Influence of Starch Content on the Thermal and Viscoelastic Properties of Syndiotactic Polypropylene/Starch Composites

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Abstract—In this study, syndiotactic Polypropylene/Starch (sPP/starch) composites were prepared using a solution mixing technique. The thermal characterization was performed using Differential Scanning Calorimetry (DSC), and the melting point was measured for all polymer composites. The thermal degradation temperature was measured using thermal gravimetric analysis. The viscoelastic measurements were performed using the Atomic Rheometric Expansion System (ARES). Both melting point and thermal degradation temperatures were found to decrease with increasing starch content. Moreover, the elastic modulus was found to decrease when the starch content increased.

Keywords-aeration; melting point; sPP/starch composites; thermal degradation temperature; elastic modulus; frequency sweep test

I. INTRODUCTION

Polymer composites are synthesized by embedding natural or synthetic materials into a polymer to increase its desired properties [1, 2]. Several studies have been conducted on enhancing the properties of polymer products [3-23]. Polymer composites with different combinations of filler and polymer are studied in order to obtain the desired and targeted properties of polymer products [3]. However, the final desired microstructure and macrostructure properties of polymers and composites depend on the nature, amount, geometry, and interfacial interactions of the components [4]. Rheology is used as a tool to study a polymer's or a polymer composite's microstructure, as the rheological response is highly sensitive to the molecular structure of polymers and their composites [5-9]. While several studies have been conducted on the synthesis and the rheology of polymer and polymer/clay composites [10-18], only a few have targeted the viscoelasticity of polymer/clay composites.

The rheological properties of polyethylene oxide/montmorillonite clay gels and multilayered films were studied in [14], using an Atomic Rheometric Expansion system (ARE-2 rheometer), and noticing a slight increase in both the loss modulus (G') and the storage modulus (G") when increasing the clay content. The thermal properties were examined using Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA), while the results were related to the microstructural properties of the composites and the films. The effect of clay content on the rheology of polypropylene/clay nanocomposites was investigated in [15], examining both linear and non-linear rheology, finding that loss modulus (G'), storage modulus (G"), and dynamic viscosities increased monotonically with organophilic montmorillonite nanocomposites. The viscoelastic properties of syndiotactic polypropylene (sPP) were investigated in [16], examining the effect of the degree of syndiotacticity on the rheological parameters, including plateau modulus and entanglement molecular weight. This study indicated that increasing the degree of syndiotacticity enhanced the plateau modulus causing a decrease in the molecular weight between entanglements. In [17], the influence of clay contents on plateau modulus and entanglement molecular weight was studied on polypropylene/clay composites, concluding that an increase in the clay content increased the plateau modulus and consequently decreased the entanglement molecular weight. The rheological properties of a drilling fluid polymer treating agent named Driscal-D using a Fann 50SL rheometer were investigated in [24]. The effects of adding polymer, electrolyte, clay type, and antioxidant on the rheological properties of a

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Driscal-D solution were examined, finding that solution's viscosity tends to increase when increasing polymer addition and decreased in the presence of an electrolyte. Furthermore, adding clay in a Driscal-D solution enhanced its rheological properties, which could improve cuttings transportation.

The current study examines the viscoelasticity of syndiotactic polypropylene/starch composites (sPP/starch), with starch content ranging from 0 to 8%, using an Atomic Rheometric Expansion System (ARES) to investigate the effect of starch content on the melt rheological response of composites.

II. METHODOLOGY

A. Polymer Composite Synthesis

1) Materials

Syndiotactic Polypropylene (sPP) having a 60% degree of syndiotacticity, supplied by Zhongwei Industrial Co. Ltd., was used as a matrix. Starch, originating from potato, was used as the filler. Xylene, provided by Shanxi Zhongwei Industrial Co. Ltd., was used as a solvent in mixing. The samples' details are listed in Table I.

TABLE I. SAMPLES' DETAILS

Number of samples	Name of samples	Percentage of starch content	Degree of syndiotacticity (%rrr)
1	sPP/S-8	8%	
2	sPP-6	6%	
3	sPP/S-4	4%	
4	sPP/S-2	2%	
5	sPP	0	60

2) Preparation of Composite Samples

Solution mixing was applied to create a set of syndiotactic polypropylene/starch composite samples with four different starch content proportions. The starch was accurately weighed and mixed with the polypropylene matrix using xylene as a solvent in a 1000ml beaker. The mixing temperature was kept at 120°C using a heating mantle until all syndiotactic polypropylene granules dissolved in a clear solution. The solvent containing syndiotactic polypropylene was initially shaken vigorously by hand and then stirred by a high-speed electrical stirrer keeping the heating conditions. The starch, dissolved in xylene, was added slowly to the syndiotactic polypropylene and xylene mixture. Vigorous and continuous stirring helped the uniformity of starch mixing and the intercalation of sPP to starch layers. The beaker operated for a few hours to evaporate the xylene. Then, the size of the prepared polymer-starch composite was mechanically reduced. After the completion of xylene evaporation, the composite samples were created by compression molding at 170°C temperature and 7Psi pressure for one and a half hour [10].

B. Polymer Composite Analysis

1) Differential Scanning Calorimetry (DSC)

The melting temperature (Tm) of all samples was measured using Differential Scanning Calorimetry (DSC). The samples, weighing 4mg, were heated up to 350°C at a constant heating rate of 40°C/min. During the heating cycle, the melting point peak was obtained. Afterward, the sample was kept under this annealing process for 7 minutes to eliminate crystallinity and remove thermal history. The analysis was performed using the instrument software TA-60 to find the melting temperature (Tm) of all samples.

2) Rheometry

The sPP/starch composites were pressed using Hot Press to prepare a uniform film for each composite. An Atomic Rheometric Expansion System (ARES) (TA Instruments), having a geometry of 8mm diameter parallel plate, was used to perform the viscoelastic tests under nitrogen atmosphere to reduce sample degradation. All experiments were carried out at a different gap depending on the sample's thickness. At first, strain sweep and stability tests were carried out. After choosing the suitable strain value (0-10%), dynamic frequency sweep tests were performed at temperatures ranging from 100°C to 200°C to obtain both elastic and viscous moduli at different frequencies and the master curves using the time-temperature superposition principle. No tests were performed below 100°C due to the faster crystallization kinetic.

III. RESULTS AND DISCUSSION

Frequency sweep tests were performed on all samples. The frequency sweep tests for samples having 2% and 6% starch contents are shown in Figures 1 and 2 respectively. It can be noted that the elastic modulus increased along with the frequency range (0 to 100rad/s), while the viscous modulus tended to decrease. Figure 1 shows a cross-over frequency at almost 1rad/s indicating that relaxation time was a little greater than 1s. Figure 2 shows that viscous was greater than elastic modulus at lower frequencies, while the elastic modulus was higher than viscous at higher frequencies. The cross-over frequency of the 6% sample was found to be greater than the one in the 2% sample, indicating that relaxation time for the 6% sample was less than for the 2%. This result also indicates that increasing starch content decreased the elastic and increased the viscous response. In other words, a strength decrease occurs when the starch content increases.

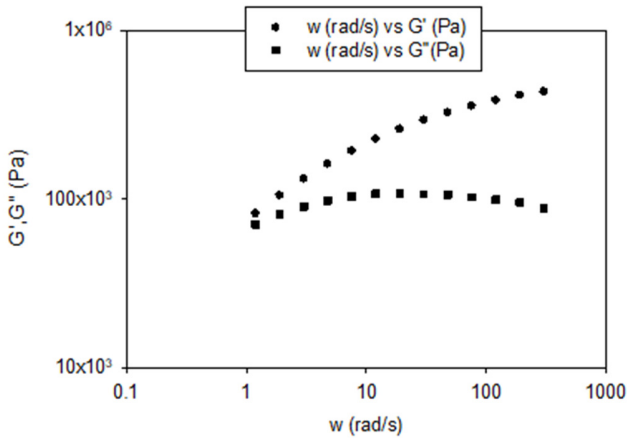

Fig. 1. Frequency sweep test for sPP/S-2 at 200°C.

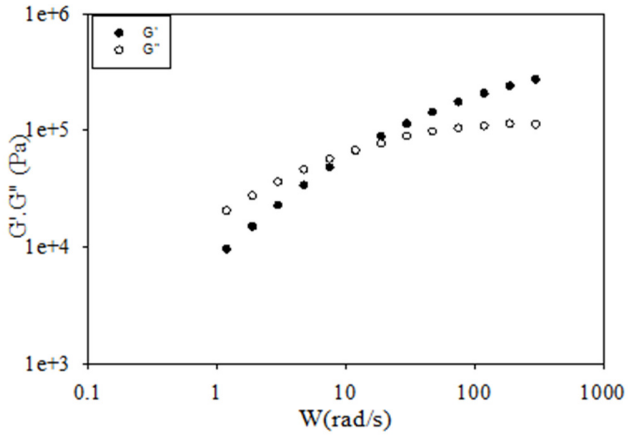

Fig. 2. Frequency sweep test for sPP/S-6 at 200°C.

A. Effect of Starch on Melting Point

The effect of starch on the melting point temperature of sPP/starch composites is shown in Figure 3. As it can be noted, increasing starch content decreased the melting point temperature of sPP/starch composites. The melting point of the composite was actually the melting point of starch. Starch's thermal stability is low compared to the syndiotactic polypropylene polymer. Therefore, increasing starch decreases the melting point temperature of sPP/starch composites.

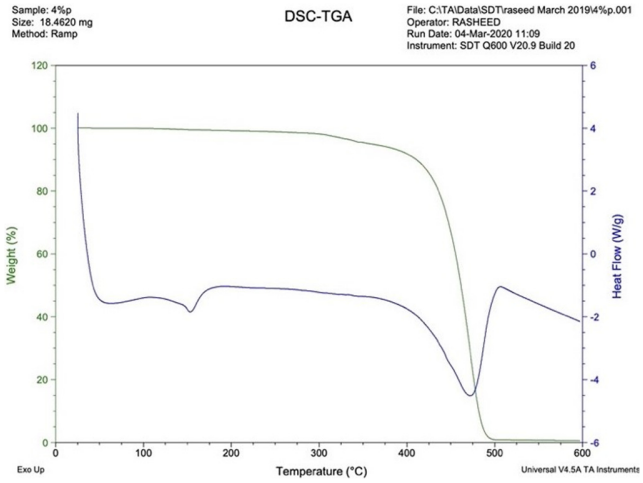

Fig. 3. Relationship between starch and melting point (T_m).

B. Effect of Starch on Thermal Degradation Temperature

The thermal degradation temperature of all composites was measured using Thermal Gravimetric Analysis (TGA). The TGA analysis for the sPP sample containing 4% starch is shown in Figure 4. This Figure depicts two drops in mass: The first drop indicates the removal of water from the composite sample, i.e. the dryness of the sample, while the second drop indicates the degradation of the sample. Thermal degradation temperature decreased when increasing starch content, as shown in Figure 5.

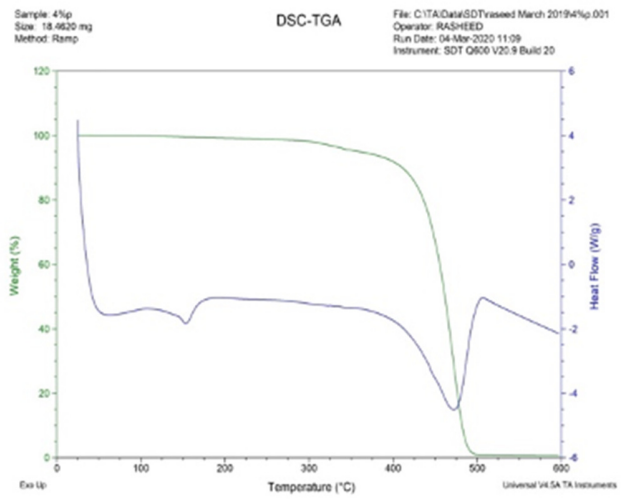

Fig. 4. FDSC and TGA analysis of sPP/S-4.

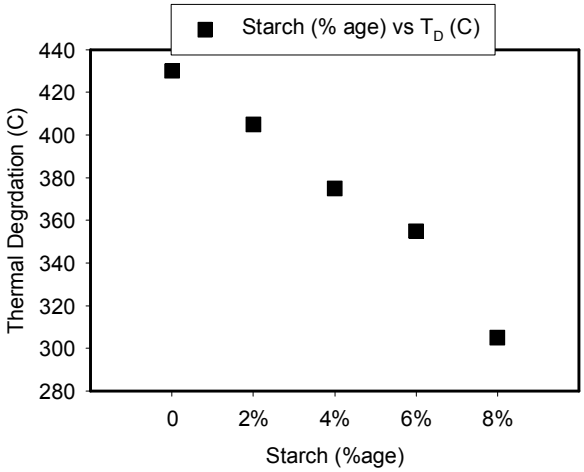

Fig. 5. Relationship of thermal degradation temperature and starch content.

C. Effect of Starch on Elastic Modulus

The elastic modulus was calculated using frequency sweep tests for all samples. The maximum value for each sample was noted. The elastic modulus indicates the mechanical response of a sample, and it was examined as a function of starch content. Increasing starch content decreased the elastic modulus, as shown in Figure 6. Therefore, increasing starch content decreased the strength of the composites. This result comes in agreement with the findings of [17], which investigated the effects of clay content on the thermal and rheological properties of sPP/clay composites. Clay content and starch affected the rheological and thermal properties of sPP/clay composites oppositely. Clay content increased the melting point temperature and the plateau modulus of sPP/clay composites. On the other hand, starch decreased both the thermal properties and the elastic modulus. An increase in clay content increased the mechanical response of the sPP/clay composites, while an increase in starch content decreased the mechanical and increased the viscous response of syndiotactic polypropylene/starch composites.

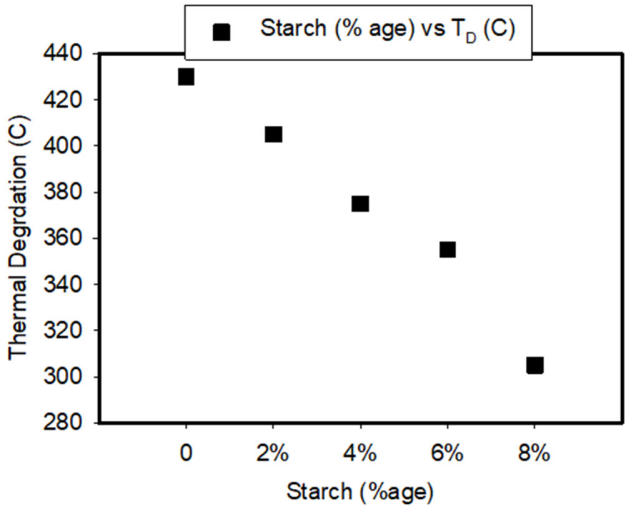

Fig. 6. Relationship between starch contents and elastic modulus.

IV. CONCLUSION

The viscoelastic and thermal analysis of sPP/starch on melting point, thermal degradation temperature, and elastic modulus depend on starch content. This stydy's findings showed that viscoelasticity is a powerful tool to investigate the microstructure and the chain parameters of polymer/starch composites. Thermal and viscoelastic properties were found sensitive to starch content proportions. Starch alters both the melting point and the thermal degradation temperatures, as increasing starch content decreased both of them. The same trend was found for the elastic modulus, as it decreased when the starch content increased. In conclusion, increasing starch content results in a decrease of the mechanical and elastic responses of the composite.

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