Influence of processing conditions on the linear and nonlinear oscillatory shear, extensional and combined dielectric-rheological properties of poly(ethylene-butyl acrylate) - graphite nanoplatelets - carbon black hybrid nanocomposites

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ABSTRACT

In this study, the nonlinear oscillatory shear and extensional rheological properties of poly(ethylene - butyl acrylate) - graphite nanoplatelets - carbon black hybrid nanocomposites have been investigated with respect to the influence of extrusion processing history on the dielectric properties of the nanocomposites. Electrical conductivity was achieved in during combined oscillatory shear - dielectric spectroscopy measurements independent of the processing history provided that the deformations are in the nonlinear regime. The onset of the conductive behavior corresponded to an increase in the nonlinearities recorded. A strain-hardening behavior in extension was observed in both unfilled as well as filled samples, with a good prediction given by the Molecular stress function (MSF) theory

INTRODUCTION

Establishing the relationship between a material's microstructure, processing conditions and resulting properties is of utmost importance for tailoring the microstructure of polymer nanocomposites to desired properties. Due to the large/fast deformations employed, polymers are subjected to nonlinear deformations during processing, with the interactions between the flow field, e.g. extrusion flow, matrix and fillers dictating the overall microstructure dynamics and subsequent material properties/performance. Therefore, it is important to probe material linear as well as nonlinear rheological properties in simple configurations and seek out the associated microstructural effects and their relationship to the materials' mechanical, electrical, barrier etc. properties. In this framework, the rheological characterization of ethylene-butyl acrylate - graphite nanoplatelets - carbon black (EBA-GnP-CB), nanocomposites with respect to the influence of processing history and resulting electrical conductivity is investigated in this study.

EXPERIMENTAL

The EBA matrix contained 17 wt% butyl acrylate, the CB was a medium-structured carbon black (CB) ENSACOő 260G, TIMCAL Graphite and Carbon, and the GnPs used were xGnP M5 from XG Sciences. The EBA-GnP-CB hybrids were compounded using twin screw extrusion. The total filler content was 5% (volume), with CB comprising 20wt% thereof. The filler content reported was preceded by optimization with respect the percolation threshold.[1] Thereafter, the nanocomposites were extruded using a 19/25D single-screw Brabender extruder using varying processing/flow histories, i.e. different screw types (compression screw (C) and Maillefer screw with a Saxton mixing unit (B)), temperatures (160 and 180°C) and (die) shear rates. The electrical conductivity of the extrudates was assessed in circuit using a two-point technique.[1] The rheological characterization of the extruded nanocomposites comprised small and large amplitude oscillatory shear (SAOS, LAOS), capillary rheometry, combined rheological methods and extensional rheological testing. Nonlinear rheological properties can be readily accessed through the use of LAOS combined with Fourier-transform (FT) rheology.[2] In contrast to linear viscoelastic experiments, nonlinear tests are more sensitive to the molecular makeup of the materials while at the same time being subjected to nonlinear conditions closer to processing flows. Dielectric analysis (DEA) quantifies molecular transport and relaxation processes via charged ions or dipoles present in the material. Such phenomena is influenced by the external mechanical constraints. Combined rheological methods, such as Rheo-DEA and DEA-DMTA, are therefore useful tools for simultaneous rheological and in situ molecular characterization. Finally, extensional rheological properties, in combination with SAOS and LAOS and the molecular stress function (MSF) theory are a very sensitive tool for understanding the behavior of long chain branched polymers.[3]

RESULTS AND DISCUSSION

The electrical conductivity of EBA-CB-GnP extruded hybrid nanocomposites was significantly influenced by the applied deformation history, i.e. screw type, and the Weissenberg numbers attained, $Wi = \lambda_1 \dot{\gamma}_a$, where λ_1 is the characteristic relaxation time of the polymer defined as the inverse angular frequency corresponding to the crossing between the dynamic moduli and $\dot{\gamma}_a$ is the apparent shear rate in the die. Given a flow history dominated by shear stresses (C-screw) and at $Wi < 20$, where orientation of the nanoplatelets is avoided, electrical conductivities of ca. 0.01 S/cm were recorded. More complex deformation histories (B-screw) appeared to generate distorted nanoplatelets[1] with typical conductivities as low as ca. 10-9 S/cm regardless of the Wi no. From rheological point of view, the EBA branching behavior can be observed observed from extensional rheological measurements,[3] as well as the instability transition sequences observed during extrusion flow in capillary rheometry. The strain-hardening behavior in extension is observed in both unfilled as well as filled samples, with a good prediction given by the Molecular stress function (MSF) theory, whereas the presence of fillers inhibits the onset of instabilities during extrusion. The third harmonic relative intensity, $I_{3/1}$, in the nonlinear viscoelastic regime and the corresponding dielectric loss, spectra time dependencies show however that under large amplitude oscillatory deformations conditions both deformation histories investigated (C-screw and B-screw) exhibit conductive behavior at $Wi = 0.07$ for the C-screw and $Wi = 0.14$ for the B-screw, corresponding to an increase in $I_{3/1}$. In the case of oscillatory tests the Weissenberg number was defined as $Wi = \lambda_1(\gamma_0 \omega)$, where γ_0 and ω are the applied deformation and angular frequency of the oscillation. In contrast, electrical conductivity was not achieved under SAOS conditions as well as in LAOS for nanocomposites containing an equivalent total filler content of GnP.

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