Measuring the Payne effect in filled rubber

VKRT meeting, May 14, 2009
As is in the name: ERT B.V. provides research and testing facilities in the rubber field for third parties.

One of the properties of filled rubber we are working on is the measurement of the Payne effect.

The Payne effect is directly related to the dynamic properties of the vulcanized rubber.
The Payne effect in filled rubber is the phenomenon of a strain dependent dynamic modulus.

In carbon black or silica filled rubber we measure a high dynamic modulus at low strains (< 1%) which decreases at higher strains (> 10%).

The reason for this phenomenon is the formation of a network formed by filler-filler interaction.

For carbon black the interactions are Van der Waals forces and for silica the much stronger hydrogen-bondings.
André Wehmeier, VKRT February 14, 2008.
Possible mechanisms for the Payne effect.

(i) the destruction-reformation of a filler network
(ii) adsorption-desorption of polymeric chains at the filler interface
(iii) disentanglement of bulk polymer from the rubber bounded to the surface
(iv) strain-softening of the glassy polymer shell surrounding the particles surfaces

In real life this means an energy loss and the intention is to minimize this effect in filled rubber (but with the reinforcement retained).
How to measure this filler-filler interaction.

The first remark about this phenomenon was in 1942 by Gehman.

The Dutch “Rubber Stichting” played a pronounced roll in the discovery of this phenomenon.

In 1954 S. de Meij and G.J. van Amerongen presented their results on the ‘DKG Tagung’ in Munich.

Part of these results were published in 1956.
Measuring device of Seel de Meij.
G’ vs. strain, A.R. Payne, RTC 1966, 365

Payne effect: \[ \Delta G' = [G'_0 - G'_\infty] \]

\[ \tan \delta \]
samples were tested in pure shear with a Metravib VA3000 analyzer
L. Guy, IRC Lyon, 2006
Measuring the Payne effect.

The Payne effect is difficult to measure in tension (single strain) and measuring in compression means that the test piece has to be glued as is done in the Metravib VA3000 analyzer.

The other modes are shear and torsion; ERT has the option make use of an Eplexor and a RPA.
**RPA** measures in torsion shear on samples which are first cured in the die of the instrument. (Wehmeier, VKRT 14-2-2008). Chosen is for 60°C and 1 Hz. The RPA measures from 0.7% up to 90% strain; below 1.0% the data are not reliable.

**Eplexor** measures on bar shaped vulcanized test pieces of 4x4 mm. Chosen is for 60°C and 1 Hz. The Eplexor measures reliable from 0.1% to 40% (this is what we did until now).

Only two compounds were measured (207-03 and 207-04).
Measurements in shear on the Eplexor.
RPA Payne effect (G') of vulcanized samples

G' (MPa)

strain (%)
Eplexor $G'$ of vulcanized samples

- **G' (MPa)**
- **strain (%)**

Graph showing the variation of $G'$ with strain for vulcanized samples 207-03 and 207-04.
Comparison Payne effect ($G'$) measurements

- **G' (MPa)**
- **strain (%)**

- RPA-03
- RPA-04
- Eplexor-03
- Eplexor-04
RPA $G''$ of vulcanized samples

- $G''$ (MPa)
- Strain (%)

Graph shows the $G''$ (loss modulus) as a function of strain for vulcanized samples 207-03 and 207-04.
Eplexor G'' vulcanized samples

Strain (%) vs. G'' (MPa)

- 207-03
- 207-04
Comparison of $G''$ vs. strain

![Graph showing comparison of $G''$ vs. strain for different materials.](image-url)
RPA tan δ of vulcanized samples

\[ \tan \delta \]

\[ \text{strain (\%)} \]

\[ 0,00 \quad 0,05 \quad 0,10 \quad 0,15 \quad 0,20 \quad 0,25 \quad 0,30 \]

\[ 0,1 \quad 1 \quad 10 \quad 100 \]

- 207-03
- 207-04
Eplexor $\tan \delta$ vulcanized samples

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    title={Eplexor $\tan \delta$ vulcanized samples},
    xlabel={strain (\%)},
    ylabel={$\tan \delta$},
    xmin=0.1, xmax=100,
    ymin=0, ymax=0.3,
    xtick={0.1,1.0,10.0,100.0},
    ytick={0.0,0.1,0.2,0.3},
    legend pos=outer north east,
]
\addplot [yellow, smooth, line width=1.0pt] table {data1.csv};
\addlegendentry{207-03}
\addplot [red, smooth, line width=1.0pt] table {data2.csv};
\addlegendentry{207-04}
\end{axis}
\end{tikzpicture}
\end{center}
Comparison of $\tan \delta$ vs. strain

- RPA-03
- RPA-04
- Eplexor-03
- Eplexor-04
Results

The **Payne effect** as measured with the RPA on cured samples is higher than measured in shear on the Eplexor

\[ \Delta(G'_{1,0} - G'_{20}) = 0.548 \text{ vs. } 0.432 \text{ MPa for 207-03 and } \Delta(G'_{1,0} - G'_{20}) = 0.307 \text{ vs. } 0.234 \text{ MPa for 207-04.} \]

The storage modulus \( G' \) is also much higher for the RPA measurements.

Both the loss modulus and the tan \( \delta \) show an unexpected increase at strains over 25%.
(Most probably due to slip in the RPA die at higher strains.)
The Payne effect of unvulcanized compounds

The **Payne effect** as measured with the RPA on unvulcanized compounds did not show this increase in loss modulus ($G''$) but the tan $\delta$ curve showed again an increase.

Note: the following curves $G'$ and $G''$ for unvulcanized compounds are smoothened below 1% strain.
RPA G' measured curves

G' (kPa)

strain (%)
Payne effect $G'$, unvulcanized compound

- Payne effect $G'$ for unvulcanized compound
- Strain (%) vs. $G'$ (kPa)

- Curve 207-03
- Curve 207-04
G'' vs. strain; unvulcanized compounds

G' (kPa)

strains (%)

0,1 1 10 100

207-03

207-04
tan δ vs. strain; unvulcanized compounds

- 207-03
- 207-04
Conclusions:

the Payne effect can not reliably be measured on vulcanized rubber with the RPA because of unreliability below 1% strain and slip above (at least) 25% strain.

For unvulcanized compounds the RPA seems to be reliable between 1.0 and 25% strain.

The Payne effect of vulcanized samples can reliably be measured with the Eplexor in shear between 0.1 and 40% strain.
The **Payne effect** was defined by A.R. Payne as the difference between $G'_0$ and $G'_{\infty}$ but this is difficult to determine.

As a measure for the Payne effect in unvulcanized compounds, the differences between the $G'$ values at 1% and 20% as determined with the RPA in torsion shear can be used in comparative studies.

As a measure for the Payne effect in vulcanized rubbers, the differences between the $G'$ values at 0.5% and 40% as determined with the Eplexor in pure dynamic shear can be used in comparative studies.