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Viscoelastic investigation of interfacial damage of glass and carbon fibers composite materials

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SUMMARY

Glass/Epoxy and Carbon/Epoxy unidirectional composite materials have been subjected to cyclic ondulated loading of three points bending specimens. The viscoelastic properties of the new or damaged materials are recorded with a POLYMER LABORATORIES PL/DMTA viscoelasticimeter working at 10 Hz. The viscoelastic behavior of samples subjected to various dynamic shear strains has also been investigated with a computer driven METRAVIB viscoanalyser.

The results show that under fatigue stresses, glass/epoxy interface has permanent damage leading to large damping while carbon/epoxy one seems to have only intermittent damage leading to lower damping and better fatigue properties.

INTRODUCTION

Composite materials have specific fatigue properties compared to polymer or metallic materials.

These properties can be related to the effect of fiber/matrix interactions at the interfacial bond and/or in the interphase zone (1). The interfacial bond is considered to have zero thickness and result from the interaction between fiber surface and matrix. The interphase zone is the area immediately adjacent to the interface, including fiber finish or size materials, and extends a finite distance into the bulk matrix material.

An extensive review of the literature (1) indicates that much work has been done on fiber/matrix interface characterization but the role of the interphase in determining composite properties is not well known.

The viscoelastic behavior of composite materials is very important : it can be predicted from constituent properties (2) and some works have been made in our laboratory to correlate viscoelastic properties with interface structure and technical properties (3-7).

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Adams (8) found that damage on specimens fabricated from fibre reinforced plastics could be detected by an increase in damping whether this damage is localised, as in a crack, or distributed through the bulk of the specimen as many microcraks.

Effect of damage on viscoelastic properties of structural components has been studied on glass (9), carbon (10), and aramid fibers (11) reinforced epoxies as well as on aluminium alloys (17).

GIBSON (9) studied crossply laminated glass-epoxy beams with a steady-state forced vibration tests : the damping increases slightly with increasing maximum strain during a first run. When the strain level is reduced, the damping remains near its level indicating permanent structural changes. The proposed explanation of the authors is Coulomb friction at the newly-created crack interfaces.

The carbon/resin composite has poor interlaminar shear strength because of the weak adhesion and poor bonding between carbon surface and matrix (12).

Adams and Flitcroft (10) studied dynamic torsion at series of increasing and decreasing amplitudes, in some fibre high volume fraction composites, there was a decrease of damping with stress at low strains followed by an increase at higher strains as they cause propagation of the delamination craks. They proposed damping as a non destructive testing measurements in the range 3- 10% of failure stress.

The coupling mechanism of carbon-resin composites involves the formation of hydrogen bonds (13) which can be increased by dipole-dipole interaction : Riess (14) prepared an interphase copolymer material, the dipole-dipole interaction couples to the carbon fiber and increases shear strength and impact toughness

In its extensive review of literature, Mc MAHON (1) concludes that in contrast to adhesion in glass fiber/epoxy composites, carbon fiber/epoxy adhesion is not simply promoted by coupling agents but rather results from physical interactions with the matrix.

Early works of ATKINS (15) proposed a new approach of carbon/epoxy in which intermittent bonding along the fiber surface was suggested. The weakly bonded sections allow debonding and fiber pullout during fracture while the strongly bonded areas enable load transfer.

In this study, we damage composite materials by cyclic ondulated loadings of three points bending specimens while we followed the viscoelastic properties at selected level of stiffness. We also applied dynamic shear at various levels of strain to follow the in-situ evolution of viscoelastic properties.

EXPERIMENTAL

Epoxy matrix is prepared with diglycidyl ether of bisphenol A (Dow Chemicals DER 332) and 4,4' diamino-diphenyl methane (Fluka) as a stoechiometric mixture. We used two types of fibers :

E glass from Vetrotex with an epoxy sizing containing DGEBA and aliphatic polyester (P185-300 EC 14 2400) and a T300 sized TORAY carbon fiber.

The impregnation of fiber has been made at 60°C (as we notice that the viscosity remains constant at a level of 0.22 Pa.s. during 1 h 30) and samples have been filament winded in a 270 x 250 x 1 mm^3 mold, cured 3 hours at 90°C followed by a 3 hours 190°C post-cure and a slow return at room temperature in the mold (5 hours). The carbon volume fraction has been measured as 0.45 and the glass volume fraction is 0.67.

Fatigue experiments have been made on a EPSIFLEX PRODEMAT machine. The specimen supports three points bending at constant strain (0.5 σ_R) and one can follow the level of stress while the frequency is 25 Hz.

Viscoelastic properties have been studied on PL/DTMA viscoelasticimeter from POLYMER LABORATORIES working at 10 Hz. The sample is a cantilever beam and the displacement is set to 16 µm (fig. 1).

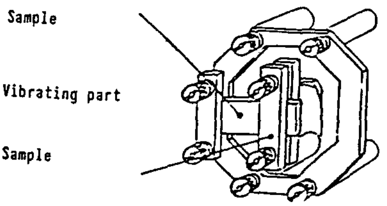


Fig. 1 : PL/DTMA sample support

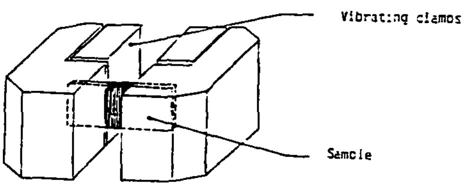


Fig. 2 : Metravib viscoanalyser sample holder

The measurements are made after 1 mn of temperature stabilization while the temperature changes are made with a 3°C/mm increase. The computer gives the real part of the complex modulus (E') and loss factor (tg δ) as the tangent of the phase angle between E' and the imaginary part E'' of the complexe modulus :

$$E^* = E' + jE''$$
$$tg\delta = E''/E'$$

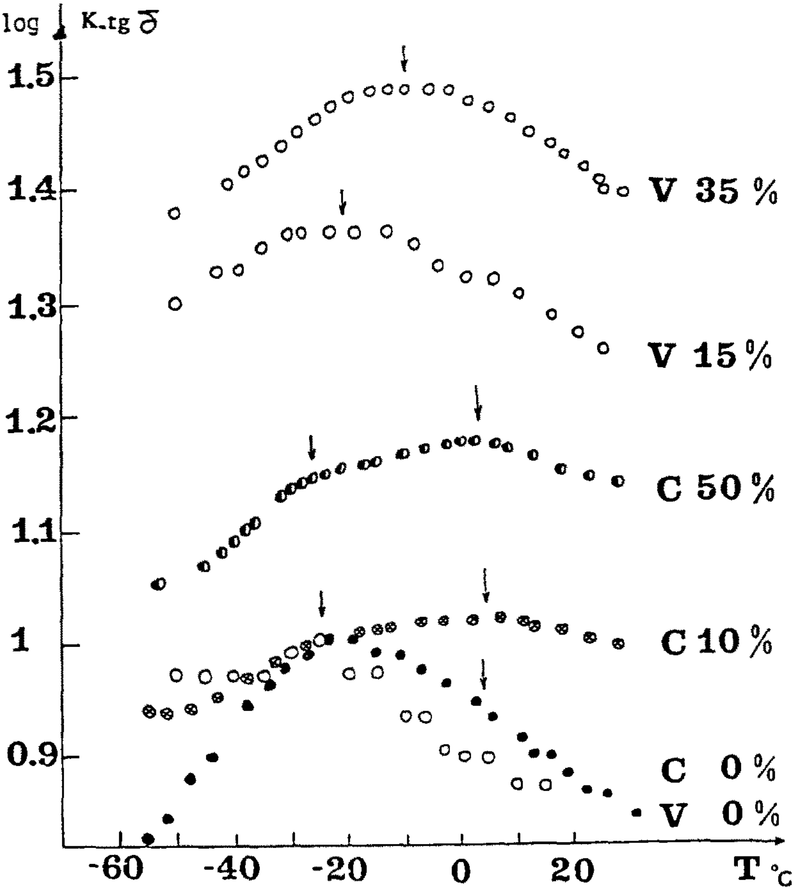
Dynamic shear damage has been followed on a computer driven METRAVIB viscoanalyser at room temperature. The sample is placed between two clamping systems (fig. 2) which allow to strain the matrix/interphase/fiber system along the fiber axis (16).

The computer drives all the system and follows the different shear displacement previously set up. This automatic drive avoid differences in time, level or measurements of any human drive. The computer calculates and prints G', G" and tgδ, the components of the dynamic shear modulus at various displacements between 0.1 µm. As the effective sample size between clamps is 7 x 7 mm^2, this lead to a strain level of 1.4 10^{-4} for each µm of displacement (which is a sufficient one for high damage of the material).

At higher damage level, the damping must decrease as there are so many interfacial craks that part of the load is no more shared by the matrix.

With T300 carbon fibers, the behavior is different : damping decreases first. This result suggests a kind of accomodation of the interphase region where significant residual stresses accumulate during elevated temperature curing as well as shrinkage of the matrix during polymerisation. The weak physical bonds of the matrix at the interface can move to a better arrangement which is known as Mullins effect is black carbon/elastomers composites (21).

Fig. 4 : Analyses of low temperature viscoelastic behavior of composites during fatigue tests



RESULTS

Evolution of viscoelastic properties with fatigue damage

Fiber epoxy composites with DGEBA-DDM matrix present a viscoelastic spectrum with three main peaks at 10 Hz :

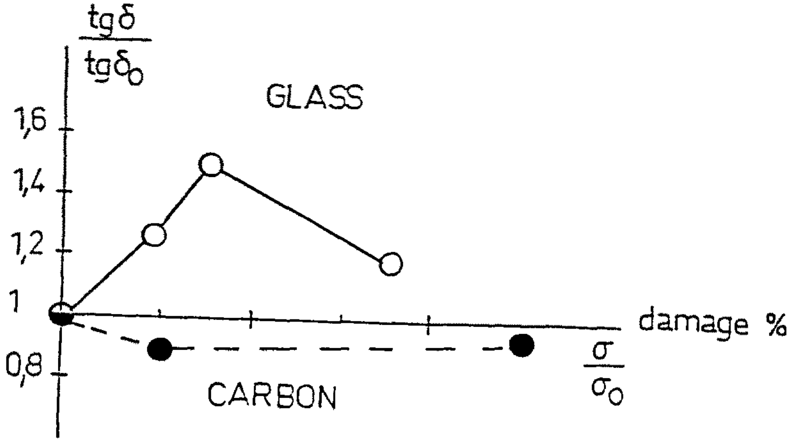
α Peak (185 ± 1°C) with an apparent activation energy of 175 kcal/mole which is the glass/rubber transition relaxation mode. With this kind of matrix, this relaxation zone is not large and is at the same place either with carbon or glass fiber.

β Peak of the resin (-25°C) has an activation energy of 19 kcal/mole and comes from the motion of hydroxyl-ether segments of the matrix (18). With treated carbon fibers as T300, this pic has a high temperature shoulder β' at 5°C which can be attributed to the relaxation of hydroxyl-ether within the interphase. The relative activation energy of the two relaxations being different, this shoulder is more easy to see at low frequencies.

α' Peak (50°C) as a very low activation energy and is very small. It seems to be due to the movements of less fixed areas or internal stresses (19) (20). In our experiments we only observed this peak with some specimens during a first run, this could mean it is caracteristic of poor curing.

The variations of damping properties are shown on fig. 3-4.

Fig. 3 : Relative variation of dampinc at the glass transition with damage



With glass fiber, the maximum of damping increases up to 20% of damage measured by the remaining stress for a constant strain level. This behavior is interpreted as Coulomb friction damping among interfacial cracks as the fatigue process goes on because of the break of some chemical links between the matrix and the silane sizing.

To have comparable results with different volume fractions, we reported relative damping by dividing all the values by the maximum value of tgδ for the undamaged carbon/epoxy composite.

Glass-epoxy composites (V 0%, V 15%, and V 35%) have a large increase of damping for rather low damage (15%) with no change in peak aspect. This means that permanent craks occur at the interface which leads to Coulomb friction as the damping shift toward higher values without structural change.

Carbon-epoxy composites are different again. Between 0% and 10% of damage, the β peak of hydroxyl-ether remains constant while the β peak of the same function within the interphase increases. As only the free hydroxyl-ether groups can relax while the hydrogen or dipole-dipole bonded cannot move, this means than more free hydroxyl ether groups exist after some dynamic stress has been applied for sometime. Over 10% of damage, the peak shifts toward higher damping as permanent ruptures of the interface take place without any more change in the peak aspect.

Effect of dynamic shear strains on viscoelastic properties

We report on Fig. 5 and 6 the results about the evolution of viscoelastic properties during several runs of increased displacement between 2 and 100 μm for the matrix itself and the two kinds of fiber reinforcements.

To have comparable results, we calculate relative changes by dividing all the results (G' and tgδ) by the values of the less damaged sample (i.e. 2 μm displacement, first run) for each kind of specimen (matrix, glass and carbon).

On fig. 5, one can see the matrix and the carbon reinforced composite show the same behavior during the first run (0-20 μm), the second one (0-50 μm) and the third one (0-100 μm).

There is just a small loss in stiffness after a first run at 50 μm displacement the remaining stiffness being 97% of the fresh one.

For glass fiber composites, after a first run up to only 30 μm, the remaining stiffness is only 93% of the fresh sample's one and it decreases again after a second run.

The damping variations on Fig. 6 show similar effects :
For the matrix, the damping presents a very small increase in damping over the displacement range and is perfectly reversible.

For carbon-epoxy composites the damping increase is larger but, however it is 4 times larger after a 50 μm bending, it comes back to its initial value when the displacement is back to 2 μm.

For glass epoxy materials the damping at 2 μm displacement is multiplied by 4 after a first run and by 5 after a second run. This is an evidence for permanent damage in glass-fiber reinforced composites while the carbon-fiber one presents at least a partial recovery of its interface properties after some damage.

Fig. 5 : Dynamic shear modulus evolution with damage

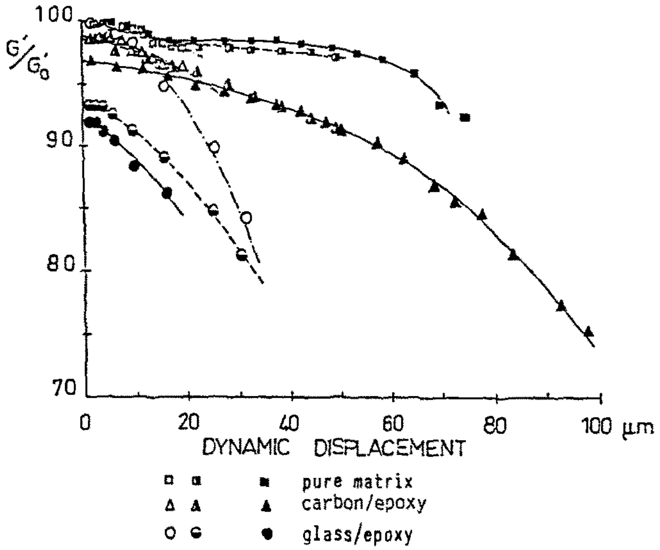
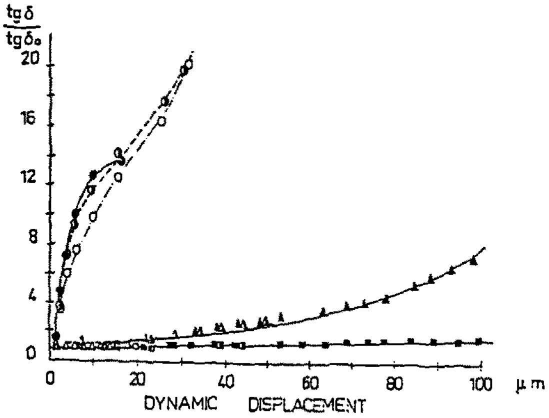


Fig. 6 : Dynamic damping of materials at various strain levels (same symbols than Fig. 5)



CONCLUSION

Viscoelastic measurements are performing tools for the investigation of interfacial damage of composite materials.

The following of viscoelastic damping during fatigue of three points bending specimens and shear test specimens show that glass/epoxy and carbon/epoxy are different :

With glass/epoxy composite materials, the strong covalent links between fiber and matrix through the silane sizing present permanent damage with large Coulomb friction damping while the weaker physical interaction of carbon/epoxy interface allows accomodation and recovery of the interface region when the sample is back to any unstressed state. It is only for the large stresses that permanent damage appears in carbon/epoxy composites, leading again to some permanent damage.

The results show that if good adhesion is necessary for good strength, stronger links between fibers and resin might no give better properties and that optimum fatigue behavior can be achieved by "tailoring" the interphase stiffness, adhesion and accomodation ability.

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