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THERMAL STABILITY AND WATER VAPOR SORPTION OF WHEAT STARCH MODIFIED WITH ISOCYANATE FUNCTIONAL GROUPS

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ABSTRACT

Wheat starch polymer was modified through the unequal reactivity of isocyanate groups in isophorone diisocyanate (IPDI) monomer. Fourier transform infrared spectroscopy (FTIR) and ¹³C nuclear magnetic resonance (¹³C NMR) confirmed the presence of both urethane and isocyanate functionalities in the modified polymer. Thermal stability and water vapor sorption properties of the modified polymer were evaluated by means of thermogravimetric analysis (TGA) and auto-dynamic vapor sorption (AVS) method, respectively. The results indicated that the modified starch polymer showed a better thermal stability (e.g. higher temperature at maximum weight loss) compared to the unmodified one. Water vapor sorption of starch polymer was considerably reduced after modification with IPDI monomer.

INTRODUCTION

Starch is the main reserve source and energy storage of plants, and it is widely available in agricultural products. Native starch has excellent applications in many industrial sectors such as food, textile, pharmaceutical, paper, and biofuel. However, it suffers from lack of water tolerance, storage stability and bonding strength [1]. Numerous studies have been performed to chemically, physically, genetically, and enzymatically modify different native starches and to enhance their functionalities for new applications.

The objective of this study was to modify native wheat starch with IPDI monomer by using the Lewis acid dibutyltin dilaurate (DBTDL) as a reaction catalyst, and to evaluate its thermal and water vapor sorption behavior

MATERIALS AND METHODS

Native wheat starch (NWS) was kindly provided by Lantmännen (Lantmännen Reppe, Växjö, Sweden). The NWS polymer was modified with IPDI monomer at a weight ratio of NCO:OH of 6:1, as described previously [2].

The chemical structure of NWS and modified wheat starch (MWS) polymers were analyzed by means of FTIR (Nicolet-Nexus, Waltham, MA, USA) and solid-state ¹³C NMR (Billerica, MA, USA). Q500 TA equipment (New Castle, DE, USA) was used to evaluate the thermal stability of the polymers from 50 to 650 °C at a rate of 10 °C·min⁻¹ under nitrogen. The vapor sorption behavior of the NWS and MWS polymers were determined using a AVS apparatus (Q5000 SA, TA Instruments, New Castle, DE, USA), as described previously [2-5].

RESULTS AND DISCUSSION

The structural change of native wheat starch after modification with IPDI was analyzed by means of FTIR and solid NMR. The FTIR spectra (Figure 1a) illustrate the vibration at 1750 cm⁻¹, bending vibration of -NH at 1530 cm⁻¹ and stretching vibration of C-N at 1250 cm⁻¹ which can be attributed to the presence of urethane bonds between IPDI and native wheat starch. The appearance of the

isocyanate band at 2266 cm^{-1} is related to the pendant $-\text{NCO}$ groups. The NMR spectra (Figure 1b) demonstrate new peaks at 129.5 ppm and 158 ppm, which are related to the secondary free $-\text{NCO}$ group and urethane linkage, respectively [2,6].

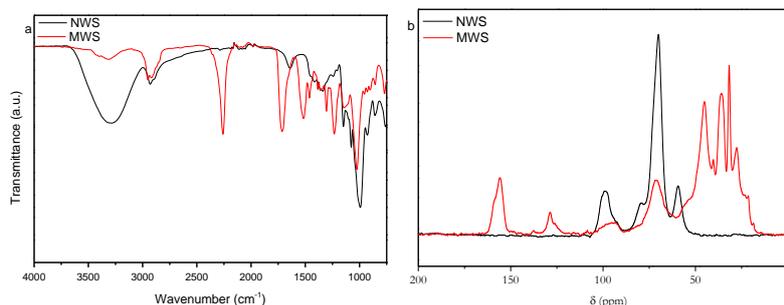


Figure 1. FTIR spectra (a) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra (b) of NWS and MWS

Water vapor sorption analysis showed an obvious reduction in moisture adsorption behavior of wheat starch as a result of IPDI modification (Figure 2a). Reduction in equilibrium moisture content (EMC) of modified starch can be due to occupation of polar $-\text{OH}$ groups by cycloaliphatic urethane moieties in the polymer chains.

The derivative thermogravimetric (DTG) curves derived by the slope of TG graphs (Figure 2b), illustrate the temperatures that maximum mass loss of the polymers occurred. This temperature was $312\text{ }^\circ\text{C}$ for NWS, and it is associated with its thermal decomposition. However, functionalization of starch with IPDI shifted the degradation temperature to $335\text{ }^\circ\text{C}$, and caused a second maximum degradation temperature at $418\text{ }^\circ\text{C}$, which can be attributed to the decomposition of urethane groups into the isocyanate and alcohol groups.

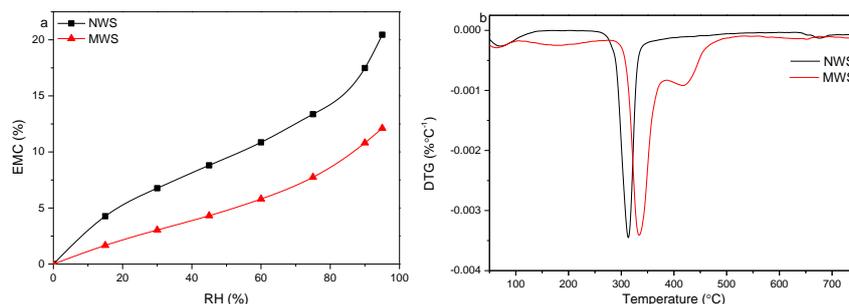


Figure 2. Water vapor sorption (a) and derivative thermogravimetric (DTG) analyses (b) of NWS and MWS

CONCLUSION

Wheat starch was modified with isophorone diisocyanate (IPDI) monomer. The presence of both isocyanate and urethane functionalities in wheat starch macromolecules after modification was confirmed by FTIR and ^{13}C NMR. The thermal stability of IPDI-modified wheat starch was remarkably improved. The moisture sorption of starch polymer was greatly reduced by IPDI modification. This study shows the potential of modified wheat starch for a wide range of applications as a reinforcement element in compatible matrices.

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