**DYNAMIC MECHANICAL BEHAVIOR OF CELLULOSICS AND CELLULOSE COMPOSITES**

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**Introduction**

The goal of our research in dynamic mechanical studies (DMTA-studies) is twofold: On the one side to provide data for application of cellulosics with regard to compete with synthetic polymers as well as to deduce general ideas for the prediction of tailored properties as glass transition temperature, stiffness of the materials etc. (1-4). On the other side we aim for simple processing procedures of advanced thermoplastic materials by easy accessible methods as the extrusion of composites with cellulose, hemicellulose, cellulose derivatives and a thermoplastic matrix as polypropylene or other thermoplastic biodegradable materials avoiding pretreatment of the filler materials.

We started the investigations in processing composites by extrusion of glass fibers with polypropylene as matrix (5, 6) and continued in 1994 by using cellulose in form of regenerated fibers and of microcrystalline particles replacing the glass fibers and obtained comparable results as with application of glass fibers in DMTA-studies. A paper concerning these new findings submitted in 1995 was turned down in 1998 with unacceptable statements by the referee. Continuing this research we found that hemicellulose can be used as an suitable filler as well and published our preliminary findings in 1998 (7). Our original paper was resubmitted to another journal and published in 2000 (8). On the other side a research proposal dealing with this subject was not supported due to unfavorable statements of a researcher who recently himself has reported results in this field and stressed the importance of his research in application.

In this note we want to report some highlights of our research in cellulosics and cellulose composites with polypropylene as matrix materials mainly by DMTA-studies. Thermal investigations (DSC) as well as X-ray diffraction and microscopic studies are added in support of the findings.

**Experimental**

**Materials: Composites.** Two types of cellulose fibers were incorporated into a matrix of polypropylene for the study of cellulose composites: Chopped strands of spun cellulose fibers (CFS; Cordenka RT; ρ = 1.4 g/cm³; length 6-8 mm) supplied by Akzo Faser AG (Obernburg) and wood cellulose microfibers (CFM; Arbocel BE 600; ρ = 1.5 g/cm³; length × thickness: 40 × 20 μm²) from leaf-wood containing >98% cellulose, supplied by Rettenmaier GmbH (Ellwangen). Xylan fillers (XL, not characterized) from birch wood were obtained from Dr. Puls (Bundesforschungsanstalt für Forst- und Holzwirtschaft, Hamburg). The data for the glass fibers and polyester fibers are given elsewhere (2) and only introduced for reasons of comparison. Isotactic polypropylene (PP; P 5000; MI = 1.5 g/min; ρ = 0.902 g/cm³; Mₗₙ = 263 x 10⁶ g/mol) supplied from the Hüls AG served as polymer matrix for the preparation of the composites. If not otherwise stated, maleic anhydride modified PP-homopolymer (MAPP; Polybond; 1.3 wt% maleic anhydride) was added as compatibilizing agent and was obtained from Vestolen GmbH (Gelsenkirchen).

Each fiber type was mixed and homogenized with the polymer matrix by a Haake twin-screw extruder TW100 model (length × diameter: 75 cm × 24 cm) and a small amount (ca. 7 wt%) of the coupling agent MAPP added. The temperatures of the four zones of the extruder were 180, 185, 190 and 190°C, respectively. The screw speed was adjusted to 40 rpm. The sample preparation for the DMTA measurements included hot pressing of the extruded granules in a hydraulic electrically heated press at 190°C for 10 min with a force of 50 kN, and after pressing, the samples (about 0.3 mm in thickness) were cooled (20°C/min) to room temperature under pressure.

**Instrumentation and sample preparation: Composites.** A DSC-7 (Perkin Elmer) served for calorimetric studies. The samples (each ca. 10 mg) were heated to 180°C and maintained at this temperature for 5 min. Then they were cooled from 180°C to 25°C at a rate of 10°C/min (cooling cycle), held for 5 min at this temperature and then heated again to 180°C at a rate of 10°C/min (heating cycle). Transition temperatures and enthalpies were determined from the thermograms.

The morphology of the composites was investigated by optical micrographs of thin specimens (~50 μm) using a BH-2 Olympus polarizing microscope. The processing procedure for the films used was the same as stated above. Fractured surfaces of composite specimens were investigated by a Hitachi S-800 scanning electron microscope, operated at 25 kV.

A dynamic mechanical thermoanalyzer (DMTA), Eplexor of Gabo Qualimeter (Ahlden, Germany) was employed for stress-strain oscillation measurements at a frequency of 10 Hz. The samples (30 x 5 mm² area and 0.3 mm thickness) were cooled to ca. -150°C and heated under a strain-controlled sinusoidal tensile loading to 170°C with a heating rate of 2°C/min. The static and dynamic strains amount to 0.15% and ± 0.05%, respectively. The viscoelastic properties, i.e. the complex dynamic modulus (E') and the mechanical loss factor (damping) tanδ = E''/E' (E'' and E' loss and storage modulus, respectively), were recorded as a function of temperature.

**Cellulosics.** The synthesis of the cellulose derivatives used in our investigations is reported in (3). The specimens for DMTA investigations of these pure cellulosics have been prepared by dissolving the materials in a suitable solvent which was evaporated and the solid films obtained (0.1 mm in thickness) cut to 30 x 4-6 mm² area. The films have been dried in vacuum at 80°C and stored for 24 h before used for measurements.

**Results and Discussion**

**Composites.** Thermoplastic polymer composites with an isotactic polypropylene matrix and cellulose fibers up to 50 wt% as well as xylan filler as a major component of hemicellulose have been produced and investigated. The melting and crystallization behavior is depicted in figure 1 as studied by DSC of neat PP and samples of PP + 30 wt% fiber (XL: xylan filler, CFM: wood cellulose microfibers, CFS: short strands of spun cellulose fibers). The melting of all these isotropic samples occurs at the same temperature which is the melting point (peak of the curves) of isotactic polypropylene. However, the crystallization temperature clearly increases for the filled samples up to 8°C as compared to neat PP which signifies that the filler acts as an efficient nucleating agent. Optical micrographs show a trans-

![Figure 1. DSC thermograms of neat PP and samples of PP+30 wt% fibers (XL: xylan filler, CFM: wood cellulose microfibers, CFS: spun cellulose fibers).](image-url)
Figure 2. DMTA spectra for neat PP and PP + 30 wt% fiber content (XL: xylan filler, CFM: wood cellulose microfibers, CFS: spun cellulose fibers).

crystalline morphology along the cellulose and xylan fibrils, and scanning electron micrographs of fractured surfaces suggest good adhesion of the filler with the matrix.

The dynamic mechanical spectra (storage modulus E' and damping factor tan δ as a function of temperature) are represented in figure 2 for the same specimens, neat PP and PP + 30 wt% filler, as shown in figure 1. Relaxation peaks are present for the tan δ curves in the vicinity of -80 °C (γ), 8 °C (β) and 100 °C (α). The dominant β-peak represents the glass-rubber transition of the amorphous portion in PP, and the peak in tan δ is assigned to the glass transition temperature T_g. At this transition a significant decrease of the storage modulus E' is initiated which drops even more at the melting range of PP.

The DMTA spectra for the composites show an increase of the storage modulus E' and a decrease in tan δ as compared to neat PP with only minor changes in the shape of the curves. These facts signify an increase of stiffness of the materials which is highest for PP/CFS. A comparison of E' at 20 °C is provided in table 1 and some values for glass fiber and polyester fiber composites added. It is remarkable that the E' modulus for PP + 50 wt% CFM without compatibilizer MAPP lies only 10% below the value with MAPP added. It seems that the cellulose with its sheet-like conformation exhibits in the central part of the sheet a large hydrophobic area which leads to good interaction with the hydrophobic polypropylene.

Table 1. Storage Modulus E’ of Isotropic Samples

<table>
<thead>
<tr>
<th>materials</th>
<th>E’ [MPa] (at 20° C)</th>
</tr>
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<tbody>
<tr>
<td>polypropylene-homopolymer (PP)</td>
<td>1560</td>
</tr>
<tr>
<td>PP + 20% glass fibers (GF)</td>
<td>2700</td>
</tr>
<tr>
<td>PP + 20% polyester fibers (PETF)</td>
<td>1840</td>
</tr>
<tr>
<td>PP + 20% cellulose fibers (CFS)</td>
<td>2170</td>
</tr>
<tr>
<td>PP + 30% cellulose fibers (CFS)</td>
<td>2725</td>
</tr>
<tr>
<td>PP + 30% cellulose microcrystals (CFM)</td>
<td>2090</td>
</tr>
<tr>
<td>PP + 50% CFM</td>
<td>2865</td>
</tr>
<tr>
<td>PP + 50% CFM without MAPP</td>
<td>2585</td>
</tr>
</tbody>
</table>

Figure 3. DMTA spectra of PP-CFM composites with different fiber content and 7 wt% MAPP as compatibilizer. Marked curve without MAPP.

The last figure in this series of experiments deals with effects observed on initially drawn specimens that is the anisotropic behavior of the composites. X-ray diffraction experiments show that the crystallites of neat polypropylene and PP composites are uniaxially oriented upon drawing and exhibit the α form of polypropylene. The melting temperature of PP as matrix materials of the composites is considerably increased with the draw ratio as detected by DSC experiments. An increase of the melting temperature of PP can also be deduced from the DMTA plots of drawn PP composites as depicted in figure 4. The steep decrease of the storage modulus curves does not join at a single melting
temperature as for the isotropic samples in figure 3, rather ends at different temperatures which represents the melting of the specimen. An increase of the melting point as compared to the equilibrium melting temperature of polypropylene indicates a melting under tension which is caused by a good adhesion between the matrix and the oriented fibers (9, 10).

From an application point of view, the increase of the $E'$ modulus with drawing ratio is remarkable for neat PP as well as for the composites. However, the $E'$ modulus for neat PP shows a relatively large drop at the glass transition temperature. This drop is quite moderate for the composites. A shift of the $\alpha$ relaxation occurs for highly drawn samples leading to stiff materials up to high temperatures (cf. table 2).

**Table 3. Storage Modulus $E'$ of Cellulose Derivatives (Original DP 200) at 25$^\circ$C for Low and High Acylated Compounds and for the Peracetylated High Acylated Compounds**

<table>
<thead>
<tr>
<th>C200-</th>
<th>$E'_{25^\circ C}$ (low)</th>
<th>$E'_{25^\circ C}$ (high)</th>
<th>$E'_{25^\circ C}$ (Ac)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pro</td>
<td>1870</td>
<td>1880</td>
<td>2080</td>
</tr>
<tr>
<td>But</td>
<td>1800</td>
<td>930</td>
<td>1320</td>
</tr>
<tr>
<td>Hep</td>
<td>1840</td>
<td>230</td>
<td>3080</td>
</tr>
<tr>
<td>Oct</td>
<td>1090</td>
<td>180</td>
<td>120</td>
</tr>
<tr>
<td>Lau</td>
<td>50</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>Pal</td>
<td>70</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 represents the storage modulus $E'$ of a homologous series of low substituted cellulose esters with 3, 4, 7, 8 and 12 C atoms in the substituent and exhibits similar behavior of the propionate and butyrate on the one side as well as heptanoate and octanoate on the other. The values of $E'$ of the derivatives with alkyl side groups $C_3$ and $C_4$ decrease from 6500 MPa to 1300 MPa, those with $C_7$ and $C_8$ from 6000 to 500 MPa in the temperature range from $-150^\circ$C to $+150^\circ$C. The storage modulus of the laurate behaves differently. Above $260^\circ$C the $E'$ modulus of all compounds increases after a short rubber plateau which may be originated by structural changes due to possible hydrogen bonding.

The highly acylated derivatives in figure 6 show a different behavior. The $E'$ modulus is lower at respective temperatures except for the propionate (cf. also table 3). The glass transition temperatures are considerably shifted of about 50 to 100$^\circ$C to lower values. The rubber plateau for the propionate, butyrate and heptanoate is quite extended and cannot be detected for the other derivatives.
Figure 7. DMTA spectra of highly substituted cellulose-propionate, -butyrate, -heptanoate, -octanoate, -laurate and palmitate (cf. figure 6) with the remaining OH acetylated.

The DMTA spectra of the peracetylated highly acylated cellulose derivatives in figure 7 resemble to some extent the spectra of figure 6 where some OH groups are still present. However, the glass transition temperatures are 10 to 30°C lower, the rubber plateau is almost non existent and the E' modulus drops for all compounds to non measurable values in the melt. Melt processing should be possible due to low melt viscosity for these derivatives in contrast to the non acetylated ones for which E' still has a finite much too high value.

Investigations with further mixed cellulose derivatives with phenlcarbamate, benzoate and tosylate substituents lead to the conclusion that the E* modulus, the glass transition temperature as well as a suitable melt viscosity can be tailored to specific needs.

The next section deals with rules and predictions of desired properties.

Figure 8. Glass transition temperatures T_g of a large number of mixed cellulose-(2.5)-acetate derivatives and acylates, carbanilates, benzoates as well as acylate-acetates from ref. (12) as a function of the solubility parameter δ_L.

Figure 9. Storage modulus E' at 25°C of a large number of mixed cellulose-(2.5)-acetate derivatives and acylates, carbanilates, benzoates as a function of the solubility parameter δ_L.

Coleman et al. (11) refined the method for estimating interaction parameters between different polymers by introducing a solubility parameter δ_L:

\[ \delta_L = \sum \left( \frac{F_i}{\Sigma V_m} \right) \]  \[ [1] \]

with V_m the group molar volume and F_i the group molar attraction constant of the molecular group i, e.g. -CH_2- or -COO-. The needed values for F_i and V_m are collected in (11). Edgar et al. (12) found for cellulose acetate as well as for various cellulose acetate derivatives with an overall degree of substitution of 2.7 and the second ester substituent from C_3 to C_7 a linear relationship with δ_L for the glass transition temperature, viscosity and flexural modulus. Extending the data base and introducing a large number of cellulose-(2.5)-acetate derivatives, cellulose acylates, cellulose phenyl-carbamates and cellulose benzoates (3) as well as the published cellulose acetate-acetate data (12), the plot of figure 8 for the glass transition T_g and of figure 9 for the storage modulus E' at 25°C with a few lesser derivatives was obtained.

The calculated solubility parameter monotonically decreases with increasing DS and alkyl substituent length. Therefore, a perfect linear relationship of T_g with δ_L is not expected and not provided in figure 8. Nevertheless, the straight line drawn in figure 8 is sufficient to obtain acceptable T_g for arbitrary derivatives of which the solubility parameter can easily be calculated. It should also be noted that the derivatives with longer side groups and DS = 1 exhibit significant deviations due to a two phase behavior and differences in stiffness of the main chains and side groups as well as extensive hydrogen bonding interactions.

The storage modulus E' at room temperature exhibits a two range behavior in figure 9 which can be represented by two straight lines. Given a known solubility parameter, the storage modulus can be estimated.

A better functional relationship between macroscopic properties as T_g (cf. figure 8) and microscopic structures may be obtained as a pure mathematical correlation function between a property, e.g. T_g, and some chosen variables established on experimental grounds. Such a correlation was established for T_g determined by DMTA or DSC, respectively, for cellulose acetate-acylates and later for further derivatives. Equation [2] represents T_g in °C as a function of DS and the number of C atoms in the acylate group n; \( r_i \) (i=1-6) adjustable coefficients for all acylate-acylates and obtained by a least squares fit of experimental data.

\[ T_g = 10^{\delta_L} \]  \[ [2] \]
Figure 10. Glass transition temperatures \( T_g \) determined by DMTA investigations and by calculation with equation [2] (full lines) for fully substituted cellulose acetate-acylates as a function of substituent length (DP: 110, 230, 200 as marked).

**Table 4. Coefficient \( r_i \) (in °C) for the Calculation of the Glass Transition Temperatures \( T_g \) of All Cellulose Acetate-Acylates According to Equation [2] (DMTA Investigations, Heating Rate 1K/min, Frequency 10 Hz)**

<table>
<thead>
<tr>
<th></th>
<th>( r_1 )</th>
<th>( r_2 )</th>
<th>( r_3 )</th>
<th>( r_4 )</th>
<th>( r_5 )</th>
<th>( r_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>198.3</td>
<td>0.6153</td>
<td>-5.437</td>
<td>-6.734</td>
<td>0.2355</td>
<td>0.2868</td>
</tr>
</tbody>
</table>

\[ T_g = r_1 + r_2 \text{DS} + (r_3 + r_4 \text{DS}) n + (r_5 + r_6 \text{DS}) n^2 \] [2]

Figure 10 represents a plot for \( T_g \) with experimental data and the calculated curves for fully substituted cellulose acetate-acylates as a function of DS and n with one set of fit parameters collected in table 4. The agreement is satisfactory between the experimental data and the predicted ones. It should be noted that the established correlation is independent of the sequence of acetylation and acylation and of the distribution of the substituents along the cellulose chain. The correlation function only depends on chemical constitution of the substituent and the degree of substitution DS as well as on the experimental conditions under which the data are collected (heating rate, frequency in DMTA investigations or if the experiments are carried out by DSC).

Conclusions
A relationship for cellulosics was established between the solubility parameter \( \delta_L \) representing the molecular structure of the cellulose derivatives and macroscopic quantities as \( \delta_L \) and \( T_g \). This correlation offers the possibility to estimate these quantities from the chemical constitution of the cellulose derivatives but the accuracy of these data is limited. Establishing a correlation function between microscopic structural parameters and macroscopic properties by analysis of experimental data is a better route to predict certain properties of cellulosics. More systematic investigations are needed to follow this route.

It was demonstrated that advanced thermoplastic composite materials can be produced by simple extrusion of two components, a filler, e.g. non surface treated cellulose, cellulose derivatives, and a thermoplastic polymer as polypropylene, cellulosics etc.

**Acknowledgement.** Figures 1– 4 have been taken from ref. 2, figures 5-10 from ref. 3.

**References**