DOI: 10.1002/masy.200651215

Nanoparticle Modified Cellulose Fibres

*Jürgen Melle, Micheal Mooz, Frank Meister**

Summary: The dissolution of cellulose in *N*-methylmorpholine-*N*-oxide monohydrate exhibits a remarkable acceptance towards well ground organic or inorganic additives up to high concentrations. Particle sizes generally in the lower micrometer range have been the most common features of all additives applied up to now. With the assumption, that it would succeed to exploit the capabilities to a surface and matrix manipulation already described for combinations of synthetic fibres and polymer bulk materials for cellulose as well, then very interesting opportunities for the development of shaped cellulosic bodies would result that possess improved product characteristics. Inorganic, hydrophilic nanoclays and different organic modified nanoparticles of various manufacturers were chosen for the investigation. The effect of the different nanoparticle types on the matrix structure after the incorporation was determined by means of X-ray wide angle scattering. Nanoadditives did not influence the structural formation of cellulose shapes significantly. Compared to a film forming process, in case of fibre spinning it was found that the nanoclays obviously underwent a preferred orientation as a result of the solvent extraction after a dry-wet extrusion process.

Keywords: cellulose; composites; fibres; nanolayers

Introduction

The ALCERU®-process, a technology variant belonging to the group of Lyocell or direct dissolution processes has independently been developed by the Thuringian Institute for Textile and Plastics Research (TITK), and represents an environmentally friendly technology for shaping native cellulose. It allows generating a wide variety of functional shaped bodies.

The dissolution of cellulose in *N*- methylmorpholine-*N*-oxide monohydrate (NMMO-MH) exhibits a remarkable acceptance towards well ground organic or inorganic additives up to high concentrations. In this way, corresponding research and development activities led to a wide variety of functional cellulosic fibre materials that are currently on the way to enter the market. However, special technological features such as the presence of water in all process steps, the comparatively low stability at elevated process temperatures ($T \geq 120\,^\circ C$) as well as increased heavy metal ion concentrations and zero shear viscosities comparable to that of polymer melts, require a considerable know-how when up-scaling laboratory results into a larger scale. Potential additives have to meet the high demands on quality parameters, especially inertness to solvent and cellulose as well as a sufficient and stable dispersion forming ability. Similar particle sizes generally in the lower micrometer range (1–20 μm) have been the most common features of all additives applied up to now.

The rapidly grown variety of nanoscaled additives was providing new capabilities for the modification of properties of shaped cellulosic bodies. Much more interesting

---

Thuringian Institute for Textile and Plastics Research, Breitscheidstraße 97, D-07407 Rudolstadt, Germany, Member of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu
Fax: (+49) 03672 37 93 79
E-mail: chemical-research@titk.de

was the fact, that decreasing particle sizes are expected to overlay the chemical properties of the resulting cellulose composite by its interfacial properties.[1]

Under the proviso, that it would succeed to exploit the capabilities of surface and matrix manipulation already described for combinations of synthetic fibres and polymer bulk materials [2–5], such as

- increase of textile-mechanical fibre characteristics (tenacity, E-modulus)
- improvement of heat resistance
- improvement of colour brilliance at reduced dye consumption
- decreased permeation behaviour of polymer films for gases and vapours
- changing heat- and electric conductivity
- influenced surface- and interfacial properties of shaped bodies
- changing swelling behaviour in liquids or retention behaviour for liquids
- change of polymer compatibility against secondary components still considered as being incompatible

for cellulose as well, then very interesting opportunities for the development of shaped cellulosic bodies possessing improved product characteristics would result.

Research activities of other groups [6,7] had shown that the change in properties as detected at composites consisting of synthetic polymers and nanoscaled additives may also apply to thermoplastic starch or cellulose composites, respectively.

Experimental Methods

Pre-treatment and Incorporation of Nanoadditives into Dopes

Inorganic, hydrophilic nanoclays and different modified nanoparticles of various manufacturers were chosen (Table 1). As process media, water (incorporation into pre-dope) and a high concentrated aqueous NMMO (dynamic mixing process) were investigated for the homogeneous incorporation of the nanoparticles into a spinning dope. Hydrophobically modified nanoclays as well as pyrogenic silicic acids were treated by a pre-dispersing step using n-hexane (nanoparticle:hexane = 1:20). A Heidolph laboratory dissolver Diax 9000 was used for this purpose. The rotation speed was varied in all trials between 8.000 (n-hexane, NMMO 1.6 hydrate) and 25.000 r.p.m. (aqueous or higher water content). The dispersion temperature was kept at room temperature when using n-hexane, $50 \pm 10\,^{\circ}C$ in aqueous or highly water-containing media and at $75 \pm 5\,^{\circ}C$ when dispersing in NMMO 1.6 hydrate. The dispersion was pre-treated with ultrasound to improve and maintain homogeneity. Swelling time and temperature have been varied between $20 \leq t \leq 60$ min and $50 \leq T \leq 90\,^{\circ}C$.

The resulting dispersions were visually assessed regarding their attained distribution and long-term stability. Microscopic images of manually cast cellulose films have been used to assess the degree of dispersion

Table 1.
Nanoadditives Used In the Investigations.

Product name	Clay type	Manufacturer	Unmodified	Organo modified
Pyrogenic silicic acids				
AEROSIL 200	–	Degussa	x	
HDK 2000	–	Wacker Chemie		x
Layered silicates				
Bentone 104	Bentonit	Elementis		x
Bentone 105	Bentonit	Elementis		x
Bentone EA-163	Bentonit	Elementis	x	
Cloisite Na^+	Montmorillonit	Southern Clay	x	
Cloisite 30B	Montmorillonit	Southern Clay		x
Laponite RD	Synthetic Clay	Rockwood	x	
Laponite RDS	Synthetic Clay	Rockwood	x	
Nanofil 948	Montmorillonit	Südchemie		x
Nanofil 1485	Montmorillonit	Südchemie		x

(laboratory microscope SM 33 of Co. Hund, Wetzlar, 80fold magnification).

Solvents/Pulps

Aqueous NMMO (50%, w/w; technical grade, BASF) was used in all experiments. It was purified by an ion exchange procedure before use and re-concentrated by vacuum evaporation to reach a desired concentration of 60% by weight. Its concentration was determined by the index of refractivity at 50 °C.

A dry-milled spruce sulphite pulp with a degree of polymerization (cupriethylenediamine) of 515 (MoDo) was used in all experimental trials.

Dope Preparation and -Characterisation

Dope preparation (Rheocord 9000, Haake, Karlsruhe) has been carried out at elevated process temperatures up to 105 °C at maximum. For larger scale investigations, a vertically arranged stirring tank being able to produce up to 6.000 g dope was at the disposal. The tank equipped with a double-mantle heating jacket is designed for stirring velocities between 60 and 100 rpm. being infinitely adjustable. An external vacuum pump generates pressures between 100 and 30 mbar.

When using a dynamic mixing process, the nanoparticle dispersion was produced immediately before blending from an aqueous or n-hexane particle dispersion and NMMO-MH, where a final NMMO-concentration of 84 ± 2% results from.

The cellulose/nanoadditive pre-dope was prepared by placing the required amount of stabilisers (0.5% gallic acid propyl ester) and caustic soda (pH = 12) into the aqueous NMMO solution needed, whereupon cellulose powder has been added together with the prepared nanoparticle dispersion. The blend was homogenised at a constant pressure of 40 mbar at 95 °C.

The progress of the dissolution process is monitored through the index of refractivity. Total solid matter contents of 10 to 13% could be realised, when preparing dopes loaded with nanoadditives (1 to 25% regarding to the amount of cellulose used) according to the common course of dope preparation. In case of a dynamic mixing step, a non-modified dope of about 12% by weight cellulose content was blended with a dispersion consisting of nanoparticles (20 to 40%) and concentrated NMMO (monohydrate ≈83%) immediately before entering the mixing chamber. Depending on the initial solid matter content of the added nanodispersion, the resulting dopes may show slightly diverging solid contents. As a consequence, the zero shear viscosities differ between some hundreds to several ten thousand Pa s, typically about 2.000 to 4.000 Pa s at the dopes investigated. The dope quality has been assessed by means of a set of parameters involving micro image, particle content and particle size as well as flow characteristics (zero shear viscosity, storage and lost modulus).[8]

Dope Shaping

The prepared composite dopes have been processed on a laboratory spinning set-up. It consists of a dope storage tank purged with nitrogen having a capacity up to 12.000 g, a spinning pump, a thermo-controlled spinning head and a multi-step washing bath.

The spun fibre bunches were wrapped around a bobbin and cut manually into staples of 38 mm length prior to finishing and drying. Depending on the fineness intended the spinning velocity was adjusted between 20 and 30 m/min. The fibres were dried at 85 °C in a hot-air circulation cabinet drier.

Determination of Fibre Properties

For fibre characterisation the fibre fineness (DIN EN ISO 1973), wet and conditioned tenacity as well as elongation at break (DIN EN ISO 5079), loop tenacity (DIN 53843, Part 2), the wet abrasion resistance[9] and the water retention behaviour (DIN 53814) have been measured.

Results and Discussion

The starting point of the research activities was to choose suitable nanoadditives, to investigate pre-treatment procedures, if required, as well as to find ways of introducing them into dopes by procedures usually applied in dope preparation.

Due to the fact that native or synthetic layered silicates (nanoclays) represent the most commonly applied modifiers at present, their structural variety may be expanded by comparatively simple methods such as hydrophobic and oleophilic modification (exchange of Mg cations in intermediate layers by ammonium cations or quaternary ammonium compounds, respectively). A wide variety of very different nanoparticles is available on the market in the meantime. It was therefore necessary to restrict the investigations to a defined group of materials.

In order to attain the desired homogeneous distribution of nanoclays in cellulosic dispersions, suitable procedures had to be found for the group of pre-selected compounding components. The initial state of additive dispersity should be maintained or only influenced in a low extent, if practicable.

Different kinds of pre-treatment and processing procedures were needed for an optimal distribution/intercalation of the various types of nanoparticles inside the spinning dopes. Thus, most of the organically modified clays had to be treated with different surface-active agents and all nanoparticles had to be pre-treated with a high-speed stirrer at about 15.000 rpm to get a homogeneous distribution inside the dopes.

As an example, organically modified nanoclays could be dispersed in the water containing solvent not before carrying out preliminary dispersion in organic media (n-hexane) or applying dispersants. Moreover, the influence of different wetting- and dispersion aids on both characteristics was investigated. Among this, the efficiency of technical grade paraffin (melting range: 28–32 °C), of low-melting polyethylene waxes (melting point: 95 °C) as well as of aqueous polyether wax dispersion was examined. Handling such dopes has turned out to be complicated, because the available experimental set-up could not provide constancy of temperature when transferring the dope to spinning devices. This led to non-reversible phase separation. Figures 1 and 2 display the achieved degree of dispersion.

Beside TEM usually applied in the manufacturing process of synthetic polymer-nano-composites, information on the nanoclay or cellulose structure could be accessible by means of X-ray wide angle scattering. For the preparation of cellulose-nanoclay films it was postulated that the lack of reflexes in the 2θ-range, where signals of clays and cellulose typically appear, may prove a sufficiently good destruction of the nanoclay within the

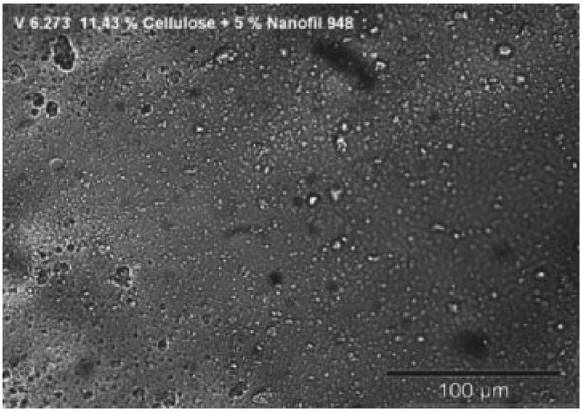


Figure 1.
Distribution of Nanofil 948 in a cellulose film without dispersing auxiliary.

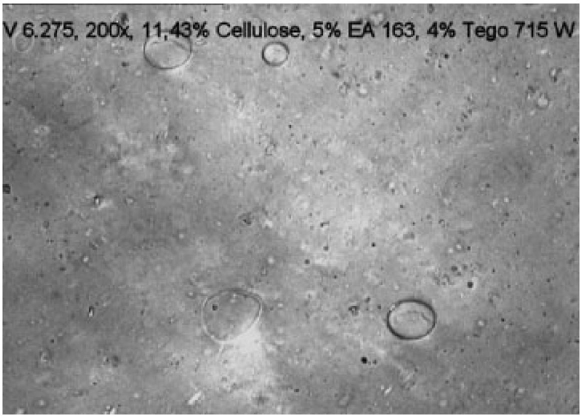


Figure 2.
Distribution of Bentone EA 163 in a cellulose film used 4% of TEGO 715 (sodium polyacrylate).

cellulose. As a consequence, signals that appear in the finger-print region of the recorded X-ray diffractograms would indicate only weak interactions between the layered silicates and the cellulose phase.

In order to evaluate the distribution of the nanoparticle layers in the cellulose matrix, manually drawn composite films obtained using a doctor coating machine have been characterised by X-ray wide angle scattering. The results are displayed in Figures 3 to 5 and 7.

The lack of strong reflexes in the XRD pattern (V 6.238 and V 6.254, manually drawn film with 4% nano-clay related to cellulose) gave rise to the assumption that it succeeded to attain a sufficiently good exfoliation of the layered silicate Cloisite Na+ in the investigated films. On the other hand a strong XRD-reflex of the nano-clays at about $2\theta = 5.5^\circ$ and of cellulose at about $2\theta = 21^\circ$ indicates only weak interaction between the clay and the cellulose matrix in fibres spun from nanoclay modified dopes.

To assess the results, a composite fibre modified with 4% Cloisite Na^+ has been prepared and has been measured by means of X-ray wide angle scattering (Figure 4).

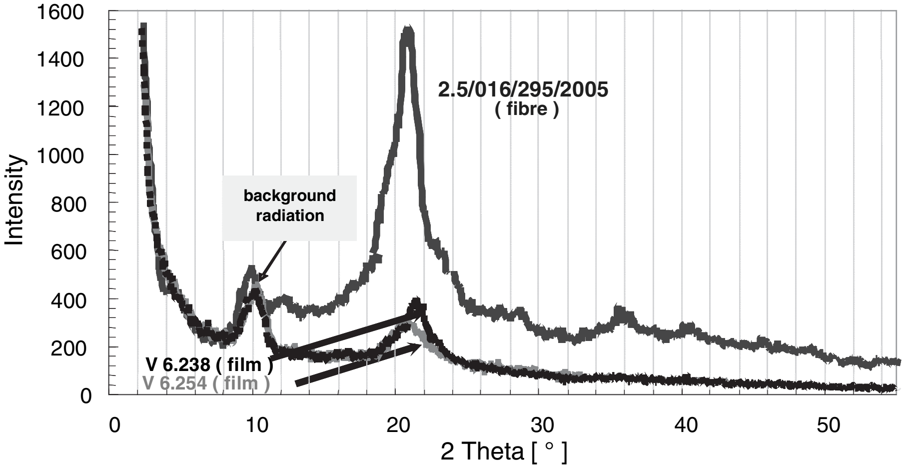


Figure 3.
Results of X-ray wide angle scattering of cellulose-nanocomposite films.

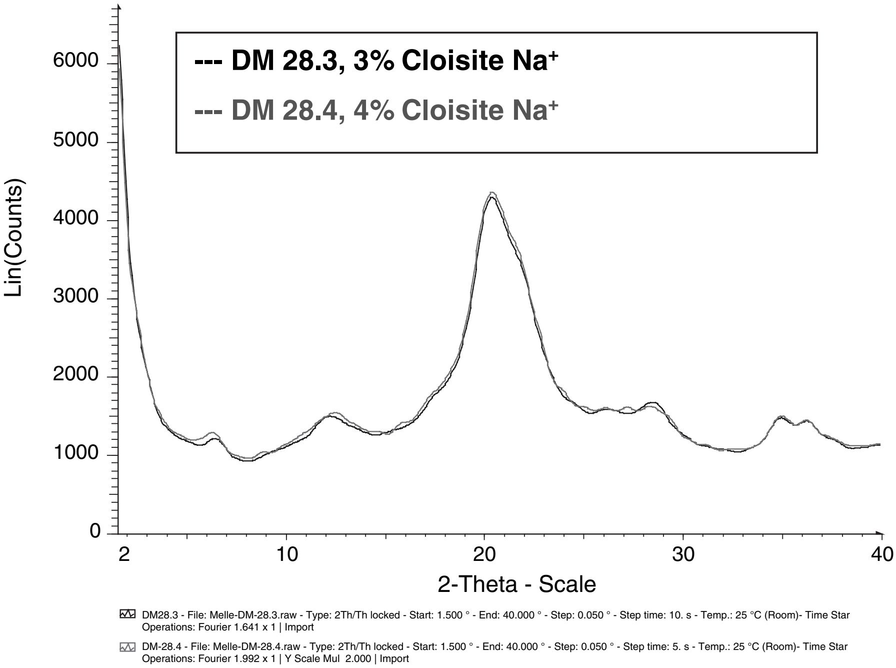


Figure 4.
X-ray wide angle scattering investigations of cellulose-nanocomposite fibres modified with Cloisite Na$^+$; experiments DM 28.3, 3% und DM 28.4, 4% Cloisite Na$^+$.

As respected, there are reflexes of the nanolayered silicates as well as of cellulose, when measuring the prepared and dried shaped bodies. Such a result indicates, that the strong shearing in the spinneret either induced a phase separation into cellulose and layered silicate or already exfoliated layered silicates are arranged in a preferred direction within the highly-viscous cellulose dopes. This finding should be investigated in more detail within the scope of further activities in order to deduct capabilities for the generation of shaped cellulosic bodies modified with nanoadditives for textile and technical applications.

The X-ray diffractograms displayed in Figure 5 have been recorded from samples having higher contents of different layered silicates. They show the reflexes in the small as well as wide angle range as expected for the components used. However, there is a remarkably different signal intensity at different Cloisite Na$^+$-contents, various clay additives as well as different dissolution procedures (V = common dissolution technique; DM = dynamic mixing technique). Composite fibres modified with 10% Cloisite Na$^+$ show the well known, but less intensive X-ray reflection, because a comparatively better intercalation has been achieved at low clay contents. This is additionally supported by a less pronounced shoulder in the small angle range. In contradiction, the distinctive signals of the cellulose point to the formation of separate phases.

The layered silicate type Bentone EA 163 shows a similar behaviour as already found for Cloisite Na$^+$. This might thoroughly be treated as a clear indication that the degree of dispersion and thus the extent of intercalation are significantly lower in these samples.

The result that a exfoliation can not be attained at contents exceeding 10% meets the results for samples loaded with 4% Cloisite Na$^+$. According to the current state of knowledge, the strongly inhibited flowability in nanocomposite solutions should be considered as the reason why higher clay contents cause such effects.

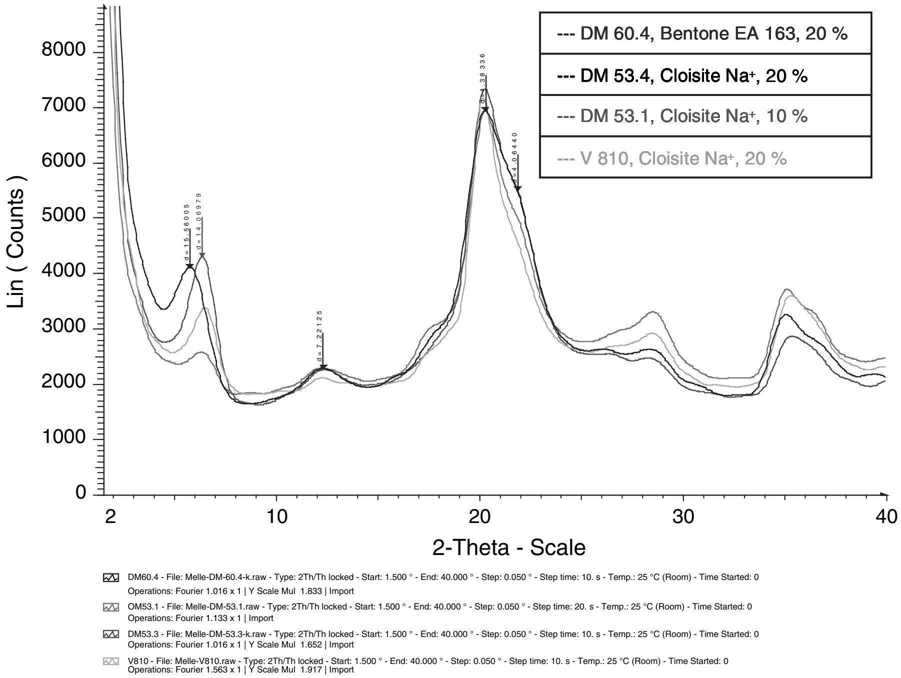


Figure 5.
Results of X-ray wide angle scattering investigations of cellulose-composite films/-fibres modified with different layered silicate additives; experiments DM 53.1, 10%, DM 53.4, 20% and V 810, 20% Cloisite Na^+ as well as DM 60.4, 20% Bentone EA 163.

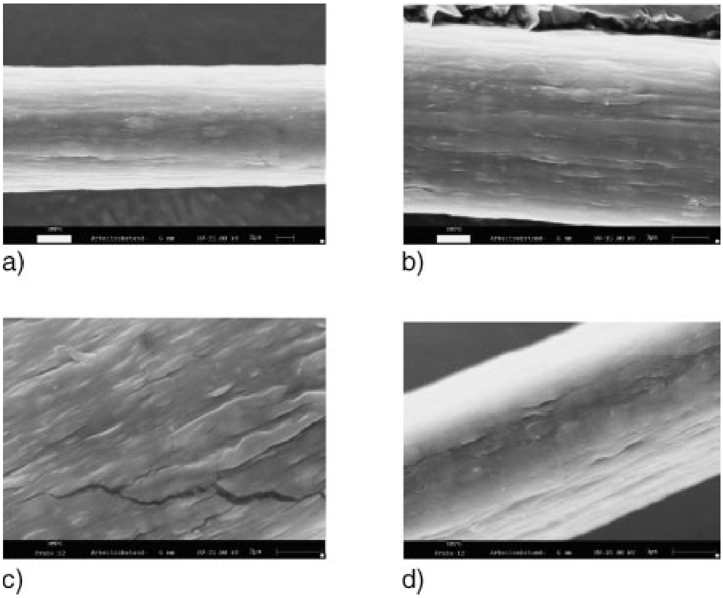
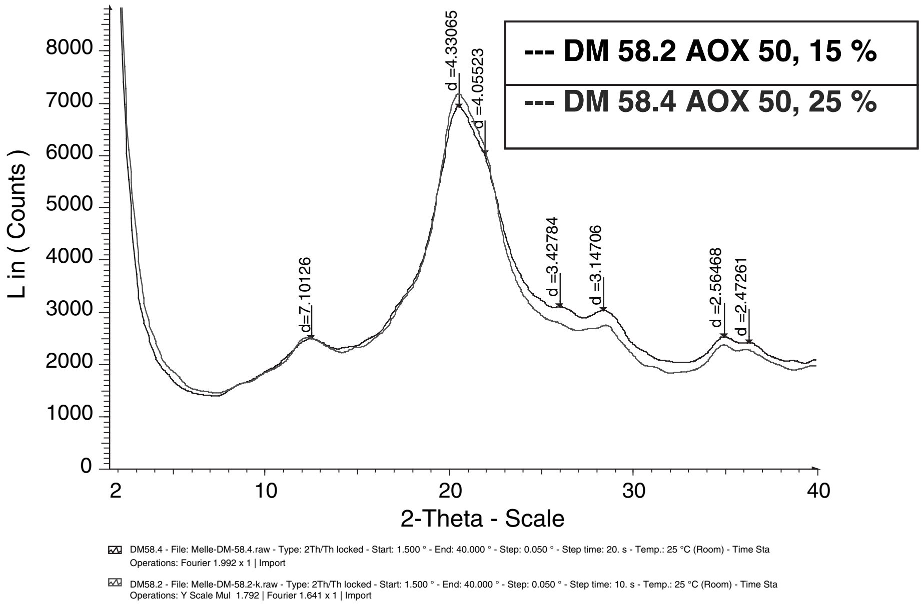


Figure 6.
REM-scans of cellulosic composite shaped bodies manufactured from different prepared dopes a) and b) DM 53.3 (dynamic mixing technique) as well as c) and d) V 810 (common dissolution technique).



```
DM58.4 - File: Melle-DM-58.4.raw - Type: 2Th/Th locked - Start: 1.500 ° - End: 40.000 ° - Step: 0.050 ° - Step time: 20. s - Temp.: 25 °C (Room) - Time Sta
Operations: Fourier 1.992 x 1 | Import
DM58.2 - File: Melle-DM-58.2-k.raw - Type: 2Th/Th locked - Start: 1.500 ° - End: 40.000 ° - Step: 0.050 ° - Step time: 10. s - Temp.: 25 °C (Room) - Time Sta
Operations: Y Scale Mul  1.792 | Fourier 1.641 x 1 | Import
```

Figure 7.
Results of the X-ray wide angle scattering of cellulose composite fibres modified with pyrogenic silicic acid AOX 50.

REM-images taken for the purpose of characterisation support such assumptions. Visible changes of structural surface features of fibres in combination with detected fibre breaks will lead to the assumption, that the flowability is seriously deteriorated during fibre forming process as shown in Figures 6a to 6d. The steady decrease of loop tenacity as well as an only moderate increase of the wet abrasion resistance of composite fibres when loaded with higher amounts of layered silicates would suggest such a conclusion.

Nanocomposite cellulose shaped bodies produced from particular, pyrogenic silicic acid do not show any signals in the small angle range as expected (see Figure 7).

The amorphous behaviour in terms of X-ray diffraction of the nanoadditives used is caused by its anisoptropic appearance. In fact, the corresponding X-ray reflections of the cellulose structure are visible in the wide angle range, but a little less pronounced compared to the reflections at incorporation of nanoclays. It can be concluded from this result, that the more hydrophobic phase of the silicic acid undergoes only a weak interaction with the more hydrophilic cellulose phase in the shaped composite body.

Conclusion

It was the objective of the activities to investigate the incorporation of nanoadditives with different aspect ratios into cellulose-NMMO-solutions in order to manufacture cellulose-nanocomposite shapes. The effect of the different particle types on the matrix structure after the incorporation was determined by means of X-ray wide angle scattering. Spherical nanoadditives do not influence the structural formation of cellulose shapes significantly. The applied nanoclays did not show an absolutely certain interaction with the cellulose matrix. Compared to film forming processes it was found in the case of fibre shaping that the nanoclays obviously undergo a preferred orientation as a result of special conditions of a dry-wet extrusion process. Based on REM-scans a high brittleness of the composite fibre surface could be detected when nanoclays have been applied.

Acknowledgements: The authors gratefully acknowledge the financial support of the project ‘‘Nano-modified Cellulose Fibres’’ from the Federal Ministry for Economy (BMWA-FKZ: 1141/03). We thank the industrial partner for co-financing and for the perfect technical and scientific steering of the research project.

[1] A. Rössler, G. Skillas, S. E. Pratsinis, *Chem. unserer Zeit* **2001**, *35*, 1.
[2] WO 2000009571 A1 (2000), Solutia Inc., USA, invs.: L. A. Goettler, S. S. Joardar, J. C. Middleton, B. A. Lysek; *Chem. Abstr.* **2000**, *132*, 152779.
[3] N. Ogata, S. Kawakage, T. Ogawa, T. Yanagawa, T. Ogihara, *Sen'i Gakkaishi* **1996**, *52*, 457.
[4] C. Zilg, F. Dietsche, B. Hoffmann, C. Dietrich, R. Mülhaupt, *Macromol. Symp.* **2001**, *169*, 65.
[5] M. Krook, M. Hedenqvist, 8 th European Polymers, Films, Laminations and Extrusion Coatings Conference, Barcelona, Spain, May 28-30, **2001**, 171.
[6] L. A. White, N. R. Bertoniere, *Polym. Prepr.* **2002**, *43*, 1279.
[7] De Vlieger, Fischer, Boersma, Berger, Jeromin, Opitz, 3 rd Intern. Symposium Materials based on natural resources, Erfurt, September **2001**.
[8] B. Kosan, C. Michels, *Chemical Fibres Int.* **1999**, *49*, 50.
[9] K.-P. Mieck, H. Langner, A. Nechwatal, *Lenzinger Ber.* **1994**, *74*, 61.