Available online at www.sciencedirect.com

ScienceDirect

Polymer 49 (2008) 2183–2196

polymer

www.elsevier.com/locate/polymer

Feature Article

Melt rheology of organoclay and fumed silica nanocomposites

Ph. Cassagnau [a,b,c,*]

[a] *Université de Lyon, Lyon, F-69003, France*
[b] *Université de Lyon 1, Lyon, F-69003, France*
[c] *CNRS UMR5223, Ingénierie des Matériaux Polymères: Laboratoire des Matériaux Polymères et Biomatériaux, University Claude Bernard Lyon 1, 15 Bvd Latarjet, F-69622 Villeurbanne, France*

Received 27 August 2007; received in revised form 18 December 2007; accepted 28 December 2007
Available online 5 January 2008

Abstract

The objective of the present work is to investigate, from the open literature, the recent developments in the rheology of silica and organoclay nanocomposites. In particular, this paper focuses on general trends of the linear viscoelastic behaviour of such nanocomposites. Hence, the variations of the equilibrium shear modulus and critical strain (limit of linearity), which depend on power laws of the volume fraction of particles, are discussed as filler fractal structure. In the third section, the strong nonlinearity behaviour (Payne effect) of filled polymers has been discussed in terms of filler nature. Typically two mechanisms arise to depict the linear solid-like behaviour and the Payne effect: particle–particle interactions is the dominant mechanism in fumed silica nanocomposites whereas particle–polymer interaction is the dominant one in colloidal silica nanocomposites at identical filler concentrations. However, these interactions are balanced in each nanocomposite systems by the silica surface treatments (chain grafting, silane modification) and the molecular weight of the matrix. Finally, we aim to unify the main findings of the literature on this subject, at least from a qualitative point of view.

We finally report on the thixotropy and modulus recovery after a large deformation in steady and dynamic shear conditions. Following this, the nonlinear rheological properties of nanocomposite materials have been discussed. The discussion is particularly focused on the effect of flow history (transient shear experiments) on the orientation–disorientation of clay platelets. Actually, the linear and nonlinear rheological properties are consistent with a network structure of a weakly agglomerated tactoids. As far as exfoliated clay nanocomposites are concerned, the inter-particle interaction is the dominant effect in the nonlinearity effect.

Keywords: Rheology; Silica; Organoclays; Nanocomposites

1. Introduction

A direct consequence of the incorporation of nanofillers in molten polymers is the significant change in the viscoelastic properties. Consequently, linear rheology is a way generally used to assess the state of dispersion of nanocomposites directly in the melt state. However, adding colloidal particles to polymers also affect the nonlinear behaviour and time dependent properties. For instance, the effect of strain-dependence of the dynamic viscoelastic properties of filled polymers, often referred as the Payne effect, is well known in elastomers since 40 years. During the past few years, intensive discussions have been hold on the rheology of nanocomposites filled with organically modified clays whereas the rheology of usual nanocomposites filled with silica particles, and more particularly fumed silica, seems to have been deserted. In particular, fumed silica is a finely divided amorphous silicon dioxide which can be seen at three main scales: primary particles of around 1–3 nm fused together in stable aggregates of around 100–250 nm which finally build up to large micron-sized agglomerates, generally named clusters. Due to the large surface area (50–400 m^2/g) of these particles, the inter-particle interactions have a major impact on the rheological and reinforcement properties of nanocomposites. Actually, this cluster structure can be viewed as an assembly of primary particles in a structure having

---

* Laboratoire des Materiaux Polymères et Biomateriaux, University Claude Bernard Lyon 1, 15 Bvd Latarjet, F-69622 Villeurbanne, France. Tel.: +33 4 72446208; fax: +33 4 72431249.
E-mail address: philippe.cassagnau@univ-lyon1.fr

0032-3861/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.12.035

a fractal dimension. Due to their fractal structure and their high specific area, fumed silica fillers are subjected to self-aggregation and can consequently form a network of connected or interacting particles in the molten polymer. As a viscoelastic result, polymer based nanocomposites exhibit a terminal plateau in the low frequency domain. Furthermore, the thixotropic nature of melt nanocomposites is also different from that of microcomposites at similar filler volume fractions.

With regard to organoclays silica nanocomposites, three layer organization scales are generally differentiated: (i) the clay layers have a micron-size scale in the polymer matrix in the case of weak interaction and/or none appropriate shearing conditions, (ii) few polymers chains are able to diffuse in the interlayer space, this structure is called intercalated, (iii) all the layers are homogenously dispersed as individual layers at a nanoscale, this structure is called exfoliated. Consequently, the exfoliation of organoclay layers increases the number of frictional interactions between layers, which is consistent with the formation a network structure of weakly agglomerated particles.

Since the rheological properties of nanocomposites are sensitive to the structure, particle size, shape and surface characteristics of the silicate phase, the rheological tool is intensively used to assess the state of the dispersion of nanocomposites directly in the melt state. A lot of papers, too many to cite them all, and reviews have been addressed to the rheology of filled polymers. The most recent review was addressed by Litchfield and Baird [1] on the rheology of high aspect ratio nanoparticles filled liquids. The main objective of our contribution is to review the viscoelastic behaviour of silica filled polymers and organoclay nanocomposites. In particular, this review focuses on linear (solid-like behaviour) and nonlinear viscoelasticity (Payne) including the thixotropy process of such composites. Actually, the exact causes of the typical viscoelasticity of nanocomposites are still a matter of investigations. This paper aims to unify the main findings of the literature on this subject, at least from a qualitative point of view.

2. Linear viscoelastic behaviour

Understanding the viscoelastic properties of nanocomposite thermoplastic polymers is of importance to get a fundamental knowledge of the process ability of these materials. At the same time, viscoelastic properties in the molten state are generally useful to determine the structure–properties relationships of these materials. As the filler nanostructure, the inter-particle and polymer–filler interactions can strongly influence both linear and nonlinear viscoelastic responses, rheology consequently appears to be a unique technique for the study of polymer nanocomposites. Few years ago, many authors have discussed on the connection which can be made between the filler morphology (structure, particle size) and the melt viscoelastic properties of polymeric materials. The theoretical understanding of the viscoelastic behaviour in the field of reinforced elastomers has been reviewed by Heinrich and Klüppel [2]. From cultural and industrial points of view, two main types of nanocomposites are generally distinguished in the scientific literature, namely elastomers (rubber) and thermoplastic composites. This difference stems from the difference in viscoelastic properties between these two types of polymers. Due to their respective viscoelasticity, the rheological developments for understanding purposes in each of these two types of nanocomposites, are generally quite different.

2.1. Fumed silica nanocomposites

Due to the small size and the high specific surface, fumed silica fillers are favorable to self-aggregation and consequently easily form three-dimensional network in molten polymer matrix. For example, Fig. 1 shows that the nanocomposite made up of unmodified silica particles (5 vol%) does not show any terminal flow zone, the elastic character of this suspension becomes predominant at low frequencies with the appearance of a secondary plateau ($G_0 \approx 3 \times 10^4$ Pa). Actually, nanocomposites filled with fumed silica show a solid-like behaviour response which includes a non-terminal zone of relaxation, apparent yield stress and a shear-thinning dependence on viscosity.

This particular rheological behaviour arises from the presence of a network structure. One argument [3] generally put forward to explain this phenomenon is that polymer chains are partly adsorbed on the filler surface and partly entangled with neighboring ones. This finding was supported by viscoelastic experiments showing that the low frequency modulus of the composites decreases spectacularly when the particles are chemically treated with organo-silane. However, the density of adsorbed chain (bound rubber) and their conformation at the filler surface are generally quite difficult to access. As for example, Aranguren et al. [3,4] determined by weight difference technique and by carbon analysis the bound rubber content of silica–PDMS suspensions. With regard to fumed silica, the adsorption of PDMS chains comes from the formation of hydrogen bonds between oxygen atoms belonging to chains sketelons and silanol groups on the surface of the

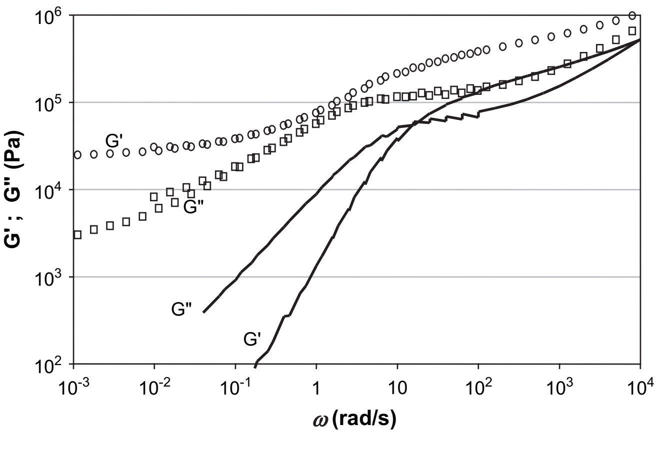

Fig. 1. Linear viscoelasticity of PS–fumed silica (5 vol%). Complex shear modulus versus frequency: master curves ($T_{ref} = 160$ °C). Open symbols: silica composite; full line: PS matrix ($M_n = 100,000$ g mol^{-1}, $I_p = 1.05$). Reprinted with permission from Polymer, Bartholome et al. [11].