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CRYOGENIC COMPRESSIVE PROPERTIES OF BASIC EPOXY RESIN SYSTEMS*

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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

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, crystallinity, and molecular weight. UHMWPE, polytetrafluoroethylene, and polyimides 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

<p>DETA</p> <p>Diethylene triamine</p>	<p>TETA</p> <p>Triethylene tetramine</p>	<p>AEP</p> <p>Aminoethyl piperazine</p>	<p>DEAPA</p> <p>Diethyl aminopropyl amine</p>	<p>BAC</p> <p>1,3-Bis(aminomethyl) cyclohexane</p>
<p>POLYCAT - 352</p> <p>N (3 aminopropyl) cyclohexylamine</p>	<p>D230</p> <p>Polyoxypropylene diamine</p>	<p>MXDA</p> <p>m-Xylylene diamine</p>	<p>BF₃-400</p> <p>Boron trifluoride-monoethylamine</p>	

SHELL Z

<p>MPDA 70%</p> <p>m-Phenylene diamine</p>	<p>MDA 30%</p> <p>4,4'-Methylene dianiline</p>	<p>BDMA</p> <p>Benzyl dimethylamine</p>	<p>DMP 30</p> <p>Tris (dimethylaminomethyl)-phenol</p>	<p>DICY</p> <p>Dicyandiamide</p>
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NMA

Nadic
methyl
anhydride

MTHPA

Methyl-
tetrahydro-
phthalic
anhydride

HHPA

Hexahydro-
phthalic
anhydride

DDSA

Dodecenyl-
succinic
anhydride

PA

Phthalic
anhydrideAMIDOPOLYAMINE V150
V140
V125 R=H or another
dimerDimerized linoleic
acid & ethylenetriamine

AMIDOPOLYAMINE EM 308

0.30 R = -C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-
Oleic acid0.25 R = -C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-
Linoleic acid 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

Diglycidyl ether of polypropylene glycol

R and R' may be methyl
n may be about 9

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	Δ L %	Resin/ Sample/ Addit.	°C-hr* /post Cure	f_{ode} 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 ^R			6420	233	16.4				31.7
TEFLON ^R			5830	169	6.0				5.0
TORLON ^R		1570	2500	188	29.9	1.2			29.9
VESPEL ^R			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

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REFERENCES

1. Kasen, et al., Vol. 26, p. 235*.
2. Dahlerup-Peterson, Vol. 26, p. 208*.
3. Evans and Morgan, Vol. 28, p. 147*.
4. Hartwig, Vol. 28, p. 179*.
5. Gauchel, et al., Vol. 28, p. 211*.
6. Hartwig and Schwarz,
Vol. 30, p. 61*.
7. Elkin, et al.,
Vol. 30, p. 977*

* All references are in "Advances in Cryogenic Engineering", Plenum Press, New York, volume and page indicated.