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THE ISSUES IN MECHANICS OF PULP-AND-PAPER MATERIALS

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INVESTIGATING THE TRANSVERSAL VISCOELASTIC PROPERTIES OF PAPER FIBERS BY ATOMIC FORCE MICROSCOPY

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In order to gain more insight on how mechanical properties of fibers are related to properties of the paper, our work focusses on the transverse viscoelastic behavior of pulp fibers at different relative humidity. Therefore, we developed a novel atomic force microscopy based method to investigate nanoscale viscoelastic properties by combining contact mechanics and viscoelastic models.

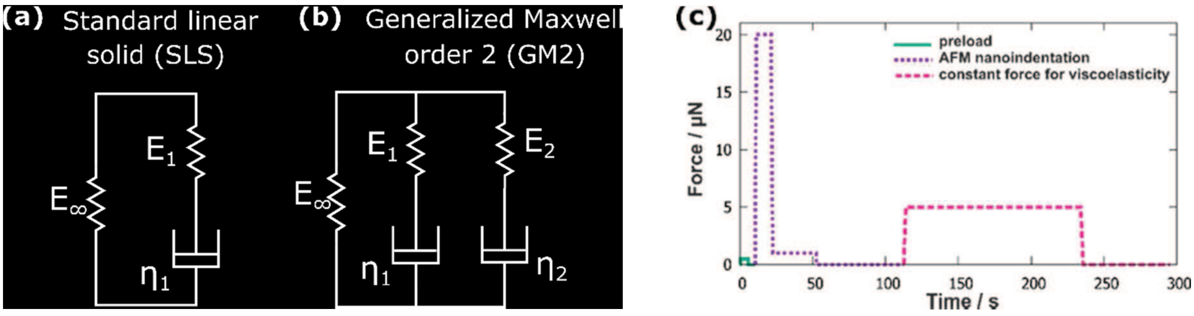
ИССЛЕДОВАНИЕ ВЯЗКОУПРУГИХ СВОЙСТВ БУМАЖНЫХ ВОЛОКОН В ПОПЕРЕЧНОМ НАПРАВЛЕНИИ МЕТОДОМ АТОМНО-СИЛОВОЙ МИКРОСКОПИИ

Для лучшего понимания связи между свойствами бумаги и механическими свойствами волокон, наша работа сфокусирована на поведении поперечной вязкоупругости волокон целлюлозы при различной относительной влажности. Таким образом, мы разработали новый метод, базирующийся на атомно-силовой микроскопии, для исследования вязкоупругих свойств в нано масштабах, путем объединения контактной механики и вязкоупругих моделей.

By probing a material with an atomic force microscopy (AFM) based method in contact mode, it is possible to gain information of the material's mechanical properties on the nanoscale since the force can be controlled precisely. In the past, AFM based nanoindentation (AFM-NI) has already been successfully employed to measure elastic and plastic properties of various kinds of cellulose based materials, in water, in air, and in an environment with controlled humidity [1–4].

In order to measure transverse viscoelastic (VE) properties of paper fibers, an AFM based method combing contact mechanics with a VE material model is used. Contact mechanics is necessary to transform the measured force and indentation depth values from AFM-NI into stress and strain, which cannot be measured directly in AFM and are needed by the VE model. The Johnson-Kendall-Roberts [5] contact model was chosen as it allows to account for adhesion forces.

To describe the bulk behavior of VE materials at the continuum scale, simple empiric VE models are often used. These consist of springs describing the elastic behavior and dash pots describing the viscous behavior. The Standard Linear Solid (SLS) model with 3 parameters is the simplest which can yield meaningful results and describes real solid behavior. A generalized Maxwell model of order 2 (GM2) was also applied and can be considered as SLS model with a second branch with a spring and dashpot. Both models are sketched in Fig. 1,*a* and 1,*b*.



a *b* *c*

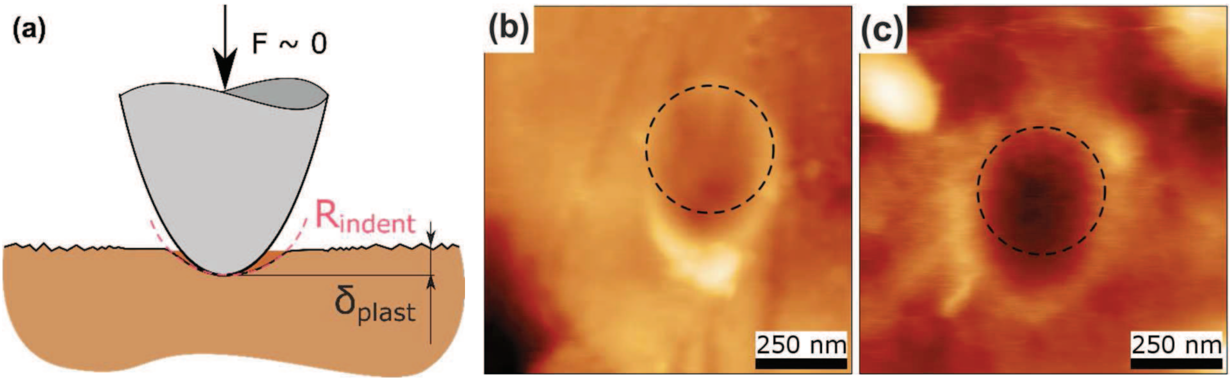
Fig. 1: Linear VE models to describe solids: *a* – Standard Linear Solid (SLS) model with 3 parameters; *b* – Generalized Maxwell model of order 2 (GM2); *c* – applied load schedule

In Fig. 1c, the load schedule for the experimental procedure is presented and shows a very simple repetition of loading to a certain force, holding and subsequent unloading to zero force. However, to create a defined surface morphology with as little roughness as possible a plastic deformation step with a maximum applied force of 20 μN was added to the load schedule. Here, the material is deformed plastically and a hole (R_{indent} in Fig. 2,*a*) with defined geometry and reduced roughness is created. In the sketch in Fig. 2,*a*, the contact of tip and surface after the plastic deformation is illustrated. In Fig. 2,*b*, AFM topography images of different investigated materials prove that the assumption of a hole is valid.

In AFM measurement usually very sharp tips, ideally one atom, are used to achieve the best possible resolution of the investigated surface. Here, AFM probes are used that have a very large radius of about 300 nm and spherical shape at the apex. This makes it possible to apply higher forces while keeping the strain underneath the tip low.

As it is extremely important to check whether such a novel procedure yields meaningful results, first a comprehensive verification has been carried out. For this purpose, poly(methyl methacrylate) (PMMA) and polycarbonate

(PC) were selected as test materials. These two materials are amorphous polymers and should be mostly isotropic and homogeneous.



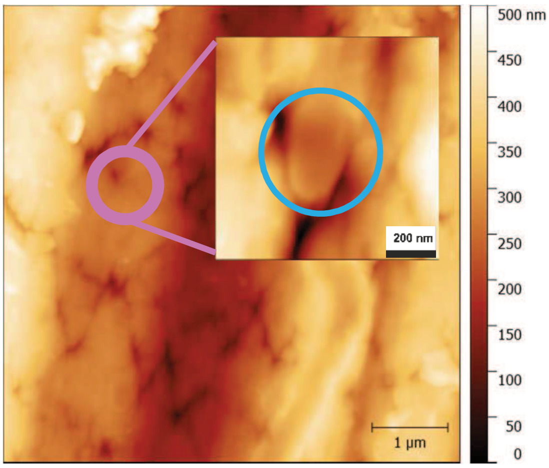
a *b* *c*

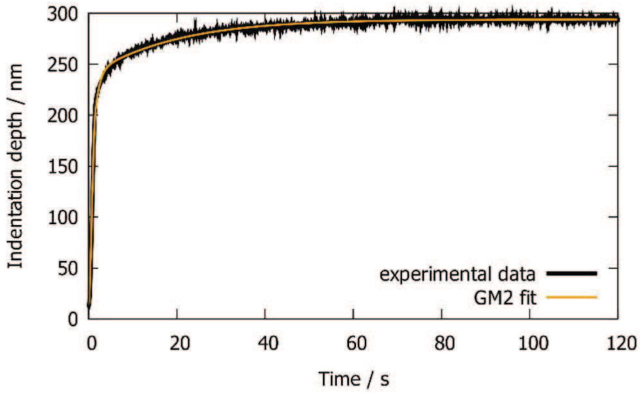
Fig. 2: *a* – Illustration of the contact between tip and surface after the plastic deformation; *b*, *c* – show 1×1 μm² AFM topography images of plastically deformed regions; *b* – PMMA surface (*z*-scale: 120 nm); *c* – PC surface (*z*-scale: 100 nm)

The verification of our method with all approaches and results is presented in detail in Ref. [6]. First, PMMA and PC were tested with tensile creep experiments where the whole macroscopic sample was loaded. Additionally, the PMMA and PC samples were investigated by classical nanoindentation. Here, the loading was chosen very similar to that of the AFM method, just higher forces were applied and an indenter with a larger radius was used (about 5 μm). Evaluation of the data showed that all three methods yielded comparable results and revealed the same trend. Especially, the nanoindentation results were well comparable to the AFM results for the SLS as well as the GM2 model. However, the influence of thermal drift and random noise to the measured AFM curves lead to a large scattering in the viscosity parameters. The indentation depths on PMMA and PC were around 20 nm - 30 nm, while noise during the measurement can cause fluctuations of a few nm.

The effect mentioned above can be overcome by using larger deformations. Therefore, a fully swollen viscose fiber in water, as presented in Fig. 3, was measured. Here, the deformations were higher by a factor of 10, although the applied forces were 5 times lower. Due to the larger indentation depth, the influence of noise is much lower and as can be seen in Fig. 3b, the experimental data is fitted very well with the GM2 model. The scattering in the viscous parts was significantly reduced as it is presented in Table 1. The resulting sums of the elastic parameters E_0 for both VE models were comparable to elastic moduli

(E_r ~ 50 MPa; recorded with a different tip) measured by AFM nanoindentation on the same type of viscose fiber [3].





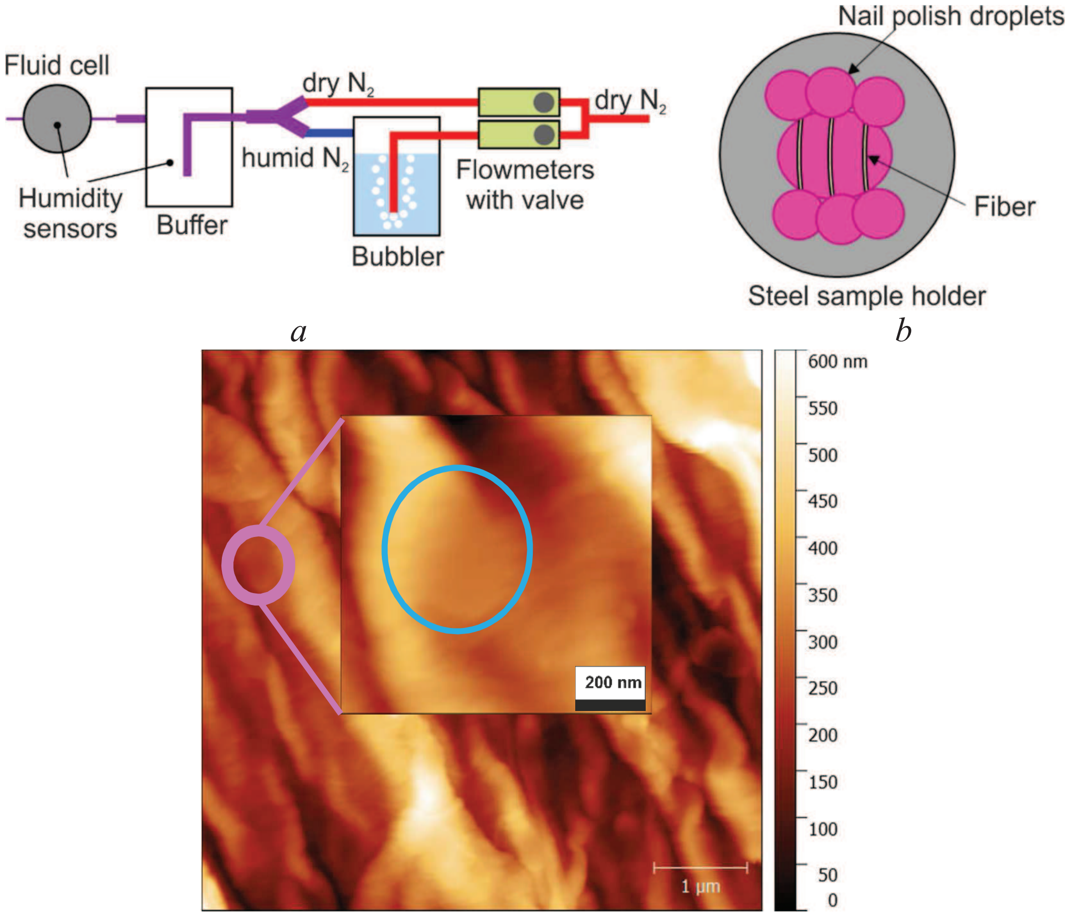
a *b*

Fig. 3. *a* – 5×5 µm² topography image of a viscose fiber and a 1×1 µm² zoom-in scan, the blue circle indicates an indent; *b* – example fit for the GM2 model on a wet viscose fiber

Table 1: Results for the evaluation of 28 measurements on a swollen viscose fiber for the SLS and GM2 model

VEM model	E_∞ / MPa	E_1 / MPa	E_2 / MPa	E_0 / MPa	η_1 / MPas	η_2 / MPas
SLS	8.6 ± 1.9	2.6 ± 1.2	-	11 ± 2.6	25 ± 11	-
GM2	8.5 ± 1.9	12 ± 5.2	1.3 ± 1.0	22 ± 6.9	7.1 ± 1.5	17 ± 14

With this successful verification, the method was finally applied to study pulp fibers at different humidity. A scheme of the setup to control relative humidity (RH) is shown in Fig. 4,*a*. Also, sample preparation of paper fibers is not trivial, as can be seen in Fig. 4,*b*. Past experiments [4] proved that embedding the fibers in nail polish works very well. The samples are unbleached and unrefined kraft pulp fibers consisting of a mixture of spruce and pine fibers. The fiber length is about 3-5 mm and the diameter ranges from 20 to 30 µm. An AFM topography image of the surface of a paper fiber is presented in Fig. 4c. As can be seen, the surface is very rough and dominated by wrinkles and fibrils. The zoom-in scan in Fig. 4,*c* shows a plastically deformed area.

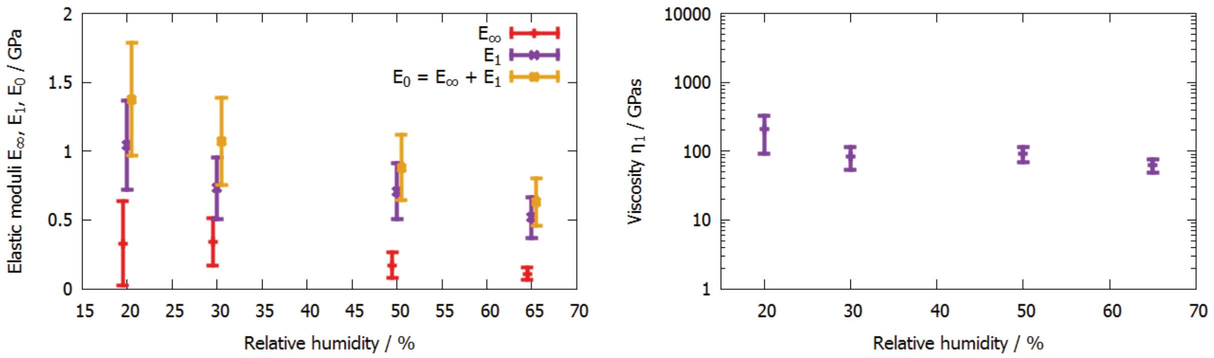


a *b*

c

Fig. 4: *a* – a schematical representation of the setup to control RH; *b* – illustration of the sample preparation; *c* – 5×5 µm² topography image of a paper fiber with a 1×1 µm² zoom-in scan, the blue circle indicates an indent

In Fig. 5, first results for a paper fiber measured at different RH (20, 30, 50 and 65 %) are presented. The results for the SLS model show (Fig. 5,*a*) that the parameters describing elastic behavior decrease with higher RH and the scattering is reduced. Especially E_∞, which is also comparable to the elastic modulus at infinitely slow loading, shows very little scattering at 65 % RH. Also, the results for the viscosity parameter of the SLS model which is presented in Fig. 5,*b* with a logarithmic scale, show a similar trend. The viscosity as well as the scattering decrease with higher RH. Here, the viscosity value drops by a factor of 2 from 20 % RH to 65 % RH.



a *b*

Fig. 5. *a* – Elastic moduli and b – (logarithmic scale) for the SLS model for one paper fiber at different RH; 30 measurements were obtained at each RH

In this work, it was demonstrated that it is possible to use an AFM based method to extract nanoscale VE properties. As a very important part the method was thoroughly tested with amorphous polymers and the results compared to established methods like macroscopic tensile testing and conventional nanoindentation. Also, first results of the transversal VE properties for a wet viscose fiber and paper fibers at different RH evaluated with the SLS model look promising and results for the GM2 model are being prepared. Now, it will be important to get reliable statistics and to measure at higher RH and in the wet swollen state, where the viscoelastic behavior should be even more pronounced.

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