



Role of polymer/filler interactions in the linear viscoelasticity of poly(butylene succinate)/fumed silica nanocomposite



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ARTICLE INFO

Article history:

Received 2 September 2013
Received in revised form 27 January 2014
Accepted 30 January 2014
Available online 7 February 2014

Keywords:

D. Rheology
C. Stress relaxation
A. Nanocomposites

ABSTRACT

The linear melt viscoelasticity of poly(butylene succinate) (PBS) nanocomposites containing different types of fumed silica nanoparticles (unmodified and modified fumed silica) was studied. Depending on the primary particle size and surface chemistry of fillers, distinct modes of polymer/filler interactions could be identified in the nanocomposites. The PBS nanocomposites containing silica nanoparticles with larger surface area appear to have higher density of temporary physical network structures leading to significantly increased modulus. Increasing the polymer–particle compatibility through introduction of a hydrophobic functionality on the surface of the particles resulted in strong immobilization of the PBS molecules. The presence of such improved polymer/filler interactions was confirmed by the secondary relaxation mode and rubber-like behavior, indicative of stronger adhesion between the modified SiO₂ and the PBS matrix. The entangled polymer dynamic theory was used to discuss the influence of polymer/filler interactions on the relaxation behavior of PBS molecules. The relaxation hierarchy can be identified from the linear viscoelastic responses of PBS/modified fumed silica nanocomposites. Dynamic mechanical measurements showed that glass transition range was widened and the peak temperature was also shifted to higher temperature in the composites with enhanced PBS/silica interactions.

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1. Introduction

Poly(butylene succinate) (PBS), is a biodegradable semicrystalline polymer that has found great properties as excellent chemical resistance, thermal stability, melt mobility, and processability [1–4]. PBS can be produced from biobased starting materials succinic acid and butane diol, and so is receiving increasing attention as a replacement for fossil-derived polymers. However, its mechanical and thermal properties are often not sufficient for commercial applications. Thus, preparation of PBS composites reinforced with nanoparticles deserves attention as a strategy for extending the thermal and mechanical properties [5–9]. Compared to neat PBS, the PBS nanocomposites are reported to possess improved physical properties such as increased modulus, yield strength [5], and resistance to creep. In addition, crystallization behavior and thermal stability can be enhanced [5,9]. Okamoto et al. [10–12] studied the structure–property relationship in PBS/layered silicate nanocomposite. A remarkable improvement of mechanical properties was found in both solid and melt states as compared with that of PBS matrix without clay. The flocculated structure was reported to play

an important role in mechanical properties of such PBS/layered silicate nanocomposites. Due to the versatile options for surface modification, silica serves as an excellent model filler to study the effects of interfacial interaction in polymer nanocomposites.

Melt rheology has found important use in nanocomposite processing behaviors, analysis and characterization since the addition of fillers dramatically changes the viscoelastic response of polymers [13–16]. Within relatively low volume fraction of nanofillers, a typical transition from liquid-like to solid-like or rubber-like viscoelastic behavior is usually observed [17]. The terminal region also shifts to lower frequencies [18]. For nanoparticles such as CNT as well as silica, mechanical property enhancement appears to depend on a strong surface–polymer interaction that physically bonds the chains to the filler surface and results in a “bridging effect” [19,20], manifested in a higher entanglement density [21–23] or a “bound polymer” immobilized layer [24,25]. In silica composites, the bound polymer layer increased with filler concentration, amount of silanols on the silica surface, and polymer molecular weight [19,26,27]. By means of advanced thermal analysis methods, Cebe et al. [28,29] introduced the concept as “rigid amorphous fraction (RAF)” to describe such an immobilized layer, where the nanoparticles behave as an attractive surface that stiffens the polymer in close proximity. Because of the

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Nomenclature

| Symbol | Meaning | |
|---------|----------------------|------------------------------|
| G' | storage modulus | CABOSIL CABOSIL fumed silica |
| G'' | loss modulus | OTS octadecyltrichlorosilane |
| $G(t)$ | relaxation modulus | $\tan(\delta)$ loss tangent |
| G_e | Plateau modulus | E_a activation energy |
| τ | relaxation time | |
| AEROSIL | AEROSIL fumed silica | |

hydrodynamic friction and thicker boundary layer, the polymer chains behave more extending and stiffer that give rise to a higher modulus. More interestingly, while silanols of the silica were substituted by particular organosilanes which contain alkyl groups, changes in reinforcement effect were reported [16,18,19,25,27,29–32], and it is expected that chemical surface modifications not only change the dispersion of fillers in polymer matrix but also the polymer–filler interaction. Recently, rheological properties of PBS nanocomposites containing silica or PBS grafted silica were reported [5,7,8]. However, the origin of the novel enhancement effect on the thermal properties and mechanical performance, were not studied with respect to the interfacial interactions between silica and the PBS matrix. There is also a lack of discussion about how the interfacial interactions affect the processing and properties of such nanocomposites.

The objective of this work is to extend the thorough investigation of polymer nanocomposite rheology to the case of PBS molecular dynamics affected by different fillers and concentrations. The influences of surface area and hydrophobic surface treatment of fumed silica on the rheological properties are investigated. Octadecyltrichlorosilane (OTS) is used to obtain functionalized silica with long alkyl chains and hydrophobic surface. The motion of PBS molecules confined by the different surface properties was studied by DMTA and stress relaxation experiments which are combined with small strain oscillatory tests to extend to the viscoelastic response time range.

2. Experimental

2.1. Materials

PBS, used in this study, was produced by Showa Highpolymer Co, LTD, with molecular weight of 90,000 g/mol (determined by GPC). Fumed silica nanoparticles under the trade name AEROSIL 300 were supplied by Evonik, with surface area 300 m²/g. Fumed silica CABOSIL M5 was obtained from CABOT Corporation, with surface area 200 m²/g. The primary particle size is around 20 nm.

2.2. Functionality of fumed silica

Hydrophobic surface modification of fumed silica was carried out using octadecyltrichlorosilane (OTS). Octadecyltrichlorosilane was added to toluene at a weight fraction of 5 wt%. The solution containing fumed silica was stirred for 72 h at room temperature. Most of the solvent was removed by membrane filter and remaining solvent was further eliminated in a vacuum oven at 373 K for 12 h.

2.3. Nanocomposites preparation

Composite mixing was achieved using a Brabender Plasticorder torque mixer with type six sigmoidal rollers. The mixing temperature was fixed at 150 °C, and the screw speed was controlled

between 40 and 50 rpm for 10–15 min until the torque leveled off. The cooled composites were pelletized using a laboratory mill (Model: Thomas-Wiley 4 1291) with a sieve of 20 mm diameter. Using those pellets a square plaque (10 cm × 10 cm × 0.3 cm) was produced by compression molding in a heated hydraulic press (Model: Dake) at 140 °C and 2.5 MPa. Before pressing the pellets, they were held at melt temperature for 10 min to allow degassing and eliminate air bubbles. They were then pressed for another 10 min. After cooling the molded plaque for 10–15 min, it was cut into the proper size for rheology test using a band saw.

2.4. SEM

The state of dispersion of the fumed silica was observed by field emission scanning electron microscopy (JSM-7401F, Jeol Co., Japan). All specimens were compression molded and cryofractured under liquid nitrogen, and the fracture surfaces were coated with thin layers of gold.

2.5. Rheology & DMA

The complex viscosity and dynamic modulus of PBS/fumed silica nanocomposites were measured by using a parallel-plate rheometer (ARES-G2, TA instrument) equipped with 25 mm diameter stainless steel parallel disks. Strain sweep measurements were used to determine the linear viscoelastic region. The critical strain values varied from 2% to 40% depended on filler concentration, as shown in Fig. 1. Oscillatory shear and transient shear measurements were performed with strain 1% at 130 °C, which is above the melting temperature ($T_m = 112$ °C). In the transient shear

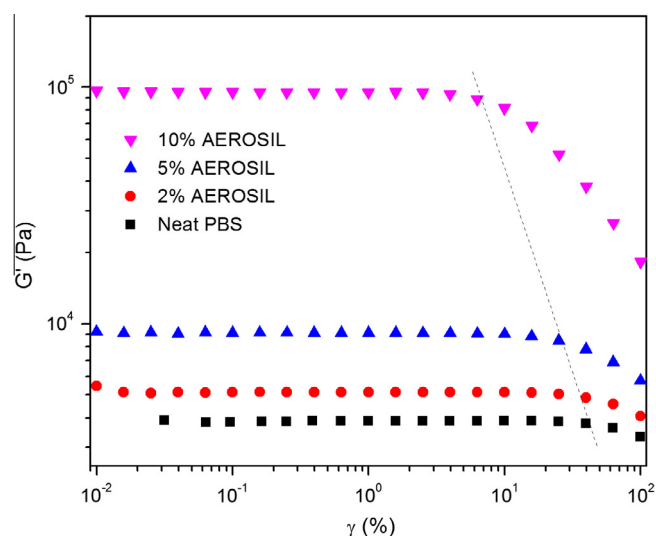


Fig. 1. Variation of the storage modulus versus deformation at different AEROSIL fumed silica concentrations in PBS; $\omega = 10$ rad/s⁻¹, $T = 130$ °C.

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