Epoxy Resins Based on Aromatic Glycidylamines. VI. Toughening of N,N,N',N'-Tetraglycidyl-4,4'-diaminodiphenylmethane by Reactive Additives

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SYNOPSIS

Mechanical properties of N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane and its mixtures with liquid bisphenol A-type epoxy resins, bisphenol A and ε-caprolactone have been studied. 4,4'-Diaminodiphenylsulfone was used as hardener. Materials with improved fracture toughness and good mechanical strength in the temperature range 20–200°C have been formulated.

INTRODUCTION

Composites have been recently used instead of metals in many applications, including aeronautics. Their utilization has brought significant weight savings. In many cases, N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) is a matrix of these so-called high-performance composites. After curing with suitable hardeners this resin keeps very good mechanical and dielectric properties up to temperatures above 200°C.[1–3] However, it is rather brittle at ambient temperature.[4] This brittleness leads to some limitations in application of the composites.

There are several ways to enhance the toughness of the cured epoxy resins. Modifying with carboxyl- or amine-reactive butadiene–acrylonitrile elastomers (CTBN, ATBN) is probably the most significant.[4] This procedure leads to two-phase systems and it was successfully used for bisphenol A type epoxy resins (DGEBA).[5,6] The results with TGDDM are much less satisfying. The addition of CTBN to TGDDM–DDS system only doubled the fracture energy (G_{IC}).[7] Moulton and Ting[8] achieved a G_{IC} similar to that of unmodified DGEBA resin

for the elastomer modified TGDMM–DDS system. Further possibilities of improving the toughness of the cured epoxy resins lie in the addition of the other soluble, insoluble, reactive or nonreactive components such as PEEK,[9] polyvinylidene fluoride,[9] bisphenol A.[10]

In previous papers in this series,[11–15] the preparation, composition, structure of the main impurities, reactivity, and long-term stability of TGDDM and its model compound N,N-diglycidylaniline were studied. The aim of the present work is to improve the properties of TGDDM after curing, especially its toughness at ambient temperature, without significant loss of T_g. Some reactive components forming a single phase system with TGDDM were used for this purpose.

EXPERIMENTAL

Materials Used

The synthesis of technically pure TGDDM was described in a previous paper in this series.[11] The product with an epoxy value 8.33 eq/kg, a total chlorine content of 0.46%, and viscosity 288 Pa·s at 25°C was used.

DGEBA (CHS Epoxy 15) was a commercial product of Spolchemie Co. (Czechoslovakia) with

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an epoxy value 4.97 eq/kg, a total chlorine content of 0.33%, and viscosity of 15.6 Pa·s at 25°C.

Bisphenol A (BPA) was also a product of Spolchemie Co. ϵ-Caprolactone (CL) and 4,4'-diaminodiphenylsulfone (DDS) were produced by Union Carbide Corp. and Bakelite Co., respectively. Sodium hydroxide, glacial acetic acid of p.a. purity, distilled water, and petrol of commercial purity were used for chemical resistance tests.

Cure Procedure

Epoxy resin or its composition with some ingredients was mixed with DDS at 120–130°C and stirred until a transparent solution was obtained. This liquid was poured into vertical steel molds and cured for 2 h at 130°C, 4 h at 180°C, and 2 h at 220°C.

Chemical and UV Resistance Tests

The weighed specimens, five of each material, were immersed in the test medium. After a certain time period (see Table II) they were taken out, dried, and weighed again. The mechanical properties were measured immediately. For UV testing, an emitter with a maximum at 360 nm was used.

Mechanical Testing

Dynamic mechanical properties were determined using a dynamic mechanical thermoanalyzer with a bending head (DMTA—Polymer Laboratories), at a frequency of 1 Hz and a heating rate of 4°C/min. The temperature range studied was −120°C to
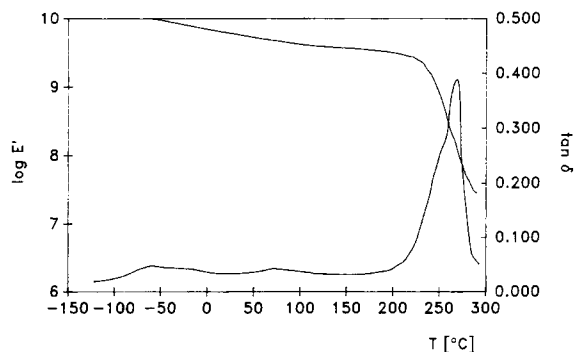

Figure 1 Temperature dependencies of storage modulus E' and loss tangent for sample 2.
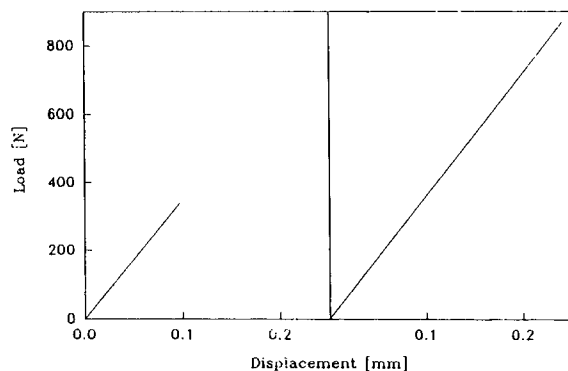

Figure 2 Load–deflection curves for the most brittle material 2 (left) and the toughened material 11 (right).

300°C. The dependences of storage modulus E' and loss tangent tan δ upon temperature are shown in Figure 1. Glass transition temperature (T_g) has been defined as the position of the maximum tan δ on the temperature axis. Determination of flexural properties at three-point loading were carried out using testing machine Instron model 1195 with a temperature chamber. The length of the span was 64 mm and the test speed 10 mm/min. Dimensions of the specimens were 80 × 10 × 4 mm. The results are an arithmetic mean of five experiments. The coefficient of variation was maximally ±15%. Fracture toughness was also measured using an Instron 1195 on specimens of the type SEN. The dimensions of the samples were 120 × 30 × 6 mm and the test speed was 1 mm/min. The samples were loaded by eccentric tension. The results are an arithmetic mean of ten experiments. The coefficient of variation was maximally ±10%. A brittle crack was observed in each case as is seen from the typical curves in Figure 2.

Thermogravimetric Measurements

Thermogravimetric (TG) curves were measured by means of a Perkin-Elmer TGS I thermobalance, in air, at heating rates 5, 10, 20, 40, and 80°C/min. The activation energies of thermal decomposition were calculated according to Ozawa's method.[16]

IR Spectroscopy

IR spectra were measured using a PYE UNICAM SP3-300 spectrophotometer in the range 200–4000 cm^{-1}, with samples in KBr pellets.

Table I   Composition of Tested Materials

Sample	Composition	T_g (°C)	K_{IC} (MPam$^{1/2}$)
	Neat resin cured with different amount of DDS		
1	TGDDM—50% DDS[a]	265	0.75
2	TGDDM—75% DDS	267	0.63
3	TGDDM—100% DDS	268	1.45
4	TGDDM—125% DDS	258	1.48
5	DGEBA—125% DDS	174	2.22
	Mixtures of TGDDM with DGEBA cured with 125% DDS		
6	DGEBA : TGDDM 75 : 25	190	2.31
7	DGEBA : TGDDM 50 : 50	212	2.05
8	DGEBA : TGDDM 25 : 75	232	1.85
	Mixtures of TGDDM with other reactive components cured with 125% DDS		
9	TGDDM : BPA 95 : 5	246	1.53
10	TGDDM : BPA 90 : 10	239	1.57
11	TGDDM : CL 95 : 5	240	1.83
12	TGDDM : CL 90 : 10	220	1.71
13	TGDDM : DGEBA : CL 75 : 20 : 5	215	1.83

[a] % of stoichiometric amount.

RESULTS AND DISCUSSION

Toughness and T_g Values

The influence of the chemical changes in our samples on K_{IC} and T_g is evident from Table I. Samples containing epoxide in excess are significantly more brittle than the samples cured with stoichiometric amounts or with excess of DDS. The changes of T_g in the samples of TGDDM cured with different amounts of DDS are negligible. Owing to its lower crosslinking density, DGEBA exhibits a much higher K_{IC} value than TGDDM and addition of DGEBA to TGDDM also influences fracture toughness favorably. In this case the drop of T_g is proportional to the content of DGEBA. Addition of 25% DGEBA leads to significant improvement in K_{IC} (about 25%), compared with neat TGDDM. T_g still remains relatively high—about 230°C. The modification with 5% CL provides practically the same improvement in K_{IC} but the decrease in T_g value is lower than in the previous case. To investigate the reason for the favorable influence of CL on fracture toughness of the cured TGDDM-DDS samples, the chemical changes of this compound during curing were followed. We supposed that aminolysis of this cyclic ester by aromatic diamine occurs at high temperatures and that the reaction product become a part of macromolecular net. IR spectroscopy has demonstrated that this is true in the case of the more basic 4,4'-diaminodiphenylmethane. However, this aminolysis does not take place in the presence of DDS; here only a decrease in the three absorption bands corresponding to the cyclic structure in the range of 1000–1100 cm^{-1} was observed, without any change in the ester group absorption. We suppose that the polymerization of CL proceeds in the composition where DDS is the curing agent. The simultaneous use of DGEBA and CL did not bring any further increase in K_{IC}, while T_g dropped significantly. The addition of BPA had practically no influence on the fracture toughness of TGDDM.

Mechanical Properties

Temperature dependencies of some bending properties of the tested materials are in Figures 3–5. Just as for the samples of neat TGDDM, the worst mechanical properties were found for material 1, containing only 50% of DDS. The compositions cured with both a stoichiometric amount and an excess of DDS have similar properties, the latter exhibiting
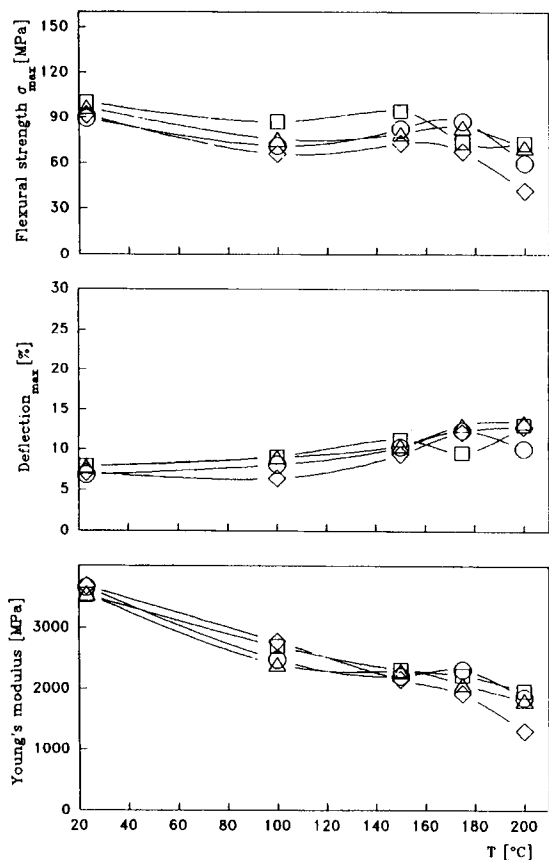
Figure 3 Temperature dependencies of the mechanical properties for TGDDM–DDS compositions: (◇) 1, (□) 2, (○) 3, (△) 4.

best mechanical properties among the TGDDM mixtures in the whole temperature range, and the highest values of K_{IC}. The samples of neat TGDDM and neat DGEBA cured with 125% of the theoretical amount of DDS were used for comparison. The results are given in Table II.

From the TGDDM compositions, the greatest drop in measured properties after the exposure to chemical agents or to UV was found for the mixture 75% TGDDM with 25% DGEBA (sample 8), which also had the lowest T_g. The least changes were observed for neat TGDDM which has the highest T_g. The chemical and UV resistance of composition 11 containing 95% TGDDM and 5% CL is very similar to that of neat TGDDM. Comparing TGDDM and DGEBA, the former seems to be more resistant. In some cases, even an improvement in the mechanical properties was found after exposure to the tested chemicals. These changes for neat TGDDM (and in one case also for its composition with CL) are greater than the coefficient of variation. The changes
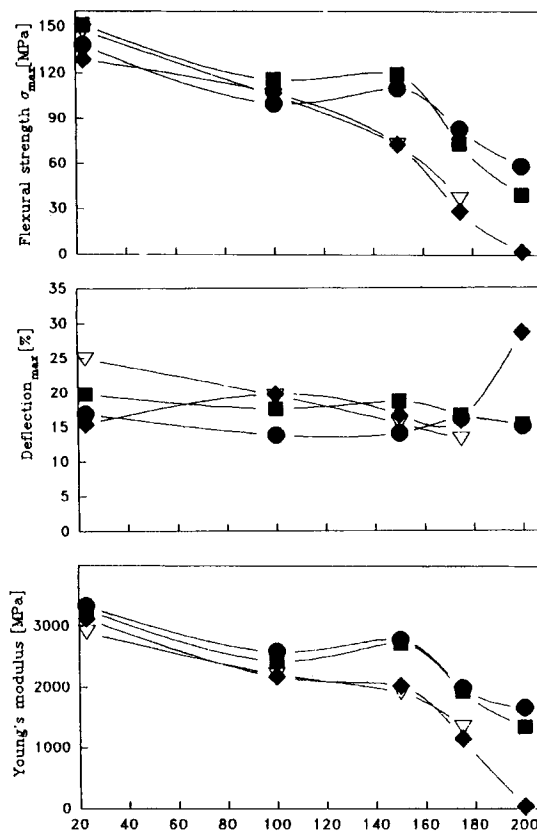
a slightly higher flexural strength up to 100°C. Compositions containing BPA were found to have relatively poor mechanical properties, especially at room temperature (Fig. 5). On the contrary, additions of DGEBA or CL lead to significant improvement. The compositions containing 25% DGEBA (sample 8) and 5% CL (sample 11) exhibit about 40% higher flexural strength at ambient temperature and only by about 5–10% lower flexural strength at 200°C, compared with neat TGDDM (sample 4). Very good mechanical properties up to 150°C were also found for samples 7 and 13, the mixtures TGDDM–DGEBA 1 : 1 and TGDDM with DGEBA and CL, respectively. However, their flexural strengths decrease significantly above this temperature because of relatively low T_g values.

Chemical and UV Resistance

Compositions 8 and 11 were used for the testing of chemical and UV resistance because they have the

Figure 4 Temperature dependencies of the mechanical properties for the TGDDM–DGEBA mixtures: (∇) 5, (◆) 6, (■) 7, (●) 8.
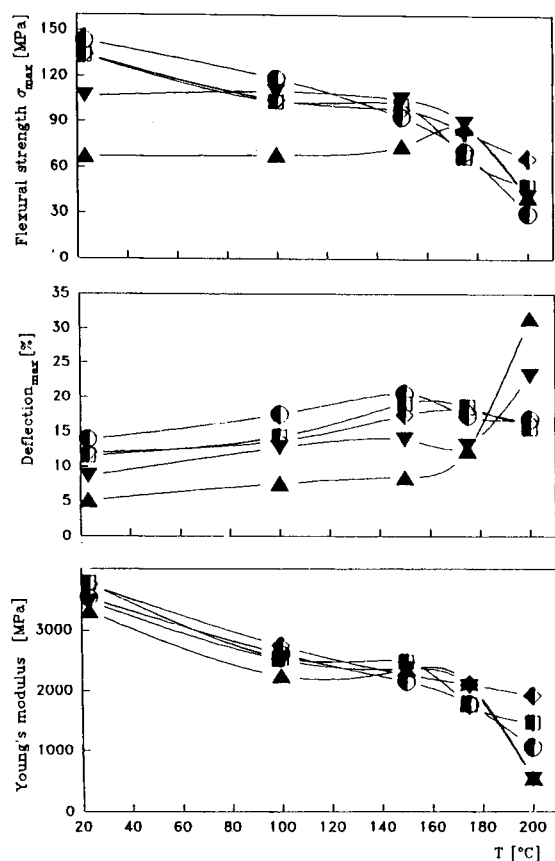
Figure 5   Temperature dependencies of the mechanical properties for the mixtures of TGDDM with different additives: (▲) 9, (▼) 10, (◊) 11, (■) 12, (○) 13.

zones are only shifted to lower temperature (change of T_g). Instead of the main peak, two secondary peaks are present in the curves of loss modulus versus temperature for all TGDDM compositions. Representative viscoelastic curves of TGDDM cured with 75% DDS are shown in Figure 1. The peak at $-70°C$ was found formerly in cured DGEBA.[17,18] It is supposed to correspond to motions of the $-CH_2-CH(OH)-CH_2-O-$ group formed during curing of epoxides with amines. The peak at $+70°C$ is missing in case of DGEBA. This peak increases with raising conversion of epoxy groups (Fig. 6). The height of this peak is inversely proportional to the content of DDS in the sample. We suppose this peak to be connected with the inter- or intramolecular reaction of epoxy groups and secondary OH groups at higher temperatures, i.e. etherification.[19,20] In the case of intramolecular reaction, the cycles have been proved.[21] The other possibility is the formation of 3-hydroxy-1,2,3,4-tetrahydryquinoline derivatives.[22] This reaction would be consistent with the observed increase in the concentration of hydroxyl groups during postcuring of the samples where epoxide was in excess, as was found using IR spectroscopy. The formation of the 3-hydroxy-1,2,3,4-tetrahydryquinoline ring was not identified in the epoxy resin based on bisphenol A.[13] The influence of these reactions on fracture toughness or on the other mechanical properties have not so far been investigated.

were observed especially for deflection and flexural strength. The stiffness of the materials remained practically unchanged, as is seen from the values of Young's modulus. We suppose that these deflection and flexural strength changes, especially in the case of cured neat TGDDM, are connected with swelling, and with the specimen's surface quality. For all tested materials, water absorption after 8 h at 100°C was between 1.1–1.4%; water absorption after 7 days at 23°C was between 0.6–0.8%. Absorption of the other media used after 7 days achieved a maximum of 0.1%, and after 63 days 0.5%.

Viscoelasticity

It follows from viscoelastic measurements that changes in the composition of TGDDM networks do not affect the shape of the transition zones between glass-like and rubber-like consistencies. The

Thermal Stability

The thermogravimetric curve of sample 1 is shown in Figure 7, and the activation energies of thermal decomposition are listed in Table III. The thermal decomposition proceeds in two main steps. The values of the activation energies of both steps depend on the composition of the resin:

1. The activation energies of the steps I and II for DGEBA are higher than those for TGDDM (123.8 kJ/mol and 207.4 kJ/mol for DGEBA, and 71.6 kJ/mol and 164.8 kJ/mol for TGDDM in the case of the same molar ratio of DDS.
2. The increasing amount of the hardener in case of TGDDM decreases the values of the activation energies (samples 4 and 1).
3. The higher the content of CL in the resin the

Table II Chemical and UV Resistance of Chosen Materials to Immersion in Liquids[a]

Changes after immersion in water

Sample	Flexural Strength		E Modulus		Deflection	
	A	B	A	B	A	B
4	104.4	107.4	100.0	100.6	116.5	121.5
5	82.5	81.6	90.2	89.7	82.1	84.7
8	65.3	86.9	87.0	97.5	55.6	79.9
11	65.1	98.1	98.7	104.3	60.0	104.2

Changes after immersion in 40% NaOH

Sample	Flexural Strength		E Modulus		Deflection	
	B	C	B	C	B	C
4	94.3	113.9	97.6	101.7	98.7	124.1
5	90.3	92.2	94.6	103.1	88.7	83.1
8	72.8	84.0	101.5	100.0	53.8	78.7
11	88.8	104.8	101.9	104.0	80.8	112.5

Changes after immersion in glacial acetic acid

Sample	Flexural Strength		E Modulus		Deflection	
	B	C	B	C	B	C
4	117.0	120.1	95.8	109.0	140.5	120.1
5	90.3	94.9	95.5	104.9	100.8	90.7
8	83.3	104.7	104.5	106.0	69.8	86.3
11	100.7	114.9	102.7	103.5	97.5	122.5

Changes after immersion in petrol

Sample	Flexural Strength		E Modulus		Deflection	
	B	C	B	C	B	C
4	127.2	135.0	97.0	111.9	176.0	154.4
5	96.6	93.9	98.1	103.1	91.9	83.4
8	67.6	93.1	100.6	98.5	51.5	75.7
11	93.7	96.3	104.3	96.8	85.8	106.6

Changes after exposure in UV

Sample	Flexural Strength		E Modulus		Deflection	
	B	C	B	C	B	C
4	94.0	130.5	102.0	104.8	142.5	126.0
5	103.3	87.8	104.2	99.1	98.4	69.6
8	78.6	72.5	107.2	100.2	68.4	53.8
11	90.6	94.0	104.3	104.9	81.3	84.6

[a] All data are given as % of initial values.
A = 8 h at 100°C.
B = 7 days at 23°C.
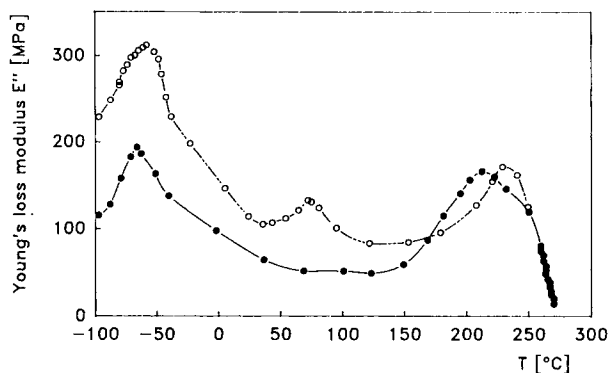C = 63 days at 23°C

Figure 6 Loss modulus E'' curves of the material 1: (●) cured 2 h at 130°C and 4 h at 180°C; (○) postcured 2 h at 220°C.

Table III Activation Energies of the Thermal Decomposition of Some Samples

Sample	Activation Energy in kJ/mol	
	Step I	Step II
1	164.8	220.5
4	71.6	164.8
5	123.8	207.4
7	112.6	195.1
8	116.7	191.1
11	117.6	179.3
12	96.5	170.1

lower the activation energy of decomposition (compositions 11 and 12).

4. The addition of DGEBA to TGDDM shifts the activation energies towards higher values.

of the same amount of hardener. The addition of DGEBA increases the thermal stability of TGDDM.

CONCLUSIONS

The difficulty in improving the fracture toughness of TGDDM on a scale comparable to DGEBA was confirmed. However, the compositions of 75% TGDDM with 25% DGEBA, and 95% TGDDM with 5% CL, especially the latter, represent very good materials with properties similar to unmodified DGEBA in the temperature range to 100°C and with very good properties above this temperature, up to 200°C. The thermal stability of the cured materials is dependent upon the composition. DGEBA is from this point of view better than TGDDM in the case
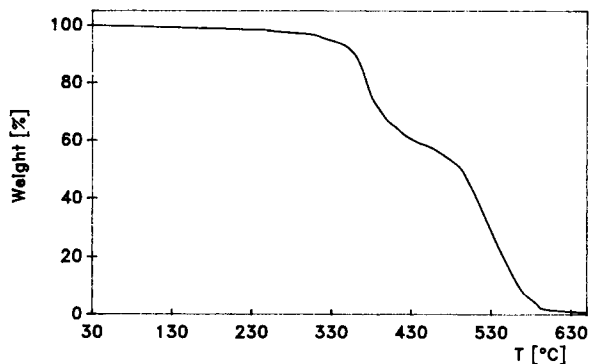
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Figure 7 Thermogravimetric curve of the sample 1.

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