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ScienceDirect

Polymer 49 (2008) 2183–2196

polymer

www.elsevier.com/locate/polymer

Feature Article

Melt rheology of organoclay and fumed silica nanocomposites

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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

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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

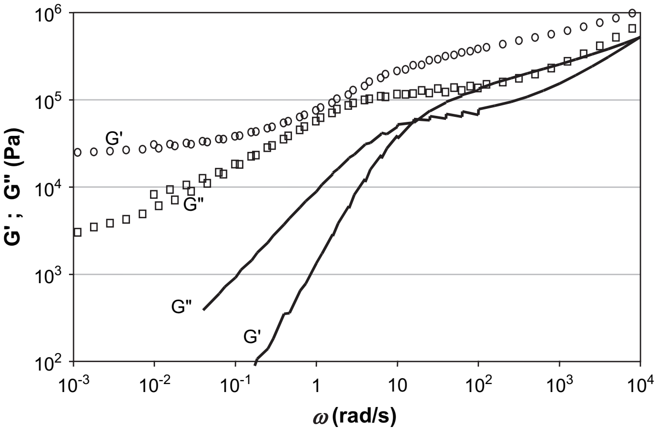

Fig. 1. Linear viscoelasticity of PS–fumed silica (5 vol%). Complex shear modulus versus frequency: master curves ($T_{ref} = 160$ °C). Open symbols: silica composite; full line: PS matrix ($M_n = 100{,}000$ g mol^{-1}, $I_p = 1.05$). Reprinted with permission from Polymer, Bartholome et al. [11].

fillers. The chain adsorption per unit area is proportional to the square root of the chain molecular weight [5–7]. Unfortunately, it is not possible to control the thickness and adsorbed density of the polymer layer around the particles and to properly establish the modeling approach. This point can be achieved in principle by grafting a polymer layer onto the surface of the silica particles to constitute model filled polymers. As for example, polybutylacrylate grafted silica nanoparticles [8] have been prepared by alkoxyamine-mediated polymerization, using a method of in situ of carbon radicals. Goel et al. [9] grafted styrene–acrylonitrile random copolymers to silica nanoparticles by in situ atom transfer radical polymerization (ATRP). The formation of the percolated filler network, even at low filler concentration (1.2 vol% SiO_2), was explained by the swelling of the corona chains by the matrix polymer that effectively form a percolated network. Nevertheless, this study was based on two samples only without any reference samples, i.e. samples filled with virgin silica. Furthermore, no discussion on silica dispersion in copolymers has been provided in this paper, therefore it is difficult to conclude on the origin of the gel-like behaviour of such nanocomposites. In a more comprehensive way, Bartholome et al. [10] used controlled radical polymerization by nitroxide-mediated polymerization (NMP) to elaborate well-defined nanocomposites with control polymer layer which can be grown with the desired thickness and composition. Polystyrene (PS) chains with molecular weights comprised between 15,000 and 60,000 $g\,mol^{-1}$ and narrow polydispersity were successfully grown from the surface of the silica nanoparticles by nitroxide-mediated polymerization. Note that the critical molecular weight entanglement of PS is $M_e \approx 18{,}000\ g\,mol^{-1}$. The linear viscoelastic behaviour of such nanocomposites, obtained by dispersing the grafted silica particles into a polymer matrix ($M_w \approx 100{,}000\ g\,mol^{-1}$) by a lyophilizing method, was characterized [11].

To summarize the combined effects of the length and the grafting density of PS chains, the storage shear modulus versus frequency are compared in Fig. 2. These results suggest a decrease of the size of the silica aggregates for PS–grafted silica in comparison to pure silica. Actually, by grafting polystyrene chains onto silica, there is a breakdown in the particle interactions because the grafted polystyrene chains create a steric repulsion between the silica particles. Regarding the influence of the grafted chain length on the viscoelastic behaviour, Fig. 2 shows that even a small amount (0.048 $\mu mol/m^2$ (sample 3)) of short chains ($M_n = 14{,}800\ g\,mol^{-1}$), with a molecular weight of the same order of magnitude than the molecular weight required for physical entanglements, is really effective to avoid the gel effect. However, when the grafting involves long chains higher than the critical molecular weight, the entanglement of these grafted polymer chains with the free chains of the PS matrix contributes to considerably increase the relaxation times of the terminal zone and even leads to the promotion of gel behaviour compared to short-grafted chains. Actually as concluded by the authors, two physical phenomena compete from a dynamic point of view: the first one concerns the existence of silica aggregate clusters and the second one is based on the modification of the relaxation times of PS chains. Finally, these model composites allow us to unify the main findings of the literature, a priori controversial. In the case of elastomers, i.e. polymers with long chains and some times with particular viscoelastic behaviour, the filler network appears to be a second order parameter affecting the viscoelastic response of the nanocomposite. On the contrary, the filler network is the first-order parameter of silica nanocomposite based on common thermoplastics, i.e. linear chains exhibiting a well-defined terminal relaxation zone in the frequency range possible to be experimentally investigated. From a general point of view, the main interesting result of these studies is the disappearance of the solid-like behaviour of the nanocomposite with increasing dispersion of the fumed silica from cluster structure (virgin fumed silica) towards primary entities. Note that the transmission electronic microscopy (TEM) clearly showed [11] that the micro-meter-sized domains of stringy-shaped aggregated silica particles are partly destroyed after polymer grafting and the silica particles appear regularly distributed within the polymer matrix.

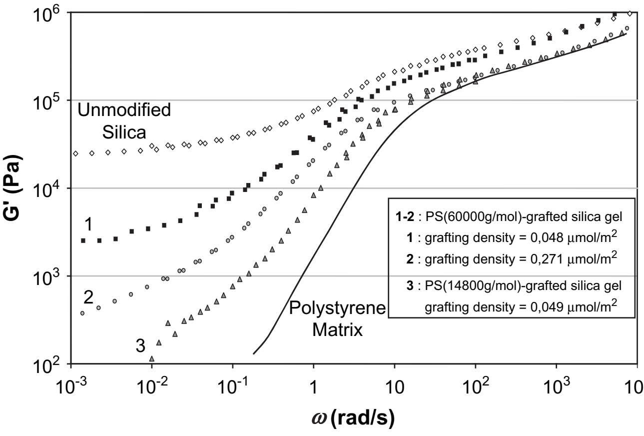

Fig 2. Storage modulus of PS nanocomposite filled with 5 vol% of silica and PS–grated silica master curve at $T = 160\ °C$. Reprinted with permission from Bartholome et al., Polymer, [11].

Furthermore, this study on model fumed silica must be compared with the work of Zhang and Archer [12] on the viscoelastic properties of colloidal silica nanocomposite materials. This work was based on narrow molecular weight distribution of poly(ethylene oxide) (PEO) containing colloidal silica nanospheres. The overall objective of this study was to determine how polymer–particle and/or particle–particle interactions influence the viscoelastic properties of nanocomposites. Due to the high surface energy of virgin silica, PEO chains are able to adsorb on the silica surface. Furthermore, it is well known that polymer molecules can adopt stretched configurations that allow them to simultaneously adsorb onto the surface of two or more particles thereby causing strong attractive interaction. Note that this mechanism is called depletion in colloidal particle suspensions. The authors observed that the viscoelastic behaviours of the nanocomposites are strongly dependent on the PEO matrix molecular weight. As a result, it can be observed a solid-like behaviour of the nanocomposite from the variation of the elastic modulus at low frequencies. In addition, this elastic modulus increases with the increase of the molar mass of the PEO chains. As silica particles are physically connected via adsorbed polymer molecules, the formed polymer–particle network is a temporary network. A priori a second relaxation zone could be expected at very low frequencies. Trapped PEO molecules may relax via their dissociation with silica particles and disentanglement (reptation) with other molecules. On the contrary, the viscoelastic response of nanocomposites filled with surface-modified silica by organo-silane is quite different as the complex shear modulus exhibits an apparent terminal relaxation zone. Actually, due to the surface modification of silica particles, the adsorption of PEO molecules on the surface is inhibited and therefore polymer–particle interactions are very weak. Finally, the authors concluded that the dominant mechanism in filler networking for spherical colloidal particles is due to the polymer–particle interactions resulting in a temporary polymer–particle network.

Finally, it can be concluded that, typically, two mechanisms arise to qualitatively depict the solid-like behaviour: the particle–particle interaction is the dominant mechanism in fumed silica nanocomposites whereas the particle–polymer interaction is the dominant one in colloidal silica nanocomposites at identical filler concentration. Obviously, these interactions are balanced in each nanocomposite systems by the silica surface treatment (chain grafting, silane modification) and the molecular weight of the matrix.

From a modeling point of view, when polymer–particle interactions dominate, conceptual models [13–15] based on the equilibrium structure of the reversibly adsorbed polymer chains on the particle surface and dynamic relaxation of polymer chains appear to be powerful to describe the linear viscoelasticity of colloidal nanocomposites.

2.2. Clay nanocomposites

The behaviour of the complex shear modulus offers valuable insight into the microstructural changes happening in melt nanocomposites filled with clay particles. Depending on the interaction between the components and the method of preparation combining chemistry and processing [16], different morphologies can be obtained when layered silicates are dispersed in polymers. In particular, two types of structures are obtained in polymer-layered silica nanocomposites, namely intercalated nanocomposites where the polymer chains are sandwiched between silicate layers and exfoliated nanocomposites, in this case the layers can be considered individually but remain more or less dispersed in the polymer matrix. A lot of papers have been published throughout the last years and it is unrealistic to review exhaustively the bibliographic references. Generally, rheological properties were determined to examine the degree of dispersion and exfoliation of organoclays and the linear dynamic mechanical properties of polymer–clay nanocomposite have been intensively studied [17–51]. More precisely, all of these papers reported an increase in shear viscosity and storage and loss moduli of the nanocomposites with increasing the clay concentration as shown in Fig. 3. Furthermore, a general rheological trend for nanocomposites studied in most of these papers is the appearance of a transition from a liquid-like behaviour to a solid-like behaviour, i.e. the apparition of a plateau (second plateau modulus) of the storage modulus at low frequency which is obviously higher than the loss modulus. Obviously, it is admitted that the increase of the clay concentration is driving this transition. Nevertheless, the influences of compatibilizing agent, polymer molecular weight and more generally interfacial properties on the linear viscoelastic properties are still open discussions [52]. Actually, the variations of the linear complex shear modulus are governed by the state of dispersion and exfoliation of clay platelets. As for example, Loiseau and Tassin [53] showed that the dispersion of laponite particles as individual entities in poly(ethylene oxide) matrix increases with the surface coverage of the particles. In particular, grafted chains appear more efficient than absorbed ones to reach the best exfoliated state. Galgali et al. [54] concluded that the rheological response of layered silicates arises from frictional

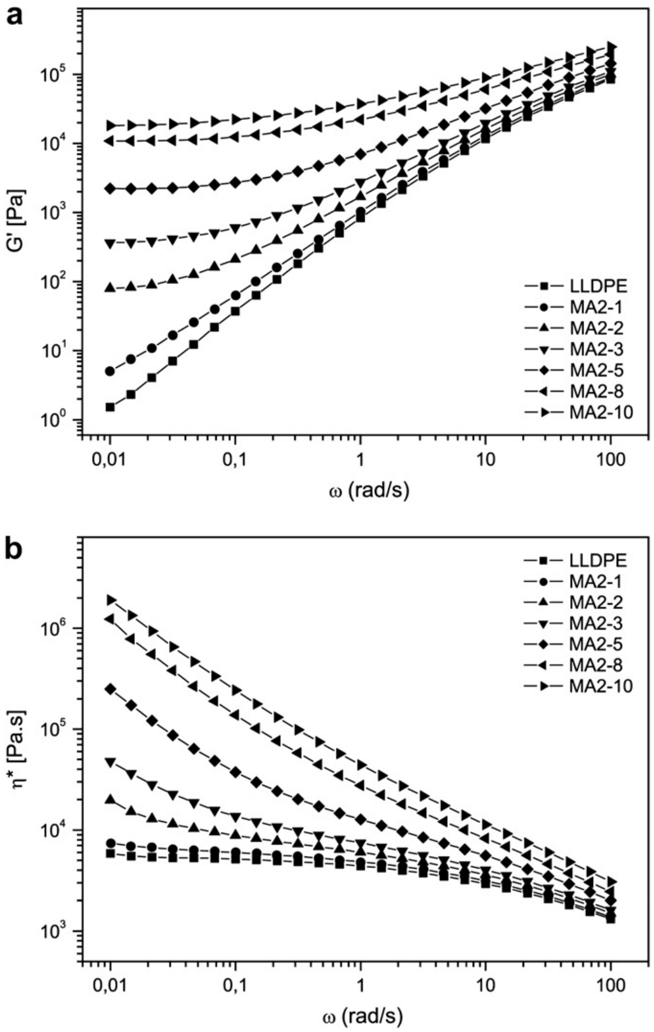

Fig 3. Viscoelastic properties of low density polyethylene (LLDPE) nanocomposites filled with different concentrations of organoclay (Cloisite 20A) using maleic anhydride grafted polyethylene as compatibilizer. Inset caption: MA-x means x phr of organoclay: (a) variation of the storage modulus $G'(\omega)$; (b) variation of the absolute complex viscosity $\eta^*(\omega)$. Reprinted with permission from Durmus et al., Polymer, [57].

interactions between the silicate layers and are not due to trapped or confined polymer chains between the silicate layers. In other words, a possible gelation in the entangled matrix is a second order parameter affecting the viscoelastic response, at least for the nanocomposites based on conventional polymers.

As a general point of view, the comparison of viscoelastic behaviour of fumed silica and clay nanocomposites leads to an apparent contradiction or paradox. Actually, the exfoliation of silicate layers increases the number of frictional interactions between the layers whereas the exfoliation of fumed silica (can we strictly use the term of exfoliation for spherical particles?) decreases the interactions between the primary silica particles. As a consequence, the percolation threshold, i.e. the filler concentration at which the transition from liquid-like to solid-like behaviour appears, decreases with increasing the exfoliation state of clay platelet fillers, whereas the percolation threshold increases with the dispersion of fumed silica at the scale of primary particles. This finding is absolutely logical and meaningful regarding the initial and final shapes after exfoliation of spherical and platelet fillers.

As a conclusion, if rheological analysis of nanocomposites offers a realistic picture to evaluate filler dispersion so that it can be used to quickly assess dispersion, a special care must be provided to the filler nature when performing and quantifying filler dispersion with rheological analysis. However, quantitative analysis of filler dispersion by rheological investigations are scarce in the literature. This is mainly due to the difficulties to model the variation of the linear viscoelastic properties depending on the filler concentration and exfoliation state. From a phenomenological point of view, Lertwimolnum and Vergnes [55] used a Carreau-Yasuda model with yield stress to describe the frequency dependence of the absolute complex viscosity $|\eta^*(\omega)|$:

$$|\eta^*(\omega)| = \frac{\sigma_0}{\omega} + \eta_0\left[1 + (\lambda\omega)^a\right]^{(n-1)/a} \tag{1}$$

where σ_0 is the yield stress, η_0 is the zero shear viscosity, λ is the relaxation time, a is the Yasuda parameter and n is the dimensionless power law index. The most interesting and important parameter is the yield stress σ_0 as it controls the increase of the complex viscosity at low frequency at constant clay concentration. Consequently, the authors related this parameter to the level of exfoliation in the nanocomposites, and consequently they were able to quantitatively study the effects of extrusion operating-conditions on the nanocomposite dispersion. Similarly, to quantify the clay dispersion by melt rheology, Vermant et al. [56] and Durmus et al. [57] used the power law dependence on the equilibrium storage modulus (see next section).

3. Percolation threshold and equilibrium storage modulus

Theoretically, the sol–gel transition for spherical particles without any interactions should be obtained at the close packing volume fraction of $\phi_c = 0.64$. From a practical point of view, the increase in the effective particle volume fraction due to particle swelling or clustering from inter-particle interaction, leads to a drastic decrease of ϕ_c. This phenomenon is generally observed for suspensions such as latex [58]. For example, the zero shear viscosity tends to infinity at volume fractions denoted by ϕ_m which are well below ϕ_c. The concept of sol–gel transition, defining the gel point or the percolation threshold can be derived to understand the rheology of cross-linked polymer network. The transition occurs during a random aggregation process of subunits into larger and larger molecules at macroscopic scales. Scaling relations have been developed to provide the divergence of the properties at the percolation threshold. Regarding filled systems, the long-range connectivity may arise from physical interactions instead of chemical bonds. Actually, the sol–gel transition for suspensions, in which the filler particles aggregate has the same features as chemical gelation, namely the divergence of the longest relaxation time and power law spectrum with a negative exponent [59]. As a result, at the percolation threshold, storage and loss moduli have the same power law frequency dependency: $G'(\omega) \propto G''(\omega) \propto \omega^{\Delta}$, where Δ is the relaxation exponent. Beyond the gel point, the material tends to behave as a Hookean solid, at low frequencies or large scales. Moreover, the loss tangent $\tan\delta$ ($\tan\delta = G''/G'$) is independent of the frequency and is given by: $\tan\delta = \tan(\Delta\pi/2)$. The importance of the gelation threshold for the description of the rheological properties of aggregating suspensions has led several researchers to consider models for particle networks based on percolation concepts [60,61]. Percolation models are concerned with the formation of cell spanning-percolating-clusters. Therefore, the properties in the vicinity of the percolation threshold can be identified by analogy with Φ_m.

Experimentally, it is more obvious to measure the sol–gel transition with the macroscopic dynamic properties than with static microscopic quantities, in particular the zero shear rate viscosity of the solution ($\eta_0 = \lim_{\omega\to 0} G''(\omega)/\omega$) and the equilibrium modulus ($G_0 = \lim_{\omega\to 0} G'(\omega)$). The growth of the equilibrium elastic modulus after the percolation threshold can be described as a function of the volume concentration ϕ by

$$G_0 \propto (\phi - \phi_c)^t \quad \text{for} \quad \phi > \phi_c \tag{2}$$

and similarly the viscosity as

$$\eta_0 \propto (\phi_c - \phi)^{-s} \quad \text{for} \quad \phi < \phi_c \tag{3}$$

Actually, the detection of the percolation threshold quantities such as η_0 and G_0, seem to depend on very difficult and precise criteria which cannot be validated experimentally. Note that in the case of latex suspensions, the exponent s can be correlated [58] with the exponent $[\eta]\phi_m$ of the Krieger-Dougherty equation [62]. However, we observed in a previous work on silica nanocomposites [63] that the predicted power law-dependency $G_0 \propto (\phi - \phi_c)^t$ with $t \approx 1.5$ is in agreement with some experimental results of the literature on carbon black filled natural rubber [64], ($t \approx 1.56$) and suspensions of silica by Yziquel et al. [65] and Rueb and Zukoski [61] ($t \approx 1.6 \pm 0.2$ and $t = 2.0 \pm 0.3$, respectively) which agree with the analogy of

De Gennes [66] who used a percolation model of a random conductor network ($t \approx 1.9$).

3.1. Silica nanocomposites

The fumed silica concentration (vol%) at the percolation threshold and the relaxation exponent on complex shear modulus were observed [63] as $\phi_c = 3.3\%$ and $\Delta \approx 0.5$, respectively. Furthermore, this percolation threshold was observed to be independent of the polymer chain regimes (entangled or Rouse regime). Inoubli et al. [67] observed in the case of polybutylacrylate nanocomposite filled with 2.5% of silica particles, that $G' \propto G'' \propto \omega^{0.5}$ in the intermediate part of the frequency spectrum. They reasonably estimated that 2.5% of the silica was very close to the percolation threshold. Moreover, Paquien et al. [68] concluded that the percolation threshold values are between 1 and 2% whatever the silica grafting ratio is (the silica surface was treated with different proportions using hexamethyldisilazane). However, the measurement of the percolation threshold is questionable in this work as the equilibrium conditions of the storage modulus were not strictly respected.

Though the calculation of the percolation threshold has not be done, Fig. 2 clearly shows that the percolation threshold strongly depends on the silica particle interactions. Actually, the trends of the storage modulus curves mean that the percolation threshold increases with the modification of the silica surface by polymer grafting. As far as fumed silica is concerned, the original silica network structure at the origin of the percolation threshold of the nanocomposite materials breaks down with steric repulsion. Consequently, the percolation threshold will be observed at higher concentrations.

As extensively reported in the literature, the elastic modulus scales with the volume fraction as following:

$$G_0 \propto \Phi^m \tag{4}$$

It is expected that this power law exponent depends on particle–particle interactions. Indeed, the elasticity should increase more rapidly as the network becomes more resistant to the suspensions composed of hydrophilic than hydrophobic silica. As for example Yziquel et al. [65], reported for suspensions in paraffin oil $m = 4.2$ and $m = 3.9$ for hydrophilic and hydrophobic silica respectively. Cassagnau [63] observed $m = 4.5$ for a suspension of hydrophilic silica in EVA copolymer. Paquien et al. [68] observed, for a silica suspension in PDMS, that m decreases for $m = 7.2$ to $m = 3.2$ depending on the silica surface treatment (from hydrophilic to hydrophobic). Zhu et al. [69] showed that $m = 3.2–3.4$ in the case of narrow polybutadiene filled with silica particle. Furthermore, this power law was observed not to be dependent on the polymer molecular weight. A priori, these findings seem to be in contradiction with the results found by Rueb and Zukoski [61] for colloidal gels which consist of sterically stabilized silica particles with different strengths of inter-particle interactions. Nevertheless, fumed and colloidal silica cannot be reasonably compared from a fractal structure point of view.

Furthermore, this scaling concept, based on a fractal dimension, is generally used to study the effect of inter-particle forces on the elasticity of aggregated suspensions [70–72]. To model the size dependence, the aggregates of silica particles are described as fractal structures with a characteristic size ξ which is the radius of the smallest particle containing N primary particles of radius a.

$$N(\xi) \approx \left(\frac{\xi}{a}\right)^{d_f} \tag{5}$$

with d_f the fractal dimension of the aggregate. Following this, the volume fraction of primary particles inside the aggregate is then:

$$\phi \approx \left(\frac{\xi}{a}\right)^{d_f - 3} \tag{6}$$

Finally, the variation of the equilibrium storage modulus versus the volume fraction of silica can be estimated according to the characteristics of the non-fluctuating fractal structure [73] as followed:

$$G_0 \propto \Phi^{5/\left(3-d_f\right)} \tag{7}$$

where d_f is the fractal dimension of silica clusters. Wolthers et al. [72] found $d_f = 2.25$ for stearyl-coated silica particles. Paquien et al. [68] observed a fractal dimension d_f equal to 2.3 for unmodified silica–PDMS composites. Furthermore, they demonstrated that the fractal dimension is very sensitive to the surface silica modification as d_f can decrease to 1.4. On the other hand, Piau et al. [73] for silica–silicone physical gel, and Cassagnau [63] for EVA/silica composite system, reported values close to 1.8. This great discrepancy between the reported data is mainly due to the different nature of the samples as well as to the different sample histories in these different experiments.

Heinrich and Klüppel [2] have considered an alternative network structure that refers to a space filling configuration of kinetically aggregated filler clusters: the cluster–cluster aggregation (CCA) model. This model is based upon the assumption that the particles can fluctuate around their mean position in a polymer matrix. Depending on the concentration of the filler particles, a flocculation process of particles or clusters leads to a filler network that can be considered as space filling configuration of fractal CCA clusters. From the calculation of the solid fraction of the fractal CCA clusters and assuming a rigidity condition for reinforcement of the polymer matrix, the authors derived the concentration dependence of the equilibrium elastic modulus:

$$G_0 \propto \Phi^{\left(3+d_{f,B}\right)/\left(3-d_f\right)} \tag{8}$$

where $d_{f,B} \approx 1.3$ is the fractal dimension of the CCA cluster backbone and $d_f \approx 1.8$ is the fractal dimension due to the characteristic selfsimilar structure of the CCA Clusters. Such an expression was already derived by Buscall et al. [74]. Eq. (8)

predicts a power law $G_0 \propto \Phi^{3.5}$ whereas experimental power laws $G_0 \propto \Phi^{4.2-7.2}$ were reported as previously discussed.

3.2. Clay nanocomposites

The threshold concentration of nanocomposites filled with organoclay platelets appears generally at concentration below 1 vol%. As for example, Loiseau and Tassin [53] obtained for well-defined laponite particles dispersed into a PEO matrix, the formation of a gel above a critical volume fraction of around $\phi_c = 0.2-0.4$ vol%, depending on the protection of the particles. Actually this critical concentration was observed to decrease when the particles are better dispersed thanks to their surface treatment. Durmus et al. [57] came to the same conclusion as they observed $\phi_c = 1.0-1.6$ vol% for LLDPE/montmorillonite (Cloisite 20A) nanocomposites depending on the compatibilizers used for the clay dispersion. Actually it is a clear fact that the type of surface treatment or compatibilizer of the particles play a crucial role on a rheological point of view since the rheological behaviour of such nanocomposites depends on the effective volume fraction due to their ability to form large anisotropic structures. These results are in opposition to fumed silica for which the critical threshold concentration is expected to increase with the dispersion of elementary particles. Actually, as previously explained, this is coherent with the formation of a gel through a network of aggregated particles.

On the other hand, Vermant et al. [56] reported a percolation threshold of $\phi_c = 1.1-1.6$ wt% for a polypropylene/montmorillonite nanocomposite and $\phi_c = 1.1$ wt% for a montmorillonite nanocomposite based on a heterophase polypropylene matrix. From a theoretical point of view, King et al. [75] equated the critical percolation threshold with the overlap of randomly oriented tactoids, taking into account the large transverse dimension of the tactoids. They predicted the percolation threshold to be 0.6 vol% or below of organoclay fraction which is consistent with the rheology data.

Above the percolation threshold, the equilibrium storage modulus exhibits a power law dependence on the filler concentration. As for example, Loiseau and Tassin [53] and King et al. [75] reported the following scaling laws $G_0 \propto \phi^{4.5\pm0.2}$ and $G_0 \propto \phi^{3.2}$, respectively. Vermant et al. [56] measured $G_0 \propto \phi^{4.8-6.0}$, depending on the polymer matrix and Durmus et al. observed $G_0 \propto \phi^{3.34-3.48}$ depending on the compatibilizer nature. These scaling laws are close, or at least of the same order of magnitude, to those previously reported on silica nanocomposites but the percolation threshold is much lower for organoclay based nanocomposites. Nevertheless, it must be pointed out that these power laws are generally measured at a lower constant frequency so G_0 may not be the true equilibrium elastic modulus. As a consequence, the accuracy and/or the validity of these power laws are generally questionable.

Among the different modeling approaches used to predict the power laws, some of them have been previously reported for silica nanocomposites. Vermant et al. [56] developed the Shih et al. model [76] as this model conceptually captures the structure of tactoid particle network. The following power law has then been derived:

$$G_0 \propto \phi^{(3+x)/(3-d_f)} \qquad (9)$$

where x is an exponent related to the filler volume fraction and the aggregate structure. The x depends on the number of tactoid particles per aggregate so that it could be linked to the degree of exfoliation. Actually, this power law is conceptually close to the CCA model (Eq. (8) with $x \equiv d_{f,B}$). Finally, Vermant et al. [56] and Durmus et al. [57] used this power law model to calculate d_f and x from experimental variation which allowed them to discuss on clay dispersion with more or less opened fractal structures.

4. Payne effect

The famous effect of amplitude dependence of the dynamic viscoelastic properties of filled polymers is often referred as the Payne [77] effect. Actually, the Payne effect was first reported for carbon black reinforced rubbers and extensively studied on silica elastomer composites. As previously discussed on the linear viscoelastic properties, the mechanism of reinforcement and nonlinearity can be based on two conceptual aspects. The concept of filler networking yields a good interpretation of the Payne effect for filled elastomers. For example, common features between the phenomenological agglomeration–deagglomeration and recent microscopical networking approaches (Particle–particle interaction) were discussed by Heinrich and Klüppel [2]. A direct experimental support for this concept was reported from electron microscopy studies [78] on elastically stretched chain-like aggregates of inorganic oxides. The concept of the temperature- and deformation-dependence of the modulus, as consequences of the variation of the topological constraint density (polymer–particle interaction) at the filler–polymer interface was reported by Maier and Göritz [79]. Sternstein and Zhu [80] suggested a common mechanism which is rooted in the macromolecular natures of the matrices as previously explained in Section 2. Their experimental results demonstrated that the nonlinearity effect is strongly dependent on the filler surface treatment as already suggested by Aranguren et al. [3].

If the Payne effect has been deeply studied for carbon black elastomers and silica nanocomposites, few works have been reported on the organoclays and the nonlinearity effect associated to tactoids fillers is generally poorly discussed. Furthermore, as nanocomposites show a thixotropic behaviour, the value of the maximum strain defining the linear region depends on the pre-shear (intensity and time) history of the composite so that rigorous experimental protocol must be applied.

As a consequence of the Payne effect, the limit of linearity γ_c decreases with increase in the volume fraction of particles according to the following power law:

$$\gamma_c \propto \phi^{-\nu} \qquad (10)$$

As previously discussed for the equilibrium shear modulus, Shih and co-workers [76] developed a scaling theory for this limit of linearity γ_c. The critical strain value follows:

$$\gamma_c \propto \phi^{-(1+x)/\left(3-d_f\right)} \tag{11}$$

As Eqs. (9) and (11) derive from the scaling theory, these equations are solved simultaneously (Vermant et al. [56] and Durmus et al. [57]) to give x and d_f. Note that the exponent x needs to exceed 1 for percolation to occur in the case of spherical particles. A lower value of d_f suggests a more open fractal structure. Nevertheless, due to the poor accuracy on the experimental determination of these exponents from Eqs. (4) and (9), it is generally difficult or at least hazardous to give a direct link with the degree of dispersion or exfoliation.

4.1. Fumed silica nanocomposites

Regarding silica particles, several experimental works reported exponent ν values. For liquid suspensions (low viscosity fluids), Rueb and Zuloski [61] observed that the exponent strongly depends on the inter-particle forces, and obtained ν values ranged from 0.7 to 4.0. Yziquel et al. [65] observed $\nu = 1.6 \pm 0.2$ for hydrophobic (R974 from Degussa) silica whereas no dependence of the linearity domain on silica concentration ($\phi \leq 7\%$) was observed for hydrophilic one (A200 from Degussa). Note that Shih et al. [76], for alumina suspensions, and De Rooij et al. [81], for latex suspensions of polystyrene observed $\nu = 2.1$ and $\nu = 2.3$, respectively. For polymeric suspensions, i.e. polymer nanocomposites, few power laws have been reported. According to works from Zhu and Sternstein [80,82], we found $\nu = 2.4$ and $\nu = 3.0$ for hydrophobic and hydrophilic silica, respectively. From our previous work [63] we calculated $\nu = 1.7$ as shown in Fig. 4.

Interestingly, Paquien et al. [68] observed, when the silica grafting ratio increases and the silica becomes more hydrophobic, that the Payne effect was reduced in PDMS/silica nanocomposite, i.e. the critical strain separating the linear and nonlinear regime increases with increasing the hydrophobic treatment of the silica. Such a result was also reported by Clement et al. [83] and Ramier et al. [84] who showed that the amplitude of the Payne effect is reduced by introducing a permanent treatment of the silica surface or by a processing aid.

From a theoretical point of view, few works on the modeling of the nonlinear viscoelastic behaviour, i.e. the variation of the complex modulus versus train, have been reported. Actually, two types of suspensions are generally concerned: suspensions in low viscosity fluids and suspensions in viscoelastic fluids, generally elastomers. Yziquel et al. [85], proposed for suspensions of fumed silica, a model able to predict the nonlinear viscoelastic behaviour, yield and thixotropic phenomenon. From a modeling point of view, when inter-particle interactions dominate, phenomenological models based on filler cluster breakdown and re-agglomeration appear to be adequate to describe this nonlinear viscoelasticity. Heinrich and Klüppel [2] reviewed these phenomenological models with more fundamental microscopic models of the nonlinear viscoelasticity of reinforced elastomers.

These models are based on the assumption that the microstructure of suspension or composites (filled elastomers) can be drastically modified under large deformations and the viscoelastic properties are then governed by the silica structure breakdown and build up. Consequently, the excess of dissipated energy is attributed to the breakdown of the particle structure. For elastomers, entanglement structure in the transition between filler surface and polymer bulk could, however, be an additional control, or even a dominant factor [80], of the energy dissipation.

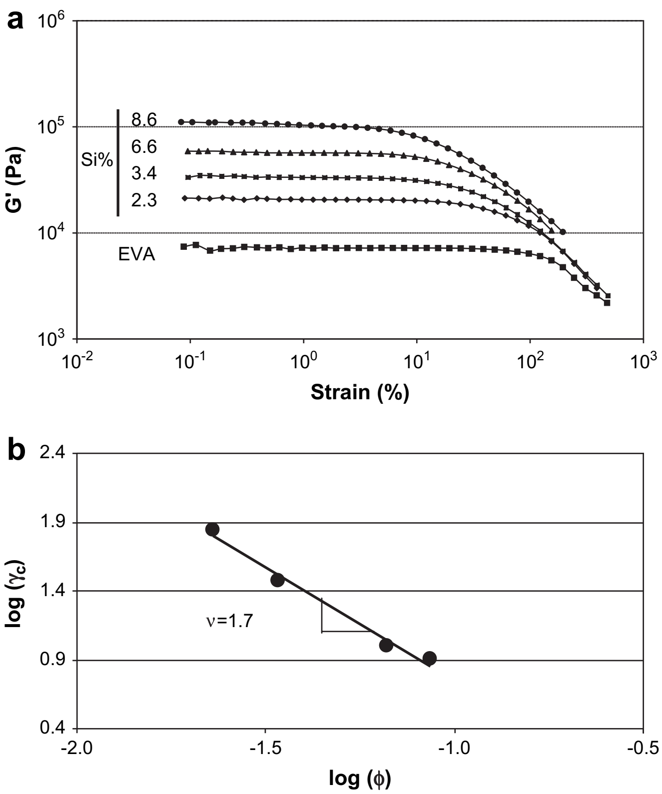

Fig 4. Payne effect in fumed silica composites. (a) Variation of the storage modulus versus deformation at different silica concentrations in a copolymer of ethylene and vinyl acetate; $\omega = 10$ rad s^{-1}, $T = 140$ °C. Reprinted with permission from Cassagnau and Mélis, Polymer, [98]; (b) Power law on the limit of linearity γ_c.

To conclude, the following general trend can be derived from this section. Silica particles and organoclays and, more generally, fillers whatever their nature (shape and chemical structure) obey the following power laws for the equilibrium shear modulus: $G_0 \propto \phi^4$ and for the limit of linearity $\gamma_c \propto \phi^{-2}$.

4.2. Clay nanocomposites

Only few works have recently been reported on the nonlinearity of clay nanocomposites. As expected, the maximum strain to which the linear viscoelastic domain extends was observed to be decreasing while increasing the clay concentration [86]. Aubry et al. [87] first observed $\gamma_c \propto \phi^{-1}$ in polyamide-12 layered silicate. Such a scaling relation was also reported by Devendra et al. [88] in the case of metallocene polyethylene montmorillonite composites. More recently, Durmus et al. [57] observed $\nu = 0.85-1.1$ in LLDPE/montmorillonite nanocomposites depending on the compatibilizer natures. Finally, Vermant et al. [56] showed $\nu = 1.8{-}1.9$ for the power variation of the limiting strain as a function of the particle concentration. Interestingly, Lertwimolnun and Vergnes [55] and Lertwimolnun et al. [89] showed that the linear viscoelastic domain, at the same concentration of organoclays, decreases with increasing the exfoliation degree of tactoids as shown in Fig. 5. This figure shows that the linear region depends on the processing conditions of the twin screw extruder. Consequently, the decrease of linear viscoelasticity can be attributed to the difference in the degree of dispersion and more precisely the degree of exfoliation. This result is of importance as it shows again that the linear viscoelastic properties of nanocomposites are governed by the particle–particle interaction of the tactoid physical network.

As a conclusion of this section, silica particles and organoclays and more generally fillers whatever their nature (shape and chemical structure) obey the following power law for the equilibrium shear modulus: $G_0 \propto \phi^4$. As far as the variation on the limit of linearity γ_c is concerned, two power laws can be distinguished according to experimental works: $\gamma_c \propto \phi^{-2}$ and $\gamma_c \propto \phi^{-1}$ for fumed silica and organoclays nanocomposites, respectively. These results mean that the fractal dimension $d_f \approx 2$ is universal for gel aggregate systems whereas x (or $d_{f,b}$), which is related to the number of particles per aggregates, strongly depends on the shape of fillers (spherical or tactoids). Note that these power exponents are extremely sensitive to the experimental criteria used by the authors. Nevertheless, most of the studies have been focused on the power law variation of both modulus and limit of linearity neglecting the importance of the front factor G_p of the power law on modulus ($G_0 = G_p\phi^m$). As discussed by Heinrich and Klüppel [2] G_p is the averaged elastic bending-twisting modulus of the different kinds of angular deformations of the cluster units. Actually, G_p depends on the dynamic relaxation regime of the polymer chains, and consequently, on the particle–particle and particle–polymer interactions. Consequently, a particular attention should be addressed to this front factor.

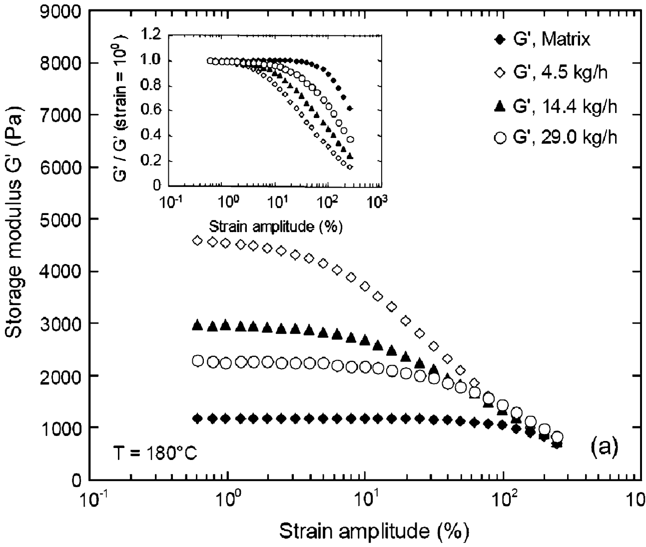

Fig 5. Strain-dependence of PP/montmorillonite nanocomposite on the exfoliation quality. From a processing point of view, the exfoliation degree is expected to decrease with the increase of the flow rate in the extruder. Reprinted with permission from Lertwimolnun and Vergnes, Polymer Engineering and Science, [55].

5. Thixotropy and recovery

Another important aspect in the mechanisms involved in the nonlinear viscoelasticity of filled polymers is the moduli restoration following the silica–polymer network destruction by a large strain perturbation. Actually, the Payne effect is a reversible process and the material should undergo a renewal of its original equilibrium structure. Under steady shear flow, the gel-like particle structure is disrupted, and it takes a long time to recover their original structures. This phenomenon, generally called thixotropy, is really a kind of viscoelasticity [90] but with typical relaxation times of a few hours. Different kinds of rheological experiments are used to quantify the thixotropic effects resulting from the presence of nanofillers.

Transient shear flow [28,29,91,92], stress relaxation [93] and creep [54] experiments have been successfully developed to investigate the evolution of the filler structure under flow. Note that stress jump experiments [94] is a useful method to study thixotropic suspensions. Furthermore, the transient stress in the start-up of steady shearing combining forward and reverse growth experiments, is also useful to characterize the evolution of the filler microstructures. The recovery of the gel structure is then studied by defining different rest times right after forward and reverse growth experiments [89,91]. The structural recovery can also be determined by measuring the linear viscoelastic properties after cessation of different pre-shear rates and applied rest times [95,96]. Under dynamic conditions, after a step-strain experiment the recovery of the complex shear modulus is measured in the linear domain of viscoelasticity. This experiment is generally called subsequent strain sweep experiments [97,98]. On the other hand, Zhu et al. [69] used oscillatory shear tests in the sequence of low, high and low amplitudes to study the Payne effect of silica nanocomposites. All these experiments in steady and/or dynamic conditions aimed to investigate the influence of the relevant parameters (polymer–filler interactions, polymer molecular weight, temperature, …) on the dispersion and orientation–disorientation of fillers under flow. From a modeling point of view, few quantitative works have been developed. As regards to colloidal suspensions, Yziquel et al. [85] proposed a structural network model based on a modified upper convected Jeffreys model with a single relaxation time and a kinetic equation describing the flow-induced network structure evolution. For clay nanocomposites, Lertwimolnun et al. [89] used two models initially developed for colloidal suspensions, the previously cited one [85] and a model on fiber suspensions based on an extension of the model used by Sepehr et al. [99] for the study of polymeric suspensions of short fibers. However, as pointed out by Lertwimolnun et al. [89] in their concluding remarks, improved or new models have to be developed to correctly describe the effects of reorganization and rest (recovery) resulting from particle–pacticle interactions in the case of anisotropic tactoids. Actually, one hypothesis of these models is based on Brownian motion of particles which governs the build up network at rest. If this hypothesis is acceptable for colloids spheres in low liquid fluids, it fails for tactoid particles in highly viscous polymeric medias.

5.1. Fumed silica nanocomposites

Under dynamic conditions, the strain amplitude dependence of the dynamic modulus is caused by a thixotropic change of the filler network structure. Such process is accompanied by the recovery of the complex shear modulus which is measured in the linear domain of viscoelasticity. Modulus recovery kinetics of elastomers filled with fumed silica have extensively been studied by the group of Sternstein [82,97]. They proposed that the recovery mechanism was entirely based on the dynamic of the filler–matrix interface and, consequently, on the physics of entangled chains. However, the agglomeration or network formation can be invoked especially at high filler concentration. In the same way, Kalfus and Jancar [100] showed that the modulus recovery time was governed by the chain relaxation processes in the polymer matrix near the filler surface. This process was successfully interpreted using the reptation concept of molten entangled chains. Consequently, filler agglomeration and/or network is less important as representing only a second contribution to the nonlinear viscoelastic response of a nanocomposite. Nevertheless, Zhu et al. [69] clearly showed that the particle–particle association was the dominant factor as the filler network broke down during the shear. In addition they observed that the particle–particle dissociation was partially and immediately recovered upon switching to dynamic linear deformation.

Furthermore, we reported in a previous paper [63] that the viscoelastic behaviour of fumed silica particles dispersed in an organic polymer solution, from diluted solution to molten polymer, and its nonlinear behaviour could be imagined [98] to be associated with both mechanisms of chain disentanglements and filler network breakdown depending on the silica concentration, silica surface treatment and deformation amplitude. This point was discussed earlier in Section 2 on linear viscoelastic behaviour and our findings confirmed the main conclusion of Bokobza [101], Sternstein and Zhu [80] and Sun et al. [102]. In other words, the nonlinearity effect is predominantly governed by the filler network breakdown (particle–particle interaction) combined with a second order mechanism originating at the polymer–filler interface (polymer–particle interaction).

Interestingly, for semi-crystalline polymers filled with fumed silica, we observed an additional particular behaviour [98]. Actually, the recovery of the complex shear modulus is not complete over a few hours. Indeed, Fig. 6 clearly shows that the linear equilibrium modulus will be never reached, even over geological times. Furthermore, Fig. 7a shows that complex modulus does not change anymore in the subsequent strain sweep. This hysteresis behaviour was not observed for composites based on amorphous polystyrene polymer and/or highly concentrated (∼30 wt%) semi-crystalline composite. Nevertheless, a new strain sweep experiment, after in situ crystallization and melting of the sample, led to a complete recovery of the modulus as shown in Fig. 7b. In other words, crystallization leads to a particular silica network structure in solid state which is not entirely spatially re-organized in the molten state under linear deformation perturbations. These results suggest that the silica network structure in molten state under linear deformation has the memory of the silica structure in solid state. The volumetric expansion of the composite at the melting transition does not allow a complete spatial isotropic recovery of silica network which is only achieved by the applications of large strain amplitudes as encountered in mixing conditions. This result clearly shows that the viscoelastic properties depend on the three-dimensional structure formed by the silica particles. Actually, this effect is well known in electrical-conductive composite polymers [103]. It is assumed to be due to the volume expansion of the thermoplastic matrix in the melting zone leading to the breakdown of the conductive paths of the filler network.

5.2. Clay nanocomposites

In the case of organoclays composites, the studies on thixotropy and recovery have been mainly developed from transient shear experiments. One of the main objective of these works was to study the origin of the tactoid disorientation process and the factors controlling it. As for example, Fig. 8a [89]

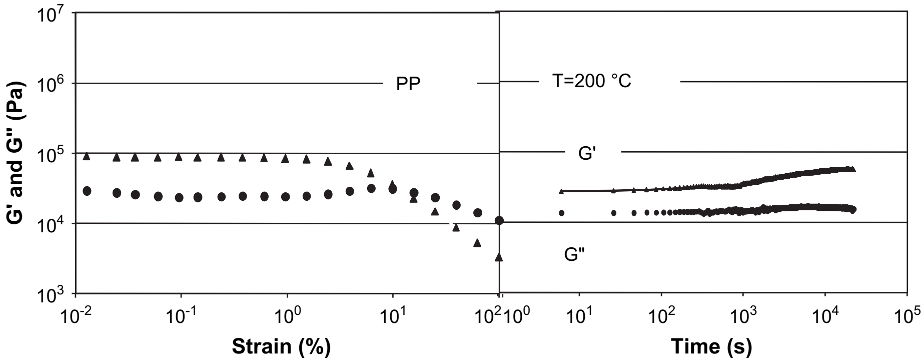

Fig. 6. Variation of the complex shear modulus versus strain amplitude ($\omega = 1$ rad s^{-1}) and its recovery versus time ($\omega = 1$ rad s^{-1} and $\gamma = 0.1\%$); PP filled with 16 wt% of fumed silica, $T = 200$ °C. Reprinted with permission from Cassagnau and Mélis, Polymer [98].

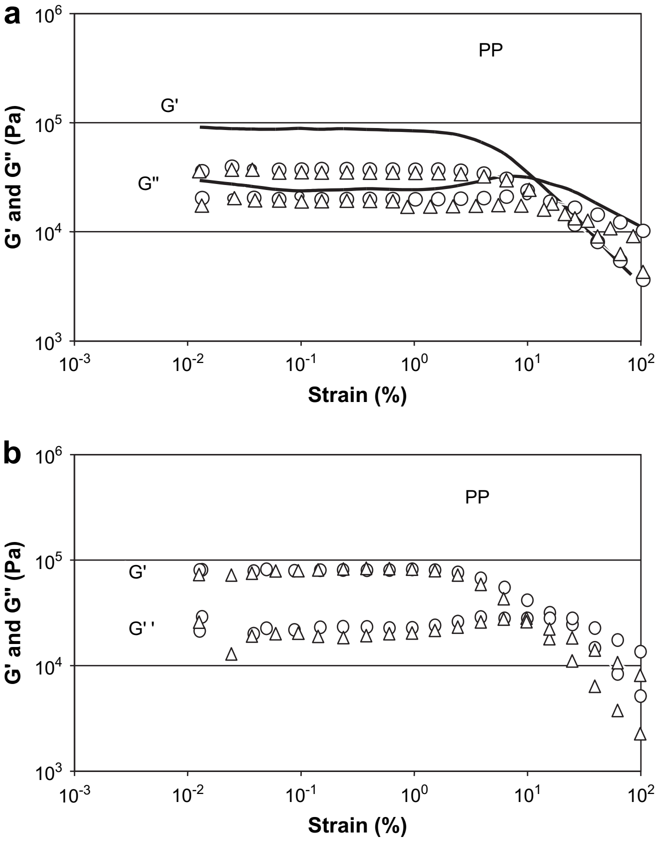

Fig 7. Subsequent strain sweep experiments. Variation of the complex shear modulus versus the strain amplitude; PP filled with 16 wt%, $T = 200$ °C. (a) Full line: first strain sweep experiment, (○): subsequent 1; (△): subsequent 2; (b) (○): subsequent strain sweep after in situ crystallization and melting compared with the first one (△). Reprinted with permission from Cassagnau and Mélis, Polymer [98].

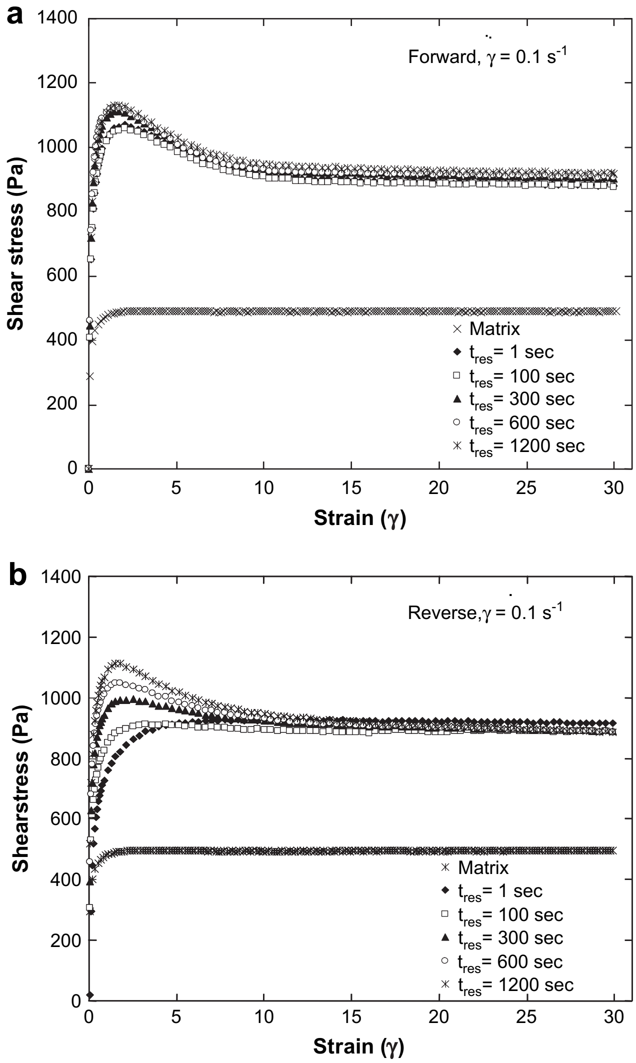

Fig 8. Shear transient experiments for polypropylene/montmorillonite (Cloisite 20A). $T = 180$ °C, $\dot{\gamma} = 0.1\ \mathrm{s}^{-1}$. (a) Forward start-up experiment showing the stress growth versus the applied strain. The different experiments show the reproducibility of the experiments. Actually, these experiments correspond to those used for the subsequent reverse start-up experiments (Fig 8b). Note that a new sample was used for each experiment. (b) Stress growth versus strain for reverse start-up experiments following the initial forward experiment (Fig 8a) after different rest times. Reprinted with permission from Lertwimolnun et al., Journal of Non-Newtonian Fluid Mechanics, [89].

shows a typical example of shear transient experiment. First, the stress overshoot can be actually attributed to the organoclay particles and not to the viscoelasticity of the polymer matrix itself. The existence of this overshoot is thus linked to the distribution of particle orientations in the hybrids and to the rupture of the network structure under flow. Furthermore, the dependence of the stress overshoot on the rest time is then a strong indication that the structure of the nanocomposites evolves. Fig. 8b clearly explains this dependence. Just after a short rest time (~1 s), the platelets are still oriented and the new start-up experiment does not show any overshoot. Increasing the rest times, the clay platelets progressively lose their orientation to return to their isotropic distribution and rebuild their network structure. Consequently, the amplitude of the observed stress overshoot increases with the rest time. The equilibrium rest time is thus the time to completely recover the initial structure of the platelets. This time is conceptually equivalent to a relaxation time. Indeed, Lele et al. [92] observed, in relaxation experiments upon cessation of shear, a relaxation time of approximately 1000 s close to the equilibrium rest time (~1200 s) observed by Lertwimolnun et al. [89] from transient start-up experiments. All the rheological studies [89,91,92,95,96,104–106] which prove the orientation of the clay platelets under shear flow well agree with the small-angle X-ray scattering studies on clay nanocomposites [92,106–109] showing that clay layers are oriented in shear flow with their major axis along the flow direction with their surface nearly oriented in the shear plane.

Possible mechanism for the structural evolution of the clay layer is the reorganization due to Brownian motion or strong thermodynamic interactions, i.e. particle–particle and particle–polymer interactions. All authors [89,91,92,95,105,106] agree with the fact that Brownian motion cannot be the driving force for such a network recovery because such relaxation processes could not occur sufficiently fast to account for the observed changes. Furthermore, Galgali et al. [106] showed that the polymer–particle interaction due to the immobilization of the confined polymer chains between the silicate layers is not the relevant process. Actually, the attractive interactions between the multi-platelet domains (inter-particle interactions) are the driving force for the structural evolution during the transient shear experiments and, more particularly, for the network recovery during rest time. Upon the flow cessation, attractive particle–particle interactions promote the reconstitution of the network.

Generally speaking, it is well known that the polymer–particle interactions, the surfactants and the melt viscosity of polymer matrix play an important role in dispersing and exfoliating organoclay aggregates. Note that the crystallization process [110] of semi-crystalline polymers can also play a determining role in the intercalation/exfoliation of clay in a polymer matrix. As for example, the presence of a compatibilizer plays a key role in influencing the rheological behaviour of nanocomposites. However, the governing parameter for the structural evolution of the clay network under shear flow is a priori the exfoliation degree which controls the structure of the platelet network. Recently, Wang et al. [95] showed, thanks to polybutadiene/clay nanocomposite systems, that the temperature could be a key factor controlling the exfoliation and orientation–disorientation of clay particles under flow. Actually, the polymer–clay interactions are temperature-sensitive. The system behaves as a system with a liquid–gel transition. This transition depends strongly on the end groups, the molecular weight of the liquid rubber and the shear field. The determination of the transition temperature is then very useful for the preparation of liquid rubber/exfoliated clay nanocomposites. At room temperature, the clay is partially exfoliated and complete exfoliation is achieved when heating above this transition temperature ($T \sim 80\ ^\circ\mathrm{C}$) with or without shearing. As discussed previously, in the case of usual nanocomposites, a shear flow induces a disorientation of the exfoliated platelets. Conceptually, Rueb and Zukoski [61] reported that such transition temperature for octadecyl silica particles in decaline. The phase diagram (depending on silica concentration) shows that the suspension is liquid-like at elevated temperatures as the silica particles are finely dispersed in the suspending liquid whereas the suspension is solid-like at low temperature since the suspension forms space filling gels. This rheological-temperature dependence behaviour is consistent with the previous polybutadiene/clay nanocomposite, similarly to a miscibility transition temperature. Actually, keeping in mind the apparent paradox on the rheology of silica and clays nanocomposite, silica suspensions behave as gel-like in the "nonmiscible domain" whereas clay suspensions behave as a gel in miscible domain (exfoliated domain). Vice versa silica suspensions behave as a liquid in miscible domain (particles individually and finely dispersed) whereas clay suspensions in nonmiscible domain (intercalated and not exfoliated clays) behave as a liquid.

6. Conclusion

Since the melt rheological properties of filled polymers are sensitive to the structure, particle size shape and surface characteristics of the fillers, rheology offers original means to assess the state of dispersion in the nanocomposites and to investigate the influence of flow conditions upon nanofiller dispersion itself. The objective of the present work was to discuss and to compare, from the open literature, the rheological behaviour of polymer composites filled with two usual fillers, namely, fumed silica and organoclays.

Generally speaking, fumed silica and organoclay nanocomposites both show a solid-like rheological response which include a non-terminal relaxation zone, an apparent yield stress and a strong nonlinearity behaviour (Payne effect). The power laws on the equilibrium elastic shear modulus G_0 and the limit of linearity deformation γ_c were investigated. Silica particles and organoclays and more generally fillers whatever be their nature (shape and chemical structure) obey the following power law (order of magnitude) $G_0 \propto \phi^4$ for the equilibrium shear modulus. Regarding the variation of the limit of linearity γ_c, two power laws can be distinguished according to experimental works: $\gamma_c \propto \phi^{-2}$ and $\gamma_c \propto \phi^{-1}$ for fumed silica and organoclay nanocomposites, respectively. These observations reinforce the idea that the moduli and the limit of linearity are related to the fraction of exfoliated layers or silica clusters which form a fractal structure. Actually, our discussion is consistent with works on elastomer reinforcements [111] and good rubber industry expertise on compounding in order to obtain optimal dispersion of fillers without completely suppressing their aggregation into larger structure. In other words, a fractal structure of fillers is required to get the best balance of reinforced properties.

Furthermore, the comparison of the viscoelastic behaviours of fumed silica and clay nanocomposites leads to an apparent paradox. Actually, both percolation threshold and limit of linearity decrease with increasing the exfoliation state of organoclay platelets whereas they increase with the dispersion of fumed silica by surface grafting of end-tethered chains. Actually, the exfoliation of organoclay layers increases the number of frictional interactions between the layers whereas the dispersion of fumed silica to the primary entities scale decreases the silica inter-particle interactions. Interestingly, such a trend is already observed for carbon nanotube (CNT) composites. Actually, the percolation threshold for NTC/polymer composites can range from 0.0005 vol% to several vol% [112] depending on the NTC "miscibility" in polymers, i.e. when improving dispersion of nanotubes by exfiolation of nanotube clusters. Note that specific and relevant discussions on the nanocomposites filled with NTC have recently been addressed [113,114].

The origin of the Payne effect, in the case of conventional fillers such as fumed silica, does not seem to be controversial anymore in the literature. Actually, common mechanisms that are rooted in the macromolecular natures of the matrices (entanglement–disentanglement of polymer chains) and the breakdown of silica aggregate are generally admitted. In the case of fumed silica nanocomposites, filler inter-particle interactions dominate the viscoelastic behaviours. As a consequence, the rupture of the filler network is the first-order mechanism in the Payne effect. On the contrary, the polymer–particle interactions which lead to a strong modification of the chain relaxation process is the dominant mechanism with colloidal silica at identical filler concentrations. The mechanism of disentanglement–entanglement should be the dominant one in the Payne and thixotropy (modulus recovery) effects with spherical colloidal nanocomposites. Of course, the respective contribution of each mechanism to the linear and nonlinear viscoelastic properties of such nanocomposite is balanced by the silica surface treatments (polymer chain grafting or organo-silane treatment). This finding means that the linear and nonlinear rheological properties are consistent with a network structure of weakly agglomerated particles (particle–particle interactions) combined with a mechanism of polymer chain relaxation at the filler surface vicinity governed by the polymer–particle interactions. However, the filler–filler interaction is the predominant mechanism in most of the cases reported in the literature.

All authors agree with the network breakdown mechanism in the case of organoclay fillers. Transient shear experiments clearly proved this finding as the attractive interactions between the clay platelet domains (inter-particle interactions) are the driving force of the structural evolution during transient shear experiments, particularly for the network recovery during rest time. Upon flow cessation, attractive particle–particle interactions promote the reconstitution of the network. Furthermore, it must be pointed out that Brownian relaxation processes do not significantly contribute to the nanocomposite rheological response.

On the other hand, we demonstrated that a third contribution to the breakdown-recovery mechanism could be arose from the volumetric expansion of the polymer matrix at the melting transition of semi-crystalline polymers.

Finally it can be pointed out, that the nonlinearity properties and the studies of flow-induced structures in organoclay composites are generally investigated from transient shear experiment whereas dynamic experiments are generally used to study the nonlinearity effects in silica nanocomposites. Actually, this trend stems from the origin of the viscoelasticity of the polymer matrix used in both types of nanocomposites. The filler concentration may be another traditional aspect. Apart from suspensions applications (coating, painting, …), one on the main development of silica particles is the reinforcement of elastomers which generally show complex viscoelastic properties in the terminal relaxation zone combined with a strong temporary elasticity. Consequently, transient shear experiment or dynamic experiments combined with pre-shear conditions can hardly be envisaged.

Acknowledgements

The author would like to thank Dr. Vergnes and Dr. Durmus for providing some of their original figures. G. Martin is gratefully acknowledged for insuring the English corrections.

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