ABSTRACT

NONLINEAR RHEOLOGICAL CHARACTERIZATION AND MODELING OF COMPLEX FLUIDS UNDER LARGE AMPLITUDE OSCILLATORY SHEAR (LAOS)

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Dynamic oscillatory shear tests have historically been one of the most common ways a rheologist probes the material response for complex fluid systems including neat polymer melts and solutions, blends, and composites. In small angle oscillatory shear (SAOS) testing, the material functions $G'$ and $G''$ describe the linear viscoelasticity of the complex fluid and may be related to the morphological changes occurring in the system. However, typical processing conditions occur at fast flow rates and generate large deformations resulting in a strain dependence on the rheological properties.

In this research, the nonlinear viscoelastic behavior of polypropylene (PP) nanocomposite melts and oligomer modified polyamide (PA) blends under large amplitude oscillatory shear (LAOS) flows was investigated using Fourier transform (FT) rheology and stress decomposition (SD) techniques. With the development of high performance data acquisition (DAQ) cards in recent years, raw voltages of angular displacement (strain) and torque (stress) from the rheometer may be Fourier transformed into discrete harmonics to probe a material’s nonlinear response. These higher order harmonics are strongly correlated to the chain dynamics and morphological changes in a polymer system.

Polypropylene-clay nanocomposites were produced using concentrations of 3 and 5 wt% of silane treated nanoclay to ensure that the system was dilute, and the filler-network contribution was negligible. To promote particle-polymer interactions, the silane treated clay was reacted with a maleated polypropylene compatibilizer. The nonlinear intensity ratio $I_3/I_1$ of the third order harmonic to the first order harmonic of the shear stress as well as the zero-strain limit nonlinearity parameter $Q_0$ were determined through FT rheology experiments. To describe the trends in $I_3/I_1$ and $Q_0$ for polymer nanocomposite systems, a nonlinear viscoelastic differential model was developed for LAOS type flows.
Blends consisting of a PA6/PA66 copolymer in an 80:20 mixture by weight were melt mixed with varying concentrations (5 and 10 wt%) and molecular weights ($MW = 750$ and 1000) of an elastomeric polyisobutylene succinic anhydride (PIBSA) oligomer and tested under LAOS conditions. The low molecular weight PIBSA acts as a plasticizer on the matrix blend, reducing its shear stress with increasing concentration. The SD technique separates the elastic ($\sigma'$) and viscous ($\sigma''$) contributions of the stress waveform, much like $G'$ and $G''$ in SAOS flows. It was found that by increasing the concentration of PIBSA, the normally viscous response of the PA blend matrix transitioned to an elastic response. By combining SD with FT rheology, it was found that the $I_{3/1}$ ratio were nearly identical for both PA blends with 0wt% and 5wt% PIBSA, while much larger values of $I_{3/1}$ were identified for 10wt% PIBSA blends at lower strains.