Dynamic Mechanical Thermal Analysis Transitions of Partially and Fully Substituted Cellulose Fatty Esters

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ABSTRACT: The main transitions of cellulose fatty esters with different degrees of substitution (DSs) were investigated with dynamic mechanical thermal analysis. Two distinct main relaxations were observed in partially substituted cellulose esters (PSCEs). They were attributed to the glass-transition temperature and to the chain local motion of the aliphatic substituents. The temperatures of both transitions decreased when DS or the number of carbon atoms (*n*) of the acyl substituent increased. Conversely, all the transitions of fully substituted cellulose esters occurred within a narrow temperature range, and they did not vary significantly with *n*. This phenomenon was explained by the formation of a crystalline phase of the fatty substituents. The presence of few residual OH groups in PSCEs was responsible for a large increase in the storage bending modulus, and it eliminated the effect of *n* on damping. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 281–288, 2003

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INTRODUCTION

The organic esters of cellulose are thermoplastic materials that can entirely be synthesized from natural, renewable products. Cellulose acetate, the most important commercial cellulose ester, requires, however, an external plasticizer for most thermomolding processes because it shows a high softening temperature. Longer linear acyl groups decrease the softening point of cellulose esters. The lateral aliphatic chain acts as an internal plasticizer of the cellulosic polymer, as first demonstrated by Malm et al.¹ Since then, the relaxation processes of fully substituted cellulose esters, that is, with a degree of substitution (DS) value very close or equal to 3, have been widely studied with dielectric measurements,² viscoelastic properties in the molten state,³ dynamic mechanical thermal analysis (DMTA),^{4,5} and differential scanning calorimetry (DSC).⁶

In contrast, studies concerning partially substituted cellulose esters (PSCEs), that is, with a DS value distinctly inferior to 3, are less abundant. They principally concern biodegradation. For instance, Buchanan et al.⁷ showed that cellu-

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