CYCLIC LOADING OF THE INTERPHASE IN SINGLE FIBRE MODEL COMPOSITES

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ABSTRACT

In composites, the interphase between the components is essential for the mechanical properties. By using a suitable sizing or finish of the fibre, the interphase may be varied, by enhancing or decreasing adhesion or by suppressing or promoting transcrystallisation of a thermoplastic matrix. The local properties of this three dimensional interphase with different property gradients play a key role in tailoring a composite's properties.

Tests on single fibre model composites are particularly sensitive to the properties of the interphase. The nature of dissipative processes and the damage behaviour can be studied in cyclic micromechanic tests. A feasibility study of a single fibre cyclic test setup is reported. Quasistatic pull-out tests on the same model composites permit insights in the interfacial characteristics such as critical interface energy release rate or adhesion strength. An AFM characterisation of the fracture surfaces of the pulled out fibres provides supplementary information.

1. INTRODUCTION

Due to excellent mechanical properties and light weight, composite materials are often used in automobile or aircraft applications, in sports equipment or construction. However, a composite is only as good as its interfaces. The interface is the area of the highest mechanical stress. In the immediate vicinity of the glass fibre, the properties of the matrix often deviate from those of the bulk, forming an interphase. The properties of this interphase are substantially influenced by the surface treatment of the fibres. If the matrix consists of a semicrystalline polymer such as polypropylene (PP), the interphase can be formed due to a crystallisation differing from that of the bulk. In a surface with high nucleating activity such as unsized glass, a large number of crystallites are nucleated, so crystal growth is limited to the direction away from the surface. The fibre is then covered by a transcrystalline layer, in contrast to the spherulitically crystallized bulk. This is expected to improve the interphase properties.

In order to study the interphase of a composite, micromechanical pull out tests are used [1]. The fibre is quasistatically pulled out of the matrix droplet, and the force-displacement curve is registered. This permits to determine local interphase parameters such as the adhesion strength at crack initiation or the critical energy release rate of the interface.

Quasistatic pull out experiments only provide information on the behaviour under a static loading. In practise it is often relevant to know how a repeated small (subcritical) load influences the durability of a composite. A dynamic load is often more

representative for a real application than a quasistatic load. This information is often sought in dynamical tests, e.g. under cyclic loading. Standard test devices perform cyclic macromechanical tests. For a more interface specific approach, cyclic micromechanical measurements may be performed on single fibre model composites in an apparatus similar to that used in the single fibre pull out test.
For a feasibility study of a cyclic micromechanical test setup, model composites with varying fibre and matrix properties are compared. Different fibre matrix combinations were selected to demonstrate the potential of this device on a wide spectrum of applications and material poperties.

2. EXPERIMENTAL

Materials

Polypropylene glass fibre composites are typical candidates for fibre reinforced thermoplasts. A variety of PP glass composites were chosen, which differ in the interfacial crystallisation and the PP chain length. Composites of PP and E-glass fibres sized to induce resp. suppress a transcrystalline interphase are hereafter called C1 resp. C2. The matrix chain length was varied, high molecular weight (MW) matrix samples are denoted by a subscript hiMW (i.e. $C1_{hiMW}$, $C2_{hiMW}$), low molecular weight samples by loMW (i.e. $C1_{loMW}$, $C2_{loMW}$).
Besides these, four model composites were chosen: C3 consists of glass fibres with an aminosilane model sizing spun at the IPF E-glass fibre spinning device which is embedded in epoxy resin matrix. C4 is a composite of Poly p-phenylene-2,6-benzobisoxazole (PBO) fibre in epoxy. PBO offers strength and modulus almost double that of p-aramid fibre, however, the surface is inert and the interphase weak. Model composites C5 consits of alkali resistant (AR) glass fibres embedded in concrete. Textile reinforcement of concrete is used for specialized architectural applications. A polymer coating in addition to the sizing can not only improve the single fibre tensile properties and protect the fibre from the alkaline environment in the concrete but also improve the adhesion between fibre bundle and matrix. Both coated and uncoated fibres were studied, subscript coat resp. uncoat denote the coated resp. uncoated fibre ($C5_{coat}$, $C5_{uncoat}$).
For the use in C1, C2 and C3, E-glass fibres were prepared on the IPF E glass fibre spinning facility and sized with aminopropyltriethoxysilane combined with either a PP dispersion (for use in C1), a PU dispersion (C2) or no further sizing component (C3). PBO Fibres were obtained from Toyobo and used in C4. For C5, alkali resistant AR-glass fibres were spun and sized at the IPF AR glass fibre spinning facility, in the case of $C5_{coat}$ the yarn was additionally coated with a polymer coating using a textile coating system (Mathis Switzerland).
For $C1_{hiMW}$, $C2_{hiMW}$, a Borealis HD120 matrix was used, it has a MFR of 8 g /10 min and is a typical injection molding PP. The matrix has been compounded with 5% Exxelor 1020 as this maleic acid grafted PP improves the matrix fibre binding. For the low molecular weight samples $C1_{loMW}$, $C2_{loMW}$, the used matrix was Borealis HH450, a typical fibre spinning PP homopolymer with a MFR of 37 g /10 min, again with 5% Exxelor 1020. For C3 and C4, Epikote L20 / Epikure 960 (Bakelite) as a typical epoxy resin was chosen. For C5, the matrix is Portland cement.

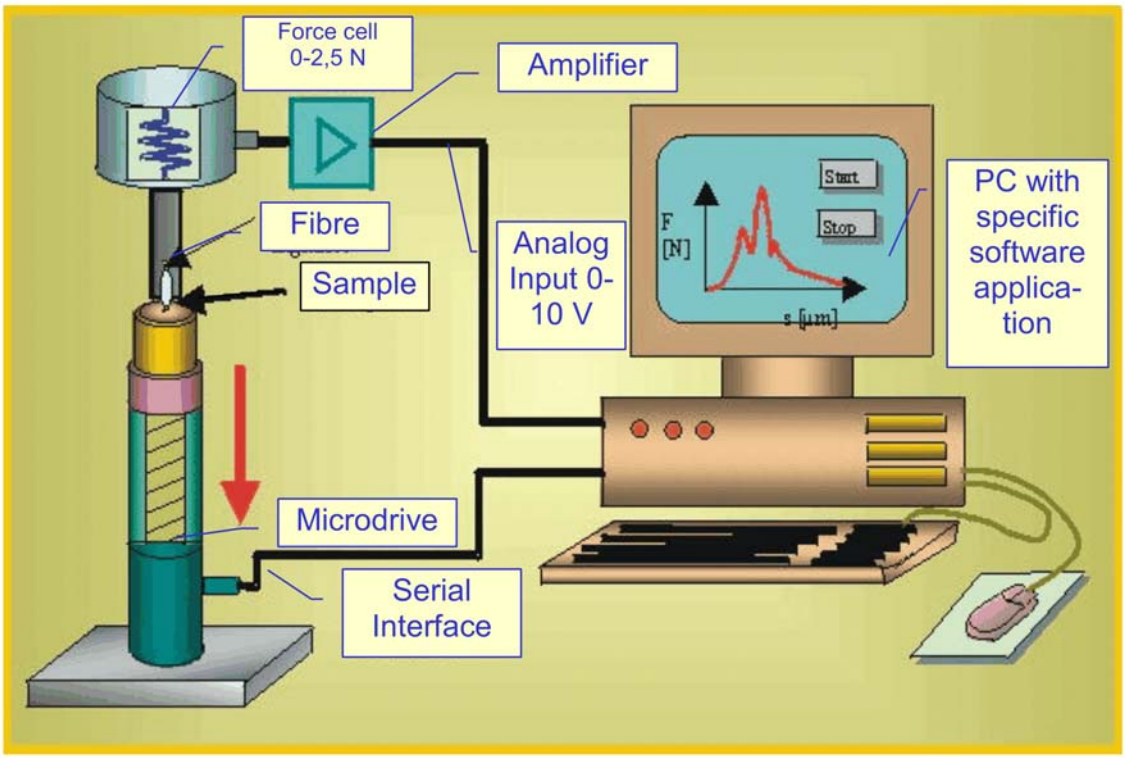

Figure 1: Setup of the micromechanical pull out test developed at the IPF. A single fibre is quasistatically pulled out of a matrix droplet.

Pull out tests and fracture surface analysis

All composites were prepared as single fibre composites: The end of a single fibre is embedded into a matrix droplet, the embedding is performed with controlled time and temperature conditions under Argon atmosphere [2]. For the C1 and C2 samples, the embedding depth is 800 µm, for the epoxy resin samples, it was set to 300 µm, for C5 it was 1000 µm. The properties of the single fibre composite are determined in a pull out apparatus developed at the IPF [1]. Additionally, AFM images of the fibre surface are taken before embedding resp. after pull out or dynamic loading to characterize the sizing distribution, the roughness resp. the failure mode. For this, a Dimension 3100 AFM with Nanoscope IIIa or IV Controller was used (Digital Instruments, USA).

Cyclic loading of single fibre model composites

The device for hysteresis measurements on single fibre model composites is institute made in order to study the damage behaviour at subcritical cyclic load (e.g. single level test) in the regime of 0.01-10 Hz. The results are treated in analogy to EN ISO 6721-1. Cyclic load studies of single fibre model composites permit to determine the critical interface parameters but also the change of the mechanical properties of the interphase in dependence on the introduced energy, the frequency and loading time. For this, the single fibre composite is exposed to subcritical alternating load in the fibre axial direction. Force-displacement-time curves are determined. For a sinusoidal signal, the phase difference between the induced displacement and the resulting force can be determined, its tangent is equal to the ratio of the loss and storage modulus and may be used for the characterisation of the interface. Fatigue, damage, and failure can be

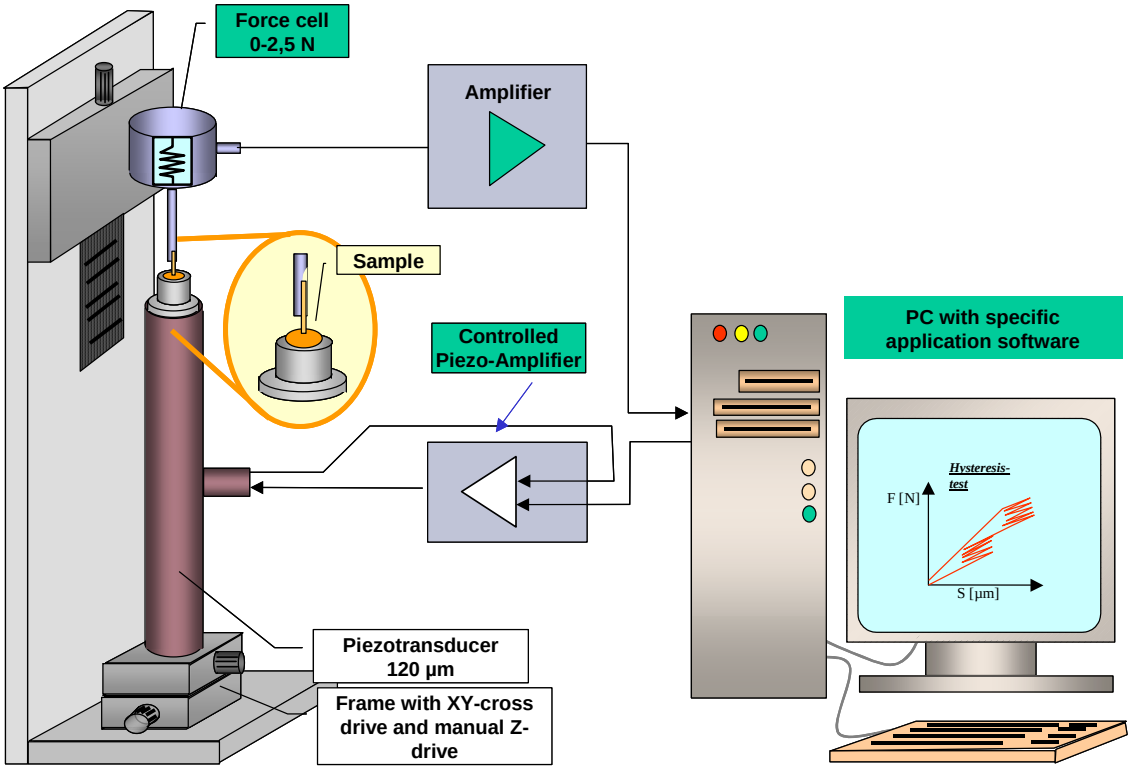

Figure 2: Setup of the micromechanical hysteresis test developed at the IPF. A single fibre model composite is exposed to cyclic load.

determined in durability tests. Alternatively, by an increase of the load amplitude from 0.1 up to 2.5 µm a load history can be imposed on the composite.
More detailed information may be gained from the analysis of the hysteresis curves. They are obtained by plotting the force-displacement curves of a load cycle. The area inside the hysteresis loop corresponds to the energy loss during the cycle, which is caused by dissipated energy (creep or friction) as well as energy contributions due to fracture. From the form of the hysteresis loop it can be determined at which strain the dissipation is increased. The evolution of the hysteresis loop over a number of cycles can be analysed for the fatigue behaviour. This permits to study the microfailure behaviour of the interface with respect to morphologic changes, induced e.g. by the interface design.

3. EXPERIMENTAL RESULTS

3.1. Interphase characterisation

Fig. 2 shows polarisation microscopic images of single fibres embedded in a thin film of PP (Borealis HD120). The sizings chosen for the PP composites do indeed either - in the case of C1 - form a transcrystalline layer easily discerned on both sides of the fibre, which is seen as a darker line crossing the image from top to bottom, or else - in the case of C2 - suppress it, so the vicinity of the fibre is occupied by bulk spherulites.

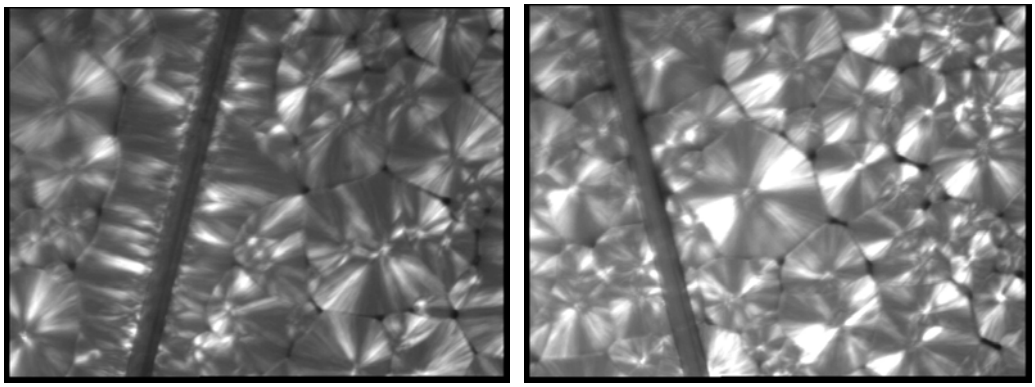

Figure 3: Polarisation micrographs of single fibres embedded in a thin film of PP. In the left image, $C1_{loMW}$ with a pronounced transcrystalline layer around the dark fibre, on the right $C2_{loMW}$ without a transcrystalline layer.

The results of the mechanical tests of $C1_{hiMW}$, $C2_{hiMW}$, $C1_{loMW}$, $C2_{loMW}$ are shown in table 1 along with the results of the single fibre pullout test. For C1 and C2, injection molded specimens were conditioned at 23°C and 50 % relative humidity and used in tensile tests according to ISO 527-2. The performance of the high MW samples is better than that of the low MW specimen. This effect is more pronounced in the single fibre data than in the injection molded specimen. The transcrystallized interphase leads to a better performance in the macroscopic composites. Pullout data are more differentiated: Here there is improvement only in the case of $C1_{hiMW}$ vs. $C2_{hiMW}$, whereas in the low MW case the apparent shear strength is comparable for both composites. The transcrystallization is expected to improve the adhesion strength due to a mechanical interlocking. However, if there is little entanglement the interface between spherulites can be weak leading to a cohesive fracture along the transcrystalline layer's outer edge. It is plausible that this effect inverting the improvement induced by the transcrystallinity is more pronounced in the low molecular weight composites.

	τ_{app} [MPa]	σ_M [MPa]	a_{cu} [MPa]	E [GPa]
$C1_{hiMW}$	25	93	55	6,5
$C2_{hiMW}$	20	83	43	6,2
$C1_{loMW}$	11	87	55	5,8
$C2_{loMW}$	13	83	44	6,1

Table 1: Apparent shear strength τ_{app} determined in the single fibre pull out test as well as results of the mechanical tests performed on injection molded specimens of the PP / glass fibre composites.

These results of the PP glass fibre composites confirm an atomic force microscopy (AFM) study of similar composites using the nanoindentation technique on polished crosssections [3], the lateral extension of the transcrystallized interphase was determined in the range of 100-300 nm, the Young's modulus of the interphase was higher than that of the bulk matrix, in a non-transcrystallized composite, the interphase modulus was lower than that of the bulk.

Tapping Mode images of the fracture surfaces after pull out are shown in fig. 4. The upper picture shows the topography (left) and tapping amplitude (which relates to the derivative of the surface, similar to a shaded electron microscopy image, right) of a fibre of $C1_{loMW}$. The topography shows several wedged together structures ranging from 100 nm to 1 µm in size. These can be interpreted as the top view of the transcrystalline layer after fracture along its outside. The phase image (not shown) is featureless aside from topography artefacts. These findings indicate a cohesive failure.

The bottom image shows topography and phase image of a fibre pulled out of $C2_{loMW}$. The topography shows an almost cylindric surface with only a few small elevations, many of which are strongly elongated in the fibre direction. This preferential direction is also evident in the phase image. This observation indicates an adhesive fracture along the fibre surface, with some sizing components bound to the surface while others are deformed or even removed during the pull out process.

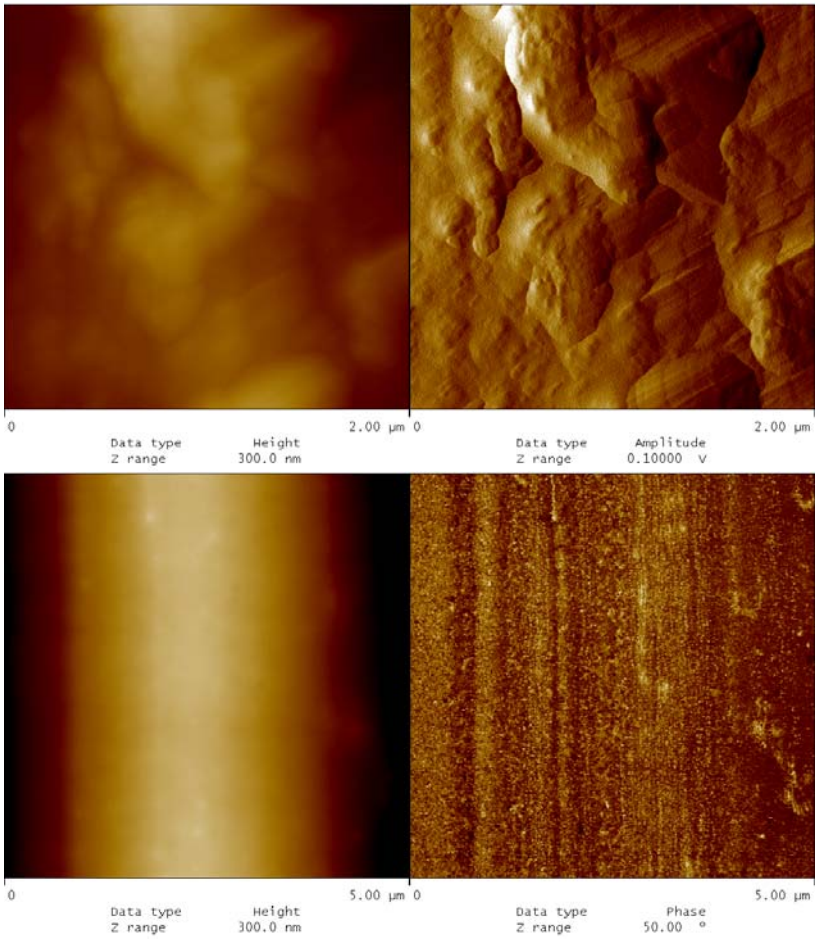

Figure 4: Tapping Mode AFM images of fracture surfaces of fibres after pull out tests. $C1_{loMW}$ (transcrystalline) top, $C2_{loMW}$ (non-transcrystalline) bottom.

3.2. Cyclic load tests of selected single fibre model composites

The results of the hysteresis measurements on the single fibre model PP / glass composites with transcrystalline interphase $C1_{loMW}$ and without transcrystalline interphase $C2_{loMW}$ are shown in fig. 5. The hysteresis curves for different cycle numbers are shown. Depending on the interfacial crystallisation, the fatigue behaviour of the model composites varies: a transcrystalline interphase deteriorates less rapidly than one where the bulk crystals reach up to the fibre surface. Besides, the area within the curve is smaller for the transcrystallized sample, it is therefore more elastic, with a lower energy loss within the interphase. Data for $C1_{hiMW}$ and $C2_{hiMW}$ are not shown, the results of measurements on these samples are very similar to the lower MW samples. There is however a tendency towards more narrow hysteresis loops, i.e. more elastic and less viscous reaction within the interface, while the slope of the curve (the "local modulus") is comparable to that seen in the low MW single fibre model PP / glass composites.

The epoxy / glass composites C3 shows an interface of high adhesion strength which is of enhanced durability and shows little dissipation upon cyclic loading. It is stable up to high cycle numbers. Measurements on epoxy / PBO composites C4 reveal the inertness of the fibre surface, and thus a lower adhesion strength. This interface seems to be less fatigue resistant and crack propagation or debonding starts at low cycle numbers and forces decrease rapidly. For the glass / cement composites, there is a difference for the coated and uncoated fibres: In hysteresis tests, the higher energy dissipation in the coated fibres is visible. The property improvement due to the fibre coating is pronounced for fibres spun and sized at the Leibniz Institutes AR glass spinning facilities, as the coating can be adjusted to the chemistry of the sizing.

The embedding depth as so far not been considered, the data are pure force data. The embedding depth for the samples was set for the resulting force data to fall in the range of 10-200 mN, the most sensitive regime of the force cell. In this range, a pull out of the fibre without fibre fracture is usually possible. This is necessary in order to determine the embedding depth after the measurement. During the embedding procedure, the embedding depth is preset to a target depth, however, there is a systematic error mainly due to matrix shrinking during hardening /cooling. Shear stresses (force divided by fibre surface area circumference times embedding depth) vary: At 1 µm displacement they are 3 MPa for the PP / glass composites, 18 MPa for the epoxy / glass samples C3, 20 MPa for the the epoxy / PBO samples C5 and 1 MPa resp. 2 MPa for the uncoated resp coated cement / glass composites, all determined for the 100^{th} load cycle.

CONCLUSIONS

Cyclic loading of single fibre model composites is an appropriate technique to study the interphase of composites. A series of application oriented model systems with varying properties were studied. The results reflect the properties of the systems, ranging from glass fibre reinforced thermoplasts to ultra high strength PBO fibre embedded in epoxy resin. The fine differences between thermoplasts with varying crystallization can be differentiated.

There are a number of limits to the method: While the shape of the hysteresis curves are fairly reproducible, the absolute values vary by about 30%, we therefore perform 10-15 fold measurements. As the measurements usually run overnight, sample throughput is low. Another issue is the temperature stability, even in an air conditioned laboratory. We are hoping this can be partially eliminated by an on-line temperature dependent displacement set according to a temperature calibration.

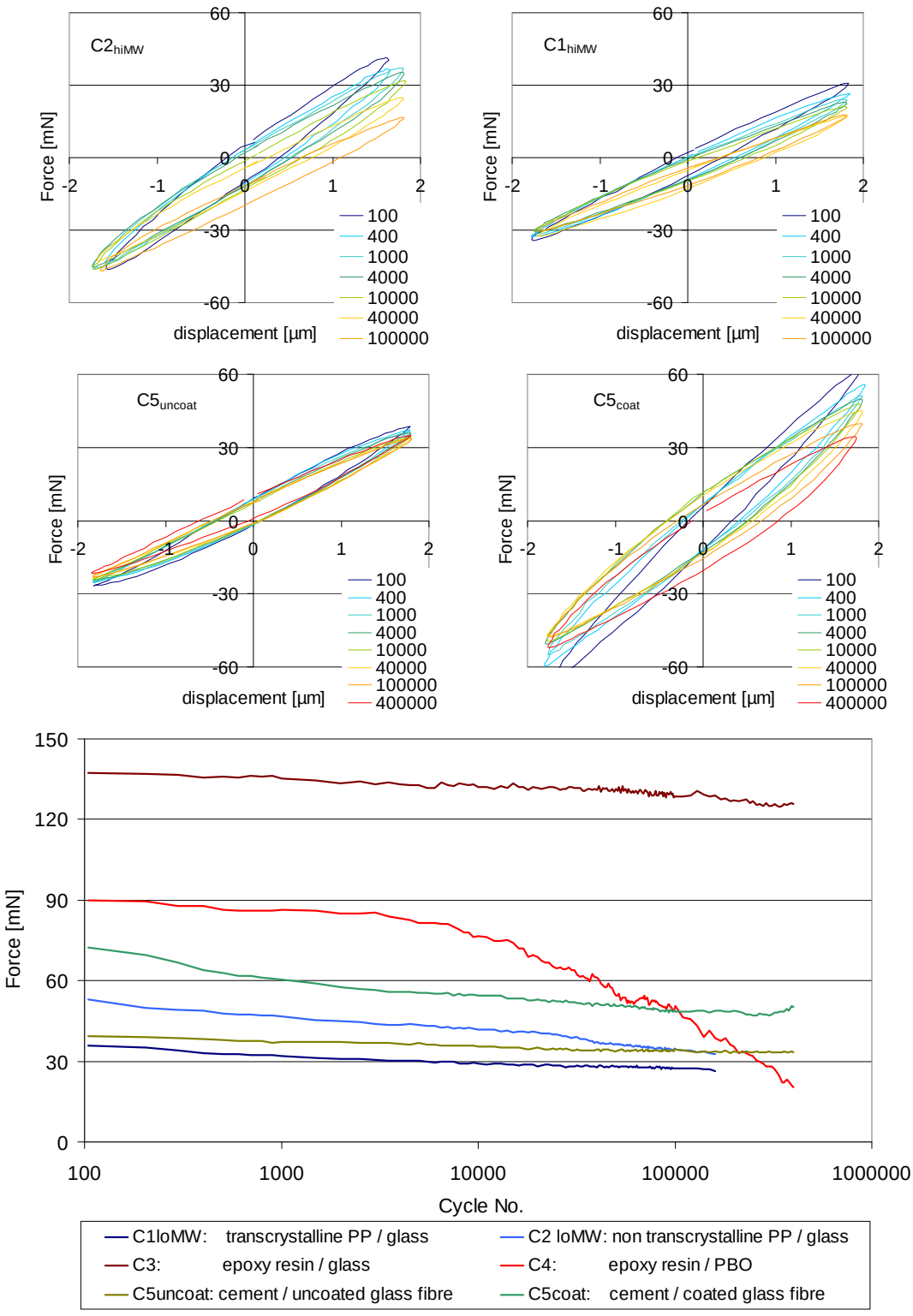

Figure 5 Top: Hysteresis curves of sine loading of PP-glass single fibre model composites $C1_{loMW}$ and $C1_{loMW}$, $C5_{uncoat}$ and $C5_{coat}$ for different cycle numbers as shown in the legends. Bottom: force/cycle data of various single fibre model composites

The results cyclic load single fibre model composite data presented in this manuscript all pertain to 10 Hz sine loads. The software also permits to perform measurements with a freely programmed load function. It is therefore possible to perform load-increase, creep or relaxation measurements on single fibre model composites. Another similar single fibre cyclic loading device permits frequency dependent measurements up to 350 Hz. Measurements on the model composites presented here are also being performed on this device and will be presented shortly.

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