A. Vidal* and B. Haidar*

Reinforcement of elastomers: Effect of polymer/filler interactions on the dynamics of elastomeric chains at the interface**

Molecular dynamics of polymer chains in elastomer/filler blends can provide indepth information on the processes taking place at the polymer/loading material interface and in the elastomeric phase surrounding the reinforcing particles (the interphase) as well. A fraction of the elastomer is in a glass-like state, even at temperatures in large excess of the polymer $T_g$. Taking advantage of physical ageing processes and using solid state NMR, one may quantify the amount of polymer which participates to the interphase and show that interfacial interactions are selective and dependent on the filler/polymer couple under investigation.

Key words: reinforcement, interaction, interphase area, testing methods

Wzmocnienie elastomerów: Wpływ oddziaływania polimer/napęlniając na dynamikę łańcuchów elastomerowych na granicy faz

Dynamika molekularna łańcuchów polimerowych w mieszaninach elastomer/napęlniając może dostarczyć wnikliwych informacji o procesach przebiegających na granicy faz polimer/napęlniając oraz w fazie elastomeru otaczająca cząstki napęlniańca. Frakcja elastomeru jest w stanie podobnym do szklistego, nawet w temperaturze o wiele wyższej niż $T_g$ polimeru. Nowoczesne metody badań, wykorzystujące procesy fizycznego starzenia i NMR ciała stałego, stwarzają możliwość ilościowej oceny polimeru uczestniczącego w tworzeniu obszaru międzyfazowego i pozwalają na obserwację współoddziaływań w tym obszarze. Oddziaływanie te są selektywne i zależą od polimerów i napęlniańczy użytych do badań.

Słowa kluczowe: wzmocnianie, współoddziaływanie, obszar międzyfazowy, metody badań

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Introduction

It is well agreed by now that the driving forces which control the so-called reinforcement effect, i.e. the improvement of properties associated with the blending of fillers with elastomers, are the result of the interactions which can take place at the polymer/loading material interface. However, in spite of the large amount of work which has been devoted to the understanding of the processes which may occur within a volume in the vicinity of the surface of the dispersed solid (the interphase) important questions still remain unanswered; particularly on the point of view of the exact nature of the interactions involved, and the distance from the filler surface at which they influence the matrix. In this paper, information on the structure and properties of the interphase between a filler and an elastomeric matrix will be obtained from the study of the molecular dynamics of the corresponding polymeric chains. In this respect two major questions will be stressed. On the one hand, how immobilized are the elastomeric chains which are interacting with the solid surface? On the other hand, is a particular structural group of the rubber chains more specifically affected by the filler surface than any other?

Filler/elastomer interactions: the interphase

The blending of a filler with an elastomer is known to be associated with the occurrence of two types of interactions which may be either purely mechanical or may result from more complex processes involving for example physical or chemical interactions.

The former, known as "occluded rubber", results from the absorption during the compounding of part of the elastomeric matrix in the voids of the filler particles. This molecular occlusion results in a shielding of the corresponding material from the strain supported by the bulk of the polymer in the compound under stress and, as a consequence, in an increase of the effective volume of the filler dispersed in the rubber [1].

The latter is the so-called "bound rubber" which corresponds to the quantity of elastomer which cannot be recovered from an uncured filler/elastomer blend upon solvent extraction. It is known to be very much dependent on the surface activity of the filler [2-4]. This bound rubber together with the neighbouring entangled elastomer molecules makes up a polymer shell of finite thickness which surrounds the filler particles and forms the interphase. Previous works have pointed at the importance of its occurrence for the observation of reinforcing effects. Indeed, the compounding of a styrene-butadiene rubber (SBR) with a reinforcing carbon black (N326) the surface of which has been deactivated by grafting of hexadecyl chains (N326C16) yields a material exhibiting a severely depressed reinforcing ability as assessed from the 100% modulus of the corresponding materials (Table 1).

Table 1. Stress strain properties of SBR compounded with different carbon blacks [5]

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ100 MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>0,9</td>
</tr>
<tr>
<td>SBR/N326</td>
<td>2,1</td>
</tr>
<tr>
<td>SBR/N326C16</td>
<td>1,0</td>
</tr>
</tbody>
</table>

Filler/elastomer interphase: structure and characteristics

Several experimental techniques allowing the obtention of informations on the interphases and their features have been selected: dynamic mechanical testing, differential scanning calorimetry, relaxational behavior of strained samples, solid state NMR spectrometry. All of them can allow an approach of the interphase through the molecular mobility of polymer chains located in the vicinity of the filler particles.

Dynamic mechanical testing

The dynamic mechanical properties of unfilled and silica filled SBR samples were studied using a Metravib viscoanalyzer. Storage moduli $E'$ and loss tangents ($\tan\delta$) were measured at 5 Hz in a -150°C to +80°C temperature range. As expected, upon increasing filler loading, $E'$ was shown to increase. Conversely, the area under the $\tan\delta$ peak which is in relation with the amount of elastomer undergoing the glass transition appeared to decrease (Figure 1). Comparison of the experimental values with the theoretical ones obtained by multiplying the area measured for the pure...
SBR by the polymer fraction in the compounded material, indicates that the former are systematically lower than the latter. Such a result suggests that a part of the polymer in a filled sample is not detected by dynamic mechanical testing as passing through the thermal transition within the considered temperature zone [6]. This could be interpreted as due either to a part of the rubber trapped in the filler particles and therefore not being submitted to the mechanical solicitation (i.e. occluded rubber) or to part of the chains immobilized in a way such as to be practically in a glass-like state over the whole temperature range (i.e. bound rubber). In order to settle between both possibilities, differential scanning calorimetry (DSC) appeared to be the technique of choice.

Differential scanning calorimetry
Experiments were performed on a Mettler DSC30 calorimeter. Values were considered out of the second run from -150°C to +180°C at a 2°C/min temperature increment. From the obtained thermograms, providing informations on first (melting, crystallization,...) and particularly second order transitions exhibited by the materials under study, the evolution of the glass transition characteristics versus filler loading was examined. While, on the average, filled compounds exhibit similar Tg as that of the pure SBR, calorific capacity changes (ΔCp) normalized for the polymer fraction only were shown to be dependent on the type of sample (Figure 2). If the ΔCp values obtained with the filled rubbers are comparable to that of the unfilled elastomer, the values obtained with the extracted samples are consistently lower [6]. Such results suggest again that part of the elastomer is not detected by DSC as undergoing the thermal transition. However, the comparison of these informations with those yielded by dynamic mechanical testing suggests that, since DSC-analyzed samples are in no way mechanically strained, the elastomer which is not detected as passing through the thermal transition within the considered temperature zone can only be associated with the formation of bound rubber.

It is thus clear that a part of the elastomer, which is in the close vicinity of the filler surface and participates to the formation of the interphase, is strongly immobilized and exhibits a glass-like behavior. However, gaining a better insight on what is the interphase requires the obtention of other informations such as the assessment of the amount of material which participates to its formation, a more precise determination of its properties and an appreciation of the degree of mobility of the corresponding polymer chains, particularly in order to evidence the occurrence of any
specificity of interactions. Two different approaches were retained to provide these informations: a relaxational approach which takes advantage of the non-equilibrium behavior exhibited by a confined polymer which, unlike a free polymeric material, is anisotropic in nature and has specific local temperature dependence, and a spectral approach (solid state NMR spectrometry) which could allow the assessment of the molecular mobility of polymer chains and as a consequence provide structural, thermal and morphological informations about the interphase.

**Relaxational approach**

It takes advantage of the so-called physical ageing process, known to happen in glassy polymers. Upon application of a static deformation the storage modulus of these materials first decreases suddenly, then increases continually (linear increase on a logarithmic time scale with a slope identified as $\mu$) \[7,8\]. If such a behavior is unobservable when dealing with pure elastomers, it is no longer the case when studying filled rubber samples. Such a result implies that at least a fraction of the matrix exhibits a low segmental mobility and hence behaves as a glassy polymer with respect to physical ageing phenomena \[10\]. Within the limits of this assumption, this tool can be used to detect the restriction of mobility exhibited by the polymer fraction which surrounds the filler particles and as such participates to the interphase. In this respect the crucial parameter is $\mu$, the rate of increase of the modulus after deformation. Its evolution versus filler volume fraction ($\phi$) points at different behaviors depending on filler loading (Figure 3). At low $\phi$, the influence of the interphase on the value of $\mu$ results from particles acting individually. At intermediate filler loadings, particles coated with an immobilized rubber shell start to interact over long distances. At high loadings, as a consequence of the formation of a tridimensional filler-interphase network, the mobility of a large part of the rubber matrix is severely depressed, although the corresponding macromolecules may not be directly immobilized on the filler surface. From this curve, one may define a critical filler loading ratio, $\phi_c$, for which particles and their interphases start to interact. Thereafter, it is possible to estimate the volume fraction of the interfacial region ($\phi_i$) as being the difference between $\phi_c$ and a theoretical value, $\phi_0$, a case in which there are no filler/matrix interactions and no matrix modification at the interfacial region (natural compactness limit). $\phi_c$ and $\phi_i$ values obtained for a reinforcing silica and a model filler (glass beads) are reported in Table 2.

**Table 2. Critical filler loading and immobilized SBR values \[9\]**

<table>
<thead>
<tr>
<th>Filler</th>
<th>$\phi_c$</th>
<th>$\phi_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0.09</td>
<td>0.34</td>
</tr>
<tr>
<td>Glass beads</td>
<td>0.41</td>
<td>0.02</td>
</tr>
</tbody>
</table>

It appears that the values of the critical filler loading ratio and of the amount of immobilized rubber, as well, are strongly dependent on the reinforcing ability of the filler. Indeed, the use of a non-reinforcing filler is associated with high $\phi_c$ values and a small fraction of the matrix being involved in the surface region.

Using the relaxational approach, it is thus possible to obtain informations on the properties of the polymer chains which are in close vicinity of a solid surface. Their mobility is strongly depressed and one may roughly quantify the amount of polymer which participates to the interfacial domain. In order to confirm these observations and obtain a better understanding

![Fig. 3. Carbon black/SBR blends evolution of $\mu$ vs filler loading ratio](image)
of the nature of the interactions which occur in the filler/matrix interphase and how they contribute to its formation, solid state NMR spectrometry was used.

**Solid state NMR approach**

At temperatures well above the glass transition of the elastomer, $^2$H solid state spectra obtained with carbon black-filled deuterated polybutadienes exhibit a double peak (Pake doublet) which is characteristic of glassy or strongly immobile deuterium together with a single and narrow peak associated with mobile $^2$H (Figure 4) [10]. Such a result confirms that part of the elastomeric chains are in a glass-like state, while at the same temperature the pure elastomer is indicating the presence of highly mobile deuterium. It is clear that these immobilized rubber segments participate to the formation of the interphase.

![NMR spectra of $^2$H-polybutadiene (a) and $^2$H-polybutadiene/carbon black blends (b)](image)

**Fig. 4. NMR spectra of $^2$H-polybutadiene (a) and $^2$H-polybutadiene/carbon black blends (b)**

Using a new approach, $^1$H high resolution high speed solid state NMR, informations may be obtained as for the specific effects exerted by the filler on the different chemical species constitutive of the polymer chains. In this respect, it was shown that it is possible, by spinning the samples at magic angle and at a 15-kHz frequency, to obtain well resolved spectra and to assess from relaxation measurements the evolution of the intensity of each peak versus relaxation time. In the case of SBR/carbon black blends (filler loading ratio in the 0 to 100 phr range) previously extracted so as to get rid of any free polymer chains and enhance as a consequence the answer of the interphase (bound rubber) we showed that the plots of the transverse magnetization relaxation functions for the different types of protons (aromatic, methine, methylene) could be fitted with a sum of two exponential decay functions corresponding to short ($T_{2s}$, relatively immobilized material) and long ($T_{2l}$, less immobilized material) relaxation times, respectively. Following the evolution of $T_{2s}$ versus carbon black loading, it was evidenced that the olefinic part of the butadiene segments is the polymer moiety which, whatever the filler loading ratio, is the most affected by the carbon black surface (Table 3).

<table>
<thead>
<tr>
<th>Carbon Black Loading, phr</th>
<th>$T_{2s}$, ms</th>
<th>Aromatic $^1$H</th>
<th>Methylene $^1$H</th>
<th>Methine $^1$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.50</td>
<td>0.22</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.52</td>
<td>0.17</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.48</td>
<td>0.16</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.45</td>
<td>0.13</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

Since butadiene polymerizes according to two different microstructures (1,2- and 1,4-), use of a series of polybutadienes (PB) of identical molecular weight but different and well controlled 1,4- content indicates, from the comparison of the slopes of the lines relating $T_{2s}$ to 1,2-polybutadiene content, that in the presence of carbon black (filler loading ratio: 50 phr) the 1,2- fractions (vinyl protons) are more immobilized than the 1,4- moieties (1,4- methylene protons) (Table 4).

This specificity of interaction was confirmed by studying the evolution of the $\Delta$Cp of the samples versus polybutadiene microstructure. One may expect of course this specificity of interactions to be dependent
Table 4. Comparison of the slopes of $T_2^*$ vs 1,2-polybutadiene content for vinyl 1,2- and methylene 1,4-protons in the case of pure, filled and extracted filled-polybutadiene [12]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope of $T_2^*$ vs 1,2-polybutadiene content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{CH}_2\cdot1,2\text{-PB}$</td>
</tr>
<tr>
<td>Pure PB</td>
<td>-0.34</td>
</tr>
<tr>
<td>Filled PB</td>
<td>-0.19</td>
</tr>
<tr>
<td>Extracted filled-PB</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

on the type of polymer used but it appeared that it also depends on the elastomer/filler couple under investigation. Thus, in the case of SBR/silica compounds the effect of the filler is felt, as seen by NMR spectrometry, at the level of all branched fractions (vinyl and aromatic groups as well). Nevertheless, assessing the intensity of the silica/elastomer interactions through flow microcalorimetry, using as solute molecules representative of the different polymer moieties, we were in a position to show that the stronger thermal effects are obtained with aromatic compounds, what would indicate that the adsorption of SBR on the surface of silica would preferentially proceed through its aromatic moieties [13].

**Conclusion**

In a filled elastomeric matrix, the effect of fillers is not limited to surface processes but is extending to the polymer phase surrounding the reinforcing particles (the interphase). Dynamic mechanical testing and differential scanning calorimetry show that part of the rubber, certainly the most affected by the presence of the filler, is not detected as passing through the glass transition temperature, thus indicating a fraction of the elastomer is in a glass-like state even at temperatures well above the polymer nominal $T_g$. Studying the relaxation behaviour of strained samples (physical ageing process) and using $^2$H and $^1$H solid state NMR, one may be in a position to evidence the presence of the interphase, to quantify the amount of polymer which is thus affected and to show that the interactions which take place at the polymer/filler interface are selective and dependent on the filler/polymer couple under investigation. The nature of the corresponding modifications and the driving forces behind them are, however, not clearly understood.

**References**

7. B. Haidar and T.L. Smith, Polymer, 31 (10), 1904 (1990)