New Insights in the Dynamic Properties of Precipitated Silica Filled Rubber Using a New High Surface Silica

The precipitated silicas are traditionally used as reinforcing fillers in rubber applications. For the soles of athletic footwear, these white reinforcing fillers give an improved resistance to wear and tear with the option of using all possible colors. In technical rubber parts, precipitated silicas are often used to increase the tear resistance or to decrease the heat build-up and in the case of colored compound achieve a good level of mechanical properties. In the tire industry, traditionally, they have been used to improve the tear resistance of truck and bus tire treads, and also to enhance adhesion between the metallic reinforcement (steel cords) and the belt rubber compounds of radial tires. Over the last several years, the use of precipitated silica has been extended to passenger car tire treads. Due to its excellent dispersion capacity, a new-generation of Rhodia’s silicas has permitted to develop the «Green Tire», which have low rolling resistance, improved wet grip and maintained longevity [1, 2].

Today, the main challenge is to extend the Magic Triangle in order to contribute to the reduction of the Tire Rolling Resistance and then to the fuel consumption reduction. As indicated in Figure 1, a new silica generation (Z Premium 200 MP [3]) with a high surface and a good dispersibility has been launched. It offers an unique morphology, resulting from a novel compromise between silica aggregate size and elementary particle size. In a classical Tire Tread recipe for Light Vehicle (sSBR/BR), using the Rolling Resistance laboratory descriptor (\( \tan \delta \) at 60 °C) [4], normally, the values increase with an increase of quantity or an increase of specific surface area. Our last results comparing Z1165MP and Z HRS 1200MP silicas [3] confirm this behaviour. But, as described in the Figure 2, the Z Premium 200 MP gives lower values than the corresponding silica (Z HRS 1200MP) in term of specific surface area. The aim of this article is to understand why the unique morphology of the Z Premium 200 MP induces a different behaviour of the energy dissipative component to the classical HDS one.

The study concerns the use of a pure elastomer (sSBR) and three dispersible silicas (Z1115MP, Z1165MP and Z Premium 200MP), used with a coupling agent (Silane: Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide or TESPT). To observe the variation of the dynamic properties, some designs of experiments (DOE) have been carried out with two parameters: silica amount / CBS amount.

To study the viscoelastic properties associated to the Tire Rolling Resistance, the lost factor parameter (\( \tan \delta \)) at 40 °C, measured at 10Hz is chosen. To describe the evolution of tan \( \delta \) at 40 °C, the approach using the Loading Interfacial Area Function already used for the carbon black [5] & silica [6] rubber compounds will be applied to our precipitated silicas. Classically, a mastercurve is obtained. The incorporation of the new Z Premium 200 MP modifies this behavior and leads to study a complementary approach based on the minimal distance between objects as for the carbon black compounds [7, 8].

Completed by previous data, these new results help us to go deeper in the interpretation of the Payne effect.

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tion of the Payne Effect (characterized by a decrease of the storage modulus ($G'$) together with the appearance of a maximum for the loss modulus ($G''$) when the strain amplitude increases [9]). This new interpretation is based on the utilization of the glassy-like rubber layer concept [10] when the temperature is far from the Tg. A mechanism will be proposed with an extension for temperatures close to the Tg including the impact of the dynamic strain.

Materials and methods

Materials

For ‘green tire’ tread compounds, the matrix is based on solution styrene–butadiene rubber (s-SBR). A solution styrene-butadiene rubber containing 50 % of vinyl-1,2 and 25 % of styrene is used. The gum is extended with 37.5 % of oil.

The fillers are highly dispersible silicas named Z1115MP, Z1165MP and Z Premium 200 MP (commercialized by Rhodia). Some characteristics of these silicas are presented in Table 1.

More especially, a new silica process permits to achieve a high dispersible silica together with a high specific surface area and a shift to higher aggregate size. The aggregate size of Z Premium 200 MP, measured by X-Ray Disk Centrifugation (XDC from Brookhaven Instruments) in a water suspension after desagglomeration in-situ using ultrasonic probe, is higher than a classical precipitated silica at the same specific surface area value (Z HRS 1200 MP). The Figure 3 shows the shift obtained in comparison with the classical precipitated silicas. As described after, some designs of experiments have been used to study the three silicas. To limit the adjustment in the recipes for each silica, we decided to work at the same total engaged surface in contact with the elastomer ($SSA_{CTAB} \times Q$).

The recipe is given in Table 2. Some ingredients have been adjusted in order to take into account the variation of the total polymer/filler contact area and the adsorption on the silica surface.

To link the silica to the rubber, TESPT is used as coupling agent. The ratio of silane is always kept constant. This value is based on the optimal overlap described by Wolff [11], and near to 1.0 - 1.2 silicium atoms by squared nanometer of precipitated silica, leading to the following equation:

\[
\text{Amount of TESPT (phr) } = 0.0005 \times Q \times \frac{SSA_{CTAB}}{m^2} \tag{1}
\]

The cure system is based on the association of CBS - DPG-TBzTD-sulphur. The CBS molecule is the second parameter, used for the design of experiments. The DPG molecule is adjusted with the total engaged surface in order to have the same adsorption behavior \([12, 13]\) for the three silicas, with the following equation:

\[
\text{Amount of DPG (phr) } = 0.00012 \times Q \times \frac{SSA_{CTAB}}{m^2} \tag{2}
\]

For the mixing process (Table 3), the non-productive stage (in two steps) is carried out in a 0.3 liter internal mixer (Speed rate: 80 rpm – Filling factor: 0.75).

<table>
<thead>
<tr>
<th>Fillers characteristics</th>
<th>Typical analysis</th>
<th>Z1165 MP</th>
<th>Z1115 MP</th>
<th>Z Premium 200 MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Specific surface area – $m^2$</td>
<td>160</td>
<td>120</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>CTAB Specific surface area – $m^2$</td>
<td>157</td>
<td>115</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Humidity (2h @ 105°C) – %</td>
<td>7.0</td>
<td>6.0</td>
<td>6.5</td>
<td></td>
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</tbody>
</table>
Under these conditions, a dump temperature close to 160 °C is reached for all the compounds. The productive stage (using a DPG-CBS-TBzTD-sulphur cure system) is performed on an open-mill. After calendaring, the green-compounds are cured at 160 °C according to their own t98 (based on the rheological data from ODR).

**Methods**

To study the rheological properties, we performed the Mooney viscosity on a MV2000E rheometer at 100 °C (ISO 289), and the vulcanization behavior on an ODR Monsanto R100S at 160 °C (ISO 3417).

To study the dynamic properties (ASTM D5992), we used a Metravib VA3000 analyzer with three kinds of deformation modes.

For the common characteristics (E*, E', E'' and tan δ), the samples (cylindrical form with a section of 95 mm² and a height of 14 mm) were tested in compression mode at 10 Hz under a temperature of 60 °C. We carried out the test with a static pre-strain of 10% and a dynamic double strain amplitude of 4%.

To characterize the viscoelastic properties on a large scale of temperatures (Fig. 4), parallelepiped samples (8 mm² section, 14 mm height) were tested in elongation mode at 10 Hz under a dynamic strain amplitude of 0.1% from -80 °C to 80 °C (speed rate: 5 °C/min).

To study the Payne effect (Fig. 5), the samples (double sandwich of parallelepiped form with a section of 8 mm² and a height of 7 mm) were tested in pure shear (γ) mode. The dynamic measurements were carried out at 10 Hz under different temperatures. The variations of the storage modulus (G’), the loss modulus (G”) and the loss factor (tan δ) were recorded between γ=0.001 and γ=0.5. The data were plotted as a function of the simple strain amplitude. The following abbreviations are used (Figure 5): G0 (elastic modulus at very low strain – γ=0.001), G max (elastic modulus at high strain – γ=0.5), ΔG’ = [G’γ=0.5 – G’γ=0.001], and tan δ max (the maximum of loss factor between γ=0.001 and γ=0.5).

For the exploitation of the results, we used the values after a first strain sweep between 0.001 and 0.5 to remove any irreversible effects [14].

**Experimental results**

The use of experimental designs based on two variables (CBS amount and engaged surface of the filler) permits, thanks to a mathematical treatment (setting up model equations), to study the rheological, mechanical and dynamic properties of the vulcanizates containing the three fillers. In the first part, to be in the operating range of the Tire Rolling Resistance, we study more specifically the dissipative energy component in pure shear mode after a dynamic strain sweep: Tan δ max at 40 °C. As described in Figure 6, the unfilled rubber compounds give a temperature value of 258 K (-15 °C) for the maximum of the viscous modulus. So, in this study, the gap between the measured temperature and the glass transition temperature (T-Tg) gives a value of 55 K. The temperature is far from the Tg (T > Tg + 50 K) with the advantage to have a low modulus at very low strain – γ=0.001, G’ (elastic modulus at high strain – γ=0.5), ΔG’ = [G’γ=0.5 – G’γ=0.001], and tan δ max (the maximum of loss factor between γ=0.001 and γ=0.5).

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be in the rubbery plateau with a molecular mobility at large-scale [15]. The Tan \( \delta \) max variations at 40 °C for the three silicas (Z1165MP, Z1115MP and Z Premium 200 MP) have been studied to obtain a master curve independently of the silica nature.

In a second part, some new results allow to go further in the interpretation of the Payne Effect using the glassy layer approach, including a geometric model to explain it.

**Parameters of the experimental design**

Three experimental designs (or DoE) have been performed: 2 containing respectively Z1115MP and Z1165MP, and one containing the Z Premium 200 MP.

These experimental designs are central composite designs with two factors: the first one is the engaged surface of the studied filler and the second one the CBS amount. The central point has been repeated three times (in order to get the variance). As, these experimental designs took into account only the interaction between the engaged surface of the filler and the CBS amount and not the quadratic interactions, the number of mixing compounds is 4 + 3 = 7.

The equation of each property can be written like:

\[
\text{Prop} = \text{Constant} + \text{Filler} \times X + \text{CBS} \times \text{Filler} + (\text{Filler} \times \text{CBS}) \times X \times Y \tag{3}
\]

In order to compare three silicas with different specific surface areas, we worked at isothermal conditions. This approach has the advantage to use the same amount of Silane (TESPT) for each point of the DoE, independently of the silica specific surface areas.

**Experimental results for the dynamic properties at 40 °C**

For the maximum of the loss factor (Tan \( \delta \) max) at 40 °C, the deformation sweep (10Hz in shear mode at 40 °C) in function of the total engaged surface (SSA \( \times Q \)), the data are plotted in Figure 7.

This approach shows very close experimental values for Z1115 MP and Z1165 MP vulcanizates which have a homothetic aggregate morphology [16]. The Z Premium 200 MP, even with a higher specific surface area, shows lower values of Tan \( \delta \).

The total engaged surface (\( S \times Q \)), indicating the total silica surface in contact with the rubber matrix, seems to be not sufficient to explain the shift of the dissipative energy component; therefore another approach is then necessary.

As described for carbon black [5] and precipitated silica [6] rubber compounds, the evolution of the Tan \( \delta \) component could be expressed in terms of Loading Interfacial Area Function (SSA \( \times Q \)). This approach leads to get a master curve for each family of fillers. In Figure 8, the Z1115MP & Z1165MP give a master curve in function of the loading interfacial area. These results are suitable with previous ones in natural rubber compounds [6]. Z Premium 200 MP is not included in the master curve.

Willing to obtain a full silica master curve for all silica systems using highly dispersible silicas and coupling agent to have a well dispersed and distributed system, an approach used for the Carbon Black compounds at the beginning of 90’s [7,8] is applied. It expresses the behavior of the loss factor (Tan \( \delta \)) in function of the minimal distances between objects following the equation:

\[
d_{\text{min}} = \frac{d_{w}}{\phi_{\text{filler}}} \left( \frac{\phi_{w}}{\phi_{\text{filler}}} \right)^{1/3} - 1 \tag{4}
\]

Where:
- \( d_{w} \) is the diameter of the filler objects (nm),
- \( \phi_{w} \) is the filler volume fraction,
- \( \phi_{\text{filler}} \) is the volume fraction at the maximal compacity.

In this hypothesis, to describe the silica aggregates, two approach have been considered: one using a spherical shape and the second one using a pseudo-fractal shape.

**Spherical shape**

For the spherical shape, the mass aggregate diameter (\( d_{w} \)) is expressed considering the CTAB surface and the following equation [17]:

\[
d_{w} = \frac{6000}{2.1 \times 5_{\text{CTAB}}} \tag{5}
\]

The calculation gives 25 nm, 18 nm & 14 nm respectively for Z1115MP, Z1165MP & Z Premium 200 MP. For the \( \phi_{\text{filler}} \) value, the spheres are supposed to be stacked under a random arrangement, given a value of 0.63 [18].

From these parameters, it will be possible to build a graph to express the Tan \( \delta \) max 40 °C value. The Figure 9 doesn’t show any master curve for all of the three silicas, even for Z1115 MP and Z1165 MP.

**Pseudo-fractal shape**

To simulate the shape of the silica aggregate, a pseudo-fractal approach is investigated.

### Parameters of the experimental designs and their limits

<table>
<thead>
<tr>
<th>Cps references</th>
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<td>or</td>
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<td>2</td>
<td>1.25</td>
<td>1.25</td>
<td>2.75</td>
</tr>
</tbody>
</table>

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The mass aggregate diameter \((d_{w})\) is expressed using the experimental value, measured by X-Ray Disk Centrifugation (XDC from Brookhaven Instruments) in a water suspension.

The \(\Phi_{sv}\) value is defined for precipitated aggregated silicas with a value of 0.36 for Z1165MP [19], 0.36 for Z Premium 200MP (Rhodia – Internal results) and 0.33 for Z1115MP (Rhodia – Internal results).

From these parameters, it will be possible to build a graph to express the \(\tan \delta\) max 40 °C value. The Figure 10 shows a master curve for all of the three silicas, even for Z Premium 200 MP.
Then, taking into account the pseudo-fractal shape, a master curve could be fitted whatever the silica family using a similar description than the carbon black fillers. The minimal distance between aggregates seems to play a major role.

This approach is extended to other dynamic parameters at 40°C like the reinforcement index of the initial elastic modulus (Ro’ = Go’/Go₀ matrix) and the non-linearity of the elastic modulus (ΔG’ = Go’ – Go₀) called the Payne Effect.

From the Figure 11, the variation of the reinforcement index (Ro’) gives a master curve for the three silicas. The same behaviour is obtained for the non-linearity values (or Payne Effect value) in Figure 12.

Then, the minimal distance between aggregates is confirmed to play a major role. Besides, from the variations of the elastic modulus at 40°C (far from the Tg), a “critical” minimal distance (d* min) could be extracted from our rubber compounds.

With a value near 25 – 30 nm, it is very close to the numerical value of the random polymer coil size for SBR as calculated before in Carbon Black rubber compounds [7]–[20]. More recently, T Chaussée [21] has observed the same behavior but applied to spherical silicas. In conclusion for this part, the Z 200 Premium MP—a shifted product—allows to show the Payne Effect value (precipitated silicas with a coupling agent) described in the next section where the glassy-like polymer layer at the filler surface is the key factor.

Discussion about the Payne Effect

To explain the Payne Effect (Fig. 5), since several decades, some mechanisms are proposed and can be classified in four groups corresponding to different local mechanisms, namely:

• Destruction-reformation of a percolating network of filler [22]—that can also involve polymer bounded to the filler (filler/rubber/filler) [23],
• Thermal adsorption-desorption of polymeric chains at the interface [24],
• Disentanglement of bulk polymer from the rubber bounded to the surface [25],
• Strain softening of the glassy polymer shell around the particles, function of the temperature [26].

The aim of this discussion is to see how to extend the approach of the glassy-like polymer layer from the silica spherical particles to the silica aggregates, using well dispersed and distributed silica rubber compounds (precipitated silicas with a coupling agent) when the measured temperature is far from the Tg (T > Tg + 50 K).

Concept of the glassy-like polymer layer on the silica surface

As shown in Figure 13, the polymer chain dynamic could be strongly reduced at the approach of a surface [27]. This specific layer is mainly due to the adsorption of rubber chains on the filler surface where the immobilization increased gradually from the bulk to the surface.

Recently, using a well dispersed filler system (Stöber silica), it has been demonstrated that the layer thickness is linked to the gap between the measurement temperature and the vitreous transition temperature with the following equation [10]:

\[ e(T) = \delta \frac{Tg}{T - Tg} \]  

where \( \delta \) is the ability of the surface to reduce the mobility of the polymer.

This result is obtained when a coupling agent is used and when the temperature is far from the Tg (T > Tg + 50 K) where the molecular mobility is at large-scale.

III-2 Extrapolation from model systems to real systems

From our previous works [28, 29, 30] we have tried to apply this concept to our precipitated silica rubber compounds (like Z1165MP or Z1115MP).

As a coupling agent is used in this system in order to optimize the filler dispersion & distribution in the rubber matrix [31], it is important to evaluate the area occupied by the silica on the silica surface. Finally, the calculation of the silane amount gives around 1.0-1.2 silicium atoms by squared nanometer on the silica surface. Based on a 6-8 Si-OH/nm² ratio for a standard precipitated silica [32], it remains a large free silica surface for an interaction with the polymer chain.

Secondly, from Inverse Gas Chromatography [33], it has been measured after OTES or TESPD grafting, that 70% of silica surface remains accessible to the probe molecule. Finally, a molecular modelling of the Silica Surface (6 x 6 nm²) functionalized with a silane (Octyltriethoxy silane) [34], confirms that a large amount of the silica surface remains accessible to the polymer chains (Fig. 14). From these observations, we can conclude using a real system having a coupling agent that the rubber chain can interact with the free silica surface. In that way, it contributes...
to the formation of the glassy-like rubber layer.

**Description of the variation of the initial elastic modulus G’o**

In the case of silica model (Stöber silicas – spherical particles), J Berriot and coworkers [26] simulated the behavior of the initial elastic modulus using the reinforcement parameter ($R’o = G’o / G’o_{matrix}$) in the linear dynamic domain (close to a dynamic deformation of 0.1 %).

To describe the behaviour of this parameter, they include the glassy layer approach in the Einstein-Smallwood’s equation:

$$ R(T, \Phi) = \frac{C'_{o}(T, \Phi)}{C'_{o}(T)} = 1 + 2.5 \times \Phi_{eff} $$

(7)

where

$$ \Phi_{eff} = k_o \times \left( 1 + \frac{e(T)}{r_{equiv}} \right) \times \Phi $$

(8)

For temperatures far from the Tg (Tg ± 50 K), in the case of a coupled rubber system, a master curve of the $R’o(T, F, \omega)$ at several volume fractions have been displayed using one single parameter $\lambda$ (around 0.3 – 0.5). This work has permitted to validate the existence of a glassy layer around the silica particle where the thickness is linked to the gap between the measured temperature and the glass transition temperature (T-Tg).

Recently, based on these results using silica spherical particles, this approach have been implemented to the silica aggregates (Z1165MP / TESPT in a sSBR matrix) [30].

To resume, assuming that the elastic modulus at 50 % (G’oo) is mainly due to the filler structure [9] (aggregated silica particles), it will be possible to determine a structure factor (koo) from Guth-Gold equation modified by Medalia [35]:

$$ \frac{C'_{o}(T, \Phi)}{C'_{o}(T)} = 1 + 2.5 \times \Phi_{eff} + 14.1 \times (\Phi_{eff})^2 $$

(9)

Using this semi-empirical equation for the initial elastic modulus (G’o), as well, we propose to complete it by the glassy-like rubber layer equation as following:

$$ R(T, \Phi) = \frac{C'_{o}(T, \Phi)}{C'_{o}(T)} = 1 + 2.5 \times \Phi_{eff} + 14.1 \times (\Phi_{eff})^2 $$

(10)

where

$$ \Phi_{eff} = k_o \times \left( 1 + \frac{e(T)}{r_{equiv}} \right) \times \Phi $$

(11)

and

$$ r_{equiv} = \frac{3000}{d_{CTAB} \times CTAB} $$

(12)

From the spherical particles to the aggregates, as the glassy-like polymer layer thickness seems to be more linked to the silica surface in interaction with the polymer chains than the aggregate volume. To define the $r$ value (equation (12)), it has been proposed to used a $r_{equiv}$ value, calculated from the CTAB specific surface area.

The evolution of the $R’o$ is described before (Fig. 15) and after adjustment (Figure 16) with the $\lambda$ parameter. A master curve with a common $\lambda$ value (0.43) can be observed for the Z1165MP/TESP system (except at 100 phr with a slight higher value $\lambda$ of 0.50). The values of $\lambda$ are close to those found by F. Lequeux et al [26].

For example, with a numerical value of 0.43, the glassy layer thickness would be close to 2.1 nm at 313 K (40 °C).

Then, the approach of glassy-like rubber layer can be applied to our systems.

The second important result is the nature of the equation which uses a quadratic function to simulate the behaviour of the elastic modulus. It seems to prove that the glassy-like rubber layers around each silica aggregate are in interaction with theirs neighbours, leading to a disturbance and more precisely an increase of the initial elastic modulus.

**Arrhenian-like behaviour of the non-linearity $\Delta G’$ far from Tg**

The second point relates to the nature of the mechanism to explain the variation of the non-linearity for the elastic modulus ($\Delta G’ = G’o – G’oo$) in function of the temperature. When the temperature is increasing, the amplitude of Payne Effect is decreasing [9].

From our previous studies [28, 29, 30], a thermally activated process would be at the source of the elastic modulus variations. To resume, it is possible to determine one or more values of activation energy, based on an Arrhenian-like temperature behavior with the following equation:

$$ \Delta G’ = G’o – G’oo = C \exp \left( \frac{E_a}{R \times T} \right) $$

(13)

where

- R: universal gas constant (value of 8.31 J K^-1 mol^-1)
- T: temperature in K
- $E_a$: activation energy (kJ/mol)
- C: pre-exponential factor

In the case of Z1165MP / TESPT [30], the value associated activation energy ($E_a$) when the temperature is far from the Tg (T > Tg + 50K – rubber state) is determined in function of the silica volume fraction (Fig. 17):

- below 0.1, the value is close to 0 — a threshold of $E_a$ values seems to exist, close to the percolation threshold [36].
• between 0.1 and 0.36, the values are between 8 and 12 kJ/mol, independently of the filler content. These values have the same magnitude than the Van der Waals interactions. Based on the existence of a glassy-like rubber layer around silica aggregate, above a certain amount of filler, a connection between these interphases [37] appears to be a percolated filler-polymer-filler network, and its destruction could be responsible of the Payne Effect. As the activation energy of the process was found to be very close to the Van der Waals between these interphases [37] appears to build a percolated filler-polymer-filler network, and its destruction could be responsible of the Payne Effect. This mechanism would be the basic source of the Payne effect. The re-adsorption process of the macromolecules chains on the free surface of the silica could explain the reversibility of the Payne effect where the energetic sites distribution would play a major role [30].

News results coming from the rubber study with the Z Premium 200 MP

From the experimental part, Z Premium 200 MP permits to investigate new fields to better understand the Payne Effect. For the energy dissipative component (tan δ max 40 °C), the total filler contact area within the rubber (Figure 8) seems to be not sufficient to explain all variations of the elastic modulus and the loss factor when the measured temperature is far from the Tg (T > Tg + 50 K).

The consideration of the minimal distance between aggregates as key factor (Fig.10) and the simulation of the elastic modulus (Figure16) using a quadratic effect (Guth-Gold equation) lead us to propose the existence of an interpenetration zone (percolation system) playing like an additional dissipative source. The second important result is the evidence of a large variation for the elastic modulus below a critical minimal distance at around 25 – 30 nm. From the literature using carbon black rubber compounds [17], this distance value is close to the random polymer coil size. Based on this assumption, the interpenetration zone (percolation system) could be due to confined elastomeric chains between silica aggregates. From all of these elements, we would like to propose a geometric model in order to better define our silica rubber systems.

Proposal of a geometric model

Approach. As shown in Figure 18, each aggregate shape (simplified by a spherical form) has a glassy-like polymer layer constituted by macromolecular segments with a progressive reduced mobility and not a glassy shell. Below a critical minimal distance, a percolation system is obtained with confined elastomeric chains. The interpenetration of the glassy-like rubber layer around each silica aggregates with theirs closest neighbors would induce an additive overlapping with the appearance between aggregates of an amplified restricted chain mobility effect. In this condition, a complex percolated 3-D network is created with certain elastic behavior and the possibility to act as an additional energy dissipative source. Impact of the temperature. As described in Figure 19, the gap between the measured temperature and the glass transition modifies the density and the thickness of the glassy-like polymer layer. The increase of the temperature would reduce the glassy layer thickness and then would induce a disappearance of the percolating diffused zone (higher mobility of the macromolecular segments due to the temperature). At the reverse, the decrease of the temperature in order to reach the vitreous transition would densify the glassy-like polymer layer with the formation of glassy bridges between the silica aggregates. In this condition, the concept of the glassy shell could be applied. Impact of an external dynamic deformation. In Figure 20, the strain-softening of the glassy layer and then the reduction of the Payne Effect are discussed. When the temperature is far from the Tg (T > Tg + 50 K), the thermal-activated adsorption/desorption of the rubber chain segments on the free silica surface could explain the destruction of the percolating diffused zone. By similarity with theoretical considerations, written by Prof PG de Gennes [38], the main mechanism could be a slippage of the macromolecular chain segments very close to the silica surface in the perpendicular axis with the deformation strain. The rubber chains would acquire a higher mobility which would lead to the strain-softening of the glassy-like polymer layer and then the disappearance of the percolating diffused zone with the generation of an additional dissipative effect.

Evolution of the activation energy for the Z1165MP/TESPT in sSBR matrix at several volumic fractions (data from reference [32])

<table>
<thead>
<tr>
<th>T &gt; Tg + 50K</th>
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</thead>
<tbody>
<tr>
<td>Glassy-like rubber layer (progressive reduced mobility)</td>
</tr>
<tr>
<td>Interpenetration zone of the glassy-like rubber layers (percolation system)</td>
</tr>
<tr>
<td>Under a critical minimal distance, confined elastomeric segments – Amplified restricted chain mobility effect</td>
</tr>
</tbody>
</table>

Geometric model to describe the impact of the minimal distance of the aggregates on the glassy-like rubber layer (T > Tg + 50K)
When the temperature decreases, as the vitreous fraction increases, the strain-softerning would lead to a plasticification of the glassy bridges by local stress amplifications mechanism with the generation of an additional dissipative effect.

In conclusion, this model would propose to conciliate several apparent contradictions, observed in the literature. The concept of the glassy-like rubber layer on the filler surface in association with the contact zones between aggregates constituted by confined elastomeric chains could explain how the Payne Effect involves on a large range of temperatures and deformations.

**Conclusion**

The new Z Premium 200 MP permits to conciliate high specific surface area (200m²/g) and large aggregate size with good dispersibility.

The new Z Premium 200 MP leads to improve our Payne Effect understanding, with the introduction of the inter-aggregates minimal distance parameter.

The approach of the glassy-like rubber layer could be applied to vulcanized and coupled HDS compounds where the confined elastomeric chains between aggregates seem to plays as an additional dissipative source.

**Acknowledgements**

The authors wish to thank C. Corriol, M. Fernandez, S. Nebut, N. Godin, A. Monton (all from Rhodia) for their contributions to this work.

**References:**


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