Syntheses of ester derivatives from natural polysaccharides and their application as bio-based plastic material

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Abstract

Polysaccharides are one of the most abundant natural polymers in the world, and are consisting of various kind of sugar units with various bonding structure. Polysaccharides are not originally thermoplastic due to their inter- and intra-molecular hydrogen bonding derived from hydroxyl groups in the polymer chain. In the present study, polysaccharide alkyl esters having different chain lengths (C2-C12) were synthesized to give them thermoplasticity, from xylan, glucomannan, curdlan, pullulan, and dextran with the goal of their application as bio-plastic material. The esterification was carried out in carboxylic acid/ trifluoro acetic anhydride (TFAA) mixed system or DMAc/LiCl system. The chemical structures, thermal and crystalline properties of the esters were characterized by NMR, GPC, and WAXD, DSC measurements. Degrees of substitution of the esters were 3.0 for all derivatives.

The esters from all polysaccharides formed transparent cast-films or thermo-pressed films. The xylan and pullulan esters could be spun into electrospun nanofibers. Tensile tests of the films revealed that their mechanical properties were dependent on polysaccharide structure and the alkyl chain length. The esters with shorter side-chains (C2-C4) exhibited higher mechanical strength (ca. 30-40MPa) compared to those of the longer chain esters (10-20 MPa). In common tendency, the mechanical strength decreased with increasing ester side-chain length and elongation at break increased with increasing in side-chain length. Pullulan esters were highly stretchable with the maximum elongation of 1200%. Among the xylan esters, xylan propionate (C3) and xylan butyrate (C4) exhibited a nucleating effect on both poly(lactic acid)(PLA) during both non-isothermal and isothermal crystallization conditions.

DSC and WAXD analyses revealed that the esters of xylan, glucomannan, pullulan were amorphous polymers and curdlan esters were highly crystalline polymers. The acetate of these polysaccharide esters exhibited high thermal stability with the glass transition temperature (T_g) of ca.180 °C. The glass transition temperature (T_g) of these esters were dependent on side-chain length and decreased from ca. 180°C for acetate and ca. 40-60°C for laurate. The melting point of curdlan esters ranged from 167 to 287 °C, depending on ester chain length.

References

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