346 | 8.5 | 1.3 | 828-1-EM | /150-2 | 14.6 |
| DDSA 116-201BDM | | 2340 | 5820 | 333 | 7.0 | 1.3 | 828-2-EM | | 13.5 |
| PA | 30 | 3540 | 6830 | 363 | 6.3 | .78 | 1001 | 120-4 | 12.1 |
| TEFLON® | | | 6420 | 233 | 16.4 | | | | 31.7 |
| TEFLON® | | | 5830 | 169 | 6.0 | | | | 5.0 |
| TORLON® | | 1570 | 2500 | 188 | 29.9 | 1.2 | | | 29.9 |
| VESPEL® | | | 5110 | 322 | 17.9 | .70 | | | 42.3 |
| PMMACRYLATE | | 3020 | 8410 | 367 | 4.7 | .88 | | | 8.2 |
| UHMWPE | | | 8210 | 325 | 18.6 | | | | 39.7 |
| TETA[1] | 14/90 | 2490 | 5940 | 202 | 3.8 | .78 | 332 | 24 | 3.6 |
| TETA[1] | 14/125 | 3130 | 6270 | 307 | 5.9 | .67 | 332 | 24 | 9.5 |
| TORLON[2] | | 7990 | 12760 | 507 | 4.7 | .29 | | | 12.5 |
| G-10CR[3] | | 15000 | 32200 | | | .26 | | | |
| ALUM | | 69600 | 89600 | | | | | | |

* - Initial cure room temperature - 4 hours. Exceptions noted; [1] - TETA/Torlon; [2] - Torlon - 40% Glass; [3] - G-10 CR Rod

ACKNOWLEDGEMENTS

The work as presented was performed at Fermi National Accelerator Laboratory which is operated by Universities Research Assn. Inc., under contract with the U. S. Department of Energy.

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