Composite Interfaces

The amine:epoxide ratio at the interface of a glass fibre/epoxy matrix system and its influence on the interfacial shear strength
--Manuscript Draft--

Full Title:	The amine:epoxide ratio at the interface of a glass fibre/epoxy matrix system and its influence on the interfacial shear strength
Manuscript Number:	TCOI-2018-0159
Article Type:	Original Article
Abstract:	The interfacial shear strength (IFSS) is commonly used for evaluating the adhesion at the interface between fibre and matrix. A glass fibre/epoxy matrix system was investigated. The surface coatings applied to glass fibres may result in a discrepancy in the amine:epoxide group ratio between the interface and the bulk matrix, consequently moving the ratio away from the optimum stoichiometric ratio most often used. The amine:epoxide group ratio in the matrix was varied to obtain the optimum ratio at the interface. The study found that the amine:epoxide ratio influenced the IFSS with an optimum just below the stoichiometric ratio. The microbond test was conducted in a thermal mechanical analyser (TMA) to determine the IFSS thus revealing an inverse dependency on the testing temperature: an increased testing temperature yields a decrease of IFSS. IFSS determined at temperatures below the glass transition temperature displays a decreasing trend at high amine:epoxide ratio whereas IFSS measured at testing temperatures above the glass transition temperature steadily increases as the amine:epoxide ratio increases. The microbond test was conducted using both a tensile tester and a TMA setup. The two microbond test setups yielded results with same behaviour of the IFSS as a function of the amine:epoxide ratio.
Order of Authors:	Helga Nørgaard Petersen, Ph.D.
	R. F. Minty
	James L. Thomason
	Liu Yang
	Yukihiro Kusano
	Povl Brøndsted
	Kristoffer Almdal

ARTICLE

The amine:epoxide ratio at the interface of a glass fibre/epoxy matrix system and its influence on the interfacial shear strength

H. N. Petersen[a], R. F. Minty[b], J. L. Thomason[b], L. Yang[b], Y. Kusano[c], P. Brøndsted[c] and K. Almdal[a]

[a]Technical University of Denmark, Department of Micro- and Nanotechnology, Ørsteds Plads 345, DK-2800 Lyngby, Denmark; [c]University of Strathclyde, Department of Mechanical and Aerospace Engineering, 16 Richmond Street, Glasgow G1 1XQ, Scotland; [c]Technical University of Denmark, Department of Wind Energy, Section of Composites and Materials Mechanics, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ABSTRACT
The interfacial shear strength (IFSS) is commonly used for evaluating the adhesion at the interface between fibre and matrix. A glass fibre/epoxy matrix system was investigated. The surface coatings applied to glass fibres may result in a discrepancy in the amine:epoxide group ratio between the interface and the bulk matrix, consequently moving the ratio away from the optimum stoichiometric ratio most often used. The amine:epoxide group ratio in the matrix was varied to obtain the optimum ratio at the interface. The study found that the amine:epoxide ratio influenced the IFSS with an optimum just below the stoichiometric ratio. The microbond test was conducted in a thermal mechanical analyser (TMA) to determine the IFSS thus revealing an inverse dependency on the testing temperature: an increased testing temperature yields a decrease of IFSS. IFSS determined at temperatures below the glass transition temperature displays a decreasing trend at high amine:epoxide ratio whereas IFSS measured at testing temperatures above the glass transition temperature steadily increases as the amine:epoxide ratio increases. The microbond test was conducted using both a tensile tester and a TMA setup. The two microbond test setups yielded results with same behaviour of the IFSS as a function of the amine:epoxide ratio.

1. Introduction

Glass fibres are produced in millions of tonnes every year for various uses. Fibre reinforced polymer composites are widely utilised in e.g. wind energy, automotive, and construction industries in great volumes. The wind energy industry alone utilises more than 100.000 tonnes glass fibres annually [1]. The wind energy industry desires larger turbine blades which in turn demand better mechanical properties of the materials used in the manufacturing [2,3].

In composites optimum stress transfer across the fibre-matrix interface is critical in obtaining the desired composite performance. A strong adhesive bond between fi-

---

bre and matrix results in a strong interface. The glass fibres are during manufacture treated with an aqueous suspension. This surface coating, called sizing, is applied in order to handle the otherwise fragile and static fibres and to ensure a strong bonding between fibre and matrix. Controlling the compatibility and the adhesion between the two constituents get complicated by the presence of the sizing at the interface. The chemistry of the sizing is typically kept as a trade secret, complicating the research outside the industry on optimising the stress transfer between glass fibre and polymer matrix. However it is known to consist mainly of a film former and a silane coupling agent both of which are chosen to compliment the desired matrix [4,5]. The epoxy resin is one of the most used thermoset polymers as matrix for fibre reinforced composites [6]. The silane coupling agent is frequently an epoxide or amine derivative of an organosilane, which makes epoxy composites of great interest since the crosslinking of epoxy resin involves amine and epoxide functional groups [5,7]. An illustration of a simplified interface structure consisting of a matrix of epoxy resin and curing agent and a glass fibre surface coated only with an amine functionalised silane as coupling agent can be found in fig. 1. The coupling agent affects the properties of the matrix at the interface and is considered to be responsible for the adhesion by the possible bond between matrix and glass fibre. Changes in the interface by changing the surface chemistry of the fibres and its compatibility to the polymer matrix will affect the adhesion and composite properties [4–6]. The interfacial shear strength (IFSS) is a generally accepted measure of the adhesion between fibre and matrix, and can be measured by different methods including pull-out, microbond, fragmentation and indentation test especially when used for qualitative comparisons [8–12].
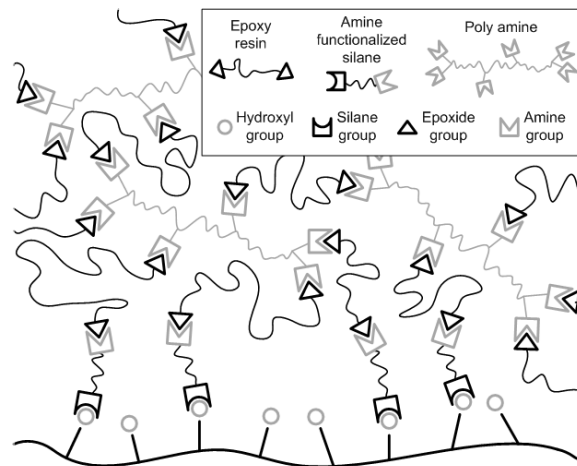

Figure 1. Schematic of network structure facilitated by the chemical groups present at the interface of a glass fibre surface coated with an amine functionalised silane and a epoxy resin polymer.

The IFSS is not only affected by the interface chemistry but also the testing temperature [13,14] where high testing temperatures resulted in low IFSS values explained by a reduction in matrix strength [15–17]. A recent study investigated the deformation caused during curing and suggests that cure shrinkage and residual stresses have a large role to play when it comes to the stress transfer at the interface [18]. Cure shrinkage and stresses in epoxy matrices are closely related to crosslinking density which is controlled by the amine:epoxide ratio and curing temperature. The glass transition temperature is an important parameter when it comes to matrix structure. It is often determined when investigating the optimal manufacturing procedure e.g. mixing of

2

epoxy resins in regards to curing agent and curing cycles. The glass transition temperature is related to the crosslinking density and structure of the material along with other material properties as strength and stiffness [19].

The glass transition temperature changes with the amine:epoxide ratio having a maximum located around the stoichiometric ratio as seen in literature [19], where also the crosslinking density is at its highest [20,21]. The IFSS has been shown to greatly vary with a clear distinction of below and above the glass transition temperature of the matrix being tested [14]. Testing temperatures above, below and around the glass transition temperature were chosen to investigate the effect of the glass transition temperature on the IFSS.

In a previous work the mixing ratio of epoxy resin and curing agent has been shown to affect the apparent IFSS [22]. The mixing ratio between epoxy resin and curing agent is usually chosen by composite manufactures at the optimum to ensure the most stable material [23]. The optimum is considered to be at the stoichiometric ratio (1:1) between amine and epoxide groups, but a small excess of amine is preferred in order to obtain complete reaction of epoxide groups as unreacted epoxide groups can hydrolyse leading to an increase of moisture absorption [24,25]. Since these functional groups also can be present in the sizing, the amine:epoxide group ratio of the interface may be shifted from the optimum towards an excess of amine or epoxide groups. Changing the sizing and hereby the chemistry of the glass fibre surface and the interface in a controlled manner is not easily done without a glass fibre manufacturer involved. Changing the chemical structure and properties of an epoxy matrix is easily done by controlling the mixing ratio of epoxy resin and curing agent. In this work the mixing ratio of epoxy resin and curing agent is varied to observe how an off stoichiometric mixing ratio will affect the interface and the IFSS. The fibres used had a sizing containing only an amine functionalised silane which was assumed to be uniformly distributed along the fibres.

The results can be used to obtain a guideline of how to optimise the amount of amine and/or epoxide groups in the sizing in agreement with the epoxy matrix mixed at stoichiometry ratio. This could lead to a better stress transfer and thereby a stronger composite through interface control.

2. Materials and Methods

2.1. Materials and Instruments

The fibres used in this work were boron free E-glass fibres sized only with γ-aminopropyltriethoxysilane (APTES) during the manufacturing by Owens Corning. The fibres were received as roving on a bobbin. The fibres have an average diameter of 17.5 μm. The fibres were used as received with no additional surface treatment. A two component matrix of Araldite 506 (poly(bisphenol A-co-epichlorohydrin)) epoxy resin and triethylenetetramine (TETA, technical grade 60%) curing agent was used, both from Sigma-Aldrich, Germany. For the microbond tests an Instron 3342 tensile tester (Instron, Great Britain) and a Thermal Mechanical Analyser (TMA) Q400EM with a MCA70 cooling accessory and an expansion probe mounted (all from TA Instruments, United States) were used. The glass transition temperature was determined using Differential Scanning Calorimetry (DSC) performed on a TA Q20 using aluminium pans (TA Instruments, United States). The dimensions of droplets and fibres were measured with a Nikon Epiphot inverted microscope with 200$\times$ magnification and the

3

image processing program ImageJ.

2.2. *Microbond Samples*

The mixing ratio of the epoxy matrix is given as the ratio between the functional groups of amine and epoxide. The stoichiometric ratio being 1:1 which was calculated to be equal to 12 wt.% TETA for this matrix system based on the equivalent weight of epoxide groups and the molecular weight of TETA. All matrix batches were made with approximately 1-2 g of epoxy resin and different amounts of curing agent. The range of the amine:epoxide group ratio varied from 0.07 to 2.49, corresponding to 1-25 wt.% TETA. After carefully stirring epoxy resin and TETA, the mixture was degassed under vacuum for a minimum of 12 minutes. Droplets were deposited on the single glass fibres. Cardboard box frame ensured the same 5 mm gauge length of all the samples both for the Instron and the TMA microbond samples. The Instron microbond samples were made with a hole in the center of the frame for the hook on the tensile tester. The TMA microbond samples were cut to fit inside the sample holder. A minimum of 60 samples for each of the ten amine:epoxide ratios were made to be tested at room temperature with the Instron. Batches of around 120 TMA microbond samples were made at a time for each of the seven amine:epoxide ratios, yielding 30 samples for each of the four testing temperatures. The droplets were subsequently cured in a convection oven heating to 60 °C with a heating rate of 2 °C/min and kept isothermally for one hour then further heated to 120 °C also with a heating rate of 2 °C/min, where it was maintained for two hours. The samples were left in the oven to cool down afterwards. The same curing cycle was used for all samples.

2.3. *Microbond test*

The dimensions of both fibres and droplets were individually measured digitally before testing by image analysis. The dimensions were determined in order to calculate the embedded interface area used together with the maximum load for calculating the apparent IFSS, see eq. 1, assuming a constant shear along the interface. The apparent IFSS will in the following just be denoted as IFSS.

$$IFSS = \frac{F_{max}}{A_e} = \frac{F_{max}}{L_e \cdot d_f \cdot \pi}, \tag{1}$$

where F_{max} is the maximum load, A_e is the embedded area, L_e the length of the droplet that embeds the fibre and d_f the diameter of the fibre.

The TMA method is described in details by Thomason *et al* [13] and was based on the principle of the previously developed method using an Instron tensile tester [26]. The principle of the method is pulling a droplet of a fibre by loading in tension until it debonds. The Instron setup uses a rig with two movable knife blades positioned to fixate the droplet while the fibre is pulled with a constant deformation rate of 0.1 mm/min and a strain rate of $3 \cdot 10^{-3}$ s^{-1}. The TMA setup uses a fixed wedge of two knife blades instead of movable blades. In the TMA the fibre is pulled by the movable quartz probe. The probe loads the paper tabs glued onto the fibre with a constant load increase rate of 0.15 N/min. The maximum load was determined from the obtained load-extension curves recorded during each test. After testing the samples were inspected using an optical microscope.

4

2.4. *Glass Transition Temperature*

The glass transition temperature determination was performed on the DSC with nitrogen as purge gas and a flow of 50 ml/min. The temperature range was between -10 - 150 °C and the heating and cooling rates were 10 and -20 °C/min, respectively. The temperature was held isothermally for 10 minutes between heating and cooling. The heating procedure was done twice and the glass transition temperature was determined from the second heating ramp. The samples were prepared using the same epoxy resin and curing agent, and curing conditions as for the microbond samples and with similar amine:epoxide ratios. The resin was degassed before being poured into a silicon mould and subsequently cured in an oven. The mould yielded three 125 mm^3 cubes that were cut into small discs of approximately 15-20 mg.

3. Results

The samples were examined before testing to obtain the dimensions of droplet and fibre which were used to calculate the embedded area of the fibre and after testing to confirm the point of debonding. An example of this can be seen in fig. 2.
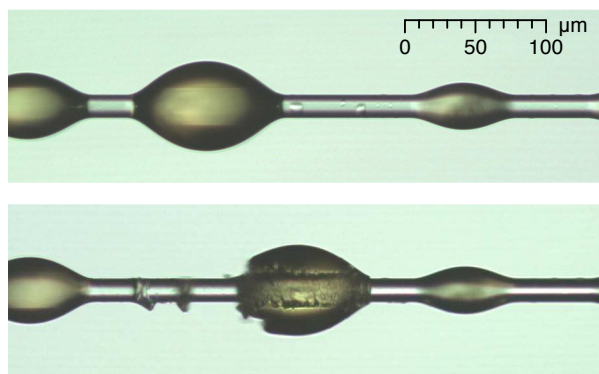
Figure 2. Droplet before and after testing.

The used amine:epoxide ratios along with the corresponding glass transition temperatures can be found in table 1. The results displayed a maximum of the glass transition temperature close to the stoichiometric ratio of 1.0 but a bit higher. The four testing temperatures (20, 50, 90 and 120 °C) were chosen for TMA microbond testing conditions as they were above, around and below the glass transition temperature of the seven batches with different amine:epoxide ratios. The crosslinking densities in table 1 were estimated based on the weight percentages and the molecular weight of the epoxy resin and the curing agent in the different amine:epoxide ratios. Densities of epoxy resin and curing agent were used for the calculation of the total volume without considering shrinkage.

For each test, both with the Instron and the TMA load-extension data were recorded in order to obtain the maximum load to use in the calculation of the IFSS, eq. 1. The maximum load is determined from the load-extension curves immediately before the load drop. The load-extension curves followed the same path for all the Instron samples with loading to a maximum where the debonding leads to a drastic drop in load, see fig. 3A. The droplet is then pushed along the fibre resulting in an increase

Table 1. The amine:epoxide ratio of the samples, the corresponding measured glass transition temperature and the calculated crosslinking density.

Amine:epoxide ratio	T_g [°C]	Crosslinking density [mol/cm^3]
0.5	48.8 ± 3.3	0.0031
0.7	67.1 ± 3.7	0.0041
1.0	82.0 ± 0.3	0.0055
1.3	87.3 ± 3.9	0.0053
1.5	78.4 ± 7.3	0.0051
1.8	70.1 ± 0.1	0.0049
2.1	59.4 ± 2.4	0.0048

of load until a steady state level is reached. The dynamic friction between droplet and fibre surface is related to this steady state. All load-extension curves obtained by the TMA looked a bit different, see fig. 3B, as the TMA measured displacement caused by linear increasing load, whereas the Instron measured load caused by linear increasing displacement. The maximum force has been marked on both curves. Only the maximum force was used for further analysis.

The average IFSS was calculated for each series of amine:epoxide ratio and testing temperature. The Instron and the TMA microbond test results are displayed in fig. 4 and fig. 5, respectively. Each of the IFSS points correspond to a minimum of 20 individual measurements. Both graphs have been added with empirical trendlines based on the data points and also the assumption that the IFSS is zero at zero amine:epoxide ratio as the curing agent and thereby the microbond droplet is a liguid.

The data points obtained with the Instron setup display a decreasing trend with increasing amine:epoxide ratio above the stoichiometric ratio as shown in fig. 4. A decreasing trend is also clear when decreasing the amine:epoxide ratio.

A distinct separation of the results obtained above and below the glass transition temperature was observed for all amine:epoxide ratios, see fig. 5 and has been described in literature [14]. The highest IFSS values were obtained when testing at temperatures below glass transition temperature. The lowest IFSS values were determined above the glass transition temperature hereby creating a gap between the series tested at 50 and 90 °C. It can be said that the strongest separation of the IFSS between the series tested
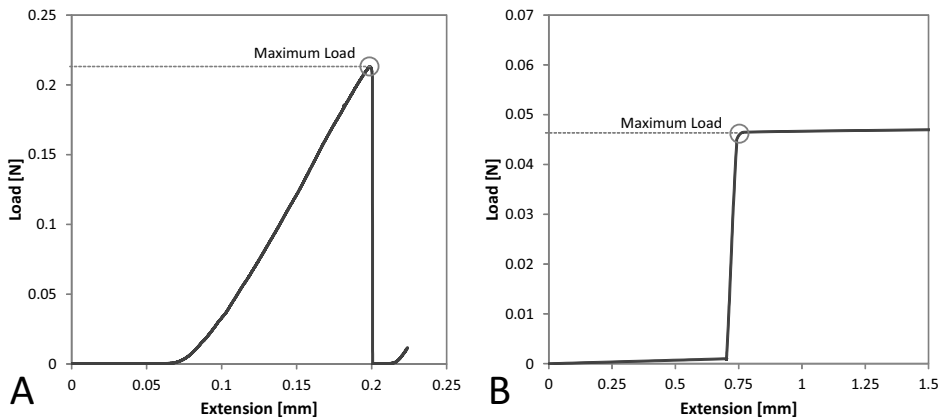

Figure 3. Load-extension curve obtained with the microbond test using A) the Instron tensile tester and B) the TMA.
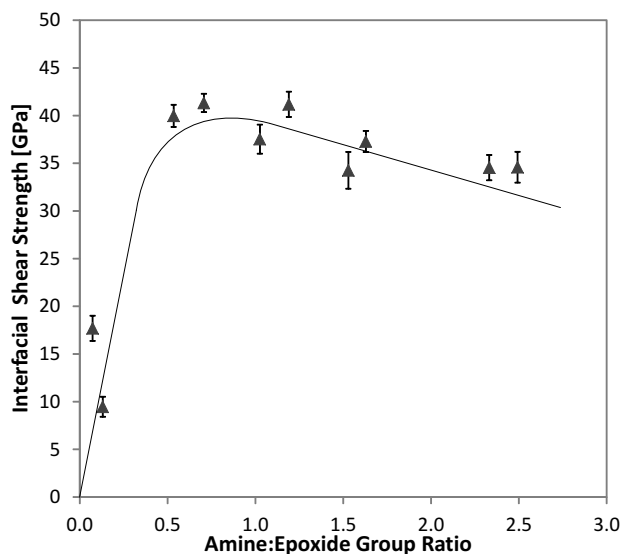
6

Figure 4. The IFSS determined at ten different amine:epoxide ratios at room temperature by use of the Instron microbond testing setup. The 95% confidence intervals are displayed.

at 50 and 90 °C was found at the stoichiometric ratio and with an amine:epoxide ratio of 0.7.

4.   Discussion

Since the glass fibres were sized only with an amino functionallised silane thus no film former nor other sizing components, interference of the amine:epoxide ratio at the fibre-matrix interface is only caused by the APTES from the sizing.

The decrease of IFSS at low and high amine:epoxy ratios is being explained by the fact, that the material is being less crosslinked as the ratio moves away from the stoichiometric ratio with either excess unreacted amine or epoxide groups. The curing agent TETA has both primary and secondary amine groups, the first being more reactive. The epoxide groups preferably react with primary amines instead of secondary amines, so an excess amount of amines (TETA) may not decrease the IFSS as much as expected. At high amine:epoxide ratios it is expected that all the primary amines are used up first, yielding a non crosslinked structure, since at least three amines of each TETA has to react to create the crosslinking. However, the excess is below an amine:epoxide ratio of 3 and secondary amines will also reach but creating a less rigid structure. A lower crosslinking density could result in a lower IFSS since the shrinkages also would be reduced [18,24,27]. At low amine:epoxide ratios less epoxide groups have reacted leading to a less crosslinked structure and possibly linear polymers [25]. This can change the physical properties of the matrix completely and the structural behaviour with a very soft material as the result. Residual stresses as a result of cure shrinkage might be reduced greatly and hereby reducing the IFSS along with it [18,24,27]. Since the droplets are soft they might not debond but rather be dragged along the fibre as can be seen in fig. 6, bottom image, where the embedded area is covered by residue.

The series tested at 90 and 120 °C behave differently with a steadily increase and a maximum above an amine:epoxide ratio of 2 suggesting that they despite the high
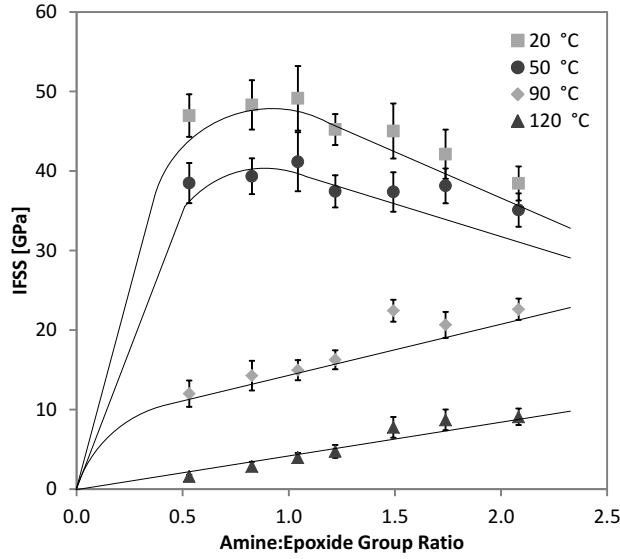
7

Figure 5. The IFSS determined at seven different amine:epoxide ratio and four different temperatures determined by the TMA microbond testing setup. The 95% confidence intervals are displayed for each data point.
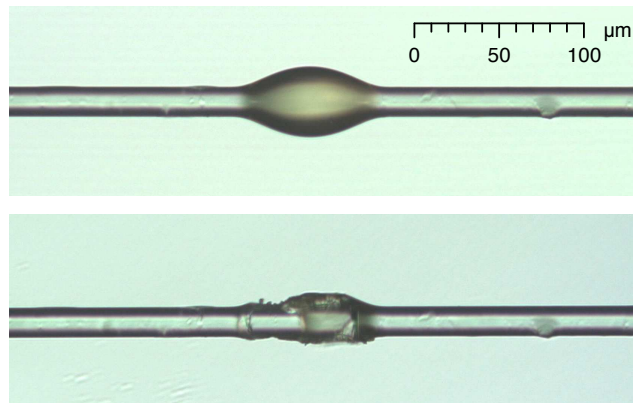

Figure 6. Droplet before (top) and after testing (bottom) at room temperature for 0.1 amine:epoxide ratio.

amine:epoxide ratio are soft as the temperature is above the glass transition temperature. The IFSS determined at both 20 and 50 °C display the same decreasing tendency above and below the stoichiometric ratio as found using the Instron setup but missing the data obtained at very low amine:epoxide ratio to verify the abrupt decrease. However it is noted that the maximum IFSS values obtained with the TMA setup is around 10 GPa higher than the results from the Instron setup. One explanation can be that the difference in loading could cause this mismatch as the loading of the droplet in the TMA setup occurs very quickly in less than a minute compared to the Instron setup with duration of several minutes. The high strain rate could result in higher shear as there is less time for deformation. To investigate this, the data obtained at room temperature for both the TMA and the Instron were normalised to the maximum value, see fig. 7. The data points overlap in such a manner that it supports the explanation that the testing speed is crucial to the IFSS determination.

The high IFSS at room temperature has been explained by residual stresses as a result of cure shrinkage but also by thermal stresses. The bulk of the curing shrinkage
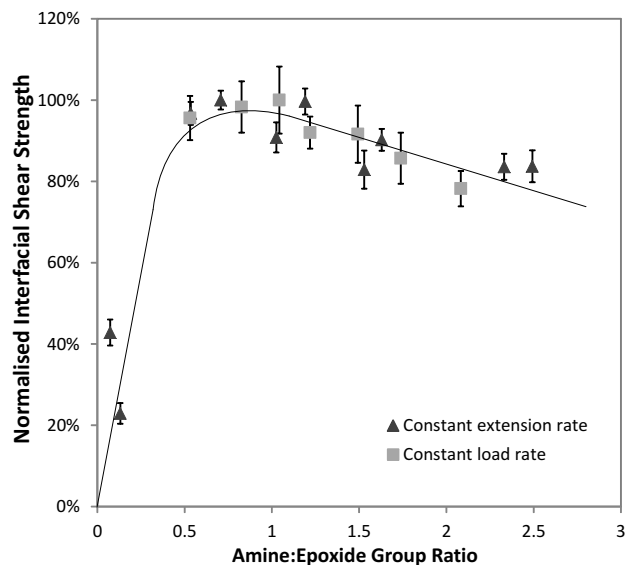
8

Figure 7. Normalised IFSS against the amine:epoxide ratio measured at room temperature with the Instron and the TMA setup.

is induced after gelation, when the crosslinking makes the structure more rigid and unable to relax [14,16–18,25,28]. Below the glass transition temperature the internal deformations could cause the determination of a higher value of IFSS [29]. Crosslinking density is responsible for the structural behaviour and therefore related to the shrinkage stresses with high crosslinking density being obtained using an amine:epoxide ratio at the stoichiometric ratio [24,27]. At high temperatures during curing the mobility of the matrix components is greater thus making crosslinking more probable than at lower temperatures. Physical properties linked to the crosslinking density will deteriorate with decreasing values, and the same applies for the shrinkage and thus the resulting residual stresses [24,27]. The risk of deformation increases with the amine:epoxide ratio and a high IFSS is expected. With testing temperatures above the glass transition temperature stress relaxation is yielding a lower IFSS [18].

The range of the glass transition temperature determined to be 49-87 °C for the chosen amine:epoxide ratios fits with the gap between the test series of 50 and 90 °C. This could indicate that the glass transition is of high importance for the IFSS as the material properties change. However the glass transition temperature might only be part of the explanation of the phenomenon as the same gap is present at the 0.5 ratio having a glass transition temperature of 49 °C. The series tested at 50 °C is not below the glass transition temperature of the 0.5 ratio and the point would thus be expected to be located at a lower IFSS. Assuming that the glass transition temperature is the same for the droplet as for the bulk samples used for the DSC.

From the glass transition temperature data and the estimated crosslinking densities the maximum IFSS is expected to be found at or close to the stoichiometric ratio [18], the results from the Instron and TMA microbond test support this as the optimum seems to be in the range of 0.7-1.2 and 0.8-1.0 amine:epoxide ratio, respectively. The maximum indicated by the TMA falls within the one from the Instron data. Despite the broad ranges the results indicate an maximum just below the stoichiometric ratio, which can be explained by the presence of the amine groups on the glass fibre surface as the fibres have a sizing containing only amino-functionalised silane. The amount of

9

amine groups from the sizing may cause a difference between the amine:epoxide ratio at the interface and the matrix expressed by the optimum just below the stoichiometric ratio.

5.   Conclusions

The IFSS is found to depend greatly on the amine:epoxide ratio of the matrix. The IFSS decreases when going below 0.5 amine:epoxide ratio and it also decreases above the stoichiometric ratio. An optimum was found to be in the range of 0.7-1.2 amine:epoxide ratio and likely just below the stoichiometric ratio around 0.8-1.0. This implies that it is possible to find an optimum amine:epoxide ratio in agreement with the presence of amine groups at the glass fibre surface from sizing. From this it is plausible that high amounts of amine or epoxide groups in sizing could move the ratio at the interface further away from the optimum stoichiometric ratio that often is used when mixing epoxy matrices. Since the matrix ratio should be kept around the stoichiometric ratio the focus should be on how to maintain this ratio at the interface through the constituents of the sizing. This knowledge about the interface ratio affecting the IFSS could be utilised when developing new sizings with respect to the concentration of functional groups and the amount of sizing. Sizings containing both amine and epoxy functionalised silanes at stoichiometric ratio could be an advantage in regard to high IFSS.

The testing temperature also influence the IFSS with the highest values obtained at testing temperatures around 20 and 50 °C depending on the amine:epoxide ratio. The results were explained to some extent by the crosslinking density of the epoxy matrix and the residual radial compressive stresses at the interface as a result of curing. The IFSS determined using the Instron and the TMA microbond setup both displayed the same behaviour with varying amine:epoxide ratio. The systematic difference between IFSS values determined using the two setups was explained by the difference in testing speed.
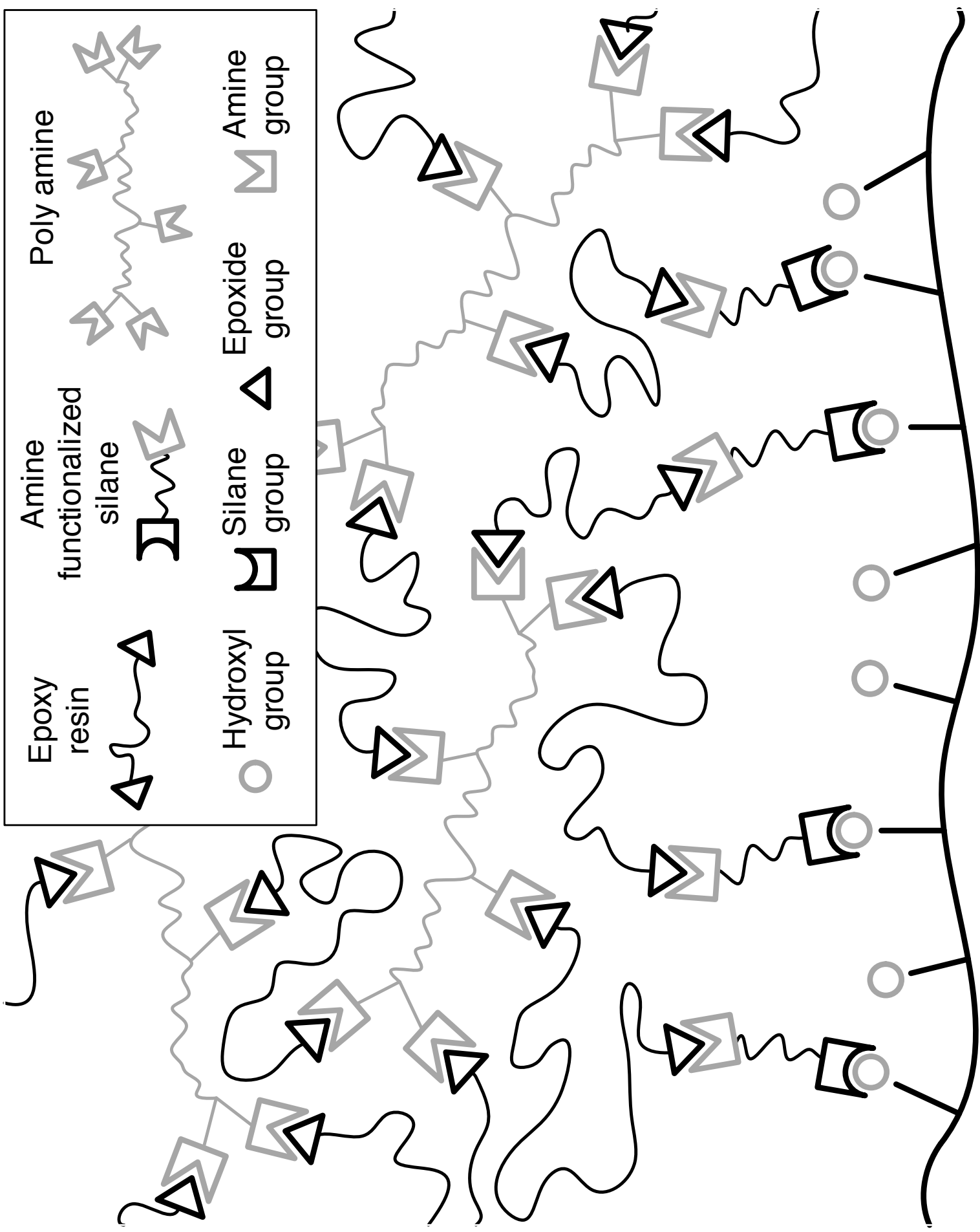
References

[1] Grande JA. Wind power blades energize composites manufacturing. Plastics Technology. 2008;54(10):68–75.

[2] REN21 2011. Renewables 2011 global status report. REN21 Secretariat, Paris; 2011.

[3] Thomason JL. Glass fibre sizings a review of the scientific literature. Glasgow, Scotland: University of Strathclyde; 2012.

10

[4] Jones FR. A review of interphase formation and design in fibre-reinforced composites. J Adhes Sci Technol. 2010;24(1):171–202.

[5] Thomason JL, Adzima LJ. Sizing up the interphase: an insider's guide to the science of sizing. Compos Part A: Appl Sci Manuf. 2001;32(3-4):313–321.

[6] Brøndsted P, Lilholt H, , et al. Composite materials for wind power turbine blades. Annu Rev Mater Res. 2005;35(1):505–538.

[7] Gorowara RL, Kosik WE, McKnight SH, et al. Molecular characterization of glass fiber surface coatings for thermosetting polymer matrix/glass fiber composites. Compos Part A: Appl Sci Manuf. 2001;32(3-4):323–329.

[8] Ash JT, Kjerengtroen L, Cross WM, et al. Estimation of the true interfacial shear strength for composite materials with the microbond test. In: Proceedings of the ASME 2013 International Mechanical Engineering Congress and Exposition, San Diego, California, USA, November 15-21; 2013. p. IMECE2013–62981.

[9] Gaur U, Miller B. Microbond method for determination of the shear strength of a fiber/resin interface: Evaluation of experimental parameters. Compos Sci Technol. 1989; 34(1):35–51.

[10] Herrera-Franco P, Drzal L. Comparison of methods for the measurement of fibrelmatrix adhesion in composites. Composites. 1992;23(1):1–27.

[11] Yang L, Thomason JL. Development and application of micromechanical techniques for characterising interfacial shear strength in fibre-thermoplastic composites. Polymer Testing. 2012;31(7):895–903.

[12] Wada A, Fukuda H. Microbond test for the fiber/matrix interfacial shearing strength. In: ICCM12 Conference, Paris, July 1999; 1999. p. 347.

[13] Thomason JL, Yang L. Temperature dependence of the interfacial shear strength in glass fibre polypropylene composites. Compos Sci and Tech. 2011;71(13):1600–1605.

[14] Thomason JL, Yang L. Temperature dependence of the interfacial shear strength in glass-fibre epoxy composites. Compos Sci and Tech. 2014;96:7–12.

[15] Dibenedetto AT, Lex PJ. Evaluation of surface treatments for glass fibers in composite materials. Polymer Engineering and Science. 1989;29(8):543–55.

[16] Pegoretti A, Della Volpe C, Detassis M, et al. Thermomechanical behaviour of interfacial region in carbon fibre/epoxy composites. Compos Part A: Appl Sci Manuf. 1996; 27(11):1067–1074.

[17] DiLandro L, Pegoraro M. Evaluation of residual stresses and adhesion in polymer composites. Compos Part A: Appl Sci Manuf. 1996;27(9):847–853.

[18] Thomason JL, Yang L, Bryce D, et al. An exploration of the relationship of chemical and physical parameters in the micromechanical characterisation of the apparent interfacial strength in glass fibre epoxy systems. IOP Conf Series: Mat Sci Eng. 2016;139(1):012048.

[19] Garcia FG, Soares BG, Pita V, et al. Mechanical properties of epoxy networks based on dgeba and aliphatic amines. J Appl Polym Sci. 2007;106(3):2047–2055.

[20] Kim JK, Sham ML, Wu J. Nanoscale characterisation of interphase in silane treated glass fibre composites. Compos Part A: Appl Sci Manuf. 2001;32(5):607–618.

[21] Schutte C, McDonough W, Shioya M, et al. The use of a single-fibre fragmentation test to study environmental durability of interfaces/interphases between dgeba/mpda epoxy and glass fibre: the effect of moisture. Composites. 1994;25(7):617–624.

[22] Minty RF, Thomason JL, Yang L. The role of the epoxy resin:curing agent ratio on composite interfacial strength and thermal performance. In: ECCM17 - 17th European Conference on Composite Materials Munich, Germany, 26-30th June 2016; 2016.

[23] Stevens MP. Polymer chemistry an introduction. Oxford, United Kingdom: Oxford University Press Inc; 1999.

[24] Pascault JP, Williams R. General concepts about epoxy polymers. In: Pascault JP, Williams R, editors. Epoxy polymers new materials and innovations. Weinheim, Germany: Wiley-VCH; 2010. p. 1–12.

[25] Strong A. Chapter 4: Epoxies. In: Strong A, editor. Fundamentals of composites manufacturing materials, methods and application. Michigan, USA: Society of Manufacturing

11

Engineers; 2007. p. 85–112.

[26] Yang L, Thomason JL. Interface strength in glass fibre-polypropylene measured using the fibre pull-out and microbond methods. Compos Part A: Appl Sci Manuf. 2010;41(9):1077–1083.

[27] Khoun L, Hubert P. Cure shrinkage characterization of an epoxy resin system by two in situ measurement methods. Polym Compos. 2010;31(9):1603–1610.

[28] Jakobsen J, Jensen M, Andreasen JH. Thermo-mechanical characterisation of in-plane properties for csm e-glass epoxy polymer composite materials - part 1: Thermal and chemical strain. Polymer Testing. 2013;32(8):1350–1357.

[29] Nishikawa M, Okabe T, Hemmi K, et al. Micromechanical modeling of the microbond test to quantify the interfacial properties of fiber-reinforced composites. International Journal of Solids and Structures. 2008;45(14-15):40984113.

12

Fig 1

Legend:

Epoxy resin

Amine functionalized silane

Poly amine

Hydroxyl group

Silane group

Epoxide group

Amine group
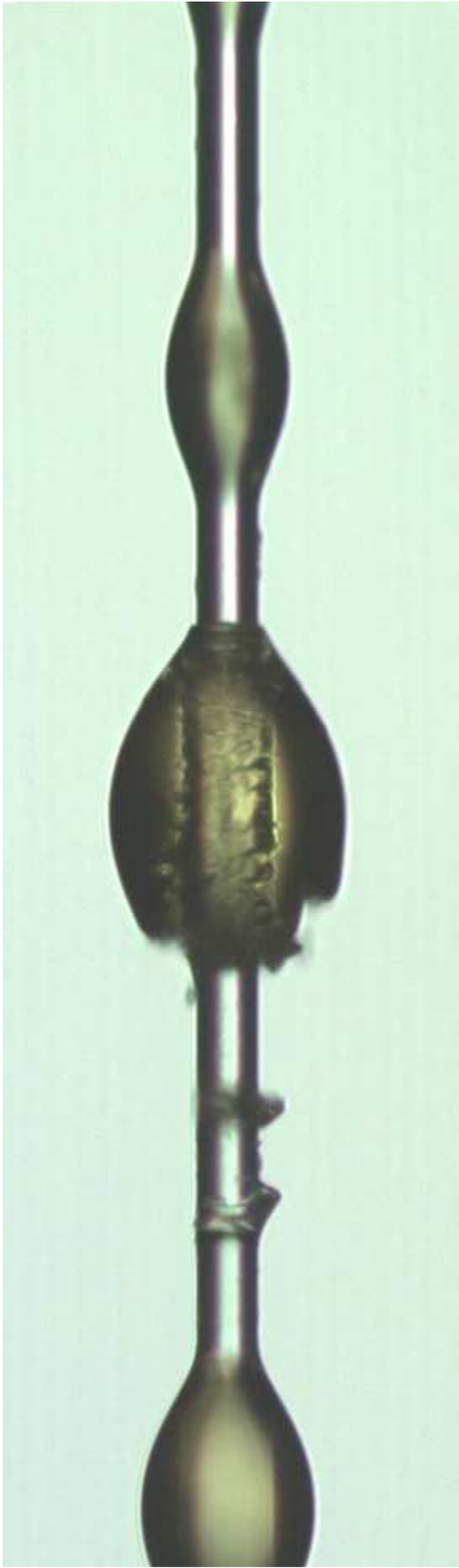
Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Normalised Interfacial Shear Strength

Amine:Epoxide Group Ratio

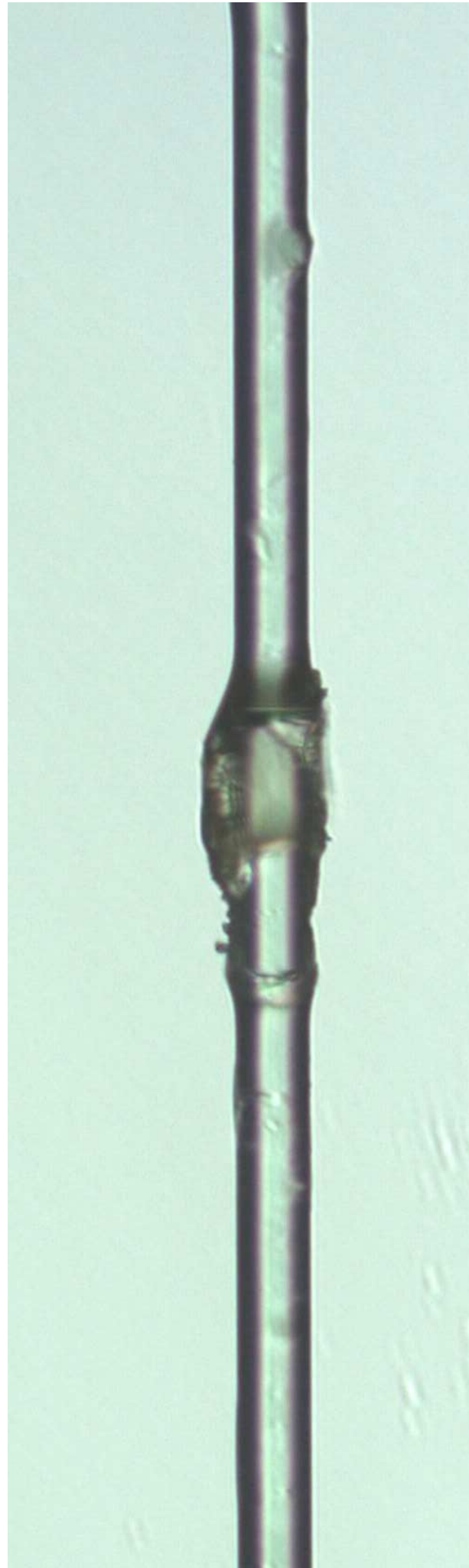▲ Constant extension rate
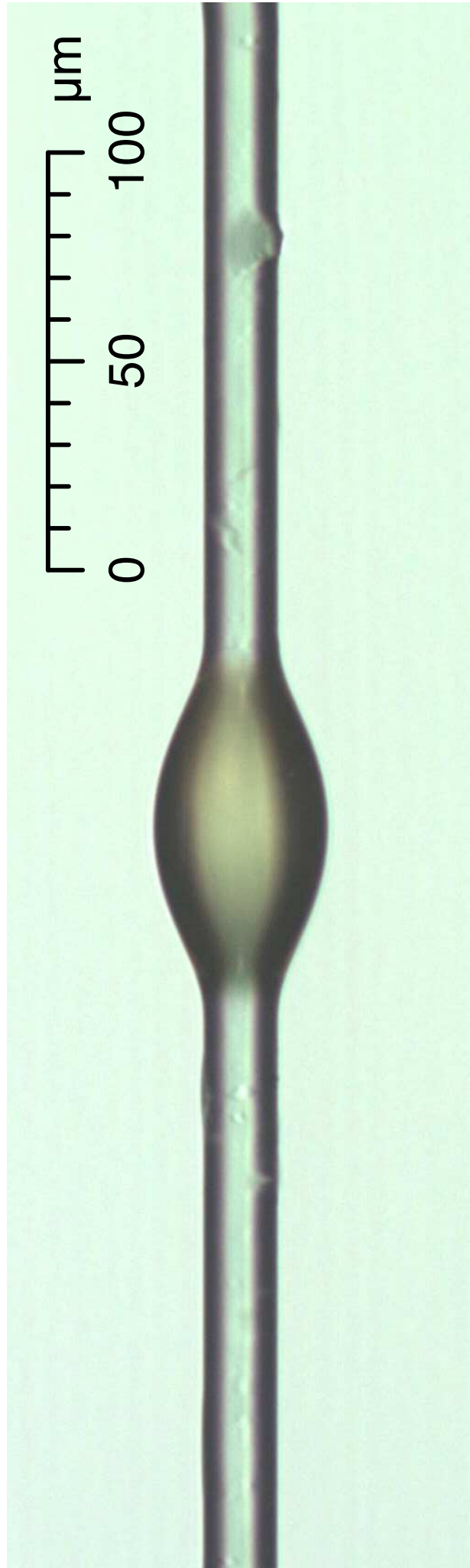■ Constant load rate

Graphical Abstract
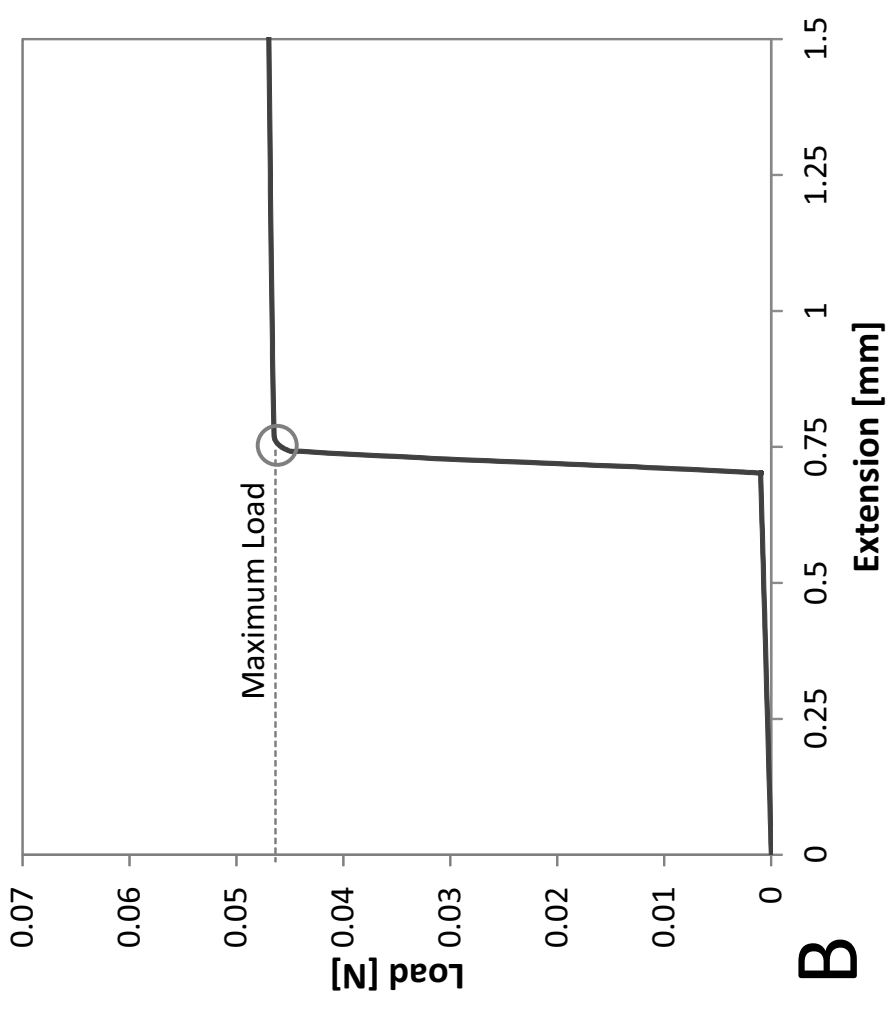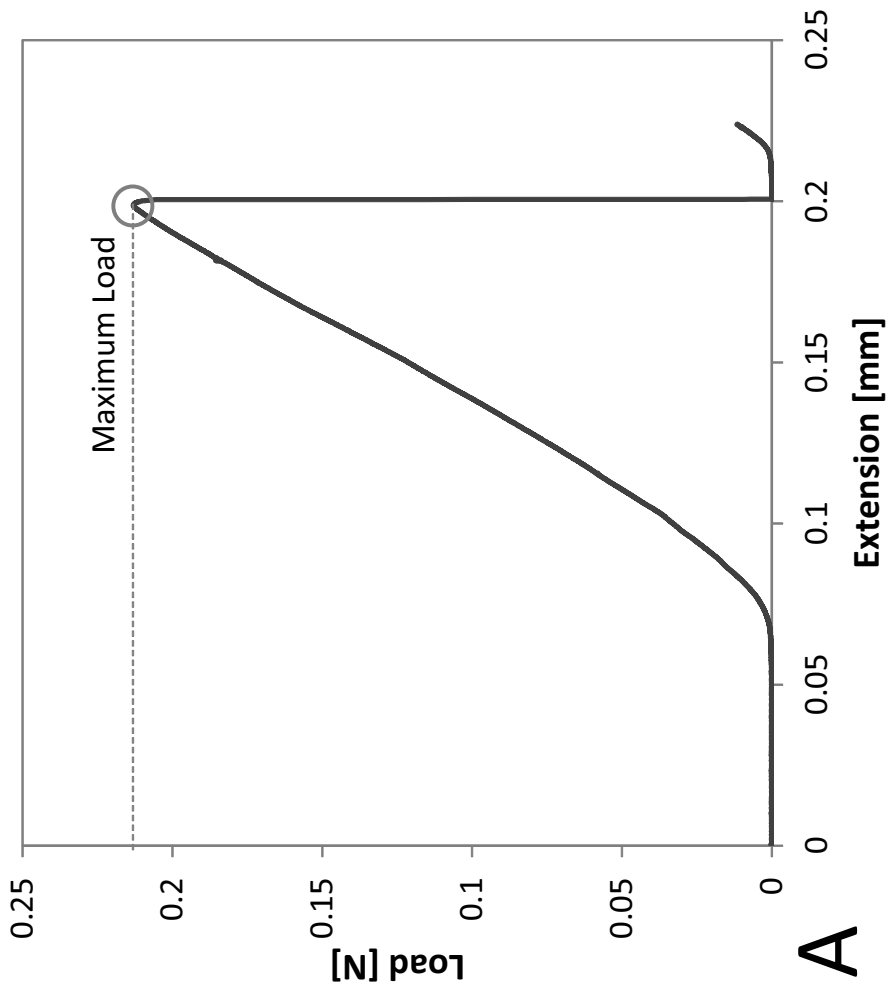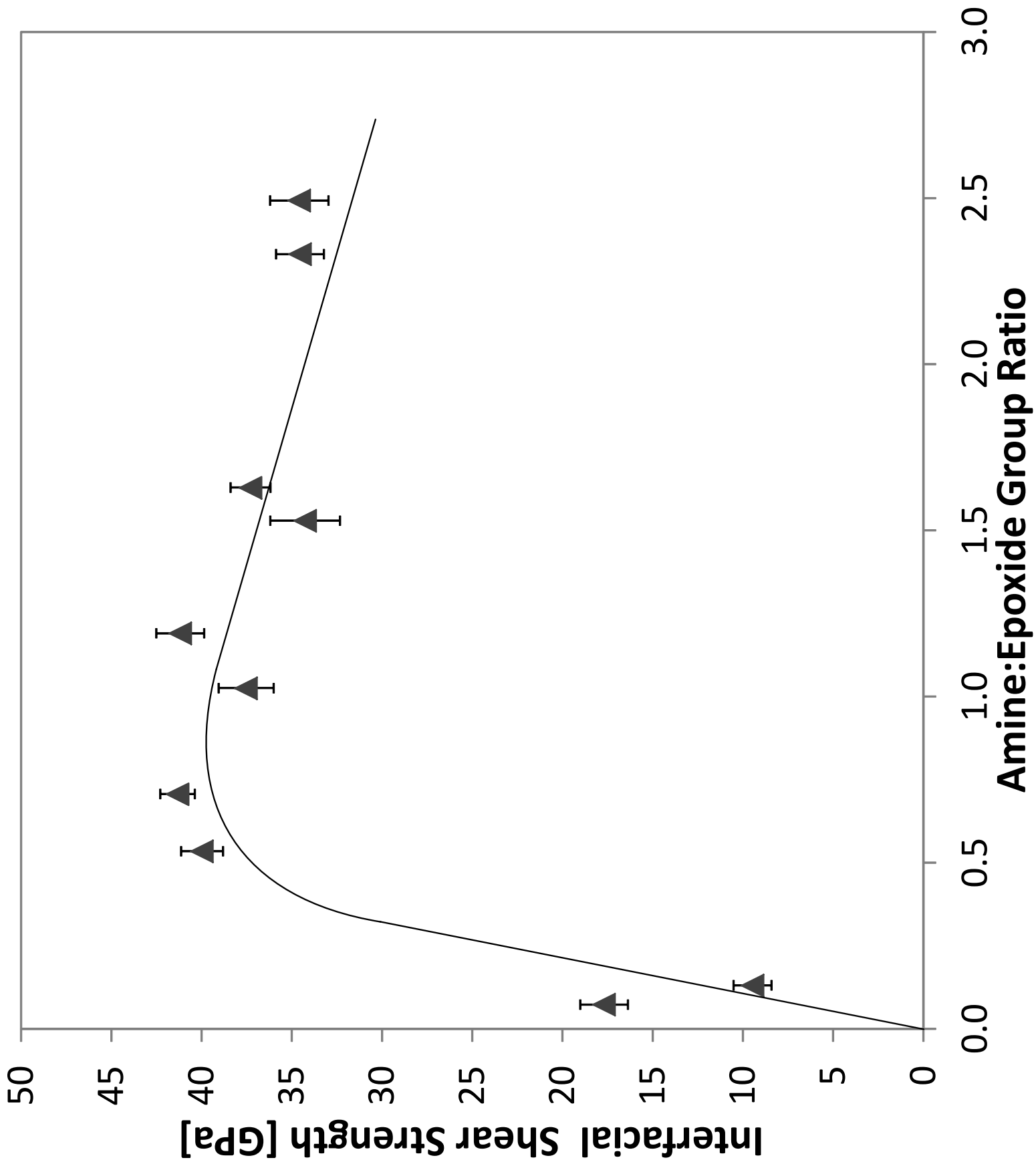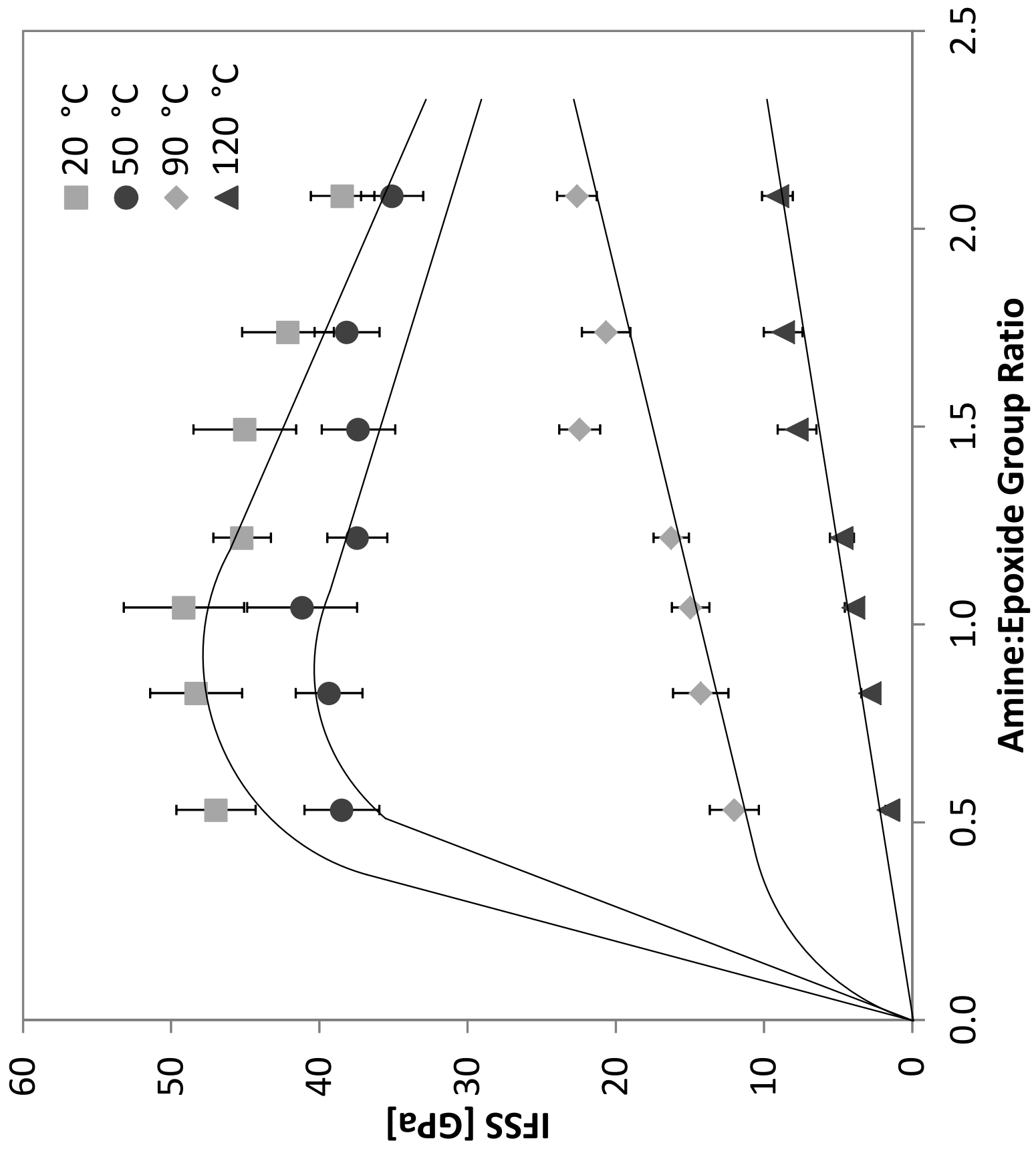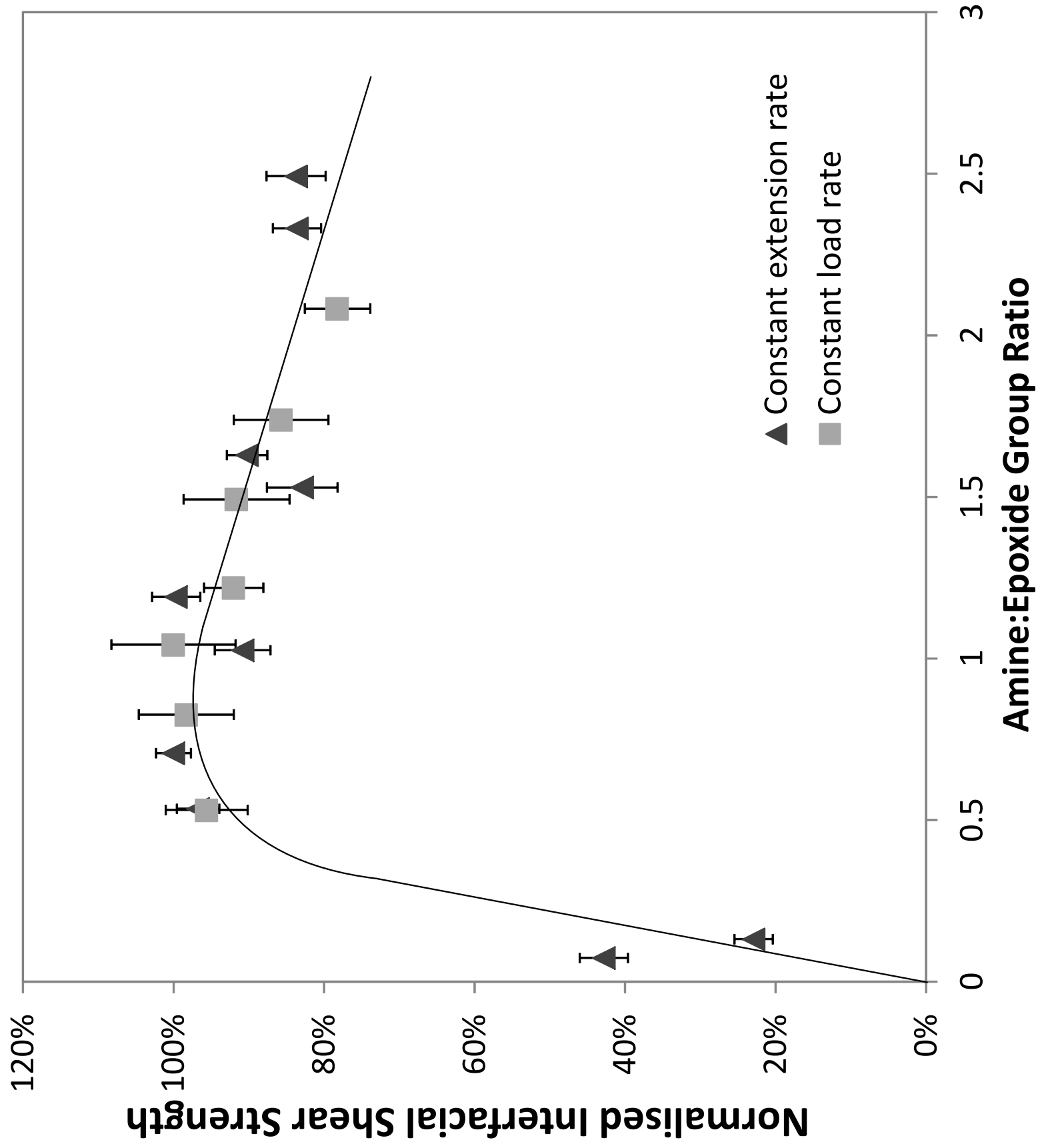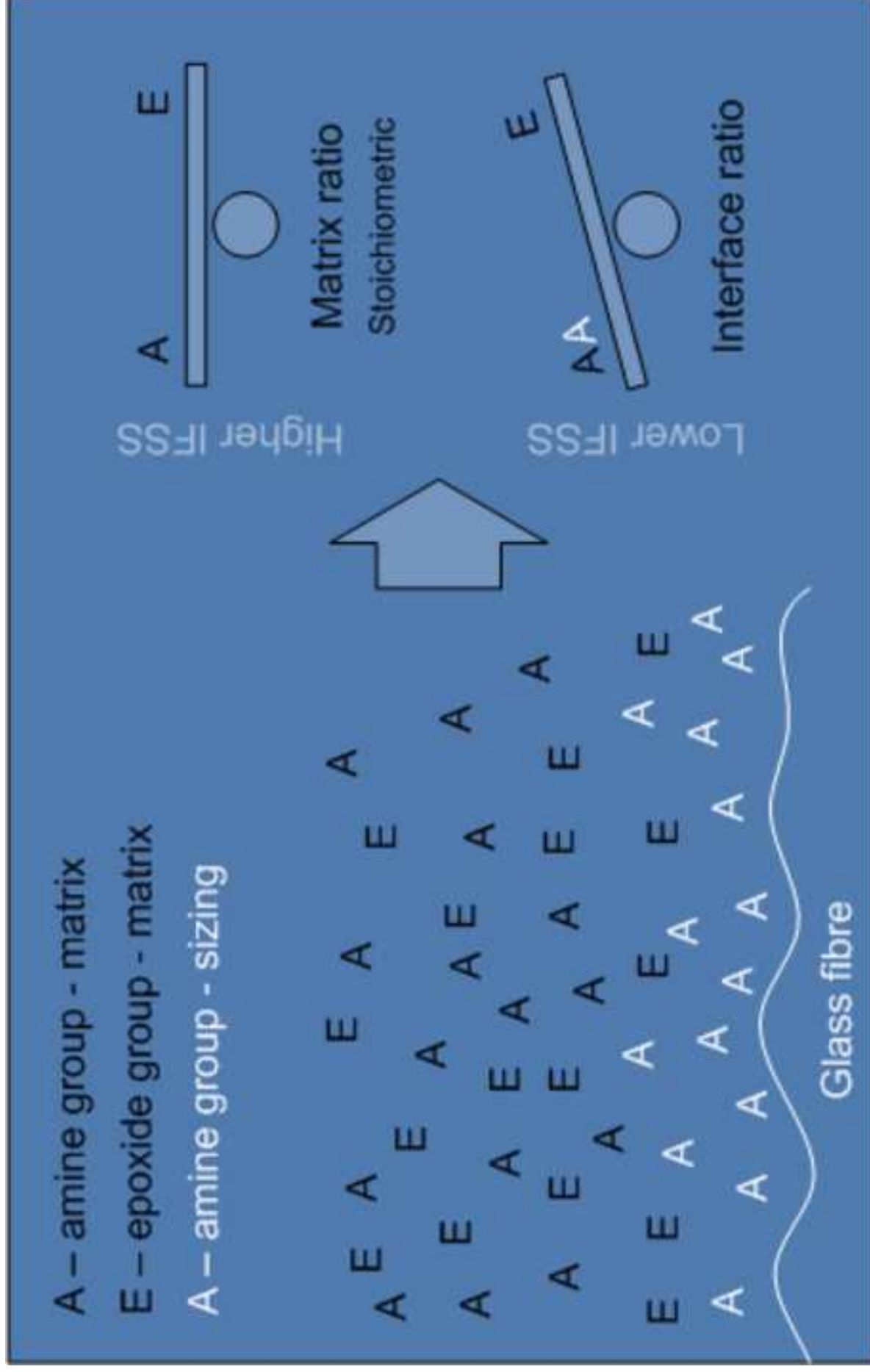
```
 1
 2
 3
 4    This is pdfTeX, Version 3.14159265-2.6-1.40.16 (TeX Live 2015/W32TeX)
 5    (preloaded format=pdflatex 2017.4.10)  23 APR 2018 07:48
 6    entering extended mode
 7     restricted \write18 enabled.
 8     %&-line parsing enabled.
 9    **./compinter_paper3.tex
10    (./compinter_paper3.tex
11    LaTeX2e <2016/03/31>
12    Babel <3.9q> and hyphenation patterns for 80 language(s) loaded.
13
14    ! LaTeX Error: File `interact.cls' not found.
15
16    Type X to quit or <RETURN> to proceed,
17    or enter new name. (Default extension: cls)
18
19    Enter file name:
20    ! Emergency stop.
21    <read *>
22
23    l.5 ^^M
24
25    *** (cannot \read from terminal in nonstop modes)
26
27
28    Here is how much of TeX's memory you used:
29     10 strings out of 493036
30     233 string characters out of 6138151
31     53513 words of memory out of 5000000
32     3649 multiletter control sequences out of 15000+600000
33     3640 words of font info for 14 fonts, out of 8000000 for 9000
34     1141 hyphenation exceptions out of 8191
35     10i,0n,7p,51b,8s stack positions out of 5000i,500n,10000p,200000b,80000s
36    !  ==> Fatal error occurred, no output PDF file produced!
37
38
39
...
```