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Mechanical properties of rubber nanocomposites: how, why... and then ?

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ABSTRACT:

Through the review of literature, this chapter will first recall the typical mechanical behaviour of rubber filled with nanofillers, from the viscoelastic linear behaviour to the large deformation one, including the ultimate properties. Then we will highlight the main filler parameters and how they seem to control these properties. In particular, we will focus on the role of filler-filler and filler matrix interactions, which are necessarily important when dealing with fillers with such high specific surface (up to several hundreds of meter square per gram). We will also see the influence of these fillers on the matrix properties, since, for instance, the filler presence can modify the matrix crosslinking kinetic or induce crystallization. Then, this description will be completed by the introduction of different modelling approaches developed to account for and eventually predict the role of nanofillers in the mechanical behaviour of these rubber nanocomposites.

Keywords : rubber, elastomer, nanocomposite, filler, mechanical properties.

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I General Introduction

Elastomers, also called rubbers, are made of long polymer chains linked to each other by cross-linking nodes. They are largely used in industrial applications, mainly in shoes, pipes and tires. For most applications, they are reinforced by stiff nanofillers [1], mostly carbon blacks or silica particles. These nanocomposites, existing well before the creation of the word “nanocomposites” have been firstly developed on an empirical basis in tire application. Their use has been extended to many other applications, such as seals, because of their very specific viscoelastic properties and wear resistance. Thanks to this large industrial interest, the mechanical properties of filled elastomers have been abundantly studied, as shown by the impressive number of publications on the subject. The development of new nanofillers (nanoclays, carbon nanotubes) [2] and the development of nanoscale characterization techniques, have reactivated the interest of both rubber industry and research community for these materials.

Indeed, the new possibilities of reinforcement offered by the development of nanoscale fillers have lead to new researches in the fields of processing [3], microstructural characterization [4],[5],[6],[7], mechanical characterization and the comprehension and modelling of the microstructure / mechanical properties relationships [8],[9],[10]. The history of the use of silica nanofillers in rubber is a good illustration. The introduction of silica has been made possible by the synthesis of appropriate compatibilizer of the hydrophilic silica with the hydrophobic polymer matrix. This improvement of nanocomposites processing has lead to the creation of new rubber materials whose microstructure and mechanical properties have been extensively characterized. Then, the discovery of optimized formulations for tire application has lead to the development of the so-called “green tire” which is claimed to decrease the car energy consumption compared to equivalent carbon blacks filled tires.

Lots of studies on rubber nanocomposites are guided by this success story. This probably explains the extraordinary number of nanocomposite formulations tested, playing with the numerous types of available elastomers and nanofillers. However, a clear evaluation of the interest of each of these formulations is often difficult. This is mainly due to the complex behaviour of filled elastomer. Indeed, besides the expected reinforcement it provides, the incorporation of small size fillers to crosslinked elastomeric matrix results in specific non-linear mechanical behaviours including high hysteresis, stress softening (Mullins effect) and strain dependent dynamic modulus (Payne effect). Various parameters are known to play a role in these phenomena i.e. (i) geometrical factors such as the shape, the size and the aspect ratio, (ii) intrinsic properties such as modulus and flexibility and (iii) surface characteristics such as specific surface and surface treatments. Most of the articles do not separate these

various factors. Consequently, it is necessary to compile the information of the literature to identify and clarify the role of each parameter in rubber nanocomposites reinforcement.

Thus, through the review of literature, this chapter will first recall the typical mechanical behaviour of rubber filled with nanofillers, from the viscoelastic linear behaviour to the large deformation one, including the ultimate properties. Then we will highlight the main filler parameters and how they seem to control these properties. In particular, we will focus on the role of filler-filler and filler matrix interactions, which are necessarily important when dealing with fillers with such high specific surface (up to several hundreds of meter square per gram). We will also see the influence of these fillers on the matrix properties, since, for instance, the filler presence can modify the matrix crosslinking kinetic or induce crystallization. Then, this description will be completed by the introduction of different modelling approaches developed to account for and eventually predict the role of nanofillers in the mechanical behaviour of these rubber nanocomposites.

II Typical mechanical behaviour of rubber nanocomposites

This first part presents the different nanofillers used to reinforce rubbers and highlights the specific aspects of the reinforcement induced by them.

II.1 The fillers and their main characteristics

Many types of nanofillers can be incorporated in rubber for reinforcement issue [11]. One of their most important characteristic is their specific surface (generally of the order of several hundreds of meter square per gram) which is directly related to their size, and which controls (at given filler content) the characteristic inter-filler distance. Another important parameter which has to be considered to describe these reinforcing elements is the average length / diameter ratio, known as "aspect ratio". This aspect ratio may change from 1 (for spheres, for instance) to values as high as several thousands.

Carbon blacks and precipitated silica are the most common nanofillers used for reinforcing elastomers. Chemically, carbon black is a form of elemental carbon consisting of 90 to 99 percent carbon, generally obtained by incomplete combustion or thermal decomposition of hydrocarbons. Amorphous silica, SiO₂, is usually prepared by vapour-phase hydrolysis or precipitation. Both types consist of aggregates of spherical particles (diameter from 10 nm) fused together (Figure 1). Note that some papers are devoted to more exotic quasi spherical shaped fillers like SiC [12], Ni et Fe nanoparticles [13],[14] and even Carbon-silica dual

phase filler (CSDP) [15],[16],[17], the latter consisting in a carbon phase including finely divided silica domains herein.

The interest of platelet like fillers such as clays (hydrous alumina-silicates) is also evaluated in many papers. The incorporation of layered silicates in polymers has been actively studied for the last two decades since the pioneer work of Toyota's researchers in the 1980's by [18]. Nanosilicates development started when amino acid treatment was found to enable the dispersion of montmorillonite clays ($(\text{OH})_4\text{Si}_8(\text{Al}_{4-x}\text{Mg}_x)\text{O}_{20}$) at an individual scale (1 nm-thick silicate layers with the lateral dimensions from 0.1 to several μm s) in polyamide 6. Nowadays, both natural clays and synthetic layered silicates have been used to process polymer nanocomposites (mica, fluoro-mica, vermiculite, hectorite, fluororhectorite, saponite...) [19]. Reports on clay chemical modification and nanocomposite elaboration may be found in the literature (see the chapter written by Karger-Coksis). The aspect ratio and the dispersion can reach very high values in delaminated composites (aspect ratio ranging from 100 to 1000) (Figure 2). Completely exfoliated clay can have a surface area of about $700\text{m}^2/\text{g}$. Clays can have a large modulus anisotropy, this is the case for montmorillonite, in which the longitudinal modulus is about 150 GPa, and the Poisson ratio is assumed to be close to 0.2, i.e. close to that of mica crystal.

Recent years have seen an increased interest for rod shaped nanofillers. Carbon nanotubes, long and thin cylinders of carbons, were discovered in 1991 by the electron microscopist Iijima who was studying the arc-evaporation synthesis of fullerenes [20]. Just few nanometres across, the cylinder can be tens of micron long, and each end is "capped" with half of a fullerene molecule (Figure 3). Nanotubes can have either a unique cylindrical wall (SWNTs) or multiple walls (MWNTs). Their structural properties depend on the diameter, length, and chirality, or twist of the nanotubes. Their predicted mechanical characteristics are remarkable (Young's Modulus $\sim 1\text{ TPa}$ [21],[22], maximum tensile strength $\sim 30\text{ GPa}$ [23]). They have excellent thermal conductivity, are chemically inert and, depending on the details of their atomic arrangement (chirality), behave as metals or semiconductors. Therefore, combined to a low density, these characteristics make them particularly attractive for reinforcement in composite materials. Increasing number of publications report their incorporation in rubbery matrices [24] such as NR [25], or silicone [26],[27],[28]. Note that these fillers, which enable a very low geometrical percolation threshold, offer the possibility of conductive properties at very low volume fraction compared to carbon blacks [29],[27],[28].

Some rod shape fillers with high aspect ratio can also be extracted from the biomass. Cellulose nano-fibrils [30] have typical diameter ranging between 5 to 10 nm, with length of several μm and they consist in the alternation of mono-crystals linked to their neighbours by disordered segments. The hydrolysis of these segments allows the extraction of quasi-perfect

mono-crystals in the nano-size range. These whiskers have been extensively studied in non cross-linked polymers [31],[32]. Actually, there is an increasing interest for nanofillers from natural origin. For instance, we can cite a recent work with waxy maize starch nano-crystals, which have been incorporated in NR [33].

To complete the picture, we can also evoke particular fillers, which are in between chemical additives and stiff fillers, like Poly Oxide Siloxane (so-called POSS). These particles are made of few silicium atoms and their surface is generally reactive with the polymer in which they are introduced [34]. They have been for instance incorporated in Poly Dimethyl Siloxane elastomer [35] or Polyurethane Elastomer [36].

To conclude, a large panel of available nanofillers can be introduced in rubbery matrices. Among them, CB, silica and clays are undoubtedly the most studied ones. A large part of literature on new nanocomposites is devoted to the optimization of the filler dispersion in the elastomer. The filler dispersion can be reached through different processing route recalled in different review articles treating of filled nanocomposites: latex route, melt mixing, or solution route [3] (a chapter is devoted to this aspect in the book). The resulting dispersion strongly depends (i) on the choice of the polymer, which controls the filler/matrix compatibility, (ii) the surface chemistry of the filler, which can change this compatibility and (iii) the fillers morphology, including their shape factor and specific surface area that impacts the amount of interfacial contact area with the polymer, the complex shape of the aggregates and therefore the rheology of the filler/matrix mix. The filler chemical modification is particularly studied, resulting in an impressive increase of the number of nanocomposite systems studied. Moreover, the complex chemistry of crosslinking of the host elastomer can also be chosen as a function of the nanofiller/polymer system [37],[3]. Obviously, all these parameters must be taken into account when one wants to understand the role of the filler incorporation in the mechanical properties of the processed nanocomposites, since they influence the microstructure (filler dispersion, crosslinking) and the different type of interaction (filler/filler and filler/matrix ones). Before going into the detail of these different effects, one can however note that the first consequence of the introduction of stiff nanofillers, like in the case of micro-scale fillers, is to increase the material modulus. This is described below.

II-2 Filler Reinforcement (modulus increase)

The commonly accepted definition of an elastomer is an assembly of long polymer chains crosslinked to each other, with a glass transition temperature below the ambient temperature. Like all polymer material, when submitted to a mechanical stimulus, elastomers show a

viscoelastic response. Many static or dynamic experimental techniques are used to characterize this behaviour. At low strain, unfilled elastomers have a linear behaviour, defined by a compliance (or modulus) independent of the applied stress level. Besides, their energy dissipation measured during a strain cycle is low; in other terms, the elastomer shows a low sensitivity to strain state, in particular at low strain (Figure 4). This pseudo-elastic behaviour above T_g is also related to a very constant modulus in the rubbery plateau, and can be relatively well described by theory (cf. paragraph IV).

The stress-strain behaviour of unfilled chemically cross-linked elastomers tested at room temperature (i.e. above T_α) is proportional to the crosslink density. The latter involves those introduced by the chemical crosslink created during the crosslinking step (usually by sulfur or peroxide), as well as those created by the entanglements. The contribution of the latter is strongly dependant on the strain rate when they are not trapped during the crosslinking, but can be negligible for highly crosslinked elastomer. The quantity of the trapped entanglements depends on the initial molecular weight of the polymer and the chemical crosslink density (figure 5).

As reported in all the articles concerning filled elastomer, when stiff fillers are introduced, the material stiffness increases. Obviously, this is also the case for nanofillers. This reinforcement increases with filler volume fraction, as clearly evidenced in all the papers devoted to nanocomposites. The reinforcement can be evidenced by Dynamic Mechanical Analysis measurements. This technique provides the viscous and elastic part of the complex modulus, as a function of temperature and at given frequency, generally around the Hz. Such measurements are suitable as long as the material behaviour is linear (otherwise the modulus calculation is wrong). This is clearly the case for strain below 1%. Some articles report also data of modulus measured with large deformation tests. In that case, the modulus is measured at different strain values, depending on the choice of the authors. However, it is noticeable that the strain chosen for such measurement is often above 100%. At these strain levels, we will see in the next paragraph that many phenomena can occur and complicate the material response. Though these difficulties, some generality can be extracted from literature.

Common filler content for CB or Silica are around 30 to 50 phr. Content of around 50 phr multiplies the DMA modulus by ten [38]. In the case of spherical Ni and Fe nanoparticles in natural rubber, El'Nashar et al. [13] reported a modulus increase of 50% with 30 phr of fillers. Such reinforcement can be obtained for lower nanofiller fraction with high aspect ratio nanofillers such as nanotubes or clays. Atieh et al. [25] report an increase from 0.3 to 2.5 MPa when introducing 10% of MultiWall Nanotubes (MWNTs) in NR (nanocomposites were processed by evaporation). The introduction of 0, 5 and 10 phr of montmorillonite clay platelet in isobutyl isoprene rubber leads to a modulus equal to 0.8, 3.2 and 4 MPa

respectively (measured in tensile test at 100% strain) [39]. Kueseng and Jacob [12] report a reinforcement of NR matrix from 0.8MPa to 1.2MPa with only 2% of SiC nanoparticles. De Falco et al. [40] report also that small quantity of MWCNT is enough to improve significantly the mechanical properties of cured SBR composites when compared to CB filled SBR. Besides, due to processing difficulties, the content of filler with higher aspect ratio is generally low, except in few studies such as that of [41]. The latter report data on a series of rubber/clay nanocomposites with a volume fraction up to 60wt% of filler in ethylene-propylene diene rubber (EPDM) styrene butadiene rubber (SBR) and epichlorohydrin rubber (ECO), leading to an important modulus increase measured by Dynamic Mechanical Analysis.

These different examples show clearly that the filler aspect ratio is the main parameter for the reinforcement efficiency, the latter being higher for high aspect ratio filler. Thus, carbon nanotubes or MMT have a much higher reinforcing capability than silica or carbon blacks, except in some few studies where the bad properties obtained with such fillers are probably due to a bad quality of the tested fillers [42]. Literature also suggests that the reinforcement is strongly dependent on the elastomer matrix, the material processing, and the filler surface treatment [43],[26]. Note that a comparison between all the different systems must be cautiously done in the specific case of elastomers since their mechanical properties are also strongly dependent on the crosslinking process of the matrix. Moreover, one can regret in many papers the lack of characterization of the fillers, of precision in the mechanical characterization (for the reason precised above) and of comparison with modeling approach, which would help the clear evaluation of the fillers interest.

II-3 Mechanical behaviour at small strain : Payne effect

Besides a strong reinforcement, the introduction of nanoscopic fillers in a rubbery matrix leads, at intermediate strain level (below 100%) to a non-linear mechanical behaviour. Once again, it can be shown by two different mechanical experiments (dynamic or classical stress-strain tests). In dynamic mechanical measurements, when submitted to successive sinusoidal deformations with increasing amplitude, rubber nanocomposite samples exhibit a decrease of their measured storage modulus, and the appearance of a maximum for the loss modulus at a deformation level around 0.1. Two plateaux are also visible, as shown in Figure 6, with what will be hereafter called low amplitude modulus (LAM) and high amplitude modulus (HAM), respectively. The main features of the Payne effect described above are general to all filled

elastomers [44],[38],[45]. Note that this non-linearity at low deformation - unrevealed in pure elastomer- is equivalently demonstrated in classical shear-stress measurements. The apparent modulus measured as the slope of the stress strain curve decreases strongly when deformation is increased. The composite presents a pseudo-plastic behavior with a strong strain rate dependence of the material response. A decrease of the strain rate of measurement decreases the amplitude of the Payne effect, which quasi-vanishes at strain rate below 10^{-6} . An increase of temperature has the same influence since it strongly decreases the initial modulus and much less the terminal one [46].

It is noteworthy that the DMA measurements presented in Figure 6 represents “fully equilibrated material response”: the storage and loss moduli measured at each strain amplitude are steady state value that would remain constant indefinitely if the strain amplitude were sustained at a constant value. However, dynamic measurements performed at increasing strain amplitude do not give the same DMA curves when measurements are performed at decreasing amplitude. In other words, the material has the memory of the modulus reduction that occurs at high strain amplitude. This memory effect vanishes with time [47],[44]. Indeed, a material submitted to a static offset, presents, after a sufficient elapsed time, the same DMA curve than without static offset [48]. The curves virtually superpose, even for deformation of 0.2, i.e. much higher than that at which the modulus decrease occurs. However, this statement is only true when considering material that has been previously submitted to strain as high as the maximum strain seen in the test. Indeed, the original stiffness of a filled elastomer is always higher than that measured in following tests. This is the feature of the so-called Mullins effect.

Both Payne and Mullins effects are general to all filled elastomer, and in particular to elastomers filled with nanofillers, like reported by Ramier et al. [38] for silica, by Qian et al.[49] for CB, by Ramoniro et al. [50] for clays, by Bokobza et al.[51] for MWNT. However, the intensity of the phenomenon depends on the filler characteristics for the reason that will be explained further (paragraph III). This strongly makes more difficult the understanding of the impact of the tested nanofillers and makes more difficult the conclusion that one can have concerning their interest.

II-4 Mechanical behaviour at larger strains

At higher strain level, rubber exhibits a strain-hardening, i.e. a rapid increase of the stress (prior to break). This hardening is related to the limited extensibility of the chains between

crosslinks. Crosslinks increase the elastic modulus but induce a decrease of the strain at break. Like at small strain, the introduction of filler leads to an increase of the stress level of the material at a given strain, as shown on figure 7. Different studies report this increase for silica in SBR [52], CB in NR [49], MWNT in NR [51], clay platelets in EPDM [53] etc... Like at small strain the main filler parameters are the filler aspect ratio, and obviously their volume fraction. Moreover, especially for high aspect ratio, one has also to consider the strong influence of the processing which might orient the fibres, like suggested by [54] for fibrillar nanosilicate (with length of few microns and diameters around 10 to 30 nm) introduced in SBR and NBR by conventional process.

However, as evoked above, filled elastomers exhibit a mechanical behavior modified after a pre-straining. This effect has been firstly shown by Holtz [55] and studied by Mullins [56], whose name has been given to the phenomenon. This so-called Mullins effect is illustrated in Figure 8. A sample is stretched at a maximum deformation ϵ_{max} . Then it is unloaded during a time in between half an hour and several days. A new loading of the sample leads to a stress-strain curve, which is below the curve obtained during the first loading, for deformation level below ϵ_{max} . For deformation above ϵ_{max} , the second curve joins the first one. Some experiments suggest that this effect is partly recoverable [56],[57] but for much longer time (in the scale of months) than that involved in the Payne effect (see above). However, a real recovery in the cited experiments is not obvious since it needs heating of the sample at temperature for which a post-crosslinking can occur in the matrix. Interesting features have been shown by Lapra [58]. He confirmed by birefringence the presence of short or strongly stretched chains during the deformation, which do not obey to Gaussian statistic. A.F.M. experiments showed that there is strong heterogeneity of deformation. This confirms the important role of the distribution of the local volume concentration of fillers, this distribution being the result of the nanocomposite processing.

II-5 Ageing, fatigue and ultimate properties

Conversely to what is generally observed with filled thermoplastic, filled elastomers with nanoscopic particles can exhibit an increase of *both* stress and strain at break. Of course, this is shown when the process enables sufficient filler dispersion and lot of processing problems can hinder such result. As an example, Figure 9a shows stress-strain-curves obtained with Styrene-Butadiene Rubber filled with untreated nanoscopic silica [59]. It is also illustrated in the case of carbon MWNTS [24] in figure 9b. The main difference between both examples concerns the amount of nanofiller (10 wt. % in the case of carbon nanofibres, 20 vol. % in the case of silica). However, most of the articles report the existence of an optimum of filler content for the improvement of the ultimate properties. This optimum can often be related to

the optimum of dispersion, which is more and more difficult with increasing filler content (see for instance Hwang et al. [60]). Thus, a lot of study on clay platelet filled rubber report an optimum around few %wt of clay [61], above which the dispersion is clearly not satisfactory.

The increase of stress can be explained by strain amplification effects [62], that are known to occur in such complex materials. However, this cannot account for the apparent increase of the ultimate strain often reported in rubber nanocomposite. In fact, the total rupture envelope of such composites must be considered. The latter can be obtained by a logarithmic plot of the ultimate stress, corrected by a factor T_{ref}/T , as a function of the ultimate strain, for different testing temperatures and strain rates. T_{ref} is the chosen reference temperature for the curve, while T is the temperature of the test. The correction factor accounts for the temperature dependence of the entropic elasticity. All the tests made at different strain rates and temperature leads to a unique curve (Figure 10). The variation of temperature or strain rate only moves the representative point along the envelope, anticlockwise for a decrease of temperature or an increase of strain rate. At high temperature and low strain rate, the reinforcement is limited (low ultimate stress and strain). At low temperature and high strain rate, the ultimate stress increases but the ultimate strain reaches a maximum and then decreases. The rupture properties are optimal in an intermediary region. A maximum ultimate strain can be determined from the envelope curve and will be hereafter call ϵ_{ultm} .

As shown on figure 10, the addition of filler in the elastomer decreases ϵ_{ultm} . However, the zone of optimal behavior is shifted toward higher temperature. For instance, Lapra [58] showed that unfilled SBR exhibits, when stretched at a strain rate of 0.1 s^{-1} , a maximum ultimate strain at 273K when the latter is observed at ambient temperature with the same SBR filled with 20 vol.% of untreated silica. The same observation was made with different surface treatments: in all cases, the decrease of the properties for temperature above the ambient is much slower than for unfilled SBR. This leads to an ultimate strain systematically higher in the filled samples than in the unfilled ones at 333K.

This improvement of the ultimate properties of the fillers is obviously searched when the materials is used in application involving large strain behavior. This is in particular the case when friction is involved. Indeed, even if their macroscopic strain is not necessarily important, elastomer submitted to friction can be submitted to very high local strain. The best example is the tire application where the abrasion resistance of the material is particularly tested. The tribological behavior of elastomers, like for any type of material –because of the very local mechanisms involved- is complex and is strongly dependent of the testing conditions. However, some main characteristic can be recalled here.

Due to the viscoelastic nature of filled elastomers and to their large deformability, the friction behavior of elastomer does not follow the Coulomb rules generally observed for rigid solid. The friction force is not independent of the form and area of the contact surface, this force is not proportional to the normal force, and the sliding of the surface is not independent on the relative displacement rate between the surfaces in contact [63]. Indeed, the elastomer, filled or unfilled can more or less deform following the surface roughness. For this reason, the friction force is higher. Moreover, the latter depends on the physico-chemical nature of the material, i.e. its formulation, the viscoelastic nature of the material, complex in the case of filled elastomer, induces a dependence on all the phenomena on the speed and temperature. Besides the direct value of the force resistance to sliding, this has also consequences on the wear behavior, since it is the complex results of the testing condition.

Given this complexity, it is quite difficult to identify the main parameter deciding the abrasion resistance of rubber nanocomposite. For instance, it appears that the ultimate stress and strain at break obtained in simple tensile test are not consistent with the abrasion resistance properties when comparing a CB filled SBR and a CB filled natural rubber [64]. This is the reason why natural rubber, which has better abrasion properties, is preferred to synthetic elastomer for truck tires application. One property, which is often examined, is the crack growth resistance of the material. Depending on the nature of the elastomer matrix and formulation, the crack propagation can present strong deviation and/or the formation of moustache [65],[66], such as those shown on Figure 11. This enables higher energy dissipation and therefore delays the material rupture. This phenomenon is related to some anisotropy development in the vicinity of the crack [67]. It is then obvious that in the case of nanofillers, such phenomenon must be considered at the nanometric scale, or even at the molecular levels. The difference between NR and synthetic rubber is then generally attributed to the crystallisation ability of NR, which favours the anisotropy development [68]. Obviously, the addition of nanofiller will have a direct impact on this phenomenon and more generally on the anisotropy development of the material response near the crack tip.

The issue of crack propagation in rubber nanocomposite is obviously a concern in the study of fatigue [69]. The progressive degradation of the material observed in such tests involves all the mechanical aspects previously addressed such as the linear and non linear (Payne effect) viscoelasticity, the Mullins effect and the ultimate properties, in addition to the environmental conditions (temperature, oxygen and ozone concentration, radiations...). The latter can promote the occurrence of complex chemical processes such as polymer chain scissions, additional crosslinking, and by-products formation, which may occur either in the bulk or at the filler surface. As rubbers are strongly formulated, this degradation strongly depends on the content and nature of antidegradants additives and of the crosslinking agents, as well as their

initial crosslinking state prior ageing. Moreover, given the large specific area of nanoscopic fillers, chemical reactions at the interface can have large impact on the one hand on the overall chemical processes, i.e. their kinetic and their homogeneity and on the other hand on the resulting mechanical behaviour of the degraded material. These intricate aspects are in the scope of the Chapter 21 of this book, written by S.K. Srivastava.

II-6 Conclusion

Elastomers display specific mechanical properties such as large deformability and small visco-elasticity. The introduction of nanofillers makes this behavior more complex with the occurrence of non linear visco-elasticity, a strong sensitivity to strain history, astonishing ultimate properties such as a possible improvement of both strain and stress at break depending on the testing conditions. This statement is general to all type of nanofillers but their influence is obviously dependent on their intrinsic parameters.

III : How to explain reinforcement in rubber nanocomposite ?

After a recall of the typical mechanical behavior of rubber nanocomposites, let's go deeper in the relationships between the microstructure and these mechanical properties. There is no doubt that the filler morphology strongly influences the mechanical reinforcement they provide to the elastomer matrix. Moreover, this morphology is also involved through the role of the filler surface and the different type of interaction it generates.

III.1 Filler morphology and filler-filler interactions

The increase of the reinforcement with the increase of the aspect ratio can found theoretical explanation that will be recalled in the paragraph IV-2. Aspect ratio has also consequences in the way fillers are spatially distributed in the matrix during the processing. First, that means that the efficiency of high aspect ratio filler such as clays is directly dependent on the way they are dispersed (« exfoliated ») in the polymer, since a too bad dispersion of the particles means the formation of aggregates or agglomerates, i.e. a smaller effective aspect ratio (this effect is illustrated in figure 12). This explains the large variation of the reported reinforcement of elastomer system reinforced by fillers such as clays, or nanotubes since their dispersion is strongly dependent on the material formulation and process. This is also the reason of the very large number of articles devoted to the improvement of the filler/polymer compatibility, via the chemical modification of filler surface [70],[71], the use of

compatibilisers [72], or the chemical modification of the polymer matrix [73],[74],[75]. Note that other parameters can influence this dispersion such as the vulcanization system and in particular the accelerators [72]. The consequence is that the efficiency of these modifications can only be understood via a deep microstructural characterization of the resulting composite. At that point, one might conclude that a total dispersion of the fillers as individual objects statistically distributed in the material is the optimum to reach. However, different works indicate that such an idea is erroneous. For instance, the influence of the filler dispersion was extensively studied by Pu et al.[76]. They prepared model colloidal silica systems in a PMA matrix (poly methyl-acrylate) in such a way as to obtain particle dispersions that were random, regular or aggregated. The mechanical properties of the three types samples were tested in both DMA and stress-strain properties (tensile and compression). They observed that the composites with randomly and regularly dispersed silica have almost identical stress-strain behavior (in both dynamic and static uniaxial tests). Conversely, the composites with aggregated silica are seen to exhibit different mechanical properties, particularly higher compressibility and extensibility. These improved mechanical properties relative to the other two types of filler is consistent with frequent observations in the rubber industry that a stop of the compounding process just before the complete filler dispersion can give the best balance of mechanical properties.

Besides, the ability of the fillers to form a sort of continuous phase or network leads to a sharp increase in the reinforcement efficiency [77]. This “percolating” network depends on their aspect ratio, and on their orientation distribution, as described in the literature [78],[79]. Thus it appears that with rigid rods randomly dispersed (in position and orientation), a aspect ratio of 100 should lead to their percolation at a volume fraction of about 1%. Moreover the percolation threshold calculated for a non-uniform length distribution is also found lower than that calculated for a uniform length distribution having the same average length [80],[79],[81]. Note that these calculated thresholds are calculated with the assumption of a statistical distribution of the fillers, without account for the interactions between fillers. The latters can strongly modify the statistic spatial distribution of the fillers and therefore can increase or decrease the threshold volume fraction [82]. The process can also favour or inhibit the formation of this network, the evaporation process being likely more favourable than process involving strong mixing.

The question that arises then is the nature of the links creating the continuity of this filler structure [83]. The very high specific surface of nanofillers suggests that the filler-filler interactions can form these links. The formation of continuous structure made via filler-filler contacts can be evidenced in the case of conductive fillers such as CB [84],[53],[27],[28],[85]. Indeed, it was found a good correlation between the LAM value

and the conductivity, suggesting that this modulus is directly the consequence of a so-called mechanical (and not only geometrical) percolation of the filler. Moreover, it has been shown (by conductivity measurement and mechanical characterization) the existence of an optimum mixing time to obtain the highest LAM, which allow a macroscopically uniform dispersion of the filler but also the existence of a filler network [84].

Within this frame, the non-linear behavior of filled elastomers can be explained. The rigidity of the filler structure depends on the rigidity of the filler –filler bonds. The deformation of the composite leads to its breakage and the loss of rigidity. During cycled deformation, as observed by DMA, there is alternately breakage and reformation of the filler bonds, which is a dissipative phenomenon at the origin of the peak of the loss modulus observed in Figure 6. Many experiments support this scheme. The decrease of the filler size down to the nanoscale leads to a statistically nanometric distance in between filler, which can favour their interaction, and their agglomeration in complex structure. This "agglomeration-desagglomeration scheme" is also suggested by the analogy between viscoelastic behavior of filled elastomer and the rheology of nanofiller filled suspension. The latter shows a decrease of viscosity with shear rate similar to the decrease of modulus with shear in filled elastomer [86],[87]. A decrease of shear modulus is also observed for suspension of carbon black particles in oil for which the role of polymer chains cannot be evoked. In that case, the only obvious mechanism is a modification of state of aggregation with shear rate [83].

To this direct effect of the filler network stiffness, one must add the role of the structure in its possibility to trap matrix inside cluster of filler agglomerates. This trapped matrix increases the apparent filler fraction, and its unshielding during the de-agglomeration of the filler enhances the modulus decrease [88]. However, the preponderance of the surface of the filler over their structure suggests that the occluded volume theory is not a key mechanism in the Payne effect [89].

However, one might argue that a filler network has a too low modulus to explain the LAM measured in filled elastomer. Moreover, it has been shown that the Payne effect is also observable in Carbon Black filled rubber even when they are non-conducting composite, i.e. without the presence of a percolating filler structure effect [89]. Figure 13 presents the influence of the surface of filler (i.e. their size) on the modulus decrease in filled elastomer during the DMA experiment described above (HAM minus LAM). The so-called structure of filler, measured by DPB measurement, and which is characteristic of the complexity of the aggregates geometry, is a very minor parameter compared to their size, i.e. to the surface of matrix/filler interface.

III.2 Filler-matrix interactions

In fact, the importance of the surface developed by nanoscopic fillers is already noticeable during the composite processing. This can be due to the filler-filler interactions (and the formation of the network previously described) but also to the filler-matrix interactions that occur here on a large surface. The latter can lead to properties of the matrix in the interphase different than in the bulk. Considering the quantity of interface of the order of several hundreds of m^2 per grams, the quantity of polymer involved by the interaction with the filler surface becomes significant. Given generally reported large reinforcements provided by nanoscale filler compared to microscopic ones [9] (though this comparison might be often questionable for different reasons developed in this chapter) many studies have been devoted to the characterization of this assumed immobilized matrix. Different techniques have been proposed to characterize it: bound rubber measurement [7], Nuclear Magnetic Resonance (NMR) [90], Positron Annihilation Light Scattering (PALS) [9], etc... Bound rubber measurement consists in dissolving the uncrosslinked polymer matrix of the composite and extracts the fillers. The rubber bound on the filler surface, i.e. the rubber not extractible, is assumed to be characteristic of the quantity of immobilized polymer. The amount of adsorbed polymer depends on the chemical nature of the polymer and of the particle surface, and also of the molecular weight of the polymer [91].

For instance, Burnside and Giannelis [92] studied Polysiloxane-layered silicate nanocomposites with filler volume fraction in the range (0, 0.04). They reported that the modulus increase with the filler content correlates with the amount of bound rubber (determined from swelling experiment in toluene). The quantity of bound rubber can be important in such experiments, leading to the calculation of a polymer layer with a modified mobility of several nm thick. More precisely, Dutta [93] has studied by NMR technique the mobility of adsorbed polymer (styrene-butadiene) at the surface of carbon black particles extracted (in solvent) from the composite. They conclude in the presence of three regions with different mobility, a bound rubber region, a loosely bound region, and the non-influenced polymer. This has been supported by other studies on similar or different systems [94],[95]. In the case of silica filled PDMS, Cohen-Addad [96] has shown that the adsorbed polymer involves a multiple link structure. Numerous monomer units are involved in a binding site which is a dynamic system consisting of bonds which form and dissociate permanently. Ten Brinke et al. [90] have performed a RMN study of silica filler NR. The fraction of immobilized polymer they found is more important in the case of untreated silica compared to those treated with silane, though the latter enable the formation of covalent bonds. Seemingly,

the silanol sites are more efficient to immobilize NR chain than silane. This result is comparable to those found in silica/polybutadiene system [97].

These results are consistent with the study of Ramier et al. [38]. In his study, different materials with a SBR matrix filled by nanoscopic silica with various surface treatments have been submitted to increasing dynamic strains in the range of the Payne effect. Figure 14 synthesizes the behavior observed for the samples with untreated silica, with silica treated by a covering agent with 8 carbons, or treated with a coupling agent enabling a covalent bond between the matrix and the filler. The grafting (covering or coupling agents) leads to a decrease of the Payne effect amplitude, i.e. basically a decrease of the initial modulus, measured between the modulus drop. It was checked that this could not be due to a modification of the silica dispersion in the material [38]. Bound rubber measurements have shown an expected decrease of the adsorption of polymer chains at the filler surface with the covering agent quantity; note that this characterisation also allowed establishing equivalence between the quantity of covering agent and the length of this agent to cover the surface of silica [71]. Moreover, a correlation between the bound rubber value and the initial modulus is found. The modulus drop in the peculiar case of the materials with coupling agents is very similar to that observed with materials with covering agents. Like the work of Ten Brinke [90], this could suggest that the formation of covalent bonds between fillers and the matrix do not counterbalance the decrease of the number of physical bonds induced by the covering of the silica surface.

Another argument for the presence of a large quantity of polymer chains with decreased mobility at the filler surface is the recovery kinetic of the LAM after deformation, at large amplitude or during the application of an offset since it is for some authors, similar to the physical ageing of polymer in the glassy state after stretching [98]. The large fraction of polymer involved by adsorption can act through two mechanisms. The first vision is to consider it as a glassy polymer. Within this assumption, the Payne effect can be considered as a decrease of the glass transition temperature of this polymer fraction activated by the deformation [99]. A second possibility is to consider the Payne effect as due to a mechanism of adhesion-desadhesion of the chains at the filler interface [100]. The adsorbed polymer might act as supplementary crosslinks in the elastomer. In addition, the distance in between crosslink being reduced, linking chains between fillers might not act in the low deformation range as predicted by the Gaussian description but more like chains at the limit of their extensibility [101]. Thus, the desadhesion mechanism would be a return to the normal entropic behavior of these chains [101].

Such assumptions can also be used to explain the Mullins effect (i.e. the irreversible modification of the material behavior after a first stretch). For instance, Wagner [102] keeps

the idea of a glassy shell of polymer around the particles and proposes that under deformation, this shell deforms quasi irreversibly (i.e. plastically) and does not contribute anymore to the reinforcement. Bueche [57],[103] early assumed the existence of adsorbed polymer chains linking two different filler particles. The distance between particles would be distributed, as well as the linking segments of chains. An increasing deformation would lead the shortest segments to reach their maximum extensibility. In that case, they would break or they would be debonded from the filler surface. The key parameters in this interpretation are the distance between particle, related to their size, and the bonding surface. Dannenberg [104] and Boonstra [105] had a very similar interpretation except that they preferred to consider a slipping of the stretched polymer chain on the filler surface (Figure 15).

Thus, to consider the filler-matrix interactions as the main parameter in the mechanical behavior of rubber nanocomposites could seem appealing. However, some objections exist against a too biased vision. It is noteworthy that all the interpretation of the non linear behavior of filled elastomers in studies which deal with a modification of these interactions via chemical treatment of the filler surface, or via the matrix chemistry, does not always take into account a possible modification of the dispersion. Moreover, the bound rubber quantities generally reported are huge. Ramier reported values up to 40% vol. of matrix in the case of SBR/silica nanocomposites. However, DSC measurements are rarely reported to confirm the modification of the glass transition of the material, or the presence of phase with different glass transition temperature. Some DSC measurements even contradict the assumption of an immobilized phase. In that case, this is explained by the mobility gradient of the polymer near the surface (with no neat difference of glass transition temperatures), or by the assumed total lack of mobility (i.e. of glass transition) of the bound rubber. These receivable arguments at least suggest that more information is needed on the molecular dynamics of the polymer in the vicinity of the filler surface. Moreover, PALS study did not show an effect of the fillers (Montmorillonites treated or not with octa-decyl-trimethyl ammonium chloride) in the bulk matrix response (a Poly styrene-co-Butadiene), whatever the process used to prepare the composite [9]. At last, some authors discuss from dynamic mechanical experiments about the presence of a second loss peak above the main relaxation temperature, (characteristic of a drop of the rubbery modulus with increasing temperature). But there is no correlation between the intensity of this peak and the quantity of bound rubber value measured with the same sample [59]. Besides, mechanical spectrometry does not show any modification of the main relaxation peak of G'' of rubber nanocomposites [76], except when they can also be explained by continuum mechanic (i.e. without the assumption of the matrix properties), or by a modification of the matrix intrinsic properties by the process (i.e. a different crosslinking, copolymerisation, or degradation or cure). Indeed, these indirect effects of nanoscopic fillers are important; they will be discussed in the next paragraph.

In any case, whatever the reality of the presence of a matrix with modified properties, filler-matrix interaction has obviously consequences in the behavior at large deformation. Given the Payne effect feature and the fact that it occurs at small strain, the modification of the bulk polymer mobility becomes a negligible phenomenon at large strain. The main characteristic to consider then is indeed the strength of the filler-matrix and filler-filler bonds. Thus, the creation of covalent bonds between the matrix and the filler through the use of appropriate surface treatment is clearly visible at large deformation where it leads to a strong hardening of the material, the fillers then acting as multifunctional crosslinks [59]. The strength of these bonds, as well as the strength of the filler-filler bonds, controls the damage process of the material, and in particular the void formation, and the “desagglomeration” processes, as evidenced in Ramier’s work [52]. Consequently, these different phenomena lead to strong heterogeneities in the deformation field and the overall response of the material...up to the material rupture.

III.3 Indirect influence of fillers on the matrix cross-linking

Nanosopic fillers can also indirectly modify the matrix bulk properties through a perturbation of the crosslinking process. Indeed, these fillers can favour an important and uncontrolled adsorption of activator, accelerator and crosslinking agents that in turn can modify the crosslinking density of the matrix in the filler vicinity [37]. Curing kinetics of rubbers are generally studied using oscillating disc rheometer that measures the torque evolution required to shear the sample (characteristic of the increase of the material rigidity during the crosslinking). Measurements are usually performed versus time at a given temperature and the curing characteristics are often expressed in terms of onset time, optimum cure time and torque value.

It is generally agreed that the incorporation of carbon black in rubber does not modify the matrix cross-linking by sulfur but has an influence in the case of peroxide [37]. The results can be extended to the case of nanotubes, as the surface chemistry is close. Untreated silica leads to a strong modification of kinetic. For instance, the introduction of 20% vol. of silica in the SBR matrix leads to a crosslinking reaction which begins earlier with a slower kinetic (Figure 16). This can be attributed to a strong affinity between silica and common accelerators. The adsorption of accelerators can be significantly reduced by grafting the surface. For instance, increasing grafting quantity of octyl triethoxy silane (noted AR8 on figure 16) leads to a kinetic close to that observed in the case of the matrix alone with accelerators (CBS). The same effect is also observed when using silane with alkyl chains of different lengths, the main parameter being the covering of the silica surface. The use of

coupling agent has also the same consequences with the difference that it contributes in the same time to the crosslinking kinetic (it accelerates it) by the coupling reaction.

Let's now consider the case of nanolayered silicates. In order to exfoliate the stacks of platelets, use is often made of ammonium salts [106]. Alex and Nah [107] report that the presence of organoclay in the case of NR matrix leads to a faster crosslinking kinetic. This is attributed to the formation of a transition complex with amine and sulfur. Similar effects have been also reported by Lopez Machado et al. [108] and Teh et al. [109] in the case of NR and by Varghese et al. [110] in the case of epoxidized NR. In the case of silicone matrix, the influence of synthetic Fe MMT on crosslinking kinetic is attributed to the presence of Fe that acts as an antioxidant [14].

Given the fact that it occurs at the filler surface, the consequences are likely a more heterogeneous final crosslinking state (i.e. the development of crosslinking gradients in the filler vicinity). However, the characterization of such heterogeneities is difficult to perform. This probably explains why it is generally even not mentioned in articles. Such omission is obviously not important when studies are devoted to qualitative aspect of the reinforcement of fillers in rubber nanocomposite; however, it might be a problem when the studies discusses about the modification of elastomer mobility through the filler-matrix interface...

III.4 Influence of fillers on rubber crystallisation

Creation of specific interactions between polymer and the filler surface can also have consequences on the crystallinity of semi-crystalline polymers. This question is important since a modification of the crystallinity can sometimes explain by itself the change of reinforcement without invoking any other physical mechanisms. This problematic is present for some rubbers, such as natural rubber (NR) and poly dimethyl siloxane (PDMS). These rubbers are known to crystallize either at temperature below room temperature (the process called cold crystallization happens around -25°C for NR and -70°C for PDMS) or under strain (strain induced crystallisation: SIC). For instance, above a strain level of 300%, NR crystallisation is instantaneous. SIC is often assumed to be to at the origin of the original auto-reinforcing character of natural rubber.

Recent results on SIC in the case of NR have clearly evidenced the critical influence of the crosslink density (see figure 17 where NR2 and NR3 are NR matrices slightly and highly crosslinked, respectively). Crystallization kinetic is ruled by nucleation when the molecular weight between cross-links is below the molecular weight between entanglements. Conversely, growth is the key factor when the molecular weight between crosslinks is above

the molecular weight between entanglements. That means that the crystallization optimum is reached when the crosslink density corresponds to the physical entanglements density [111]. Besides, it is well established that the addition of nanoscopic fillers in natural rubber can indeed strongly increase rigidity, abrasion resistance, tear strength, and stress at break... The direct relationship between these improvements of the mechanical properties and the influence of the filler on the crystallisation under strain is still an open debate. Actually, the first role of the filler is the strain amplification of local strain [112]. Therefore, as a first step, it can be interesting to consider the influence of fillers on the cold crystallisation (that does not imply strain amplification). For this reason, Dewimille et al [113] have studied the cold crystallization of poly dimethyl siloxane (PDMS) networks filled with in situ generated silica particles. Chenal et al. [114] were interested in cold crystallization of filled natural rubber (NR), with carbon black (CB) and silica. In both cases, the reduction in the ability of polymer to crystallize in the presence of filler is observed. The main effects of the fillers are related to the fact that they can create excluded region for crystallization and a region with perturbed mobility where the kinetics of nucleation and/or growth are slowed down, the rest of the matrix being unperturbed. The respective volume of the different regions depends on the filler parameters. The results may also be regarded as the consequence of an increase in the apparent cross-linking density due to polymer-filler interactions. This interpretation is close to that reached by Gent [66] in studies on the effect of the network cross-linking density on the crystallization characteristics of NR.

Let's now discuss the effect of fillers on SIC. Most of the recent studies are based on Synchrotron wide angle X rays scattering (WAXS) during stress strain measurements performed on NR with different crosslink densities, unfilled or filled with nanoscopic silica, carbon black, clay, or calcium carbonate. Toki et al. [115] and Trabelsi et al. [116] have explained that the mechanical hysteresis observed, during tensile cycle tests, in all filled and unfilled NR samples is essentially due to the supercooled effect. Chenal et al. have demonstrated that the Mullins effect decreases the intensity of the SIC. The Mullins effect being highly dependent on the mechanical history of the material, it is therefore necessary to "demullinise" the samples to study properly the influence of the material parameters on SIC. Another aspect investigated by Poompradub et al. [117] Trabelsi et al. [116] and Chenal et al. [111], [118] using WAXS was the evolution of the crystallite sizes versus strain in the case of filled NR. In each study, it was shown that, when fillers are introduced, the crystallite sizes are decreased as well as the degree of crystallite orientation.

Several teams have demonstrated, regardless of filler nature, that the strain at the crystallization onset decreases with the addition of filler, due to strain amplification. Y. Wang et al. [10] have prepared NR-clay nanocomposites by co-coagulating the NR latex and clay aqueous suspension. From the results of tensile tests, they explained that the presence of

nanoclay (more than 10 phr) inhibits the development of crystallization of NR. To understand this result, the nanoparticles must be considered as new effective crosslinks. From this point of view, Rault et al. [119] have proposed the concept of effective crosslink density (ν) deduced from the sum of the chemical crosslinks ($\nu_c \sim 1/M_c$), entanglements ($\nu_e \sim 1/M_e$) and elastomer chains adsorption on the filler ($\nu_G \sim 1/M_G$) densities. By using this concept, Chenal et al. [118] have given a coherent description of SIC, i.e. the evolution of crystallization rate and crystallite size (Figure 18a and 18b). Two different regimes, at weak and high effective crosslink density, were highlighted and the molecular weight between physical entanglements in natural rubber ($M_e \sim 7000 \text{ g.mol}^{-1}$ and $\nu_e \sim 1.3 \cdot 10^{-4} \text{ mol.cm}^{-3}$) seems to correspond to the boundary between both regimes. Below the critical value (ν_e), when a sample is stretched, nuclei number increases and the medium mobility decreases with the increase of effective crosslink density. Even if the growth step is slightly hindered, the nucleation step is so promoted that the crystallization rate increases. Simultaneously, the crystallites size slowly decreases until it drops at ν_e . Above the critical value, the restriction of the medium mobility becomes significant and hinders not only the growth but also the nucleation step. Thus, the crystallization rate slows down. The origin of this decrease of the nucleation rate can be related to the creation of an excluded volume for crystallization in the filler vicinity because of a reduced mobility.

These modifications of crystallisation kinetic are related to the material ultimate properties. Tosaka et al. [120] have proposed that SIC induces a microfibrillar structure which can be seen as a network stronger than that created by the sole chemical crosslinks. This structure may significantly contribute to crack growth resistance as suggested by studies that focused on strain-induced crystallization in the crack tip region of CB filled elastomer [68],[121].

III-5 Conclusion

As for microscopic particles, the aspect ratio of the nanofiller introduced in rubber appears as a very important parameter for the reinforcement efficiency. Moreover, the very important surface of interface amplifies the problem of dispersion that often needs supplementary chemical step - such as surface treatment and polymer compatibilisation - or more efficient mixing. This dispersion step can first modify the effective aspect ratio of the particles and therefore have a direct effect on the reinforcement efficiency of the fillers. Moreover, the possible interactions of this interface with the complex formulation of the rubber (needed for its vulcanization) can modify the crosslinking kinetic and therefore the spatial distribution of the crosslinks and the matrix intrinsic properties. Besides, different experiments suggest a decrease of the polymer chain dynamic in the vicinity of the filler. At last, due to the small

inter-filler distance, the filler-filler and filler matrix interaction can more easily play a role in the formation of a continuous filler network whose the reinforcement efficiency is much higher than that of the individual particles. Thus, given the difficulty to dissociate the contribution of each type of interaction, the current author opinion, largely accepted in the community, is to consider that the reinforcement of rubber nanocomposites, the mechanisms of the Payne and Mullins effects probably involve *both* the filler structure and the adsorbed chain. As normally expected with fillers, their presence, by strain amplification phenomenon, leads to an earlier occurrence of crystallisation (when dealing with crystallisable elastomer), but the interfacial interactions also modify the crystallisation kinetic of the materials. Obviously, the ultimate properties of rubber nanocomposites strongly depend on all these phenomena, which control the development of strain anisotropy and damage.

IV Modelling attempts

Given the difficulty to dissociate experimentally all the complex phenomena involved in the mechanical properties of rubber nanocomposite, it seems that a true evaluation of the interest of the introduction of the nanofillers can only be done if some efforts are put in their understanding. Thus, the aim of this last part is to present the different available modelling methods, which can be found in literature, to analyze the mechanical behavior of rubber nanocomposites. The mechanical response of filled rubbers is sometimes seen has the sum of different contributions i.e. that of the polymer network, the hydrodynamic effect and the contribution of filler-filler and/or filler-matrix interactions.

IV-1 Polymer network contribution: modelling the rubber behaviour

The mechanical response of an elastomer is directly deduced from the modelled behavior of one polymer chain, free from interactions with the other chains. The simplest model is the Gaussian one, which models the chain as an assembly of independent segments free of rotation. The elasticity of the chain is entropic and is deduced from a statistical description of its possible conformations. The behavior of a network of such chains can be done with the affine assumption that the macroscopic deformation of the material is proportional to that of each chain. The simplest theoretical description is based on a 3 chain unit and, under simple shear, with the affine deformation of the representative network cell; this leads to the known formula available for low amplitude deformation [122].

$$G=NkT \quad (1)$$

where G is the shear modulus, T the temperature and N the number of active chains per unit volume.

This model can be refined at different levels: (i) at the level of the chain description by considering its maximal extensibility (the Gaussian description is replaced by the Langevin equation), and (ii) at the level of the network description, by accounting for the crosslink spatial fluctuations [123], by using a 8 chain models or a random distributed chain model [124],[125], (iii) at the level of the chain environment by accounting also on the entanglements presence and their role in the chain dynamic [126],[127],[128]. In the later case, lateral fluctuations of the polymer strand are limited by the presence of neighbouring chains leading to a certain confinement of the individual chain in a determined volume with a tube-like geometry.

For instance, Rubinstein [127] gives the evolution of the Mooney function as a function of the extension ratio λ (length over the initial length):

$$f^*(\lambda^{-1}) = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-0.5} - 0.35} \quad (2)$$

where G_c is the modulus contribution of the chemical crosslinks and G_e is related to the entanglement density. f^* is the Mooney ratio defined in tensile test as:

$$f^*(\lambda^{-1}) = \frac{\sigma}{\lambda^2 - \lambda^{-1}} \quad (3)$$

where σ is the tensile stress.

An alternative to these physical models is to adopt a phenomenological description based on the definition of elastic potentials as a function of the different strain invariants, or of the different elongation variables [129],[130]. Note that the number of parameters to evaluate, and therefore of experiments to perform, depends on the accuracy required for the fit of the experimental curves and the strain range that the model wants to account for.

Some authors proposed to extend the expressions used for unfilled elastomer (Ogden or Mooney type) to the composite modelling without accounting explicitly for the specific phenomena induced by the filler presence. Obviously, in such a phenomenological approach, there is no physical meaning of the parameters. The difficulty met by these models, (like in the case of more physical based models) is to account for the viscoelastic response of the material when submitted to a complex stress-strain history. This is done through the parameterisation of the time dependence of the parameters. In addition, the account for non linear character of this viscoelasticity (Payne effect) or the irreversible damage of the material (such as the Mullins effect, and cavitation) can be rendered through the introduction of functions giving the evolution of the parameters during deformation [131],[132],[133]. An intermediate solution can be the introduction in the network model of a second network corresponding to the contribution of the filler, as done for instance by Bergstrom et al. [134].

All these approaches, even the physical based ones, generally consider the elastomer network as homogeneous. In fact, in elastomers, except when they are processed by crosslinking at the ends of chains whose length distribution is known, intercrosslink distances can be widely distributed. The consequences of this distribution can be very important, especially in the large deformation range, where the non linear hyperelastic behavior of the polymer chains is involved. The account for such effects in models needs a more complete description of the network architecture. One can cite in this domain the pioneering work of Termonia [135].

IV-2 Filler contribution: how to describe the composite effect?

Of course, the introduction of filler makes more difficult the modelling of the mechanical properties of the material. The first effect of the introduction of the fillers is what we would call the “composite” effect, i.e. the reinforcement provided by the introduction of the more rigid filler phase. Different models describe the reinforcement of composite materials. Three general kinds of models can be distinguished.

The first series concerns boundary models, based on variational methods, which define the extreme elastic behaviours of composites (for instance Voigt and Reuss bounds which assume a uniform stress (serial model) or a uniform strain (parallel model) in both phases respectively). This is possible for elasticity and for linear viscoelasticity too. However, in the case of filled rubbers, the modulus contrast between both phases is huge (e.g., shear modulus of silica ~ 30 GPa, rubber ~ 1 MPa), so that the obtained bounds (of first, second and third order using respectively first, second and third-order correlation functions) are generally too far apart to be of practical use for comparison with experimental data.

The second set of models involves phenomenological approaches that introduce one or more adjustable parameters. For instance, the serial-parallel model of Takayanagi [136] gives a direct uniaxial representation of the assumed mechanical coupling through an adequate distribution of phases serially or in parallel. This distribution is controlled by one fitting parameter. In specific cases, physical arguments (percolation [137] or filler distribution from morphological observations) can be used to set the adjustable parameter of this type of model.

The last series concerns micro-mechanical modelling, developed in the framework of homogenization theory. They propose an explicit connection between given morphological information on the microstructure of a “representative volume element” (RVE) of the considered material and the overall mechanical response of the associated “equivalent homogeneous medium” (EHM). In the Christensen and Lo 3-phase model [138], the composite is seen as an inclusion surrounded by a matrix immersed in the unknown EHM.

The Herve and Zaoui n-phase model [139] generalized this so-called self-consistent estimate by an iteration technique, embedding the different phases or more specific patterns in the EHM itself [140]. Three-phase predictions are satisfactory when particles are well dispersed in the matrix and far enough from each other [141]. However, as soon as particle aggregation occurs and especially when the rubbery plateau modulus is concerned, the 3-phase model leads to too soft predictions.

This 3-phase model for spherical inclusion has an equivalent in the domain of long fibres, then assumed with an infinite length [142]. When these fibres are short, the calculations are performed using the Eshelby calculation [143] for an ellipsoidal inclusion with the aspect ratio in a matrix taken as the homogenous infinite medium (this calculation was initially proposed by Mori and Tanaka [144]). The general solution for the modulus in the direction of the large axis of the ellipsoid has a strong dependence on the modulus contrast of both phases and on the form factor. One can define a reinforcement factor A with the formula:

$$E_c = E_m(1 + A\phi) \quad (4)$$

Its evolution as a function of the form factor and of the modulus ratio is recalled on Figure 19. One can notice that for a modulus ratio below 100, fibres with form factor above 100 have the same effect on the predicted reinforcement than infinitely long fibres. Moreover, the highest the form factor, the largest the influence of the modulus contrast. These calculations can be applied to the simple case of composites with unidirectionaly oriented fibres. The calculation for a transversely isotropic or totally isotropic material needs the calculation of an average of the reinforcement on all the orientations, calculated in the unidirectional case, as proposed by Tandon and Weng. [145]

The absence of an analytical solution for such calculations leads Halpin and Tsai to propose an empirical equation equivalent to the Mori-Tanaka calculation [146]:

$$\frac{M_c}{M_m} = \frac{1 + \zeta\eta\phi}{1 - \eta\phi} \quad \text{where } \eta \text{ writes: } \eta = \frac{\frac{M_f}{M_m} - 1}{\frac{M_f}{M_m} + \zeta} \quad (5)$$

Where ϕ is the filler volume fraction, ζ is a factor depending on the filler form and M the modulus with indices f for filler, m for matrix and c for composite.

Ashton and al. [147] have shown that the equations can be used for the reinforcement of unidirectional fibre composites. They advised the use of $\zeta=2a/b$ for the calculation, where a the fibre length and b the fibre diameter, of the longitudinal modulus E_{11} , $\zeta=2$ for the transverse modulus E_{22} or E_{33} , $\zeta=1/(3-4\nu_m)$ for the shear modulus G_{23} , and $\zeta=1$ for shear moduli G_{12} or G_{31} with $\nu_{31}=\nu_{12}$. The Halpin and Tsai formula is also often used for the modulus calculation of laminated. In this case, the modulus tensor is the average on all the

orientation of the moduli tensor of each ply, weighted by the volume fraction. The Halpin-Kardos model leads to the analytical formula of a laminate containing 4 plies in which fibres are oriented respectively at 0° , 45° , 90° , and 135° . Tsai and Pagano, from these calculations, have proposed a simplified expression of a transversely isotropic composite [148] :

$$E_{2D} = 0.375 E_{//} + 0.625 E_{\perp} \quad (6)$$

Where $E_{//}$ is the longitudinal modulus of the ply, and E_{\perp} its transverse modulus.

The modulus of an isotropic composite can be obtained by a three-dimensional average such as that proposed by Van Es [149]:

$$E_{3D} = 0.184 E_{//} + 0.816 E_{\perp} \quad (7)$$

Even if his process is questionable, the results are equivalent to the calculation of Tandon and Weng [145].

All these models have been first developed in the linear domain and they are useful to compare experimental data with predicted modulus values taking into account the filler parameters such as modulus and shape. However, they are adimensional and do not predict any effect of the filler size. Moreover, the interface between filler and matrix is assumed to be perfect. When applied to nanocomposites, they generally underestimate the reinforcement, especially in the case of thermoplastics above Tg or rubbers [150]. This is however not always the case. For example, in the case of CNT filled nanocomposites, even at low nanotubes concentrations, the experimental data can be below predictions from the Halpin-Tsai model [146]. The gap between the predictions and experimental results has been attributed to imperfect dispersion and poor load transfer. Actually, even modest nanotube agglomeration may impact the diameter and length distributions of the filler. This will decrease the aspect ratio, and this can even reduce the modulus of the filler relative to that of isolated nanotubes given the weak interaction forces between nanotubes [151].

To go further in the account for the complexity of elastomer behavior, two different fields of mechanical modelling are presently developed. First, the impact of agglomeration can be evaluated through the adaptation of the micro-mechanical approaches cited above. Chabert et al. [141] presented a homogenization method based on generalized self-consistent schemes to model polymer-based nanocomposite behavior using different structure patterns. For a silica filled SBR, Mélé et al. [152] defined three phases: silica particles, bound rubber (the rubber close to the particle), and unbound rubber. Their self-consistent model introduces the viscoelastic properties of the different phases in a representative morphological pattern that depends on the particle content. Some authors proposed to apply the self consistent 3 phase model in successive steps [45]. The Finite Element Method (FEM) is sometimes used to

calculate stresses and strains in the Representative Volume Element (RVE) containing one [153] or several inclusions with different sizes in random positions for soft inclusions [154] or rigid particles for a nanocomposite [155]. A stochastic and deterministic model was proposed by Minakova et al. [156] for the macrostructure geometry of polymer materials containing dispersed fillers and allowed describing the agglomeration and desagglomeration for filler of complex structure.

The second field concerns larger deformation, for which non linearity should be introduced. Because filled rubbers are often used in situations involving large deformations, it is of practical, as well as theoretical interest, to develop adapted constitutive models. But the models must be simple enough to be implemented in standard finite element codes and to be able to carry out simulations at the structural level (“structural” in the sense of piece design). To extend the micro-mechanical models to higher strains, it is necessary to consider both the non-linear behavior of the phases and a specific scale transition rule, which takes into account the non-linear accommodation of stress heterogeneities between the phases. Lopez-Pamies et Ponte Castanada [157] develop non linear homogenization modelling (second-order) that takes into account the evolution of the microstructure (fibres orientation) and the possible onset of macroscopic instabilities in fibre-reinforced elastomers subjected to finite deformations. Tomita et al. [158] propose a computational simulation based on a plane strain rubber unit cell containing CB fillers under monotonic and cyclic strain with a non affine molecular-chain network model. The results reveal the substantial enhancement of the resistance of the rubber to macroscopic deformation, which is caused by the marked orientation hardening due to the highly localized deformation in the rubber. The chains disentanglement during the deformation of the rubber results in the magnification of the hysteresis loss during cyclic deformation processes. Such an approach has also been applied to evaluate the effect of aggregation.

IV-3 Account for the filler-filler and filler-matrix interactions

As seen above, lots of models only introduce the role of interactions through the assumed permanent and perfect load transfer between the matrix and the filler. Nevertheless, filler – filler and filler-matrix interactions are known to play a more complex role in non-linear manifestations such as Payne and Mullins effects.

In the filler structure models, the filler-filler interactions are considered as preponderant. Under this assumption, the strain dependencies of both the viscous and elastic moduli have been modelled by Kraus [159], assuming Van der Waals interactions between particles. The contribution given by interaction forces between aggregates to the modulus is proportional to

the number of contacts whose rigidity is governed by the size and the form of the aggregates. Their separation occurs at a given strain that corresponds to the maximum restoring force. The concept of occluded elastomer is also often introduced in these filler aggregation models [7]. Nevertheless, the model of Kraus does not predict nor the values of the high and low amplitude moduli, neither the strain necessary for the modulus decrease and the influence of temperature. The estimation of the modulus at high amplitude can be performed using the models presented above (Guth equation, Christensen and Low 3-phase model...). To estimate the low amplitude modulus, some authors prefer to consider the filler structure from the percolation theory [160]. They make the assumption that it has a scale invariance of a fractal object [161]. The reinforcement is deduced from the calculation of the rigidity of the cluster objects forming the network. It is found a power law dependence of the modulus with the filler content. The composite deformation leads to the breakage of the cluster in smaller and smaller units, which lose their effectiveness [162]. This description leads to the same Kraus formula in which the parameters are related to the description of the filler structure: its fractal dimension and its connectivity [160]. Gerspacher [163] uses a different formalism to describe the process of rupture and reformation of contacts between aggregates. He assumes a distribution of pair of aggregates in the material, from a linked state to a separate state. The alternation, during DMA measurements, of these states (linked-detached-linked) is responsible for energy dissipation.

A second set of models used to describe the Payne effect assumes that the matrix-filler interactions are responsible for this effect [164]. These models are based on the idea of adsorbed polymer chains at the filler surface (bound rubber) that display a decreased molecular mobility and/or may act as supplementary cross-links in the material. Then, under the increase of strain, a mechanism of adhesion and de-adhesion of polymer chains at the filler interface is proposed. In a purely entropic description of the viscoelastic behavior of the material, Maier and Goritz [100] then assimilate these bonds to supplementary crosslinks, the initial modulus being then the direct consequences of an increase of active chains in the elastomer, and its drop the consequence of a rupture of these bonds. This vision has the advantage to nourish the debate on the importance of matrix-filler interactions on the Payne effect but the model deduced from this is too global (homogenising) and leads to meaningless theoretical crosslink densities. Indeed, the reinforcement provided by the filler non deformability (compared to the matrix one) cannot be forgotten.

Besides, the multifunctional crosslinking nature of the fillers might be at the origin of an immobilized polymer phase in their vicinity, or at least of a polymer phase with a mobility gradient. Different modelling scales are explored to evidence it. The presence of filler with average distance between them of the same order as the gyration radius of the polymer chain

decreases the chain conformational freedom, and perturbs the entropic elasticity response of the matrix. Mark has worked for many years on this aspect and has developed Monte Carlo based simulation of filled elastomer [165]. Natural rubber network in presence of saponite or carbon black (N234) [166] has been evaluated by applying the tube model theory. This results in a marked decrease of the tube dimensions due to nanoparticle/elastomer interactions, which restricts the movement of the rubber chains to a lower volume. More and more work is devoted to molecular dynamics accounting extensively for all the different interactions involved at the atomistic level. We are only at the beginning of these types of simulation whose capabilities increase with the growing calculation efficiency of the computing facilities [167],[168],[169].

Instead of the description of the material at the molecular level, some might prefer a less refined but more straightforward approach. Thus mesoscopic scale modelling is developed in order to capture the complex role of the filler-matrix microstructure in the elastomer nanocomposites: so-called discrete numerical model simplifies the material description by considering only the mechanical junctions between points. This enables to explicitly account for the filler spatial organization in the matrix and the nature of contacts between the filler particles and the filler particles and the matrix [170]. This modelling is easy to handle in the linear domain and therefore can be useful to estimate the material modulus. However, the description of phenomena such as the Payne effect or the Mullins effect needs the introduction of viscoelastic contact and criteria for the rupture of either the matrix filler or filler-filler contacts. If developed, this approach can take benefit from the early work of Bueche et Halpin [171]; they proposed for the Mullins effect and the material rupture a molecular model of propagation of rupture of polymer filament, with a dependence of the crack propagation with the viscoelastic properties of the material. Boonstra [172] and Dannenberg [104], added in the interpretation the slipping of chain at the polymer filler interface, that was included in the modelling of Ambacher et al. [173]. These ideas could be advantageously introduced to describe the material behaviour from the linear range up to its rupture.

IV-4 Conclusion

To conclude, all the experimental evidences and theoretical calculations seem to indicate that both filler structure and adsorption of polymer chains are involved in the non-linear viscoelastic behaviour of nanoparticle filled rubber. The modulus measured is obviously the result of a viscous mechanical coupling of the matrix with a complex structure of more or less aggregated fillers. The deformation of this ensemble is very heterogeneous and involves complex dissipative mechanisms such as rupture of the different type of interactions, filler

reorganization and cavitation. Two approaches can be followed to describe this complexity: the first one consists in forgetting it by the use of phenomenological macroscopic constitutive equation. The second approach wants to account for the phenomena occurring at the filler scale (filler spatial repartition, more or less refined) or even at the molecular level (filler-filler and filler-matrix interaction). In addition to the comprehension it brings to the experimental observation, the advantage of this second approach is to feed the macroscopic modelling with meaningful physical parameters. This work is in progress. It is quite advanced in the domain of small deformation but is still a challenge in the domain of large strain, when damage (bond rupture, void formation, spatial reorganization of the fillers) makes the problem very difficult.

V General Conclusion

To conclude, in literature, a large number of papers are concerned with rubber nanocomposite mechanical behaviours. Among the different types of filler that have been tested, some are already extensively used in industry (carbon black, silica) whereas others are still under evaluation. Prior to any mechanical studies, fillers have to be dispersed in the host elastomer. To do so, several strategies are reported in literature, including different processing routes, the use of surface treatments or the modification of the matrix. The obtained dispersion state is more or less rigorously controlled, thanks to dedicated characterization techniques at various scales (such as SAXS, TEM, AFM..) or by an indirect approach based on the discussion of mechanical performances.

HOW nanofillers impact on the mechanical behaviour of rubber nanocomposites is the point addressed in numerous papers. Actually, the introduction of nanoscopic filler strongly modifies the mechanical behaviour of unfilled rubbers. In the small deformation range, instead of the quasi linearity observed in shear with unfilled elastomer, one observes a typical non-linear viscoelastic behaviour, so called Payne effect. In the large deformation range, the stress is remarkably increased for a given strain, the hysteretic loss during deformation cycle is enhanced, a strong sensitivity to the first deformation, so-called Mullins effect, is revealed, and the ultimate properties such as wear resistance and rupture behaviour can be improved. Lots of experimental evidences of the improvement of mechanical behaviour of rubber nanocomposites are reported in literature. However, due to the large number of parameters that can be changed in the formulation and the process, the empirical optimization of the mechanical properties might not be the most relevant approach.

Indeed, to go further, it is important to understand WHY nanofillers are so efficient for rubber reinforcement and why they lead to all these complex non linear phenomena. Through the discussion of literature data, several main features can be captured. First of all, as for all heterogeneous materials, the nanocomposite macroscopic behaviour depends on the behaviour of each phase, their volume fraction, their topological arrangement (dispersion, orientation) and on interfacial properties. The latter become of first importance in nanocomposites because the small size of the filler leads to a high interface/volume ratio, and the average distance between domains, i.e. between filler surface can be of the order of the macromolecule coils dimensions. Reinforcement is sometimes attributed to the presence of a rigid phase (immobilized interphase) whose volume fraction can be non negligible. In addition, the existence of a filler network, which is never discussed for classical, i.e. micrometer scale composites, is often evidenced for nanocomposites, and can be analyzed through the percolation concept. The properties of this more or less flexible network is ruled by the filler/filler (direct bonding between neighbouring fillers) and filler/ matrix interactions (when macromolecules that are adsorbed or chemically linked onto the filler surface link together two (or more) fillers). These interactions appear to play a preponderant role at small and large strain. In the later case, the analysis of the mechanical behaviour is even more complex as strain heterogeneities, desagglomeration and decohesion processes may take place.

Thus, one can wonder THEN what to do and what are the next challenges. To study more deeply the incidence of the various parameters already mentioned (size, shape, interfacial energy, topological distribution, etc.), one route can be to process model materials trying to modify only one of these parameters. However, this is a tricky task as it is not easy to produce fillers having the same chemical structure with different shapes (rod, platelet, sphere), or even with different sizes and identical surface properties. An alternative way involves the comparison of experimental data with prediction obtained from modelling approaches at different scales (micro mechanical approaches, mesoscopic discrete modelling or atomistic Monte Carlo based simulation). Unfortunately, at the present time, most of the models display insufficient prediction capabilities. Progresses can be expected from development of techniques able to characterize the 3D spatial distribution of filler at pertinent scale (filler network) and to give insight on contact force between filler (filler-filler interactions, through or not a matrix layer). Indeed, these data are necessary to improve the modelling of the mechanical behaviour especially at large strain, when modification of the filler distribution cannot be neglected anymore, neither cavitation and decohesion phenomena.

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Figure 1:

Transmission Electron Microscopy of primary carbon black particles coalesced into primary aggregates and further associated in agglomerates. After T.Prasse, PhD. Thesis, Technical University Hamburg-Harburg, 2001

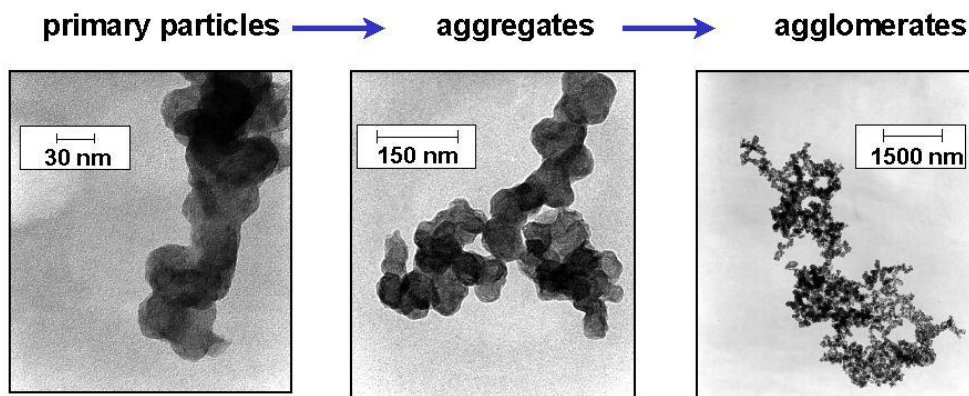


Figure 2:

Electron microscopy of intercalated and delaminated platelet-like nanofillers in a PA6 matrix. After E. Reynaud, PhD. Thesis, Institut National des Sciences Appliquées de Lyon 2000

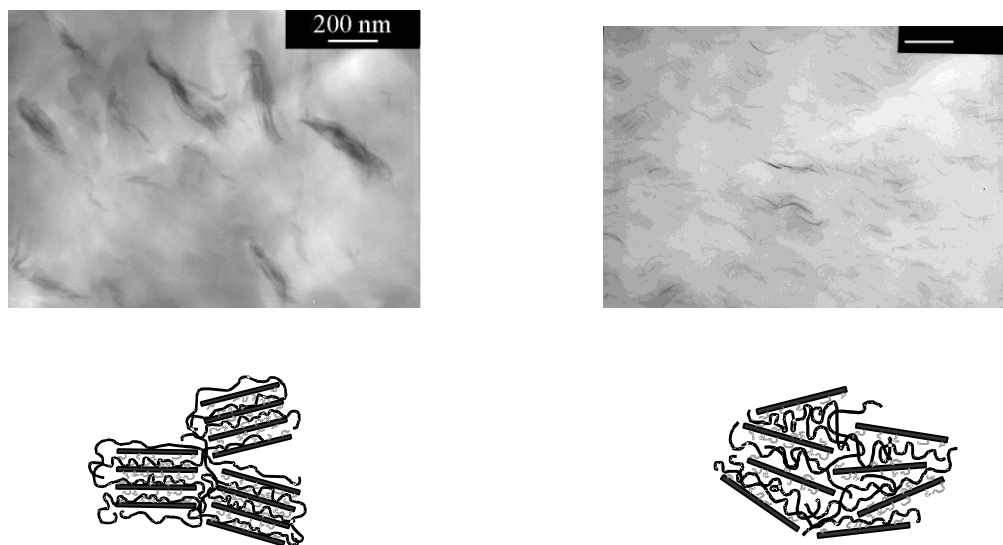


Figure 3

Transmission Electron Microscopy of Multi Wall Carbon nanotube. After F. Dalmas, PhD. Thesis, Institut National des Sciences Appliquées de Lyon 2005.

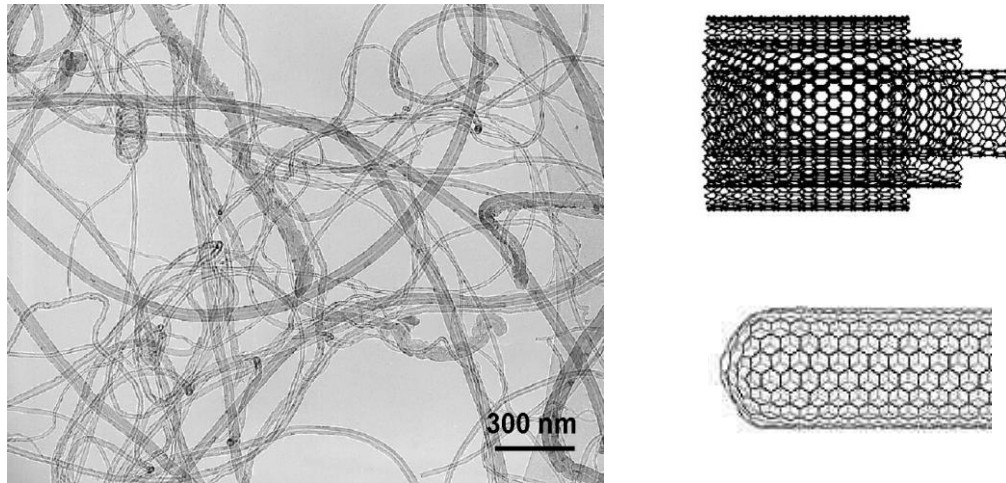


Figure 4

Shear stress-strain curve of unfilled NR and silicone (at low strain) at different strain rate, from $2.5 \cdot 10^{-5}$ up to $2.5 \cdot 10^{-2} \text{ s}^{-1}$. Reprinted with permission from L. Chazeau et al. Polym. Compos. 21, 202 (2000). © 2000 Society of Plastics Engineers.

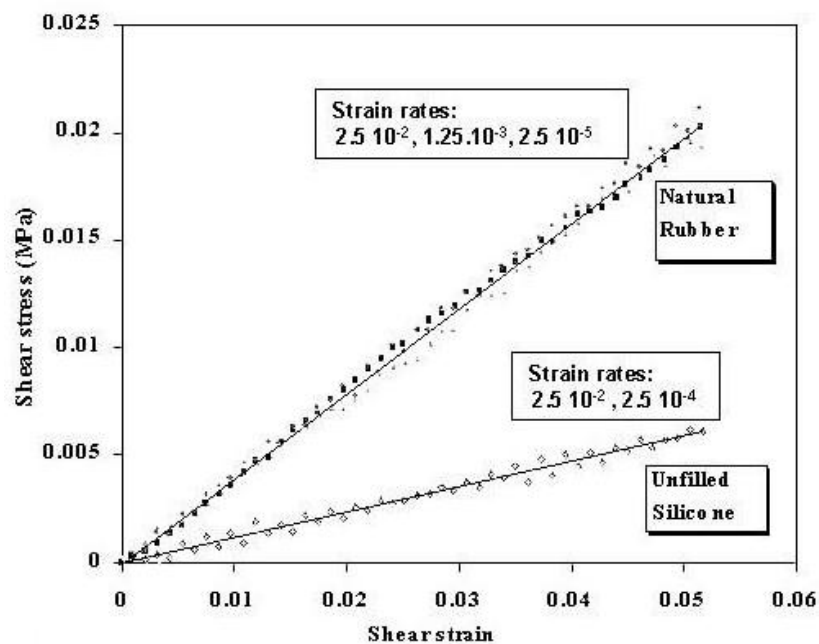


Figure 5

Scheme of the molecular structure of an elastomer: crosslinks (black dots), (a) entanglements, (b) trapped entanglements.

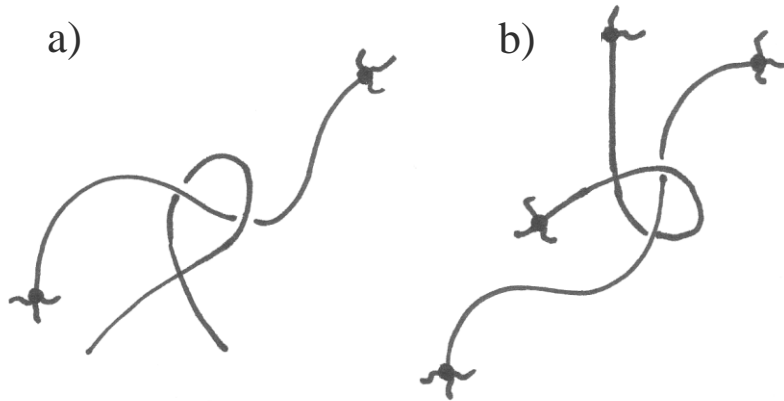


Figure 6

Payne effect measurement of a carbon black filled NR : elastic (G') and viscous (G'') moduli a function of the shear amplitude (at 1Hz). The measurement is performed at increasing shear amplitude. Reprinted with permission from L. Chazeau et al. Polym Compos 21, 202 (2000).© 2000 Society of Plastics Engineers

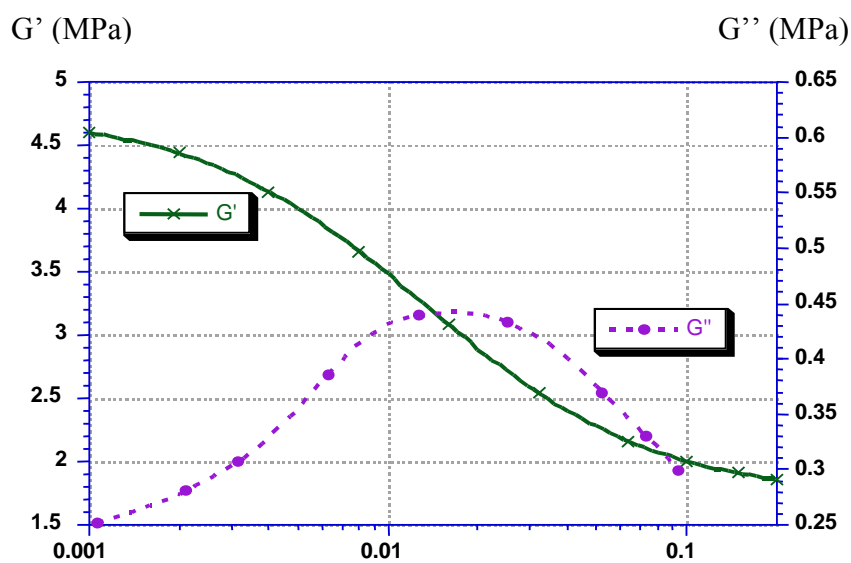


Figure 7

Stress-strain curves of pure NR and NR /MWNTs composites. Reprinted with permission from L. Bokobza et al. Polym Int 55, 1090 (2006) © 1999-2008 John Wiley & Sons, Inc.

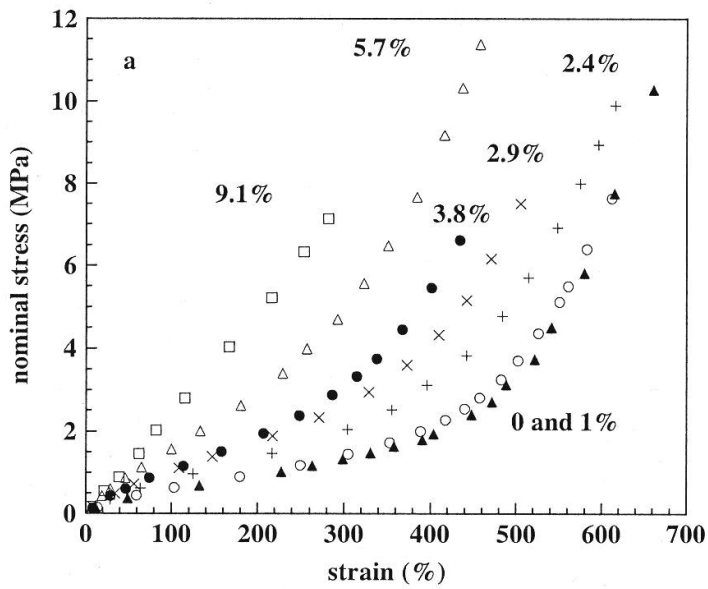


Figure 8

The Mullins effect on stress-strain curves in reinforced elastomers. The modulus on second and subsequent curves is lower than obtained on first extension.

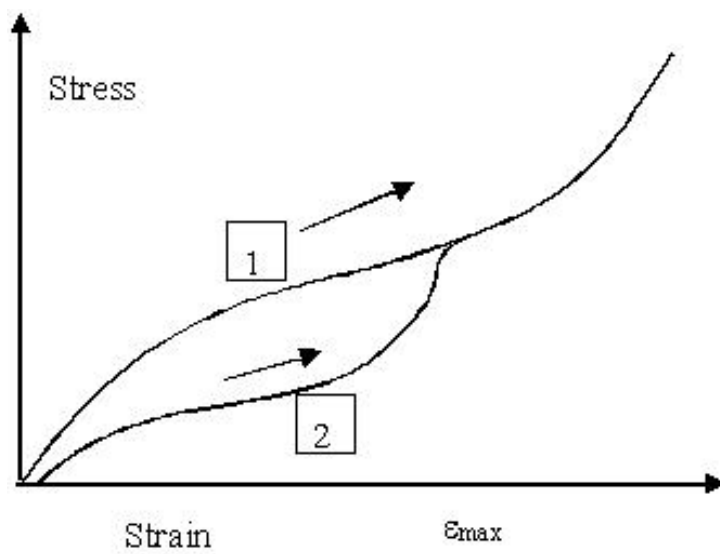
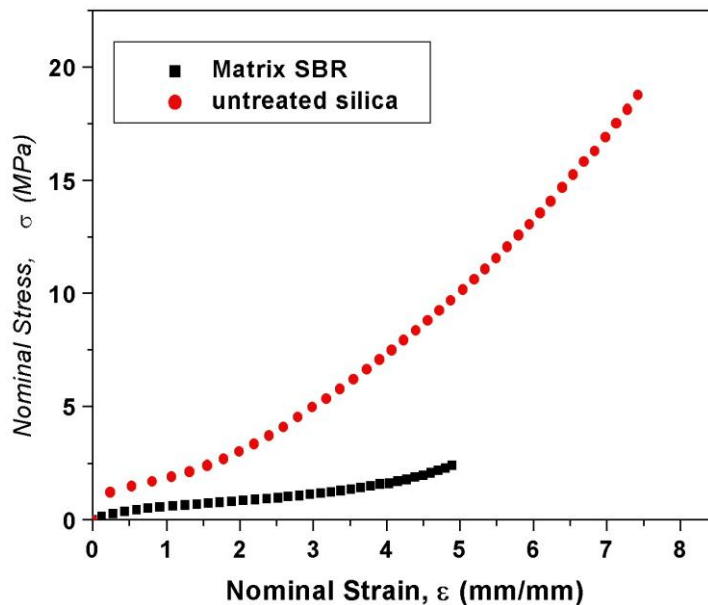


Figure 9

a) Stress strain curve of SBR and 20 %vol. silica filled SBR (at 298K with a strain rate of $4 \cdot 10^{-1} \text{ s}^{-1}$). Reprinted with permission from L .Chazeau et al. Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites, 2, 63 (2003) © 2003 by American Scientific Publishers.



b) Stress–strain curves for pure SBR and MWNT/SBR composites. The filler content is expressed in phr (phr = parts per hundred parts of rubber) Reprinted with permission from L. Bokobza et al. Polymer 48, 4907 (2007) © 2007 Elsevier B.V.

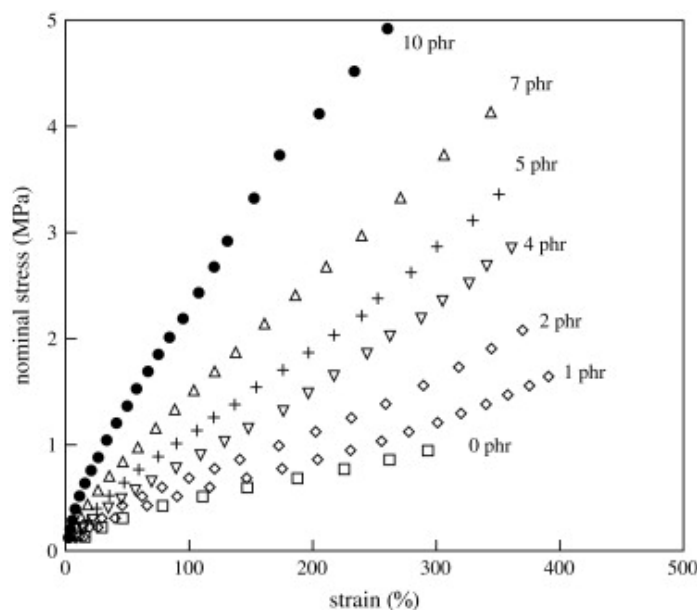


Figure 10

Rupture envelope for SBR elastomer filled with different concentrations of carbon black. Theoretical curve (full lines) deduced from the combination of creep curves and the Bueche-Halpin theory. Reprinted with permission from F. Bueche et al., J. appl. Phys., 35, 36, (1964) ©1964 by the Institute of Physics.

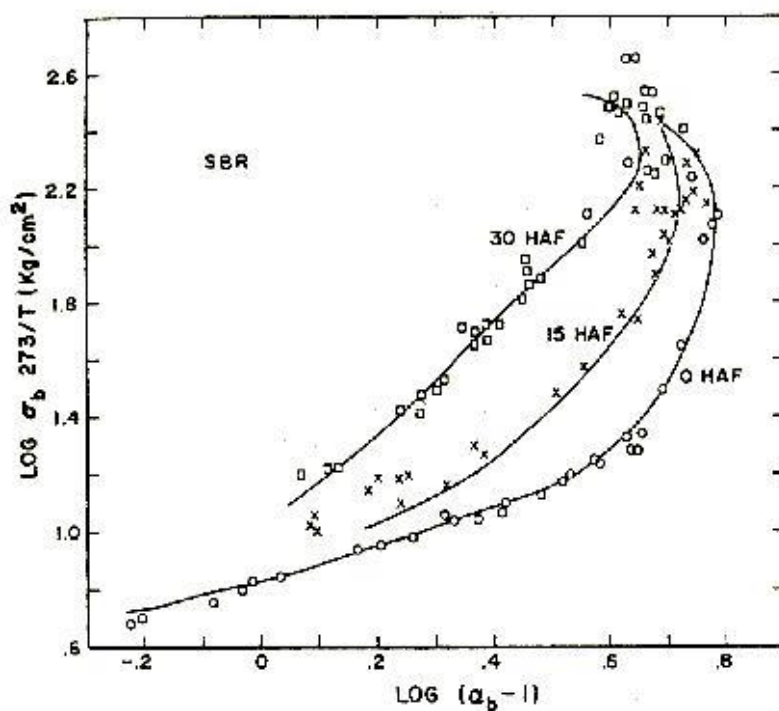


Figure 11

Crack propagation in CB filled NR can present a strong deviation (tensile strain on notched samples performed at room temperature with an initial strain rate 0.01 s^{-1}).



Figure 12

Effect of dispersion and aggregation of the silica on the mechanical properties of the composites having a silica content of 35 wt%. Reprinted with permission from Z.Pu et al.. Chem Mater 9, 2442 (1997) © 1997 American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

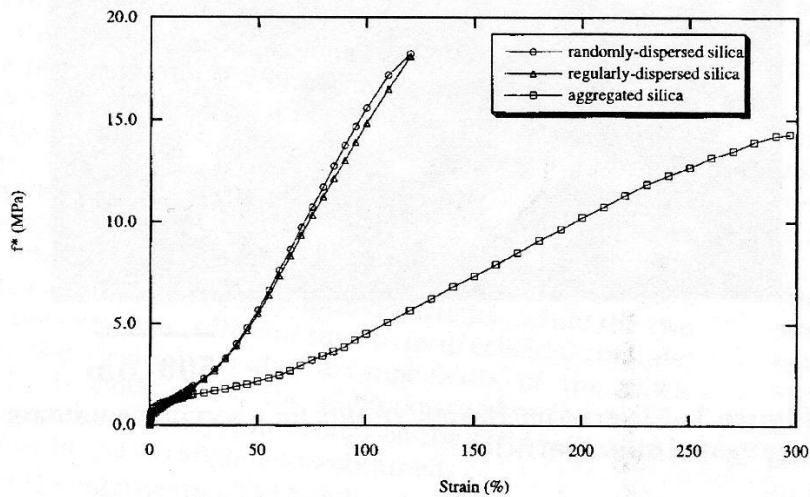


Figure 13

Influence of the filler content on the Payne effect amplitude (i.e. the modulus drop value). Carbon blacks with two specific surface (GSu for large surface, PSu for small) and twodifferent DBP structures (GSt et PSt) have been studied. The influence of the structure is of second order compared to that of the specific surface. Reprinted with permission from L. Chazeau et al. Polym Compos 21, 202 (2000).© 2000 Society of Plastics Engineers.

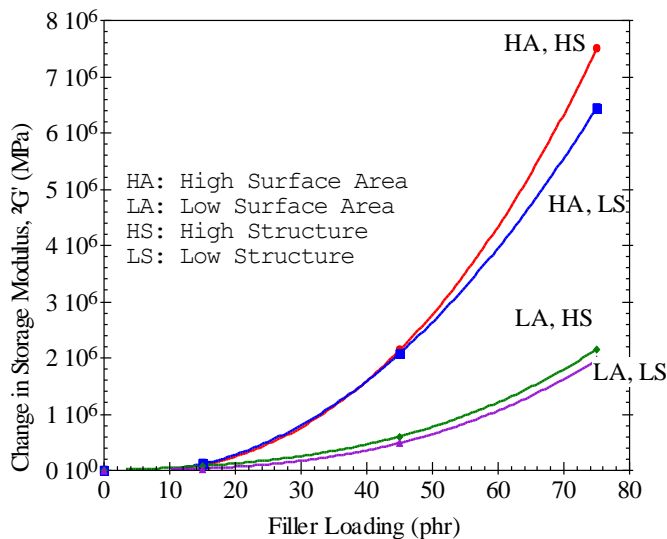


Figure 14

Storage modulus versus dynamic amplitude for Si (neat silica), AR (silica grafted with covering agent) and AC (silica grafted with coupling agent) filled SBR (20 %vol. silica). Test performed at room temperature and 5 Hz. Reprinted with permission from J. Ramier et al.. J Polym Sci Part B 44, 143 (2006) © 1999-2008 John Wiley & Sons, Inc.

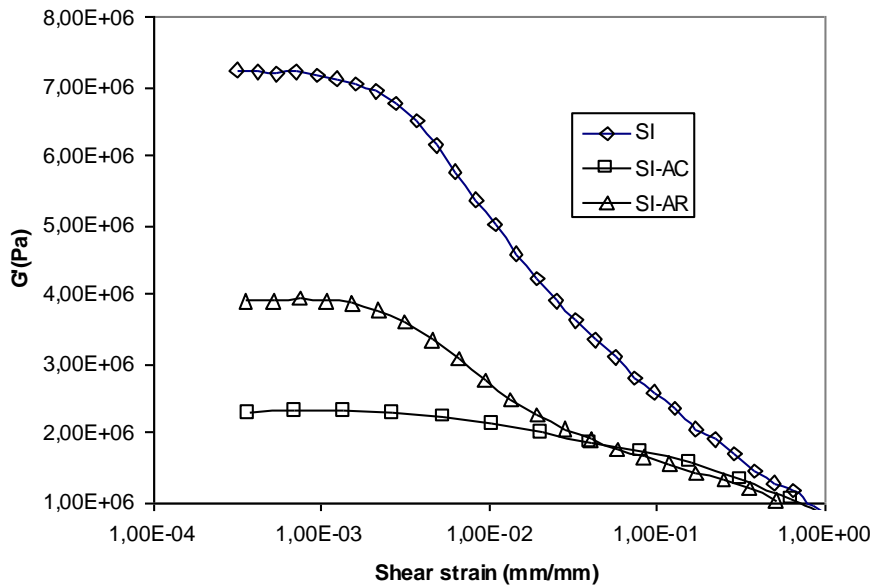


Figure 15

Physical interpretation of the Mullins effect as described by Dannenberg.

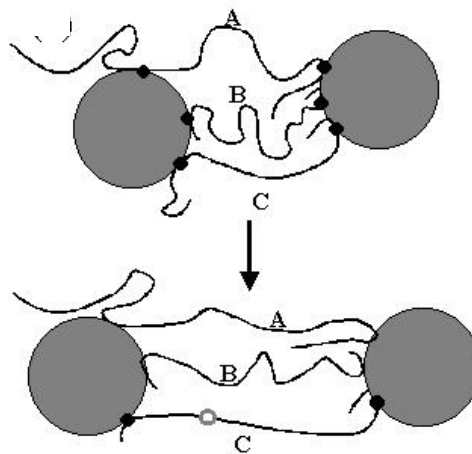


Figure 16

Effect of covering agent ratio on vulcanization kinetic : ◆ Silica, ▼ AR8-3, ▲ AR8-6, ● AR8-8, ■ AR8-14, - Matrix.

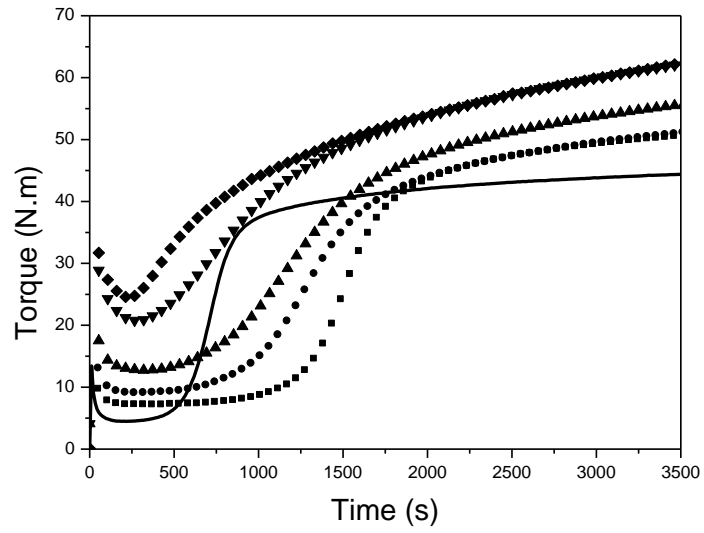


Figure 17

Crystallization versus strain for a) Silica (S5-S9: 50 phr) or b) Carbon Black (S1-S3: 45 phr) filled and unfilled NR matrices (NR1-3). Tests are performed at room temperature and strain rate 0.25 min^{-1} . Reprinted with permission from J.M. Chenal et al. Polymer 48, 6893 (2007) © 2007 Elsevier B.V.

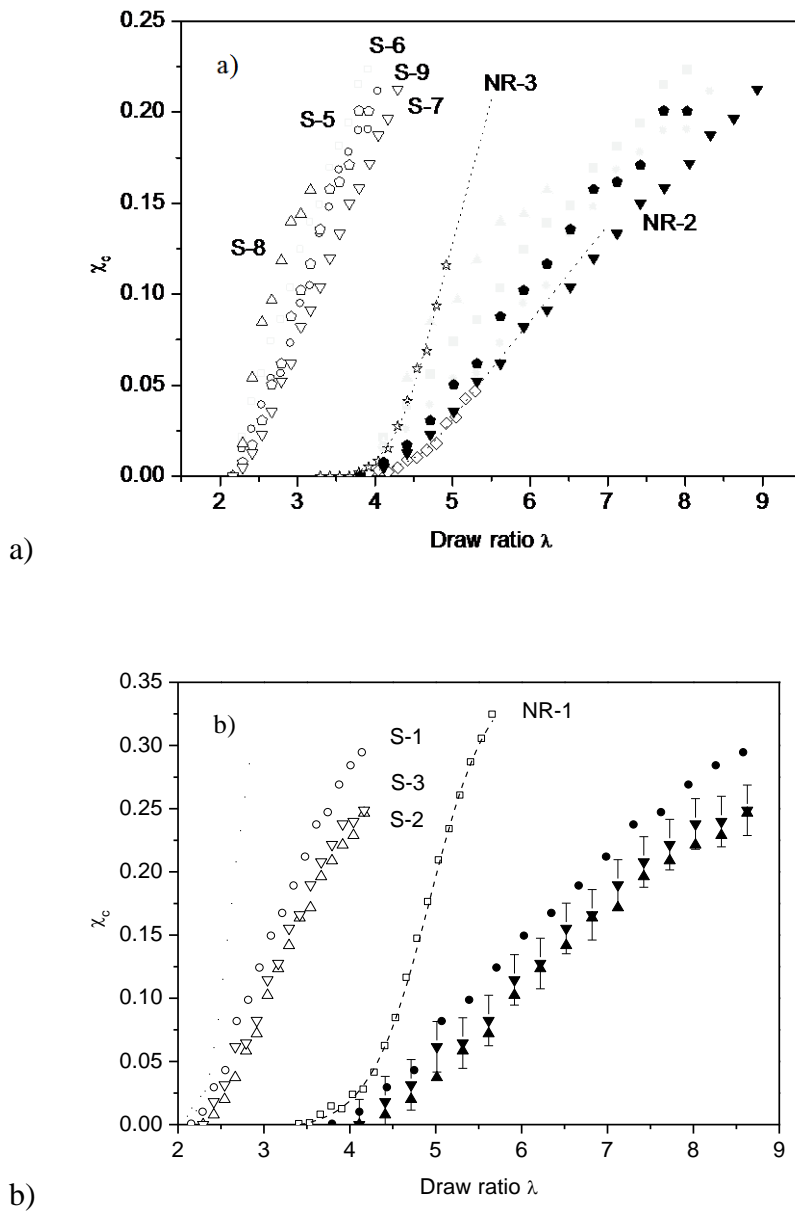


Figure 18

a) Variation of average crystallites' volume versus effective crosslink b) Crystallization rate versus the effective crosslink density. Reprinted with permission from J.M. Chenal et al. Polymer 48, 6893 (2007) © 2007 Elsevier B.V.

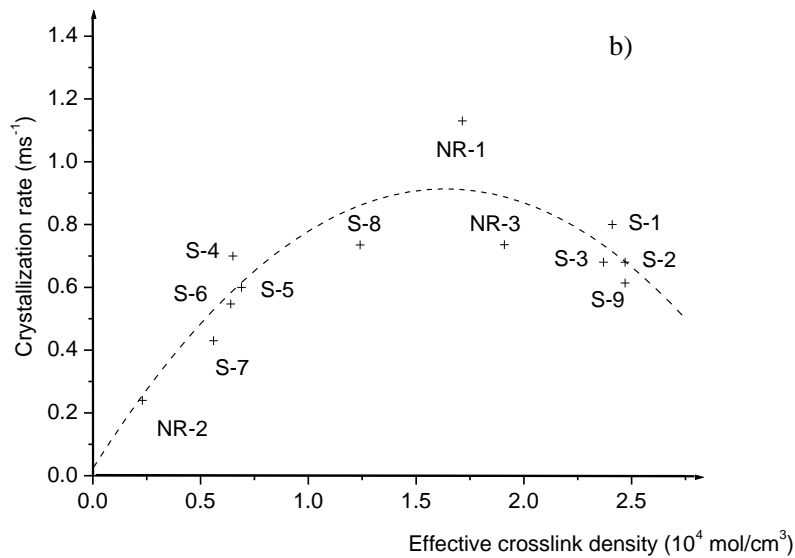
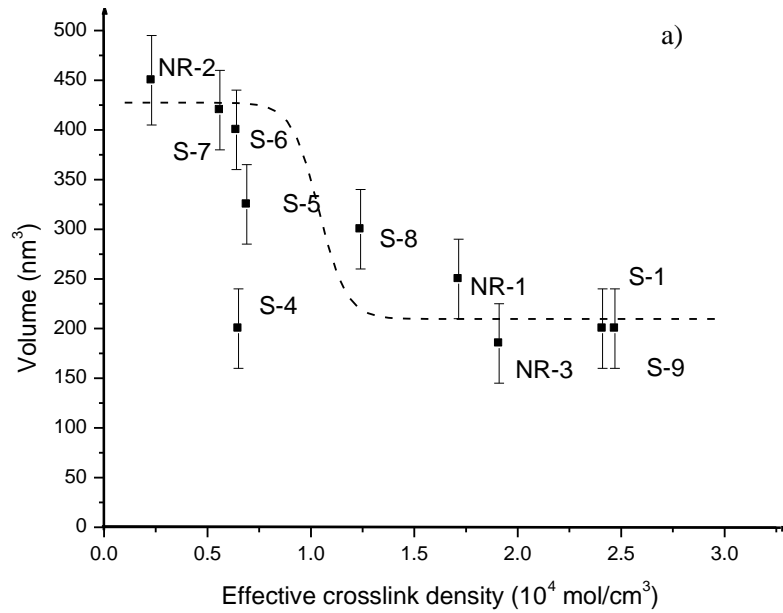


Figure 19

Influence of the filler length on the reinforcing factor A (cf equation 4) as a function of the inverse filler aspect ratio ξ and the filler-to-matrix modulus ratio E_f/E_m . After R.M. Christensen, "Mechanics of Composite Materials" Wiley, Chichester, 1979 © 1979 Wiley

