Smart Surfaces in Biobased Materials

By

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(Abstract)

The self-assembly blends of cellulose propionate (CP) and fluorine (F)-containing cellulose derivatives was examined on a model system of solvent cast films. The F-containing derivatives were either high molecular weight statistical cellulose esters with a number of F-containing substituent evenly distributed along the backbone (F-esters), or F-terminated CP-segments with exactly one F-containing endgroup. The F-esters were synthesized in a homogeneous phase and identified by ^{19}F-NMR. Thermal analysis showed improved thermal stability of the F-esters when compared to F-free derivatives.

1-monohydroxy functionalized CP-segments were synthesized by HBr depolymerization using either a commercially available CP with residual OH-groups or a perpropionylated CP (CTP). The hydrolysis using the commercial CP yielded only segments of a minimum DP of 50 and the Mark-Houwink constant declined from 1 to 0.6. The results indicate that in the presence of free hydroxyls branches are formed by transglycosidation. The hydrolysis from perpropionylated CP resulted in segments with a minimum DP of 7, which is in accordance to previous studies.

F-terminated CP segments were synthesized by coupling of the appropriate F-containing alcohol to the CP segment via toluene diisocyanate.

Solutions containing F-terminated CP-segments showed typical critical micelle behavior. The critical micelle concentration depended on the molecular weight of the CP segment and the type of F-containing endgroup. The micelles are thought to consist of a core of the F-endgroups and a corona made-up of CP. Films containing the oligomers cast from micellar solution revealed a linear decrease in wetting force according to the blend composition of the oligomer, i.e. behavior according to the rule of mixing. This indicated the absence of surface segregation of the F-endgroup and it is explained with the fact that the micellar structure is retained in the solid state, suppressing surface segregation. The solid state micelles were visualized as dome-like protrusions by height image atomic force microscopy. In systems blended with CP the distance between the protrusions was found to increase with increasing CP content which was explained by a dilution process.

Films containing F-esters were characterized by wetting force measurements and x-ray photoelectron spectroscopy (XPS). The wetting force decreased dramatically at low blend content of the F-ester and at the same time an F surface-concentration higher then expected from the blend composition was found by XPS. This indicated self-assembly by surface segregation of the F-containing species during film formation. The extent of surface segregation was found to depend on the type of the F-ester group as well as on the blend concentration of the F-ester.

Dynamic wetting force measurements revealed hysteresis in films containing either F-esters or F-terminated CP segments. The hysteresis was found to be both kinetic (water sorption and reorganization) and thermodynamic (surface roughness and surface coverage with F-moieties) in nature. Consecutive force loops revealed an increase in the wetting force (advancing

and receding) with increasing loop number, indicating the increased hydrophobicity of the surface. The force increase was determined to be due to water sorption as well as due to surface reorganization. An increase in the size of the F-groups signified a decrease in reorganization rate due to a decreased mobility of the group. The process of reorganization was fully reversible, a behavior which is congruent with the definition of smart behavior.

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Glossary

DP degree of polymerization

CP cellulose propionate

CTP cellulose tripropionate

FTIR fourier transform infrared

M_n number average molecular weight

GPC gel permeation chromatography

NMR nuclear magnetic resonance

DS degree of substitution

DS_F degree of substitution of an F-containing substituent

T_g glass transition temperature

T_m melting temperature

TGA thermogravimetric analysis

CMC critical micelle concentration

AFM atomic force microscopy

XPS x-ray photoelectron spectroscopy

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