Effect of 12-Hydroxystearic Acid on the Structuration of Blends with a High Content of Renewable Raw Materials

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Abstract

-The substitution of mineral waxes by renewable raw materials is possible by the use of organogel, via the incorporation of an organogelator, 12-hydroxystearic acid (12-HSA). However, the physico-chemical characteristics of renewable vegetable raw materials differ from those of mineral waxes. The aim of this research is to study the effect of 12-HSA content on the structuration of blends with a high content of renewable raw materials. For this purpose, 4 blends (made of 70% of organogel with different contents of 12-HSA) were compared to a reference blend (mainly composed of petrochemical paraffins). The impact of different concentrations of 12-HSA on the structure of blends, in particular on their microstructure was investigated. The structure was then analyzed at three scales: at the molecular scale, using the infrared spectra, at the microscopic scale, by polarized light microscopy to characterize the size distribution of the crystals, and at the overall scale by measuring the thermal behavior by differential scanning calorimetry.

The structure of the blends in which they are used is modified. The addition of 12-HSA promotes the creation of weak bonds, as hydrogen bonds with the liquid fraction, particularly rapeseed oil; thus, allowing the gelling of 12-HSA-rapeseed oil blend. A carboxylic acid dimerization is observed at 1695 cm-1 corresponding to a gelation of the rapeseed oil by 12-HSA. The intensity of this peak is all the more important when the 12-HSA content is high. The peak corresponding to the O-H bond stretch is very wide (between 2400 cm-1 and 3400 cm-1) and centered on the peak of the C-H stretching region showing hydrogen bonds between the carboxylic functions of vegetable raw materials and the hydroxyl group of 12-HSA. This was shown by infrared spectroscopy. The study of the microstructure of blends containing 12-HSA by polarized light microscopy shows that the addition of 12-HSA also results in a modification of the crystal microstructure: the crystal lattice is denser, and the crystal size is reduced. The crystallization of blends in which 12-HSA is incorporated is thus limited; the homogeneity of the blends is therefore improved. In addition, by increasing the density of the crystalline network of the blends in the presence of 12-HSA, the exudation of blends is reduced by trapping the rapeseed oil via capillary forces. The higher the 12- HSA content, the less the exudation. The modification of the crystal lattice has an impact on the phase transition of the blends. The addition of 12-HSA causes a change in the thermal behavior of the blends, as measured by differential scanning calorimetry. The higher the 12-HSA content, the higher the onset temperature of crystallization. Nevertheless, only blends with a 12-HSA equal or higher than 4.9% have higher onset temperatures of crystallization compared to the reference blend. The enthalpies of crystallization and melting are divided by two with respect to the reference blend, containing a majority of petrochemical paraffins. In addition, the higher the 12-HSA content, the higher the values of the enthalpies of crystallization and melting. Thus, these results show an improvement of the strength of the interactions between the 12-HSA molecules and between 12-HSA and rapeseed oil. To conclude, the incorporation of an organogel makes it possible to obtain a solid texture with a high content of liquid vegetable oil by modifying the structure of blends at all scales. All these observations highlight the benefits of adding 12-HSA: increasing the rate of renewable raw materials as a substitute of petrochemical paraffins, limiting the crystallization of raw materials by the modification of the crystal lattice by acting as a crystallization initiator and thus improving the macroscopic aspect of the finished products.