Rheology of Thermoplastic Cellulose-Esters

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ABSTRACT

We study rheological properties of cellulose modified by linking of aliphatic acids onto the cellulose backbone in media of ionic liquids. Viscoelastic properties of melt were studied in rotational flow and oscillation modes. As a reference material of flow properties we use commercially available low density polyethylene (LDPE) of M_w = 120,000 g/mol (by Borealis polymers).

INTRODUCTION

The problem of cellulose modification to make it applicable for rheological measurements is of a great interest as native cellulose does not allow us to study it in molten state. In opposite modified cellulose exhibit thermoplastic properties even at low rate of OH group substitution. Thus acylation of cellulose with fatty acids is a promising way to achieve "thermoplastic cellulose". Moreover derivatives with long substituents show plasticization ability even without adding special plasticizing agents[1]. This will help to elucidate the perspectives of developing cellulose-based plastics which is urgent in trend of renewable resources implementation in polymer materials production.

MATERIALS

A series of cellulose esters (CEs): Cellulose-Stearate (CS) and Cellulose-Laurate (CL) with low degrees of substitution (DS ≤ 0.4) have been obtained by linking aliphatic acid chlorides (lauroyl chloride, stearoyl chloride) on to cellulose backbone in media of ionic liquids (1-butyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium acetate)[2]. Molecular mass of commercial available cellulose (by Avilon Ltd.), M_w = 100,000 g/mol was estimated by viscometry in ethylenediamine-copper(II) (CuEn) using Mark-Houwink equation[3]. All these materials were characterized by Fourier-Transform-Infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR ^{1}H, ^{13}C) spectroscopies, differential scanning calorimetry (DSC) and saponification method for estimation of DS.

MEASUREMENT

Rheological characteristics studied at Anton Paar Physica MCR501 rheometer with cone-plate measuring geometry. All measurements were carried out in nitrogen atmosphere at temperature 190 °C. We use gap = 0.051 mm for Cellulose-Stearate and gap = 0.12 mm for Cellulose-Laurate. Temperature dependence of viscosity was studied in range of 190 − 80 °C. All curves were compared to LDPE.

Viscosity curves were obtained in range of $\dot{\gamma}$ = 0.001-100 1/s. Oscillation tests were performed at ω = 0.01 ÷ 1000 1/s with strain

γ = 5% determined via linear viscosity region in amplitude sweep test.

RESULTS AND DISCUSSION

Raw data of measured viscosity vs. shear rate is represented in Figure 1. As could be seen all samples show similar behaviour. In non-Newtonian flow region CL shows viscosity similar to LDPE but CS unexpectedly goes much lower. Also Newtonian flow range for CL is one decade shorter ($\dot{\gamma}_0 \approx 0.01$ 1/s) than for CS and LDPE ($\dot{\gamma}_0 \approx 0.1$ 1/s). This could be an evidence of strong influence of rigid cellulose chains onto viscosity of CL than CS. Taking into account that molecular weights of both derivatives is quite close: laurate branches has molecular weight M_w = 183 g/mol and stearate branches M_w = 267 g/mol, both they are linked to cellulose with the same low degree of substitution. The difference in branches M_w could not affect viscosity so much, so we assume that CL stays in viscoelastic state even at very low shear rate.
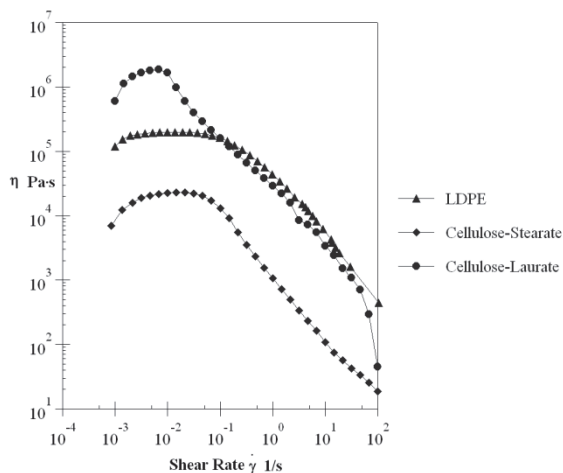

Figure 1. Viscosity curves.

This suggestion could be approved when testing viscosity by amplitude sweep in oscillation mode at frequency of 1 Hz (Figure 2.).

From this plot we could see that storage modulus G' for both derivatives is much bigger than loss modulus G". This could be

when too much elasticity comes from cellulose backbone; in opposite LDPE shows very different behaviour – it is more viscotic and less elastic.
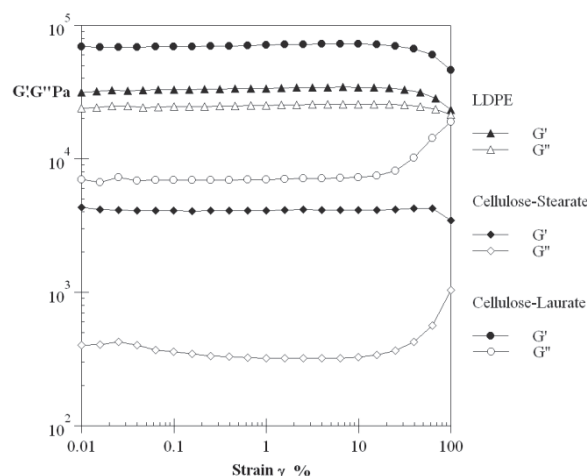

Figure 2. Dependence of storage G' and loss G" moduli on strain.

We partly diminish the amount of hydrogen bonds between hydroxyl groups in cellulose by substitution them with fatty acid branches, this certainly improve cellulose flexibility so we obtain possibility to melt modified cellulose before thermal degradation starts. On the other hand the lengths of branches affects inter- and intramolecular interactions of derivatives, their structure and the way of chain packaging[4].

But it is still unclear why dynamic viscosity of CS is much lower than those of LDPE and CL. The difference in viscosities is ten times and this could not be explained by difference in packaging or branch length of different CEs. Oscillation test with amplitude ramp at frequency of 1 Hz gives us the similar results for complex viscosity in linear viscosity range (see Figure 3.).

Moreover, linear viscosity range for CS is wider than for CL and LDPE. This could correlate with viscosity of CL and ideas that enhanced elasticity due to rigid cellulosic backbone. As well LDPE behave in flow much viscotic and it has let's say "simpler" structure, so we could expect Newtonian

flow in wider range of strain than for cellulose derivatives, but did not get it experimentally. The explanation could be that soft and flexible fatty acid branches fill in the space between cellulose backbones and play a role of plasticizing agent that prevents significant changes in melt structure under applied shear. Thus we do not see layering or strong deformation and orientation of CEs molecules which could deflect viscosity curve at low enough values of strain.
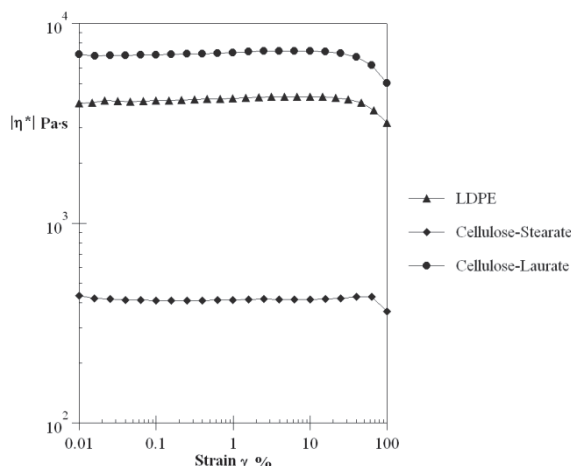

Figure 3. Dependence of complex viscosity on strain.

Figure 4. Dependence of complex viscosity on angular frequency.

Figure 5. Dependence of storage G' and loss G" moduli on angular frequency.

On Figure 4. complex viscosities are depicted in dependence on angular frequency. Viscoelastic behaviour of all systems remains the same in all range of frequencies up to 1000 rad/s. Elastic response in cellulosic materials remains dominating, thus the slope of both curves for CEs is bigger than that of LDPE – viscous response grows much faster with decrees of oscillation frequency.

We found interesting to take a look at oscillation frequency dependence of storage and loss moduli (see Figure 5.). At 190°C LDPE whole frequency range cover region of transition flow but for CL and CS we see only rubbery region with no chance to get cross points neither in transition nor in higher transition region.
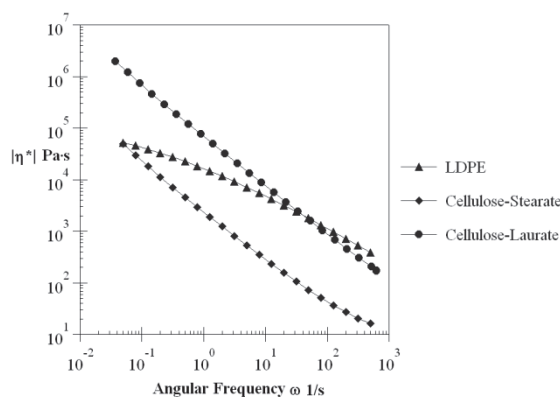
CONCLUSIONS

In this study we obtain new information about viscoelastic properties of cellulose esters and the influence of cellulose structure changes on its melt properties. At first cellulose could be transferred into thermoplastic state with viscosity low enough to be processed at conditions similar to other well-known thermoplastic polymers. Second low degree of substitution keeps cellulose backbones too rigid what makes CEs melt too viscoelastic and not suitable for industrial usage.

We could conclude that by changing the degree of substitution we can widely influence the elastic properties of this novel material. On the other hand changing the length of fatty acid branches we easily can

improve compatibility of CEs with polyolefin. Thus application of CEs as thermoplastic material itself is not convinced at fist experimental take but it could operate as strength enhancing "fiberlike" agent or as plasticiser and compatibilizer in polymer mixtures containing cellulose or wood fibres. Also relatively easy and inexpensive modification makes possible to obtain additives with wide variable properties based on renewable and ecologically friendly material.

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