

Cellulose Stearate in Melt and Plant Oil Suspension

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ABSTRACT

The flow behavior of cellulose stearate (CS) has been studied in mixtures with rapeseed oil. Cellulose stearate has limited solubility, mostly in high volatile solvents like chloroform and toluene. We studied suspensions of CS in plant oil: the influence of temperature and shear rate onto viscous properties of double phase systems. The rheological properties of suspensions are compared with melt properties. As far as CS has melting temperature close to 40-45 °C this allows us to study melts and suspensions at the same conditions. The thermal stability of cellulose fatty ester derivatives with long substituents is rather high¹ one could guess the perspectives of CS applications as compatibilizer for pure cellulose and wood pulp to widely used olefin polymers like polyethylene and polypropylene.

INTRODUCTION

Cellulose stearate is very promising thermoplastic material and showed good processability by extrusion and pressing but it is difficult to develop processing techniques for producing such products as films and they appear very brittle. At the same time it is rather difficult to study its melt properties: viscosity of CS drops very fast with increasing of applied external force (see figure 1). Storage modulus G' remains independent up to rather high angular

frequencies but loss modulus G'' changes dramatically (see figure 2).

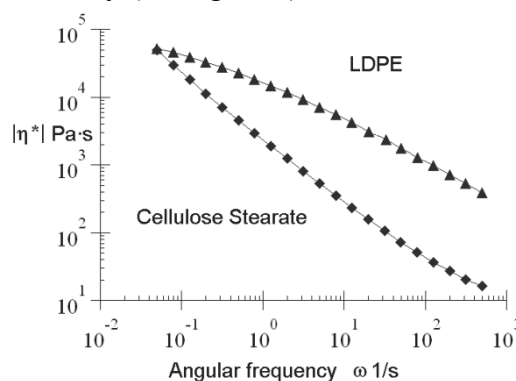


Figure 1. Complex viscosity dependence.

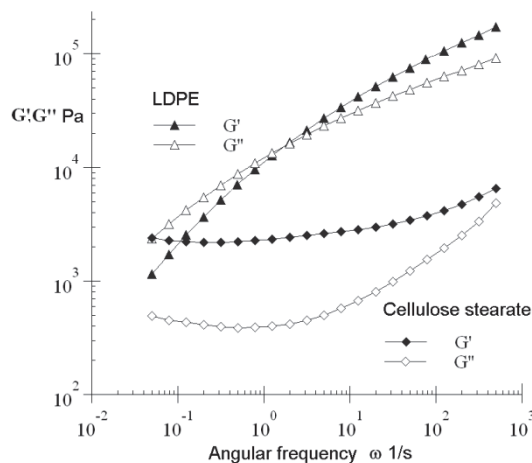


Figure 2. Storage G' and loss G'' moduli dependence.

Taking into account this phenomenon we guess that most of CS mobility under shear mostly coming from freely deformable

stearate branches motion but cellulose backbones remain rigid and their motion is hindered.

The calorimetric studies show only one melting peak so we see only one phase transition near 40°C and it might correspond to well pronounced melting of stearate branches but nothing can be told about cellulose backbone. Similar ideas were concluded by Vaca-Garcia et al.².

So we could expect that in studied temperatures range cellulose backbone keep its conformation unchanged, and the melt of CS has structure of rigid cellulose chains slithering in layers of soft stearate branches (surface of rigid macromolecules is greased by chemically bonded soft chains).

To prove this idea we make blends of CS in rapeseed oil, which has chemical structure very close to the stearate branches, thus we could study CS macromolecules behavior in flow started from “greased” state to state in which they will be separated by thick layer of fatty acid. CS is not soluble in oil, thus it keep microstructural properties of CS remains the same and material will be dispersed in oil.

MATERIALS

A series of cellulose esters cellulose stearate with low degrees of substitution (DS \approx 0.5) have been obtained by linking stearyl chloride on to cellulose in media of ionic liquid (1-butyl-3-methyl imidazolium chloride)³. The results of synthesis were proved by Fourier-Transform-Infrared spectroscopy (FTIR) spectroscopy, purification quality controlled by differential scanning calorimetry (DSC) and DS determined by saponification and acid-base titration method.

Mixtures in oil swelled for few of hours, mixed manually, than suspensions were blended in Thermo Scientific MiniCTV compounder at 150 rpm for ten minutes.

MEASUREMENT

Rheology studied at Anton Paar Physica MCR501 rheometer with plate-plate measuring geometry with gap = 1 mm. Measurements were held in nitrogen atmosphere at temperature 80 °C. Temperature dependence of viscosity was studied in range of 40 – 90 °C.

Flow curves were obtained for shear rate $\dot{\gamma}$ in range of 0.001-100 1/s. Oscillation tests were performed at $\omega = 0.1 \div 100$ 1/s with strain $\gamma = 0.1\%$ determined via linear viscosity region in amplitude sweep test.

Pure CS was pressed into discs 26 mm in diameter at 80°C and pressure 50 bar, oil suspensions were not capable for film pressing, and thus we started from 50% CS content in oil mixture, which was soft enough to uniformly cover surface under measuring plate.

RESULTS AND DISCUSSION

The linear viscosity range (LVR) and the shape of the amplitude sweep curves have similar shape. This could be explained as particles involved in motion in melt and in oil mixture has similar structure and mechanical properties.

The unexpected thing is that LVR is very short such behaviour is usual for systems filled with hard and rigid fillers. In our case this could happen if CS particles separated by layer of oil which disrupts at very low deformation.

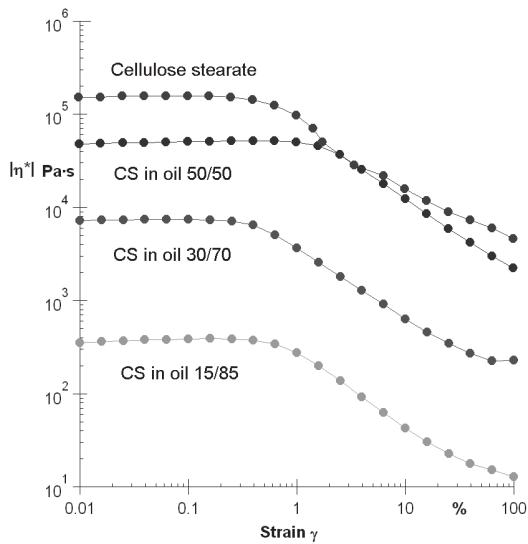


Figure 3. Dependence of complex viscosity on strain.

Similar results can be seen from flow curves: in all range of shear rates all samples show strong pseudoplastic (shear thinning) behaviour. One could guess that an oil layer disrupts easily and all further flow motion corresponds to rotation and deformation of CS particles.

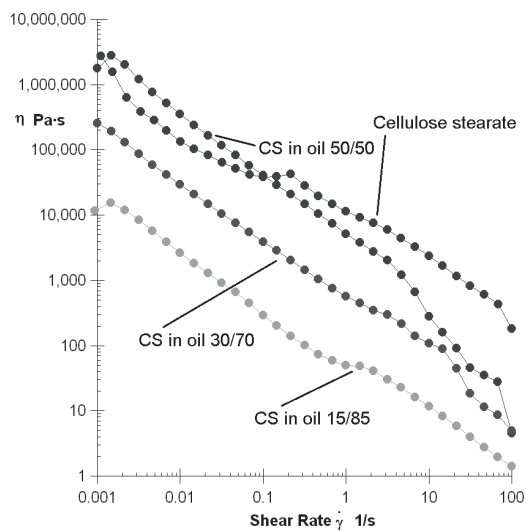


Figure 4. Dependence of dynamic viscosity on shear rate.

On figure 5 the dynamic moduli plotted the slopes of all curves remains the same telling us that in studied range of oscillation frequencies no significant deformations of particles could be seen.

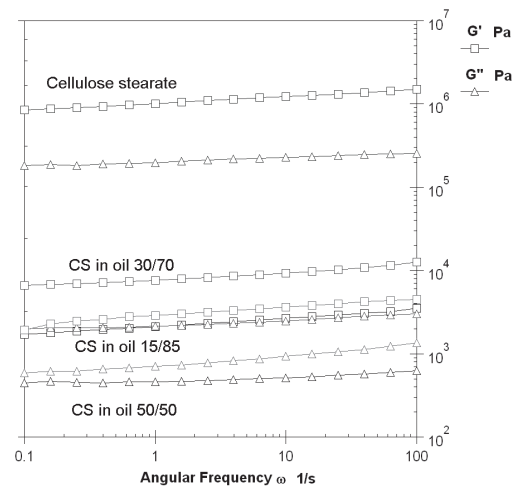


Figure 5. Dependence of dynamic moduli on angular frequency.

We also studied temperature dependence of viscosity, as it can be seen from figure 6 viscosities of samples is totally dominated by CS. When temperature goes close to melting point in pure CS and 50/50 mixture CS particles became so hard that flow failure happens and the contact between sample and measuring plates lost, so we observe slippage of the measuring system.

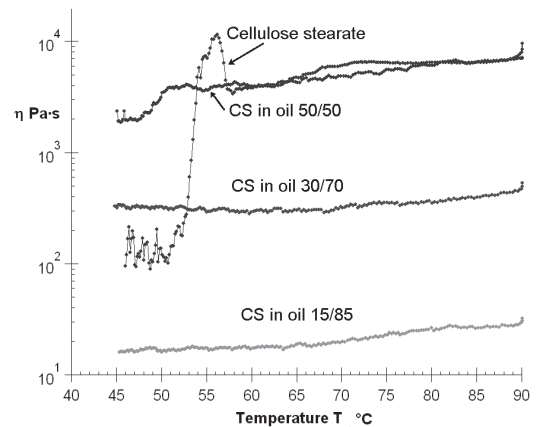


Figure 6. Temperature dependence of dynamic viscosity.

As could be seen from plot dynamic viscosity slowly grows with temperature increase such behaviour is not usual for polymers and suspensions. We could guess that this phenomenon caused by thermal expansion of CS particles but not disentanglement and unfolding of cellulosic backbone. This could happen if there is still

some cellulose crystals remain in material after chemical modification.

So we could assume that solution of cellulose in ionic liquid cannot destruct 100% of cellulose crystals and further acylation links some stearate branches to cellulose chains but also some onto the surface of crystalline phase remains. Thus we obtain particles with hard crystalline core and rigid unfolded cellulose tails all together covered by soft stearate branches.

CONCLUSIONS

Taking into consideration obtained rheological data for cellulose stearate and cellulose stearate suspension in rapeseed oil we could suppose realistic model of CS macromolecules and describe the morphology of CS particles. Our guess needs further investigation and validation by other experimental methods. Nevertheless it seems to be important that basic statements for structural properties of such complicated systems could be achieved by relatively simple and fast rheological measurements.

REFERENCES

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