

Influence of Filler–Rubber Interactions on the Viscoelastic Properties of Carbon-Black-Filled Rubber Compounds

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ABSTRACT: The specific role of filler–rubber interactions in dynamic properties was investigated. Natural rubber compounds, filled with N330 carbon black, were used, and the filler surface was modified through a gas treatment in the solid phase. The effects of this filler surface treatment on the dynamic properties were systematically studied at equal filler dispersion levels. The dynamic properties were assessed for both uncured and vulcanized compounds, and a number of advanced investigative techniques were used to characterize not only the modification of the carbon particle

surface by an oxidative treatment but also the structure of the filled rubber compounds. Particular attention was paid to techniques that gave access to the segmental mobility to explain the benefit observed with modified carbon black. A molecular interpretation, based on NMR measurements, was considered that took into account physicochemical parameters. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 577–588, 2004

Key words: elastomers; interfaces; dispersions

INTRODUCTION

Rubber materials must be vulcanized to offer interesting elastic properties. However, their elastic performance attracts limited interest if it is not combined with other properties, such as modulus and abrasion resistance. In addition, processing and economic considerations require the development of often complex formulations in which a delicate balance must be achieved between the level and nature of the various compounding ingredients. Such considerations, among others, call for the introduction of reinforcing fillers in elastomers. However, increasing the modulus and tensile properties through higher filler loadings generally leads to greater energy loss and heat dissipation under dynamic conditions. This phenomenon is crucially important because it can affect the service life of a material and other properties with respect to specific application constraints (e.g., tires and engine mounts).

Quite complex mechanisms are responsible for the filler effects on dynamic properties, and they are not yet completely understood, despite a number of compounding rules that relate the level and nature of certain ingredients with experimentally demonstrated effects; not all interactions are known today. Indeed, it is very difficult to evaluate the specific influence of

any given filler because its chemistry, physics, or both vary with the processing steps; this calls for quite delicate physicochemical characterization.

It is nevertheless well known that a part of the elastomer is in direct contact with the filler particles,¹ this phenomenon being affected by the chemical structure of the elastomer and the surface properties of the filler. Apart from the hydrodynamic influence of the filler,² three aspects are expected to be strongly influential: the physical properties of the interfacial shell of the polymer surrounding the filler,³ the connecting filaments of the polymer that link aggregates to one another,⁴ and interaggregate interactions.⁵

In a periodic sinusoidal shear or compressive strain situation, the elastic dynamic modulus of cured and filled elastomers decreases with increasing strain amplitude or temperature at a constant frequency.⁶ At the same time, a higher viscous component is observed, leading to an increase in $\tan \delta$. This phenomenon, the so-called Payne effect, is crucially important with respect to the development of compounds for dynamic applications, as discussed previously.

The Payne effect was first assigned to a filler network, which, being destroyed under a higher strain amplitude, would lead to energy dissipation. This theory is supported by the model of Kraus,⁷ and there are some experimental proofs for the existence of the filler network offered by numerous studies by electron microscopy.⁸

A decrease in the elastic modulus is also observed in shear experiments with uncured samples. Nevertheless, a different mechanism might be involved because no $\tan \delta$ peak is observed.

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The existence of a complex rubber–filler interphase, characterized by a mobility gradient of the rubber chains from the filler surface to the rubber matrix, has been well recognized too, for instance, through NMR studies by McBrierty et al.⁹ Recently, it has been demonstrated with polymer-grafted fillers that the interface between a filler and a rubber is of primary importance when dynamic properties are considered,^{10,11} but the interpretation of the phenomena observed is essentially based on dispersion improvement due to reduced contact between filler particles. It is, however, hard to believe that the sole role of the rubber–filler interface concerns dispersion, without a strong and active role of this interface.

The goal of this study was to determine the specific role of filler–rubber interactions in dynamic properties. Natural rubber (NR) compounds, filled with N330 carbon black, were used, and the filler surface was modified through a gas treatment in the solid phase. The effects of this filler surface treatment on the dynamic properties were systematically studied at equal filler dispersion levels. Eventually, a molecular interpretation, based on NMR measurements, was considered to determine the physicochemical parameters.

EXPERIMENTAL

Test compounds

Master batches of an NR-based compound were prepared via mixing in a Banbury internal mixer (volume = 1180 cm³) with 100 phr GN10CV NR, 40 phr N330 (treated or not treated) carbon black, 5 phr zinc oxide, 2 phr stearic acid, 2 phr antidegradants (*N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline), and 1 phr paraffin 50/52. All master batches were prepared at the same mixing energy level, that is, 1500 MJ/m³. A sulfur-based curing system was added on an open mill (5 min at 55°C).

Filler surface treatment

To purposely modify the rubber–filler interaction, we modified N330 carbon-black samples (400 g) with an oxidative gas mixture for 5 days at room temperature and 40% relative humidity. The temperature of the carbon black was stable during the treatment.

Electron spectroscopy for chemical analysis (ESCA)

XPS analysis was performed with a VG Escalab spectrometer (VG Scientific, England) with an Al K α X-ray source. The pressure in the chamber was less than 1 \times 10⁻⁵ Pa. Two survey spectra were recorded on each carbon-black sample (50 mg) with a surface area of

approximately 400,000 μm^2 . Detailed spectra, which allowed chemical functions to be identified, were made on a surface area of approximately 150,000 μm^2 . After the subtraction of a nonlinear background from the spectra, a Gaussian function was used to decompose C₁–C₅ and O_{1s} peaks.

Measurement of the surface energy

The surface energy was assessed by inverse gas chromatography. The experiments were made with columns 20 cm long and 1/8-in. in diameter, conditioned for 15 h at 200°C, with helium as a vector gas at a rate of 10 mL/min. The probes used for the determination of the surface energy were pentane, hexane, heptane, and octane. The adsorption free energy was obtained from the net retention volume (V_G) with the relationship $\Delta G_a(\text{probe}) = -RT \ln V_G$, where V_G is equal to $t_N D_c$, D_c is the corrected rate of the vector gas (He), t_N is the net retention time, T is the temperature, and R is the gas constant. The dispersive component (at 180°C) of the surface energy was derived from the slope $\Delta G_a(\text{CH}_2)$ of the linear plot of ΔG_a versus the atomic number of a series of linear alkanes:

$$\gamma_s^D = \frac{1}{\gamma_{\text{CH}_2}} \left(\frac{\Delta G_a(\text{CH}_2)}{2N_{\text{AV}}a_{\text{CH}_2}} \right)^2 \quad (1)$$

where N_{AV} is Avogadro's number, γ_{CH_2} is the surface energy of one CH₂ group [$\gamma_{\text{CH}_2} = 36.5 - 0.056(T - 20)$, where T is the temperature (°C)], and a_{CH_2} is the surface area of one CH₂.

The nanorugosity of the filler surface was assessed through the so-called morphology index (MI), which was calculated by the division of the retention volume of ramified probes [$V_G(\text{M})$] by the retention volume of linear alkanes [$V_G(\text{C})$]; this assumed the same surface accessibility for linear and nonlinear alkanes:

$$\text{MI (branched probe)} = \frac{V_G(\text{M})}{V_G(\text{C})} \quad (2)$$

The specific component was obtained from I_{sp} , which was calculated from the difference between the adsorption energies of the polar probe and the *n*-alkanes with the same molecular surface, that is, $[\Delta(\Delta G)] / (N_{\text{AV}}a_p)$, where a_p is the surface area of the polar probe. The polar probe used was benzene. The determination of the distribution of the adsorption energy was made at 30°C with 2,3-dimethylbutene as a probe, with the method usually described in the literature.¹¹ The specific surface area of samples of carbon black was also determined with this method.

Assessment of the bound rubber

The bound rubber was measured according to a technique previously described,¹² with toluene as a sol-

vent. Samples (ca. 0.5 g) were cut into small pieces and introduced into a steel-wire basket, which was immersed in 100 mL of toluene at room temperature. The solvent was renewed several times until complete extraction was achieved. The extracts were collected and evaporated *in vacuo* for the assessment of the unbound rubber. The amount of extracted rubber was calculated:

$$m_c(t_i) = m_w(t_i) \left[1 - \frac{m_{\text{sample}} \text{phr}_{\text{sol}}}{\text{phr}_{\text{tot}} m_{\text{ext}}} \right] \quad (3)$$

where $m_c(t_i)$ is the corrected mass of rubber extracted at extraction time t_i , $m_w(t_i)$ is the weighted mass at extraction time t_i , m_{sample} is the mass of the sample, phr_{sol} is the concentration (phr) of soluble ingredients in the compound, phr_{tot} is the total concentration (phr) of the formulation, and m_{ext} is the total extracted mass.

The complete extraction of the unbound rubber was checked by the plotting of the extracted rubber versus time (i.e., the so-called extraction curve) and by the observation that a plateau value was indeed obtained. The bound rubber content (%BdR) was finally assessed by the fitting of the extraction curve:

$$[\% \text{Extr}]_t = (100 - [\% \text{BdR}])[1 - \exp(-bt)] \quad (4)$$

where $[\% \text{Extr}]_t$ is the unbound rubber extracted at time t and b is the kinetic extraction parameter.

NMR measurements

NMR measurements were performed with a Bruker Analyser Avance DSX 300 solid instrument operated at 300.13 MHz. The proton spin-spin relaxation time (T_2) was determined by the solid echo sequence with a 90° pulse of 3 μs and an 8.6- μs interval between pulses. T_2 was obtained by the fitting of the total normalized relaxation by a mixed Gaussian-exponential expression:

$$f = A \exp \left[-\left(\frac{t}{T_{2S}} \right)^2 \right] + B \exp \left[-\left(\frac{t}{T_{2L}} \right)^i \right] \quad (5)$$

where $1 < i < 2$. The decomposition was determined with Sigmaplot software (Jandel Corp.).

TABLE I
Evolution of the Elemental Composition of N330 After Surface Treatment

Survey spectrum sample	Surface elemental composition (atom %)		
	C	O	S
Reference N330	98.9	0.7	0.4
Modified N330	96.4	3.1	0.5

TABLE II
Effect of Surface Treatment on Functional Groups on the Surface of Carbon Black

Element	Binding energy (eV)	Type	Reference N330 (%)	Modified N330 (%)
C1	≈285.0	Polyaromatic carbon	73.9	74.6
C2	≈286.0	C—O	12.9	10.7
C3	≈287.5	C—O	5.8	5.6
C4	≈289.4	COOH	3.0	3.5
C5	≈291.0	Plasmon	4.3	5.6
O1	≈533.6	—OH	100	66
O2	≈532.3	=O	0	34

Rubber testing

Rheological measurements of the uncured materials

The rheological measurements were performed with an RPA 2000 rubber process analyzer (Alpha Technologies) in the dynamic mode. First, a strain sweep test from 0.6 to 100% strain, at 110°C and a frequency of 0.314 rad s⁻¹, was carried out. Then, frequency sweep tests were performed at 60, 100, and 120°C and a 7% strain amplitude, and the master curve was built with respect to a reference temperature of 100°C.

Dynamic measurements of the cured systems

The samples were optimally cured at 150°C and tested for their dynamic properties with a Metravib visco-analyzer. Strain sweeps were performed at different temperatures at a frequency of 5 Hz, with the strain varying from 0.01 to 10%. The activation energy of the structure at the origin of the low strain modulus was determined by the plotting of $\ln[(E'_{0.01\%}/273)/T]$ versus $1/T$ in an Arrhenius-type graph.

RESULTS

ESCA

The compositions of the reference (untreated) and treated carbon-black samples are given in Table I.

The oxygen atomic percentage increases to a large and significant extent ($\times 4.4$) after the surface treatment. This indicates the high reactivity of carbon black to the oxidative surface treatment. The type of function introduced into the filler has been assessed through a detailed analysis of the spectra, and the results are reported in Table II.

Carboxy groups cannot be detected on the reference carbon black, and this indicates 100% hydroxy groups. Moreover, the proportion of OH groups seems to predominate after the surface treatment (66 vs 34% for C=O groups). This may mean that the oxidative treatment is relatively sweet because an aggressive treat-

TABLE III
Effect of Surface Treatment on the Surface Energy of Carbon Black

Sample	γ_S^D (mJ/m ²)	I_{sp} (kJ/mol)
Reference N330	120.0 ± 6.5	1.1 ± 0.5
Modified N330	134.1 ± 5.6	4.9 ± 0.5

ment would have converted all oxidized species into acid groups.

The peaks at 291 eV are related to the presence of carbon atoms with conductive electrons,¹³ being related to polyaromatic structures. On the treated carbon black, those types of carbon are more abundant than on the reference carbon black (+28%). Therefore, the treatment is likely increasing the level of polyaromatic structures on the surface of the carbon black. However, the C2 concentration decreases by 17%, and the concentration of C4 groups increases by 17%. Although this may be an artifact, it is also possible that the increase in the number of carboxy groups is linked to the initial level of hydroxy groups. With respect to the asymmetric form of the carbon peaks and the absence of a chemical mechanism that could explain such an effect, such a comment should be considered with care.

Surface energy

An infinite-dilution chromatography technique has been used to detect changes due to the surface treatment. The dispersive and specific components of the surface energy of the two carbon blacks are reported in Table III. The dispersive component increases sharply (+10%) with respect to the sensitivity of the measurement. This may be due to the elimination of surface impurities.¹⁴

With respect to the nanorugosity of samples of carbon black, as reflected by MI, no significant changes arise because of the surface treatment (Table IV).

As shown before (Table III), I_{sp} is multiplied by 4.5, in agreement with ESCA measurements. It can be concluded that the main effect of the surface treatment is to develop polar groups on the surface, without

TABLE IV
Effect of Surface Treatment on the Nanorugosity of Carbon Black

Probe	Reference N330 MI	Modified N330 MI
2,2-Dimethylpentane	0.59 ± 0.02	0.63 ± 0.03
2,2,4-Trimethylpentane	0.57 ± 0.01	0.59 ± 0.01
2,2-Dimethylhexane	0.65 ± 0.01	0.61 ± 0.01
Cycloheptane	0.37 ± 0.01	0.36 ± 0.02
Cyclooctane	0.38 ± 0.01	0.35 ± 0.01

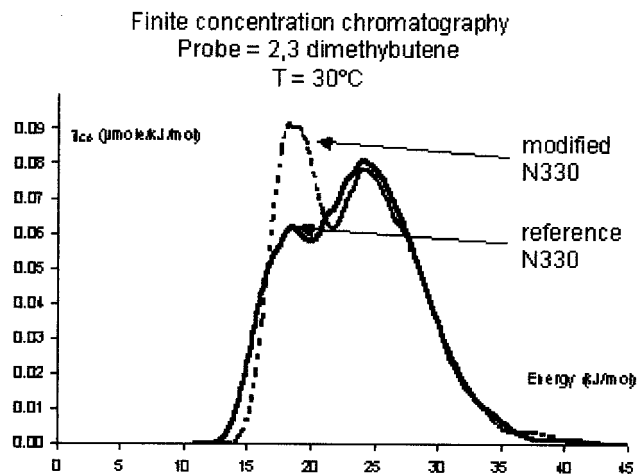


Figure 1 Effect of the carbon-black surface treatment on the distribution of energy sites.

changing the surface energy (or nanorugosity) to a significant extent.

The distribution of energy sites is shown in Figure 1. The shape of the curves confirms the heterogeneity of the surface of carbon black.¹⁵ The energies corresponding to the peaks are 18, 24, and 38 kJ/mol, with the two major ones at low energies. The proportion of high-energy sites (≈ 38 kJ/mol) is modified by the surface treatment, but in such a manner that it does not seem significant. However, the increase in the peak at 18 kJ/mol is highly significant with respect to the precision of the measurement. It is thus likely that the modification does affect the graphitic planes of the filler, the amorphous carbon regions, or both.

The specific surface areas found for carbon black are 62.6 and 69.3 m²/g (+11%) for the reference and treated carbon black, respectively. These values are smaller than usual for a nitrogen adsorption (N_2 SA) surface area because of the higher molecular surface of the probe. However, these results suggest that the oxidative treatment is bringing surface defaults of significant width (approximately the size of one NR segment) to particles of carbon black.

Compound properties

Dynamic properties of the uncured compounds

The effect of the carbon-black surface treatment on the rheological properties is shown in Figure 2. The compound filled with the reference carbon black exhibits the expected nonlinear behavior of the dynamic storage modulus (G'), even at the lowest strains. At a 14% strain, the compound filled with the treated carbon black has a 26% higher elastic modulus than the reference material. This variation is significant with respect to the reproducibility of the RPA 2000 (5%). However, the dynamic loss modulus (G'') does not

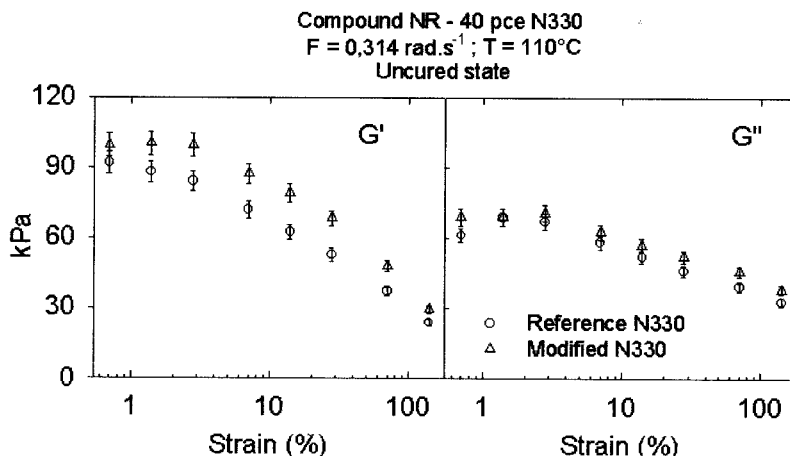


Figure 2 Effect of the carbon-black surface treatment on rheological properties: strain sweeps on uncured compounds.

show a significant variation at the same strain. Using the modified carbon black seems to induce a linear domain up to a 3–4% strain, whereas the compound filled with the reference carbon black is clearly non-linear. The carbon-black/elastomer structure induced by the carbon-black surface treatment seems, therefore, to better sustain the strain. This structure is also sensitive to the frequency, as shown by the master curves in Figure 3.

At a low frequency (e.g., 0.21 rad s⁻¹), the elastic modulus increases by 20% after the carbon-black treatment, whereas the viscous modulus increases by 15%. From 10 to 900 rad s⁻¹, the difference between the two compounds is lower than the reproducibility of the RPA for the viscous modulus and only slightly higher for the elastic modulus. This suggests that the modulus increase originates not only in hydrodynamic ef-

fects (otherwise the plots would remain parallel) but possibly also in a different structure induced by the modified carbon black, which affects principally the long relaxation time mechanisms, in comparison with the reference carbon black.

Dynamic properties of the vulcanized compounds

The effect of the surface treatment is shown in Figure 4. In contrast with the uncured state, the elastic modulus of the cured compound filled with the modified black is significantly lower than that of the reference compound (30% in the linear domain). The Payne effect is thus reduced to a large extent. In the same manner, tan δ is reduced significantly (-45% at the tan δ peak). In terms of the dynamic behavior, the surface treatment of the filler brings interesting properties

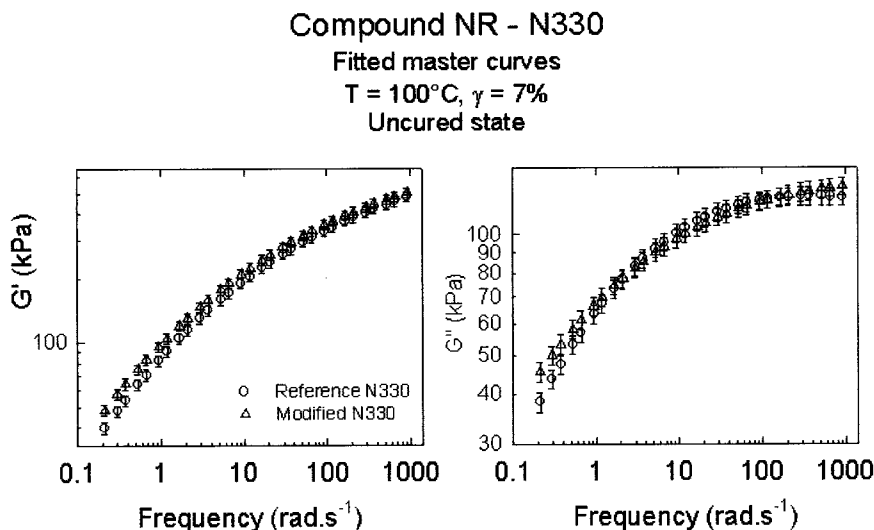


Figure 3 Effect of the carbon-black surface treatment on rheological properties: G' and G'' master curves of uncured compounds.

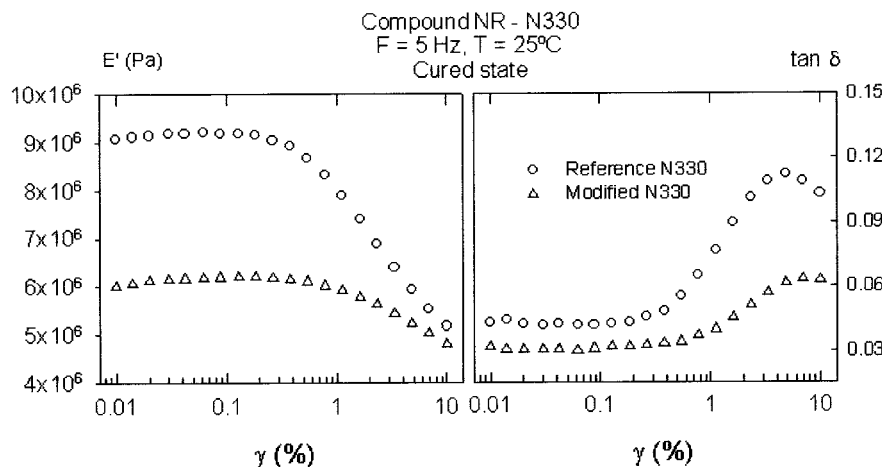


Figure 4 Effect of the carbon-black surface treatment on dynamic properties: the Payne effect on cured materials.

with respect to applications such as tires or engine mounts.

At first sight, the decrease in the elastic modulus can be assigned to a lower efficiency of the acceleration system due to the surface acidity of the treated carbon black. However, a decrease in the reticulation density would not induce a decrease in $\tan \delta$. Consequently, it is not possible to explain the observed effect by a modification of the number or distribution of sulfur bridges between macromolecular chains. We must consider other mechanisms to explain such results.

Bound rubber

The level of rubber/carbon-black interactions is considered with respect to bound rubber measurements (see Fig. 5). With the reference black, the bound rubber concentration is 30%; with the modified carbon black, it is 40%. In other words, the surface treatment of the filler leads to a 33% increase in bound rubber. This variation is highly significant with respect to the precision of the method and confirms other studies:^{16,17} the surface treatment appears to favor increased compatibility between carbon black and rubber because the surface treatment should not have any significant effect on the gel content.

NMR measurements

To understand more precisely the structure generated by the surface treatment, we have performed an analysis of segmental mobility for both extracted and unextracted compounds. Figure 6 shows the variation in relaxation times T_{2S} and T_{2L} and the fractions of the different components with a temperature variation of 230–330° K. Indeed, the mixed two-term exponential–Gaussian equation satisfactorily fits the free-induction decay signal, without the need of a third (intermedi-

ate) component, contrary to what is usually shown in the literature. The well-known behavior of the rigid part ($T_{2S} \approx 17 \mu s$) of the elastomer—the so-called tightly bound rubber—is observed, and this confirms the permanent quasiglassy state of this part of the rubber. The other part of the bound rubber (the mobile fraction) appears to have a glass-transition temperature of about $-30^\circ C$ and represents 90% of the bound rubber at about $40^\circ C$.

With respect to the fractions of both the rigid and mobile phases, no significant differences can be seen between the two compounds. Between 20 and $60^\circ C$, a slight difference is observed as T_{2L} of the compound filled with the modified carbon black is some 3–11% lower (depending on temperature) than T_{2L} of the

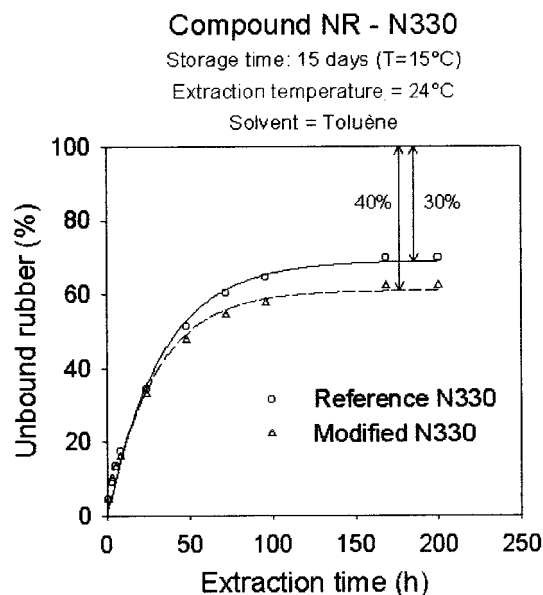


Figure 5 Effect of the carbon-black surface treatment on bound rubber.

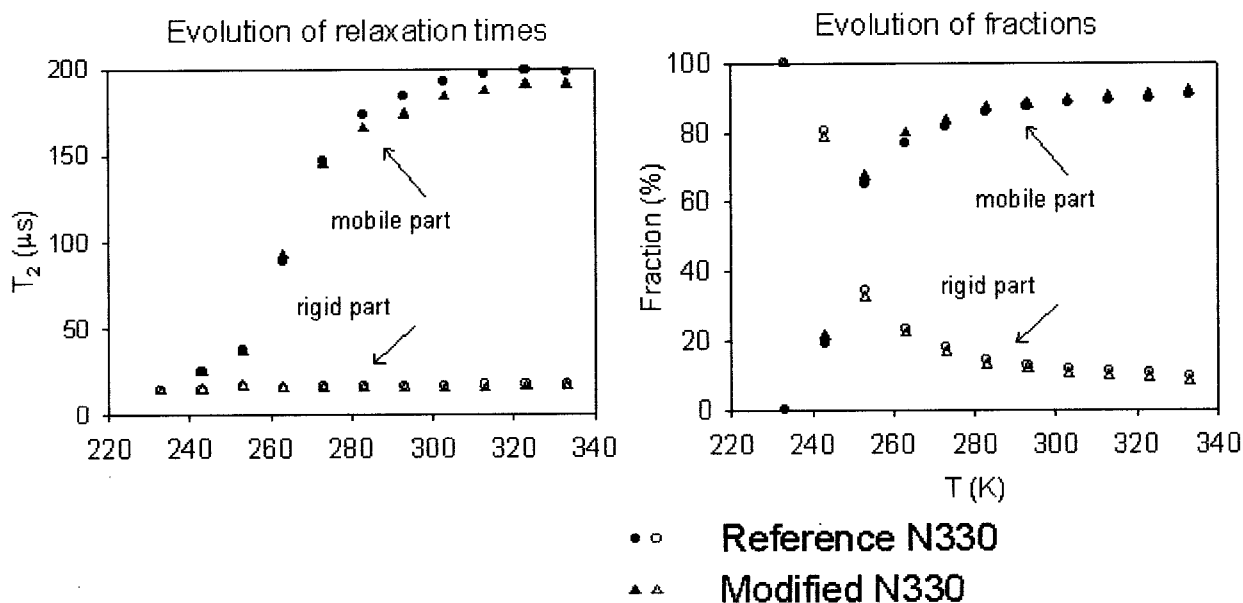


Figure 6 $^1\text{H-NMR}$ experiments: the effect of the carbon-black surface treatment on the segmental mobility of bound rubber (extracted samples).

compound filled with the reference black. However, this difference is small and perhaps lacks significance.

These results somewhat contradict other experiments, and two hypotheses can be drawn at this stage: either the surface treatment does not produce any significant change in the structure of the rubber/carbon-black network or the extraction procedure changes the morphology of the compound because, by the extraction of the free rubber matrix, the spatial support of the three-dimensional rubber-filler structure is lost.

The relaxation times measured at 40 and 60°C for unextracted compounds are reported in Table V. The T_{2S} relaxation times are of the same order as those of extracted compounds, and the treated and untreated carbon black cannot be distinguished in this way. The percentage of the immobilized phase (5–6%) is twice as small as the percentage in extracted compounds because the elastomer matrix is not extracted and, therefore, reduces the proportion of the immobilized phase. Second, it must be specified that the mobile

phase characterized here is different from the one in extracted samples: this phase is made of both loosely bound rubber and extractable elastomer. Therefore, the long T_{2L} 's are larger than the ones measured for extracted samples. Moreover, the T_{2L} relaxation times are lower than the ones usually found in the literature, likely because of the specific nature of the mobile phase characterized here.

The T_{2L} relaxation times of the compound filled with the modified carbon black are significantly higher than for the compound filled with the reference black: at 60°C, a 23% increase is observed, which is significant with respect to the precision and the reproducibility of the measurement. Apparently, the surface modification of the carbon black does manifest itself locally in the rubber matrix far from the filler surface, it is not seen at the filler surface, and it consequently does not appear in extracted samples. Indeed, for the two carbon blacks, the segments that are not expected to be influenced by the carbon black (i.e., extractable matrix) should have the same mobility because they belong to the same polymer in the free state. Therefore, it is logical to assume that, in unextracted samples, the mobile bound phase has a larger mobility in the presence of treated carbon black than in the presence of the reference black.

The nature of the functionalities introduced onto the surface of carbon black could induce the formation of chemical links, the mobility of which, in comparison with that of adsorbed segments, is not known. Figure 7 shows the ^{13}C spectra obtained for both extracted and unextracted compounds.

The measurements were made as follows:

TABLE V
Effect of Surface Treatment on the Segmental Mobility of Unextracted Compounds

	Reference N330 compound		Modified N330 compound	
	40°C	60°C	40°C	60°C
F_{T2S} (%)	6.0	5.3	5.8	5.0
F_{T2L} (%)	94.0	94.7	94.2	95.0
T_{2S} (μS)	19.0	20.1	18.4	20.2
T_{2L} (μS)	219.0	224.6	269.9	276.0

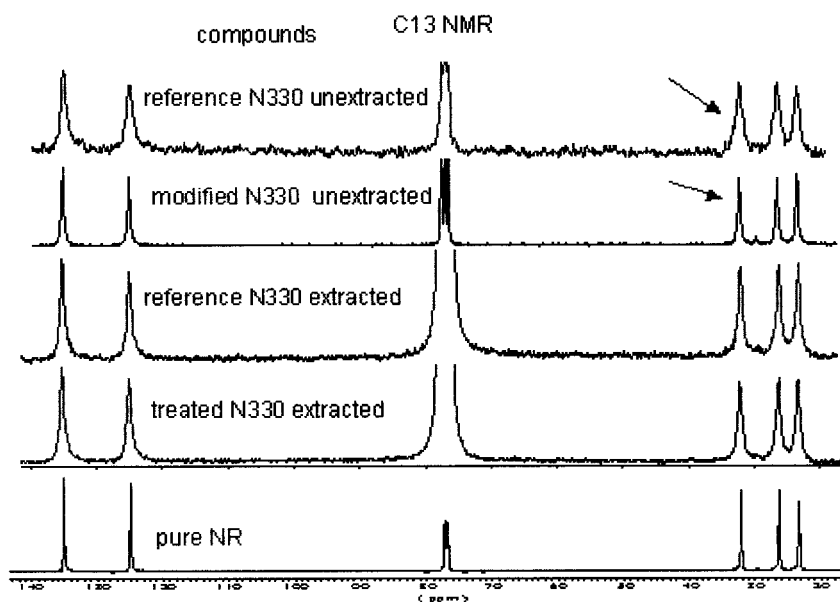


Figure 7 ^{13}C -NMR experiments: the effect of the carbon-black surface treatment on ^{13}C spectra.

- With a Bruker/C DRX 500 instrument at 125 MHz.
- With CDCl_3 (77 ppm) as a solvent at room temperature.
- With a nutation angle of 20° , a relaxation time of 10 s, 1000 scans, a spectral width of 200 ppm, and FT at 64 K.

No chemical shift is observed with respect to the treated carbon black. Therefore, if chemical links exist with the treated carbon black, they are very low in number because they cannot be detected, being at best a part of the 10% tightly bound rubber and hence at the limit of detection of the technique. Other techniques could possibly reveal the presence of chemical links, but at this stage of the work, it can be concluded that there are surely no sufficient links to explain the variations observed in the dynamic properties.

Nevertheless, the ^{13}C -NMR results confirm the results obtained by ^1H -NMR. Indeed, the half-width at maximum is smaller for the modified N330 unextracted compound than for the reference black (30 vs 55/65 Hz, which is a 45/55% difference, as shown by peaks indicated by arrows in Fig. 7). Because the widths of the bands are affected by heteronuclear dipolar interaction (the more restricted the mobility is, the larger the band is), the global segmental mobility is enhanced by the surface treatment; this has been observed with two different NMR techniques.

Filler dispersion

Among the techniques available for assessing carbon-black dispersions, transmission electronic microscopy

(see Fig. 8) is preferred for conductivity measurements, an indirect method of characterizing dispersions. Moreover, the latter technique raises a number of difficulties linked with the variation of carbon-black conductivity according to its nature or surface chemistry.

The objects observed (aggregates) are around 250 nm for both compounds. This value is close to the weight-average diameter found in the literature,¹ if one takes into account that the measured dimensions correspond to the surface projected areas.

No difference in the carbon-black dispersion can be seen in a comparison of the two samples. Therefore, the improvement of the dynamic properties shown in

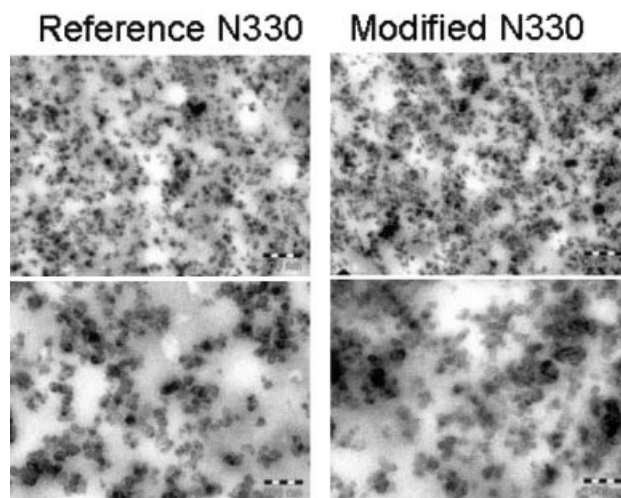


Figure 8 TEM images of the dispersion states of treated and untreated reference carbon black.

Figure 4 can be assigned not to any change in the filler–filler interactions but rather to a modification in the rubber–filler interface when we consider the significant differences shown with respect to the segmental mobility characterized by two different NMR techniques.

DISCUSSION

The following discussion is an attempt to propose a phenomenological mechanism that can explain the observed effects on uncured and cured compounds.

Average molecular weight of the adsorbed rubber chains

- In a filled rubber compound (NR or SBR), the bound rubber increases with storage time.¹⁸ This effect has been tentatively explained by a progressive substitution of the initially adsorbed short chains by longer chains through segmental diffusion mechanisms. This hypothesis has recently been confirmed.¹⁹
- As a result of the competition between the adsorption enthalpy of a segment on the carbon-black surface and the thermal energy at room temperature, it is likely that adsorbed segments are in a constant process of adsorption and desorption at the filler surface.

The molecular characteristics of rubber chains follow Gaussian statistics, but a simpler view can be purposely taken by the consideration of only two fractions: shorter and longer chains. The longer chains having obviously more segmental units than the shorter ones, the probability that segments belonging to longer chains can be adsorbed onto the surface is, at equilibrium, higher than for segments belonging to shorter chains. This hypothesis explains the increase in the amount of bound rubber in a system in which neither the specific surface area nor dispersion varies.

Segmental mobility of the mobile phase in the unextracted compounds

It has been shown²⁰ that in filled compounds an increase in the molecular weight of the polymer increases the segmental mobility of the mobile phase. The interpretation is based on the fact that long chains have a tendency to form long loops. Moreover, it has been shown that the introduction of chemical functions onto the carbon-black surface can increase the segmental mobility of the mobile phase.²¹ This phenomenon has been interpreted by the enhanced formation of long loops.

Experimental observations

We have shown that

- The surface treatment introduces chemical functionalities onto the surface.
- These chemical functionalities change the surface energy distribution of the carbon black.
- The mobility of the mobile phase is enhanced by the surface treatment.
- The bound rubber increases after the surface treatment of the filler.

Hypotheses and explanations

Chemical functionalities on modified carbon black lead to more difficult segmental adsorption than for untreated black. This hypothesis is related to the increase in the proportion of low-energy sites. By a process similar to the maturation mechanism, the shorter chains, which do not have many chances of adsorbing onto the surface, are likely substituted by longer ones because of the filler surface treatment. The increase in the mean molecular weight of rubber segments at the filler surface may be the reason for the increased bound rubber after the surface treatment. The formation of long loops, connecting filaments, or both may also favor the mobility of the mobile phase. These interpretations are illustrated in Figure 9 with respect to the sketch by McBrierty et al.⁹

The hydrophilic nature of the treated carbon-black surface is, therefore, responsible for a modification of the distribution of the adsorbed macromolecular chains and tends to enhance the adsorption of molecules of larger macromolecular weights.

Uncured dynamic properties

In the linear viscoelastic domain, the microstructure of the compound corresponds to an equilibrium state, which depends on the stability of the initial structure of the material with respect to the deformation.

It has been observed (see Fig. 2) that the compound filled with treated carbon black is less sensitive to strain. It is generally accepted that the nonlinearity of filled compounds can be attributed to the filler because the nonlinearity of unfilled compounds is observed at higher deformations. For the experiments reported here, no difference in the dispersion has been observed between reference and modified carbon black. Another explanation can, therefore, be considered: at a constant dispersion state, the connecting filaments between aggregates play an important role with respect to the elastic modulus. An increase in the number of connecting filaments gives both an increase in the elastic modulus and a decrease in the deformation sensitivity. Note that at a 140% strain, at an un-

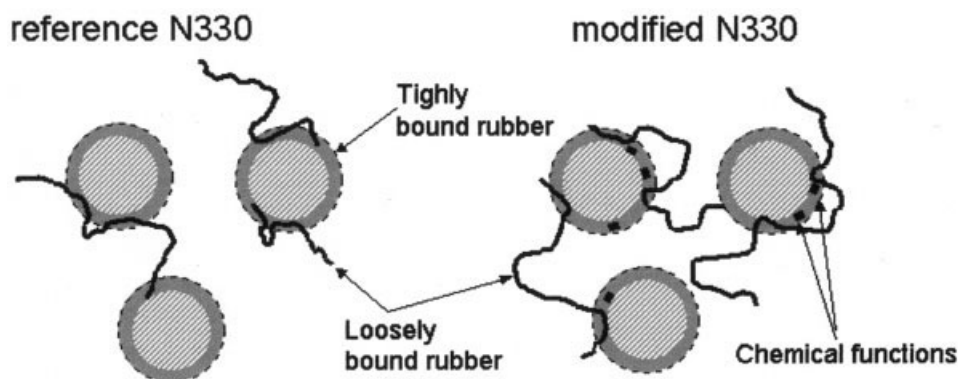


Figure 9 Schematic representation of a possible structure generated by the surface treatment of carbon black.

cured state, the modulus of the treated carbon-black compound is still 23% higher than that of the reference compound. It is difficult to believe that this phenomenon is not due to a network structure. When the strain increases, the connecting filaments are destroyed, and then the elastic modulus decreases.

Vulcanizate properties: Payne effect

The cured dynamic properties have been analyzed in the linear domain (see Fig. 4). The mechanism under increased strain amplitude might be different for a cured material than for an uncured material because a $\tan \delta$ peak is only observed in the cured state. Indeed, it seems that in the uncured state under increased strain amplitude, the carbon-black/rubber interface is not fully constrained because the rubber matrix is able to flow. Connecting filaments are thus expected to play a significant role.

In the cured state, connecting filaments are obviously vulcanized and are part of the whole rubber matrix; they cannot, therefore, be broken or destroyed. The carbon-black/rubber interface, which is made of weak (physical) links in comparison with the chemical links of the vulcanized network, can be much more constrained. Under increased strain, those weak links are broken, and this results in higher energy dissipation. This explanation, suggested by the work of Maier and Göritz,³ meets the observed results because the chemical functions at the carbon-black surface will hide the so far unidentified sites at the origin of energy dissipation.

Figure 10 shows the variation of the plateau modulus as a function of the inverse temperature.

The activation energies of the structures characterized here are 5.9 and 4.8 kJ/mol for the compounds filled with the reference and modified carbon black, respectively. Because the dispersion does not vary, these typical activation energies should be assigned to the behavior of the part of the elastomer that is very close to the filler surface. It can, therefore, be con-

cluded that the importance of the enthalpic phenomena associated with the introduction of the filler is lower when the modified carbon black is used. As the number of sites responsible for energy dissipation decrease, the probability of their desorption under thermal energy is lower as well.

The analysis of the mechanical properties gives further support to the aforementioned explanations (see Table VI).

In the work reported here, higher 100 and 300% moduli were obtained with the treated carbon black, in comparison with the reference black, at an equivalent tensile strength (probably because of an equivalent dispersion). It is likely that sliding segments are less favored for the surface-treated carbon black, with the immediate result of a lower ultimate elongation due to a less heterogeneous distribution of energy dissipation between the rubber matrix and the filler-rubber interphase. Because of the moderate content of

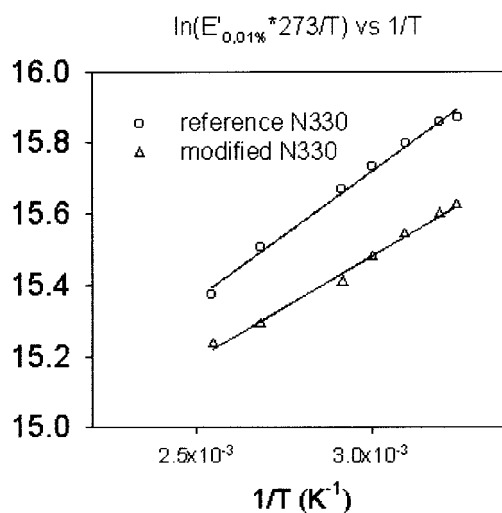


Figure 10 Arrhenius graph of the plateau modulus for vulcanizates filled with reference and modified carbon black.

TABLE VI
Effect of Surface Treatment on the Mechanical Properties

Property	Reference N330	Modified N330
σ_{100} (MPa)	2.9	3.6
σ_{300} (MPa)	14.9	18.9
Tensile strength (MPa)	26.7	26.6
Elongation at break (%)	460	390

acidic groups on the carbon-black surface, the curing system seems not to be damaged and allows interfacial phenomena to predominate.

It has been reported in the literature²² that rubber-filler contacts should only play the role of spatial supports for filler networks at small strains. The aforementioned results suggest the opposite: at a cured state, the carbon-black aggregates could play the role of supports for the spatial repartition of carbon-black/rubber interfaces in the compound. At an uncured state, the filler network is an active part of the compound because of its three-dimensional nature.

The objectives of this work were to further refine the correlations between rubber compound properties and physicochemical characterizations. Similar correlations have been observed between long T_2 relaxation times and $\tan \delta$, but through variations of the filler content. Indeed, Yastuyanagi²³ has shown that when the filler volume fraction increases, T_{2L} decreases and $\tan \delta$ increases. However, no characterization of the dispersion was made by these authors, and it is, therefore, difficult to assign the evolution of $\tan \delta$ to the occurrence of any kind of structure. With respect to the results reported here, we can assume that a reason for increased $\tan \delta$ with the filler content may be the restriction of the mobility of the rubber matrix (higher internal frictions) coupled with an important increase in the number of unstable links, rather than enhanced filler-filler contacts, which, under increased strain, would create highly constrained regions near the particle surface.

This hypothesis could also bring an alternative explanation for the properties of compounds with a silica/coupling agent. Generally, the reason given for the low Payne effect of silica-filled rubber is an improved dispersion due to the coupling agent, which reduces the amount of polar filler-filler contacts. In this case, the rubber chains are not in contact with the filler surface but are linked to it through an intermediate mobile interface made of condensed silane molecules. The constraints exerted by the rubber matrix are, therefore, lower than for standard carbon blacks, in which case the formation of trains and short loops could have the effects mentioned previously. Moreover, there should be only a few instable links in the case of silica compounds, and the Payne effect should

be studied with respect to the specific nature of the interphase. This hypothesis is supported by the modeling of Tokita et al.²⁴ and by another study²⁵ that shows that T_{2L} in coupled silica-filled systems is systematically higher than in carbon-black-filled systems.

Finally, with respect to surface energy measurements in relation to mechanical properties, it appears that carbon-black reinforcement (modulus) can be highly influenced by the introduction of low-energy sites, which limit the molecular sliding of rubber at the carbon-black surface and, therefore, lead to a modulus increase.

CONCLUSIONS

The high reactivity of carbon black with respect to the surface treatment has been established. The main observed effects are (1) a grafting of —OH and —OOH functions onto the surface and a corresponding increase in the specific component of the surface energy, (2) a modification of the distribution of energy sites (an increase in the number of low-energy sites), and (3) slight increases in the specific surface area and the surface defaults.

With respect to physicochemical characterizations, no variations of the fractions and mobility of rigid and mobile phases for extracted compounds have been observed, whereas an increase in the mobility of the mobile phase has been noted with unextracted compounds and has been assigned to the formation of long loops and connecting filaments.

In terms of rubber properties, an increase in the elastic modulus of an uncured material can be observed when carbon black is modified, and decreases in the elastic modulus at a low strain (a decrease in the Payne effect) and $\tan \delta$ peak of 45% can be noted for cured compounds. Modifying the carbon black also leads to higher 100 and 300% moduli, but no change in the filler dispersion is observed.

Therefore, that the specific role of the rubber/carbon-black interface is clearly underlined by this study. The dispersion of the filler (filler-to-filler contacts) is obviously crucial for the practical uses of rubber compounds (fatigue and service-life performance), but its role in dynamic properties may be indirect, resulting from a modification of the mobility of the rubber matrix: the more mobile the matrix, the lower $\tan \delta$. Under dynamic strain, the deformed vulcanized rubber matrix may have a spring effect on the rubber/carbon-black interphase. If less unstable links are subjected to this strain, the dynamic properties are improved. Therefore, it seems that the carbon-black surface can be improved in such a manner that the adsorption of trains will be less favored and the formation of long loops will be enhanced. Huber and Vilgis²⁶ recently modeled the adsorption of polymer segments under the physical or chemical modification

of the carbon-black surface. They concluded that the disorder-induced enhancement of adsorption was confirmed and was shown to be much more significant for the heterogeneous interaction strength than for the spatial roughness. With respect to this hypothesis, and comparing our results with those of Gronski et al.,²⁷ we can conclude that a disordered adsorption on the carbon-black surface may improve the dynamic properties.

As the content and type of carbon black are currently fixed by crucial properties, such as the abrasion resistance, hardness, and mechanical properties, it seems that a good way of improving the dynamic properties is to use the elements offered by filler-rubber interactions, the efficiency of which only relies on an understanding of interfacial phenomena.

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