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CRACK TOUGHENED EPOXIES FOR ROOM TEMPERATURE APPLICATIONS

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ABSTRACT

Ordinary epoxy resins used for laminating glass fiber reinforced plastics are glassy polymers and are known to be brittle. A manifestation of this brittleness is the ease with which microcracking of laminates made with such resins takes place, even at low levels of loading. Recent work has shown that it is possible to toughen epoxies by reacting them with small concentrations of a liquid carboxyl-terminated butadiene/acrylonitrile copolymer. If the proper microstructure of the resulting polymer is achieved, its surface fracture energy is typically an order of magnitude higher than that of the unmodified system. When such toughened epoxies are used for laminating, microcracking, which ordinarily can be extensive, is reduced or even eliminated under conditions of cyclic fatigue loading.

Application of toughened systems published to date has been difficult in the case of large lay-ups because of the need to use are described herein in which a simple prereaction technique is used to make possible toughened resins which then can be cured at room temperature.

INTRODUCTION

Composite materials are favored at the present time for the construction of sailplanes because of their great strength-to-weight ratio and the ease with which they can be formed to aerodynamically favorable shapes. Nevertheless, certain weaknesses are inherent to such materials; one notable one in the case of glass-reinforced plastics (GRP) being the development of microcracks in the matrix. The cause of these cracks has been established as the "strain-expansion" (dehnungs-vergrosserung) which exists in the matrix between the glass fibers oriented at 90 deg to the direction of loading (Ref. 1). Because of the differences in modulus between the glass fibers and the resin, strains in the matrix may be fifteen to thirty times that of the composite as a whole (Ref. 2). As a result, a GRP composite subjected to a tensile load experiences microcracking in the direction perpendicular to the load along the fibers in that direction. This accounts for the well-known "knee" in the stress-strain diagram for a glass composite having fibers in the direction perpendicular to the tensile load. The "knee" coincides with the strain at which the onset of microcracking may be observed.

Ways of avoiding microcracking have been suggested. The simplest is one offered by Puck (Ref. 3), dimensioning the structure large enough so that the "knee" strain is not exceeded under the specified service load. This amounts to reducing the maximum allowable stress in the structure to a value far below the actual ultimate tensile strength. Thus the superior tensile strength of a glass-fiber laminate, when compared to other typical aircraft materials, may be illusionary. It may be noted that, even if the strain is limited as above, microcracking will still take place after a few thousand cycles of fatigue (Ref. 4), which would be a small percentage of the fatigue life.

A second method could be spacing the fibers uniformly since the microcracking starts more readily in areas where the fibers are most closely packed together (Ref. 5). In practice, this method seems unattainable, at least in a hand lay-up.

The third method is the one discussed here, that of toughening the matrix against crack propagation by altering its chemical composition. Polymers may be toughened in various ways; one being the dispersion of a rubbery polymer in the glassy matrix. This method has been used quite successfully in thermoplastics like ABS and rubber-reinforced polystyrene for which fracture surface energies of 10^8 ergs/cm^2 have been reported (Ref. 6). The two-phase structure resulting from the rubber additions can be obtained without a great decrease in heat-distortion temperature or modulus as is ordinarily the case with plasticization. The need for sufficiently high heat-distortion temperature in aircraft construction is self-evident; the influence of matrix modulus on laminate compressive strength has been found to be quite pronounced (Refs. 7, 8).

TWO-PHASE EPOXIES

The first actual use of a rubber copolymer to toughen an epoxy was reported in 1968. Reference 9 describes the pioneering work of McGarry in the field. It was found that by adding 10 pph of a carboxyl-terminated butadiene/acrylonitrile copolymer, CTBN, to Epon 828, a standard bis-A epoxy, and curing it with 6 pph of DMP-30 (2, 4, 6-tridimethylaminoethylphenol) at 250^{o}F, the surface fracture energy was tripled; and further that, if laminates were made with 181-style glass fabric and subjected to a tensile fatigue test, those made with the rubber-modified epoxy showed no microcracking while those made with the unmodified resin showed appreciable cracking as shown in Fig. 1. Later work at B. F. Goodrich Chemical Company showed that the addition of CTBN caused a four to seven-fold reduction in the crack density of composites in flexural fatigue after 10-million cycles.

FIGURE 1

Many factors influence the amount of toughening to be expected from CTBN additions (Refs. 10, 11); and, unless the proper microstructure of the cured product is obtained, the modification of the basic epoxy may only degrade the physical properties (Ref. 12). A necessary but not sufficient condition for toughening is that small (2,000 A to 30,000 A) rubbery particles precipitate during the cure. The reaction chemistry involved has been discussed briefly by Drake, Siebert, and Rowe (Ref. 10). In addition to the cross-linking of the epoxy, the epoxy-rubber reaction should also be catalyzed. This can be done by using tertiary amines, either alone or in combination with other types of curing agents. Furthermore, the epoxy-rubber esterification reaction does not proceed rapidly at room temperature. Formulations published to date have all required the application of elevated temperatures to promote this reaction. This has, therefore, made difficult the use of these formulations in a large layup.

ROOM TEMPERATURE SYSTEMS

Since the epoxy-rubber reaction requires heat, but the cross-linking of the epoxy can be accomplished at room temperature, it was hoped that the two reactions could be carried out separately, and that the resulting system might still be toughened. Fortunately, this turned out to be the case. Attention was first directed at selecting a room-temperature, low viscosity laminating resin showing high tensile strength and elongation since these properties were also expected to extend the composite fatigue life. The system chosen was Araldite 6005*, a standard bis-A epoxy resin; Araldite RD-4, a cycloaliphatic epoxy; and triethylenetetramine (TETA), in the proportion 84:16:19. In addition to the excellent physical properties for this system, a heat distortion temperature of 102°C is listed by the manufacturer as opposed to a value of around 80°C, the value normally expected of low viscosity laminating resins. The surface fracture energy for this system was measured and found to be approximately 7.5×10^4 ergs/cm^2; the cure cycle was 12 hr at room temperature plus 12 hr at 50°C. This fracture value is less than the base value McGarry found for the DMP-30 cured system ($\nu = 4 \times 10^5$ ergs/cm^2). Thus, microcracking would be expected to be more severe for a TETA-based system than one cured with DMP-30, although the cure schedules were not the same. To toughen the system, CTBN** was mixed with Araldite 6005 in the proportion 3:1, CTBN/6005, and cooked for three hours at 150°C. The mixture was then allowed to cool to room temperature, and more 6005 and RD-4 were mixed in; finally, TETA was added to cure the system, which was cast for testing. The final recipe was 6005/RD-4/TETA/CTBN-84:16:17:10. The TETA concentration was reduced slightly from stoichiometric (19 pph) because published data with heat-cured systems, using Shell Agent-D (which gives higher fracture values than DMP-30 systems) used subnormal concentrations of that curing agent. The specimen blank was cut to shape and cleaved, following the technique described in Ref. 13; fracture work was approximately 8×10^5 ergs/cm^2, an order of magnitude higher than the value for the straight resin. Thus, the method of pre-reacting the CTBN was found to successfully toughen the resin, although the fracture value was still short of that for heat-cured systems. The next step was to measure the tensile strength of the toughened resin. Here the performance was disappointing. The addition of 10 pph of CTBN dropped the tensile strength from 8.25 kg/mm^2 to 5.32 kg/mm^2, a decrease of 36 percent. Heat-cured systems normally showed decreases of only 5 to 15 percent and a published cycloaliphatic system actually gained 60 percent in tensile (Ref. 12); these data seemed to indicate that higher tensile performance than achieved could still be reasonably expected. The elongation with and without rubber was about 3 percent, although CIBA data shows 10 percent for the unmodified system when post-cured eight hours at 100°C.

Attention was turned to other curing agents to replace TETA. DMP-30 can be

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*Ciba-Geigy Corporation

**Hycar CTBN, B.F. Goodrich Chemical Co., Cleveland, Ohio used to obtain room temperature cures as well as heat cures, so, on the basis of its success in toughening at elevated temperatures, it was tried using the same approach as had been used with TETA. The fracture results were not only inferior to those found when heat curing it, but were actually lower than the TETA values.

A cycloaliphatic amine, aminoethylpiperazine (AEP) was next considered. Several advantages were expected: its Izod impact value was listed as two to three times that of TETA, thus it would give naturally tougher cures than TETA. Also, it produces sweat-out free castings which most aliphatic amine systems like TETA do not. Other physical properties are very similar to those obtained with TETA. A fracture test of EPON 828 and AEP, (100:22), post cured 12 hr at 50°C, gave ν of 10^5 ergs/cm^2. This is three to four times the value found for 828-TETA but still not considered especially high; however, AEP's high Izod impact values are obtained only if post cures at 100°C are carried out for at least two hours (Ref. 14). so the moderate value of fracture work is not surprising. AEP can be used in less than stoichiometric proportions; and, indeed, the experimentally determined optimal mix ratio of 21 pph (based on tensile strength) is less than the calculated ratio, referring now to the 6005-RD-4 blend. The addition of 3 pph Methylon 75108* based on total epoxy weight is not thought to have significantly affected this result; the Methylon was included in the mix because AEP alone does not provide full RT cures in thin sections.

The first attempt at toughening the AEP system consisted of mixing a 3:1:0.05 batch of CTBN, 6005, and tributyl amine (TBA). The TBA was added to promote the desired epoxy-rubber reaction. This mix was heated to 175°C and then allowed to cool to room temperature. The rest of the components were then stirred in; the complete composition was 6005/RD-4/AEP/75108/CTBN/TBA - 84:16:25:3:10:0.16. Fracture work was 17 x 10^5 ergs/cm^2 but tensile strength was only 4.47 kg/mm^2. The fracture work was at a value equal to that of good heat-cured systems but tensile was still inferior, although tensile elongation had roughly doubled. Next the AEP concentration was varied. From Table I it may be seen that the tensile values were independent of AEP concentration in the range tested.

TABLE I

	A	B	C	D
AEP, pph	25	23	21	19
Tensile strength, kg/mm^2	4.47	4.50	4.42	4.40
Elongation at break, %	5.5	4.8	--	--

Lowering the CTBN level to 5pph and using AEP at 21 pph raised the tensile value to 5.57 kg/mm^2; while elongation rose to 6.5 percent. Putting all the 6005 into the premix with the CTBN instead of mixing at 3:1 as had been done previously, leaving out the TBA and cooking the premix for one hour at 175°C, brought the tensile strength up to 6.08 kg/mm^2, a value equal to that of a typical heat-cured system. Varying the AEP concentration with the rubber at 5 pph now and omitting the 65108 gave these results.

TABLE II

	A	B	C	D
AEP, pph	19	17	15	13
Tensile strength, kg/mm^2	5.87	6.07	6.57	6.42
Elongation at break, %	2.6	3.2	3.8	3.6

Comparing these data with the previous data, two observations may be made. As was the case with 10 pph CTBN, tensile strength is relatively insensitive to the amount of amine in the system, although the

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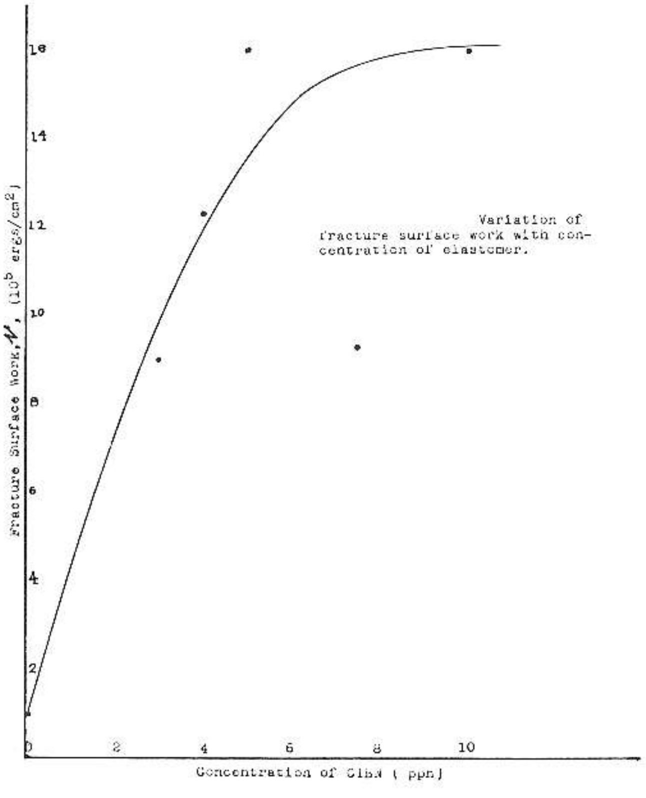
*phenolic resin, General Electric Co., Plastics Dept.

variation is stronger at 5 pph (and much stronger with no CTBN). Furthermore, the use of Methylon 75108 has a very beneficial effect, since elongation with it was 6.5 percent and without it around 3 percent, at least with 19 to 21 pph AEP. Testing the 15 pph system with 3 pph Methylon resin raised the tensile to 7.17 kg/mm^2; again, the Methylon is seen to be beneficial. Doubling the Methylon level to 6 pph had no appreciable effect on the tensile value; elongation with 3 pph Methylon was 3.8 percent.

Figures 2 and 3 show the variation of fracture work and tensile strength of the 21 pph AEP system with CTBN content. The best balance of properties is obtained with about 5 percent rubber; 10 pph seems to overload the system.



Variation of fracture surface work with concentration of elastomer.

FIGURE 2

ADDITIONAL TESTS

In the course of the testing, the importance of using Methylon resin together with the CTBN eventually became apparent. An additional variation of the cure cycle was, therefore, tried--including the Methylon in the preheated mix instead of adding it with the AEP for the actual cure of the epoxy. Figure 4 shows the results, now in terms of the stress-strain diagram for the material. There is no decrease in tensile strength, and elongation goes from 3.0 to 7.6 percent. Actually, the test values for the unmodified resin varied from 5.83 to 8.05 kg/mm^2. This is an unusual amount of variance but is attributed to the flaw sensitivity of the untoughened system. Normally test scatter for straight resins was around 10 percent and about 4 percent for toughened resins. From the figure, the increase in ductility is obvious. The on-set of stress-whitening is easily observable on the toughened test specimen at about 3.5 percent strain. Fracture work was found to be 15×10^5 ergs/cm^2. Summarizing the mixing procedure: Mix together the following and cook for one hour at 175°C with stirring:

Hycar CTBN	5 parts
Ciba 6005	84 parts
Methylon 75108	3 parts

Cool to room temperature and stir in 16 parts Ciba RD-4 (the RD-4 was considered to be too volatile to include in the heated mix). To cure, add 21 parts AEP. Post cure 12 hours at 50°C.

The above procedure gives good toughness with good tensile strength, and it is strongly suspected that the procedure will also toughen systems using a variety of aliphatic and cycloaliphatic amine curing agents and epoxies with negligible loss in tensile strength. Single tests with TETA and methane diamine indicated this to be the case, although AEP gives the best toughness and elongation.

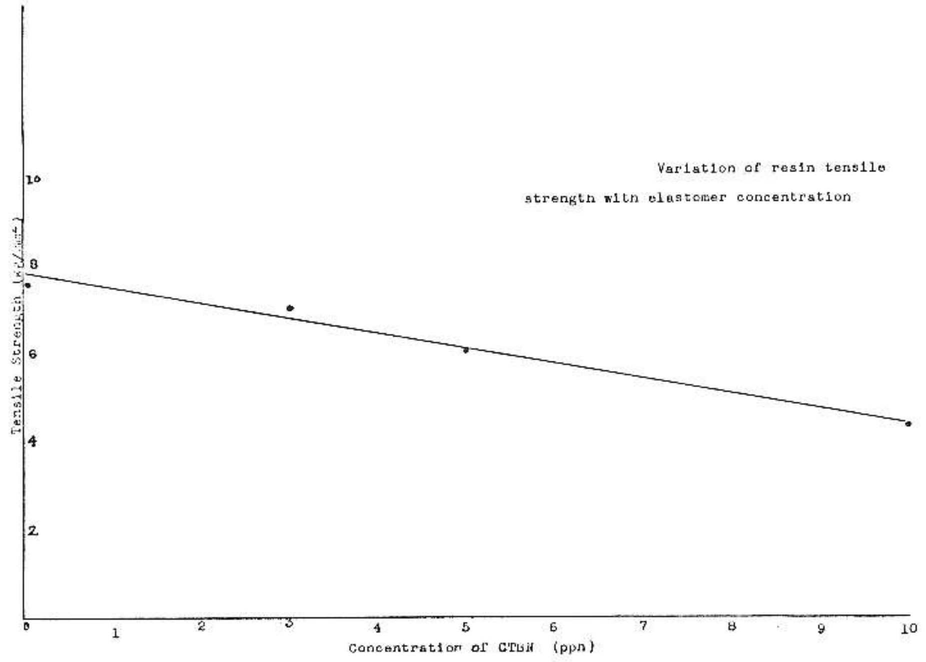


FIGURE 3

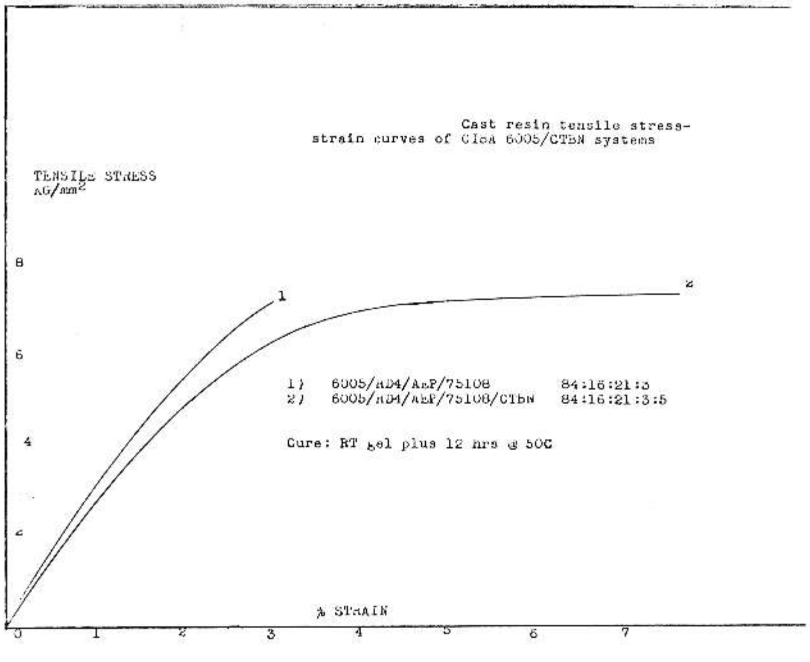


FIGURE 4

FINAL REMARKS

Published data by resin manufacturers, as well as by independent laboratories, indicate that the toughness of unmodified, aliphatic amine cured epoxies is very slow in coming (weeks), even though they gel in a matter of hours, thus it is expected that the systems described herein may well require the 50°C post-cure to obtain the toughness in a reasonable period of time. This is not considered a disadvantage, comparatively, since aircraft manufacturers have found it necessary to use a post-cure with unmodified resins, both for the reason mentioned above and to increase the heat distortion temperature.

Another factor deserving consideration is the strong dependence of surface fracture energy on temperature. Data obtained with a heat-cured system (Ref. 5) indicate that at a temperature of 0°C, ν is about one-third of its room temperature (20°C) value. At temperatures above 20°C, the slope of the curve is even greater. Since white painted surfaces may experience a 12°C rise in temperature above the air temperature because of solar heating (Ref. 15) and the air itself can be as high as 38°C on a hot summer day, the fracture values on sunny days would be expected to far exceed those reported in these tests. On the other hand, on wintry days the values would be much less. Fracture energy of unmodified resins does not vary much with temperature in the -40°C to +30°C range.

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ment diameter and sizing; (2) the resin system, and (3) the process such as lay up, vacuum bagging or matched die molding. Keep in mind that although there are a number of variables to be considered, their proper choice can pay off in a composite structure with definite performance advantages.

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REFS. CONTINUED FROM P. 7

AVERAGE PROPERTIES OF EPOXY LAMINATES
REINFORCED WITH 181 FABRIC
VOLAN A FINISH
E-GLASS COMPOSITION

	Strength (PSI)			Modulus (PSI x 10^6)		
Property	ECE 225 1/3 Yarns	ECG 150 1/3 Yarns	ECDE 75 1/0 Yarns	ECE 225 1/3 Yarns	ECG 150 1/3 Yarns	ECDE 75 1/0 Yarns
Tensile	53,400	51,500	56,100	2.63	2.77	2.70
Compressive	47,500	49,900	44,100	4.25	4.05	4.94
Flexural	80,500	80,800	88,100	3.84	4.15	4.03
Interlaminar Shear	2,770	2,780	2,790	--	--	--

TABLE 7

AVERAGE PROPERTIES OF EPOXY LAMINATES
REINFORCED WITH 181 FABRIC
S-GLASS COMPOSITION

	Strength (PSI)		Modulus (PSI x 10^6)	
Property	Volan A	901	Volan A	901
Tensile	74,700	97,700	3.29	3.15
Compressive	58,800	67,400	4.67	4.60
Interlaminar Shear	2,405	3,040	--	--

TABLE 8