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Non-linear viscoelastic behaviour and modulus recovery in silica filled polymers

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Abstract

The viscoelastic properties of different silica filled polymers were investigated. A variety of rheological observations was studied in the molten state, such as Payne effect and modulus recovery kinetics, in ethylene vinyl acetate, polystyrene and polypropylene filled with non-porous silica. The concept of the filler network breakdown seems to be adequate in describing the strain-dependence of dynamic mechanical properties of composites. Recovery tests of the complex shear modulus performed by subsequent strain sweep or time sweep experiments show evidence that the initial equilibrium network structure cannot completely restore within several hours. Furthermore, new strain sweep experiment after in situ crystallisation (or glass transition in polystyrene composites) of the sample leads to a total recovery of the linear modulus suggesting that the silica network structure in molten state have the memory of the silica structure in solid state. On the other hand, the complex shear modulus measured at lower strain for cross-linked EVA composites are perfectly recoverable in few seconds as proven by subsequent strain sweeps.

Keywords: Payne effect; Silica composite; Modulus recovery

1. Introduction

A direct consequence of the incorporation of filler in rubbers is the significant change in the dynamic mechanical properties. The effect of amplitude-dependence of the dynamic viscoelastic properties of filled rubbers, often referred to as the Payne effect [1], has been extensively investigated these last years. Payne found that the three-dimensional structure network constructed by the aggregation of carbon black significantly influences the dynamic viscoelasticity properties of rubbers. Furthermore, rheological experiments [2–6] 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 in low frequency range in a dynamic deformation experiment. As reviewed by Heinrich and Klüppel [7], the theoretical understanding of the behaviour of filled elastomer has been extensively treated so that a connection can be made between the filler morphology (structure, particulate size) and the viscoelastic properties of rubber materials. Due to the small size and the high specific surface, silica fillers are favourable to self-aggregation and consequently easily form three-dimensional network in molten polymer matrix. Consequently, the Payne effect, i.e. the decrease of the modulus with increasing deformation ratio, is generally explained in terms of the breakdown process occurring in the agglomerates. For example, common features between the phenomenological agglomeration–deagglomeration Kraus [8] approach and recent microscopical networking approaches were discussed by Heinrich and Klüppel [7].

Nevertheless, the mechanisms for reinforcement and non-linearity remains controversial. For instance, Maier and Göritz [9] have developed a model describing the temperature- and deformation-dependence of the modulus as a consequence of the variation of the topological constraint density at the interface with temperature and deformation. In addition, Sternstein and Zhu [10] reported that the non-linear viscoelastic properties of the nano-filled polymer melts bear striking similarity to what is observed in filled rubbers suggesting a common mechanisms that is

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rooted in the macromolecular natures of the matrices. Furthermore, their experimental results demonstrated that the non-linearity effect is strongly dependent on the filler surface treatment. Consequently, they argued that filled elastomers and polymer melts should share a fundamental mechanism regarding the origin of the non-linear viscoelasticity. However, characterization of the cross-linking density at the filler–elastomer interface by ^{1}H NMR measurements on model filled elastomers [11] shows that far from the particles, the polymer network is not affected by the covalent bond connecting the polymer chains and the interfaces. Furthermore, we reported in a previous paper [6] viscoelastic behaviour of inorganic particles dispersed in polymer organic solution from diluted solution to molten polymer and the non-linear behaviour can be then imagined to be associated with both mechanisms of chain disentanglements and filler network breakdown depending on the silica concentration and amplitude deformation. Actually, a general frame unifying both kinds of concepts is still lacking.

Another important aspect in Payne effect is the recovery kinetics of the shear modulus following a large strain perturbation. In previous works of the Sternstein's group, Chazeau et al. [12] showed that modulus recovery is complete but requires thousands of seconds whereas about 0.5–0.6 of the fractional recovery occurs in a time of 10 s or less. Nevertheless, most of the studies on the non-linearity or recovery kinetics of the complex shear modulus were performed on filled amorphous polymers having glass temperature (T_g) lower than the room temperature. Semi-crystalline polymers or amorphous polymers of high T_g have not been so widely studied whereas the electrical non-linear phenomena in such conductive filled [13,14] polymers have received considerable attention for filler concentration around the percolation threshold in such higher T_g systems.

The present paper aims to contribute to the understanding of the non-linear dynamic and modulus recovery in molten polymers of different nature (ethylene vinyl acetate copolymers, polypropylene and polystyrene) filled by fumed silica. Only composites with low silica concentrations just above the percolation threshold, (typically, 16 wt%), will be investigated in this study.

The first part of this work will investigate the effects of nature of the thermoplastic polymer (EVA, PP and PS) on Payne effect, pointing out the specific effect of the molecular weight of thermoplastic or cross-linked EVA samples.

The second part is devoted to the modulus recovery phenomenon. The investigations will particularly focus on the modulus recovery kinetics and on the memory effect resulting from a volumetric expansion of the matrix at the T_g for PS sample and at the melting transition for EVA and PP semi-crystalline polymers.

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.

EVA samples of different melt flow index were supplied by Atofina. The amount of acetate groups contained in these copolymers is about 28 wt%. These EVA28 copolymers were named in the present study EVA28-03, EVA28-40 and EVA28-420 with a melt index of 3, 40 and 420, respectively. PS sample was also supplied by Atofina. PP sample with a melt flow index of 2 was kindly supplied by Exxon. The respective zero shear viscosities of these different samples are reported in Table 1 at the temperature of $T = 200$ °C.

Furthermore, it can be pointed out that the molecular chains of EVA28-03 are entangled because the molecular weight $M_w \approx 56,000$ g/mole is higher than the critical molecular weight $M_c \approx 12,000$ g/mole calculated in a previous work [15]. Nevertheless, we did not measure by size exclusion chromatography, the molecular weight distribution of the two other EVA28-40 and EVA28-420 samples. Assuming a power law on the zero shear viscosity in entangled regime as: $\eta_0 \propto M_w^{3.4}$, we can estimate the zero shear viscosity at M_c from EVA28-03 data (Table 1). Then, $\eta_0 = 15$ Pa s for $M_w = M_c \approx 12,000$ g/mole. Consequently, EVA28-40 copolymer chains are slightly entangled ($M_w = 25,000$ g/mole) and the molecular weight of EVA28-420 is near to M_c leading to the conclusion than EVA27-420 chains are not entangled.

2.2. Sample preparation

The polymer–silica melt samples were prepared by mechanical mixing in a internal mixer at the rotational speed of 50 rpm of the counter-rotative blades (Rheomixer 600 from Thermo-Haake) during 10 min at the temperature of 1601 °C for EVA samples and at the temperature of 200 °C for PS and PP samples. All molten filled samples were found to be optically clear, as a result of good dispersion of the silica particles. The collected molten materials were compression-molded into 1 mm-thick plates by hot pressing under 100 bar for 20 s at $T = 150$ °C for EVA samples and 200 °C for PS and PP samples.

One set of EVA samples was cross-linked by radical

Table 1
Zero shear viscosities of polymer samples at $T = 200$ °C. Crystallinity of EVA and PP samples

	EVA28-03	EVA28-40	EVA28-420	PP	PS
η_0 (Pa s)	2800	180	14	17,000	1200
Crystallinity %	13	10	7.5	50	–

reaction by addition of dicumyl peroxide (DCP, Aldrich product) at the concentration of 2% by weight. DCP was first mixed with EVA copolymers in the internal mixer. The temperature was regulated at 100 °C and the rotor speed was fixed at 50 rpm. After 5 min of mixing, silica particles were then mixed with EVA/DCP system. For a mixing time of 10 min and for these processing conditions, no cross-linking occurs. The chemical network was formed in a molten state by curing the samples between heating parallel plates at $T = 200$ °C for 10 min.

2.3. Rheological measurements

Dynamic measurements were performed using a Rheometrics strain-controlled (RMS800) rheometer using a plate–plate geometry. EVA samples were analysed at the temperature $T = 100$ °C in order to avoid thermal degradation. Obviously, the sample deformation is not homogenous as it depends on the plate radius. Actually, from an experimental point of view, a plate–plate geometry is more suitable than cone plate geometry for the gap control of the geometry cell for samples having a high viscosity or a permanent elasticity.

The testing of non-linear behaviour of all the samples were performed in the range of deformation from 0.1 to 100%.

3. Results and discussion

3.1. Payne effect: uncross-linked samples

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 constant 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 well defined peak. Fig. 1a–c displays the variation of the storage modulus G', loss modulus G'' and tang δ loss factor, respectively, versus strain amplitude for EVA28-03, PS and PP composites. As expected, the storage modulus is not strain dependent in the low strain region for $\gamma < 1\%$, whereas a strain-dependent behaviour appears over two decades at high strain. The variation of the storage moduli with strain does not exhibit any fundamental difference between these polymer samples as all composites show nearly identical behaviour with strain amplitude. The critical strain amplitude, where the non-linearity effect occurs, is however slightly affected by the polymer nature. Moreover, the storage modulus of EVA28-03 composite is substantially higher than the two other composites. The general behaviour of the loss moduli with strain is similar to the behaviour described for the storage moduli. The similarities observed for these polymer composites are striking in view of the different nature of their interaction with silica particles. For example, displacement experiments have shown that EVA completely displaces PS from silica surface [16]. The effects of matrix molecular weight on the non-linearity effect were studied using thermoplastic EVA composites. Fig. 2a–c shows the variation of the storage modulus G', loss modulus G'' and tang δ loss factor, respectively, versus deformation for EVA28-03, EVA28-40 and EVA28-420 composites filled with 16 wt% silica.

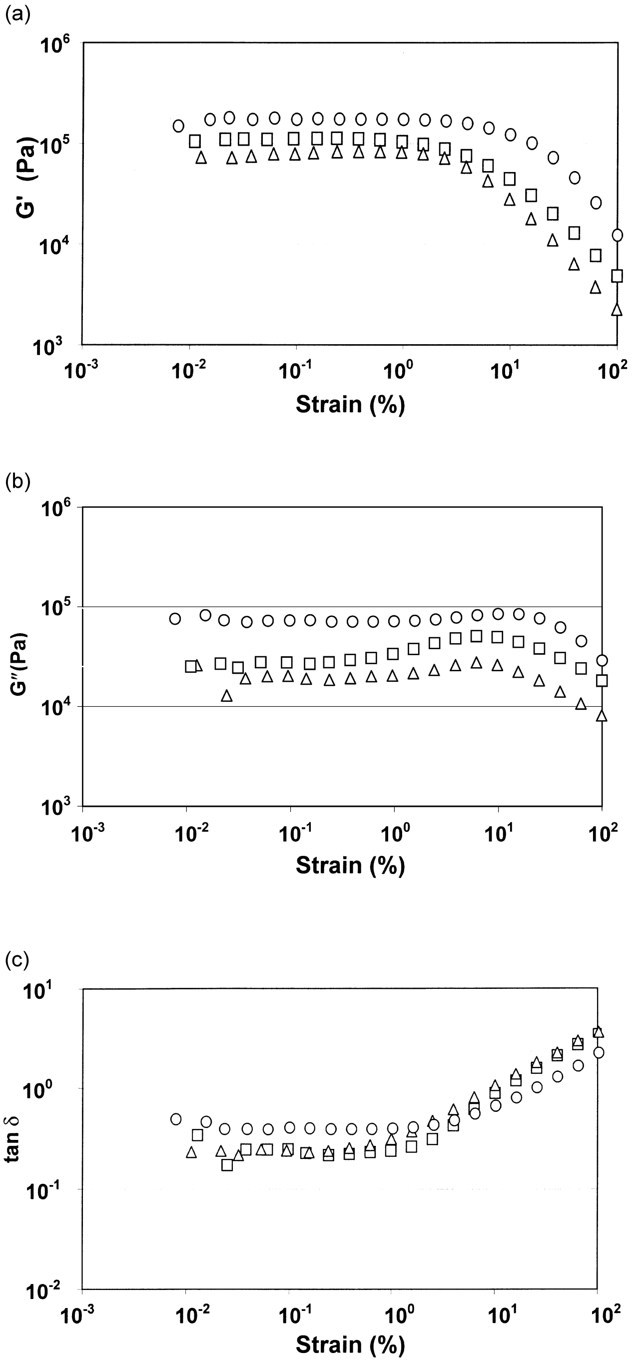

Fig. 1. Variation of the viscoelastic properties versus strain amplitude of different composites. Silica 16 wt%, $\omega = 1$ rad/s. (a) Storage modulus $G'(\gamma)$, (b) loss modulus $G''(\gamma)$, (c) tan $\delta(\gamma)$, EVA28-03 (○, $T = 100$ °C), PP (△, $T = 200$ °C) and PS (□, $T = 200$ °C) composites.

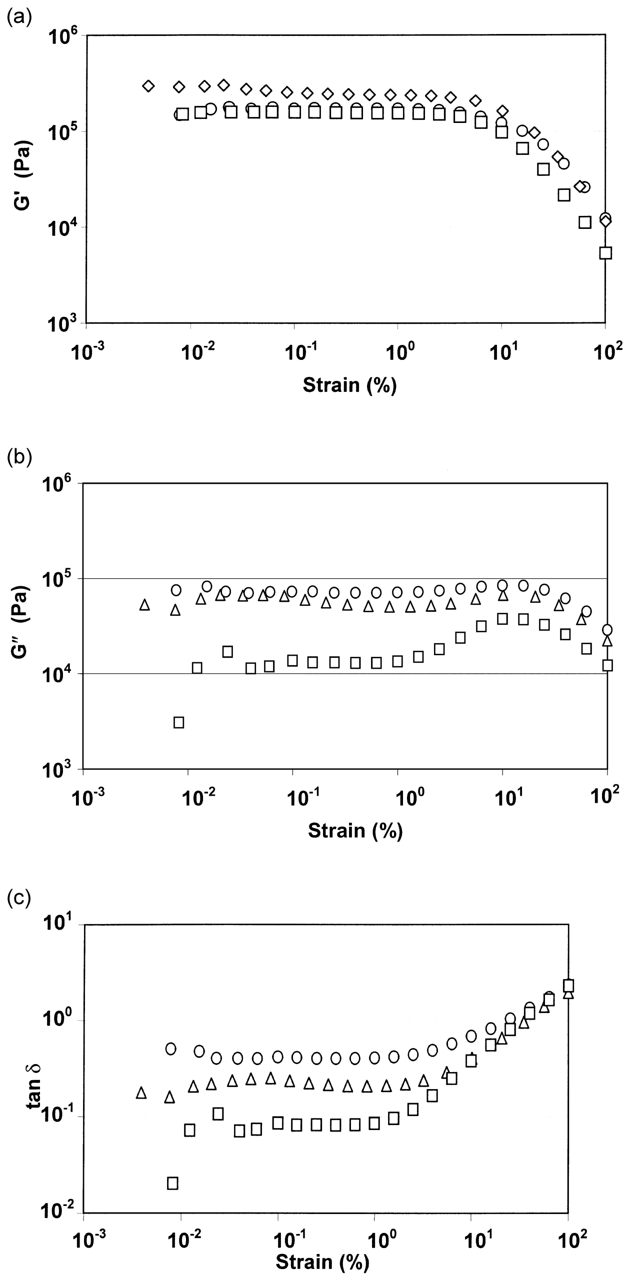

Fig. 2. Variation of the viscoelastic properties versus strain amplitude of different EVA28 composites. Silica 16 wt%, $\omega = 1$ rad/s, $T = 100$ °C. (a) Storage modulus $G'(\gamma)$, (b) loss modulus $G''(\gamma)$, (c) tan $\delta(\gamma)$, EVA28-03 (○), EVA28-40 (△) and EVA28-420 (□) composites.

Fig. 2a shows that an increase in molecular weight decreases the loss modulus for all strains whereas the storage modulus is less affected. Furthermore, the amplitude of the loss modulus maxima near the critical strain is substantially emphasized for the EVA28-420 composite. Aranguren et al. [4] observed that the maximum in G'' appeared only when working with untreated silica dispersed in PDMS. Then, they assumed that it is related to the energy dissipation produced by the breakdown of silica aggregates. In other words, the dependence of loss moduli on strain should depend on silica dispersion. Nevertheless, TEM analysis did not allow us to observe any difference on the silica dispersion in our EVA copolymers. Additionally, Fig. 2c displays a loss factor that decreases with matrix molecular weight at strains lower than the critical strain. These composites exhibit a loss factor that is lower than that of the neat polymers at all strain. Indeed, the loss factors of neat EVA are higher than unity at the frequency applied in the present work. These results indicate (i) a greater effect of the silica fillers on the storage modulus than on the loss modulus and (ii) the importance of the matrix molecular weight in determining the viscoelastic properties of the composites. Sternstein and Zhu [10] postulated that the reduction of storage and loss moduli with increasing applied strain is related to filler–polymer interactions including the aspects of trapped topological entanglements. Moreover, in the linear region, Aranguren et al. [4] concluded that the storage modulus-dependence should increase as the molecular weight of the polymer increases. Nevertheless, it can be pointed out that EVA48-420 chains are not entangled since their molecular weight is lower than the critical molecular weight M_c of EVA28 copolymers. As a result, chain entanglements should not play any role in Payne effect. Moreover, we showed in a previous work [6] that diluted EVA composites in good solvent (xylene) have a higher storage equilibrium modulus than that observed for filled molten polymers or concentrated solutions at the same silica concentrations. Consequently, the concept of bonding and debonding between polymer chains and fillers surfaces cannot exclusively be invoked to explain the Payne effect. Indeed, it may be also related to the filler network formed in the polymer matrix suggesting that there is a change of filler structure with increasing dynamic strain. A direct experimental support of this concept was reported from electron

Table 2
Shear elastic modulus G' ($\omega = 1$ rad/s), 16 wt% silica

	Neat	Cross-linked	Silica filled	Cross-linked silica filled
EVA28-03	1.35×10^4	3.3×10^5	1.7×10^5	6.4×10^5
EVA28-40	1.6×10^3	2.4×10^5	2.5×10^5	7.8×10^5
EVA28-420	2.0×10^1	1.1×10^5	1.6×10^5	6.4×10^5
PP	5.2×10^3	–	8.4×10^4	–
PS	1.0×10^2	–	1.1×10^5	–

Neat EVA, cross-linked EVA, EVA composite and cross-linked EVA composites: $T = 100$ °C; neat PP, PS and corresponding composites: $T = 200$ °C.

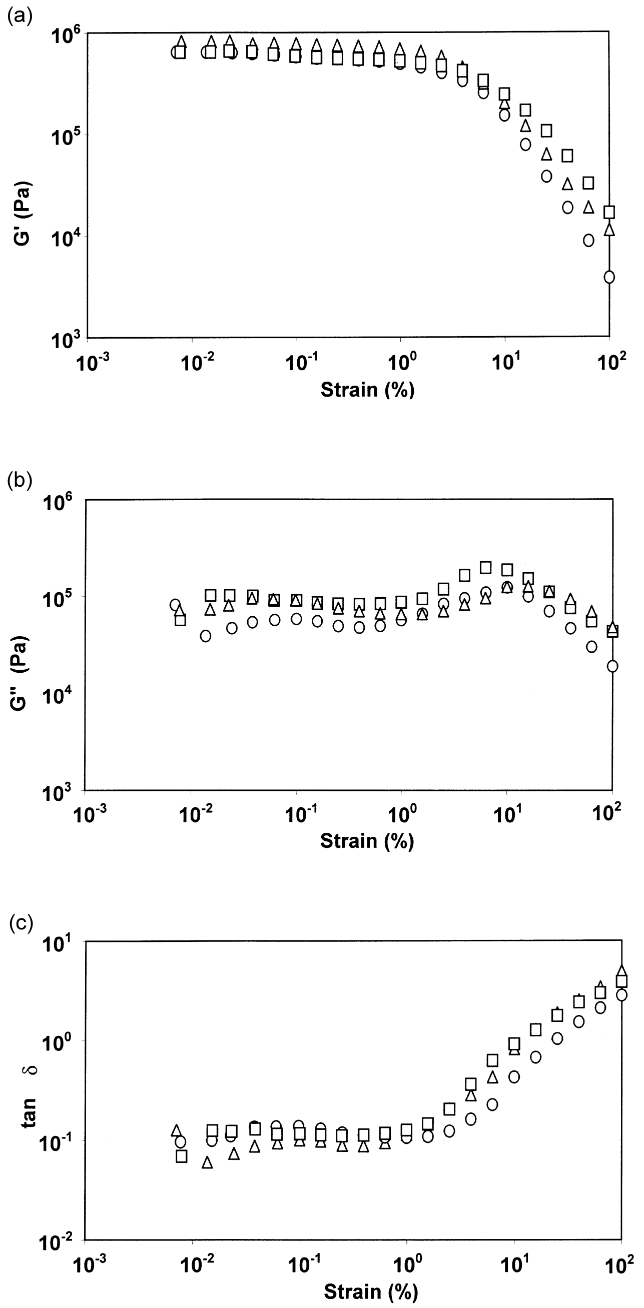

Fig. 3. Variation of the viscoelastic properties versus strain amplitude for different cross-linked EVA28 composites. Silica 16 wt%, $\omega = 1$ rad/s, $T = 100$ °C. (a) Storage modulus $G'(\gamma)$, (b) loss modulus $G''(\gamma)$, (c) tan $\delta(\gamma)$, cross-linked EVA28-03 (○), EVA28-40 (△) and EVA28-420 (□) composites.

microscopy studies [17] on elastically stretched chain-like aggregates of inorganic oxides.

3.2. Effect of cross-linking on the Payne effect

In a second experimental approach of the Payne effect, the non-linearity of filled cross-linked EVA copolymers were studied. Fig. 3a–c shows that cross-linked EVA composites display similar non-linearity effect on dynamic mechanical properties. All cross-linked EVA composites show nearly identical shear complex modulus with strain amplitude. More particularly, all samples show a well-defined maximum in G'' which appears in the critical strain region. Moreover, the high reinforcement observed for the storage modulus is far larger than the values expected from usual composite models. Table 2 shows data of the shear modulus measured in the linear domain ($\gamma = 0.1\%$) at $\omega = 1$ rad/s. A same chemical cross-link density for EVA samples can be expected as they were cross-linked with the same amount of peroxide. The magnitude of the elastic modulus reflects the density of network strands terminated by both topological entanglements and chemical cross-links. Indeed Table 2 shows that the elastic modulus of EVA cross-linked samples (without silica) decreases with decreasing molecular weight suggesting that the proportion of physical entanglements which are trapped decreases with decreasing molecular weight. This result agrees well with the different data published on the effects of trapped physical entanglements on the magnitude of elastic modulus.

The storage modulus magnitude of these cross-linked silica filled samples is similar for all samples. This result implies that the contribution of the silica network to the reinforcement of the elastic modulus for cross-linked sample is more efficient for lower molecular weight (six times higher for EVA28-420) than for higher molecular weight (only two times higher for EVA28-03). Furthermore, it can be observed for EVA28-03 and EVA28-40 sample series that the modulus of cross-linked silica filled samples is close to the sum of the moduli of cross-linked and uncross-linked silica filled samples. In a first assumption, we can then imagine for entangled polymers an additive contribution of the chemical network (plus trapped entanglements) and silica network. Nevertheless, this assumption cannot explain the high reinforcement of the non-entangled EVA sample (EVA28-420). Moreover, it can be pointed out that the elastic modulus of cross-linked non-reinforced EVA decreases with decreasing the molecular weight. Such mechanism is generally accounted for by taking into consideration, the effective elastic strands in the chemical network. The chemical reaction of cross-linking is a random radical reaction through the CH_2 sequence of EVA copolymer so that the density of the chain ends, non-effective elastically, increases with decreasing molecular weight. Furthermore, assuming that the adsorption of EVA chains on silica particles decreases the end chain proportion, or at least their length, the chemical network is more effective for silica reinforced matrix than for unfilled matrix at the same cross-linker concentration.

3.3. Modulus recovery

Another important aspect in the mechanisms of non-linear viscoelasticity in filled polymers is the restoration of moduli following the silica network destruction by a large strain perturbation. From literature data [4], thixotropic phenomenon are generally reported on shear flow behaviour of dispersions of fumed silica in PDMS. When the fluid is deformed, the microscopic structure of the dispersion is partially destroyed and the microstructure is increasingly disrupted as the shear rate is increased. When the shear rate is decreased, the microstructure of the filler is not immediately recovered. Indeed, the flow-induced structure is erased only after hours (or days) of quiescence. In dynamic conditions, comparable results [18,19] also suggest that the strain amplitude-dependence of the dynamic modulus is caused by a thixotropic change in the structure of the filler clusters and associated with filler network reorganisation. Another non-linear mechanical behaviour, the Mullins effect [20], involves a non-linear elastic behaviour under static load at large strains. These effects can be described as a stress-softening phenomenon of the material after a primary load leading to a material alteration. Further results presented here show that the present experimental work is only concerned by the phenomenon associated to the Payne effect.

Fig. 4a–c shows subsequent strain sweep experiments immediately performed on filled (16 wt%) EVA28-420, PP and PS and composites. These figures show that almost all dynamic stress softening is achieved in the first strain sweep and only minor effects take place in the subsequent sweep. In other words, the filler network is changed in the first strain sweep experiment followed by a partial recovery of the modulus. The complex modulus does not change any more in the subsequent strain sweeps. Furthermore, it can be observed from these figures, that the linear complex modulus of the filled PS sample is recovered in a larger extent than that of PP and EVA composites. Fig. 5a and b shows recovery experiment performed on EVA28-420 and PP composites, respectively. Immediately, after a strain sweep experiment, the linear modulus recovery was explored as a function of time at low strain amplitude ($\gamma = 0.1\%$). These figures show that about 60% of the recovery occurs in a time of 10 s or less (10 s is the characteristic time of the experiment between strain sweep and time sweep). Nevertheless, the recovery of the complex shear modulus is not complete within several hours. Furthermore, it is clear from an extrapolation point of view, that the equilibrium modulus will be reached only for geological times.

Furthermore, for more concentrated suspensions, such as 30 wt% silica in EVA28-420, this hysteresis behaviour is not observed as the complex modulus entirely recovered its behaviour of the first strain sweep as shown in Fig. 6. Such a phenomenon was already observed in the literature [21] on PDMS suspensions under steady shear flows. It can be pointed out that the degree of non-linearity increases with filler concentration.

Actually, the relationship between the observed viscoelastic behaviour and filler micro-structure leading to an apparent hysteresis behaviour is unclear for the present composites. Moreover, it is well known that the crystallisation of a semi-crystalline matrix often reduces the resistivity of conducting composites. Such a reversible phenomena was also observed in filled amorphous thermosets though they do not present a large volume expansion compared to a semi-crystalline polymer matrix. It has often been admitted in the literature that this non-linearity effect resulting from a disturbance in the continuity of the conductive network is principally due to the volumetric

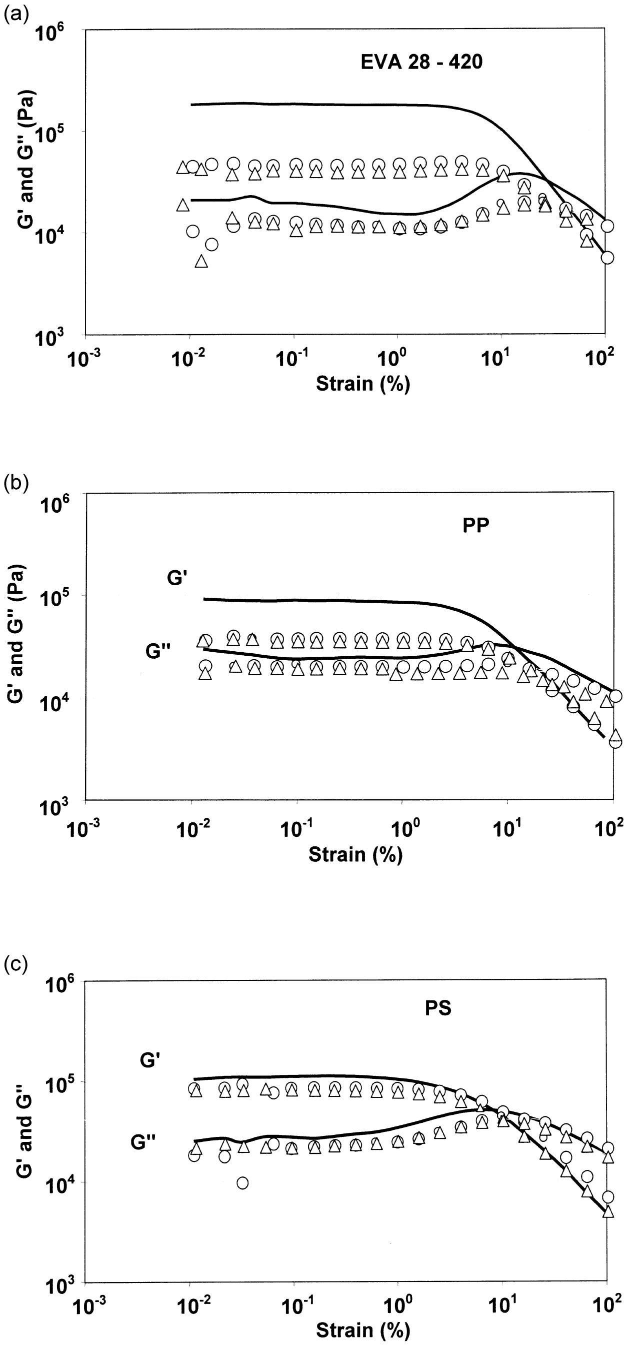

Fig. 4. Subsequent strain sweep experiment. Variation of the complex shear modulus G^* versus strain amplitude for different composites. Silica 16 wt%, $\omega = 1$ rad/s. (a) EVA28-420, $T = 100$ °C, (b) PP, $T = 200$ °C, (c) PS, $T = 200$ °C. Full line: first strain sweep. (○): subsequent 1, (△): subsequent 2.

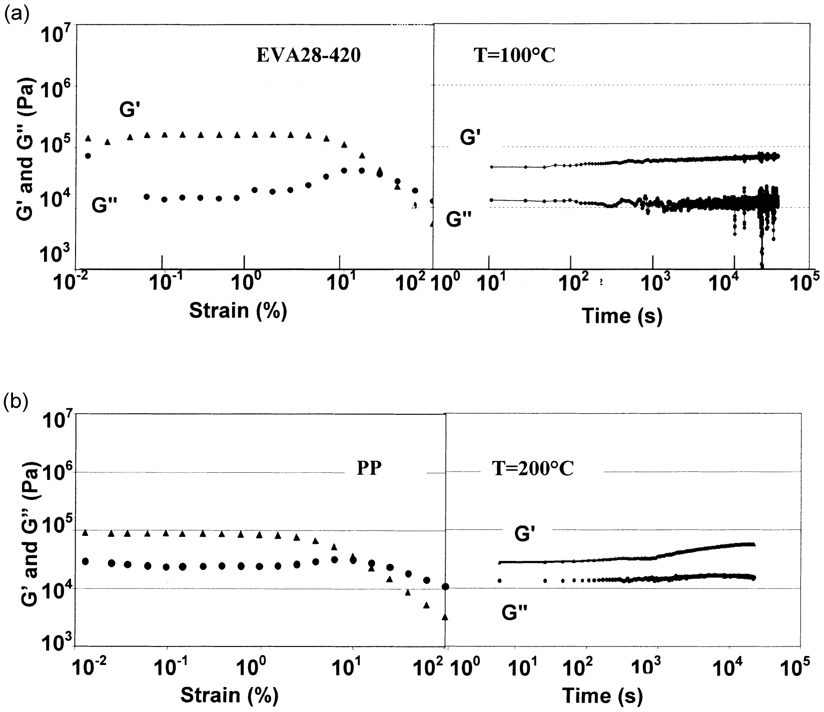

Fig. 5. Variation of the complex shear modulus versus strain amplitude ($\omega = 1$ rad/s) and complex shear modulus recovery versus time ($\omega = 1$ rad/s and $\gamma = 0.1\%$). (a): EVA28-420, Silica 16 wt%, T = 100 °C. (b): PP, Silica 16%wt, T = 200 °C.

expansion of the matrix. In other words, the volumetric expansion of the matrix can change the spatial filler network formed by silica clusters. This phenomenon should be emphasized in semi-crystalline polymers, because the silica particles are necessarily located in the amorphous zone of the polymer and volume expansion is more important for semi-crystalline polymer at the melting point than for amorphous polymer at T_g. The following experiments were made in order to test this assumption. At the end of the strain sweep experiment, the temperature of the sample between the two plates was fixed at a temperature below the crystallisation temperature of PP ($T_c \approx 135$ °C) and EVA28 ($T_c \approx 45$ °C) or below the glass temperature of PS composite ($T_g \approx 100$ °C). The temperature was then fixed again at the previous one in molten state ($T = 200$ °C for PS and PP samples and $T = 100$ °C for EVA28-420 sample). At this equilibrium temperature, a subsequent strain sweep experiment was performed. Fig. 7a–c shows the dependence of the complex shear modulus on the strain amplitude for PS, PP and EVA28-420 composites, respectively. In each figure are compared the data of the first strain sweep (circle symbol) with data of the subsequent strain data (triangle symbol), performed after in situ crystallisation or solidification of the matrix. These figures show a perfect recovery of the complex shear modulus by volumetric expansion of the matrix which can be qualitatively explained taking into account the different processing step from sample elaboration to subsequent strain sweep in rheometer. In the preparation step, the composite is cooled from molten state, the matrix retracts and some rearrangements may then occur in silica network, especially for semi-crystalline polymer as the silica particles are expulsed in the amorphous zone. In rheological testing, this composite is heated and the matrix expands. Then, the complex shear modulus in the linear domain characterises a network structure of silica network in molten state. The increase of the strain amplitude, up to 100%, leads to a high modification of this network structure out of this equilibrium state. A recovery test of several hours in the linear domain does not allow restoring entirely the initial equilibrium network structure. Nevertheless, a new strain sweep experiment after in situ crystallisation and melting of the sample leads to a total recovery of the modulus. In other words, crystallisation or solidification leads to a particular

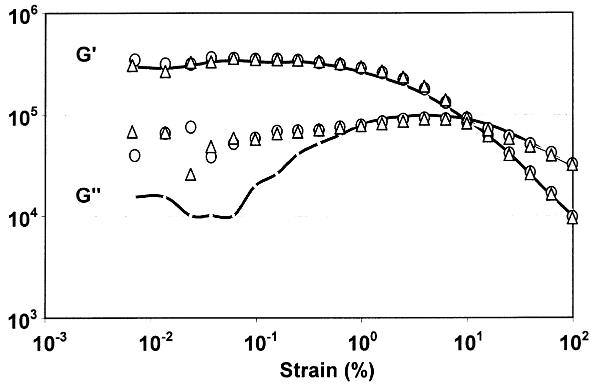

Fig. 6. EVA28-420 composite variation of the complex shear modulus versus strain amplitude. Silica 30 wt%, $\omega = 1$ rad/s, $T = 100$ °C. Subsequent strain sweep experiments. Full line: first strain sweep. (○): subsequent 1, (△): subsequent 2.

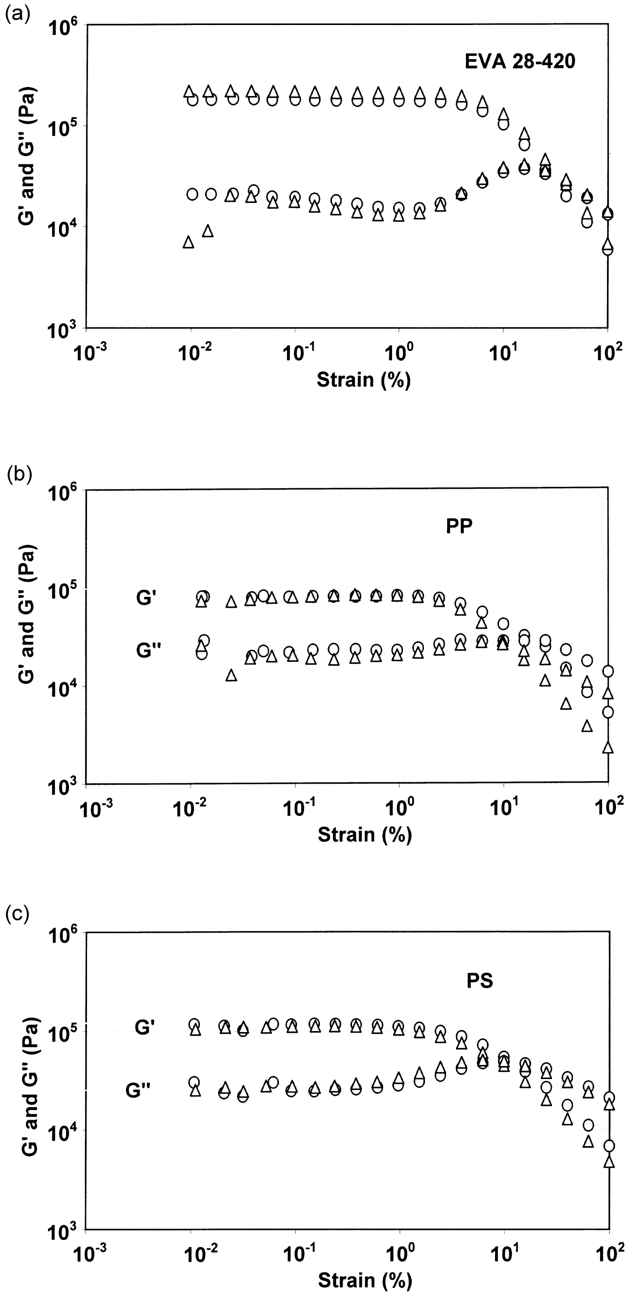

Fig. 7. Complex shear modulus recovery by volumetric expansion of the matrix. Subsequent strain sweep after crystallisation and melting (EVA28-420 and PP) or solidification and heating (PS) of the matrix. Silica: 16 wt% (○) first and (△) subsequent strain sweep.

silica network structure in solid state which is not entirely reorganised in the molten state under linear strain perturbation. Rheological experiments in low strain (linear viscoelasticity) of molten composites give a qualitative estimation of this structure which has been partially conserved during the melt processing under static conditions. This memory effect of this silica network structure completely vanishes when reaching the non-linear viscoelastic behaviour.

Lastly, it can be pointed out that the shear complex modulus of cross-linked EVA28-420 composites are perfectly recoverable in few seconds as proved by subsequent strain sweeps plotted in Fig. 8. We can then imagine that the chemical network restores in few seconds the silica cluster network which does not change any more with volumetric expansion of the matrix.

4. Conclusion

The concept of filler networking yields a good interpretation of the Payne effect both for filled cross-linked polymers and filled uncross-linked polymers. This behaviour is attributable to the characteristics of cluster structure formed by dispersed particles which depend on the interaction between particles and disperse polymeric medium. The increase of the strain amplitude leads to a high modification of this network structure out of this equilibrium state. Recovery tests carried out by subsequent strain sweep or time sweep proved that the initial equilibrium network structure could not be completely restored within several hours. On the other hand, a new strain sweep experiment after in situ crystallisation (or solidification for PS) and melting of the sample leads to a total recovery of the modulus. These results suggest that the silica network structure in molten state have the memory of the silica structure in solid state. The volumetric expansion of the sample does not allow a complete volumetric reorganisation of the network silica structure which is only achieved by the application of large strain amplitudes. Thus, the viscoelastic properties of the molten state composites depend on the three-dimensional structure formed by silica structure during crystallisation or solidification of the matrix. On the other hand, the complex shear modulus of cross-linked EVA composites are perfectly recoverable in few seconds as proven by subsequent strain sweeps meaning that the cross-link chemical network screens this memory effect.

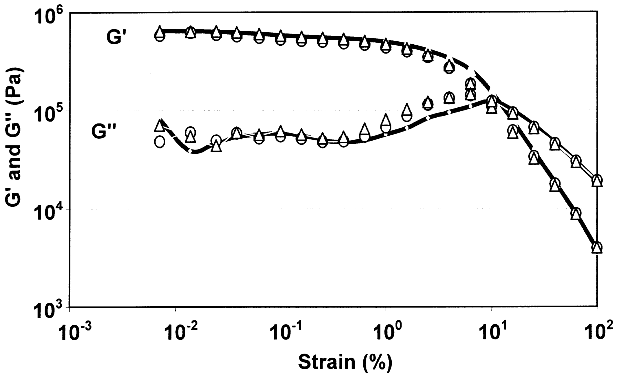

Fig. 8. Subsequent strain sweep experiment for cross-linked EVA28-420 composites Full line: first strain sweep. (○): subsequent 1, (△): subsequent 2.

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