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Improving the fracture energy of carbon fibre-reinforced plastics by delamination promoters

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The effect of delamination promoters on the Charpy impact energy and other mechanical properties of carbon fibre-reinforced plastic has been studied. These delamination promoters consist of thin sheets of metallic or organic materials which make the multiple splitting of samples at the time of impact, a process involving a greater energy absorption, much easier.

1. Introduction

Fracture of carbon fibre-reinforced plastics (CFRP) is of growing interest due to the anticipated large use of these materials for aircraft in the coming years.

Several models of fracture behaviour have been reported. Compared to this plethora of theoretical contributions, a relatively small number of applications and developments have been reported. Papers such as those recently published by Adams [1, 2], provide a basis for consideration of recent theoretical models. Other workers (e.g. [3, 4]) have tried to apply some of the new ideas to the behaviour of specially formulated composites.

2. Background to the work

Crack deflection along the interfaces was first reported by Cook and Gordon. The extent of this mechanism in the total fracture energy was then evaluated for several CFRPs by Novak and de Crescente [5] who found that this contribution was between 2 and 20%, depending closely on the shear strength of the material. That these longitudinal cracks propagate before the fibres break constitutes a separate mechanism of energy absorption.

An estimation of this energy is given by Aveston [6] who considers one longitudinal crack extending the whole length of the test bar in three-point bending. The maximum energy is three times the fracture energy in the "brittle" mode. Aveston further notes that if the sample repeatedly delaminates according to the successive neutral axes of the bar, more energy can be absorbed. Hancox [7] took advantage of this fact for carbon-glass sandwich composites: the work of fracture, measured by the Izod test or the slow bend test, was found to be greater than the calculated work from the flexural strain energy stored in the bars.

The delamination process in CFRP failure has been well documented by Bader [8] who reported that an extensive delamination of the test pieces is associated with a greater energy absorption. This "multiple shear" fracture mode may absorb three times as much energy as the simple "brittle" mode within certain limits of the dimensions of the test-piece and span-to-depth ratio.

Bader and Ellis [9] showed that when various CFRPs are compared on the basis of the standard Charpy test, there is a transition from one mode to the other. This transition takes place when:

$$\frac{\sigma_c}{\tau_i} = \frac{2L}{D-d} \qquad (1)$$

In Equation 1, σ_c and τ_i are the flexural strength and the shear strength, i.e. materials parameters, respectively. L, D and d are the test parameters, i.e. span and depth of beam and notch length respectively.

For a given sample geometry and test conditions, various types of CFRP may exist having different σ_c/τ_i ratios. Dorey [10] and Bradshaw *et al.* [11] have emphasized the importance of the Equation 1 when unidirectional composites are impacted with a flexural stressing mode. From this it can be concluded that increasing delamination before the fibres break is one way of increasing the fracture energy of CFRps. One of the different attempts to obtain this fracture mode is the subject of this paper. This is the effect of thin layers of isotropic materials incorporated between the plies of fibre resin material.

3. Experimental

3.1. Materials

Courtaulds Grafil carbon fibres have been used in the form of 10 000 filament yarns of various types: HT, HTS, HM, HMS and A. Some difference in the fibre properties was occasionally observed between the manufacturer's specifications and our own control tests (based on single fibre testing). The data given below, therefore, must only be compared with proof-mouldings with fibres of the same batch.

HT, HM and A types were used unsized ("bare yarn"); HTS and HMS received an epoxy and a phenolic finish, respectively. The matrix was a medium-viscosity DGBA epoxy (Araldite LY 556, Ciba) hardened by an anhydride (HT 907 + DY 063) or an amine (HT 972). The cure cycle was 2h/100° C + 3h/160° C.

Any other resin or additive used is indicated elsewhere.

3.2. Elaboration

Impregnation of the carbon yarn and precure of unidirectional sheets were made conventionally and plies were cut in the prepregs. At the time of stacking of the plies in the mould (8 plies resulting in a 3 mm thick composite plate), the thin monolayers of isotropic materials were intercalated. The whole mass was then cured in a press.

The fibre content was determined using the dimensions of the cured plate and the number of lengths of fibre. Void content was calculated from the density and fibre content.

SEM observations were made on polished samples electrolytically coated with silver. A deposition of metal on the extremity of each single fibre gave a good contrast.

3.3. Testing

Table I gives the dimensions of the test samples.

Resilience was measured on a Wolpert CPSA Charpy-type machine of maximum capacity 40 daNcm (40 J). The specimens were unnotched, and a sensitivity of 20 daNcm was used. The specimens were struck in the stacking direction.

TABLE I Dimensions of test specimens

	Length (mm)	Breadth (mm)	Height (mm)	Span-to depth ratio
Flexion	60	12.5	3	16
Interlaminar shear	20	10	3	4
Resilience	60	3	3	13.4

4. Results for standard CFRP mouldings

The results of mechanical tests on basic materials (carbon fibres + resin) differ in no way to those reported elsewhere. For comparison purposes, a parallel will be drawn in each case between these results and those of the "improved" plates.

At this point we wish to draw attention to the delaminations which eventually occur when basic materials are broken in the Charpy test. Basically, there is no cleavage, but splitting into two or three pieces possibly occurs in one of the many samples of a set. Sometimes, all the samples in a set are cleaved. In the first case, the initiation of the longitudinal failure is caused by local defects (voids, loss of adhesion, etc); in the second case, imperfections in the production of the composite is suspected ("hard" prepreg). Two examples of these irregular features are presented below.

4.1. Accidental splitting

The results of Charpy tests are given in Fig. 1 for an HTS/LY 556 composite: 6 samples from the same plate have been tested. Samples 4 and 6 absorbed more energy than the others. Moreover, a complete longitudinal splitting of samples 4 and 6 has occurred at a point $\frac{2}{3}d$ of the thickness. This mode of fracture is unusual for this material whose breakage is generally very clean.

4.2. Generalized splitting

The data for two sets of samples based on HT/LY 556 material are given in Fig. 2. The samples of laminate 1 are thoroughly split and the original laminate configuration (8-ply lay-up) can be easily recognized. In this case, there was an excess

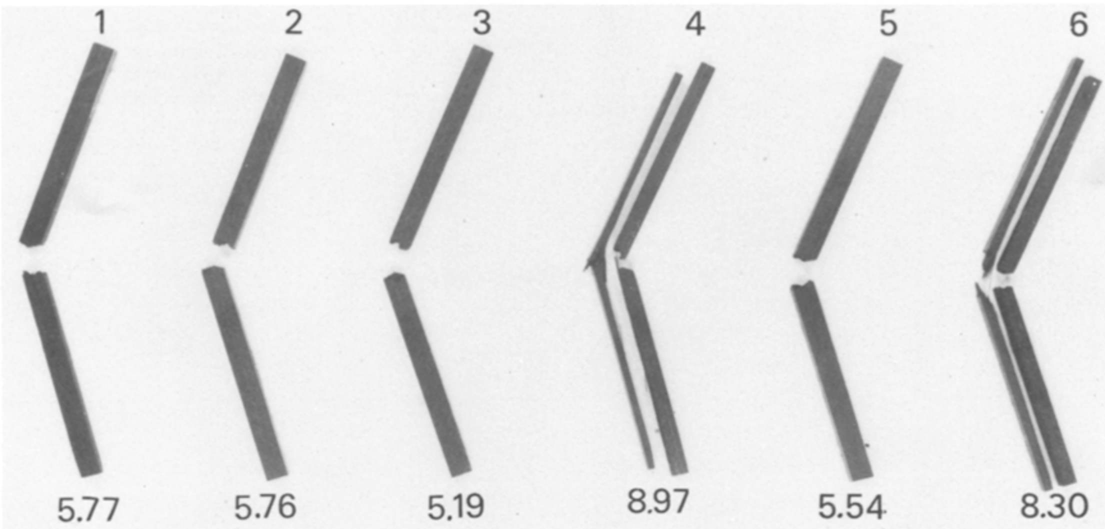

Figure 1 Broken Charpy impact specimens of a HTS/LY 556 composite. Charpy impact energy in $\mathrm{J\,cm^{-2}}$.

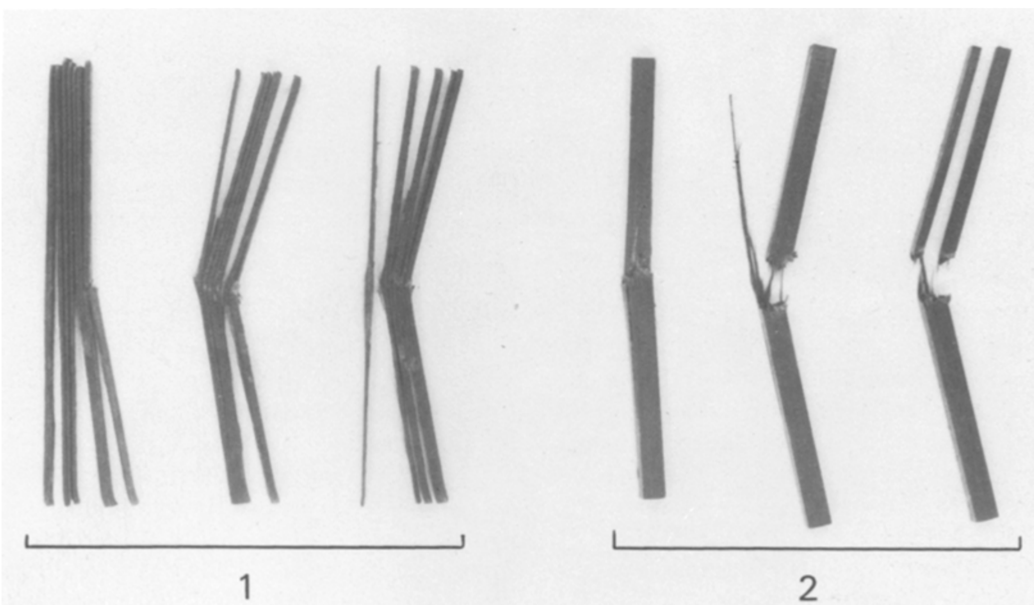

Figure 2 Broken Charpy impact specimens of HT/LY 556 composites. (1) Laminate showing generalized splitting. (2) Standard laminate.

of prepreg precuring before the final moulding and inadequate mixing of the layers. Lines of flattened voids (total void volume fraction ≈ 0.1) in a direction parallel to the layers can be seen in Fig. 3, which shows a view of a polished section.

The mean energy is $9.26\,\mathrm{J\,cm^{-2}}$ (15 specimens) with a maximum variation of $\pm 1.5\,\mathrm{J\,cm^{-2}}$. There is no obvious difference with data for a well-made HT/LY 556 laminate whose resilience is $8.4\,\mathrm{J\,cm^{-2}}$ when the modes of fracture are quite different (compare in Fig. 2).

Other mechanical properties suffered as a consequence of generalized splitting: a drop of 70% in the flexural strength is seen compared to the sound HT/LY 556 material of the same batch of fibres ($240\,\mathrm{N\,mm^{-2}}$ versus 780) and 30% in the

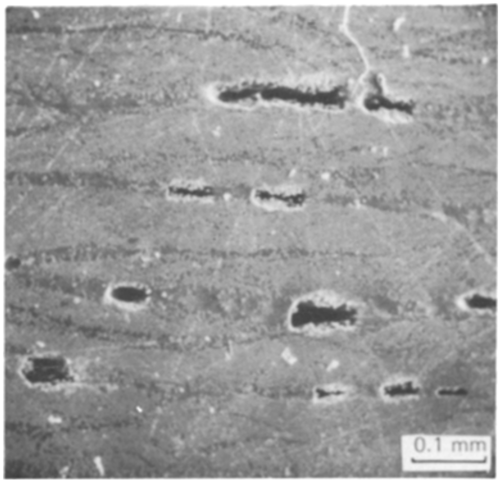

Figure 3 Section of a HT/LY 556 composite (laminate 1 of Fig. 2) with flattened voids between the plies.

interlaminar shear strength (23.1 $N\,mm^{-2}$ versus 32 to 33.4). Part of the loss of strength must be assigned to the high level of porosity.

These observations led to the following conclusions:

(1) Induction of splitting is an advantage when no other energy absorption mechanism exists in the well-elaborated composite. In HT/LY material, where pull-out of fibres occurs, splitting is of no concern.

(2) Moderate cleavage (sample broken into two or three pieces) is occasionally observed for composites with a high shear strength (e.g. HTS fibres) and otherwise brittle fracture. This cleavage is accompanied by an increase in fracture energy and apparently does not affect the shear strength.

Further work is related to a possible extension of the preceding observations.

5. Results for composites supplied with delamination promoters

Several films were introduced between the piles of prepreg in order to make the fracture by "multiple shear" easy. Details of the films are given in Table II. The only property required of the film material was its thermal stability at the cure temperature and chemical resistance to the attack by epoxy groups; characterized release films were also discarded.

TABLE II Nature and origin of films

Film	Thickness (nm)	Commercial designation	Origin
Aluminium	30		
Nylon-6	50	Capran-80	Allied Chem.
Polyester metallized on one-face	50	Mylar	Du Pont
Polyquinazoline	60		ONERA
Polyimide	12	Kapton	Du Pont
Polycarbonate metallized on one-face	12.5	KG-Makrofol	Bayer

The films were incorporated in the lay-up without special treatment, except for the aluminimum foil, which was either degreased or bichromate-treated to improve adhesion. Films of polyquinazoline are obtained in both a dry state and swollen by tetrachlorethane (25% wt/wt); both films were used.

5.1. Selecting the optimal lay-up

Variable numbers of 50 nm thick nylon-6 sheets were incorporated into a series of HTS/LY 556 composites to determine the optimal content of layers and the most favourable disposition.

The results of mechanical tests (Charpy fracture energy and ILSS) are plotted against the number of layers, in Fig. 4: it can be seen that with 2 sheets of nylon, the Charpy fracture energy increases from 4.5 to 12 $J\,cm^{-2}$. At the same time, the interlaminar shear strength decreases from 66 to 50 $N\,mm^{-2}$. Addition of more nylon sheets is of

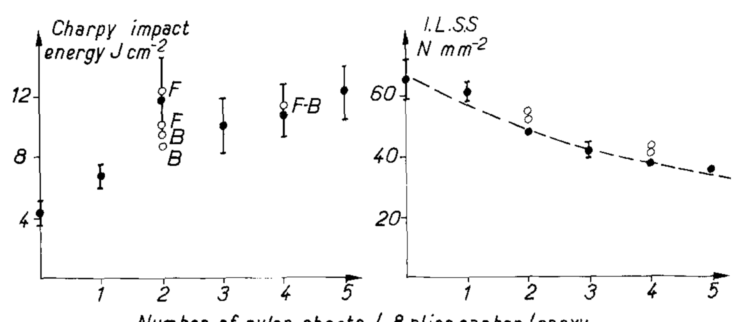

Figure 4 Mechanical properties versus number of nylon sheets. •, symmetrical lay-up; ○, asymmetrical lay-up. F, nylon forward; B, nylon backward.

TABLE III Mechanical properties of an asymmetrical lay-up (notation: numbers refer to carbon/epoxy piles and A to nylon; arrows indicate divertion of impact)

Property	Notation	
	→ 5A1A2	→ 2A1A5
Flexural strength ($MN\,m^{-2}$)	1060	970
ILSS ($MN\,m^{-2}$)	52.5	53.2
Charpy resilience min. ($J\,cm^{-2}$)	8.9	9.7
max.	9.6	12.0

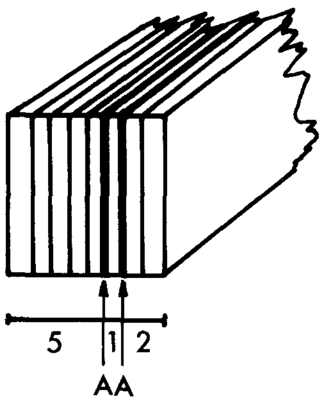

Figure 5 Structure of the specimens.

no further interest for the impact strength as the ILSS curve continues to fall.

Evolution of the flexural strength with number of sheets is difficult to appreciate up to 3 sheets: values in the range 800 to 1100 $N\,mm^{-2}$ were obtained. Over 3 sheets, the strength is very low although the fibre volume fraction is still 0.55 to 0.60.

The positioning of the two sheets is unimportant: a symmetrical lay-up with respect of the neutral plane of the sample or an asymetric one with the nylon oriented towards one face give almost equal results; for the asymmetrical orientation, however, anisotropy in the mechanical properties can be observed according to the direction of the stress: fracture energy and flexural strength behave conversely with each other (Table III). The structure of the specimens is shown in Fig. 5.

When the samples are fractured in the Charpy impact machine, as many pieces are yielded as separated blocks in the original laminate. On examining the fragments, it appears that fracture occurred in different manner to than in the samples containing no nylon: from Fig. 6, it can be seen that the compression area is very reduced and fibre pull-out more accentuated.

5.2. Comparison of different films

Table IV gives the results of mechanical tests on composites containing metallic or organic films as described previously. It must be noted that not all films behave as anticipated: Kapton and surface-treated aluminium do not fracture into the lamellae when tested. On the other hand, when adhesion between film and matrix is weak, e.g. in

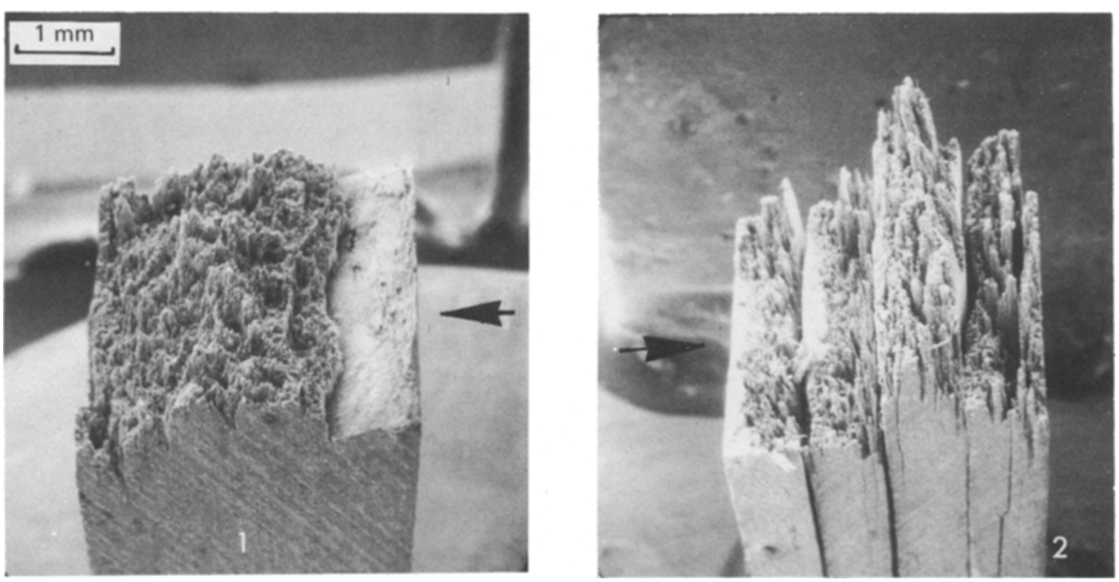

Figure 6 Scanning electron micrograph of impacted samples. Arrows indicate direction of impact. (1) HTS/LY 556. (2) HTS/LY 556 containing 3 sheets of nylon.

TABLE IV Change in mechanical properties of CFRP with delamination promoters. Fibre: Grafil HTS; resin: Araldite LY 566 + HT907 + DY063. Fibre volume fraction: 0.5 to 0.6 av (arrows indicate direction of impact)

Film	Number of sheets	Notation	Flexural strength ($MN\,m^{-2}$)	ILSS ($MN\,m^{-2}$)	Resilience ($J\,cm^{-2}$)
aluminium	3	2A2A2A2	–	34.5	11
(surface treated aluminium)	3	2A2A2A2	1000	52.0	4.7
nylon-6	2	→ 2A1A5	970	53.2	10.8
		→ 5A1A2	1060	52.5	9.3
polyimide	2	→ 2A1A5	1000	63.0	6.3
		→ 5A1A2	920	63.0	6.5
polycarbonate	2	→ 2A1A5	725	55.5	10
		→ 5A1A2	–	61.5	8.8
dry polyquinazoline	2	→ 2A1A5	–	43.1	10.8
		→ 5A1A2	–	40.3	10.5
swelled polyquinazoline	2	→ 2A1A5	1050	59.8	13.1
		→ 5A1A2	–	61.6	9.6
control (no film)		8	1000	65.0	5

degreased aluminium or perfectly dried polyquinazoline film, the lamellae are easily cleaved and there is a dramatic reduction in shear strength.

This contrasting behaviour has been represented schematically in Fig. 7, 1 and 4. Fig. 7, 2 and 3 depict the most interesting modes of fracture: with nylon or one face-metallized polycarbonate, adhesion of the film is high enough to prevent a complete peeling-off; tearing or even splitting of the film occurs (see Fig. 8). This is representated by Fig. 7, 2: here an increase in the fracture energy is obtained at the expense of a small diminution in shear strength.

Finally, Fig. 7, 3 agrees well with the case of swollen polyquinazoline films. As the moulding takes place in the press, there is very close contact between the film (containing 24% wt/wt tetrachlorethane behaving as a plasticizer) and the epoxy matrix. When the Charpy test is performed, breakage of this contact yields lamellae with a very rough surface (Fig. 9). Related to this is the strength of the adhesive bond (practically restrained ILSS) and the amount of work required to break this intricate bond (resilience × 2.5 in the optimal configuration).

5.3. Process generalization: other fibres and matrices

Incorporation of isotropic thin sheets into composites other than the basic HTS/LY 556 system studied so far, has also been attempted.

5.3.1. Other fibres

Delamination promoters do not produce any advantage in the case of HT or HM types of fibre. The mode of fracture of the original fibre/resin material is not fragile and is controlled by pull-out (for HM) and pull-out/delamination mechanisms. This agrees well with the earlier conclusions (Section 4.2).

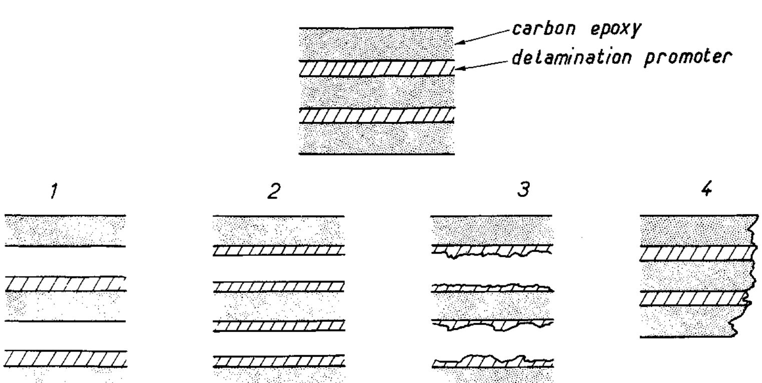

Figure 7 Idealized mechanism of film-promoted splitting.

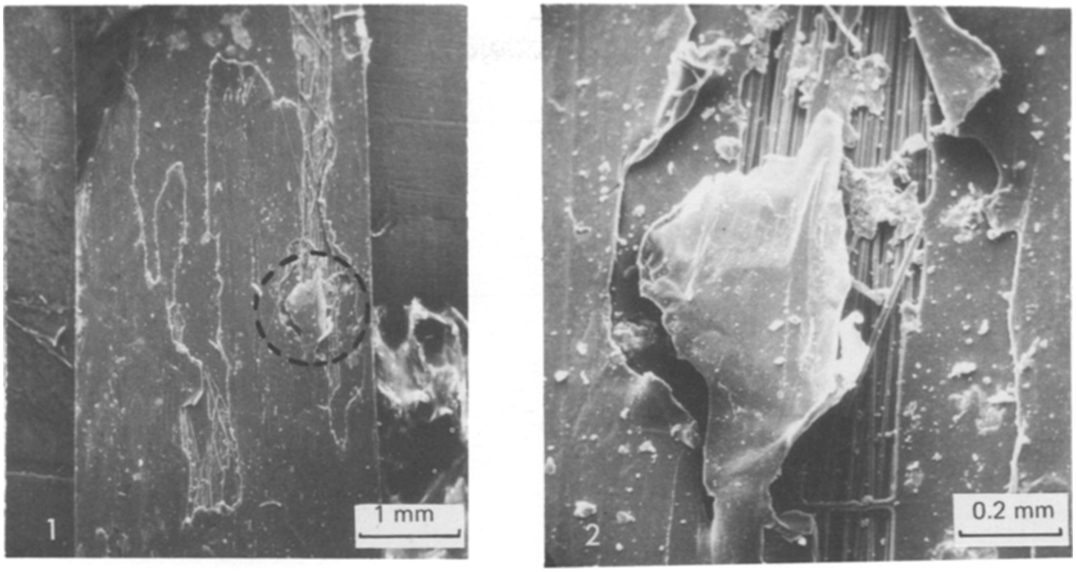

Figure 8 Tearing and splitting of metallized polycarbonate film at the surface of a lamella produced by the fracture of a sample. (*1*) General view of the lamella. (2) Detail of the circle in (1). Subjacent fibres can be seen.

Figure 9 Surface of delaminated polyquinazoline film.

For type III Grafil A fibre, the composite with seven layers of nylon-6 exhibits twice as much resilience (6.3 to 12.1 $\mathrm{J\,cm^{-2}}$) but there is a rough counterpart in shear strength: 61 to 25.5 $\mathrm{N\,mm^{-2}}$, in agreement with previous observation of the behaviour of shear strength with the number of nylon layers (see Fig. 4).

No obvious conclusion was reached for the two other types of fibre, HMS and AS, due to differences in the operating conditions. HMS type fibres were coated with a phenolic resin, and AS type fibres were directly used as a prepreg with NARMCO 588 resin. Nevertheless, improvement in fracture energy has been reported for the latter systems, but there was evidence that the nylon and polyquinazoline films did not fit well with the two resins used.

5.3.2. Other matrices

For HTS fibres, the film products used so far successfully function when other resins are substituted for LY 556. A few results are given in Table V for a cycloaliphatic epoxy resin (formerly manufactured Union Carbide's ERLA 4617) and a bismaleimide epoxy resin (KERIMID 601, Rhône-Poulenc). As noted previously, nature of film must be taken into consideration with regard to the resin, i.e. chemical and thermal stability, film/resin bond strength, etc.

Careful selection of the proper film is required to optimize such conflicting properties as fracture energy and interlaminar shear strength.

6. Conclusions

For unidirectional composites which have a brittle

TABLE V Variation of mechanical properties of CFRP with delamination promoters and various matrices. Fibre: Grafil HTS, volume fraction: 0.5 av

Matrix (curing cycle)	Film	Flexural strength ($MN m^{-2}$)	ILSS ($MN m^{-2}$)	Resilience ($J cm^{-2}$)
ERLA 4617 + mPDA	0	1200	92	5.8
(16h/120° C + 1h/160° C)*	nylon	1100	63	11.9
	aluminium	–	62	8.3
	polyester	–	43	10.
Kerimid 601	0	1000	68	4.9
($1\frac{1}{2}$ h/250° C)	aluminium†	1000	51	8.0

*Manufacturer's conditions of cure not observed lest film's injury.
†Aluminium only available at this temperature.

mode of fracture, e.g. type IIS or III carbon fibre-reinforced plastics, the conditions of fracture may be modified by thin metallic or polymeric sheets incorporated into the lay-up and acting as delamination promoters. The volume fraction of these promoters is small (≈ 0.03 when the 3 mm thick plate contains two sheets of 50 nm thick nylon) and generally does not affect the longitudinal properties of composites (static as well as fatigue strength).

The chemical nature and the surface conditions of the films must match the impregnation resin. Film/resin peeling tests should be carried out.

Delamination promotion by isotropic films is inadequate for composites where energy-absorbing mechanisms (pull-out, debonding, delaminations) are extensively involved.

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