Effect of Acetylation on the Mechanical and Thermal Properties of Soy Flour Elastomers

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ABSTRACT: Biobased fillers were utilized as components in soy-elastomer composites. Soy flour is lightweight, low cost, and high strength, which makes it an ideal alternative to petroleum-derived fillers. However, poor interfacial adhesion and low dispersion within the polymer matrix are limiting factors for composite performance. Soy flour chemically pretreated by acetylation was compounded with synthetic rubber elastomers. In general, soy flour (as received) concentration in the composite is proportional to the ultimate strength. However, soy-elastomer composites with acetylated filler performed similar to the neat elastomer. In addition, the pretreated composite's thermal stability increased and exhibited less phase seperation compared to the untreated composites.

KEYWORDS: Acetylation, soy flour, thermoplastic, elastomer, composite

1 INTRODUCTION

In an effort to reduce the demand for petroleum products and our dependence on them, the use of agricultural fillers in plastics as an "environmentally friendly" alternative to petroleum products has gained the interest of industry. Agricultural fillers are potential lightweight, low cost alternatives, and can have unique mechanical and thermal properties compared to synthetic fillers. Fillers, such as soy bean co-products, represent a potential biofiller for plastic composites because they are widely available commercially and relatively inexpensive. However, producing homogenous composites with good interfacial properties that exhibit good mechanical and thermal characteristics can be a challenge.

In 2011, Omni's technical report, "Rubber Compounds: A Market Opportunity Study," pointed out the potential for soy protein to be utilized in the synthetic polymer industry [1]. Soy protein has been used in recent studies as a filler in natural rubber [2–5] and elastomeric materials [6–8]. Soy flour, in particular, is a lower cost filler than soy protein isolate or soy concentrate mainly because of the lower processing costs of purification. Soy flour contains approximately 56% protein compared to the 90% protein content for isolate and 65% for concentrate; however, this lower protein content also contributes to soy flour's ability to absorb more water and exhibit hydrophilic characteristics [9].

When native soy flour is compounded with synthetic rubber resin, the hydrophobic nature of the polymer counteracts the hydrophilic nature of the filler, which results in poor interfacial adhesion. Several approaches to solve this issue have been identified, including crosslinking [10], alkoxy silane treatment [11], copolymerization [12–14], acylation [14], and esterification. Esterification, in particular, has been proven to alter the hydrophilic nature of wood flour particles [15]. Thellen *et al.* used polyethylene and soy flour composites produced via co-extrusion to create multilayer packaging films [16].

In this study, we used esterification through acetylation to chemically treat the filler and then tested the mechanical and thermal properties of soy flour-elastomer composites. We hypothesized that this technique would decrease the hydrophilic nature of the soy flour particles, resulting in better interfacial adhesion between the soy filler and the polymer resin. Chemical conversion was verified by solid-state nuclear magnetic resonance (SS-NMR), and scanning

electron magnification (SEM) was utilized to visually characterize the behavior of the soy flour particles. Mechanical properties were characterized via tensile testing. Thermal properties were characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Samples were created at 10 wt%, 15 wt%, and 20 wt% soy flour loadings and compared to the neat polymer.

2   EXPERIMENTAL

2.1   Materials

A 7B, defatted soy flour was supplied by ADM (Archer Daniels Midland; Decatur, IL). Moisture was reduced by oven heating at 100 °C for 12 h. The synthetic elastomer used was a poly(styrene-butadiene)-triblock copolymer (PolyOne; Romeoville, IL).

2.2   Modification of Soy Flour

Soy flour (SF) particles were chemically modified through an acetylation reaction to change their functionality. Protein and carbohydrate hydroxyl (-OH) groups of the soy flour were replaced with acetyl (-OCOCH$_3$) groups [8]. This was completed by dispersing ten grams of dried, defatted soy flour in a solution of acetic anhydride (57.17 g, 56 mmol/g SF), dimethylformamide (DMF) (10.23 g, 14 mmol/g SF), and a potassium carbonate (K$_2$CO$_3$) (1.5 g, 1.1 mmol/g SF) catalyst [9]. The reaction was allowed to cool after it was heated to 100 °C for 3 h. The mixture was precipitated at room temperature after 3 h through Soxhlet extraction. The extracted material was washed with deionized water for 6 h and then with a 4/1/1 (parts) mixture of toluene, ethanol, and acetone for 6 h before being dried at 40 °C for 24 h. After drying, samples were ground into a powder with a mortar and pestle. This procedure was adapted from previous research focused on wood flour and plastic composites [15, 17, 18].

2.3   Sample Preparation

Samples were compounded with a single-stage, single screw Brabender extruder (C.W. Brabender Instruments; South Hackensack, NJ) with an L/D ratio of 30:1 at 165 °C and 60 rpm. According to Du *et al.*, extrusion intensifies crosslinking due to either disulfide bonds or intramolecular contact that affects the mechanical properties [19]. The SF filler was added on a weight basis of 10, 15, and 20%. The composites were extruded through a 3 mm, circular die, pelletized, and compression molded into dog-bone samples according to ASTM standard D638 [20].

2.4   NMR Procedures

Nuclear magnetic resonance (NMR) is a powerful spectroscopic technique that can be used to determine the type and quantity of atoms in a local bonding environment. Solution NMR is regularly used by organic chemists to determine the structure of molecules synthesized in the lab. In this work, we have conducted our analyses via solid-state NMR (SSNMR) due to the insoluble nature of the flour particles. In solution NMR, molecules tumble freely in solution, averaging the molecular orientation, and producing a spectrum with very sharp lines. Due to the random ordering of particles in an SSNMR sample, the sample must be mechanically rotated via magic angle spinning in order to produce a spectrum where only the isotropic chemical shifts remain.

With NMR, quantitation is determined by calculating the area under a peak resonance. Quantitation of ^{1}H solution NMR spectra is a common procedure for organic chemists and provides the relative ratios of protons in different bonding environments in the molecule. While ^{1}H solution NMR is commonly used for molecular structure determination and quantitation for soluble organic molecules, ^{1}H SSNMR suffers from broad lines that prevent the collection of much useful integration data. Thus, we must turn to ^{13}C SSNMR in order to obtain quantitative spectra and identify the different carbon bonding environments in our flour samples. Quantitative ^{13}C SSNMR spectroscopy is possible via a direct polarization pulse sequence where a single pulse is applied to the ^{13}C spins, immediately followed by detection. Quantitation is still challenging due to long [13]C T1 relaxation times, particularly for carbonyls and quaternary carbons, and necessitates acquisition of spectra under long recycle delays. Direct polarization ^{13}C SSNMR spectra also suffer from sensitivity issues due to the low natural abundance of ^{13}C spins. Another common SSNMR technique is known as cross polarization, which enables the transfer of magnetization from an abundant spin (typically ^{1}H) to a less abundant spin (^{13}C), followed by detection of the less abundant spin. This technique greatly enhances ^{13}C sensitivity, but suffers from the fact that the spectra are no longer quantitative. Our ultimate desire is to combine the quantitative nature of direct polarization ^{13}C experiment with the sensitivity of the cross-polarization experiment.

The MultiCP sequence [21] was developed in order to yield quantitative ^{13}C spectra under cross-polarization conditions. The MultiCP pulse sequence is able to produce quantitative spectra through the use of repeated blocks of cross polarization separated by delays in which the ^{1}H and ^{13}C magnetization are stored along the z-direction, and the [1]H

magnetization can recover almost to an equilibrium state. The MultiCP experiment produces a pair of spectra, obtained with and without gated decoupling. Gated decoupling is a spectral editing technique that eliminates the resonances of carbons strongly bonded to protons, allowing for filtering out of CH and CH$_2$ resonances. Although methyl carbons are obviously bonded to protons, the rapid rotation of the methyl group results in a weak ^{13}C–^{1}H coupling, and thus the CH3 peak also remains in a spectrum acquired under gated decoupling. The first spectrum in the pair, with gated decoupling, shows only the quaternary, carbonyl and methyl resonances, and the second spectrum, without gated decoupling, shows all resonances. The spectrum under gated decoupling features a clean methyl peak with no overlapping CH$_2$ resonances, and this peak is representative of the acetyl groups in the flour samples. In this analysis (Figure 1), we are primarily interested in monitoring the relative increases and decreases of the carbonyl and CH$_3$ resonances in order to verify the conversion of hydroxlyated carbons (–OH) to acetylated carbons (–OCOCH$_3$) after the esterification reaction. For our purposes, comparing the peak integration of the modified soy flour to that of the unmodified provides the percent change of various functional groups that occurs after sample treatment.

In order to ensure quantitative spectra, the pulse sequence power levels and delays are calibrated using unlabeled N-t-Boc-L-Ala, which contains carbonyl and methyl resonances. Adjusting the parameters within the MultiCP sequence allows the user to obtain a 3:1 integration ratio between the carbonyl and methyl peaks. Using the same parameters with other compounds has been shown to be a reliable method of producing quantitative spectra on more complex systems.

Solid-state ^{13}C NMR measurements of the soy flour samples were performed on a Bruker Avance II spectrometer with a 14.1 T wide-bore magnet using a 4 mm triple resonance MAS (magic angle spinning) probe in double resonance mode. TopSpin 3.0 software was used for data acquisition and processing. The operating frequencies for 1H and ^{13}C on this spectrometer are 600.13 MHz and 150.90 MHz, respectively. MultiCP spectra [21] spectra were obtained under MAS at 14 kHz, 1H SPINAL decoupling at 62 kHz, and stabilized at a temperature of 298 K. Spectra were typically acquired with 1536 scans and a recycle delay of two seconds. The final spectra were externally referenced to glycine Ca resonance at 43.5 ppm.

2.5 Thermal Analysis Procedures

A Q2000 differential scanning calorimeter (TA Instruments; New Castle, DE) was used with liquid nitrogen and equilibrated at −80 °C for one minute under isothermal conditions to characterize the sample phases. A 15 mg sample was hermetically sealed in an aluminum pan where the onset temperature was ramped at a rate of 20 °C/min. The maximum temperature was 200 °C.

A Q50 thermal gravimetric analyzer (TA Instruments; New Castle, DE) measured the change in mass as a function of temperature to determine outgassing and degradation. This was conducted in a nitrogen atmosphere at a heating rate of 20 °C/min reaching a maximum temperature of 600 °C [22].

3 RESULTS

3.1 Solid-State Nuclear Magnetic Resonance (SSNMR)

Figure 2 shows a stacked spectrum of the untreated and treated (acetylated) soy flour samples. The comparison between the two spectra indicates a change in concentration of the functional groups before and after the acetylation process.In general, the ppm value for NMR references corresponds to the local electronic environment of the observed nucleus. The chemical
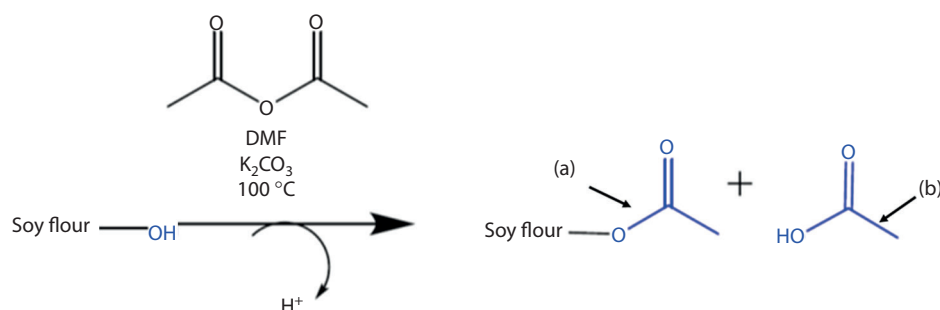

Figure 1 Acetylation of soy flour from hydroxyl groups (-OH) to acetyl groups (-OCOCH$_3$), (**a**) and (**b**), attached to the surface of the soy flour.