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Furthering the understanding of the non linear response of filler reinforced elastomers

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ABSTRACT

The cyclic deformation of filler reinforced elastomer compounds results in energy losses caused by a partial hysteretic breakup and subsequent reformation of the filler network. This phenomenon has significant socio-economic consequences as it affects the rolling resistance of tires and consequently the fuel economy of cars. The results of experiments with an on line rheometer provide more detail on our earlier reported findings that this filler network does not exist after the elastomer compounds are first mixed but forms on storage by a flocculation process particularly at higher temperatures to which rubber compounds are exposed to during shaping and vulcanization. Additionally they suggest that the formation of a filler network does not only depend on the type and volume fraction of filler but also on the thermodynamic interaction between the host polymer and the polymer chains which attach themselves physically and/or chemically to the filler surface during composite mixing. Since the embedded fillers resemble core/shell nanoparticles we drew on the results of published theoretical studies on the stabilization of colloidal systems to help define key factors contributing to the stability and equilibrium morphology of filler reinforced elastomers. The insight gained offers an explanation on why composites made with end group functionalized polymers have a reduced filler network manifested by a significantly lower excess storage modulus $\Delta G'$.

1. Introduction

Elastomers need to be reinforced with significant quantities of fillers such as carbon black (CB) and silica (Si) to achieve the physical properties needed for high performance application in tires and other products. The addition of such fillers in quantities of up to about 25 vol % result in high tensile strength, good cut growth resistance and a maximum extension of the vulcanized compounds to several hundred percent. However such high filler loading also causes the low strain deformation to become very non linear. In cyclic deformation one measures a very high storage modulus G' at low strains which diminishes with increasing strain amplitude reaching asymptotically a value of $G'(\infty)$ but G' partially recovers when the strain is removed. The loss modulus G'' reaches a maximum at the inflection point of the storage modulus curve. As a result repeated cyclic deformations such as encountered in rolling tires lead to significant hysteretic energy losses (proportional to G'' or $\tan\delta$ depending on the mode of deformation) that increase the tire rolling resistance and thus lower the fuel efficiency of vehicles equipped with such tires. It is for this reason that this phenomenon has received much attention as means are being sought to reduce this hysteretic non linear response of tire compounds.

The non linear behavior of CB filled rubber compounds was first observed by Payne [1,2], who proposed that the non linearity is caused by a filler network which is disrupted even by small strains but can reform to a certain extent once the stresses are released. This phenomenon later called the Payne effect has in later years been the subject of many studies [3–11] addressing the effect of filler level, type and treatment, theories that had been proposed for the Payne effect etc. including a good review article by Wang [11]. More recently it was also discovered [12–16] that the non linear response can be reduced by the use of polymers having a functional group which can react with CB and thus get attache to the filler surface. Some of these efforts led to the development of a number of end group modified elastomers mainly for use in tires.

Up to that time it was assumed that this filler network is generated when the elastomer is mixed with the filler during the preparation of rubber compounds. However Bohm and Nguyen showed [17,18] that the network does not exist at that time but is later formed on storage after the secession of shear and increasing in rate with temperature. Hence most of the network is formed during molding and particularly during the first few minutes of vulcanization. The authors further argued that the network is

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generated as a result of filler flocculation and showed that if the vulcanization is done at room temperature such as can be accomplished by radiation induced crosslinking instead of conventional sulfur based vulcanization at about 160 °C the non linearity is significantly reduced. This paper summarizes the results of follow up experiments performed with an on line rheometer which were only briefly abstracted in conference proceedings [18]. Also presented is a simple model describing factors governing filler flocculation and the hysteresis improvements seen with end group functionalized polymers.

2. Experimental

2.1. Materials

The polymers used and the compounds prepared for this study are listed in Table 1. Two random 23/77 styrene-co-butadiene copolymers (SBR) were prepared by anionic polymerization in hexane. Both had a cis/trans/vinyl microstructure of 29/43/28, molecular weights of 120 and114 kg/mol respectively, a molecular weight distribution M_w/M_n of about 1.4 and Tg's of −53 °C. One was initiated with BuLi, the other with Bu_3SnLi and both were later terminated with iPrOH. Also used was a Ni catalized high cis-polybutadiene with a cis-1,4 content of 96% made by the Firestone Polymer Company and four low molecular weight polybutadiene probe polymers made by anionic polymerization with a. cis/trans/vinyl microstructure of 38/51/11, molecular weight distributions M_w/M_n of about 1.15 and Tg's of −93 °C. Two, initiated with Bu_3SnLi, had molecular weights of 5 and 10 kg/mol respectively and thus had Sn end groups which can react with functional groups on the carbon black surface. The two other polybutadienes had the same molecular weights and microstructure but lacked the Sn end groups as they were initiated with BuLi.

The N347 and N339 carbon blacks were obtained from the Cabot Corp. and the HiSil 210 silica from PPG Industries Inc. The coupling agent used in Si compounds was bis-(3 triethoxysilylpropyl)tetrasulfide produced by the Degussa/Huls Corp.

The composition of all the carbon black and silica filled compounds is described in Table 2 along with details on the mixing procedures applied. Mixing was done in a Brabender Plasticorder, preheated to the indicated temperature T_o following which the compounds were sheeted on a heated mill. To assure a high level of filler dispersion particulary for silica filled compounds an additional mixing step of 5 min (remill) was used. The filler concentration in all these compounds (A-G) was 16 and 18 vol% respectively.

All the compounds for the on-line rheometer experiments were prepared by this two stage mixing process and thus did not contain any vulcanization inducing compound ingredients. A few of the compounds were also molded into plaques and vulcanized at 160 °C for 20 min for the testing of physical properties in the vulcanized state. In those cases the ingredients needed for vulcanization were first added in a short additional (third) mixing step with the Brabender Plasticorder preheated to 90 °C.

2.2. Bound rubber and graft density measurements

To determine the weight fraction of end group functionalized polymers reacting with the carbon black surface 10 phr of the four low molecular weight probe polymers listed in Table 1 were added during the mixing of a standard carbon black filled compound prepared with 100 phr of the high cis PBD and 50 phr of N339 carbon black. This exposed the probe polymers to the temperature and shear environment normally encountered in a compound mixing process. Bound rubber measurements were subsequently conducted on all four compounds (H–K) as well as compounds A and D by solvent extraction in toluene at room temperature for three days. The fraction of the low molecular weight probe polymer which had not reacted with carbon black during the mixing of the compound was determined from a GPC analysis of the solvent extract with the results shown in Table 1. As anticipated both non functional probe polymers did not get retained in the bound rubber fraction as polymer of such low molecular weight are neither expected to contribute to bound rubber formation to any significant extent nor could they get chemically bound to the carbon black surface. In contrast about 50% of the functional polymers added to compounds I and K became attached under the experimental conditions used.

2.3. Rheology measurements

The rheological tests were conducted with a Dynastat Viscoelastic Analyzer produced by Rheometrics to determine the storage and loss modulus under cyclic deformation as a function of strain, frequency and temperature. For the study of filler flocculation a modified on - line rheometer of the former Rheometrics Company was used with Fig. 1 showing a schematic diagram of the equipment. The mixed compounds were fed into a small extruder which pumped the material through a test chamber with an oscillating cylinder having attached torque sensors to measure the rheological response at different temperatures and strains either during flow of the compound through the apparatus or after the secession or absence of such flow.

3. Results

In our earlier study [17] it was shown that a filler network does not exist to any great extent after the polymer and filler are first combined during mixing when the filler is at first distributed and

Table 1
Polymers, fillers and additives used in compounds along with bound rubber and graft density data.

Compound	Matrix Polymer		Probe Polymer		Filler		Si- 69	Bound Rubber	Probe Polymer Extracted	Graft Density
	Type	Mn (kg/mol)	Type	Mn (kg/mol)	Type	Vol %	(phr)	(%)	(%)	nm^{-2}
A	SBR	120			N347	18		26		
B	SBR	120			N339	18				
C	SBR	120			N339	16				
D	Sn-SBR	114			N347	18		36		0.05
E	SBR	120			HiSil 210	18	0			
F	SBR	120			HiSil 210	18	4			
G	SBR	120			HiSil 210	18	8			
H	Cis PBD	83	PBD	5	N339	18		28	99	0
I	Cis PBD	83	Sn-PBD	5	N339	18		30	43	0.15
J	Cis PBD	83	PBD	10	N339	18		27	97	0
K	Cis PBD	83	Sn-PBD	10	N339	18		32	48	0.075

Table 2
Compounds formulations and mixing procedures.

Formulation			Mixing Procedure		
	CB Compound	Si Compound	Addition Sequence (min)	CB Compound	Si Compound
Rubber	100	100	**Masterbatch** $T_o = 130\ ^\circ C$		
Carbon Black (CB)	50		0	Rubber	Rubber
Silica (HiSil 210)		80	0.5	½ CB	½ Si and pigments
Coupling Agent (CA)[a]		8	1.0	½ CB and pigments	
Zinc oxide	3	3	5.0	***Drop MB***	***Drop MB***
Stearic acid	2	2			
Antioxidant	1	1	**Remill** $T_o = 130\ ^\circ C$		
Subtotal	***156***	***194***	0	Load MB	Load MB
Sulfur	1.5	1.5	0.5		½ Si and CA
Accelerator	1	1	5.0	***Drop Remill***	***Drop Remill***
Total	***158.5***	***196.5***	**Final**$T_o = 90\ ^\circ C$		
			0	Remill	Remill
			0.5	Sulfur and Accelerator	Sulfur and Accelerator
			1.5	***Drop batch***	***Drop batch***

[a] bis (3 triethoxysilylpropyl)tetrasulfide.

later dispersed to a certain degree depending on mixing conditions. The experiments, following the strategic outline of Fig. 2, revealed that the network forms by a filler particle flocculation process during subsequent storage and particularly when exposed to higher temperatures which increases the molecular mobility required for filler particles to come into close proximity and ultimately to build up an interconnected network structure to a degree depending on filler type and concentration as well as thermodynamic conditions. Fig. 3 highlights schematically one of the key results of that study. It compares the strain amplitude dependence of the storage shear moduli for two compositionally identical samples molded into 0.15 cm thick plaques at 100 °C for 10 min. One compound was subsequently radiation cured at room temperature immediately following the mixing, milling and short molding steps while the other was first heated to 160 °C for 20 min (the temperature and time often used for a sulfur vulcanization) before radiation curing at room temperature under the same conditions. As can be seen the avoidance of the high temperature heating steps lead to an approx. 55% reduction of the strain amplitude dependence ($\Delta G'_{\text{Rad}} \sim 0.45\Delta G'_{\text{Heat + Rad}}$) which was ascribed to a suppression of filler flocculation. Heating of the former sample to the same temperature following the radiation cure at room temperature did not affect the results appreciably because the C–C crosslinks introduced by radiation exposure increase the viscosity of the elastomer eventually leading to its gelation. This of course greatly reduces the molecular motion needed for additional flocculation to occur. Moreover in a later unpublished experiment, the authors quickly quenched a rubber sample in liquid nitrogen following the mixing and brief sheeting on a mill prior to radiation crosslinking at room temperature thus forgoing the plague molding at 100 °C which also must have contributed to some filler flocculation. The strain dependence of that sample was only 15% of the value measured on the sample which had been heat treated at 160 °C prior to radiation crosslinkung ($\Delta G'_{\text{Rad}} \sim 0.15\Delta G'_{\text{Heat + Rad}}$). This clearly suggested that the filler network does not exist to any significant extent following the mixing step but is developing over time by filler flocculation with the flocculation rate strongly dependant on temperature.

The experiments with the on-line rheometer confirm and solidify this hypothesis. Fig. 4 shows the storage modulus of a carbon black filled rubber compound during and after the secession of flow through the rheometer. As can be seen G′ shows a rapid response following stoppage of the extruder by increasing at first very quickly and then gradually approaching a value representing a certain filler network achievable under the chosen experimental conditions (vol % filler, filler type and dispersion level, annealing temperature etc.) However as soon as rubber flow is restored G′ drops quickly returning to the original value within a very short time and depending on temperature and the shear rate rate applied. The same results were obtained when the process was

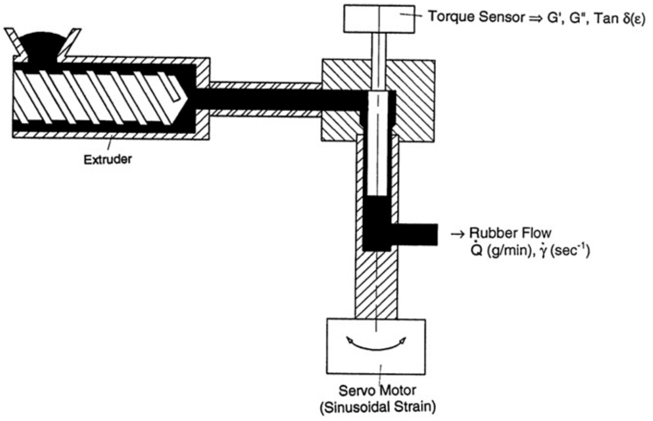

Fig. 1. Schematic diagram of the on-line rheometer with attached extruder to feed the elastomer compounds to the equipment for rheological tests conducted either during flow or when the compound is at rest.

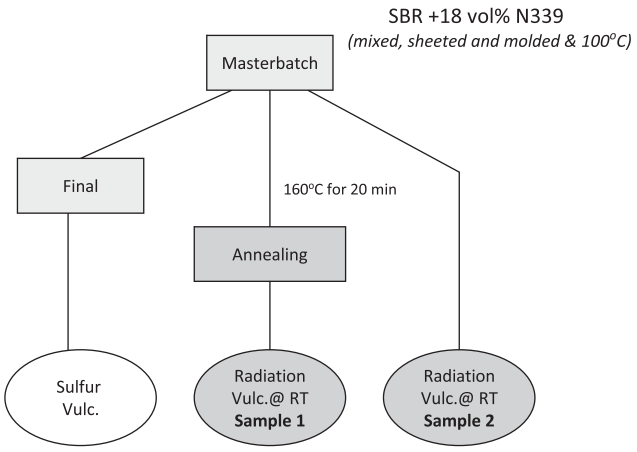

Fig. 2. Strategic outline for flocculation experiments.

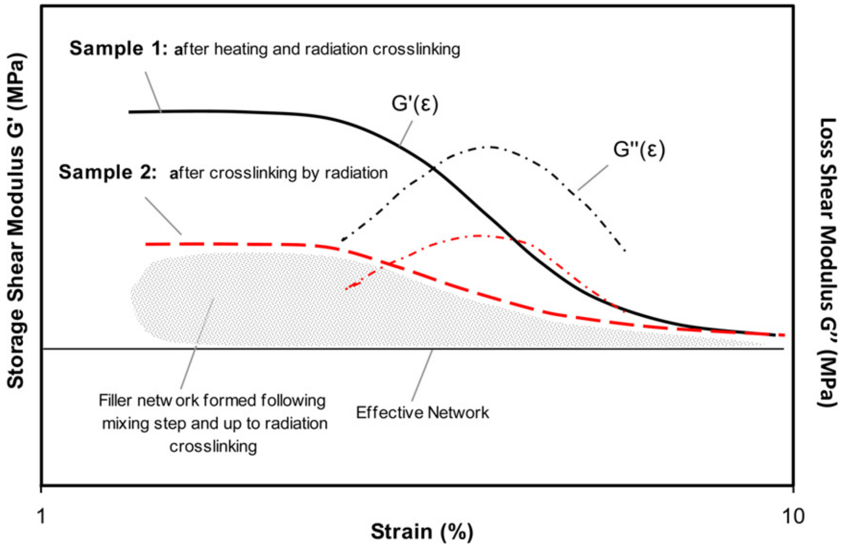

Fig. 3. Summary of a key result from our earlier study [17] showing the storage shear modulus as function of strain amplitude for a carbon black filled rubber compound following two different treatment conditions.

repeated several times. The same experiment was also carried out with an unfilled SBR polymer used in the former compound with the G′ traces also shown in this figure. The only response seen is a very small but rapid increase in G′ probably caused by a re-entanglement of the polymer molecules as they transition from a partially disentangled state induced by the imposed shear rate of $\dot{\gamma} = 12\ \mathrm{s}^{-1}$ to their equilibrium conformation after stoppage of rubber flow.

To confirm that the G′ increases are indeed caused by a flocculation induced formation of clusters which gradually lead to an increasingly connected filler network quick strain scans were also carried out at different times following the secession of flow with the results shown in Fig. 5. This data is somewhat compromised by the fact that several processes are expected to occur during this experiment. While filler flocculation takes place during annealing at 100 °C the compound is also probed by four consecutive strain scans which will cause some disruption of the filler network formed up to that moment particularly when reaching higher strain amplitudes. However as can be noted the network disruptions were far less potent than those caused by the onset of rubber flow through the rheometer. The data also shows that G′(∞) is much greater than G′ measured during rubber flow which implies that a portion of the initial rapid increase in G′ noted in Fig. 4 and later experiments is not filler network related but most likely caused by the earlier referred to re-entanglement following the secession of flow. In the filled reinforced compounds this may also involve entanglements between host polymer molecules and molecules of the bound rubber layer covering the filler surface with the contribution depending on the mobility and conformation of the outer bound rubber layer.

The rate of filler flocculation can be projected based on the simple assumption that the rate of flocculation should be proportional to the number of carbon black aggregates that exist in a non associated state.

$$dS/dt = (1 - S(t))^n \tag{1}$$

where S, the structure parameter defined by $S(t) = \Delta G'(t)/\Delta G'_R$ [17] is the fraction of the carbon black which has flocculated at the time t and $\Delta G'(t)$ and $\Delta G'_R$ are the excess storage moduli at time t and at $t = \infty$ respectively. The rates determined in our first paper [17] did

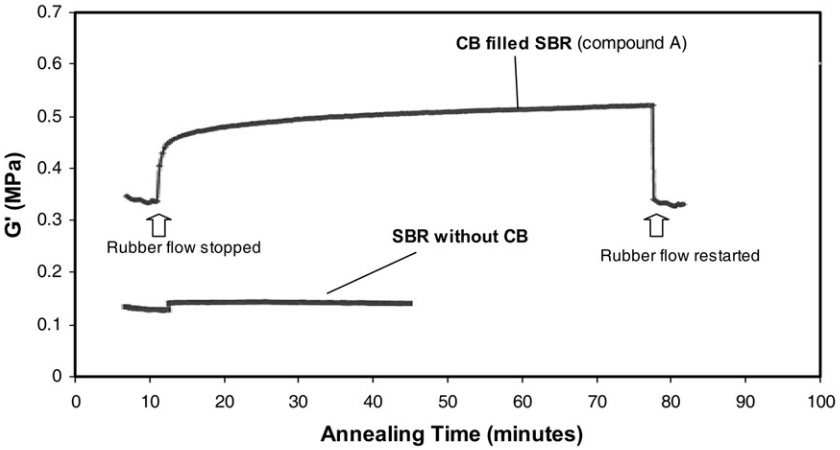

Fig. 4. Storage shear modulus G′ at 1% cyclic strain of carbon black reinforced compound A during flow through rheometer at $\dot{\gamma} = 12\ \mathrm{s}^{-1}$ and after the cessation of flow during annealing at 100 °C. Also shown is the response of the unfilled polymer used to prepare compound A under the same conditions.

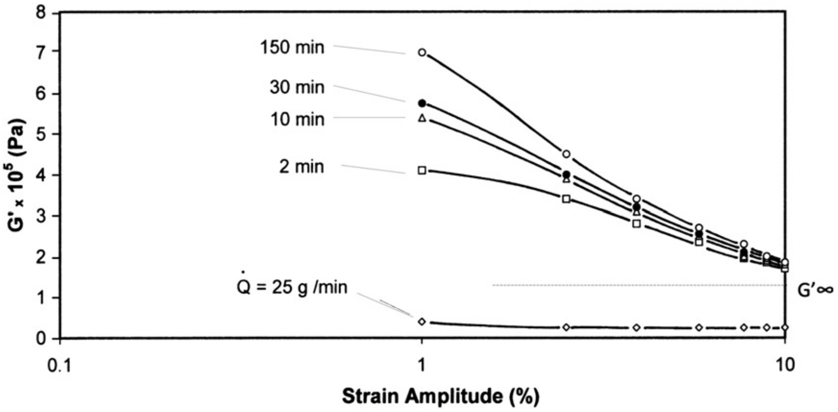

Fig. 5. Shear storage modulus G′ of carbon black reinforced compound B as function of strain amplitude during flow as well as during annealing at 100 °C in the absence of flow.

fit the solution to this equation for $n = 1$ however the data obtained from the on line rheometer experiments (Figs. 4–10) does not. The reason is that the rheometer experiments also recorded the initial steep G′ increase occurring during the first few minutes a time period which could not be accessed in the first study. Plotting the new data of Fig. 4 (compound A) according to the solution of a first order rate equation, ie, $n = 1$ in equation (1) Fig. 6 shows again a linear relationship for $t > 10$ min with a rate constant at 100 °C of 3.5×10^{-2} min^{-1}. The insert shows a plot of the shorter time data according to equation (1) from which an exponent n of 3.9 was derived. While equation (1) with $n = 2$ would offer a reasonable fit of the whole network recovery data it would be premature to interpret the results in terms of a certain system cooperativity suggesting a second order kinetics as proposed by Heinrich et al. [7]. The reason is that two or perhaps even three distinct processes with different kinetics are likely contributing to the initial rise in G′ immediately following the secession of flow in which the system is not yet in an equilibrium state. In addition to filler flocculation facilitated by Brownian diffusion, stress relaxation may also contribute to particle motion and finally there is some earlier referred to evidence that, unrelated to the filler network, a re-entanglement of brush and matrix polymer chains is involved in the rapid G′ increase observed. Further experiments are ongoing to solidify our understanding of the origin of the initial G′ increase.

The effect of different flow rates on the breakdown and recovery of the filler network was also studied with the results shown in Fig. 7. G′ measured during flow decreased with increasing flow rate as should be expected by the shear rate dependence of viscosity and G′ of these compounds as well as by the likely shear rate dependence of the filler breakup process. Here we assume that the degree to which the filler network and its clusters are destroyed depends on shear rate. At low shear rates there may be a rate below which no breakup will occur and conversely one can expect that the number and size of the clusters will diminish with increasing shear rate even after the filler network has been broken up by shearing. The increased flow does not seem to influence the filler network forming over longer annealing periods once the rubber flow had stopped. However the

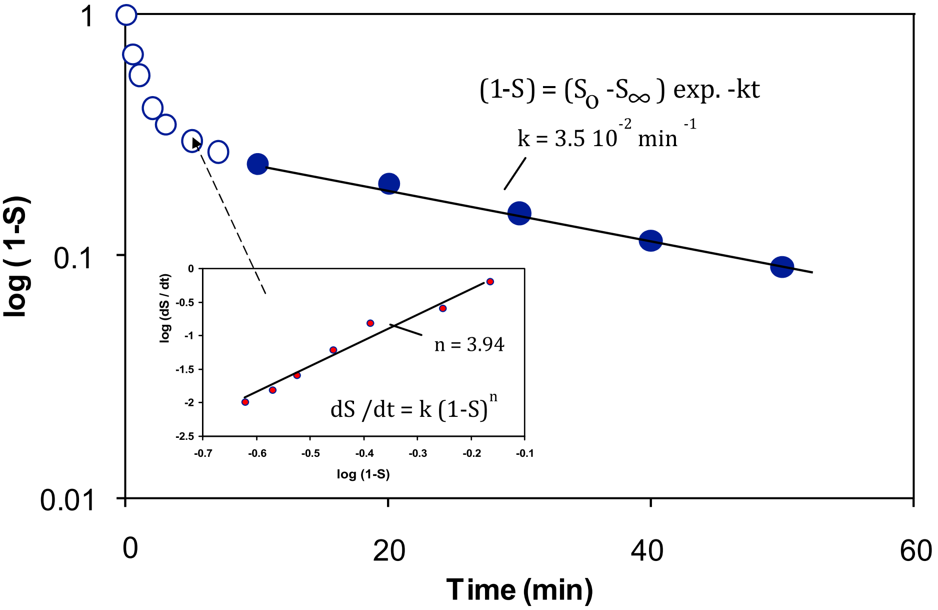

Fig. 6. Kinetic analysis of filler structure recovery following secession of flow. First order plot of data for compound A at 100 °C. Insert shows recovery plot data according to equation(1) for short time data of $t < 10$ min.

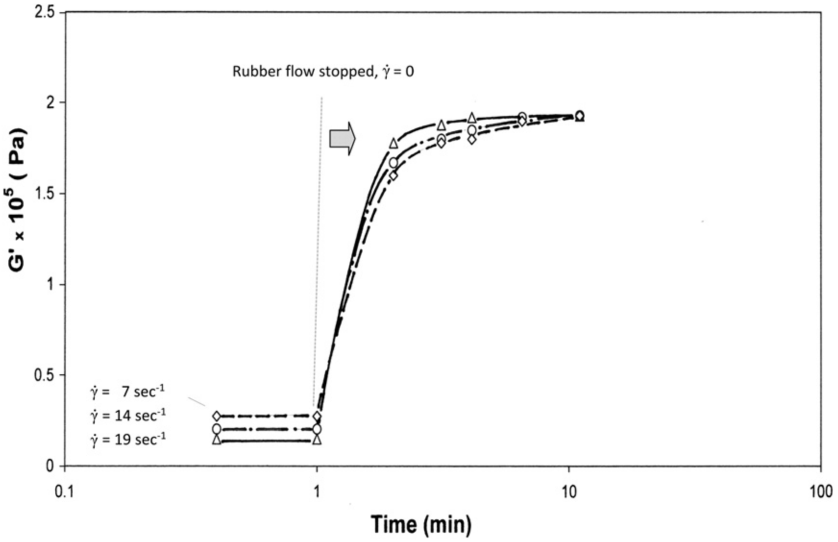

Fig. 7. Shear storage modulus G′ at 1% cyclic strain of carbon black reinforced compound C as function of time during annealing at 100 °C in the absence of flow following a rubber flow at different shear rates.

rate of recovery during the first 2 min increases with the magnitude of the shear rate applied during the preceding flow period. This can be anticipated from Equation 1as an increased breakup of the flocculated filler structure at higher shear rates is expected to result in a faster recovery. In Figs. 8 and 9 the results with CB filled compounds are compared with those of Si filled compounds. Fig. 9 also shows the drastic effect silane coupling agents have on filler dispersion and subsequent flocculation on storage. The findings with silica are not surprising as it is difficult to disperse a polar filler with strong self association through hydrogen bonding in an essentially non polar elastomer such as SBR unless dispersion aiding additives such as silane coupling agents are used. In the absence of such dispersing agents the high shear forces acting on the Si agglomerates are not able to overcome the strong cohesive bonding between Si particles and thus a significant portion of agglomerates may still exist after prolonged mixing giving rise to a high viscosity and extreme difficulties in processing. Finally Fig. 10 shows the effect an end group functionalized elastomer has on the flocculation of carbon black filled compound D. There again a quick increase in G′ occurs on secession of flow and after a slight overshoot the storage modulus remains essentially constant in contrast to compound A prepared with a non functionalized polymer of essentially identical structure where we see a further but relatively slow rise in G′ as anticipated by a continuing flocculation process.

4. Discussion

4.1. Flocculation process

The results of our earlier study and the findings of this investigation are very complimentary even though the experimental procedures used and the parameters measured are rather different. In our earlier work filler flocculation was induced by annealing uncured filler reinforced compounds at temperatures ranging from 125 to 175 °C for up to 60 min yet the filler network was probed at room temperature in the vulcanized state. In contrast essentially all the flocculation related data of this study was generated with the on-line rheometer using unvulcanized compounds at 100 °C. These differences need to be recognized when drawing on the results of both studies to assess the validity of any proposed mechanism for filler flocculation.

Given that and assuming that the ΔG′ increases are mostly due to filler flocculation, we can draw the following preliminary

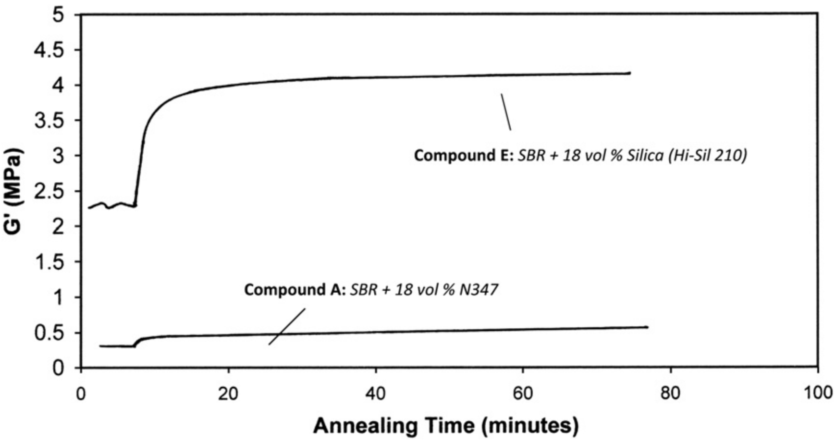

Fig. 8. Comparison of shear storage moduli G′ at 1% cyclic strain of Si and CB filled compounds E and A during flow and after the cessation of flow during annealing at 100 °C.

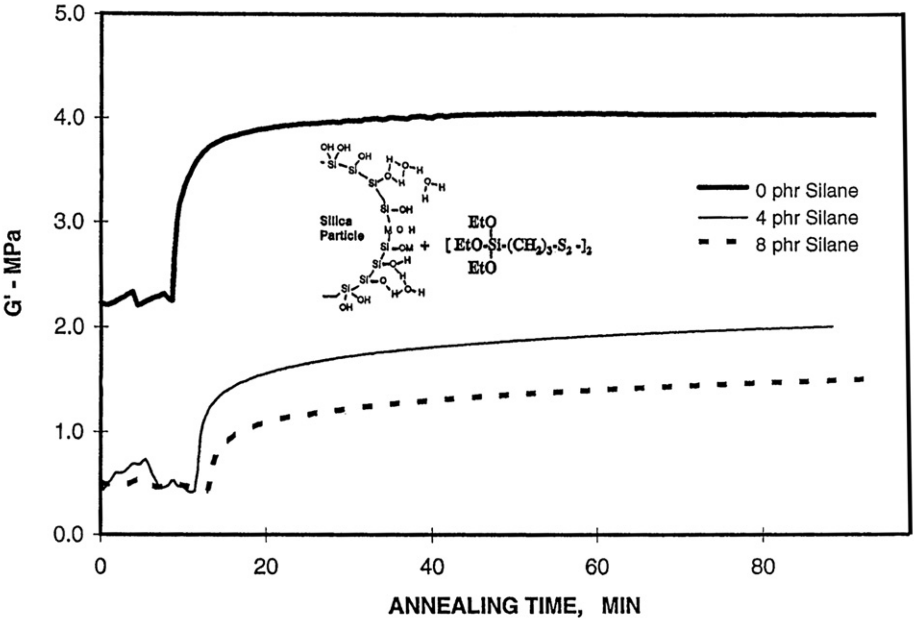

Fig. 9. Shear storage modulus G′ at 1% cyclic strain of three Si reinforced compounds E, F and G comprising different levels of silane coupling agents as function of time during flow as well as after the cessation of flow during annealing at 100 °C.

conclusions about the filler related events which occurred in the compounds of this study during the mixing, shaping and ultimately vulcanization.

The initial dispersion of carbon black and silica fillers achieved in typical rubber mixing equipment depends on a number of equipment, process as well as material related parameters. In the case of compounds A-D good macrodispersions were achieved under the conditions used. Most filler agglomerates were broken up and the aggregates dispersed by the high shear forces of the mixing process which was confirmed by microscopy. One additional event also occurred during the mixing process which we will later show, has a significant effect on the low strain performance of the compounds as well as on other properties. Rubber molecules have become attached to the surface of carbon black particles with the portion one cannot remove by solvent extraction generally being referred to as bound rubber. Hence the compounds now comprise free elastomer molecules and elastomer coated filler particles in addition to other ingredients normally being added to stabilize the polymer, to initiate a vulcanization etc. After mixing stops and the compound is removed from the equipment there is an opportunity for carbon black aggregates to form initial clusters which progressively can lead to the formation of a contiguous network provided that the volume fraction of filler Φ_{filler} exeeds $\Phi_{\text{filler}}^{\text{crit}}$, the treshold value predicted by percolation theory. $\Phi_{\text{filler}}^{\text{crit}}$ values for different carbon blacks were determined by electrical conductivity measurements [9]. Since the volume fraction of carbon black in all the compounds of this study ($\Phi_{\text{filler}} \sim 0.18$) is larger than the treshhold volume concentration for typical furnace blacks ($\Phi_{\text{filler}}^{\text{crit}} = 0.12$) the formation of a filler network by flocculation should be possible. Figs. 4–10 certainly show that flocculation occurs at 100 °C after a secession of flow except in compounds prepared with a Sn end group functionalized polymer where no further G′ increase is seen beyond the rapid initial surge (Fig. 10) in line with the findings of others [12–16] indicating that vulcanized compounds comprising Sn functional polymers show significantly lower excess storage moduli ΔG′ than compounds prepared with non functional polymers of identical macro and microstructure. In all other cases flocculation continues at decreasing rate as predicted by equation (1). In commercial elastomer compounds used for tires and other products filler flocculation will occur during molding and the early part of vulcanization until a crosslinking of the matrix polymer by vulcanization (using sulfur, peroxides etc) decreases the flocculation rate due to the resulting increase in the viscosity of the rubber phase. As the polymer gels and continues to crosslink longer range motion such as required to perpetuate flocculation will essentially cease. Even though only a few experiments were conducted with silica reinforced compounds the data suggests that the above stated basically also holds for those compounds.

This cursory interpretation raises several questions as to the nature and magnitude of the forces acting on the filler aggregates to cause cluster formation, the reason why an end group functionalized matrix polymer impedes filler flocculation, what fraction of the G′ increase noted on annealing is due to flocculation etc. Some of these questions will be addressed following a brief description of the rubber/filler interphace which represents a large volume fraction in any composite comprising significant quantities of nanoscale sized particles such as carbon black and silica.

4.2. *Characterization of the bound rubber layer*

The formation of bound rubber has been studied over the last few decades by many investigators [19–24]. The amount of rubber being adsorbed by carbon black depends mainly on the polymer and on the surface area and surface activity of the carbon black aggregates etc. It is generally understood that carbon black has a very rough geometrically disordered surface which fractal down to molecular dimensions. Moreover the energy distribution of surface adsorption sites is rather broad ranging from low energy sites of the basaltic layer to the highly energetic cavities between carbon black crystallites. This is the likely reason for the dependence of polymer de-sorption from carbon black surfaces on solvent type and temperature noted in bound rubber measurements. Polymers

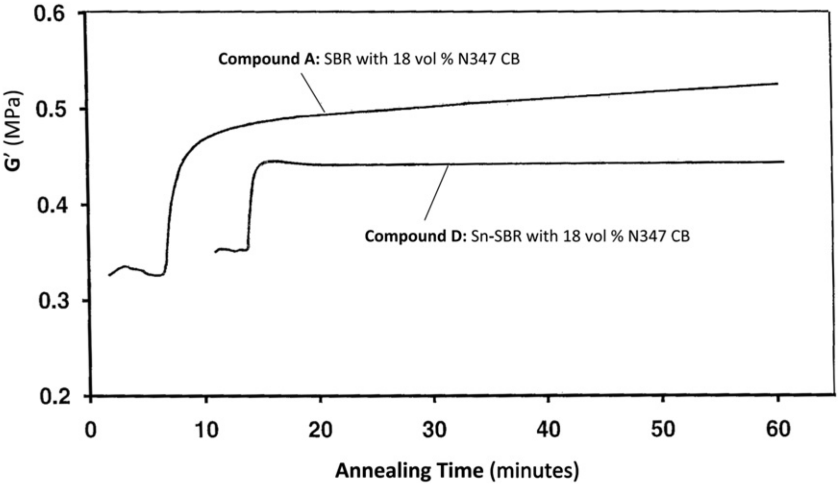

Fig. 10. Shear storage moduli G′ at 1% cyclic strain of carbon black reinforced compounds A and D as function of time during flow as well as after the cessation of flow during annealing at 100 °C. The compounds have essentially the same composition except that the SBR molecules used in compound D have one Sn functional end group.

adsorbed on such disordered surface can assume unusual configurations which deviate strongly from an unperturbed Gaussian coil shape and in these localized conformations the size of the polymer perpendicular to the surface can become independent of chain length. This can be qualitatively understood by the argument illustrated in Fig. 11. A polymer molecule being adsorbed on a flat surface (Fig. 11a) would gain the most energy if all segments were adsorbed on the surface yet that would result in a very large entropy penalty and thus adhered molecules are somewhat extended forming loops and trails with only a fraction of the segment attached. However when the molecules get adsorbed on a highly disordered random surface (Fig. 11b) they can gain energy by adsorption without paying an entropy penalty.

On the other hand the bound rubber layers are expected to assume a different shape if they are formed by reactions of end group functionalized polymers with surface groups such as carboxyl or lactone functions. The reach of these surface grafted polymers should extent further away from the carbon black surface (Fig. 11c–e). At low graft densities one may expect the formation of mushroom type structures and more brush -like conformation with an extended chain structure at higher graft densities. When the functionality on the polymer is not at the end but randomly placed on the chain the brush conformation will have a reduced range away from the surface. A similar conformation may also develop with end group functionalized polymers when one or more chain segments first form physical bonds with

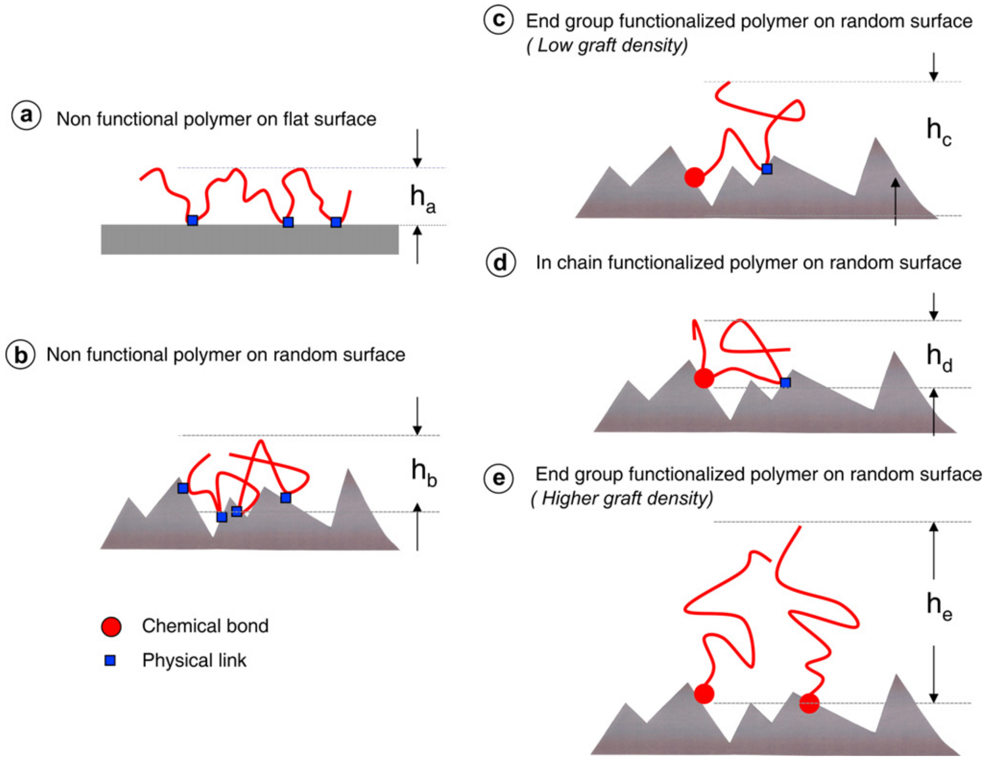

Fig. 11. Schematic description of the physical adsorption to and chemical reaction of polymers with flat and highly disordered surfaces such as carbon black.

the surface which also reduces the chance for the functional end group to subsequently find a suitable reaction site on the surface which then depends on the remaining surface density of such chemical surface groups and the length of the dangling chain portion ending with a functional group.

This matter is further complicated by some evidence that the locus on the carbon black surface of physical and chemical interaction is different [11]. Physical bonding is expected to occur on the small patches of quasi-graphitic crystallites whereas the chemical groups are believed to be located at the edges of the graphitic basal planes of these crystallites. A number of oxygen containing groups (phenol, carbonyl, quinone, lactone, ketone and pyrone) have been identified with the concentration on a typical furnace black such as N220 varying from 1 to 2 for COOH/nm^2 to 2–4 for OH/nm^2 with the oxygen content normalized to a reactive oxide such as carbonyl or phenol [11].

Using the results of experiments with compound D comprising a Sn functionalized SBR one can determine the graft density from

$$\sigma = X_{BR}/X_{CB}A\,M_n^{-1}S^{-1} \tag{2}$$

where x_{BR} and x_{CB} are the weight fraction of bound rubber and CB in the compound, Mn is the number average molecular weight of the grafted polymer, S the surface area of the CB and A is Avogados's number.

Using equation (2) and assuming that all the bound rubber molecules are endlinked to the filler surface a σ of 0.05 nm^{-2} is obtained. However this number is probably overestimated because the brush is most likely formed by both chemically endlinked as well as random physically attached molecules. Moreover given that the functional groups appear to be located on narrow islands on the edge of graphitic basal planes conformations of endlinked brush molecules cannot be deduced from an average graft density. One may also question whether there are sufficient number of chemical groups on the surface, capable of reacting with Sn to allow all the molecules of the bound rubber layer to attach themselves by end linking reactions. The experiments with the probe polymers can shed some light on this. In compounds I and K about 50% of the low molecular weight probe polymers added during compound mixing attached themselves to CB based on which graft densities of 0.075 nm^{-2} (for $M_n = 10$ kg/mol polymer) and 0.15nm^{-2} (for the $M_n = 5$ kg/mol polymer) can be derived. This would indicate that the density of chemical groups on the CB surface $\sigma_{\text{chem.. groups}}$ capable to react with Sn-SBR is equal or greater than 0.15. However our experiments cannot clarify why only 52% of the probe polymer of Mn = 10 kg/mol had reacted with the CB and why the lower molecular weight probe polymer was able to react with a larger number of chemical groups. One may have to assume that access to these chemical groups was impeded by the concurrently occurring physical adsorption of the high molecular weight high cis-PBD host polymer particulary in light of the very unfavorable weight ratio of probe to host polymer (0.05–0.1) in the compound. A similar process may also limit the graft density achievable with high molecular weight Sn-SBR in compound D. Also to consider is the dynamics of the grafting process in a high shear field applied during mixing. These issues are presently being investigated in another study [25].

The case of silica filled compounds is different in that a non polar PBD or SBR molecule will not attach itself to the highly polar hydrophilic surface of the Si particle and as earlier mentioned bare silica particles will stay in a highly agglomerated state even after extensive mixing of the compound. A dispersion of Si can only be achieved by a shielding of the polar surface with chemicals such as glycols and amine compounds and/or by coupling agents which first react with and thus bond to the silanol goups on the silica particle surface and later attach themselves to the host polymer at a random position on the chain once the temperature exceeds a certain value during in the mixing process. The conformation of this now attached host polymer molecule may, unperturbed by any interaction with the Si surface, approach an equilibrium configuration of a nature depending on graft density etc. Likewise the reaction of certain end group functionalized polymers of high molecular weight with the silanol surface groups also result in grafted polymers with brush conformations. These options thus mimick the approach used with CB but they benefit from the abundance of homogeneously distributed silanol groups (4–7 silanol groups/nm^2) [11] available as grafting sites and the absence of any surface interference on the graft polymer conformation. As implied earlier these Si modifications are being used not only to disperse the Si in a non polar elastomer but also to successfully suppress the formation of a Si network after the mixing step just as in the case of CB filled compounds. A more detailed description of these treatment options has been publishes earlier [26].

4.3. *Interaction between rubber coated filler particles*

Filler flocculation may occur in a rubber composite as part of a process in which the composite drifts to its equilibrium state. The starting non-equilibrium state may be the result of preparing the composite involving mixing, molding etc. or, as in the case of our experiments, it may be caused by a shear induced disturbance of the system. Depending on the equilibrium state of a given system this process may or may not involve a filler flocculation. If, for example, the equilibrium state represents conditions in which particle/particle interaction is minimized an agglomeration of the filler may not take place. Even in cases where an agglomerated filler state is thermodynamically favored flocculation may not be observed in the time frame of the experiment because of a slow kinetics. To learn more about the equilibrium morphology of such systems on can be guided by studies conducted on colloidal core/shell particles which, to a certain degree, resemble the carbon black particles of this study. Such studies addressing colloidal systems with an interface between brushes and melts of chemically identical chains were started by de Gennes [27] and later pursued by several others investigators [28–32] using self consistent field theories as well as Monte Carlo simulations in more recent years. The results impact on a range of processes such as micelle aggregation, the flocculation of protected colloidal particles, the phase separation of homopolymer- copolymer mixtures etc. Hasegawa et al. [28] and Wang et al. [30] also reported on experimental data relevant to their theoretical analysis. From these efforts one can conclude the following:

The total free interaction energy between two particles F_{int}^{total} consists of two contributions.

$$F_{int}^{total}(d) = F_{pol}(d) + F_{vdw}(d) \quad \text{with } F_{vdw} = -AD/12d \tag{3}$$

where F_{pol} is the polymeric interaction energy between the molecules of the bound rubber layers. F_{vdw} is the van der Waals attraction which has a negative value and depends weakly on the distance d between the two particles with D being the diameter of the particles and A the Hamaker constant [33].

Using the results published let us examine the simple case where the particles are composed of small solid cores with brush molecules covalently endlinked to the surface and embedded in a matrix polymer. For that idealized filler structure one can then attempt to project how the polymeric and van der Waal terms of equation (3) are expected to contribute to the equilibrium morphology of this system which is schematically illustrated in

Fig. 12. We will assume that the chemical structure of the grafted and the free polymer molecules is identical in which case the polymer interaction parameter $\chi_{G/FP} = 0$ and any interaction between the free and grafted polymer will be purely entropic in nature. Scenario A represents the case of a core/shell particle where the free polymer is deeply interpenetrating the brush ("wet brush") as manifested in the plot showing the volume fractions of grafted polymer (brush) Φ_G and the free polymer molecules Φ_{FP} between two interacting particles. In this scenario the van der Waals interaction (dashed line) is partially offset by a hard core like repulsion of $F_{pol}(d)$ (dotted line) originating from the excluded volume effect between the two grafted polymers. This can be seen in the graph inserted to the right (taken from reference 28). This type of interaction is mainly promoted when $N_G/N_{FP} > 1$, by a low graft density and small particle diameters. As the graft density increases the thickness of F_{pol} (d) increases which in turn decreases the depth of the F^{total}_{int} minimum. Thus at low graft densities the maximum attraction decreases with increasing graft density which in turn helps the dispersion of the particles.

However as the graft density increases further the chains become more stretched and at one point the entropic gain associated with the penetration of the mobile chains into the brush will not be able to compensate for the elastic deformation of the grafted chains and as a result free polymer molecules will be increasingly ejected from the brush. This situation is depicted in scenario B for a dry brush with the associated volume fraction graph showing that the interaction between the brush and the free polymer is now limited to a very small interphase. $F_{pol}(d)$ will now also have an attractive part and its depth increases with increasing graft density. This situation is most likely to occur when $N_G/N_{FP} < 1$, at high graft densities and larger particle diameters. This minimum F_{int} lying between the wet and the dry brush scenario corresponds to the transition from a negative to a positive interfacial energy between the brush and the matrix polymer. It represents the state with the lowest particle/particle attraction and is thus offering the greatest system stability. The equations shown below were derived by three of the referenced investigators, published in the chronological order shown, to predict conditions for the occurrence of this transition.

$$\sigma_c = a^{-2}N_G^{-1/2} \quad \text{for } N_{FP}/N_G = 1 \quad \text{by Hasegawa [28]} \tag{4}$$

$$\sigma_c a^2 N_G^{1/2} = (N_{FP}/N_G)^{-2} \quad \text{by Ferreira et al. [29]} \tag{5}$$

$$N_{FP}/N_G = 1.4\left(a/R_o\sigma_c v^2\right)^{1/3} \quad \text{by Wang et al. [30]} \tag{6}$$

where N_G and N_{FP} are the degree of polymerization of the graft (brush) and the matrix polymers, σ_c is the critical graft density, R_o is the particle radius, a the monomer size and v a term varying between 0 and 1 and depending on the curvature of the particle. Hasegawa's equation applies strictly only for $N_{FP} = N_G$. Equations (5) and (6) also cover cases where $N_{FP} \neq N_G$ and equation (6) includes the effect of surface curvature.

One can point to at least two studies where particle dispersion results were reasonably well predicted by the results of this theoretical analysis.

In an experiment with ABS particles consisting of poly(acrylonitrile –co- styrene) (AS) grafted onto polybutadiene (PBD) particles suspended in a linear AS matrix polymer Hasegawa et al. [28] confirmed the trends predicted by mean field theory. In their case $N_G > N_{FP}$ and thus the onset of the attractive force was mainly controlled by the graft density σ. They were able to show that the particle dispersion improved with increasing AS grafting but when

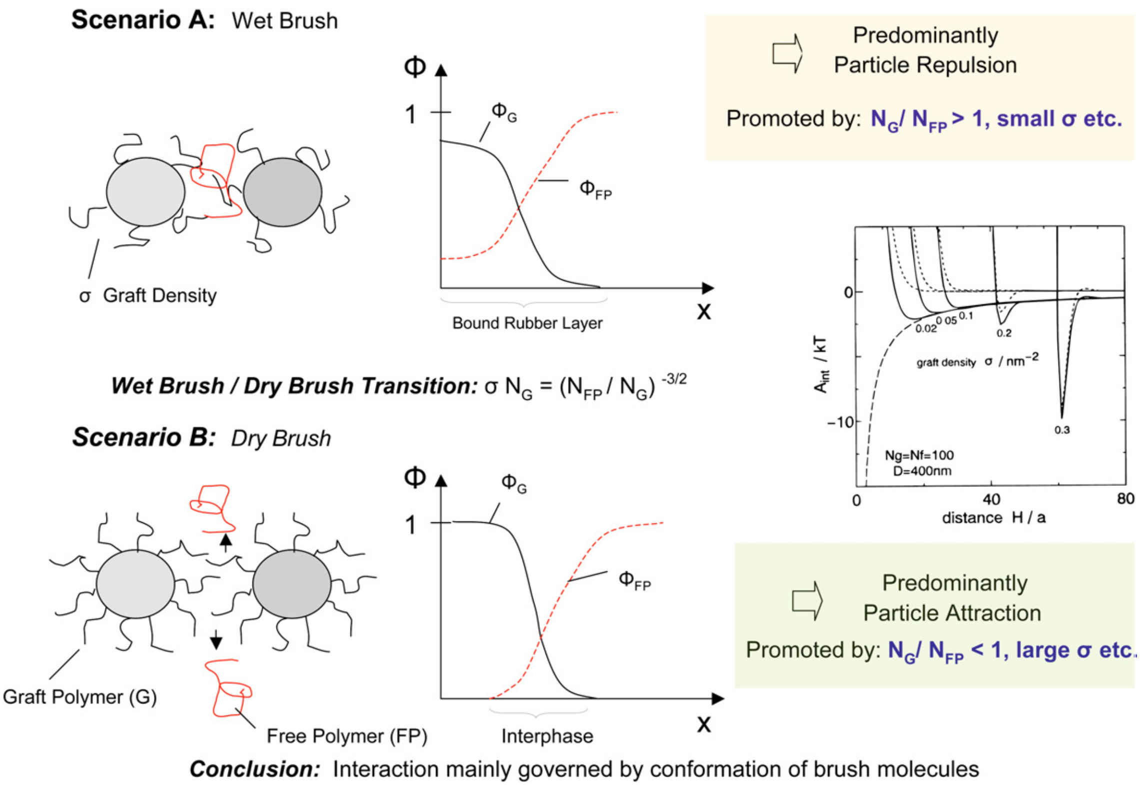

Fig. 12. Schematic diagram illustrating how different free energy terms interact to control the dispersion of hairy nanoparticles resembling bound rubber coated fillers such as carbon black and silica.

σ was increased beyond a critical graft density σ_c defined by equation (4) the dispersion became much worth.

Experiments by Wang et al. [30] involved dispersions of nanoparticles having crosslinked polymeric hard cores and polybutadiene (PBD) brushes dispersed in a PBD matrix polymer identical in microstructure to the brush molecules. It was shown that a transition from a transparent to an opaque flocculated state occurred when $N_{FP}/N_G > 2.4$ for $\Phi_{NP} < 0.1$ in line with theoretical predictions of equation (6).

Thus for the simple case of well defined core/shell particles in a polymer melt the theoretical studies predict that conditions may exist (defined by graft density, polymer interaction parameter, matrix and brush macrostructure etc.) when such a system can have different equilibrium states ranging from a single phase with randomly distributed filler particles stabilized by their brush structure to a two phase morphology with insufficiently stabilized highly agglomerated filler particles.

Real carbon black particles generally differ from this simple case in ways described earlier. The core structure is not a single particle but an aggregate of several nanoscale sized particles fused together during the manufacturing process. The characteristic features of the brush molecules attached to the core aggregates such as the conformation and density of the physically or chemically attached chains etc. are generally unknown. Given that one can not apply the results of these theories to quantitatively predict the thermodynamic stability of the more complex und insufficiently characterized carbon black compositions. However the physics elaborated on in these theoretical studies can be expected to apply and thus efforts to reduce the flocculation of carbon black fillers in rubber compositions can, in the short term, benefit from an understanding gained about system parameters controlling particle/particle interaction and thus the stability of the composite. Once carbon black filler composites are better characterized one should be able to elaborate in more detail on this matter. However for now one can distinguish between three possible scenarios:

1) The brush is formed by a physical attachment of a matrix polymer during the mixing process. Then $\chi_{AB} = \chi_{AA} = 0$ and the brush/matrix interactions are purely entropic in nature. The polymer interaction of the dangling ends shown in Fig. 10b with the matrix polymer is not expected to contribute strongly to particle stability and thus a two phase equilibrium morphology with filler networking can be expected for most commercial filler reinforced rubber compositions which has indeed been observed by many investigators.
2) The brush is formed by the chemical attachment of an end group functionalized matrix polymer to the filler surface. $\chi_{AB} = \chi_{AA} = 0$ and $N_G/N_{FP} \sim 1$ (in the absence of additional physical links to the surface) which favors a wet brush conformation with improved particle stability and thus a less agglomerated equilibrium state with reduced flocculation.
3) The brush is formed by a physical or chemical attachment of polymer A to the filler surface and the resulting polymer coated filler is then embedded in polymer B. Then if $\chi_{AB} > 0$ the additional enthalpic interaction will tend to reduce brush/matrix interpenetration and favor a dry brush configuration with the above discussed consequences. However when $\chi_{AB} < 0$ a wet brush conformation could be encountered even under conditions when it would not be favored under $\chi_{AB} = 0$

This is the trend we see in our experiments. The vulcanized compound A of our study comprising a non functional SBR polymer developed an extensive carbon black network with an excess shear modulus of $\Delta G' = 5.6$ MPa whereas compound D prepared with a structurally identical polymer except for the functional Sn end group showed a much reduced excess shear modulus of $\Delta G' = 2.8$ MPa. A similar difference was observed in the unvulcanized compounds during the system recovery following shearing in the on-line rheometer. In other published experiments referred to earlier intermediate $\Delta G'$ values were measured in cases where blends of functional and non functional polymers of the same structure and molecular weight were used or when comparing the results obtained with two functional polymers, one having the functional group at the end and the other having the same group located randomly along the chain. In the latter case one may expect bound rubber layers with less extended polymer conformations somewhat intermediate between those of end group functional polymers and non functional polymers. This analysis is also expected to apply to Si filled compounds except that the conformation of the bound rubber molecules will depend on the earlier discussed means by which the molecules are attached to the silica filler surface. Polar interaction will also need to be considered.

5. Conclusions

Experiments were carried out with an on-line rheometer to study the dynamics of filler network formation responsible for the non linear response of filler reinforced elastomers and the underlying mechanism. The results confirm our earlier findings that the filler network does not exist to any great extent after mixing of the elastomer compound but is formed by a subsequent flocculation of the filler particulary at higher temperatures such as encountered during vulcanization. In the uncured state the filler network breaks up easily when shear is applied. A storage modulus data based kinetic analysis of the recovery phase, following the secession of shear flow, shows a slowly progressing increase of G' due to stress relaxation and Brownian motion induced flocculation causing filler clusters and later a contiguous filler network to form. This process slows down as the concentration of unstructured carbon black aggregates diminishes. This slow increase in G' is preceded by an initial steep rise with experiments pointing to a non filler related process such as a chain re-entanglements involving matrix as well as bound rubber molecules.

The study also concludes that the formation of filler networks is not merely the consequence of incorporating in a rubber compound a given type filler in access of a threshold volume fraction but is also influenced by the thermodynamic interaction between the matrix polymer and the brush molecules which physically or chemically attach themselves to the filler surface during the mixing process. The results of experiments with end group functionalized and non functional matrix polymers illustrate this point. This interaction governs the thermodynamic stability of filler reinforced rubber composites, a point which has been largely ignored in the literature. The detailed mechanism involved in forming a stabilized carbon black reinforced compound by controlling the particle/particle interaction is currently not well understood but an attempt was made to learn more about the thermodynamic stability of such systems from theoretical as well as experimental studies conducted on colloidal core/shell particles which resemble the embedded carbon black particles to a considerable degree. No quantitative conclusions can be drawn from this comparison, due in part to a lack of data on the bound rubber molecules such as conformation, graft density, distribution etc. but it offers an explanation for the reduced filler network of composites comprising end group functionalized polymers and some guidance for exploring other hysteresis reducing options.

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