

# Rheology Properties of Poly(butylene succinate-co-butylene adipate)/Attapulgit Nanocomposites

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**Abstract**—Attapulgit (ATP) reinforced poly(butylene succinate-co-butylene adipate) (PBSA) nanocomposites were prepared by melt mixing in a HAAKE mixer. The fracture surfaces of PBSA/ATP nanocomposites showed superior interfacial linkage between ATP and PBSA matrix. The dynamic rheology properties of PBSA and PBSA/ATP nanocomposites were studied in this paper. The results showed that complex viscosity, storage modulus and loss modulus increased with increasing the clay content. Because of the interactions between polymer–filler and filler–filler, the network-like structures were formed.

**Keywords**—poly(butylene succinate-co-butylene adipate); attapulgit rheology; nanocomposite

## I. INTRODUCTION

The physical or chemical properties of nanocomposites with small amount of clay were greatly improved compared with the homogeneous polymer [1]. In recent years, attapulgit (ATP) has been regarded as an economic and effective natural one-dimensional reinforcing filler for preparing nanocomposites with high performance[2]. A lot of study works had focused on polymer/ATP nanocomposites, such as polyethylene/palygorskite nanocomposites[3], nylon 6/attapulgit nanocomposites[2], poly (ethylene terephthalate)/attapulgit nanocomposite[4]. But all of them are difficulty in recycling and biodegradation. In order to solve this dilemma, many biodegradable polymers had been exploited in the past decades. Properties of poly(butylene succinate) (PBS) and its copolymers poly(butylene succinate-co-butylene adipate) (PBSA) have attracted a lot of attention. Their soften temperature, yield strength and elongation at break was equivalent to daily use polyolefin materials[5]. But, the insufficient stiffness, low melt viscosity, slow crystallization rate, easy aging and high product cost have limited their further applications. Chen [6] found that PBS with ATP would bring the nucleation effect and elevated Young's modulus.

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Ray[7] and Eslami[8] studied rheological properties of polymer nanocomposites under molten state to understand the processing and structure property relationship of materials. Wu[9] et al. studied the rheological behavior of the intercalated PBT/clay nanocomposites. He found that the formation of the liquid crystalline-like phase structure in the nanocomposites was the major drive force for the formation of the percolated nanoclay network. In this research project, the PBSA/ATP nanocomposites were prepared by melt mixing. The dynamic rheological properties of PBSA and various PBSA/ATP nanocomposites were studied to investigate the influence of clay on the rheological behaviors[10].

## II. EXPERIMENTAL

### A. Materials

PBSA with 5 mol% adipic acid comonomers was kindly supplied by Anqing Hexing Chemicals Co., Ltd., China. The intrinsic viscosity was 1.38 dL/g in 50 wt%:50 wt% phenol and 1,1,2,2-tetrachloroethane mixed solvent at 25 °C. Attapulgit were kindly supplied by Jiuchuan Nano-material Technology Co., Ltd., Jiangsu, China. The chemical compositions detected by X-ray fluorescence were showed as follows: SiO<sub>2</sub> 68.84%, MgO 12.68%, Al<sub>2</sub>O<sub>3</sub> 9.20%, Fe<sub>2</sub>O<sub>3</sub> 5.98%, K<sub>2</sub>O 0.90%, P<sub>2</sub>O<sub>5</sub> 0.66%, TiO<sub>2</sub> 0.65%, CaO 0.61%, Na<sub>2</sub>O 0.29%, MnO 0.08%, Cr<sub>2</sub>O<sub>3</sub> 0.06%, NiO 0.04%, and ZrO<sub>2</sub> 0.01%.

### B. Preparation and characterization of PBSA/ATP nanocomposites.

The PBSA/ATP nanocomposites (nano-PBSA/ATP) were fabricated by melt mixing with a Germany RS600 HAAKE mixer. The mixing was carried out at 140 °C and the rotary speed was 60 rpm. The fabrication of the nano-PBSA/ATP with 7 wt% ATP content was depicted as follows: 46.5 g PBSA was first added into HAAKE mixer at 140 °C for 2 minutes for premelting. Then, 3.5 g attapulgit was added into the melt and

mixed for another 10 minutes. Other nanocomposites containing 1.0, 3.0 and 5.0 wt% attapulgite were fabricated in the same procedures and homogeneous PBSA was also processed at the same conditions.  $\phi$  25×2 mm disc-shaped specimens were prepared for the rheology test by a USA DACA instruments-50000 injection machine.

### C. Characterization

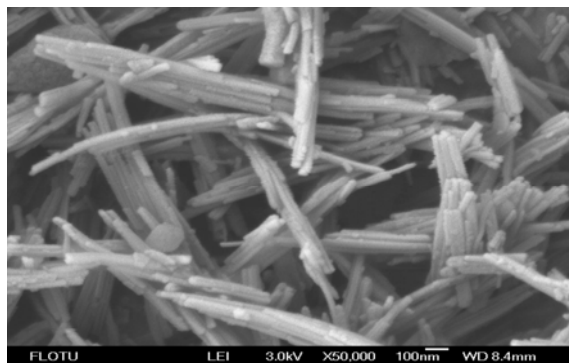
The morphologies of attapulgite and nano-PBSA/ATP were examined by scanning electron microscopy (SEM) on the Japan JEOL JSM-7401 at an accelerating voltage of 3 kV and 1 kV, respectively. Nano-PBSA/ATP samples were prepared by thermoforming the sheet at 160 °C, and then it was put in liquid nitrogen for 10 min before fracture. The attapulgite surface and fracture surfaces were all coated with platinum prior to examination.

The dynamic rheological measurements of PBSA and nano-PBSA/ATP were performed in an Anton Paar MCR301 stress/strain controlled rheometer. The diameter of parallel plates was 25 mm with a gap of 1 mm. The operation was in oscillatory shear mode at 140 °C by frequency sweep from 0.01 to 100 Hz and at 1% strain.

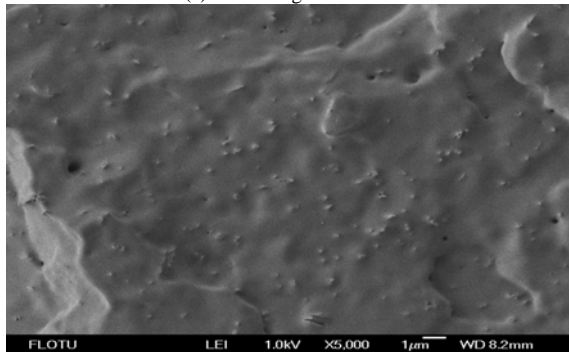
## III. RESULTS AND DISCUSSION

### A. Scanning electron microscopy analysis

Scanning electron microscopy (SEM) analysis was conducted to investigate the ATP morphology, dispersion states in polymer matrix. The results are showed in Figure 1.



(a) SEM images of ATP



(b) SEM images of fracture surface of 1 wt% PBSA/ATP nanocomposite

Figure 1. SEM images of ATP and PBSA/ATP nanocomposites

Figure 1 (a) gave SEM images of ATP and showed the morphology of original ATP presented a fibrous and formed bundle. Its diameter was about 20-30 nm and the length was about 500-1000 nm. Figure 1 (b) showed the fracture surface of 1 wt% nano-PBSA/ATP. ATP presented single fiber form in PBSA matrix. ATP was separated from bundles to single fiber by the function of shearing force and heating. Therefore, ATP could disperse and embed in the PBSA matrix without noticeable aggregates.

### B. Rheology properties

Figure 2 (a)-(c) showed the results of (a) dynamic complex viscosity  $|\eta^*|$ , (b) storage modulus  $G'$ , (c) loss modulus  $G''$  of PBSA and various nano-PBSA/ATP, respectively.

In Figure 2 (a), all  $|\eta^*|$  values of homogeneous PBSA and various nano-PBSA/ATP decreased with the increasing frequency. They presented a non-Newtonian behavior over the entire frequency range and pronounced a shear thinning characteristics. The nano-PBSA/ATP exhibited a stronger shear thinning behaviors than homogeneous PBSA. The reinforcement effect at low frequency was more significant than high frequency. Because of the interactions between polymer-filler and filler-filler, interconnected or network structures were formed. Vassiliou [11] et. al. studied the interactions in poly (butylene succinate)/fumed silica by using rheometer and confirmed the network structures.

Both  $G'$  and  $G''$  increased monotonically with increasing ATP content at all frequency. The enhancement effect was more significant at low frequency than high frequency, as demonstrated in Figure 1 (b-c). At low frequencies, the values of modulus increased with the increasing ATP content, and seemed to form a plateau of all nano-PBSA/ATP. Because there was enough time for the chains to unravel the entanglements so that a large amount of relaxation occurred. On the contrary, at high frequencies, the values of modulus increased than those of at low frequency, since the chains did not have time to escape from the entangling tube. The relaxation behaviors of the typical filled-polymer composites systems was also found in the previous works[13-15]. Therefore, because of the interactions between ATP surface and PBSA matrix, their network structures are confirmed by rheology properties of nano-PBSA/ATP.

## IV. SUMMARY

The morphology of ATP and nano-PBSA/ATP were investigated by scanning electron microscopy (SEM). The fracture surfaces of nano-PBSA/ATP showed superior interfacial linkage between ATP and PBSA matrix. The dynamic rheological measurements of PBSA and PBSA/ATP nanocomposites were performed in an Anton Paar MCR301 stress/strain controlled rheometer.

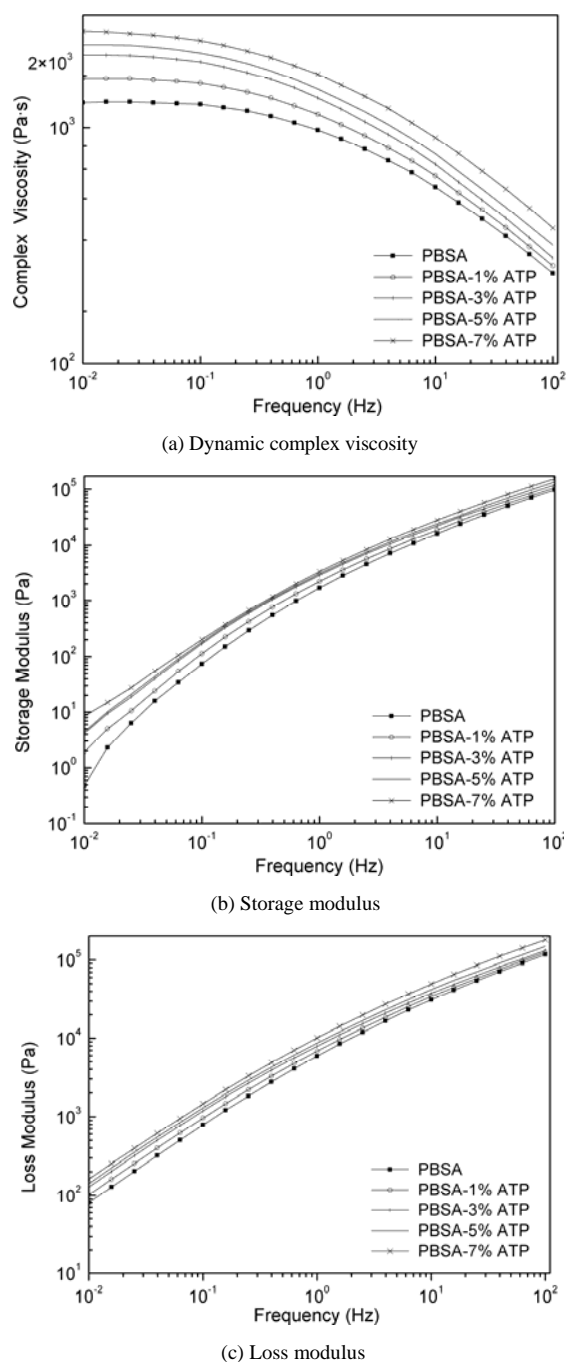


Figure 2. Rheology properties of PBSA and nanocomposites

All  $|\eta^*|$  values of homogeneous PBSA and various nano-PBSA/ATP decreased with the increasing frequency. They presented a non-Newtonian behavior over the entire frequency range and pronounced a shear thinning characteristics. Both

$G'$  and  $G''$  increased monotonically with increasing ATP content at all frequency and this enhancement effect was more significant at low frequency. At high frequency region, the values of modulus for all samples had little difference. The rheology results confirmed that the network structures were formed because of the interactions between polymer–filler and filler–filler

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