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# Payne effect and shear elasticity of silica-filled polymers in concentrated solutions and in molten state

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**Abstract**

The viscoelastic properties of silica-filled copolymer in concentrated solutions and melts were investigated. A wide variety of rheological observations, such as Payne effect, percolation threshold and elastic effects, of non-porous silica dispersed in a ethylene vinyl acetate copolymer (EVA, 60 wt% of vinyl acetate) were studied in the molten state or diluted solutions in xylene. The concept of the filler network breakdown seems to be adequate in describing the strain-dependence of dynamic mechanical properties. Nevertheless, the degree of non-linearity was found to be the highest for the highest dilution. It appears for silica concentration lower than the percolation threshold of the filler suggesting another mechanism associated with trapped entanglement. On the other hand, we observe a silica content ($\Phi_c = (3.3 \pm 0.1) \times 10^{-2}$) for the onset of a gel-like behaviour in the terminal zone. This critical level, defined as the percolation threshold, appears to be independent of EVA dilution in xylene. Furthermore, this liquid–solid transition can be expressed in the same general relaxation patterns as chemical gelation systems with a self similar behaviour at the rheological gel point. However, the universal properties of percolation are not properly described and elastic effect are better depicted by the cluster–cluster aggregation model. On the other hand, the concentration-dependence of the equilibrium storage modulus of EVA at different dilutions in xylene yields evidence of a screened effect of copolymer chains in the entangled regime ($\varphi \geq \varphi_c$) of elastic bending–twisting interaction between filler particles.
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*Keywords:* Payne effect; Percolation; Viscoelasticity

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## 1. Introduction

The addition of filler in elastomers usually leads to improve or modify the physical properties of rubbery materials. In particular, the incorporation of filler in rubbers is the significant change in the dynamic properties. As reviewed by Heinrich and Klüppel [1], the theoretical understanding of filled elastomer has been extensively treated that now a connection can be made between the filler morphology (structure, particulate size) and the viscoelastic properties of rubber materials. The effect of amplitude-dependence of the dynamic viscoelastic properties of filled rubbers, often referred as the Payne effect [2], has been also extensively investigated these last years. Payne found that the three-dimensional structure network constructed by the aggregation of carbon black significantly alter the dynamic viscoelasticity properties of rubbers. Furthermore, rheological experiments [3,4] have shown that melt polymers filled with fine particles exhibit a well defined yield stress, i.e. a stress below which there is no flow or the appearance of a plateau in the storage modulus at low frequencies in a dynamic deformation experiment. The existence of this behaviour in its physical meaning is correlated with the density and strength of a structure formed by the interaction between the filler particles. The concept of filler networking yields a good interpretation of the Payne effect for filled compounds. A direct experimental support for this concept was recently reported from electron microscopy studies [5] on elastically stretched chain-like aggregates of inorganic oxides. These results clearly show that the networking structure effects of the filler promote the Payne effect primarily. Nevertheless, the mechanisms for reinforcement and non-linearity remain controversial. For example, Sternstein and Zhu [6] reported that the non-linear viscoelastic properties of the nano-filled polymer melts bear striking similarity to what is observed in filled rubbers

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suggesting a common mechanisms that is rooted in the macromolecular natures of the matrices. The molecular weight of the matrix, the entanglements characteristics of the polymer and trapping of polymer chain loops at the filler surface appear to be the primary factors determining the non-linear viscoelasticity.

On the other hand, adsorption of polymers on the particles should play a role in the stability and viscoelastic response of inorganic particles dispersed in polymer aqueous solutions [7]. For example, Kawaguchi et al. [8] performed rheological measurements of Aerosil silica suspensions in aqueous solutions of (hydroxypropyl)methyl cellulose (HPMC) that absorbs onto the silica particles as a function of the concentration on silica, HPMC molecular weights and its adsorption kinetics on silica.

However, only a few works have been reported on the viscoelastic behaviour of inorganic particles dispersed in polymer organic solution from diluted solution to molten polymer. Furthermore, there is little information regarding non-linear viscoelastic properties at low filler concentration around the percolation threshold. In this paper, in order to have additional and complementary information of role of the silica dispersed in such media, rheological measurements have been performed by varying the fraction of silica and concentration of polymers. This paper deals with the characterization of the Payne effect, percolation threshold and elastic effects of non-porous silica dispersed in ethylene vinyl acetate copolymer (EVA, 60 wt% of vinyl acetate) diluted in xylene.

## 2. Experimental part

### 2.1. Materials

Non-porous Aerosil 130 silica (Degussa AG, Germany) with a surface area of 130 $m^2/g$ and a primary particle diameter of 16 nm was used as the inorganic filler and cleaned at 300 °C before use.

*p*-Xylene purchased from Aldrich was used as a solvent (polymer diluted solution) without further purification.

EVA was kindly supplied by Dupont de Nemours. The amount of acetate groups contained in this copolymer is about 60 wt% and this EVA copolymer was named EVA60 for the present study. Molecular weights were measured by size exclusion chromatography in tetrahydrofuran (THF) at room temperature using polystyrene standards. The molecular weights of this copolymer is as follows: $M_w = 138,000$ g/mol and $M_n = 30,000$ g/mol. The EVA copolymers are generally assumed to be amorphous for vinyl acetate concentration higher than 40 wt%. However, we observed from dynamic rheological experiments that EVA60 exhibits a slight crystallinity effect for temperature lower than 50 °C.

### 2.2. Samples preparation

The EVA60–silica melt samples were prepared by mechanical mixing in a internal mixer (Rheomixer 600 from Thermo-Haake) at 160 °C for 10 min at the rotational speed of 50 rpm of the counter-rotative blades. The collected molten materials were compression-moulded into 1 mm-thick plates by hot pressing at 150 °C under 100 bar for 20 s.

The EVA–silica–xylene diluted solutions were prepared in a vessel as follows: EVA was first dissolved in xylene at 50 °C. 24 h later, the amount of silica was added in the EVA–xylene solution and manually mixed at room temperature. The rheological experiments were then performed 24 h later after a last manual mixing of the solution just before the experiment.

The concentration of EVA in xylene and the concentration of silica in melt EVA or in diluted EVA are expressed by volume taking into account the following densities at room temperature: $\rho_{\mathrm{Xylene}} = 0.866$; $\rho_{\mathrm{EVA60}} = 1.04$; $\rho_{\mathrm{silica}} = 2.22$.

### 2.3. Rheological measurements

Dynamic measurements were performed using a Rheometrics strain-controlled (RMS800) and a stress-controlled (SR5) rheometers. EVA60–silica melt samples were analysed by the strain-controlled rheometer at different temperatures and plotted in a master curve at the reference temperature $T = 140 \pm 0.5$ °C using the time–temperature superposition principle. EVA–xylene–silica diluted samples were analysed by the stress-controlled rheometer using a plate–plate geometry at the temperature $T = 21 \pm 1$ °C. The measurement system was modified with an aluminium cover to limit solvent evaporation. The testing of non-linear behaviour of all the samples were performed using the strain rheometer in the range of deformation from 0.1 to 1000%.

## 3. Results and discussion

The adsorption of homopolymers with different chemical structures onto silica surfaces have been performed and have led to common conclusions that the polymer molecules preferentially adsorb to the surface. For example, Botham and Thies [9] reported that polystyrene were desorbed by EVA copolymer and that EVA copolymers with higher vinyl acetate content replaced those with lower content in trichloroethylene solvent. Furthermore, the rate of polymer displacement is completed within 5 h. It can been then concluded, for our present system, that the adsorption of EVA60 chains on silica in a non-polar solvent such as xylene is fast and completed in few minutes. Furthermore, when concentration of silica and polymer increased, chain entanglements and polymer bridging can occur leading to further enhancement of rheological responses [8] of the silica suspensions. Actually, it is well known [10] that a fundamental distinction exists between dilute polymer solution and more concentrated solutions where the chains are entangled ($c^*$ theorem). Consequently, the terminal viscoelastic parameters are strongly affected by the concentration $\varphi$ of the polymer in the solution. The critical entanglement onset $\varphi_c$, i.e. the transition point between Rouse and entanglement behaviour depends on the critical molecular weight in zero shear viscosity $M_c$ as:

$$\varphi_c = \left(\frac{M_c}{M_w}\right)^{1/1.25} \tag{1}$$

with $M_w$ the mass molecular weight of the polymer, $M_w = 138{,}000$ g/mol, and with $M_c = 2M_e$ where $M_e$ is the molecular weight between two entanglements. $M_e$ can be calculated from the plateau modulus using the Ferry formula [11]:

$$M_e = \rho \frac{RT}{G_N^0} \tag{2}$$

In the present study $G_N^0$ was measured by a method derived by Fulchiron et al. [12] of extrapolation of the storage modulus from the calculation of relaxation time distribution $H(\tau)$ :

$$G_N^0 = (5.0 \pm 0.2) \times 10^5 \text{ (Pa)} \tag{3}$$

The melt density at 140 °C of the EVA60 is about 1. Thus, the deduced value of $M_e$ is of the order of 13,500 g/mol and consequently:

$$\varphi_c \approx 0.16 \tag{4}$$

Then, one can expect a quite different behaviour of EVA-xylene-silica samples at the concentrations below or beyond $\varphi_c$. The following concentrations of EVA60 diluted in xylene were prepared as discussed in Section 2: $\varphi = 0.075$, 0.12, 0.16, 0.22 and 1.

### *3.1. Payne effect*

The Payne effect refers to the effect of strain-dependence of the dynamic viscoelastic properties of filled polymers in amorphous state above $T_g$. For a specific frequency, the storage modulus decreases with increasing deformation from a linear plateau value to a lower plateau at high amplitude of the deformation, whereas the loss modulus exhibits a pronounced peak. Fig. 1(a)–(c) shows the Payne effect at different silica fractions for the following EVA/xylene compositions: 100/0, 22/78 and 7.5/92.5, respectively.

The storage modulus is less strain-dependent in the low strain region for $\gamma < 1\%$, whereas a strain-dependence behaviour occurs over two decades at high strains. For the EVA concentrations below the entangled regime, Payne effect is still observed even at low concentration of silica particles ($\Phi < 3.3$ vol%) below to the percolation threshold as calculated later. This observation evidences that the non-linear behaviour associated with trapped entanglement cannot be considered as relevant here. Indeed, the Payne effect is observed for non-entangled dilution. Moreover, the non-linear behaviour associated with break down of particle network cannot be invoked, as Payne effect is observed at silica concentration far below the percolation threshold. Actually, the non-linear behaviour can be imagine associated with both mechanisms of chain disentanglements and filler breakdown depending of silica concentration and amplitude deformation. Indeed, the degree of non-linearity increases continually with filler concentration for filled

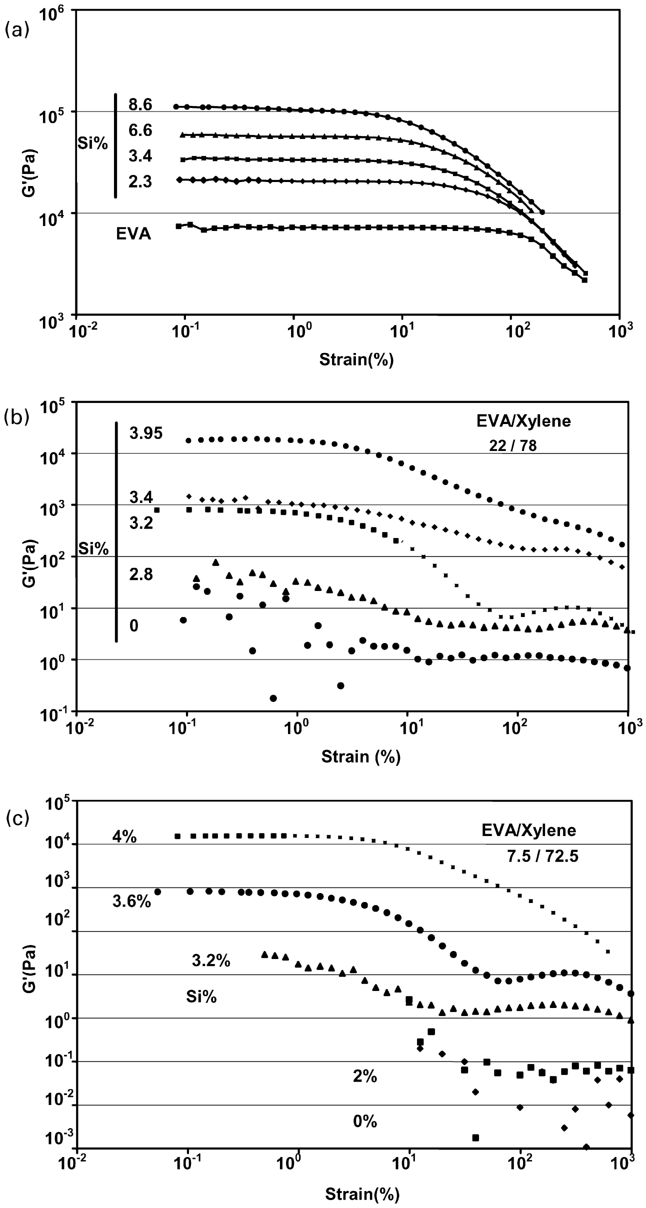

Fig. 1. Payne effect, variation of the storage modulus versus deformation at different silica concentrations. $\omega = 10$ rad/s (a) EVA/xylene: 100/0, melt EVA, $T = 140$ °C, (b) EVA/xylene: 78/22, $T = 21$ °C, (c) EVA/xylene: 92.5/7.5, $T = 21$ °C.

molten EVA (Fig. 1(a)) whereas, the degree of non-linearity seems to be constant for diluted solutions whatever the concentration in silica (Fig. 1(c)) and concentrations in polymer below $\varphi_c$ (Fig. 2).

Furthermore, a singular behaviour is observed at strains above 10% for diluted solution of EVA in xylene. Usually, a sigmodal decline is observed leading to a lower plateau at high deformations. Fig. 1(c) shows that for diluted solution the storage modulus slightly increases for deformation higher than 100% and goes through a maximum around 300% before decreasing again. However, this behaviour is less pronounced for concentrated solution ($\varphi \geq \varphi_c$) as the amplitude dependence of the storage modulus only exhibits a shoulder around 300% (Fig. 1(b)). It can be pointed out that same trends were observed for the variation of the loss modulus. This singular behaviour could be explained by a re-arrangement of the filler particles in the flow direction after the break down of the equilibrium filler network. However, another explanation could be the stress-induced debonding of polymer chains from the filler surface at high deformation.

### 3.2. Percolation threshold

The concept of sol–gel phase transition or gel point was extensively used for understanding the rheology of crosslink polymer networks. The transition occurs during a random aggregation process of subunits into larger and larger molecules. Scaling relations have been developed to provide the divergence of the properties at the percolation threshold [13]. On the other hand, the long-range connectivity in the filling material may arise from physical interactions instead of from chemicals bonds. The liquid–solid transition for suspensions in which the filler particles aggregate into sample spanning complexes have the same features as for chemical gelation, namely the divergence of the longest relaxation time and power law spectrum with negative component [14].

Experimentally, it is more obvious to measure the sol–gel transition with the macroscopic dynamic properties than with static properties, in particular the zero shear rate viscosity $\eta_0$ of the media and the equilibrium modulus $G_0$. Indeed, the detection of the gel point quantity such as $\eta_0$ seems to depend on very difficult and precise criteria which cannot be experimentally validated. Furthermore, it is rash to apply zero shear predictions to measurements which have been performed at non-zero shear rates. On the other hand, oscillatory dynamic experiments in the domain of the linear viscosity are the suitable methods to study the viscoelastic behaviour due to particle interactions because they directly probe these interaction without any influence of the flow field imposed in steady shear experiments. As a consequence, the self-similar regions of the composite were examined at different length scale by measuring the complex shear modulus at various concentration of silica. Furthermore, it can be expected that the liquid–solid transition manifests in the same general relaxation frame as chemical reaction, with a self-similar relaxation time spectrum at the gel point. Such transition was reported by Castellani and Lomellini [15] for rubber particles dispersed in acrylonitrile–butadiene–styrene (ABS).

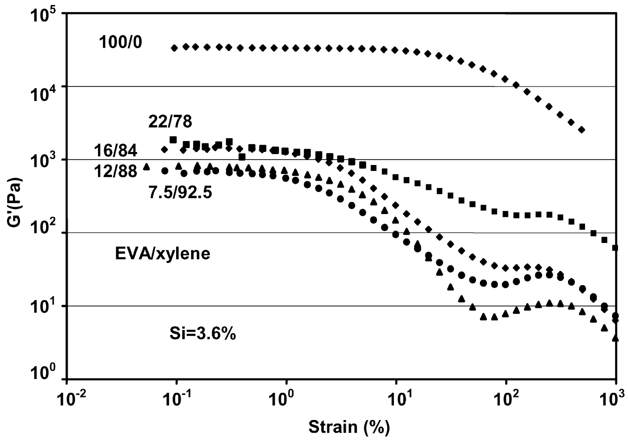

Fig. 2. Payne effect, variation of the storage modulus versus deformation at different EVA dilution (EVA/xylene). Si = 3.6%.

The variation of the complex shear modulus versus frequency for EVA/Si and EVA/Xylene (22:78 and 7.5:92.5) composites are shown in Fig. 3(a)–(c), respectively. In order to clarify these figures, three complex shear modulus ($G'$ and $G''$) curves are plotted describing the rheological behaviour of the composite far below the gel point, around the gel point and far beyond the gel point. Furthermore, Fig. 4(a)–(c) shows the variation of tan $\delta$ versus frequency for a filled molten EVA and diluted EVA/Xylene composites at different silica concentrations. Below the gel point one still observes at low frequencies the classical liquid behaviour ($G''\alpha\omega^1$ and $G''\alpha\omega^2$) and tan $\delta$ is a decreasing function of the frequency. However, the main feature of the storage modulus below the gel point, as shown in Fig. 5(a)–(c), is the appearance of an intermediate elastic plateau in the low frequency region followed by a decrease toward lower frequencies. That is the signature of an additional process of relaxation due to an adsorption of polymers chains on the silica surface. Vignaux-Nassiet et al. [16] studied the rheological behaviour of narrow polybutadiene samples filled with rigid silica spheres of 3 μm diameter. The results have been interpreted by an adsorption of polybutadiene chains on the silica surface that creates a mono-molecular layer whose thickness is comparable to the bulk radius of gyration of the chains and whose relaxation time scales in the same way as branches of star polymers. Nevertheless, it can be pointed out that the silica structure developed in the present study from nano-particles is quite different of silica structure from individual spheres with a diameter of few microns. Transmission Electronic Microscopy (TEM) allowed us to visualise the scale of segregation of silica particles at different concentrations in EVA melt samples. Fig. 6(a)–(c) clearly shows that silica aggregates in clusters. Furthermore, Fig. 6(c) shows that the

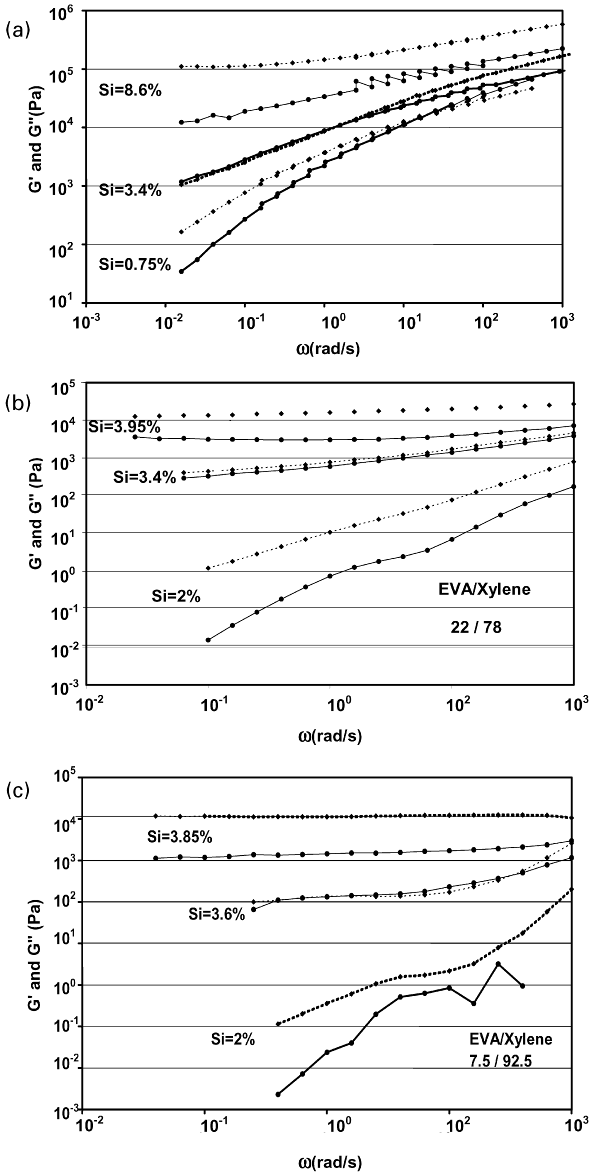

Fig. 3. Variation of the complex shear modulus at different silica concentrations for different EVA dilutions. Power law at the gel point. $G'$ : (●, full line) and $G''$ : (◆, dotted line) (a) EVA/xylene: 100/0, melt EVA, $T = 140$ °C, (b) EVA/xylene: 78/22, $T = 21$ °C, (c) EVA/xylene: 92.5/7.5, $T = 21$ °C.

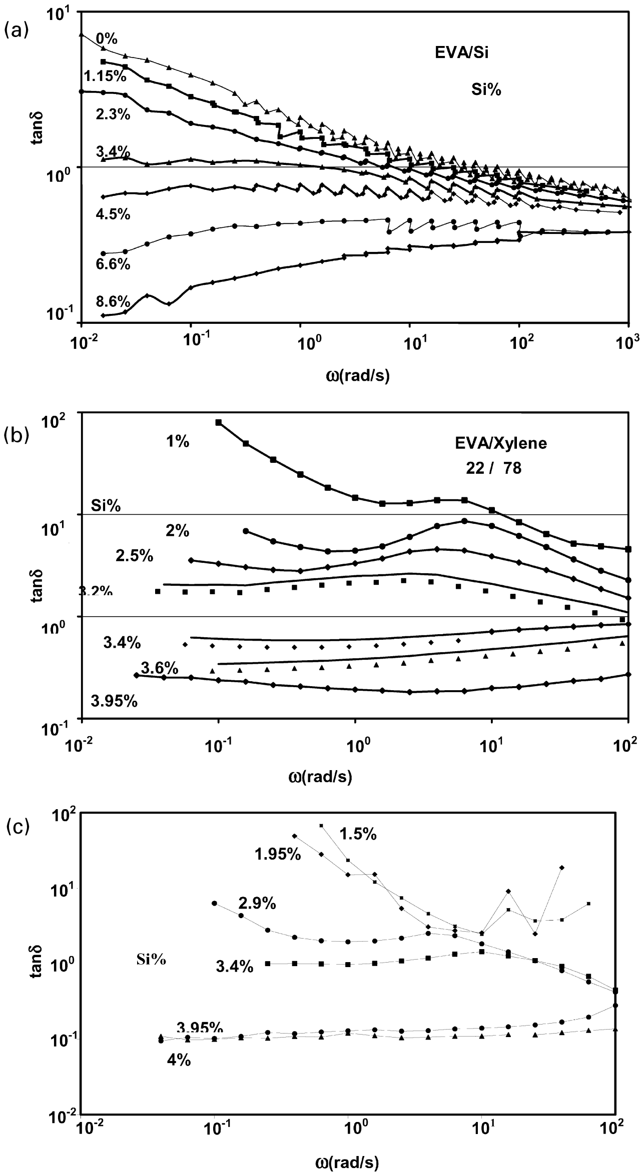

Fig. 4. Variation of tan δ versus frequency at different silica concentrations for different EVA dilutions (a) EVA/xylene: 100/0, melt EVA, $T = 140$ °C, (b) EVA/xylene: 78/22, $T = 21$ °C, (c) EVA/xylene: 92.5/7.5, $T = 21$ °C.

agglomeration tendency of these clusters at high concentrations leads to the formation of a percolation-like filler network.

Beyond the gel point, the materials represents the case of a viscoelastic Hookeen solid at low frequencies or large scales ($G'\alpha\omega^{\circ}$; $G' = G_0$). Near the gel point, the storage modulus crosses over the loss modulus and the rheological criterion for the definition of the gel point is the same power law for $G'(\omega)$ and $G''(\omega)$ :

$$G'(\omega)\alpha G''(\omega)\alpha\omega^{n} \tag{5}$$

where $n$ is the relaxation exponent.

Moreover, the loss tangent, tan δ, is independent on frequency and is given by:

$$\tan\delta = \tan\left(\frac{n\pi}{2}\right) \tag{6}$$

which is a second condition for the occurrence of the gel point.

Considering the EVA/Si molten composite, the behaviour of $G'(\omega)$ and $G''(\omega)$ exhibits a same power law $G'(\omega)\alpha G''(\omega)\alpha\omega^{1/2}$ with $\tan\delta \approx 1$ at lower frequencies, i.e. $\omega < \omega_0 = 20$ rad/s with $\omega_0 = 1/\lambda_0$ defining a characteristic relaxation time which is the onset of the rubbery relaxation phenomenon of EVA60 molten polymer. This result suggest [15] that a self-similar relaxation time spectrum is observed at the gel point in the same relaxation patterns as chemical reaction.

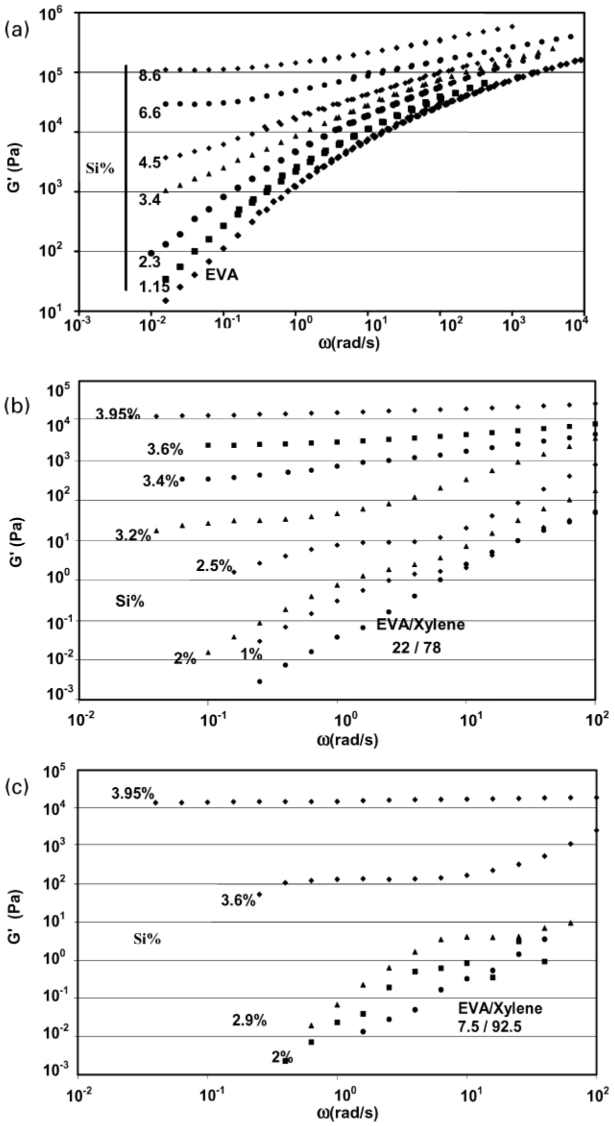

Fig. 5. Variation of the storage modulus at different silica concentration for different EVA dilutions: (a) EVA/xylene: 100/0, melt EVA, $T = 140$ °C, (b) EVA/xylene: 78/22, $T = 21$ °C, (c) EVA/xylene: 92.5/7.5, $T = 21$ °C.

For diluted composites, the characteristic relaxation time $\lambda_{0,\varphi}$ decreases as observed for diluted polymers [17]:

$$\lambda_{0,\varphi} = \lambda_0 \varphi^{1.75} a_\varphi \tag{7}$$

where $a_\varphi$ is the free volume correction and $\varphi$ is the volume fraction of polymer in solution.

As a consequence, the self similar spectrum in diluted composites is valid at shorter angular frequencies ($\omega_0 \leq 100$ rad/s) than those observed in bulk. Fig. 3(b) and (c) exhibits a same power law on $G'(\omega)\alpha\, G''(\omega)\ \alpha\omega^{1/2}$. A same power law with $n \approx 1/2$ was already observed by Castellani and Lomellini [15] from the study of the dynamical viscoelasticity of ABS melts with different particle size of dispersed rubber. However, the three dimensional network of rubber particles is quite different of the present silica network and the authors reported a percolation threshold between 19 and 31% depending on the inter-particle distance.

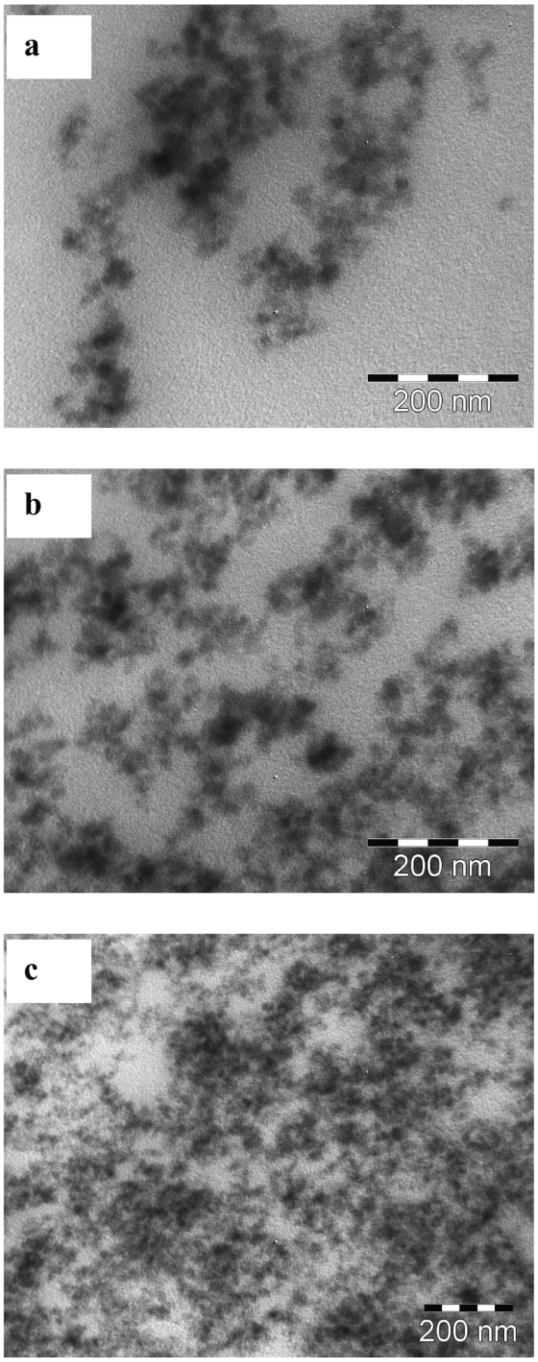

Fig. 6. TEM pictures for different silica concentration in melt EVA (a) $\phi = 0.0075$ ($< \phi_c$), (b) $\phi = 0.034$ ($\approx \phi_c$), (c) $\phi = 0.086$ ($> \phi_c$).

Finally, the silica concentration by volume at the gel point and the relaxation exponent on complex shear modulus were observed to be: $\Phi_c = (3.3 \pm 0.1) \times 10^{-2}$ and $n \approx 0.5$, respectively. These results show that the percolation threshold is not dependent on the polymer chains regimes (entangled or Rouse regime) and reflects a same self-similar structure of the filler clusters at the percolation threshold. Furthermore, it can be pointed out that this value of the percolation threshold is much lower than those predicted or experimental measured. For instance, it is calculated to be 31.2 vol% for the three-dimensional simple cubic lattice model [18] and electrical conductivity experiments [19] of carbon black filled natural rubber measure a threshold filler level around 15 vol%. Nevertheless, from rheological experiments performed on poly(ε-caprolactone)–clay nano-composites [20] it can be deduced that the percolation threshold for such systems is lower than 3 wt%.

### 3.3. Equilibrium storage modulus

The growth of the storage modulus beyond the percolation threshold can be described as a function of the silica concentration $\Phi$ by:

$$G_0 \propto (\Phi - \Phi_c)^t \quad \text{for } \Phi \rangle \Phi_c \tag{8}$$

The Fig. 7 shows that the variation of $\log(G_0)$ versus $\log(\Phi - \Phi_c)$ are displayed in two groups of data obeying a same power law with $t \approx 1.5$. The data were obtained from molten EVA/Si composite and diluted EVA/xylene composite (EVA/Si: 22/78; 16/84, 12/88 and 7.5/92.5). Furthermore, $G_0$ data of bulk EVA composite were calculated at 21 °C from data measured at $T = 140$ °C assuming that the rubber-like elasticity, i.e. entropic elastic behaviour, of the EVA/Si network dominates the overall temperature dependence of the filled EVA sample, i.e. $G_0 \propto T$ at $T > T_g$. The fact that Fig. 7 displays two curves means that the coefficient of proportionality of Eq. (8) depends on the composite nature. Indeed, we observe that this coefficient is lower for filled EVA sample for which the EVA chains are entangled ($\varphi > \varphi_c$). This particular point will be discussed later.

The predicted power law-dependency $G_0 \propto (\Phi - \Phi_c)^t$ with $t \approx 1.5$ is in agreement with experimental results of the literature [21] on carbon black filled natural rubber ($t \approx 1.56$) and with the analogy of De Gennes [22] using a percolation model of a random conductor network ($t \approx 1.9$). However, Heinrich and Klüppel argued that the universal properties of percolation are not correctly considered as the predicted power law $G_0 \propto (\Phi - \Phi_c)^t$ with $t \approx 3.6$–$3.7$ is in discrepancy with the cited experimental data and that is confirmed by the present work. Consequently, Heinrich and Klüppel 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 rubber matrix. Depending on the concentration of 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 rubber, the authors derived the concentration dependence of the equilibrium elastic modulus. Furthermore, the rigidity condition implies that the elastic modulus of the cluster $G_a$ is much higher than that of the rubber so that $G_0 \cong G_a$ and finally:

$$G_0 \approx G_p \Phi \frac{3 + d_{f,B}}{3 - d_f} \quad \text{for } \Phi \rangle \Phi_c \tag{9}$$

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 self similar structure of the CCA clusters.

$G_p$ is the averaged elastic bending–twisting modulus of the different kinds of angular deformation of the cluster units. Eq. (9) predicts a power law $G_0 \propto \Phi^{3.5}$ for the elastic whereas an experimental power law $G_0 \propto \Phi^{4.5}$ was measured from Fig. 8. This scaling law is very close to the values found by Piau et al. [23] on silica–silicone physical gels ($G_0 \propto \Phi^{4.2}$) in agreement with a formulation of the non-fluctuating fractal concept ($G_0 \propto \Phi^{5/(3-d_f)}$). Furthermore, as early observed in Fig. 7, the data obtained from samples at different polymer dilutions and melt displays two groups of data depicted by a same power law but with pre-factor which seems to depend on the critical

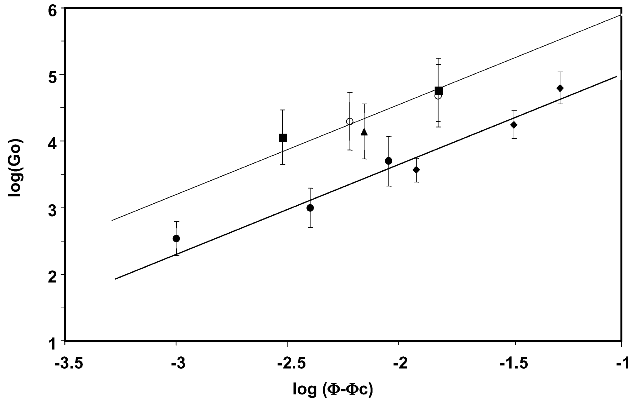

Fig. 7. Power law dependency $G_0 \propto (\Phi - \Phi_c)^t$ with $t \approx 1.5$ EVA/xylene: (◆): 100/0, (●): 22/78; (○): 16/84, (▲): 12/88, (■): 7.5/92.5.

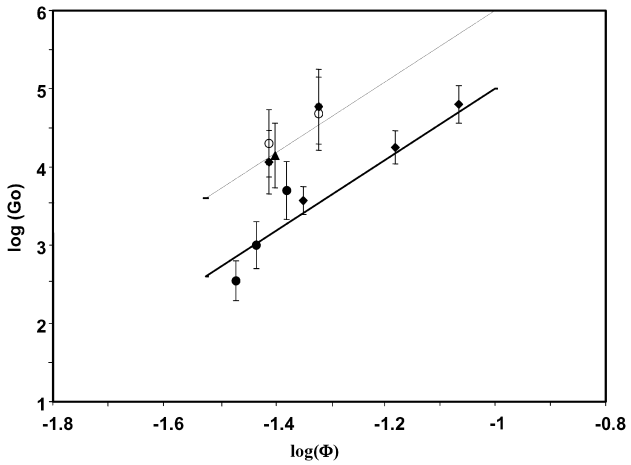

Fig. 8. Power law dependency $G_0 \approx G_p \Phi^{4.5}$. EVA/xylene: (◆): 100/0; (•): 22/78; (○): 16/84; (▲): 12/88 (■): 7.5/92.5.

dilution $\varphi_c$ separating the Rouse regime and entangled regime of polymer chains. Eq. (9) is a scaling invariant relation in regard to the particle size-dependence of the elastic modulus. However, Heinrich and Klüppel [1] proposed to consider the action of the adsorbed chains on the elastic modulus of CCA-clusters by introducing a mechanically effective solid fraction of the clusters. They predicted a strong impact of the layer thickness on the elastic modulus. Consequently, the influence of the particle size becomes important and $G_0$ increases significantly as the particle diameter becomes smaller. However, the authors assumed that the adsorbed layer is a glassy layer of immobilized polymer chains. Actually, this assumption cannot be considered for the present study as the $T_g$ of adsorbed chains of EVA60/xylene diluted composites is obviously lower than the room experimental temperature as the xylene is a good solvent of EVA chains. Furthermore, the EVA molten composites, for which an immobilized layer could be assumed, have a lower modulus $G_0$ compared with diluted composites for the same silica concentrations. Another assumption is to consider the average elastic bending–twisting modulus dependence on particle interactions. This elastic constant is usually assumed to be controlled by the rubber phase around the fillers. However, it can be also imagined that the average force of different kinds of angular deformation is controlled by the molecular dynamic of the bulk chains. In the entangled regime, as defined by $\varphi\rangle\varphi_c$, the changes of angles between singly particles of a filler network chain is screened by topological polymer chain interactions. Such assumption implies for diluted EVA composite a higher value of $G_p$ than that observed for filled molten polymer or concentrated solutions. It can be pointed out that the concentration of silica in our composites is much lower than the concentration of filler, carbon black for example, usually used in rubber composites.

## 4. Conclusion

The viscoelastic properties of filled molten EVA and diluted EVA/xylene were examined and the main conclusions of the present work can be summarised as follows:

(i) The non-linear behaviour (Payne effect) can be imagined to be associated with both mechanisms of chain disentanglements and filler network breakdown depending on silica concentration and amplitude deformation. Furthermore, a singular behaviour was observed at strains higher than 10% for diluted solution of EVA/xylene composites. This behaviour was explained by a re-arrangement of the filler particles in the flow direction after the break down of the filler network.

(ii) We have shown that the liquid–solid transition can be expressed in the same general relaxation frame as chemical reaction. We measured that the silica concentration by volume at the gel point was $\Phi_c = (3.3 \pm 0.1) \times 10^{-2}$ and we deduced the relaxation exponent on complex shear modulus to be $n \approx 0.5$. However, a model of percolation structure appeared too qualitative for the modelling of filled elastomers.

(iii) The CCA model depicts well the dependency of the equilibrium elastic modulus $G_0$ on filler volume fraction for $\Phi\rangle\Phi_c$. However, the average elastic bending–twisting modulus, $G_p$, depends on the dynamic relaxation regime of the polymer chains. We propose that the changes of angles between singly particles of a filler network chain is screened by topological polymer chain interactions in the entangled regime for composite such as $\varphi\rangle\varphi_c$.

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