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# Carbon Black Networking

Carbon black is a truly remarkable material. Known and used as a colorant in antiquity, it is still used in large quantities in the modern age. In particular, it is a raw material of prime importance in the manufacture of rubber goods, especially automobile and truck tires. Highway and air transportation as it is known today would not be possible without carbon black-reinforced rubbers.

Carbon black consists of irregular, chain-like, branched aggregates of firmly fused nodular subunits. It is suggested that these aggregates are "interacting" together in order to form agglomerates and/or a network when dispersed in supporting media.

The objective of the studies, summarized in this paper, is to confirm the existence and quantify the filler network within polymeric matrices.

Previous studies have shown [1,2] that strain dependency is much more important than the influence of frequency (up to 30 Hz) or temperature in distinguishing the reinforcing role of carbon black in polymeric compounds.

For many years the dynamic mechanical properties of rubber reinforced carbon black systems have been studied, and an excellent review has been written by A. Medalia [3]. In this review Medalia emphasized the role of strain measurement to distinguish the behavior of carbon black in compounds. Dynamic test equipment suitable to evaluate the role of the filler in a compound therefore has to be able to measure accurately over a strain range from 1/10 to at least 10 to 12 % strain.

The low strain data presented were all obtained using a Rheometrics SIV mechanical spectrometer. The deformation in a "rotational shear" mode was done at 1 Hz and 30 °C.

A viscoelastic body subjected to sinusoidal strain :

$$\gamma = \gamma_0 \sin \omega t$$

$\gamma_0$  : max. strain amplitude  
 $\omega/2\pi$  : frequency (Hz)

will exhibit a sinusoidal stress of identical frequency but out of phase ( $\delta$ ) with the strain (linear viscoelasticity). In that case the stress can be expressed by :

$$\sigma = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t]$$

thus defining two shear moduli,  $G'(\omega)$  and  $G''(\omega)$ . The storage modulus  $G'$  is a measure of energy (elastic) stored and recovered in cyclic deformation ; the loss modulus  $G''$  is a measure of energy dissipated as heat. The ratio  $G''/G'$  is than  $\delta$ , the loss tangent.

It is worthwhile to note that in a prescribed strain cycle experiment where  $\gamma_0$  is the maximum strain amplitude, the energy lost per cycle (hysteresis) is given by the following expression :

$$2\pi (\gamma_0)^2 G''(\omega)$$

and not by than  $\delta$ , which in this case is related to the energy dissipated per unit energy stored and not per unit energy input.

Based on all the above considerations, it is clear that to characterize a material exhibiting viscoelastic behavior the usage of two parameters is required. Therefore the couple ( $G'$ ,  $G''$ ) is used to fully define the fundamental behavior at low strain of carbon black filled compounds. Since the strain is the predominant factor, the representation of  $G'$  and  $G''$  as function of strain is essential. Fig. 1 shows a typical example of these curves.

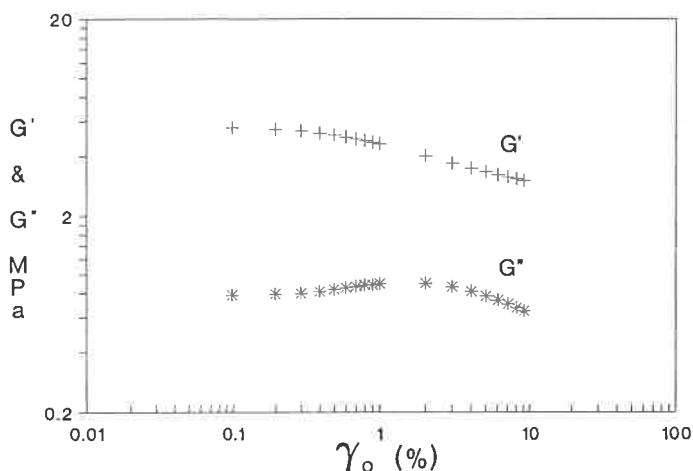


FIGURE 1.

It is also recognized that there exists a relationship between  $G'$  and  $G''$ . Indeed, a high/low  $G''$  corresponds to a high/low  $G'$ . It was therefore interesting to consider  $G' = f_1(\gamma_0)$  and  $G'' = f_2(\gamma_0)$  as a parametric representation of a general equation :  $G'' = f_1(G')$ . This function exhibits similarities with the known «Cole-Cole» plots [4] established for complex dielectric permittivity.

A generalized representation of this equation, called a <G-Plot>, is shown on Fig. 2 ; specific <G-Plots> of four carbon blacks (N220, N330, N550, and N660) in SBR on Fig. 3. It can be shown [5, 6] that all <G-Plot> curves studied (22 carbon blacks from N110 to N782 in SBR and NR) can be shifted to a "master" curve. Indeed, all <G-Plots> obtained with the different fillers in one type of compounds can be shifted to a "reference curve". Specifying, for example, the NR-N110 <G-Plots> as a reference curve, all the other NR <G-Plots> can be shifted using two factors,  $a_1^{NR}$ ,  $b_1^{NR}$ , to the above-mentioned reference curve. Indeed, using different "affinities" for each curve (translation and expansion along the  $G'$  axis followed by a different expansion along  $G''$  axis), it is possible to shift all these curves ( $r_i$ ) to the reference curve ( $r_0$ ). Mathematically ( $r_0$ ) is defined by N coordinates :

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$(X_{0,1}, Y_{0,1}), \dots, (X_{0,N}, Y_{0,N})$

whereas each of the  $r_i$  curves are defined by :

$(X_{i,1}, Y_{i,1}), \dots, (X_{i,N}, Y_{i,N})$

and the transformation consists first to switch :

$(X_{i,1}, Y_{i,1})$  to  $(X_{0,1}, Y_{0,1})$

and then to bring by two « affinities » ( $a_i, b_i$ ) the  $k$ th point of  $r_i$  to the  $k$ th point of  $r_0$ , both  $k$ th points corresponding to the same  $\gamma_{0,k}$  :  
 $(X_{i,k}, Y_{i,k})$  to  $(X_{0,k}, Y_{0,k})$

The method described by Tricot [6] gives :

$$a_i = \frac{\sum (X_{i,k} - X_{i,1}) \cdot (X_{0,k} - X_{0,1})}{\sum (X_{i,k} - X_{i,1})^2}$$

$$b_i = \frac{\sum (Y_{i,k} - Y_{i,1}) \cdot (Y_{0,k} - Y_{0,1})}{\sum (Y_{i,k} - Y_{i,1})^2}$$

All the <G-Plots> obtained for a given polymer were shifted to the reference N110 <G-Plot> and the results can be summarized as follows.

$G'$  and  $G''$  are not independent moduli.

All shifts are remarkably good. The shiftability criterion [6] was generally met with a high degree of confidence.

The "a<sub>i</sub>'s" are generally smaller than the "b<sub>i</sub>'s", but in all cases a linear relationship exists between  $b_i$  and  $a_i$  for a given polymer (slope of 1.2 with SBR and 1.5 with NR).

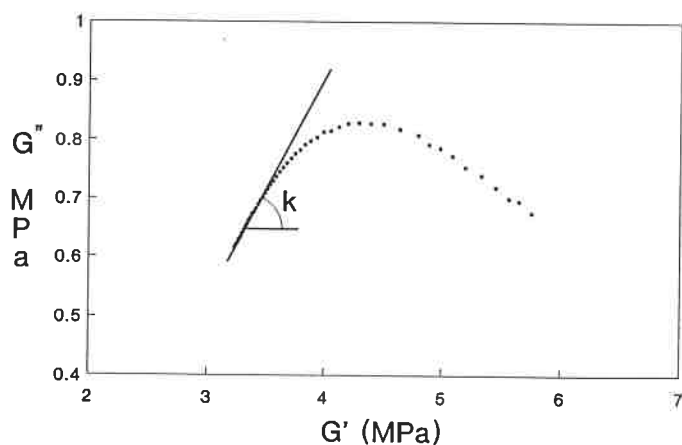


FIGURE 2.

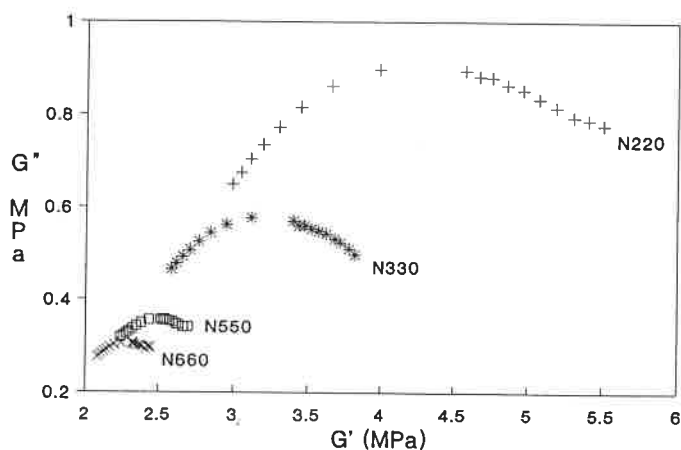


FIGURE 3.

Moreover, if the  $a_i$ 's and  $b_i$ 's for tread black are calculated from the shift to N110 <G-Plot> and the  $a_i$ 's and  $b_i$ 's for carcass black from a shift to a carcass black reference <G-Plot> (i.e., N539) then the linear relationship of  $b_i$  with  $a_i$  for "tread black" is identical to the linear relationship for the "carcass black". Here again the slopes of these lines are polymer dependent (1.36 for SBR, 1.64 for NR).

By shifting all <G-Plots> (NR and SBR) to the same reference curve (i.e., <G-Plot> N110 SBR) the above-mentioned observations are also true. In this case the slope of  $b_i$  vs.  $a_i$  is 1.7.

All these results show that all the <G-Plots> are "affined" indicating that regardless of the polymer studied (NR or SBR) and regardless of the carbon black used, a unifying mechanism must be operable to explain the low strain behavior of carbon black filled compounds.

From a more practical standpoint, one can imagine that using this approach could reduce substantially the testing requirements necessary to choose a carbon black for a given low strain dynamic application, since knowing the  $a_i$ 's and  $b_i$ 's all low strain properties can be predicted from one <G-Plot> for a series of carbon blacks.

The mechanism proposed to address these observations is the formation of an independent filler network, the cohesion of which is a function of the filler. The above-mentioned shift factor characterizing one filler reflects that dependency ; and if one shifts all the <G-Plots> to a master curve obtained with the most reinforcing carbon black, the lower the shift factor the stronger the network. This type of relationship between  $G''$  and  $G'$  is not restricted to carbon black dispersed in elastomeric matrices but is also valid in other media of much lower viscosity and/or chemical nature.

A study was conducted wherein N110 carbon black was mixed with low molecular weight polydimethylsiloxane (PDMS) at varying filler concentrations (0 to 40 phr). At higher loading levels, the shape of  $G'$  vs. strain plot (Fig. 4) is typical. However, two additional observations can be made based on that study :

- (1) At 10 phr N110 in PDMS, the  $G'$  of the compound is lower than pure PDMS regardless of the strain ;
- (2) At higher loading (i.e., 30 phr) the elastic modulus of the sample drops below the modulus of the pure polymer above 10 % strain.

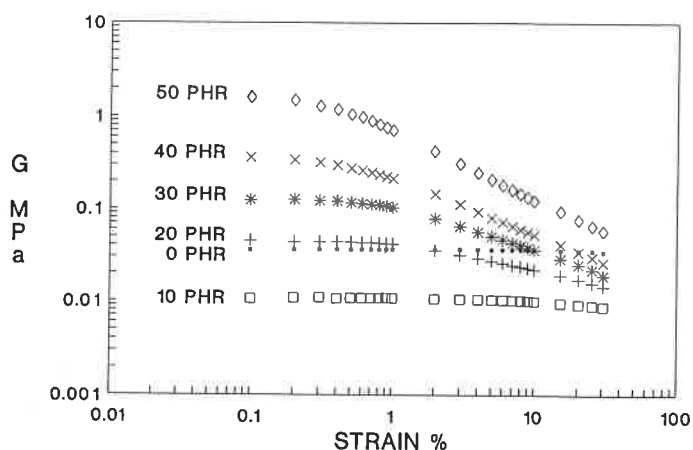


FIGURE 4.

These observations lead to the conclusion that before percolation (i.e., 10 phr) the carbon black forms a set of non-connected subnetworks (not deformed by strain relative to the low molecular weight polymeric matrix and therefore  $G'$  is lower than the non-filled compound) ; whereas, after the full network is formed and increase of strain "shatters" the continuous network into a set of non-connected subnetworks resulting in a prepercolation

morphology. This behavior is not noted in SBR or NR compounds since the viscosity of the polymeric matrix overshadows the subnetworking cohesion.

Previous studies [7] have postulated the existence of this network and calculated the "network cohesion energy". This networking energy  $E_n$  was measured for all the studied carbon black by studying the role of temperature on  $G'$  and has confirmed a "Van der Waals" type network [5]. The "network cohesion energy" is proportional to the low strain reinforcing potential of the filler. (i.e., the higher  $G'$  the higher  $E_n$ ) (Fig. 5) The representation (Fig. 6) of  $L_n G'$  versus  $1/T$  from which  $E_n$  is calculated shows for all studied samples a well-marked transition point around 90 °C, which indicates a change in the material behavior. It is postulated that as this transition point the network is broken.

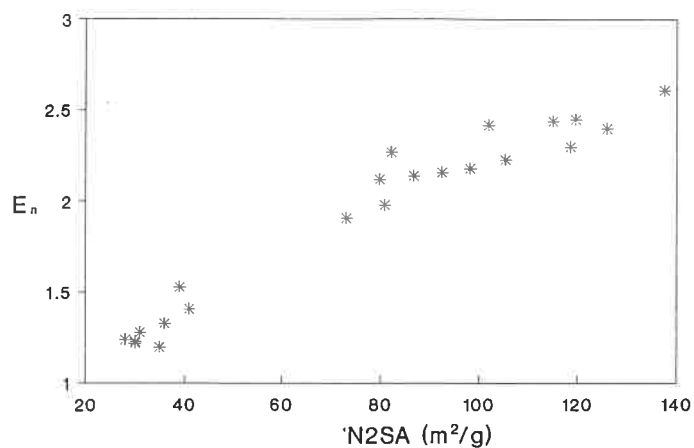


FIGURE 5.

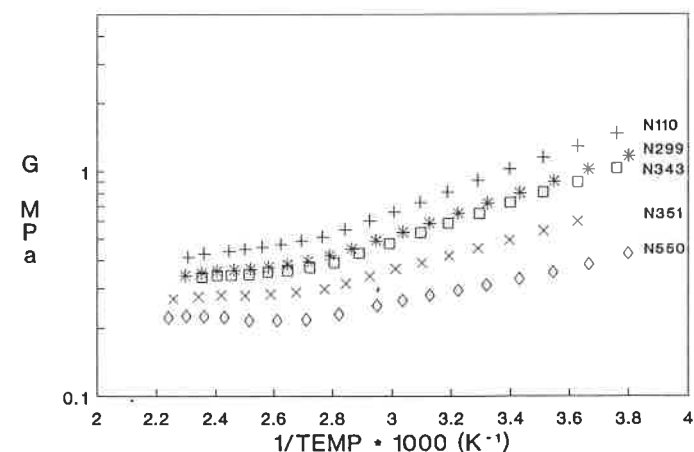


FIGURE 6.

This network is very sensitive to strain amplitude and has been shown via conductivity measurements [8] to vanish with increasing strain.

The analysis of the <G-Plot> confirms this network breakdown. If one considers that a higher strains  $dG''/dG'$  is becoming strain independent the reinforcing carbon black network has vanished. All the obtained <G-Plots> are characterized by a linear part

(Fig. 2) where :

$$\frac{dG''}{dG'} = k = \text{cst}$$

It is interesting to note that for "tread black" this linearity starts around 6 to 7 % strain ; whereas, for "carcass grades" the network influence disappears around 5 to 6 % strain, indicating that the tread black network is stronger than the carcass black network.

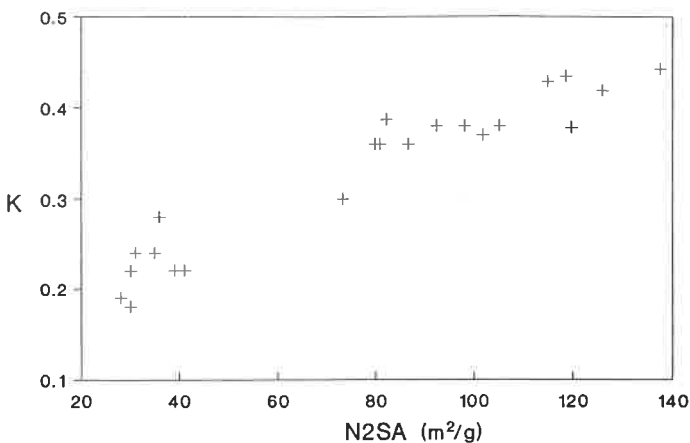


FIGURE 7.

The "k" values of the different <G-Plot> are essentially carbon black-dependent and can be related to geometrical parameters of the filler, indicating that after the network breaks down, the effect of the filler is reduced to solely a "hydrodynamic type" effect, hindering the polymeric chain flow upon straining. As expected, and as shown on Fig. 7, this effect is more pronounced with a smaller filler entity (larger specific surface area). This phenomenon, and as reported elsewhere (5), has also to be taken into consideration when studying high strain properties of carbon black-filled compounds. In particular it is shown that at higher strain (>20 % strain) the energy dissipated ( $E_D$ ) per unit strain energy input ( $E_I$ ) is independent of the strain (i.e.,  $E_D/E_I = K'$ ). It is shown that  $K'_{\text{SBR}} = K_{\text{SBR}}$  for SBR compounds ; whereas,  $K'_{\text{NR}} > K_{\text{NR}}$  in NR compounds, which might be due to the strain crystallization of the polyisoprene.

## References

- [1] M. Gerspacher, C. Lasinger, Paper # 7, *ACS Rubber Div. Meeting*, April 1988.
- [2] M. Gerspacher, J.-B. Donnet, Paper # 42, *ACS Rubber Div. Meeting*, May 1989.
- [3] A.I. Medalia, *Rubber Chem. Tech.*, 1978, 51, 437.
- [4] K.S. Cole, R.H. Cole, *J. Chem. Phys.*, 1941, 9, 341.
- [5] M. Gerspacher, C.P. O'Farrell, H.H. Yang, to be published.
- [6] C. Tricot, private communication.
- [7] E.R. Fitzgerald, *Rubber Chem. Tech.*, 1982, 55, 1547.
- [8] L.C. Burton, K. Hwang, T. Zhang, *Rubber Chem. Tech.*, 1989, 62, 838.