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Krzysztof Kurek and Andrzej K. Bledzki

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What is This?

Fatigue Behavior of Composites with Foamed Matrix

KRZYSZTOF KUREK
Zentrum für integrierten Umweltschutz
Landgraf-Karl-Straße 2
34131 Kassel, Germany

ANDRZEJ K. BLEDZKI
Institut für Werkstofftechnik
University of Kassel
Mönchebergstraße 3
34109 Kassel, Germany

ABSTRACT: Fiber reinforced epoxy foams laminates are a new group of fiber composite materials. The microporous structure of these fiber composites is achieved by adding siloxanes as an expanding agent during the hardening reaction with amino-hardeners. Hydrogen released during the cross-linking reaction expands the polymer matrix.

Fiber reinforced epoxy foams laminates have already found widespread industrial use. A foam system with glass fiber reinforcement was used in the production of the first load-bearing primary structures of fiber reinforced thermosets. The underbody of the Z1 model of BMW exhibts a high degree of inherent stiffness and strength. Fiber reinforced epoxy foams systems have also become successfully established in sports and in the electrical and building industries.

Epoxy foams reinforced with glass and carbon fibers were selected for mechanical and microscopic tests. Given a micropore content of 27.4 vol. %, densities of 1.4 g/cm³ were achieved with glass fiber fabric reinforced epoxy foams with a glass fiber content of 42 vol. %. Carbon fiber fabric epoxy foams exhibit the following values: density of 1.25 g/cm³ with a carbon fiber content of 50 vol. % and micropore content of 15 vol. %.

The dynamic increasing load tests showed that the damping progress of glass fiber reinforced epoxy foams laminates does not depend on the micropore content. The damping progress by carbon fiber reinforced epoxy foams laminates is largely independent of the micropore content, the stresses at break diminish with increasing micropore content. The Wöhler fatigue tests on glass fiber fabric reinforced epoxy foams laminates with different micropore content produced similar Wöhler curves, which are relatively close together.

In view of the initial results it can be assumed that the structure of the fiber reinforced epoxy foams laminates can favourably influence the dynamic characteristics of these composite materials. There is evidence that the porous structure which is developed during the

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*Author to whom correspondence should be addressed.

expansion of epoxy resin can restrict the crack progression. The crack progression depends on the size and distribution of the micropores in the resin matrix. This means that the dynamic behavior of completely pore-free laminates need not always be linked to the better dynamic behavior of such materials.

LIGHTWEIGHT CONSTRUCTIONS SAVE ENERGY
AND RELIEVE THE ENVIRONMENT

THE SEARCH FOR ever lighter materials that are at the same time more resistant to mechanical strain opens up new areas of use for non-reinforced and fiber-reinforced foamed plastics. However lightweight construction has also become an important factor in environmental protection. An automobile weighing 100kg less saves 0.4 l of fuel per 100 km, with 1 l of fuel burning up to about 2.6 kg CO_2. Thus, by replacing the steel flat springs and the steel driving shaft by fiber composite a vehicle on a 150 km driving stretch would relieve the environment by approx. 1250 kg CO_2 [16].

FOAMED PLASTIC PRODUCTION

History

Foamed plastics made of thermosets, namely on the basis of von urea-formaldehyde-resins, have been known since the early thirties. In the late forties a certain commercial interest began in foamed plastics of those made of polystyrene. In the early fifties, of those made of crumby PVC, and at the end of the sixties, of those made of polyethylene (LDPE), i.e., in each case about 20 to 25 years after, the respective thermoplastics began to be produced on a large scale [1].

EXPANDING AGENTS AND NUCLEATORS

Mainly low-boiling liquids such as pentane and fluorinated hydrocarbons, e.g., freon, are used as *physical expanding agents*. Above boiling point, an increase in volume results upon transition to a gaseous state, and the plastic smelt is thereby swelled. The physical expanding agents have become generally accepted for almost all polymer materials and production procedures and so are used for all foam processes in which a regular low density is required. The simplest physical expanding agent is water [6], which, however, does not boil until 100°C.

The *Chemical expanding agents* break down, separating a gaseous product above their disintegration temperature. The gas yield from this breakdown product varies and determines the necessary addition quantities to achieve a prescribed density [7]. The azo compounds constitute approximately 95% of all chemical expanding agents for foamed plastics and the sulfohydrazides approx. 2%. In all, the chemical expanding agents are treated approx. 90% with PVC, the remaining 10% with polyethylene, polypropylene, polystyrene, polycarbonate, etc., [8].

The *reaction expanding agents* react chemically with the polymer matrix, sep-

arating a gaseous product. A good example of this context is the production of epoxy resin foams, whereby a siloxane is used as expanding agent.

Citric acid, for example, and sodium hydrogene carbonate, which acts at the same time as a expanding agent, can be used as *nucleators*. They cause regular formation of the gas cells in the production of vacuum plastifiable sheets made of EPS [1].

Foamable Unsaturated Polyester Resins [2–4]

In the production of Legupren foamed plastics from the Bayer AG, the following components are necessary:

• resin, a foamable Leguval type
• hardener, an orgainc peroxide, e.g., benzoyl peroxide
• expanding agent that, upon chemical disintegration, develops a gas at room temperature, e.g., carbonic acid, derivates of the general formula:

$$R_1-C-O-C-O-R_2$$
$$\underset{O}{\|}\qquad\underset{O}{\|}$$
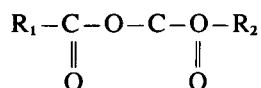
Here, $R1$ and $R2$ refer to similar or different saturated and/or unsaturated aliphatic or cycloaliphatic as well as aromatic residues.

When combined with suitable activators, compounds of this nature break down at room temperature, and eliminate carbon dioxide. The residue containing ester groups in UP-resin compatible, practically soluble in water, and can if necessary, be incorporated in the copolymerisation of the UP resins.

Without altering the whole system essentially, the use of di- or polyisocyanates offers further advantages on foaming,—in the adhesive strength and in the final properties, e.g., higher E-module and higher heat resistance. The pore structure is also affected. The pressure development is affected by formulation, temperature, mould surface, foam height and by the mould tightness. During repeated experiments, pressures of 0.07 bar were measured, in special cases up to 0.6 bar.

Epoxy Resin Foams

The epoxy resin foams have been known for a long time. In the early fifties the first epoxy resin foams were developed [6]. At that time, hardener systems such as aconite acids, amino boranes, trimethoxyboroxine, or gas separating compounds, such as diphenylosulfon—disulfohydracide were used as expanding agents. However, only foamed plastics with a relatively high volumetric weight could be produced using these expanding agents. Products with low volumetric weight did not become available until the foaming process was considerably simplified by the use of the fluorine hydrocarbons, especially freon 11 (monofluorine trichloromethane) [13]. In the early seventies the epoxy foams were used in the aviation industry [14, 15]. Aluminium honeycomb epoxy foams, for example, were used in the production of the DC 10 passenger aircraft.

Meanwhile, the epoxy resin foams are also used in the construction industry [12].

- grouting electronic components
- grouting of cable sleeves in low voltage and telecommunications area
- sealing of pipe and cable penetrations through walls in civil engineering

Fiber Reinforced Epoxy Resin Foams

The fiber reinforced epoxy resin foams represent a new group of materials, used industrially only since recently. The foaming of the matrix material takes place as a result of a chemical reaction between the resin and the expanding agent, whereby hydrogen is released. Thereby a porous structure in the material is produced.

The uncomplicated processing of this systems distinctly improves [9] the production economy. A good example of this is the use of the reinforced epoxy resin foams in the manufacture of surfboards. The introduction of the reinforced epoxy resin foams has resulted in reducing by half the production time for a standard surfboard [12]. The time saved depends on the expansion and the resulting flow progress of the resin, which saturates the reinforcing fiber bundles independently. The epoxy gelcoat layer is thereby laminated, agglutinated to the core material, and hardened in a single operation. The use of the epoxy foams has reduced the weight of the standard surfboards from 22 to 12 kg while retaining the same stiffness.

The underbody of the Z1 model by BMW is one of the first load-bearing primary structures made of plastic to be used in standard automobile construction [10]. The underbody has a high intrinsic stiffness, strength, shape retention at a temperature of 140°C, and fire-resistant behavior. By means of a sandwich construction with a PUR foam core and covering layers made of glass fiber reinforced epoxy resin foam, these properties are secured [11].
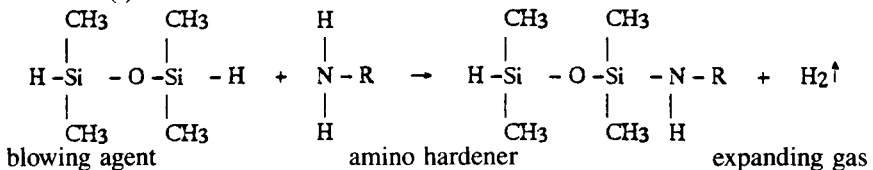
The Federal German Railway used reinforced epoxy foams for the production of large-area, nonwarping laminates for the lining of the whole roof and windows of the ICE (Inter City Express) wagons [12].
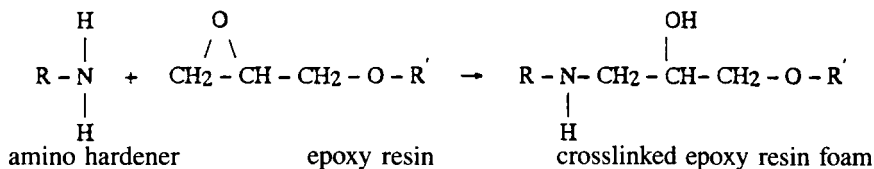
EXPERIMENT

Principle of the Procedure used for Foaming Epoxy Resin

The foaming of the epoxy resin results chemically. Before processing, a siloxane is added to the epoxy resin components, which releases hydrogen as a expanding agent in the hardening reaction with aminio-hardeners [10].

Reaction (I):

$$\begin{array}{ccccccc}
CH_3 & CH_3 & & H & & CH_3 & CH_3 \\
| & | & & | & & | & | \\
H-Si & -O-Si & -H & + & N-R & \rightarrow & H-Si & -O-Si & -N-R & + & H_2\uparrow \\
| & | & & | & & | & | & | \\
CH_3 & CH_3 & & H & & CH_3 & CH_3 & H
\end{array}$$

blowing agent   amino hardener   expanding gas

Reaction (II):

$$\underset{\text{amino hardener}}{\overset{\displaystyle H}{\underset{\displaystyle H}{R - N}}} \quad + \quad \underset{\text{epoxy resin}}{CH_2 - \overset{\displaystyle O}{\overset{/ \ \backslash}{CH}} - CH_2 - O - R'} \quad \rightarrow \quad \underset{\text{crosslinked epoxy resin foam}}{\overset{\displaystyle OH}{R - \underset{\displaystyle H}{N} - CH_2 - \overset{|}{CH} - CH_2 - O - R'}}$$

In a closed slightly heated mould, the still liquid matrix builds up a weak expansion pressure. The resin permeates all marginal zones of a complicated mould. The wetting of the reinforcing material is also simpler than with conventional epoxy resin composites.

Production of Reinforced Epoxy Foams

The 4-mm-thick laminates were produced in a press between two heated steel plates. The reaction time was approx. 15 minutes at 80°C. For variation of the pore content in the resin matrix 0.2 to 2.0 weight parts of the polysiloxane were added. The characteristic values of some manufactured laminates are listed in Table 1. The dependence of the micropore content on the expanding agent content as shown in Figure 1 is also affected by the kind of reinforcing material. The glass fiber fabric is woven denser than a random mat and therefore creates a greater obstacle to the excaping blowing gas. A higher volume content of the reinforcing fabric restricts the expansion of the matrix, which may explain the difference between the course of the micropore content in the g-fabric and c-fabric laminates.

Table 1. Manufactured laminates.

Material Components /Laminate Name	Expanding Agent Content [Weight Parts]	Pore Content [vol. %]	Density [g/cm³]
Epoxy foam + glass fiber fabric	2.0	27.4	1.42
g-fabric	1.0	20.7	1.50
	0.2	11.4	1.62
Epoxy foam + endless glass	2.0	20.3	1.52
fiber mat	1.0	18.3	1.54
g-mat	0.2	14.8	1.27
Epoxy foam + carbon	2.0	14.8	1.27
fiber fabric	1.0	7.0	1.37
c-fabric	0.2	2.0	1.43

Fiber content approx.:
   g-fabric   42.5 vol. %
   g-mat   43.3 vol. %
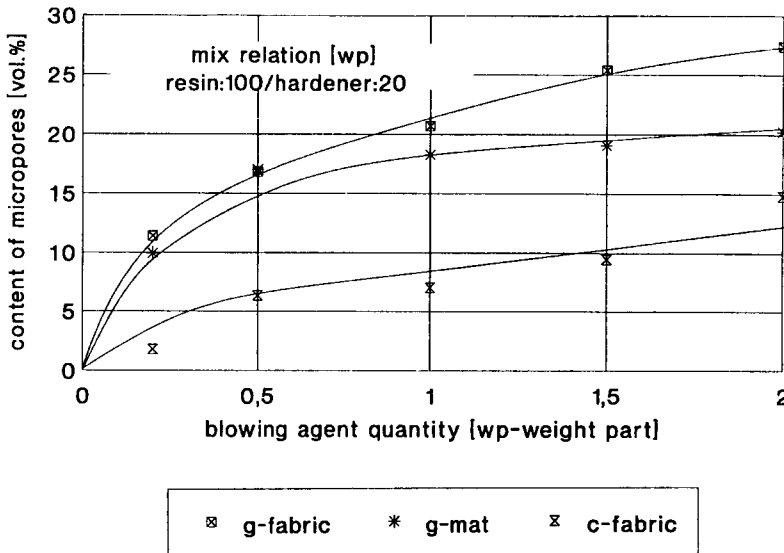   *c*-fabric   50.0 vol. %

Figure 1. *Content of micropores vs. blowing agent quantity.*

Resin System and Reinforcing Material Used

The epoxy resin system from Ciba Geigy GmbH was used as matrix material: Resin LY 5054; expanding agent DY 5054; hardener 970R.

Glass fiber fabric:	plain weave, weight 300 g/m², type 21 091, Brochier S. A./France
Endless glass fiber mat:	weight 450 g/m², type U 816, Vertotex/Germany
Carbon fiber fabric:	plain weave, weight 245 g/m², type 98150, Interglas AG/Germany.

RESULTS OF MECHANICAL TESTING

Static Experiments

The static experiments (tensile test pursuant to EN 61) were carried out with 8 samples in each case. With increasing micropore content, strength does indeed become slightly reduced (Figure 2), but a standardization by density profides practically the same characteristic values for all micropore contents examined. With increasing micropore content, the E-modulus remains almost constant with the carbon fiber as also with the glass fiber reinforcement (Figure 3). A standardization of the density would mean an increase of the E-Modulus with increasing micropore content.
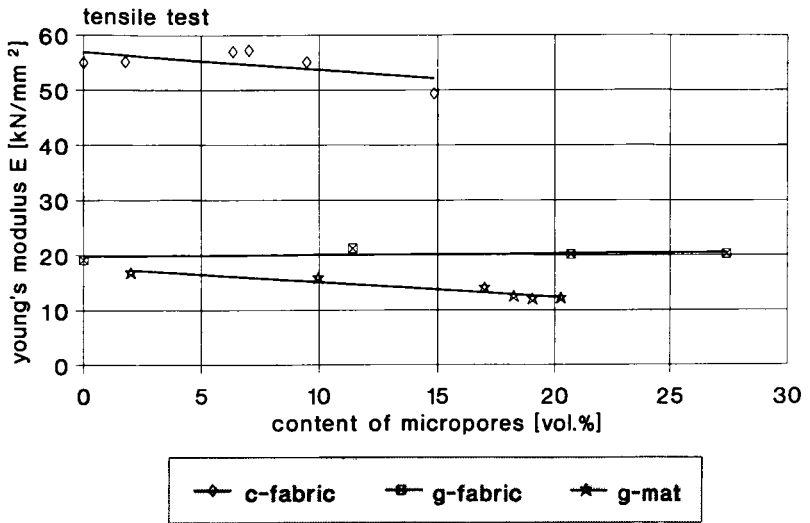
Figure 2. E-modulus vs. content of micropores.
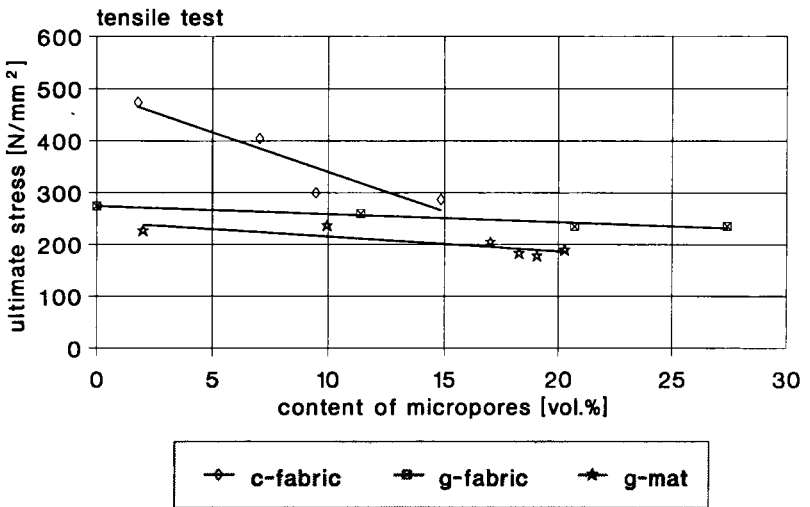
Figure 3. Ultimate stress vs. content of micropores.

Dynamic Behavior of Fiber Reinforced Epoxy Resin Foams

Since the use of these fiber composite materials will lie increasingly in the area of dynamic loading, knowledge of the dynamic behavior is necessary for the component arrangement. First dynamic experiments of fiber reinforced epoxy resin foam have shown that the microporous structure of the laminates can have a positive influence on the mechanical behavior [17,18].

Due to the visco-elastic behavior, a phase shift in the polymer materials between applied stress and extension of the material. The extension comes some time after the application of stress. A sinus-shaped stimulation of the sample, e.g., with a hydropulser, results in a sinus-shaped extension of the sample. The two sinus curves are separated by a phase angle (δ) for each other (Figure 4). Overlaying the two measurement signals in a tension extension diagram results in a hysteresis loop. The reconstruction of the hysteresis loop from the tension- and extension signal is shown in Figure 4. InDyMat, (*In*telligent *Dy*namic *Ma*terial *T*esting), the computer programme developed at the Institut Für Werkstofftechnik records the hysteresis loops at certain intervals (approx. 1,000 values each time) and evaluates them, the most-used characteristic values of the dynamic test being defined as in Figure 5. The whole of the system for dynamic material testing, constructed at the Institut für Werkstofftechnik, is shown in Figure 6. A sinus-shaped load is put on the test sample between two jaws of a hydropulser. Using an extensiometer, measured extension is amplified, digitalized, and fed into a DOS computer. The load measured by the dynamometer is also amplified, digitalized, and fed into the computer. Optionally, the sample temperature can be measured accordingly and registered. The stress or the extension, depending on whether tension or extension control is tested, are taken as true values with the given index values. Any eventual corrections to the load put on the sample are thereby made possible by using a function generator (controller).

The course of the characteristic values can be followed during the experiment on the screen. After the experiment, the measured values are available as appropriately prepared files, which can by read in, processed, and printed out in conventional graphic programmes.

Load Increase Experiments

The load increase experiments serve as a speedy material characterisation on cyclical on cyclical loading and help to register the course of the damage. The test pieces were loaded in the tensile stress range at a stress ratio (understress/overstress) of 0.1.

In various reinforcing materials substantial differences resulted in the course of the damping. The two fabric laminates (*g*-fabric and *c*-fabric), Figures 7 and 9, show basically similar behavior with regard to the course of the damping. After an initial slight increase in the damping there were indications more or less of a decrease in damping, which was probably caused by the stretching of the fabric threads in the loading direction. A stretched thread contributes more to the general stiffness of the composite, thus the composite is more stiff and the damping decreases thereby. Since the carbon fibers are heavily anisotropic
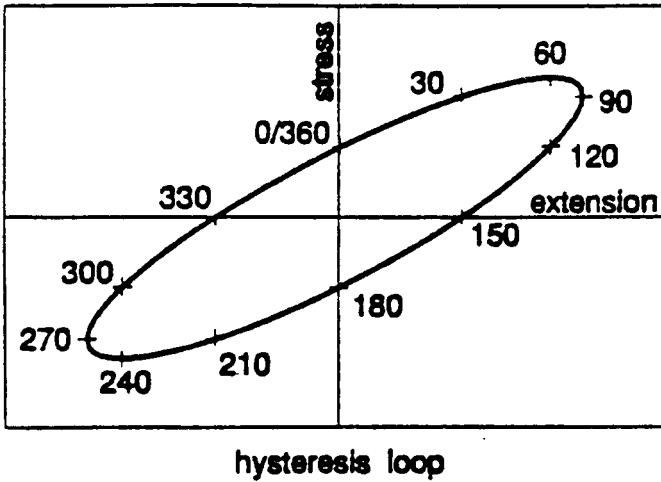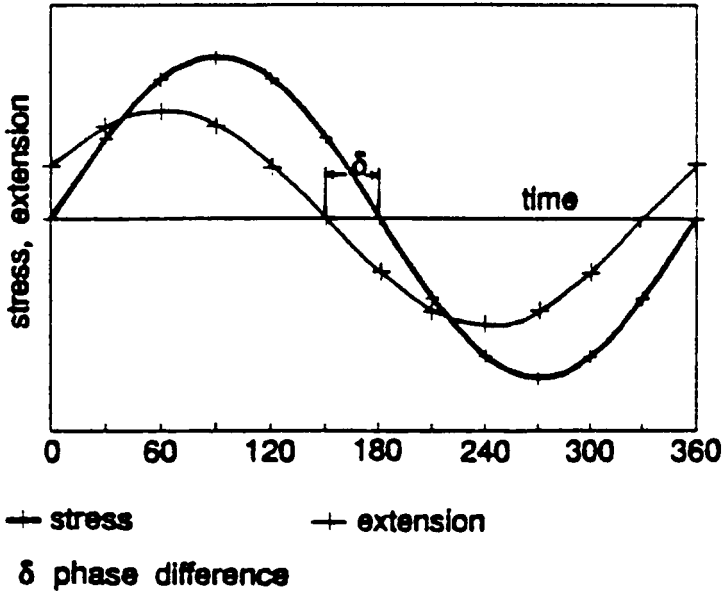
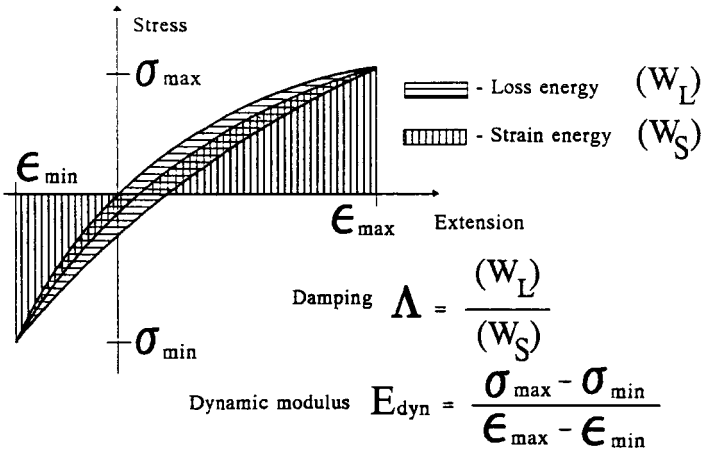Figure 4. Reconstruction of hysteresis loop from stress and extension signal.
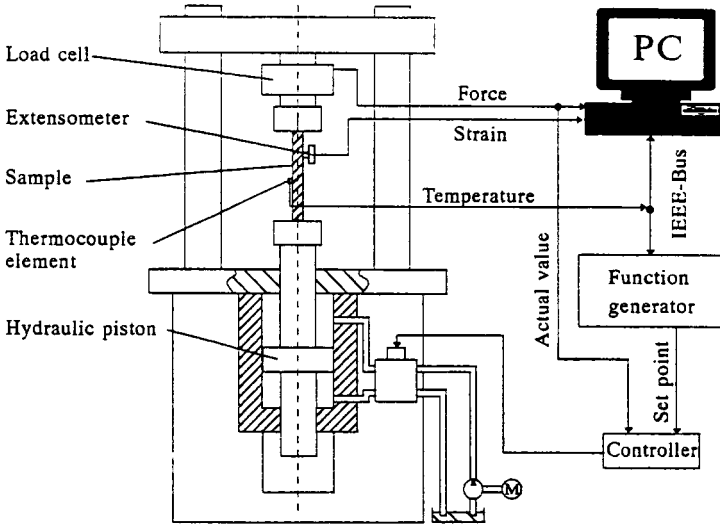
Figure 5. *Definitions of damping and dynamic modulus.*

$$\text{Damping} \quad \Lambda = \frac{(W_L)}{(W_S)}$$

$$\text{Dynamic modulus} \quad E_{dyn} = \frac{\sigma_{max} - \sigma_{min}}{\epsilon_{max} - \epsilon_{min}}$$

Figure 6. *Experimental arrangement for dynamic tests.*
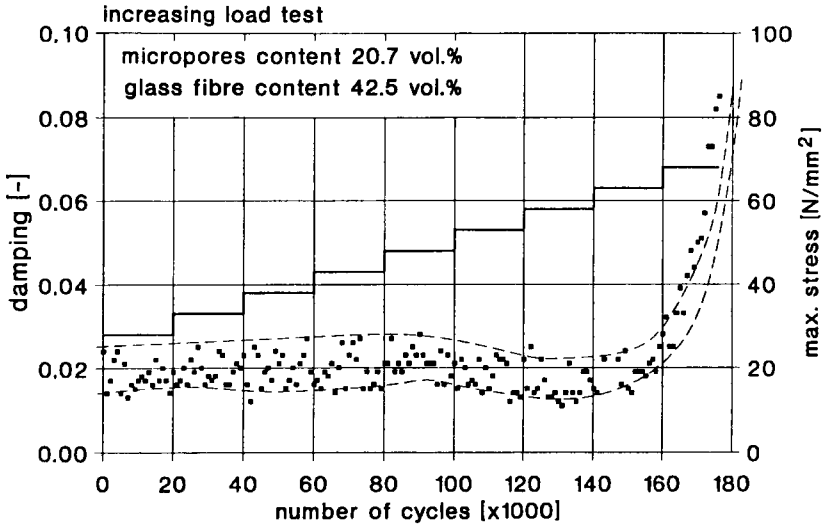
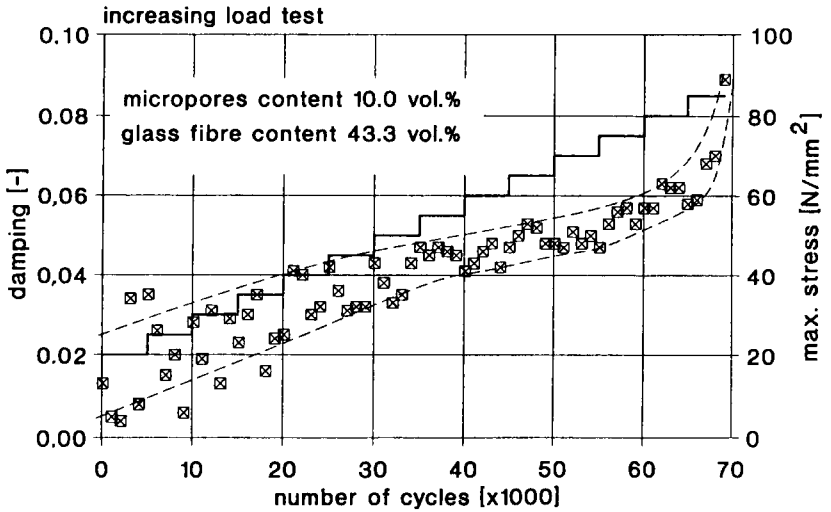**Figure 7.** *Characteristic progress of damping for g-fabric-laminates.*

Figure 8. *Characteristic progress of damping for g-mat-laminates.*

increasing load test
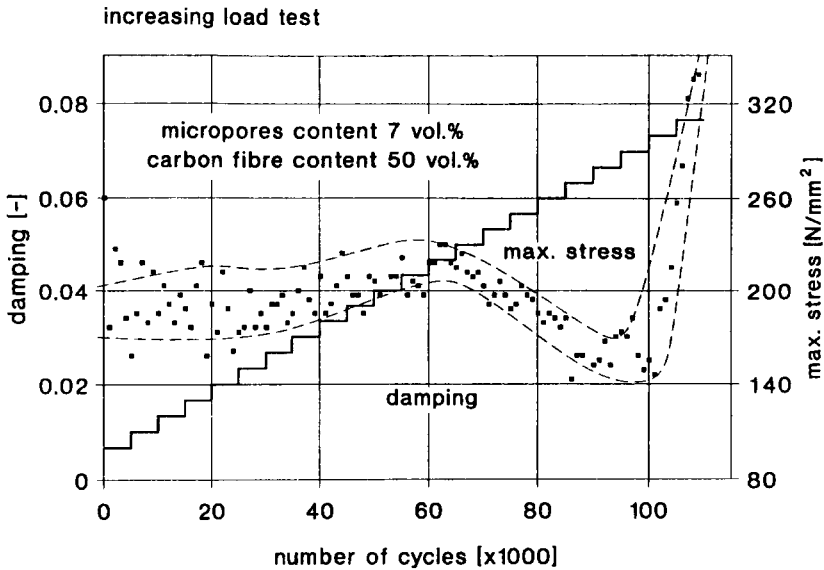
Figure 9. *Characteristic progress of damping for c-fabric-laminates.*

($E_{lengthwise}$ = 230 [kN/mm2], $E_{crosswise}$ = [14 kN/mm²]), the reduction in the damping is more pronounced than in epoxy foams reinforced with glass fiber fabric.

The characteristic course of the damping in *g*-mat laminates appears different (Figure 8). The damping does indeed increase steadily but with varying intensity. The initial, relatively strong increase in damping is followed by a zone of constant damping. Shortly before failure, the damping increases rapidly as also in the case of fabric laminates.

Only in the case of a foam reinforced by glass fiber fabric is the whole course of the damping independent of micropore content. The samples with varying micropore contents fail with similar load levels and stress cycle figures (Figure 10).

Examination of the dynamic behavior in the load increase experiment of the *c*-fabric and *g*-mat laminates show basically similar behavior (Figures 11 and 12). The course of the damping curve is indeed similar, however the failure load cycle figures with increased micropore content are puched towards low values.

The course of the dynamic modulus in place of the tested *C*-fiber laminates can be seen on Figure 13. The same tendencies have resulted here as is the course of damping. For the foams reinforced by glass fiber fabric the dynamic modulus is independent of micropore content. Then again, in the case of the *g*-mat and *c*-fabric laminates, there was a shift of the failure load cycle figures with increasing micropore content toward lower values.
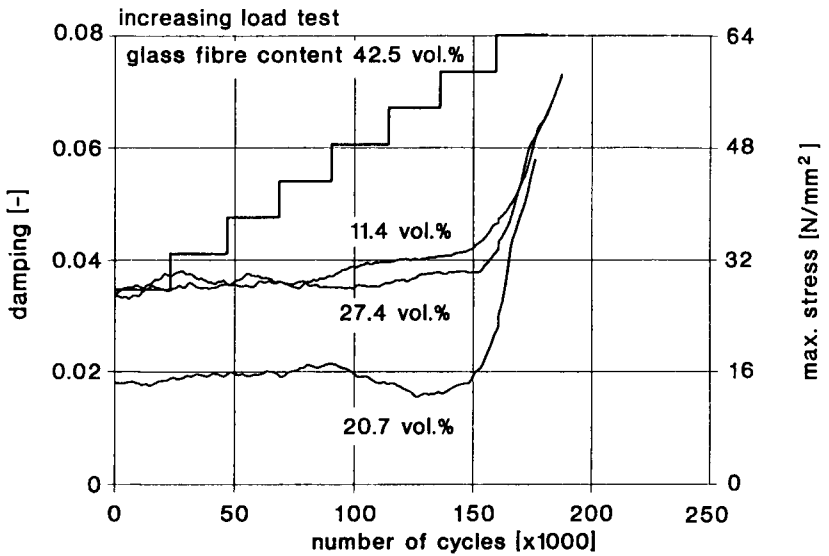
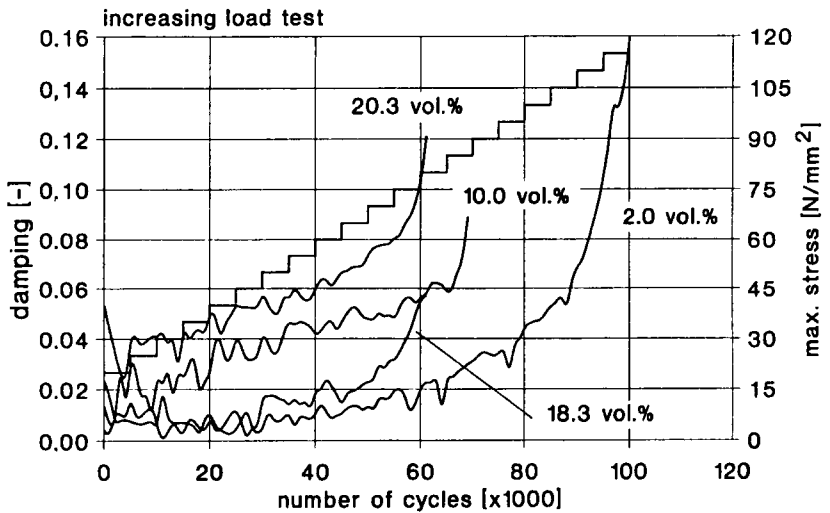**Figure 10.** *Progress of damping depend from content of micropores for g-fabric-composite.*

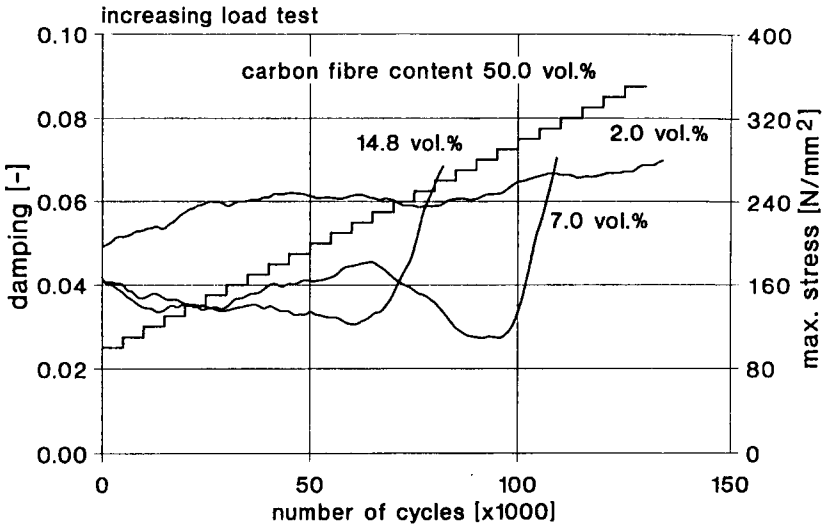**Figure 11.** *Progress of damping depend from content of micropores for g-mat-composites.*

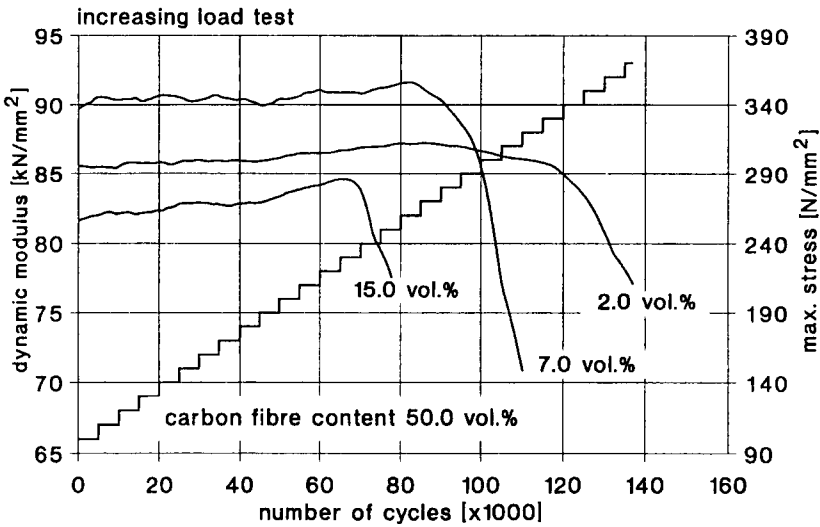**Figure 12.** *Progress of damping depend from content of micropores for c-fabric-composites.*

Figure 13. *Progress of dynamic modulus depends from content of micropores for c-fabric-composites.*

Wöhler Experiments

Since the Wöhler diagrams remain the most important construction aids in the arrangement of dynamically stressed components, the two glass fiber reinforced foams were tested with 4 load levels each at a stress ratio of $R = 0.1$. The fatigue limit of the materials was established in accordance with DIN 50100. The glass fiber fabric reinforced epoxy foam showed (something that was could already be observed during the load increase experiment) that the influence of the pore content on the tensile stress strength is only small. The representation with reference to density of the Wöhler curves (Figure 14) shows the best strength properties of the laminate with the highest micropore content (27.4 vol. %). Here the difference to the conventional laminate has become negligible. Figure 15 shows the Wöhler curves of the glass mat reinforced epoxy foams. All curves lie very close to one another, whereby the distribution of the failure load cycle figures is totally typical of fiber composites. Whether it is a case of laminates with 2 or 20 vol. % micropores, the fatigue limit lies in the same range.

The dynamic experiments that were carried out have given evidence that the influence of the micorpores on the dynamic behavior of the fiber composites is only limited. With increasing micropore content, however, the density of the laminates decreases, which is of particular importance for lightweight constructions. By using the reinforced epoxy foams the components could be easier arranged while retaining the same strength and there by contribute to saving energy. The experiment results of the dynamic behavior of reinforced epoxy foams also raise questions about the efforts of the processors in producing micropore-free parts. The
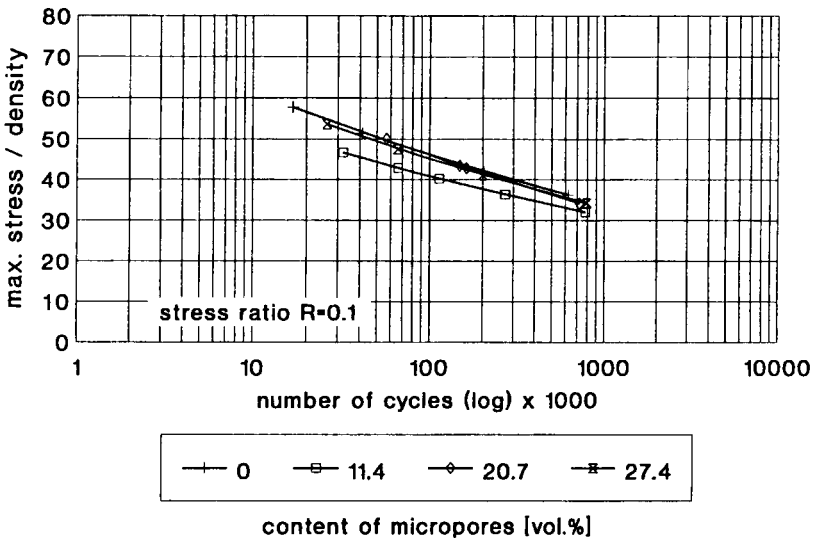

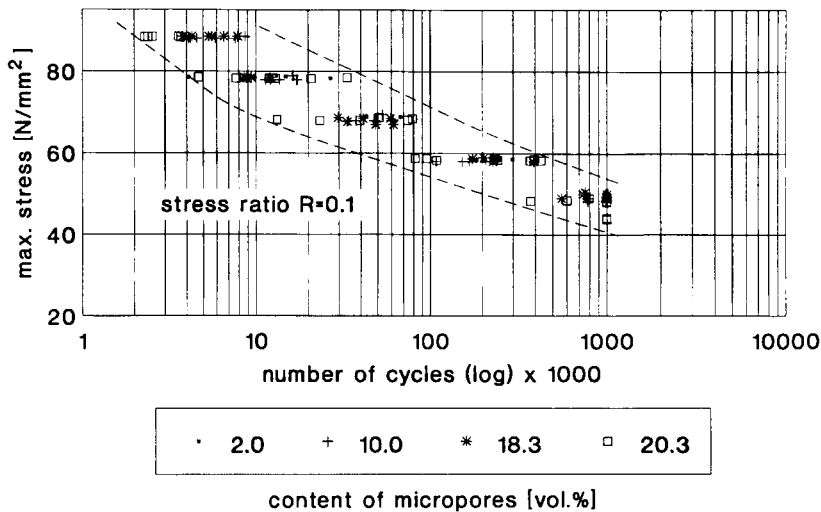**Figure 14.** *Wohler-curves for g-fabric-composites.*

Figure 15. *Woher-curves for g-mat-composites.*

deterioration of the dynamic characteristic values of these compositee with an increase in the micropore content is only small.

MICROSCOPIC EXPERIMENTS

The documentation of the material structure before mechanical testing was carried out using reflected light micrographs with an enlargement of 20:1. Figure 16 shows the structure of the examined glass fiber fabric reinforced epoxy foams. The gradation of porosity, caused by the graded expanding agent content, is clearly evident. The regularity of the micropor distribution may be termed good. However, in various matrix areas larger pores have also formed. The microscopic experiments of the damaged samples have shown that the cracks run through the micropore as well as beside the micropore (Figure 17). There are indications that the micropores are an additional obstacle to the spread of the cracks and thereby could also have a retarding effect on the proliferation of the cracks. The cracks run through the micropores, when such a possibility exists. Certainly this requires a certain amount of energy so that the crack can break through the pore surface.

CONCLUSIONS

Fiber reinforced epoxy foams were tested. The microporous structure of these composites is achieved by adding an expanding agent that released hydrogen during the cross-linking reaction. The static and dynamic tests showed similar characteristics values for all micropore contents. The cracks run throught and beside micropores losing energy by breaking the pore surface.
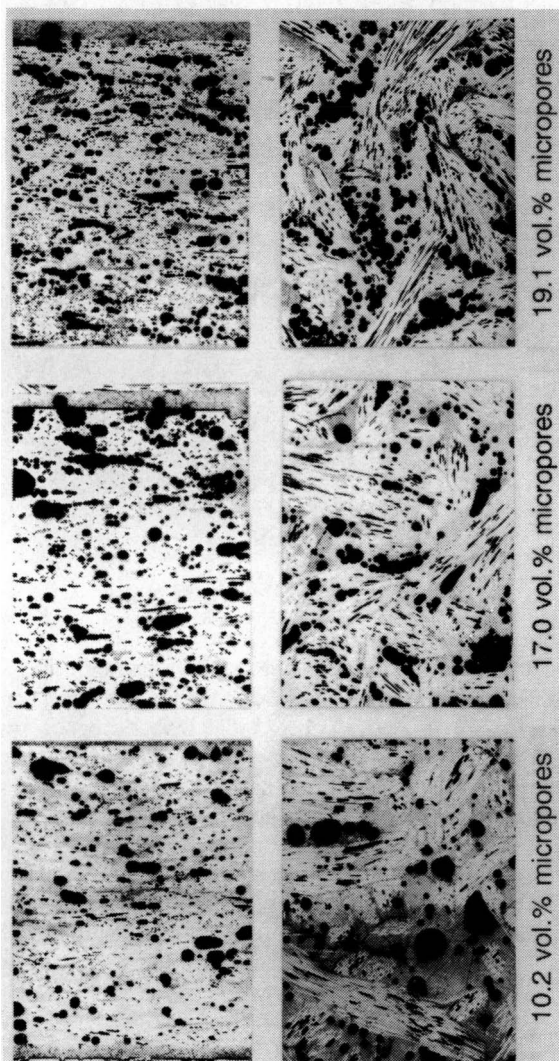
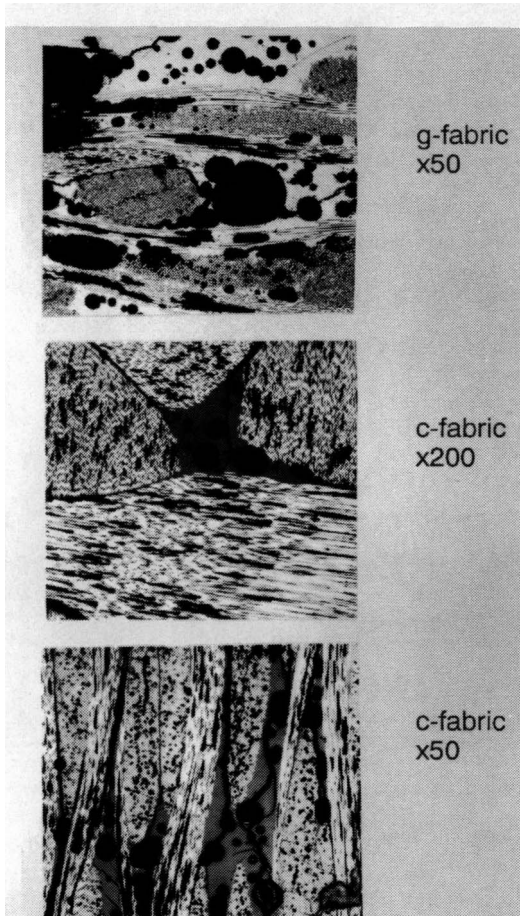Figure 16. Microscopical structure of glass fibre mat foams, enlargement 20:1.

Figure 17. *Microscopical structure of fatigue reinforced foams.*

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